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REACTIONS OF POLY(VINYL ALCOHOL) IN THE PRESENCE OF
METAL COMPLEXES AND PEROXIDES

by

ANDREW AUERBACH

A dissertation submitted to the
Graduate Faculty in Chemistry in
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1974

This manuscript has been read and accepted for the University Committee in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

Poly (vinyl alcohol) (PVA) in the presence of t-butyl hydroperoxide (t-BuOOH) and cobalt (II) and (III) acetylacetonates undergoes an autoxidation and a cleavage reaction in dimethylsulfoxide (DMSO) and aqueous solutions. Measurements were made at 42°C on cleavage of PVA viscometrically; autoxidation of PVA by means of a gas burette; t-BuOOH decomposition iodimetrically; and cobalt concentration changes spectrometrically. The effect of varying the concentration of PVA, t-BuOOH, and cobalt (II) and (III) acetylacetonate, temperature and solvent (DMSO and aqueous solution) were investigated for each process studied. Empirical rate equations of the form, rate of reaction = $k[\text{Co}]^a[\text{t-BuOOH}]^b[\text{PVA}]^c$ were used to describe the effect of the concentration of the reactants on each process.

In the investigation of t-BuOOH decomposition, it was found that the exponents which were experimentally obtained for the empirical equation were dependent on the concentration of the reactants, as well as the solvent used. A more complex equation was used to describe the t-BuOOH decomposition process. An equation was derived by using the assumption of a complexation reaction between the cobalt (II) and/or (III) acetylacetonate and the t-BuOOH. NMR evidence is presented, which supports this assumption.

In the autoxidation of PVA, the empirical equation proved to be inadequate to describe this data in DMSO and aqueous solution, since the values of a, b, and c of the empirical equation varied with the concentration of the reactants. A more complex equation was utilized which was derived from the assumptions that the autoxidation reaction could be viewed as being composed of propagating and nonpropagating reactions, which were separate interdependent processes and that initiation reactions in autoxidation take

place within a polymer solvent cage.

In cleavage reactions of PVA it was found that cleavage took place under a nitrogen atmosphere at a comparable rate to that under an air atmosphere or a 100% oxygen atmosphere, implying that cleavage of PVA is not a direct function of the autoxidation of the polymer. Periodate cleaved PVA, which contains only 1,3 glycol units, exhibited no further cleavage in the presence of *t*-BuOOH and cobalt (II) and (III) acetylacetonate. The possibility of a cobalt (II) acetylacetonate-PVA or cobalt (II) chloride-PVA complex initiating cleavage was investigated with the use of contact shifting phenomena in the nmr. These reactions in DMSO-water mixtures were also studied.

Cobalt (II), cobalt (III), chromium (III), copper (II), manganese (II), manganese (III), iron (II), iron (III), nickel (II), vanadium (III), cerium (III), and aluminum (III) acetylacetonates were used to catalyze the autoxidation and cleavage of PVA, *t*-BuOOH decomposition, and spectral changes of each metal acetylacetonate were followed on the U.V. spectrometer in DMSO and aqueous solution, solubility permitting.

Cobalt fluoride, chloride, bromide, and iodide were studied in a similar manner.

Hemin, hematin, chlorophyllin, and cobalt, copper, iron, and vanadyl phthalocyanines were used to catalyze *t*-BuOOH decomposition and PVA cleavage in DMSO and cytochrome c was tested in aqueous solution. In general, these metals were more active in *t*-BuOOH decomposition and PVA cleavage than metal acetylacetonates and halides.

A comparison was made between the rates of autoxidation and cleavage of PVA and *t*-BuOOH decomposition in the presence of PVA, *t*-BuOOH, and cobalt (II) and (III) acetylacetonate in DMSO and aqueous solution. The rate of autoxidation was more rapid in aqueous than in DMSO solution, while

the rate of peroxide decomposition was less rapid in aqueous solution.
Several alternatives are discussed to explain the experimental results.

INTRODUCTION

The mechanism of polymer autoxidation is still a subject of much speculation in the scientific literature. A great deal of work has centered on polypropylene and low molecular weight saturated hydrocarbons in non-polar organic solvents or in bulk. The initial purpose of this study was to investigate autoxidation reactions of PVA. This system has not been studied extensively. Polar media were employed for this study (DMSO and water) owing to solubility of PVA in these media.

PVA showed a cleavage reaction, as well, under the conditions studied. This cleavage reaction was studied in addition to the autoxidation reaction. The autoxidation initiator consisted of cobalt (II) and (III) acetylacetonate plus *t*-BuOOH. Trace amounts of metal acetylacetonates are used in these studies (10^{-5} - 10^{-4} M) in order to limit radical metal reactions. In addition to the cobalt acetylacetonates other metal acetylacetonates of chromium (III), copper (II), manganese (II), manganese (III), iron (II), nickel (II), vanadium (III), cerium (III), and aluminum (III) and cobalt fluoride, chloride, bromide and iodide were employed in order to assess the effect of different metals and ligands on peroxide decomposition, autoxidation and cleavage reactions. Metals of biological interest, such as metal phthalocyanines of cobalt, copper, iron, and vanadium and hemin, hematin, chlorophyllin were also assessed to their effectiveness in catalyzing these reactions in DMSO and cytochrome c was investigated in aqueous solution.

PVA autoxidation is a reaction of industrial importance, since the aging characteristics of polymers is of vital economic importance

to industry. Mechanistic studies may shed light on methods which could inhibit the degradation of polymeric materials. The mechanism of this reaction undoubtedly has relevance in biochemistry, as well. Presumably, materials such as cellulose and starch, which are also polyhydric alcohols undergo reactions of a similar nature to PVA. Lipids, as well as many other substances have been found to autoxidize in living organisms. Processes such as aging in the body may be tied to free radical autoxidation reactions. The information gathered about these processes might find relevance in the study of the degradation of biological materials.

I. Historical

Autoxidation

Interest in the deterioration of polymers in the presence of oxygen dates back to 1861 when A. W. Hoffman¹ studied the deterioration of rubber and linked it to oxygen absorption. Thomson² found that if copper was in contact with the rubber, the rate of deterioration of the rubber increased. Ostwald³ observed that the rate of oxygen uptake vs. time was autoaccelerating, the curve of oxygen uptake of rubber with time exhibiting a sigmoidal shape. Much of the early work on rubber deterioration was inconsistent owing to the difficulty of obtaining pure rubber and of controlling oxidative reactions which occur subsequent to the reaction. Moureu and Dufraisse used highly purified materials and indicated that rubber oxidation could have arisen from the formation of peroxides, owing to exposure to air.⁴ These peroxides could cause rubber to degrade, even in the subsequent absence of an oxygen atmosphere.

Subsequently, polymer autoxidation was seen as a free radical process, involving peroxides in a self perpetuating, autoaccelerating chain mechanism.⁵ The British Rubber Producer's Association devised a basic autoxidation scheme. As for any chain reaction, there are three main processes involved: initiation, propagation, and termination.

(I) Initiation

Initiation involves the production of radicals by the decomposition of free radical sources. Initiators (peroxides) may be added which are capable of undergoing homolysis under relatively mild thermal conditions. Initiation may also take place through the action of light, in the presence or absence of a photosensitizer.^{6,7}

Peroxides might be formed initially in a reaction mixture, either by direct interaction of oxygen or by the intermediacy of some external energy source such as light, heat, ionizing radiation, or a combination of these to cause homolytic bond cleavage followed by reaction with oxygen.⁸ Since the peroxide is both product and initiator, the autoxidation reactions can be autocatalytic.

Thermal decomposition of peroxides can proceed by unimolecular or bimolecular kinetics, depending on the peroxide concentration. At low peroxide concentrations, decomposition of the peroxide homolytic cleavage of the O-O bond is involved (Reaction 1), where higher peroxide concentrations may involve the breakage of the OH bond as well (Reaction 2).⁹



The difference in endothermicity between reaction (1) and (2) is 20 kcal/mole (50kcal/mole) on the basis of bond dissociation energies.

There is a possibility of substrate peroxide interaction in the initiator process. Nieman has indicated that in the uncatalyzed oxidation of isotactic polypropylene the inclusion of steps (3) could explain the kinetic dependencies observed.¹⁰



Metal species are known to facilitate the decomposition of peroxides and lower the energy of activation of this process. Reaction (4) and (5) are known to occur in metal peroxide systems.



Generally, the activity of the various metals is dependent on the availability of other oxidation states or the redox potential of the metal. Depending on whether the metal is a strong oxidizing or reducing agent,

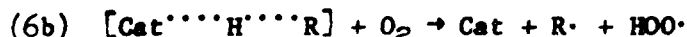
reaction (4) or (5) will predominate.¹¹

The solvent used in peroxide decompositions can affect rates appreciably. Aqueous media compared to organic media, generally reduce the activity of metals. This is related to dielectric constant, catalyst deactivation, and a lower degree in catalyst solubility. In addition, the effect of the medium on complex formation is of great importance and can affect the activation or deactivation of the catalyst.

A metal hydroperoxide complex has been invoked to explain copper 2-ethyl hexanoate catalysed decomposition of *t*-BuOOH in chlorobenzene by Richardson.¹² NMR and visible absorption spectrum were used to support this view.

Woodward and Mesrobian have found the occurrence of a steady, maximum rate for tetralin autoxidation catalysed by cobalt (II) acetate with the occurrence of steady concentrations of hydroperoxide accompanying this maximum rate.¹³ The maximum rate is attributed to the fact that the rate of peroxide formation equals the rate of decomposition, which leads to rate expressions which are independent of cobalt concentration.

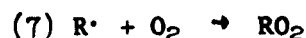
Initiation of atactic polypropylene autoxidations was shown to be first order with respect to catalyst, substrate, and oxygen concentration in the absence of added peroxide. Jadrnicek, Stivala, and Reich were able to demonstrate this by adding an inhibitor, diphenylpicrylhydrazyl, which produced an induction period in the autoxidation of polypropylene in bulk.¹⁴ It was found that this induction period was first order with respect to oxygen, substrate, and catalyst (cobalt (III) acetylacetonate) as expected. The involvement of all three components suggested the possible initial interaction of the catalyst with the substrate, followed by reaction of this complex with oxygen.



A similar scheme was proposed by Bawn and Chaudhri for the autoxidation of atactic polypropylene in trichlorobenzene in the presence of manganese salts (Mn(III)).¹⁵ An order of .5 was found with respect to manganese. This was attributed either to the presence of manganese (II) which could react with peroxy radicals or to possible interactions of the inhibitor (beta naphthol) with peroxides to form hydroperoxides.

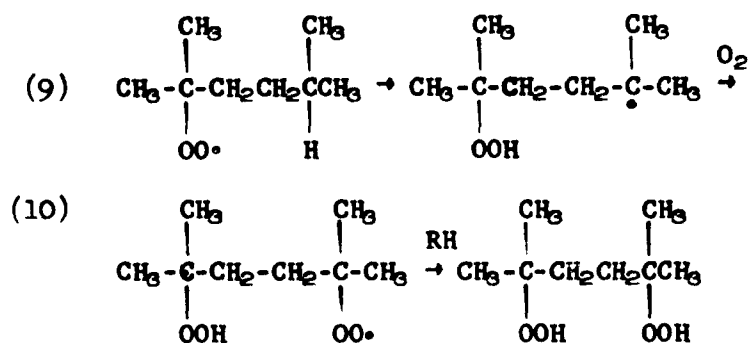
(2) Propagation

The propagation steps involved in polymer autoxidation are associated with the addition of oxygen to a carbon radical and the attack of the radical on another polymer substrate site. Reaction (7) is essentially a rapid coupling reaction.



The relative radical coupling rates of oxygen with a free radical in comparison with styrene towards a polystyrenyl radical are on the order of 1×10^6 .¹⁶

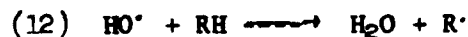
In aliphatic systems, intramolecular hydrogen abstractions are likely to be important. Rust found that the liquid phase oxidation of 2,5 dimethyl hexane could best be interpreted by an intramolecular attack of the initially formed tertiary peroxy radical upon the remaining tertiary hydrogen atom, followed by the formation of a second peroxy group.¹⁷



This result is relevant to work done on isotactic polypropylene and poly (butene-1) in trichlorobenzene, where different dependencies of oxygen concentration are found between isotactic and atactic polypropylene. This difference was attributed to the formation of peroxide groups in close proximity in the isotactic species, which could undergo a bimolecular termination reaction between the two peroxy moieties more readily in the isotactic case than in the atactic case.¹⁸

Hydrogen abstraction (reaction (9)) is expected to occur more readily at stabilized tertiary positions. Boardman assumed that all initiator radicals formed were oxidized to the corresponding peroxy radical and that this radical abstracted hydrogen from the substrate to produce another substrate radical, in his study of p-cymene.¹⁹ This same assumption has been applied to polymer autoxidation kinetics.

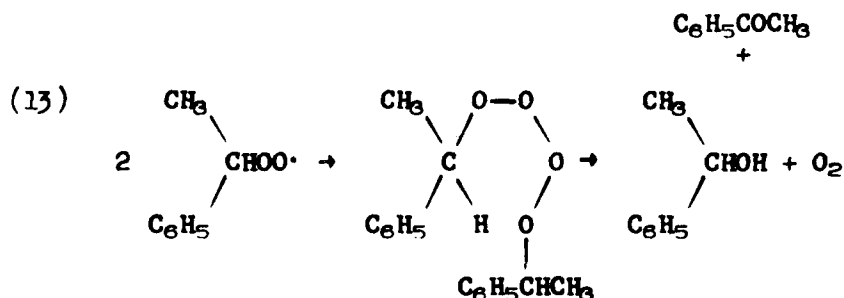
Chien and Boss included propagation steps which involved alkoxy radicals.²⁰



This study was done on polypropylene (about 50 per cent crystalline) in the bulk phase.

(3) Termination

Termination is essentially the combination of two radical species to form an inactive product. Termination usually involves the recombination of two peroxy radicals at oxygen pressures greater than 50-100 mm. This is also seen from the fact that cumene oxidation is independent of oxygen pressure.²¹ In general, disproportionation mechanisms are invoked to explain the products from primary and secondary peroxy coupling reactions. On the basis of stoichiometric considerations and the relatively low deuterium isotope effect for the termination reaction of ethyl benzene, a tetroxide mechanism was postulated²² (Reaction 13).



This mechanism has also been used to explain termination in tertiary peroxy radicals, where methyl migration would be involved.

In polymer autoxidations in the solid phase, two approaches are generally used. In one approach, termination in solid phase oxidation is postulated involving recombination of polymeric peroxy radicals similar to that proposed for liquid phase oxidations.²³⁻²⁶ In another approach, such a termination step is considered unlikely energetically and is therefore excluded, since it would depend upon two very small concentrations requiring polymer-polymer interaction in a medium of very high viscosity.²⁷

Tobolsky and co-workers emphasized the following termination steps in the autoxidation of amorphous polypropylene in the presence of

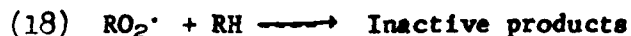
benzoyl peroxide.²⁸ (Reactions 14-16)



Tobolsky obtained the expected linear plots on the basis of the kinetic equations derived from these expressions (refer to page 11). An activation energy of 17 kcal/mole was obtained. This is considered too high, by Stivala in comparison to hydrocarbon oxidations. Chien and Boss used similar termination steps as Tobolsky.²⁹

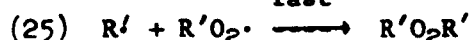
Good correspondance was obtained between the theoretical values of k_i (rate constant for radical formation) and experimental values for polypropylene hydroperoxide decomposition obtained in another study.³⁰ Mayo has criticized this approach because of the presence of carbonyl and alcohol products in the degraded polymer, which would invalidate its comparison to pure polypropylene hydroperoxide.³¹

These approaches differ from that of Reich and Stivala and Bawn and Chaudhri. Reich and Stivala employed a kinetic scheme which did not involve termination by recombination of polymeric peroxy radicals.³²⁻³⁴ The total termination scheme proposed by them is listed below, where Ca^+ is the catalyst.



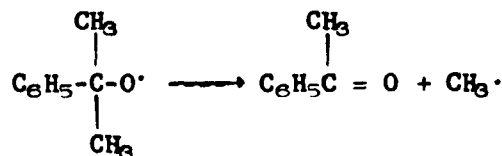


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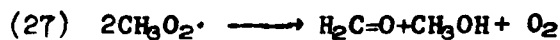


Step 17 involves catalyst deactivation of $RO_2\cdot$ radicals. Kamiya and Ingold in the cobalt (II), tetralin, chlorobenzene system found that at high cobalt (II) concentrations a critical catalyst concentration was reached, producing a maximum autoxidation rate.³⁵ The addition of more cobalt (II) produced lower autoxidation rates. This was attributed to a chain termination process similar to step 17. Steps 19 and 20 involve non-radical decomposition of hydroperoxides. Stivala and Jadrnicek found a linear correlation between oxidation-reduction potential of various metals and the maximum rate of non-volatile carbonyl formation during the autoxidation of atactic polypropylene in bulk phase.³⁶ A mechanism for a step similar to step 19 involving an epoxide has been advanced by Fish to explain rearrangements in gas-phase oxidations.³⁷ Steps 18, 19, 21, 22, 23 and 24 have been used in conventional autoxidation reactions of hydrocarbons.³⁸ A step similar to (21) has been advanced to explain cumene autoxidations.³⁹

(26)



This would correspond to the production of a more mobile radical than the tertiary radical. The methyl radical could combine with oxygen (step 23) and then disproportionate to give the indicated products.



It is assumed that the small $\text{CH}_3\text{O}_2\cdot$ radical can diffuse through the polymeric medium much more readily than polymeric tertiary peroxy radicals.

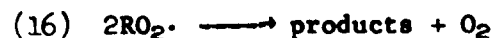
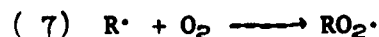
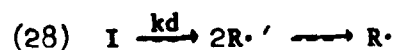
Chain termination is reported to be much more rapid for secondary than tertiary peroxy radicals.⁴⁰

Carlsson and Wiles have presented I.R. evidence which suggested that two ketone products are formed in the oxidation of atactic polypropylene. One of these was apparently formed by the loss of a methyl radical, while the other ketone product could form by chain cleavage.⁴¹ Reaction (25) is included as a cross termination step, but reaction (24) is much more likely in an oxidizing medium. Reaction (22) is not considered likely, since consumption of $R'O_2\cdot$ radicals in previous termination steps is favored.

Significantly, Bawn and Chaudhri have used a similar kinetic scheme to explain the autoxidation of atactic polypropylene in trichlorobenzene in the presence of manganese (III).⁴² A reasonable adherence to the kinetic consequences of the equations postulated by Reich and Stivala has been obtained.

Kinetic Consequences

Tobolsky studied the benzoyl peroxide initiated autoxidation of polypropylene and devised the following kinetic scheme.²⁴



From this it can be seen $-dO_2/dt = k_7[R\cdot]O_2 - \frac{k_{16}}{2}[RO_2\cdot]^2$ and assuming the rate of initiation is equal to the rate of termination $R_i = k_{16}[RO_2\cdot]^2 = k_7[R\cdot][O_2] - k_8[RO_2\cdot][RH]$. Using the steady state approximation for the production of $RO_2\cdot$ radicals and the production of $R\cdot$ radicals we have upon combining equation (29).

$$(29) \quad -dO_2/dt = R_i + \frac{k_p [RH] R_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}$$

Plotting $-dO_2/dt/R_i$ vs $R_i^{-\frac{1}{2}}$ should yield a linear plot, with intercept equal to one. Factors such as the initiation efficiency and the evolution of volatiles were utilized to explain the value of the intercept of this equation, which was less than zero.

Mayo, Niki, Dekker studied the effect of viscosity on di-t-butylperoxylate induced autoxidations of polypropylene in bulk and in the presence of solvent.⁴³ It was found that most of the pairs of peroxy radicals interact by a first order reaction in a polymer cage mechanism. The fraction that escapes gives hydroperoxide in a reaction that is half order in the rate of initiation. In interaction of polymer peroxy radicals, in or out of the cage, about one third give dialkyl peroxides and immediate chain termination and two thirds give alkoxy radicals. About one third of the latter cleave at 45°C. The rest abstract hydrogen to give hydroxyl groups and new polymer and polymer peroxy radicals. The primary peroxy radicals from cleavage account for the rest of chain termination. It was found that polymer peroxy radicals account for 70% of the oxygen absorbed. Polymer peroxy radical concentrations were found to be approximately $10^{-3}M$ at 58-63°C by use of the esr detection of these radicals.

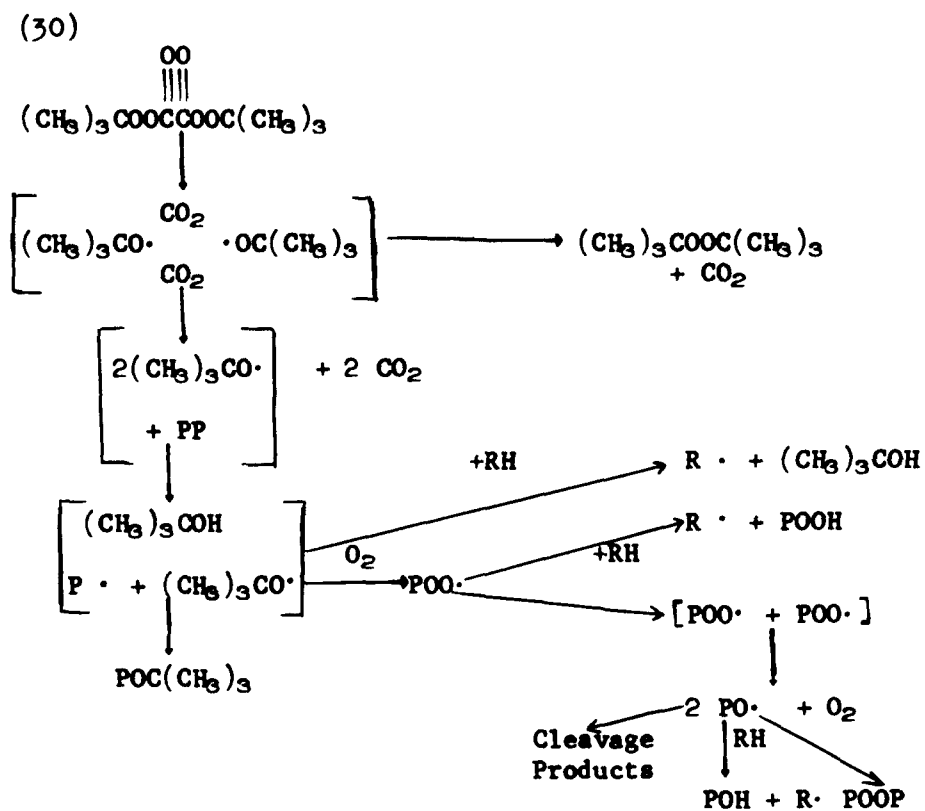
Reactions of initiator radicals within a polymer cage is essentially independent of polymer concentration. Oxygen uptake is proportional (proportionality constant a) to the rate of initiation ($dO_2/dt = aR_i$). If a radical escapes the polymer cage and abstracts a hydrogen from a polymer molecule outside the cage then propagation reactions can take place. We can use Tobolsky's mechanism to represent this propagation mechanism. The rate of oxygen uptake can be taken as equal to the rate

of hydroperoxide formation $(-dO_2/dt) = k_8(RO_2\cdot)(RH)$. If we employ the steady state approximation for $R\cdot$ and $RO_2\cdot$ radicals and add these two steady state equations we obtain $R_1 = 2k_1 (ROO\cdot)^2$.

Substituting this into the equation for the rate of hydroperoxide formation we obtain $dO_2/dt = \left(\frac{R_1}{2k_t}\right)^{\frac{1}{2}} k_p (RH)$. Adding the oxygen uptake

for cage and propagating mechanisms we obtain $dO_2/dt = a R_1 + \left(\frac{R_1}{2k_t}\right)^{\frac{1}{2}} k_p (RH)$.

The form of this equation is similar to the equation obtained by Tobolsky, but was derived from a different set of assumptions. Mayo's kinetic scheme allows the inclusion of viscosity effects to the overall rate of oxygen uptake.⁴⁴ This arises from the fact that the a value is a complex function which is partially dependent on viscosity. It is suspected that the efficiency of initiation is in part dependent on viscosity as well, and is related to a .

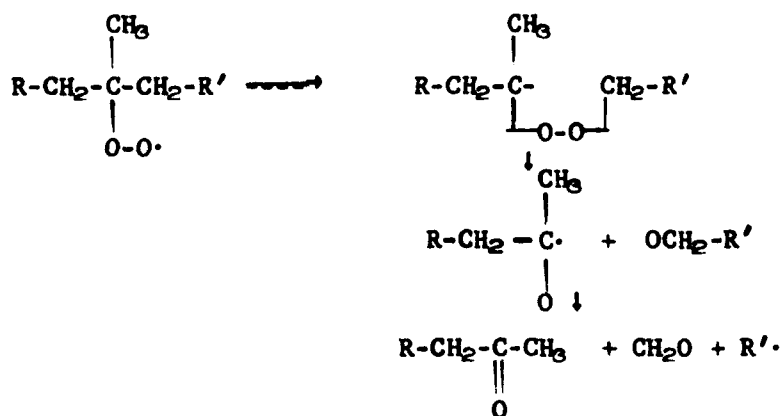


Equation 30: Reaction scheme for di-t-butylperoxyoxalate initiated autoxidation of polypropylene in bulk as proposed by Mayo, Niki, and Dekker.⁴³

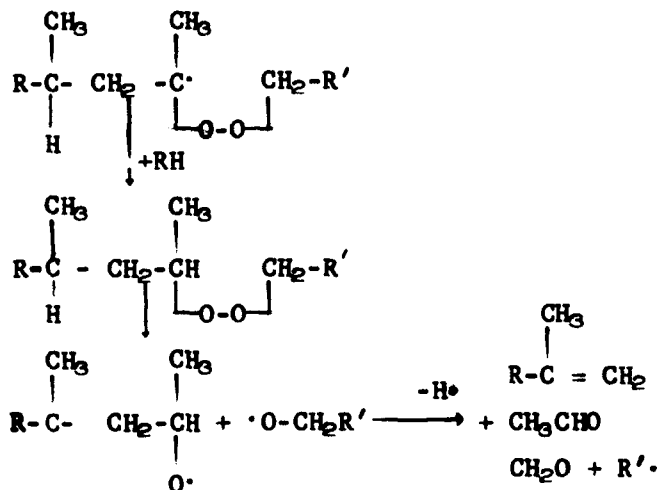
Cleavage Reactions

Cleavage of the polymer chain can come about as a result of autoxidation. Products from the oxidation of polypropylene have included water, formaldehyde, acetaldehyde, acetone, methanol, hydrogen, hydrogen peroxide, carbon monoxide and carbon dioxide. One mechanism postulated for this reaction involves reaction (31):⁴⁵

(31)



or isomerization



Other mechanistic steps have also been postulated. Peroxide concentration seems to affect the rate of formation of product, supporting the conclusion that all secondary products resulted from the breakdown

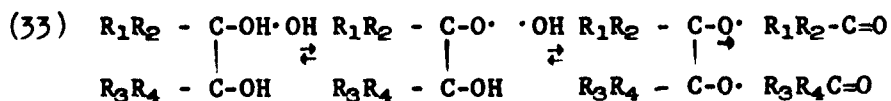
of hydroperoxides.

PVA, a polymeric alcohol has the additional possibility of free radical oxidative cleavage at its alcohol linkage sites. Two basic units exist in PVA (32 a&b), the 1,2 and 1,3 glycol sites.

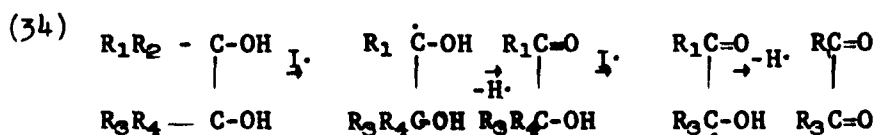


Cleavage reactions of 1,2 glycols are well known. Waters demonstrated that 1,2 diols such as ethylene glycol and 2,3 butylene glycol can yield cleavage products in strongly buffered solutions (neutral conditions) employing Fenton's reagent (hydrogen peroxide plus a ferrous salt.)⁴⁶

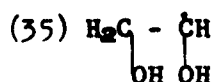
Oxidation products not involving cleavage are also found.



Under concentrated conditions where molecular hydrogen peroxide is in large excess, the free hydroxyl radical would have a very short life time. As a result the main reaction proceeds as:



This occurs by a non chain mechanism and is the predominant reaction with Fenton's reagent.⁴⁷ It is suspected that a radical such as (35) is involved.



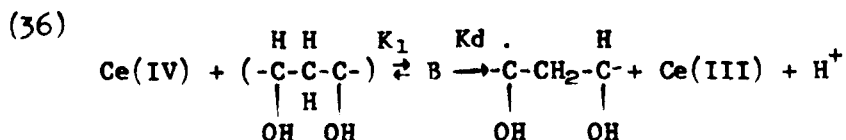
The absence of a chain reaction from (35) indicates that radicals of this type must be somewhat less reactive than the radicals derived from monohydric primary or secondary alcohols and presumably this must be

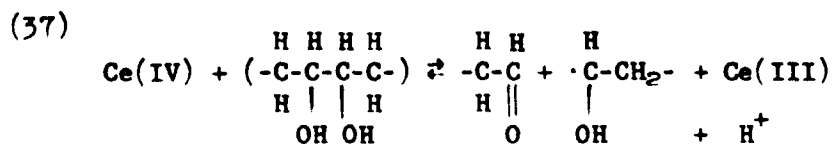
due to the proximity of the second hydroxyl group. As a result the alcohol radical does not initiate new chains by a reaction with the peroxide. 1,3 glycols do initiate oxidation in a chain process, however.

Cleavage reactions at 1,3 glycol sites in hydroperoxide solutions have also been studied. Sicilio employed a mixture of titanium trichloride, sulfuric acid, and hydrogen peroxide in aqueous solution with PVA in order to study its cleavage reactions spectroscopically by using an ear spectrometer.⁴⁹ Radicals were found which were attributed to chain cleavage, but a mechanism for this reaction could not be adequately supported.

Another cleavage reaction has been studied involving the use of cerium nitrate and perchlorate on α glycols.^{49, 50} Duke and Forist studied cerate oxidation of 2,3 butane-diol in nitric acid solution.⁵¹ A coordination complex between cerium and the diol was postulated which could disproportionate into cleavage products. By using conditions which would change this equilibrium, the nature of the complex was investigated. It appears to be monoglycolated at low concentrations and polyglycolated at higher concentrations.

Mino, Kaizerman, Rasmussen investigated this reaction for PVA. Ceric nitrate was used in nitric acid in PVA oxidations. It was found that oxidations were selective for 1,2 glycol sites in PVA. The following scheme was hypothesized:



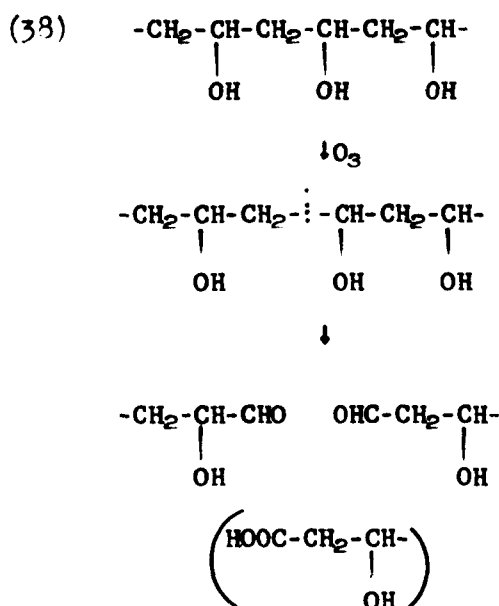


B represents a ceric alcohol complex, while C represents a ceric ion glycol complex. The glycol free PVA was shown to have a much slower rate of oxidation and to follow different kinetics. It was assumed that only monoalcohol complexes form. At 20°C and for a solution containing .2M nitric acid and .57M hydroxyl groups present in glycol free PVA, the rate coefficient for the reduction of ceric ions is $3 \times 10^{-4} \text{sec}^{-1}$. When similar PVA, containing glycol units at a concentration of .0057M in solution, was oxidized under similar conditions, the rate coefficient was $1.8 \times 10^{-3} \text{sec}^{-1}$.

Additional research has been done on PVA oxidation and cleavage. Ozonolysis reactions, carried out in neutral, acidic, or alkaline solutions (N/10-N/100) in the presence of air or oxygen at 60°C has been found to degrade PVA oxidatively.⁵³ The velocity of the reaction in alkaline solution was found to be fifteen times larger than that in neutral or acidic solutions, while the velocity in acidic solution is slightly greater than neutral solutions. It was found that both carbonyl and carboxyl end groups were formed with the carbonyl accounting for about seventy per cent of the end groups found. A possible mechanism listed involves chain scission at 1,3 glycol sites. (38)

Potassium dichromate is also known to cleave PVA in aqueous acidic solution. Five potassium dichromate molecules are consumed for every cleavage of the main chain at 30° to 60°C. Carbonyl groups are seen to be in excess.⁵⁴

Trudelle and Niel placed chromic anhydride in different acid environments i.e. HCl, H₂SO₄, H₃PO₄, HClO₄, and HOAc.⁵⁵ Degradation



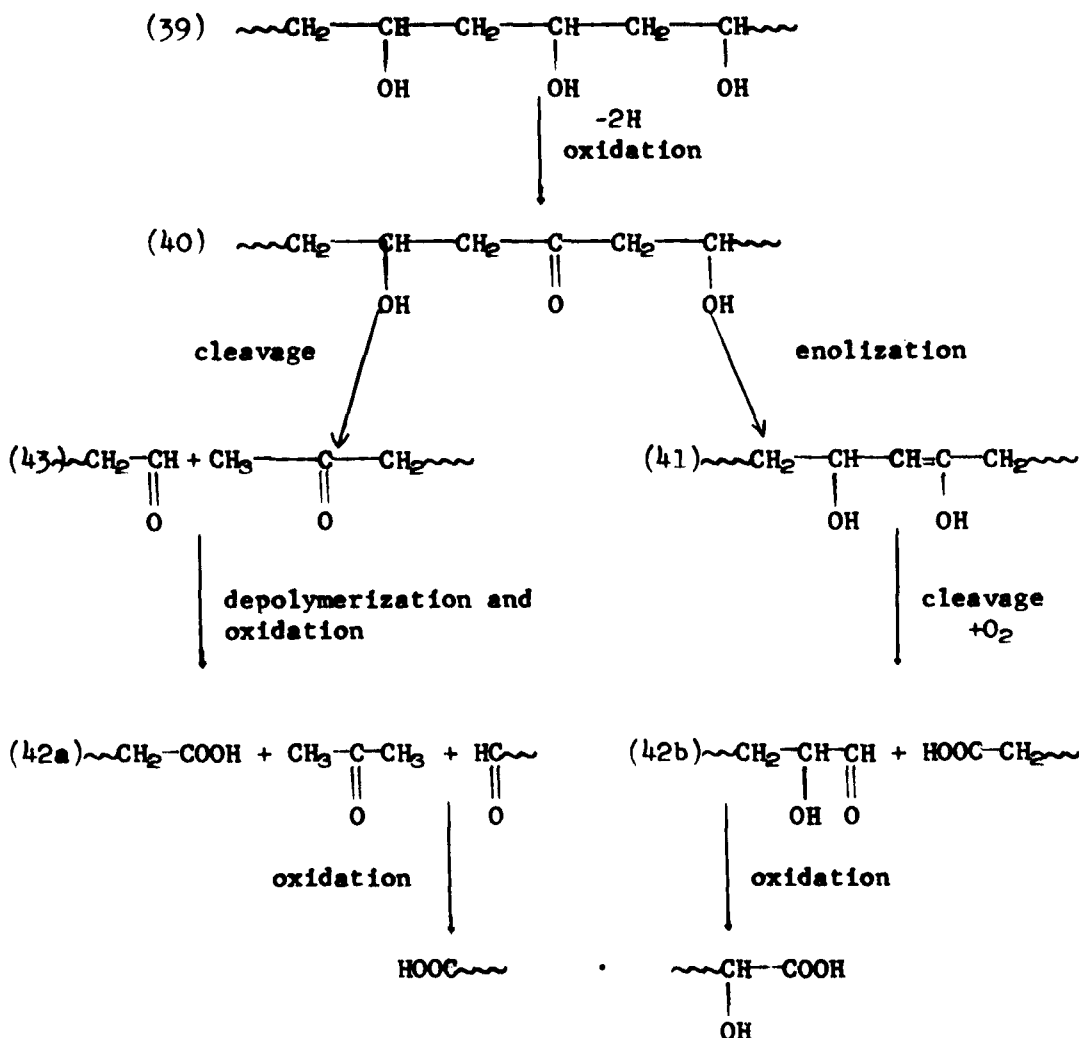
of PVA as measured viscometrically was in the order of: $\text{HClO}_4 > \text{HCl} > \text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HOAc}$. It was found that the scission of 1,2 glycol bonds was much more rapid than 1,3 bond scission. A certain portion of chromium (III) was reportedly on the surface of the polymer after precipitation of the polymer from solution.⁵⁶ Units such as $-\text{C}(\text{C}=\text{C})_n-$ and $-\text{HOC}(\text{C}=\text{C})_n-$ were

detected by U. V. spectroscopy. An intermediate complex with the chromate, followed by oxidation of the alcohol to a ketone function was given as the initiating reaction, followed by dehydration and chain scission. The process is more rapid at 1,2 glycol linkages. It is thought that the action of the acids, either changed the oxidation reduction potentials of hexavalent chromium or modified the rate of the dehydration reactions according to Trudeau and Niel.

PVA degradation has been studied in H_2O_2 solution.^{57,58} G. Takayama has utilized viscometric techniques to measure chain cleavage in neutral 1% H_2O_2 solutions at 60°C. Both carbonyl and carboxyl group content

was determined in the polymer. The polymer appeared to exhibit a strong absorbance at 270 μ , which increases in intensity with increasing carbonyl content in the polymer as a result of oxidation. The carbonyl group content seems to be much greater than carboxyl group content in the polymer under the conditions studied. It was found that PVA that had already been partially degraded or oxidized by another method (e.g. photooxidation, irradiation) degraded more rapidly with hydrogen peroxide.⁵⁹ It is thought that this arises from the production of β diketone groups as a result of oxidation, which facilitate chain cleavage reactions. Oxidation of the polymer appears to proceed through a non cleavage mechanism, which results in the oxidation of the polymer chain.

Shiraishi and Matsumoto studied a similar system except that the pH was varied from 2.5 to 13 to observe its effect on PVA degradation.⁶⁰ It was noted that in acidic solution (pH=2.5) no chain scission was observed. In basic solution, however, a rapid increase in scission occurred (pH=13). A rapid leveling off of chain cleavage seems to occur with time. Carbonyl formation seems to be twice as likely as carboxyl formation. The energy of activation of the oxidation of carbonyl to carboxyl was found to be 2.3 kcal/mole and the energy of activation of the degradation of the polymer was found to be 9.2 kcal/mole (reaction temperatures of 60°, 70°, and 80°). The carboxyl content was seen to increase linearly with the carbonyl content according to the expression $a_t = 2 a_c + .015$ where a_t is the carboxyl content, a_c is the carbonyl, and .015 is the carbonyl content of the original sample. A mechanism was proposed which reflects previous work on alkali degradation of PVA.⁶¹



It is interesting to note that under ordinary oxidation conditions at 22°C in solid state PVA seems resistant to oxidative aging.⁶² In addition it seems to be resistant to most common organic solvents. It was found that even under 660 Kg pressure at 70.4°C for 8.6×10^5 sec that PVA plastic remained almost unchanged as indicated by a comparison of mechanical properties. In a study by Hans Vink on the degradation of a variety of cellulose derivatives and PVA, PVA seemed to be resistant to cleavage by transition metal ions in acidified aqueous

solution.⁶³

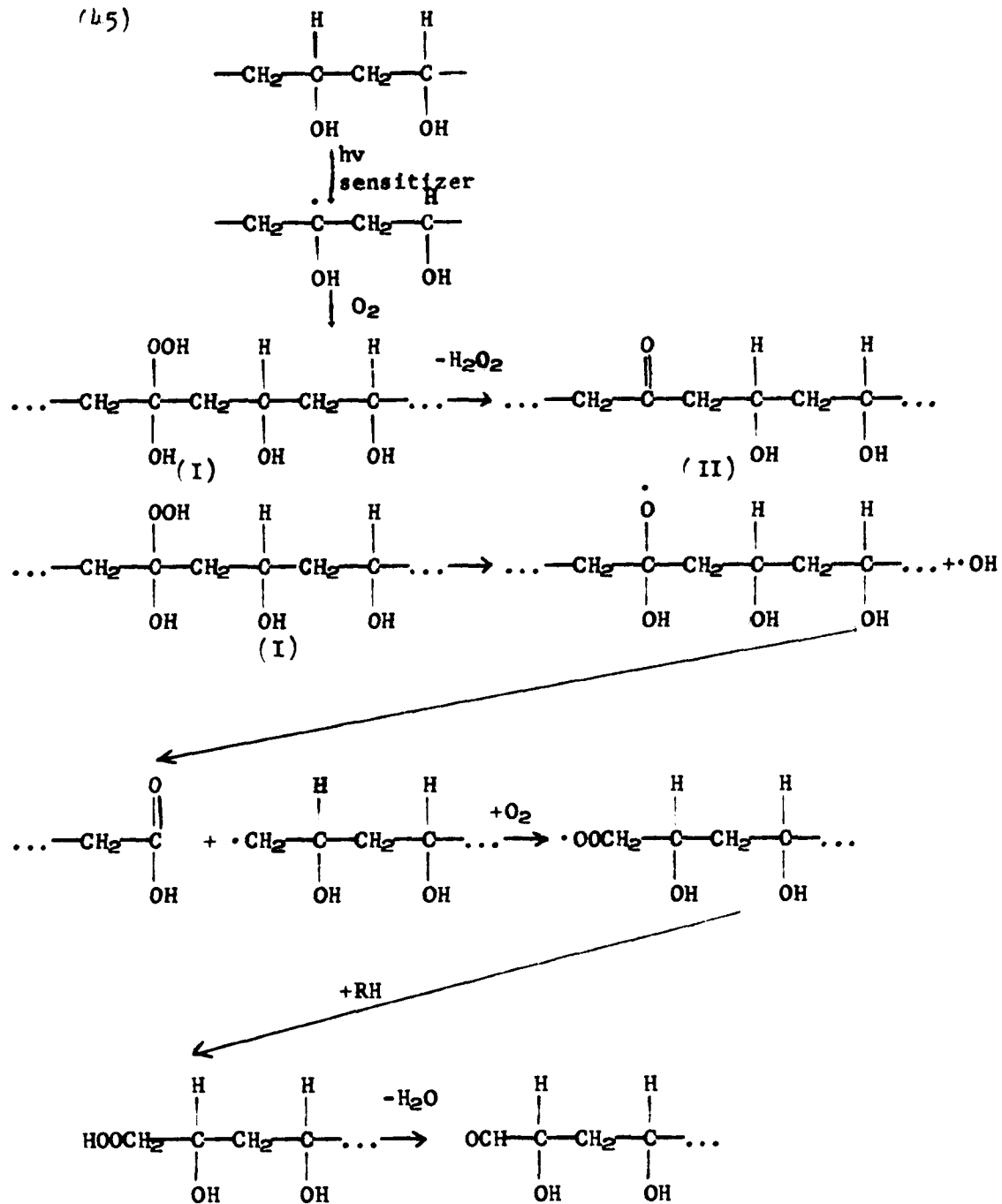
Oxidation of PVA, in bulk, has been reported over long periods of time (134 days) at elevated temperatures (140°-150°) and was found to be similar in rate to that of poly (ethylene).⁶⁴

Under photochemical conditions autoxidation is possible at lower temperatures. Van Lothar Dulong et al have studied a photosensitized autoxidation of PVA in aqueous solution at 30°C.⁶⁵ Degradation products which were detected included hydrogen peroxide, carbon dioxide and polymeric acids. Chain cleavage was determined viscometrically on the reaction solution and on precipitated polymer. Titration with NaOH was also performed to determine the number of acid end groups formed per chain cleavage. It was found that one carboxyl end group resulted per chain scission on the average. Approximately 20 to 25 molecules of O₂ are taken by the solution for every carboxyl end group formed. The reaction was found to follow statistical cleavage by comparing the degree of polymerization before and after cleavage to the equation of Jellinek.⁶⁶

$$(44) \quad \frac{1}{\bar{P}_{NS}} = \bar{k}t + \frac{1}{\bar{P}_{NO}}$$

$\bar{P}_{NS}$ is the degree of polymerization of the original non-degraded polymer and $\bar{P}_{NO}$ is the degree of polymerization of the degraded polymer. At the beginning of the reaction little chain cleavage is found, presumably because initial oxidation of the chain (without cleavage) must take place. The following reaction mechanism was presented to account for these facts:⁶⁵

(45)



The sensitizer concentration decreased linearly with oxygen uptake, indicating that the autoxidation was photosensitized. The role of 1,2 glycol linkages in PVA in this reaction was not discussed. Also, it should be realized that an ionic mechanism for chain cleavage could also explain the indicated observations.

Cobalt Catalyzed Reactions

Since the main part of this thesis involves the kinetics of reactions in the presence of cobalt complexes, a brief survey of cobalt catalyzed decomposition of t-BuOOH and cobalt catalyzed autoxidations, will be presented and some general remarks on the structure of cobalt complexes.

Cobalt compounds have been employed as catalysts in a variety of systems. They have been used in hydrogenation reactions⁶⁷ and amination reactions of olefins,⁶⁸ in the catalytic synthesis of alcohols,⁶⁹ in hydroformylation reactions,⁷⁰ for the catalyzed oxidation of organic compounds by oxygen,⁷¹ and as paint driers.⁷² The high activity of cobalt as a catalyst in oxidation reactions is attributed to cobalt's high redox potential or the ease with which it can transfer an electron.⁷³ Cobalt (II) acetylacetonate has been cited by N. Indictor and T. Jochsberger as the most effective metal acetylacetonate in the decomposition of t-BuOOH in octyl chloride solution.⁷⁴ As a catalyst in polymer autoxidations it is frequently cited as the most effective catalyst.⁷⁵⁻⁷⁷

Cobalt has also been shown to have biological significance. Minute quantities of cobalt salts are apparently essential to plant and animal growth, and in microorganism metabolism. Cobalt is a constituent of vitamin B-12, said to be involved in the bodies oxidation-reduction

system.⁷⁸ The role of oxygen binding to cobalt species has also been investigated.⁷⁹

Cobalt (III) is characterized by the formation of six coordinate, octahedral complexes which exhibit the structural integrity usually attributed to the formation of covalent bonds. The amine and aquo complexes of cobalt have been studied extensively. The hydrated complexes are much less stable than the amines and cobalt (III) ion will react with water to liberate oxygen and will be reduced by hydrogen peroxide. It is also observed that H_2O is very rapidly exchanged in $[Co(H_2O)_6]^{3+}$ molecules.⁸⁰

Cobalt (III) is diamagnetic, indicating the six 3d electrons are entirely paired. Some cobalt complexes are para magnetic. This is accounted for by assuming that no bonding occurs in the 3d orbitals, giving rise to four unpaired electrons. Cobalt (III) acetylacetonate was originally reported as paramagnetic, and later found to be diamagnetic.⁸¹ Cobalt (III) ions have exhibited ion pair formation, either with ligands of opposite charge or with other metal ions.

Oxidation-reduction reactions of cobalt operate through two primary mechanisms: (a) direct electron transfer (b) electron transfer via a bridged intermediate. The true direct electron transfer process is expected in systems where a bridged intermediate is unlikely, because of one or both reactants are substitution inert and contain no ligands in its coordination sphere capable of forming a second coordinate bond. Systems involving electron transfer between cobalt (II) and (III) such as $(Co(NH_3)_6^{3+} - Co(NH_3)_6^{2+})$ are thought to satisfy this condition. Acetylacetonates are thought to utilize bridged intermediates and exhibit slow electron transfer processes. This is consistent with the Frank-Condon

principle which implies that either cobalt (III) must undergo a transition to a spin free state or cobalt (II) must undergo a transition to a spin paired state for electron transfer to occur.⁸²

The order of electron transfer is slowest for ligands of intermediate bond strength (ligand field strength), increasing both with increasing and decreasing field strength. High ligand field strength favors formation of the cobalt (II)-spin paired state while weak ligand fields favor the cobalt (III) spin free state of cobalt (III).

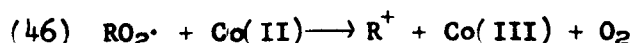
Electron transfer via a bridged intermediate is probably related to ability of the electron to influence the environment just prior to electron transfer. It is seen by Taube and Meyers that ligand exchange occurs upon electron transfer, when a substitution inert oxidant reacts with a substitution labile reductant.⁸³

Cobalt (II) complexes are generally associated with tetrahedral, octahedral, square planar and trigonal bipyramidal configurations. Where cobalt (III) complexes are covalent and nonlabile, cobalt (II) complexes tend to react rapidly, reaching equilibrium in the time of measurement. Halogen complexes are tetrahedral and the relative stabilities are $F > Cl > Br > I$. In the tetrahedral coordination sp^3 or σ bonding is generally utilized, leaving three unpaired electrons. It should be noted that other oxidation states of cobalt exist, namely plus one, zero, and minus one.⁸⁴

Dean and Skirrow studied the decomposition of t -BuOOH in the presence of cobaltous acetate in glacial acetic acid (an anhydrous medium).⁸⁵ Products isolated were oxygen, t -butyl alcohol, formaldehyde, acetone, di- t -butyl peroxide and small amounts of water. Kinetic study was performed by determining oxygen volumetrically, t -butyl hydroperoxide iodometrically and the cobalt spectroscopically. It was found that water

was produced in small amounts in the cobalt (II) reaction but none in the cobalt (III) reaction. This can be explained by reaction (5)

$\text{Co(II)} + \text{ROOH} \rightarrow \text{Co(III)} + \text{RO}\cdot + \text{OH}^-$. Only 10% of the hydroperoxide seems to react this way. The overall cobaltic reaction with hydroperoxide seems to be faster by a factor of 250-300. Thus during the cobaltous reaction the stationary concentration of cobaltic ion is immeasurably small. There is kinetic evidence presented for the formation of a hydroperoxide and cobaltous complex (see previous section on initiation). In the cobalt (II) reaction, reaction (46) is rejected since no t-butyl acetate is formed.



Water is seen to play a marked role in the reaction of cobalt (II) in acetic acid solution, but not in the cobalt (III) reaction. It is thought that the hydrated cobalt (II) ion, which results from the displacement of acetic acid molecules or acetate ions is probable formed in preference to the hydroperoxide complex, lowering the overall rate of decomposition.

Richardson conducted a study which contrasted the behavior of cobalt acetate tetrahydrate and cobalt 2-ethyl hexanoate in acetic acid and chlorobenzene solutions respectively.⁸⁶ Polarographic and spectrometric measurements were used to determine $[\text{Co(III)}] / [\text{Co(II)}]$ content in the solution. Product yields were found to differ from Dean and Skirrow, in cobalt (II) acetate-acetic acid system. Approximately 95-98% cobalt(II) in acetic acid was found to be present at the completion of the reaction as compared to 45-48% in the chlorobenzene. A plot of molecular complexity vs. cobalt (II) 2-ethyl hexanoate concentration indicated a dimeric structure. Consistent with this is an absence of an esr signal, which might suggest that the unpaired electrons are being shared in a common orbital. The mechanism of Richardson is similar to Dean and Skirrow's

except that cobalt is treated as a dimer, e.g. $(\text{CoII})_2 \text{ROOH}$. The order of hydroperoxide decomposition varied with temperature.

Hiatt, Mill, and Mayo studied the metal catalyzed decompositions of $t\text{-BuOOH}$ in chlorobenzene, mixtures of chlorobenzenes, with acetic acid or alcohols, and refluxing alkanes.⁸⁷ It was found that order with respect to metal ion varied from .05 to 3 depending on solvent, catalyst concentration, and temperature. Cobalt carboxylates were the most frequently used catalysts, but iron phthalocyanine, acetylacetonates of cobalt (II) and (III), iron (II) and (III), manganese (II), vanadium (III), copper (IV) and Nuodex solutions (octanoates) of lead, copper, vanadium, and manganese were also tested. $t\text{-BuOOH}$ in protic solvents appeared to have very short radical chains in initiated autoxidations. It has been recognized that metal ion induced decompositions are subject, to some extent, to concomitant radical induced chain decomposition. Alkoxy radicals may undergo SH_2 attack upon C-H bonds such as,



The kinetic consequences of introducing this branching step are profound, and in certain cases non branching initiation may be negligibly small.

E. Y. Scott investigated the cobalt (II) and (III) acetate initiated decomposition of benzyl hydroperoxide in acetic acid at 25°C under conditions of low peroxide concentration.⁸⁸ He criticized other investigators such as Kamiya⁸⁹ and Heath, for employing high peroxide concentrations of tertiary hydroperoxides, where radical induced decomposition of hydroperoxide may become the preferred reaction, as being unrealistic inasmuch as steady state concentrations of hydroperoxide in many autoxidations are less than catalyst concentration. As a result steps such as





might become more relevant. A greater than first order dependance was found with respect to the steady state concentrations of cobalt ion.

Benzaldehyde was found to be the major product of the reaction. Scott concluded that the higher oxidized state of the catalyst is probable regenerated from the lower state by reaction with peroxy radicals derived from the reactant hydrocarbon or from the aldehyde formed by decomposition of hydroperoxide.

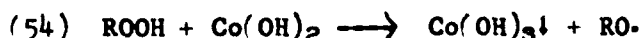
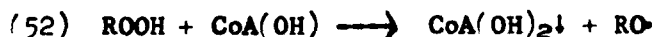
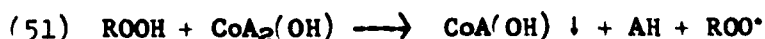
Hiatt also makes a distinction between stoichiometric reaction in which the ratio of peroxide to catalyst is near 1:1 and catalytic decomposition, in which each metal ion decomposes many hundreds of hydroperoxide molecules.⁹⁰ Catalytic decompositions are typified by cobalt carboxylates or iron phthalocyanine. The uniformity of products and the bimolecular rate expressions suggest a radical induced decomposition of the usual type initiated by metal ion-hydroperoxide interactions, as in equations (4) and (5) in the initiation section. If catalyst dimers and hydroperoxide complexes are temporarily left in abeyance, a first order dependance in metal and peroxide (see kinetic section) is derived. Catalyst dimers, as mentioned previously can be accounted for provided that the degree of aggregation remains fairly constant over the concentration range used. Complexing between catalyst and hydroperoxide may occur prior to equations (4) and (5), but it appears to have no important consequences other than retardation caused by other materials which also form strong complexes with the catalyst.

Hiatt found little importance to metal ion reactions with alkoxy or peroxy radicals because of the low concentration of the catalyst. Cobatous ion appears to react with t-butoxy radicals (t-BuO $\cdot$) much less

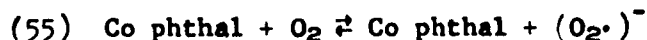
rapidly than other metals. Decompositions of t-BuOOH under conditions where only one valence state of cobalt is active [cobalt (III) acetate in acetic acid] have approximately 1:1 stoichiometry. Apparently under these conditions ROOH competes effectively with cobalt (II) for RO $\cdot$.

Metal radical interaction and specifically cobalt ion peroxide radical interaction has been investigated by the use of esr. Tkac studied cobalt (II) acetylacetonate reaction with t-BuOOH in toluene.⁹² A maximum concentration of radicals of $1 \times 10^{-4}M$ was obtained at 25°C at a 10/1 ratio of t-BuOOH to metal. It is suggested that the observed radicals are t-butyl peroxy radicals (t-BuOO $\cdot$) forming a complex with the cobalt central atom. Acetylacetonates of manganese (II), cobalt (II) and (III), and vanadium (III) undergo similar reactions. At higher temperatures little complexation is found. It is found that polar compounds such as water, t-butyl alcohol, and acetone inhibit the radical metal complexation reaction.⁹³ It was found that cobalt (II) acetylacetonate exists as a dimer or tetramer in non-polar solvents.⁹⁴ $Co(acac)_2 \cdot OH$ is the active species in its reaction with t-BuOOH in toluene.

Deactivation reactions of the catalyst are other phenomena which must be accounted for. Kamiya has found that in the cobalt catalyzed autoxidation of tetralin in chlorobenzene or undiluted tetralin that the rate of autoxidation decreases with the amount of oxygen absorbed by the reaction mixture.⁹⁵ A reaction sequence such as (50) - (54) was postulated, where A represents the anion attached to cobalt. A black precipitate was isolated from the reaction mixture, which exhibited characteristic -OH peaks, and upon X-ray examination with a focusing camera the precipitate was shown to be amorphous. Water was found to



accelerate this process. In acetic acid no deactivation was found since the hydroperoxide would react with the acetic acid and be regenerated to the acetate. Metal porphyrin compounds appear to be deactivated less easily, since at low concentration they are more effective promoters of autoxidation and may be correspondingly less susceptible to deactivation. Cobalt phthalocyanine (a porphin like compound) however, appears to be deactivated during the autoxidation of cumene.⁹⁵ It should be noted, however, that the reaction mechanism for phthalocyanine reactions may involve the formation of oxymetal complexes.



This reaction can be retarded by products being formed in the reaction, since it can block the reaction site.

Deactivation reactions in cumene hydroperoxide-cobalt (II) and (III) acetylacetonate initiation system have been ascribed to both initiation and termination reactions. Four possible alternatives were investigated in order to explain the apparent loss of activity of cobalt (II) and (III) acetylacetonate with time in the autoxidation of cumene. Deactivation of cobalt (II) and (III) acetylacetonate may occur as a result of initiation or autoxidation products blocking cobalt (II) and (III) acetylacetonate sites thereby preventing peroxide from reacting with the catalyst. Another possibility is that the solvent is actively promoting ligand exchange or that the reaction of cobalt (II) and (III) acetylacetonate with the peroxide

results in ligand exchange. Radical-cobalt (II) and (III) reactions may affect the catalytic activity of the metal. Finally, the acetylacetonate ligand may be autoxidized causing the destructive oxidation of the ligand involved.⁹⁷

It was suggested that the cobalt (II) and (III) acetylacetonate is converted to the hydroxide during initiation. Added acetylacetonate appears to slow the deactivation of the catalyst. Products formed during the initiation and termination reaction e.g. water, dimethyl phenylcarbinol, and acetophenone seem to have only a limited effect on autoxidation rates (~5%).

K. Saito and K. Masada found that both water and acid catalyze the exchange of aluminum (III) acetylacetonate with water or the solvent.⁹⁸ C. H. Bamford and A. N. Ferrar found that DMSO is a catalyst for ligand exchange of acetylacetonates including manganese (II) and cobalt (II) and (III) acetylacetonate.⁹⁹ This reaction appears to be free radical in nature, since vinyl polymerization reactions were also observed. 1,2 Diaminopropane also initiates ligand exchange. This initiation process appears to be insignificant compared to peroxide decomposition.

In line with Tkac's work, cobalt (II) and (III) acetylacetonate may also capture a $RO_2^{\cdot}$ radical and be deactivated.⁹² Vigorous oxidative conditions, may actually cause the destructive oxidation of the ligand involved. H. Freiser found that at 100°C in phenyl ether that metal acetylacetonates underwent destructive oxidation to biacetyl, water, acetic acid, mestityl oxide, and acetylacetone.¹⁰⁰ Oxygen was taken up by the system, but was absorbed at different rates by different metal acetylacetonate. Hammett σ values for the abstraction of a hydrogen atom by *t*-butoxy radicals from a acetylacetonate metal complex, were

tabulated by Gritter and Pattmore and may be correlated with Freiser's data.¹⁰¹ It was concluded by Lombard and Knopf that metal deactivation in the initiation step was a most important influence in reaction retardation.

It should be noted that Kamiya found that under conditions where initial hydroperoxide concentration is large relative to cobalt concentration the rate of hydroperoxide decomposition rapidly drops to zero (cobalt salt-tetralin system) due to deactivation.¹⁰² In chlorobenzene each cobalt salt molecule is capable of decomposing about 120 molecules of hydroperoxide before becoming deactivated. Kamiya found that the maximum rate of oxygen uptake is affected by initial hydroperoxide up to a certain limiting concentration. This implies, of necessity, that the rate controlling chain initiation reaction between cobalt and hydroperoxide is not a simple bimolecular reaction. Instead, the rate controlling step must involve the slow decomposition of a rapidly formed complex. It should also be pointed out that under conditions of low cobalt and high hydroperoxide concentration a reaction with the substrate could be rate determining.



Bull used a reaction such as this to explain toluene autoxidation in which more than simple branching is required to explain autoxidation rates.¹⁰³ Wallace and Skomorski found cumene at 104°C to undergo immediate autoxidation with no induction period in the presence of copper (II) and cobalt (III) cyclohexane butyrates.¹⁰⁴ However, the rates were inhibited by addition of cumene hydroperoxide. With iron (II) and nickel (III) salts, oxidations commenced only after appreciable induction periods, and addition of hydroperoxides shortened the induction periods and increased

catalyzed rates. Iron (II) and nickel (III) salts appear to function as peroxide decomposers, while cobalt (II) and copper (II) salts also function as true initiators. Retardation by added hydroperoxide reflects competition between hydroperoxide and hydrocarbon for the higher valence form of metal catalyst.

Metal Ligand Effects

The metal ligand plays a role in the initiation process and the influence of the ligand falls into five main categories. These are solubility of the salt in the solvent, aggregation of the catalyst in solution, the steric bulk of the ligand, the changes in redox potential of the metal as a result of different ligands, and the protection a ligand may afford the metal from deactivation.

First, the solubility of the catalyst can have an effect on the overall rate of reaction. It is sometimes found that reaction products tend to solubilize the metal salt. In fact, Hiatt suggests that the variety of metal reaction orders found (.05 to 3) in various peroxide decomposition studies is due to the lack of true solubility of the metal catalyst in organic solvents.⁸⁷ Catalyst aggregates in solution appear to contribute to nonlinear behavior with respect to temperature and solvent. Catalysts appear to fall into two categories, those that undergo reactions which are first order in metal ion and have an E_a of 9-12kcal and those with higher order of E_a 's of 17-22kcal. Increasing temperature may decrease the aggregate size (and increase the effective catalyst concentration) resulting in an extraordinarily large E_a .

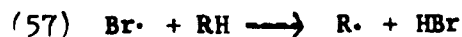
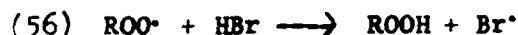
A. Chalk and J. Smith have found that at low peroxide concentrations the steric bulk of a ligand as well as the number of coordination sites it occupies on the metal may have considerable influence on the rate of

autoxidation.¹⁰⁵ If electron transfer can take place over longer distances this factor may not be as significant. Various groups may also protect the catalyst from deactivation. For instance, in benzene solutions of autoxidizing linoleic acid, malic acid was found to deactivate cobaltous stearate, but to have no effect on such catalysts as cobaltous and ferrous phthalocyanine, and heavy metal porphyrin derivatives. The reactivity of porphyrin complexes is remarkable, since the central atom appears to be completely embedded in the complex.

The fourth factor involves change of redox potential as a result of chelation, which may be either favorable or unfavorable towards peroxide decomposition. In relation to acetylacetonates, Wallace and co-workers found that iron acetylacetonate was a less active catalyst than various organic acid metal salts in decomposing cumene hydroperoxide in xylene.¹⁰⁶ The author attributes this to the low redox potential of the metal in this media.

A special type of rate enhancement seems to exist for cobalt halides. Numerous examples exist in the literature¹⁰⁷ in which cobalt bromide or hydrogen bromide significantly enhances the rate of autoxidation reactions.¹⁰⁷ K. Onuma studied the effect of adding lithium chloride and bromide to the cobalt acetate-*t*-BuOOH system.¹⁰⁸ Contrary to a synergistic role in autoxidation the addition of bromide or chloride seemed to inhibit decomposition and create an apparent induction period. Molecular bromine appears to be formed from hypobromite, which is produced in the reaction. A rationale for the inhibitory effect of lithium bromide is that cobalt (II) bromide is a tetrahedral where as cobalt (II) acetate is an octahedral complex. The cobalt (III) form of either is octahedral, suggesting that the halide requires additional energy to undergo a valence change.

It is known that HBr can provide a low energy pathway for propagation in autoxidation reactions.



Cobaltous bromo acetate has been thought to serve as a reservoir, providing a low steady concentration of HBr, which might account for its increased catalytic behavior. An alternative explanation by Bawn is that cobalt (III), a very powerful oxidizing agent, oxidizes Br^- to $\text{Br}^\bullet$ which in turn produces new radicals.¹⁰⁹ Onuma has suggested that cobalt catalyst in the presence of bromide may aid in propagation reactions.¹⁰⁸ This is in line with Bawn's work on p-toluic acid oxidation, where it was shown that only oxidation steps which involved a chain mechanism of propagation were affected by bromide ion.

Z. Osawa, T. Ishizuka, and Y. Ogiwara have suggested that the extent of ionic character in the bonding of the ligand to the metal may effect the rapidity of the autoxidation reaction of isotactic polypropylene in bulk.¹¹⁰ In fact cobalt (II) and (III) acetylacetonate which are active catalysts, are partially ionic in character, where cobalt (III) N,N diethylseleno carbamate has a pronounced inhibitive effect for the oxidation of the polymer and is highly covalent in character. Other cobalt salts showed similar behavior. Osawa, T. Ishizuka and Y. Ogiwara conducted studies on different metal N,N diethylseleno carbamates. It was decided that there inhibitory action results from the decomposition of peroxides into stable products such as alcohols rather than carbonyl compounds.¹¹¹

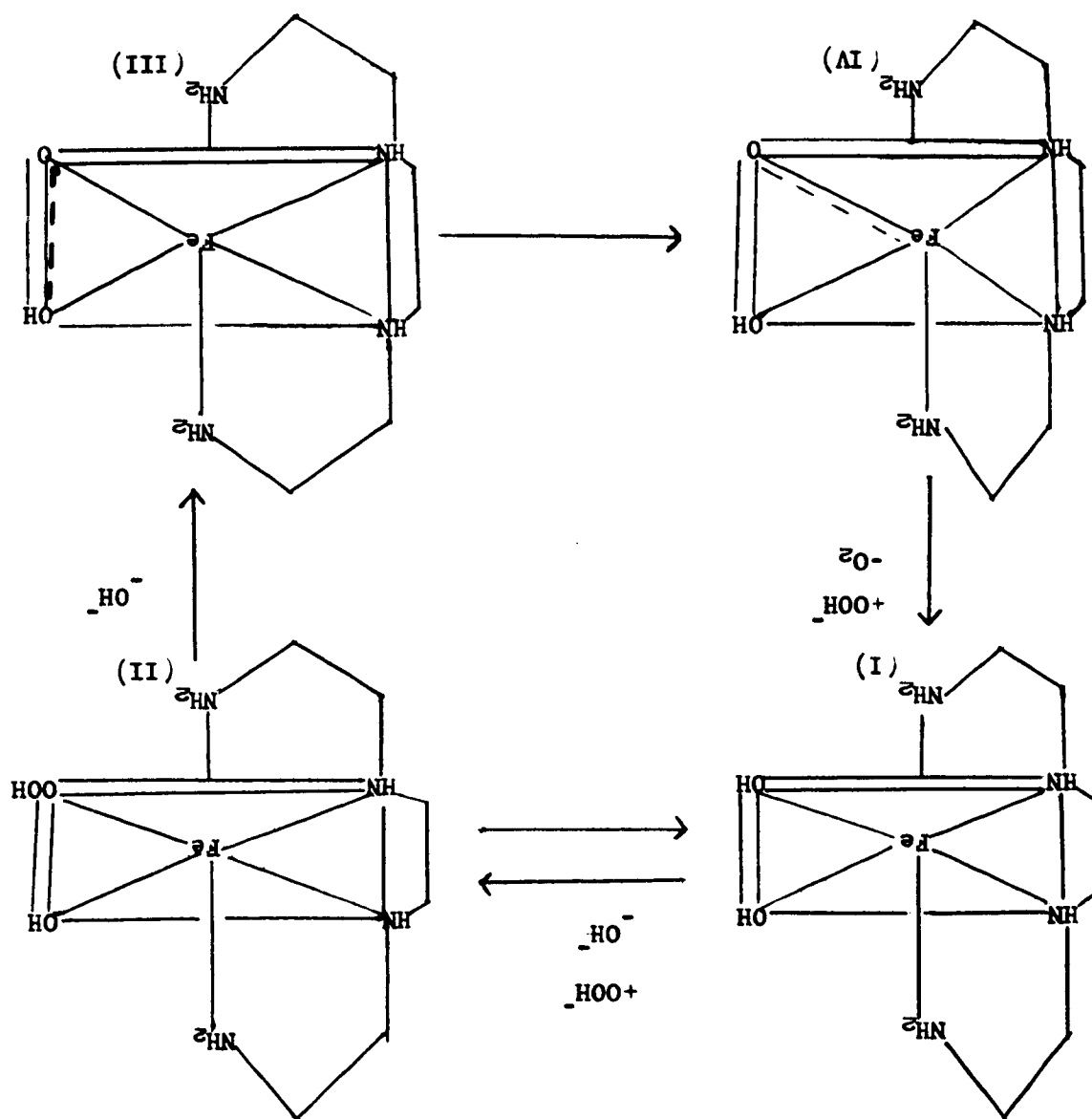
As has been previously mentioned both phthalocyanine and porphyrin compounds seem to be quite active catalysts. This may be due to their

ability to protect the catalyst from deactivation.¹¹² Numerous phthalocyanine compounds have been used to catalyze peroxide decomposition and autoxidation. Iron phthalocyanine has been shown to have an exceptional ability to promote the decomposition of H_2O_2 and tetralin hydroperoxide.¹¹³ This result is of biochemical interest because of the structural relationship between phthalocyanine and porphyrins and chlorophylls. It is the iron atom associated with the four pyrrole nitrogen atoms which leads to catalytic activity.¹¹⁴

Kropf has made an extensive study of kinetics and reaction mechanism of the autoxidation of cumene, with copper, cobalt, vanadium and nickel phthalocyanines.^{115, 116} An oxygen-metal complex was hypothesized in order to explain initiation as opposed to the standard metal peroxide redox cycle. Tobolsky's theory of limiting rates was dismissed without serious consideration, mainly because when copper phthalocyanine was used as a catalyst there was almost quantitative production of cumene hydroperoxide at temperatures below 105°C where thermal decomposition is negligible.

Kamiya has criticized this interpretation of data. He suggests that hydroperoxide could be the main product if chain lengths are long. The Tobolsky limiting rates, if calculated for infinite catalyst concentration, agree well with the rate theory. The values are $7.3 \times 10^{-4}(\text{Co})$, $2.6 \times 10^{-4}(\text{Ni})$, $4.7 \times 10^{-5}(\text{Cu})$, and $7.5 \times 10^{-6}\text{mole/l sec (V)}$.¹¹⁷ Deactivation does seem to occur in these reactions since peroxide concentrations above 100mMol decreases the autoxidation rate.

J. H. Wang has synthesized model porphyrin compounds and feels that decomposition of H_2O_2 by these compounds is nonradical in nature and involves the metal binding of OOH^- molecule in order to facilitate O-O bond rupture.¹¹⁸



(58)

Many transition metal ions are known to bind hydroperoxide ion, OOH^- , and catalyze its decomposition. A complex of ferric ion and triethylene tetramine (TETA) was found to bind OOH^- as a bidentate ligand under strain and hence rendered OOH^- more reactive. Steric considerations show that it is energetically unfavorable to have four N atoms and the iron (III) ion of the complex in one plane.

Steps (II) to (III) represent OH^- exchange with bidentate OOH^- . Since the O-O bond length is normally $1.3\text{\AA}$ it should be under strain in compound III and rapidly change to IV. This splitting of the O-O bond (33kcal/mole) is partially compensated by the formation of stronger Fe-O bonds. Compound IV can then extract a hydride ion rapidly from a second OOH^- to produce oxygen and regenerate I. In fact, the rate constant for decomposition is 10^4 times higher than hematin but lower than catalase an enzymatic peroxide decomposer. Other metal TETA complexes involving cobalt (III), copper (II), nickel (II), chromium (III) were found to be inactive. Only iron (III) and manganese (II), which are isoelectric, show high catalytic activity. It is expected that hematin catalysis is not operating through this mechanism, but that catalase would. One possible mechanism for hematin involves the formation of $(\text{TETA})\text{Fe}(\text{OOH})_2^+$ from the double replacement of OH^- by OOH^- . A transfer of two electrons from one OOH^- to the other through the iron (III) ion would cause decomposition of the substrate to form oxygen and two OH ligands.

A homolytic decomposition of peroxide with the production of free radicals is an alternate and predominant pathway in between the metal and the peroxide, followed by a homolytic unimolecular scission of the -O-O- linkage. This forms hematin (M-OH) and an alkoxy radical. No

valence change of the metal is necessary in any of these reaction mechanisms.

A. L. Tappel points out hematin is a very effective catalyst in the autoxidation of linoleic acid and does not appear to undergo any change in valence.¹¹⁹ Hematin was destroyed in the process of initiation and at 40°C the ratio of peroxide decomposed to hematin destroyed was 300:1. Alpha tocopherol, (Vitamin E) a phenolic compound is capable of inhibiting this autoxidation process. This indicates that the reaction is free radical in nature.

The Effects of Different Metals

Studies have been conducted by Lombard and Knopf to assess the effect of varying the metal group in a variety of acetylacetonates in order to assess their effect on the autoxidation rate and the peroxide decomposition rate of cumene and cumene hydroperoxide respectively.¹²⁰ The order of reactivity was $\text{Co(III)} > \text{Mn(III)} > \text{Co(II)} > \text{Fe(III)} > \text{Ni(III)}$ with respect to peroxide decomposition. This order follows their redox potentials to some extent (Table XXII). The low activity of nickel and iron acetylacetonate was attributed to the comparatively small equilibrium constant for the formation of the metal hydroperoxide complex as well as catalyst deactivation. The relatively low equilibrium constants were attributed to the octahedral structure of the iron chelate and the trimeric structure of the nickel chelate in non polar solvents, which made the formation of a metal chelate hydroperoxide complex difficult. It was noted by Lombard and Knopf that anilino, dipyridyl, and a nitrous acid modified acetylacetonate complex had modified the activity of nickel. The dipyridyl complex was particularly active even at relatively long reaction times. This activity was explained in part by the planar configuration of the

dipyridyl complex, which favored the formation of a metal catalyst-peroxide complex. The stability of such a complex should be favored by electron donating properties of pyridine. The apparent inactivity of iron acetylacetonate was ascribed to its low oxidation potential in that solvent. T. Jochsberger and N. Indictor studied metal acetylacetonate-t-BuOOH catalysis of 1-octene in octyl chloride at 30°C.¹²¹ A similar order of reactivity was obtained for t-BuOOH decomposition and oxygen uptake. The order was $\text{Co(II)} > \text{Mn(III)} > \text{Co(III)} > \text{Cu(II)} > \text{Fe(III)} > \text{Al(III)} > \text{Ni(II)}$. Iron appears to be much more active oxidatively than its ability to decompose t-BuOOH would indicate. It was noted that no direct correlation existed between activity of the metal in autoxidation, styrene polymerization and olefin epoxidation. This holds true for amine oxidation in the presence of metal acetylacetonates and t-BuOOH as well.¹²²

K. Osawa correlated the ability of metal salts of stearic and lauric acid to decompose t-BuOOH to the metal's ability to oxidatively degrade polypropylene in bulk. There seemed to be a good correlation, except for copper (II) and iron (III) salts, which accelerated the thermal oxidative degradation of polypropylene, but did not accelerate the decomposition of t-BuOOH markedly. His order was $\text{Co(II)} > \text{Mn(II)} > \text{Cu(II)} > \text{Fe(III)} > \text{V(III)} > \text{Ni(II)} > \text{Al(III)}$. This order was similar to both Jochsberger and Indictor's work and Lombard and Knopf's work.¹²⁰

Kamiya did an extensive study on tetralin autoxidation catalyzed by various metal decanoates in pure tetralin and on metal acetates in acetic acid at 50°C.¹²⁴ Kamiya found that manganese (II) has a substantial induction period in the autoxidation reaction, which Kamiya attributed to manganese (II) decanoate's inhibitory properties. Deactivation of the

catalyst seems to occur in manganese (II) catalyzed autoxidations in an analagous manner to cobalt (II) catalyzed autoxidations (see previous section), but at a more rapid rate. Products formed during the autoxidation reaction seem to solubilize undissolved manganese (II) and as a result the reaction reaches a second maximum. Copper (II) decanoate seems less subject to deactivation and is an active catalyst, where nickel seems rather inactive. Nickel (II) seems to have a low peroxide-nickel equilibrium constant, which is indicated by the fact that the kinetic dependencies with respect to metal concentration and peroxide are unaffected by increasing peroxide concentration. Iron (III) also appears to be inactive. The rate constant for the decomposition of the metal-peroxide complex is smaller with iron than any other metal and the equilibrium constant for formation of the complex is low. The order of the metal activity seems to be related to experimental conditions. Peroxide must be added to manganese (II) and iron (III) decanoates for a reaction to occur. Copper (II) decanoate appeared to be deactivated when acetic acid was added to the tetralin solution. Qualitatively, however, cobalt, manganese, and copper were the most active and iron and nickel were the least active. A. Chalk and J. Smith provide similar results for the autoxidation of cylcohexane in the presence of metal heptoates.¹²⁵ They suggest that the ferric salt does not undergo a change of valence and does not initiate autoxidation effectively. Manganese (II) has a large induction period, which is accounted for by radical termination reactions of manganese (II). It was shown that diphenylpicrylhydrazyl reacts with manganese (II) to convert it to manganese (III) state.

Solvent Effects

The solvent may play a significant role in the autoxidation process also. In terms of initiation the solvent may alter the redox potential or compete with the hydroperoxide for sites on the metal. Solvation of the carrier radicals may influence propagation and termination rates. Solvation of the hydroperoxide may accelerate branching homolysis or promote heterolytic decomposition. Kamiya has found that a correlation exists between the dielectric constant of the medium and the rate of autoxidation.¹²⁶ He investigated a tetralin-cobalt decanoate system in a 1:1 solution of benzene to a given fatty acid. Six acids were used and a linear correlation was obtained between the dielectric constant vs. the rate of oxidation. This was attributed to an interaction of the solvent with the dipolar transition state of the propagation reaction. J. Howard and K. U. Ingold demonstrated that *o*, *o'* azo-bis-isobutyronitrile initiated are also sensitive to the dielectric constant of various solvents which were used.¹²⁷ Y. Kamiya and K. U. Ingold demonstrated that similar results and rate data could be obtained by cobalt, manganese, and copper decanoates under conditions where the hydroperoxide reaches a steady state concentration in these solvents.¹²⁸ Accordingly, metal peroxy radicals do not play any important role in oxidation of tetralin in these solvents under the experimental conditions employed. It should be noted that at low cobalt and high peroxide concentrations an inverse relation exists between dielectric constant of the medium and the oxidation rate. Under these conditions, the hydroperoxide concentration has not yet reached a steady state concentration. Fatty acids under these conditions can exert an influence on catalytic efficiency by blocking metal sites from peroxide. As a result, fatty acids of high dielectric constant would be more effective at inhibition than fatty acids of lower dielectric

since a more polar molecule would associate itself with the metal.

The formation of specific solvates of solvent with peroxide can increase oxidation rates. Chlorobenzene has been shown to form a specific solvate with cumene hydroperoxide as have other polar solvents and therefore caused an increase in the rate of autoxidation. The activation energy for peroxide homolysis was shown to decrease systematically with increasing polarity. Addition of caproic acid to t-BuOOH, accelerates overall autoxidation in decane. This suggests possible formation of a specific H-bonded complex. In metal catalyzed oxidations, however, acids generally decrease the rate of autoxidation due to their ability to coordinate with the metal interfering with hydroperoxide complex formation. However, when acids increase the relatively low catalyst solubility, the rate should increase. Kamiya observed that in non-polar media the addition of heptanoic acid increased the rate of oxidation of cobalt (II) catalyst but decreased the rate of autoxidation for manganese (II), copper (II), and nickel (III) catalysts.¹²⁴

Water may also play the dual role of both inactivating the metal catalyst and solubilizing the catalyst in non-polar media. Kamiya and Ingold found that the addition of 10% by volume of water increased the oxidation rate of tetralin in non-polar media in the presence of manganese, copper, and nickel decanoates.¹²⁴ However, Dyer found that water could inhibit the cobalt (II) catalyzed decomposition of tetralin hydroperoxide in cyclohexane in the presence of water.¹²⁹ Similar effects have been noted in relatively polar media. Dean and Skirrow studied the cobalt (II) catalyzed decomposition of t-BuOOH in acetic acid and found that water inhibited the reaction, apparently by hydrating the cobalt complex.⁸⁵ Water may also decrease the reactivities of the carrier radicals. This may increase reaction sensitivity. In the autoxidation of n-butane to

butanone, water retards the reaction, but improves the yield of ketone by stabilizing the 2-butyl peroxy radical and suppressing carbon-carbon bond scission.¹³⁰ It has been noted that in highly polar protic solvents (1-butanol, acetic acid, water), 2-butanone-3-hydroperoxide decomposition is relatively insensitive to changes of solvent. Activation energies are within 1 kcal.¹³¹

In general, the propagation rate constant is generally increased as the solvent medium is changed from non-polar to polar; it is maximized at some fairly high extent of polarity, and highly polar protic solvents such as water generally stabilize the peroxy radical sufficiently to reduce the value of k_p . The value of k_t is decreased in a similar manner.¹⁰⁷ In this discussion, k_p is the reaction constant for the propagation reaction (8) and k_t is the reaction constant for the termination reaction (16).

The termination reaction between two $\text{HO}_2^\cdot$ radicals was shown to be pH sensitive by Cyapski and Bielski in an esr study of H_2O_2 in aqueous solution. A maximum rate of recombination of peroxy radicals was shown to occur at a pH of 4.5, with a very sharp decrease in rate below a pH of 4.¹³²

Products formed from the autoxidation reaction may have variable effects on the autoxidation rate. It was mentioned previously that Kamiya found that manganese-tetralin autoxidation system would experience a second maximum due to the apparent solubilization of the catalyst by products of the reaction.¹²⁴ The influence of *t*-butyl alcohol (a decomposition product) on the decomposition of *t*-BuOOH by cobalt octanoate in chlorobenzene was one of severe retardation. Initial rates were only $1/100^{\text{th}}$ as fast as in pure chlorobenzene.⁹⁰ In part this is due to the enhanced rate of cleavage of *t*-butoxy radicals and the inhibition of the radical induced chain. This factor can only explain a factor of 8-10 at most.

The most likely explanation is that the alcohol affects the rate of metal ion hydroperoxide reactions, possibly by competing for ligand sites in the metal ion complexes. It should be noted that other workers have found that reaction products may have little effect on the autoxidation rate.¹³³ Reaction products may also have an effect on the metal valence state. In the oxidation of *n*-decane it was reported that the concentration of manganese (III) passes through a maximum, in which 20-30% of manganese existed in its trivalent state. It was thought that the oxidation products might react with the metal in order to reduce manganese (III) to manganese (II).¹³⁴ In fact, Denison and Emanuel, employed this reaction in an overall kinetic treatment of *n*-decane oxidation and were able to obtain a curve for manganese (III) concentration vs. time which closely resembles the actual curve.¹³⁵

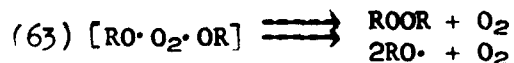
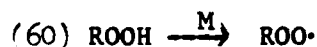
It should be noted that cobalt (III) rapidly oxidizes formaldehyde and methyl and ethyl alcohols in aqueous acid solution. The results would appear to be consistent with a direct electron transfer between cobalt (III) ion and the organic compound with the generation of a free radical.¹³⁶

Viscosity can have an effect on the autoxidation process. Hiatt and Traylor¹³⁸ and Mayo¹³⁹ studied the effect of viscosity on the formation of decomposition products from di-*t*-butylperoxyoxalate and found that changes in medium viscosity caused changes in the amount of various products formed. It was found that the yield of di-butyl peroxide increased strongly with solvent viscosity, suggesting that the peroxide results from cage combination of *t*-butoxy radicals. This interpretation was substantiated by carrying out the decomposition of di-*t*-butylperoxyoxalate in cumene hydroperoxide solutions where *t*-butoxy radicals are

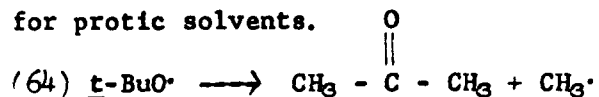
readily trapped by reaction (59).



Bartlett and Gunther discuss cage effects in the Pb tetraacetate- $\underline{t}$ -BuOOH initiating system.¹⁴⁰ Cage effects which are large, generally decrease slowly with rising temperature, corresponding to the competition between a coupling reaction with almost zero activation energy and a diffusion reaction conditioned by the temperature coefficient of fluidity of the solvent. In the following mechanism the $\underline{t}$ -butoxy radicals, which



escape the cage at elevated temperatures should be able to abstract a hydrogen from the peroxide, extending the radical chain. It was found at lower temperatures that the radical chain length decreased markedly in line with this mechanism. Hiatt found that in di- $\underline{t}$ -butyl peroxy oxalate induced decomposition of $\underline{t}$ -BuOOH a similar relationship with respect to chain length existed. Chain lengths as high as 50 (in the gas-phase at 100°) and as low as 1 (in Nujol at 35°) were found.⁸⁷ It should be noted that a 2.5 fold change in solvent viscosity corresponds to an apparent activation energy of 2.3 kcal/mole for diffusion. It is noted by Walling and Wagner¹⁴⁴ as well as Hiatt that below .2M $\underline{t}$ -BuOOH cleavage reactions for $\underline{t}$ -butoxy radicals become an important reaction and this is especially true for protic solvents.



Participation of $\text{CH}_3\cdot$ or $\text{CH}_3\text{O}_2\cdot$ in rapid termination reduces chain lengths.

It should be noted that Reich and Stivala³² and Bawn and Chaudhri⁴² have devised mechanisms for the autoxidation of polypropylene which do not require polymeric peroxy termination in a medium of high viscosity, but instead involve decomposition of tertiary oxy radicals and subsequent termination through primary polymeric radicals or $\text{CH}_3\cdot$ or $\text{CH}_3\text{OO}\cdot$ radicals. This mechanism was discussed in greater detail earlier in the thesis.

In the α, α' azo-bis-isobutyronitrile initiated autoxidation of polypropylene C. Bawn and S. Chaudhri found that the high viscosity medium of polypropylene in trichlorobenzene might exert an effect on the initiation process.¹⁴² Recombination of the initiator radicals of α, α' azo-bis-isobutyronitrile may occur when they are still in the same cage where they are formed, or they may undergo secondary recombination after slight diffusion (geminate recombination) or may combine with radicals from other dissociations. The extent of geminate recombination will be controlled by the rate of diffusion of the radicals, and the overall rate of production of free radicals in the system. It was found that in the autoxidation reaction the order with respect to initiator was .85 and with respect to polymer .37 to .12 over the concentration range studied.¹⁴² A model system (2,6,10,14 tetramethyl pentadecane) had reaction orders with respect to α, α' azo-bis-isobutyronitrile of .55, and with respect to substrate of 1.0. At low polymer concentrations, a higher order with respect to polymer is obtained. These results suggest that the high viscosity medium of concentrated polymer solutions favors geminate recombination of free radicals as an additional termination step, concurrent with the usual bimolecular termination of radicals. Kinetically this can lead to an increased dependance of α, α' azo-bis-isobutyronitrile with

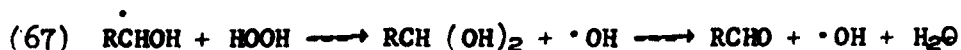
a decrease in importance with respect to polymer substrate. Bawn regards the treatment of geminate recombination as too complex to treat quantitatively.

The work of Mayo⁴³ and Kamiya⁴⁴ on the effect of solution viscosity on di-t-butylperoxyoxalate decomposition and polypropylene autoxidation was discussed in an earlier section. It should be noted that macroscopic viscosity increases due to increased polymer concentration in solution seem to have little effect on the efficiency of di-t-butylperoxyoxalate initiation reactions. Mayo found that polymer autoxidations seem to occur predominantly within a polymer cage in bulk. Solvent addition seems to increase the efficiency of initiation over bulk phase initiation. Cage recombination of t-butoxy radicals varies directly with the viscosity of the solution employed for solvents with similar properties.

Y. Kamiya found that the extent of cage recombination may be influenced by a specific interaction of t-butoxy radicals with the surrounding solvent molecules. This explanation was used to account for the decreasing formation of cage products in solvents of increasing polarity. The order was found to increase in the order of aliphatic, olefinic, aromatic, and protic solvents. A similar order is found with respect to solvent effects in t-butoxy radical cleavage. Alcohols completely suppress the formation of the cage product. A similar complex is expected to account for the effects observed in both these phenomena. Protic solvents would then be expected to suppress termination reactions.

Alcohol Oxidations

Alcohols may undergo both oxidation and cleavage with Fenton's reagent. J. Merz and W. Waters have described a simple chain process for the oxidation of various alcohols by Fenton's reagent.¹⁴³



Low alcohol concentrations

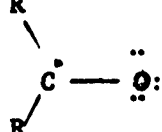


High alcohol concentrations

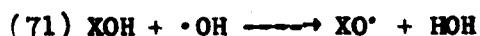


It should be noted that reaction (69) could explain glycol splitting as a disproportionation reaction of the alcohol radical. It was found that reaction (68) seems to be insignificant kinetically, since the ratio of k_{68}/k_{65} is not affected by addition of ferric sulfate.¹⁴⁴ Likewise, the representation of process (66) as an equilibrium process to explain a decrease in the ratio of $\frac{\Delta\text{RH}}{\Delta\text{Fe(II)}}$ with dilution seems to have little basis in fact, since it is unlikely that the alcohol radical can oxidize water to hydroxyl. At high alcohol concentrations $\Delta\text{Fe (II)}/\Delta\text{R-H}$ appears to approach an upper limit. This was explained by a disproportionation reaction (69). A later article by Merz and Waters suggested that disproportionation occurs only in a small number of reactions.¹⁴⁴ A unifying explanation for these two phenomena was suggested by the fact that free carbon radicals will tend to lose electrons, where oxygen radicals will tend to acquire an electron. However, by the loss of a proton both can give the same mesomeric

radical anion in which it is impossible to associate the odd electron exclusively with either the carbon or oxygen atom.



As a result, equations (71) and (72)

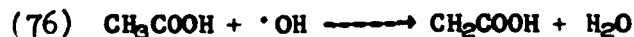
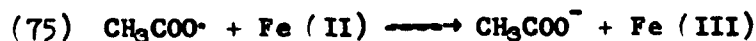


can be used to obtain kinetic expression (with eqns 65, 66, 67, 68) which could account for the dilution and saturation effects.

Kolthoff and Medalia have proposed an alternative explanation for the oxidation of ethanol.¹⁴⁵ The propagation reaction (67) could be replaced by reaction (73)



followed by fresh $\cdot\text{OH}$ radical production by the Fe(II) produced. This alternative is now generally accepted. Merz and Waters values for $\frac{k_{68}}{k_{65}}$ are on the order of 2-3 which seem implausibly high and have been criticized by Uri.¹⁴⁶ Kolthoff and Medalia have also found that certain substances such as acetic acid and acetone (products of acetaldehyde oxidation) interfere with Fenton reagent chains. Here processes such as (74) and (75)



have been suggested, although (76) is a plausible alternative since the product radical could also readily act as an oxidizing agent to give relatively stable enolate anion. The data strongly supported the view that acetic acid and ethanol compete for the active intermediates formed in the reaction between ferrous ion and hydrogen peroxide.

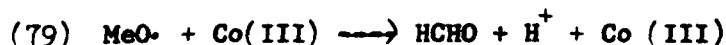
The acetate radicals do not give rise to decomposition of hydrogen peroxide, while hydroxyethyl free radicals do. Thus acetic acid suppresses the induced aut oxidation of ethanol observed in the reaction between ferrous iron and hydrogen peroxide.

Various sugars and alcohols (especially α keto alcohols) have been shown to have a catalytic effect on various free radical reactions (e.g. polymerization) with Fenton's reagent. One author has attributed this to activation by an iron-sugar complex.¹⁴⁷ It is possible that the alcohol radicals formed might be more effective in initiating polymerization,¹⁴⁸ for instance, or that oxidation products of the sugar are effectively reducing the ferric ion to ferrous ion.¹⁴⁹ In the simplest view, the chemical process consists of reduction of ferric ion to ferrous ion by sugar, followed by oxidation of ferrous to ferric iron by peroxide, with free radicals which are the active initiating agents formed only in the latter step.¹⁴⁷ It should be noted that the peroxide and sugar in the absence of iron can under certain circumstances achieve comparable polymerization rates, suggesting a direct reaction between the reactants.

Cobaltic ion has been hypothesized to react directly with alcohols and aldehydes in an electron transfer reaction between cobaltic ion and the organic molecule with the formation of an alkoxy radical.¹⁵⁰ Specifically,

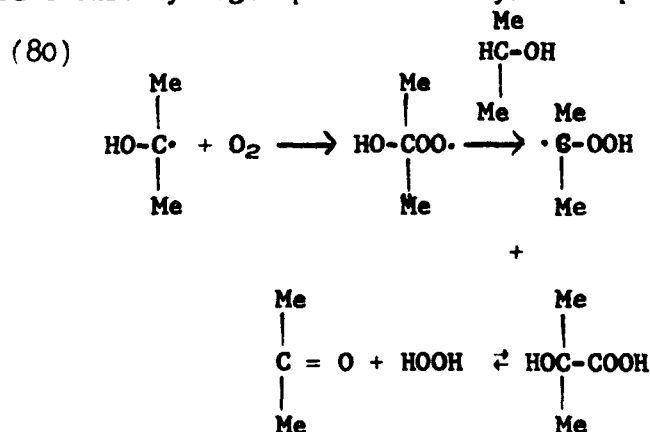


in the case of methanol in 5N sulphuric acid the presence of an induction period and the effect of acid concentration militate against this simple scheme. The radical produced may react with the solvent, the original organic compound, or further radical, or a cobaltic ion.



The aldehyde formed may react further to form the acid, Ethyl and propyl alcohol follow similar kinetics.

Various mechanisms involve secondary alcohols undergoing auto-oxidation reactions. The primary products are ketone e.g. acetone from isopropyl alcohol ¹⁵⁷ and cyclohexanone from cyclohexanol. ¹⁵² In secondary alcohols the hydroxyl group exerts a moderate activating effect upon the geminal C-H bond. Consequently peroxy radicals, like carbon radicals abstract this hydrogen preferentially. The preferred mechanism is



Indeed the first products of cyclohexanol autooxidation is 1-hydroxy 1-hydroperoxycyclohexane. ¹⁵² If these autooxidations are carried out in the absence of H_2O_2 decomposition catalysts, equivalent amounts of ketone and H_2O_2 are found in the reaction mixture.

It is commonplace that alcohols often retard other autoxidizing systems. This appears to arise from a combination of two factors: intermolecular deactivation of the peroxy radicals via hydrogen bonding and intramolecular hydrogen bonding of the alcohol derived peroxy radicals. ¹⁵³ The effect of general radical solvation is to lower k_p

and k_t for the secondary alcohol radical. In this case, k_p is the propagation rate constant for a reaction similar to reaction (8) and k_t is the termination rate constant for a reaction such as (16).

II RESULTS

TABLE I

U.V. SPECTRAL CHANGES^d FOR PVA, COBALT (II) AND (III) ACETYLACETONATE
AND t-BuOOH IN DMSO SOLUTION AT 42°C

$[\text{Co} \times 10^5]_0$ M	$[\text{t-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	B_1^a	B_2^b	U^c
<u>Co(acac)₂</u>					
4.12	.016	.53	.85	.92	.88
4.21	"	1.06	.86	.87	.78
4.53	"	1.60	.84	.85	.81
9.42	"	.53	.85	.91	.85
9.25	"	1.06	.87	.89	.87
9.60	"	1.60	.85	.82	.83
17.1	"	.53	.78	.85	.85
17.5	"	1.06	.87	.83	.85
17.4	"	1.60	.87	.80	.84
<u>Co(acac)₃</u>					
1.86	.016	.53	.10	.78	.78
1.95	"	1.06	.11	.80	.75
1.75	"	1.60	.13	.80	.75
4.37	"	.53	.16	.70	.80
4.56	"	1.06	.19	.72	.81
4.25	"	1.60	.16	.74	.80
30.7	"	.53	.10	.69	.75
31.2	"	1.06	.12	.72	.76
30.2	"	1.60	.13	.70	.74

$$a \quad B_1 = \frac{[Co(acac)_2]}{[Co(acac)_2 + Co(acac)_3]} \quad \text{measured at } 1 \times 10^4 \text{ secs}$$

$$b \quad B_2 = \frac{[Co(acac)_2]}{[Co(acac)_2 + Co(acac)_3]} \quad \text{measured at } 2 \times 10^5 \text{ secs}$$

$$c \quad U = [Co(acac)_2 + Co(acac)_3] / [Co(acac)_n]_0 \quad \text{measured at } 2 \times 10^5 \text{ secs}$$

d In vacuo

TABLE II

U.V. SPECTRAL CHANGES^d FOR PVA, COBALT (II) AND (III) ACETYLACETONATE
AND t-BuOOH IN AQUEOUS SOLUTION AT 42°C

$[\text{Co} \times 10^5]_0$ M	$[\text{t-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	B_1^a	B_2^b	U^c
<u>Co(acac)₂</u>					
17.5	.016	.53	.57	.22	.81
17.5	"	1.06	.57	.19	.80
17.5	"	1.60	.57	.25	.77
39.1	"	1.06	.48	.32	.81

<u>Co(acac)₃</u>					
10.1	.016	.53	.29	.16	.81
10.3	"	1.06	.23	.14	.80
10.5	"	1.60	.23	.16	.83
35.1	"	1.06	.25	.20	.75

$$a \quad B_1 = \frac{[\text{Co(acac)}_2]}{[\text{Co(acac)}_2 + \text{Co(acac)}_3]} \quad \text{measured at } 1 \times 10^4 \text{ secs}$$

$$b \quad B_2 = \frac{[\text{Co(acac)}_2]}{[\text{Co(acac)}_2 + \text{Co(acac)}_3]} \quad \text{measured at } 1 \times 10^5 \text{ secs}$$

$$c \quad U = [\text{Co(acac)}_2 + \text{Co(acac)}_3] / [\text{Co(acac)}_n]_0 \quad \text{measured at } 2 \times 10^5 \text{ secs}$$

d In vacuo

TABLE III

RATES OF PEROXIDE DECOMPOSITION; ^{a, c} t-BuOOH IN THE PRESENCE OF COBALT
(II) AND (III) ACETYLACETONATES AND PVA IN DMSO SOLUTION AT 42°C

$[Co \times 10^5]_0$ $[t\text{-BuOOH}]_0$ $[PVA]_0$ $-[t\text{-BuOOH}/\Delta t] \times 10^9$ $[\tau_1^0 \times 10^{-5}]$
M M g/dl M/sec $\frac{1}{2}$ secs

DIMETHYL SULFOXIDE

<u>Co(acac)₃</u>				
4.12	0.16	.53	16.3	6.80
4.21	.016	1.06	18.8	5.90
4.53	.016	1.60	22.7	4.88
9.42	.016	.53	24.3	4.56
9.25	.016	1.06	30.2	3.67
9.60	.016	1.60	34.2	3.24
17.1	.016	.53	33.2	3.33
17.5	.016	1.06	40.1	2.76
17.4	.016	1.60	46.7	2.37
2.72	.160	.53	27.5	40.3
2.72	.160	1.06	32.5	34.1
2.72	.160	1.60	38.6	28.7
6.85	.016	.53	20.1	5.51
6.85	.060	.53	25.1	16.6
6.85	.160	.53	41.2	26.9
6.85	.660	.53	82.3	55.6
6.85	.960	.53	78.1	85.2
6.85	.016	1.06	24.5	4.52
6.85	.060	1.06	32.5	12.8

6.85	.160	1.06	52.0	21.3
6.85	.660	1.06	98.0	46.6
6.85	~~.960~~	~~1.06~~	~~94.7~~	70.3
6.85	.016	1.60	29.0	3.82
6.85	.060	1.60	67.0	16.5
6.85	.660	1.60	131.0	34.9
6.85	.960	1.60	118.2	56.2
13.7	.016	.53	29.0	3.82
13.7	.160	.53	60.1	18.4
13.7	.660	.53	115.1	39.7
13.7	.016	1.06	38.0	2.92
13.7	.160	1.06	82.0	13.5
13.7	.660	1.06	163.1	28.0
13.7	.016	1.60	46.3	2.39
13.7	.160	1.60	101.1	11.0
3.66	.660	1.06	78.1	85.2

Co(acac)₃

1.86	.016	.53	9.6	11.55
1.95	.016	1.06	11.5	9.64
1.75	.016	1.60	13.0	8.53
4.37	.016	.53	14.2	7.81
4.56	.016	1.06	17.0	6.52
4.25	.016	1.60	21.2	5.23
30.7	.016	.53	37.5	2.96
31.2	.016	1.06	48.1	2.31
30.2	.016	1.60	55.1	2.01
1.95	.660	1.06	46.2	99.0

a The rate of peroxide decomposition = $.693 [\text{t-BuOOH}]_0 / \tau_{\frac{1}{2}} \times 10^9$

b $\tau_{\frac{1}{2}}$ = the half life for the peroxide decomposition

c In vacuo

TABLE IV

INITIAL RATES OF PEROXIDE DECOMPOSITION a, c FOR PVA, COBALT (II) AND (III) ACETYLACETONATE, AND t -BuOOH IN AQUEOUS SOLUTION AT 42°C

$[Co \times 10^5]_0$ M	$[t\text{-BuOOH}]_0$ M	$[PVA]_0$ g/dl	$-(\Delta t\text{-BuOOH}/\Delta t) \times 10^9$ M/sec	$\tau_{1/2}^b \times 10^{-5}$ sec
<u>Co(acac)₃</u>				
17.5	.016	.53	5.50	20.2
17.5	.016	1.06	6.91	16.0
17.5	.016	1.60	8.65	12.8
2.0	.016	1.06	2.45	45.2
39.1	.016	1.06	10.95	10.12
17.5	.060	1.06	13.50	30.8
17.5	.160	1.06	28.30	39.2
2.0	.660	1.06	27.10	169.0
17.5	.660	1.06	91.20	50.2
<u>Co(acac)₂</u>				
10.1	.016	.53	3.45	32.1
10.3	.016	1.06	4.71	23.5
10.5	.016	1.60	5.51	20.1
2.0	.016	1.06	2.15	51.6
35.1	.016	1.06	8.45	13.1
10.6	.060	1.06	9.31	44.7
10.6	.160	1.06	19.50	56.9
2.0	.660	1.06	17.50	261.4
10.6	.660	1.06	65.6	69.7

- a The rate of peroxide decomposition = $.693[\text{t-BuOOH}]_0 / \tau_{\frac{1}{2}} \times 10^9$
- b $\tau_{\frac{1}{2}}$ = the half life for peroxide decomposition
- c In vacuo

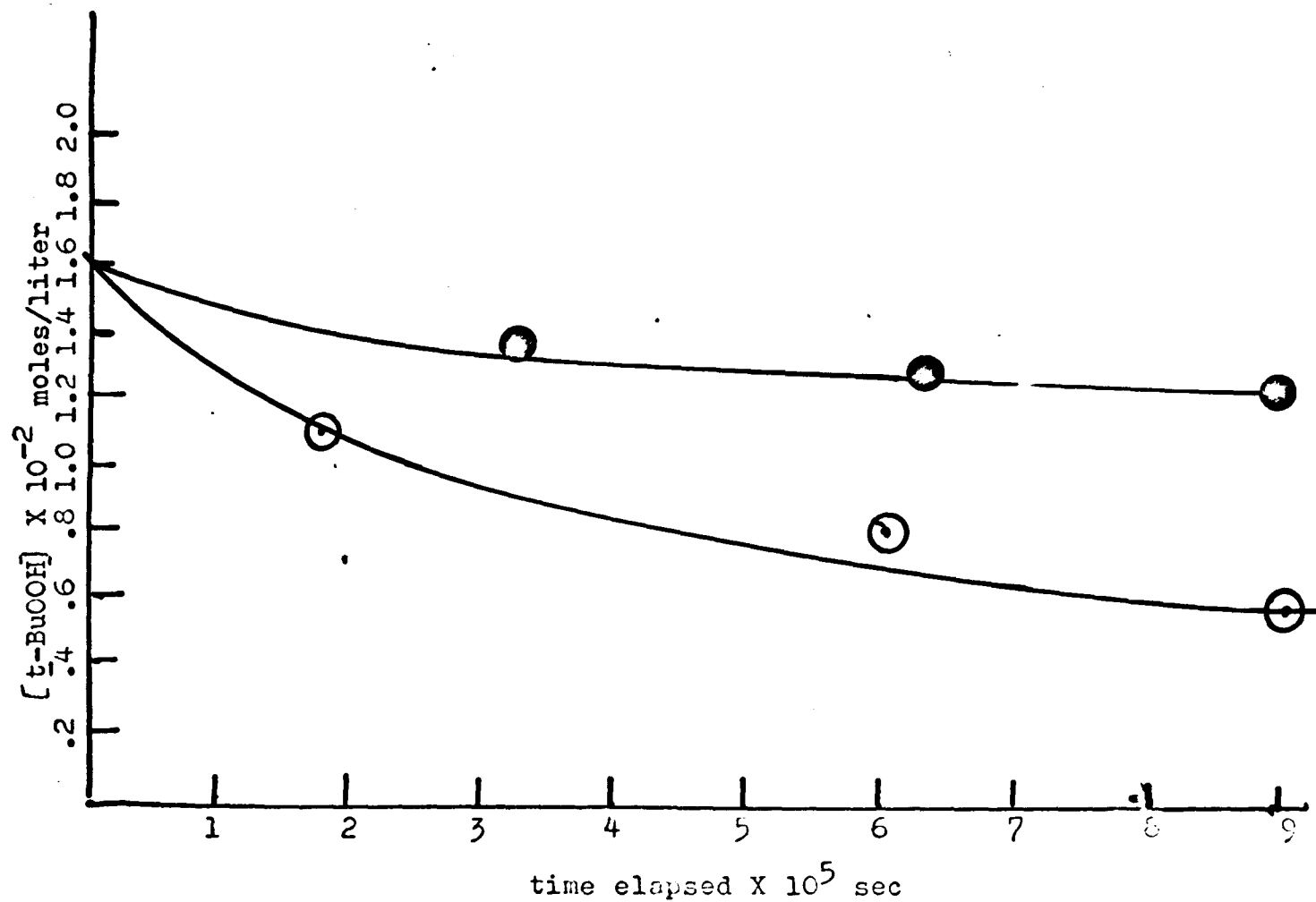


Figure (1) : The decrease of t-BuOOH with time in the presence of 4.2×10^{-5} M cobalt (II) acetylacetonate, .016M t-BuOOH, and 1.06 g/dl PVA in a DMSO and aqueous solution at 42°C .

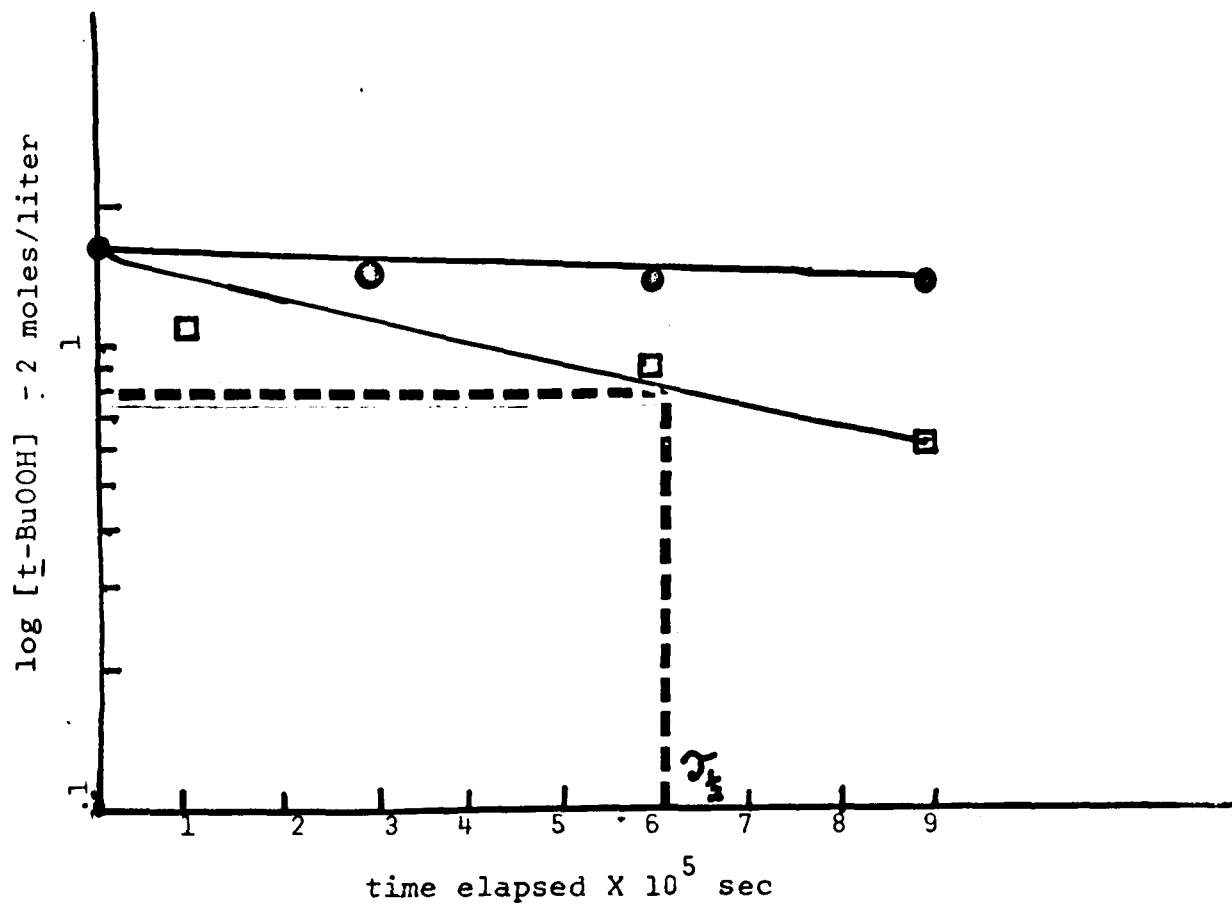


Figure (1b) : The logarithm of the $[t\text{-BuOOH}]$ vs time elapsed in the reaction for $\square$ DMSO and $\bullet$ aqueous reaction mixtures under identical conditions as employed in Figure (1a).

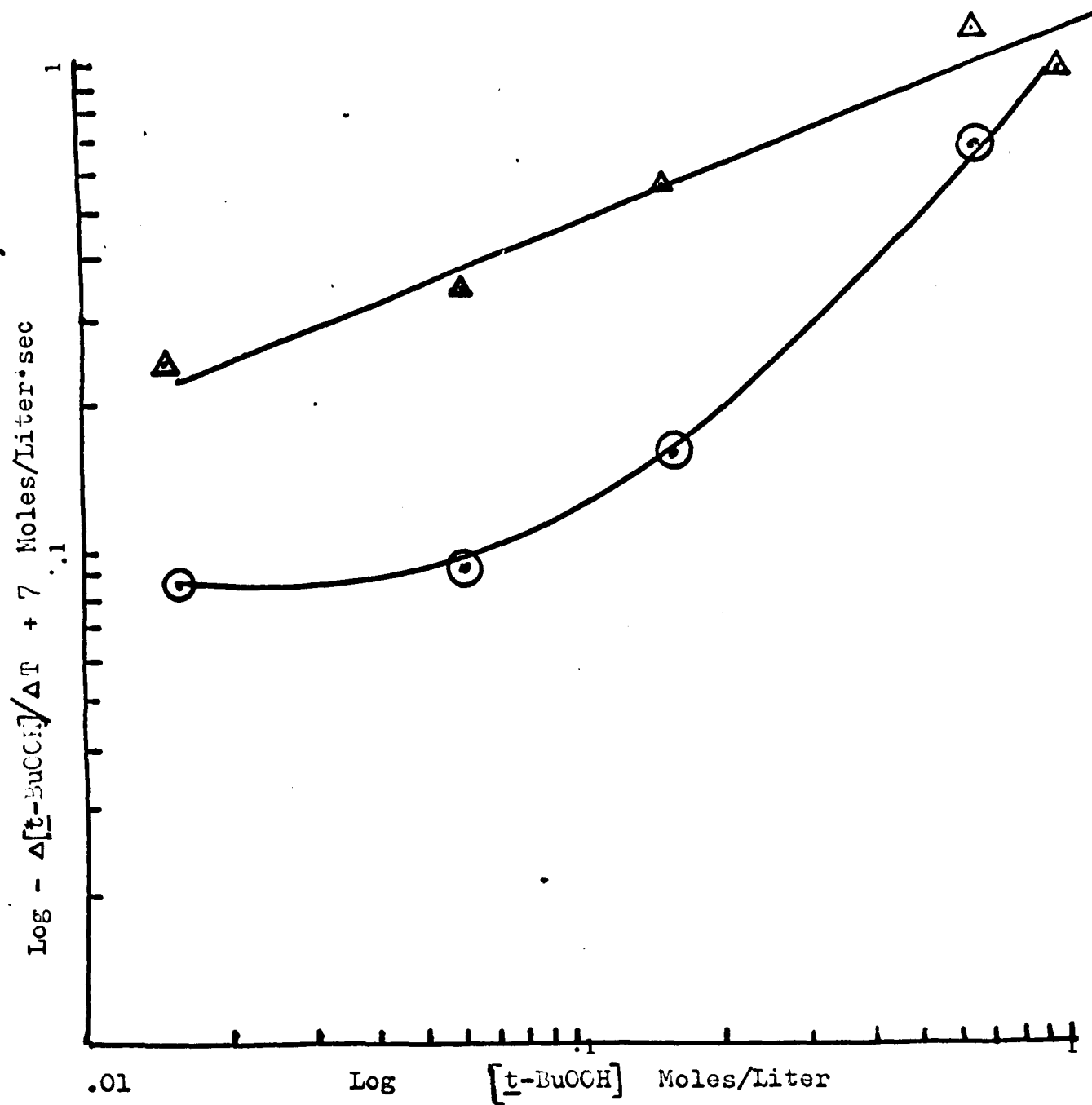


Figure (2) : The rate of peroxide decomposition as a function of peroxide concentration in the presence of 6.85×10^{-5} M cobalt (II) acetylacetonate and 1.06 g/dl PVA in Δ DMSO and $\circ$ aqueous solution at 42°C .

TABLE V

EMPIRICAL RATE EQUATIONS AND THE EVALUATION OF EXPONENTS FOR t-BuOOH
DECOMPOSITION IN DMSO SOLUTION AT 42°C

$$- \Delta[\text{t-BuOOH}] / \Delta t = k [\text{Co}]^a [\text{t-BuOOH}]^b [\text{PVA}]^c$$

$[\text{Co} \times 10^5]_0$ M	$[\text{t-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	a	b	c	$k^a \times 10^4$
<u>Co(acac)₃</u>						
4.12-17.5	.016	.53-1.60	.55±.01			.12±.02
2.7 -13.7	.16	.53-1.60	.55±.01			.60±.03
6.85	.016-.06	.53-1.60		.14±.01		.10±.02
6.85	.06-.96	.53-1.60		.47±.02		.61±.03
4.12-17.5	.016-.66	.53-1.60			.35±.05	.60±.05
<u>Co(acac)₃</u>						
1.86-30.7	.016	.53-1.60	.52±.02			.41±.03
1.86-4.50	.016	.53-1.60			.35±.05	.42±.04
30.5	.016	.53-1.60			.30	.41
2.0	.016-.66	1.06		.48		.40

a Units of $[\text{PVA}]_0$ are grams of polymer/(GMW of monomer unit x liters)
for the calculation of k

TABLE VI

EMPIRICAL RATE EQUATIONS AND THE EVALUATION OF EXPONENTS FOR t -BuOOH
DECOMPOSITION IN AQUEOUS SOLUTION AT 42°C

$$-(\Delta t\text{-BuOOH}/\Delta t) = k[\text{Co}]^a [t\text{-BuOOH}]^b [\text{PVA}]^c$$

$[\text{Co} \times 10^5]_0$ M	$[t\text{-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	a	b	c	$k^a \times 10^4$
<u>Co(acac)₂</u>						
2.00-39.1	.016	1.06	.50±.05			.13
17.5	.016-.16	1.06		.66±.04		.12
17.5	.16-.66	1.06		.81±.10		.26
17.5	.016	.53-1.6			.47±.03	.13
<u>Co(acac)₃</u>						
2.00-35.1	.016	1.06	.49±.05			.072
10.6	.016-.16	1.06		.53±.06		.073
10.6	.16-.66	1.06		.78±.10		.16
10.6	.016	1.06			.46±.03	.071

a Units of $[\text{PVA}]_0$ are grams of polymer/ (GMW of monomer units x liters)
for the calculation of k

TABLE VII

ACTIVATION PARAMETERS FOR THE AUTOXIDATION AND CLEAVAGE OF PVA AND THE
DECOMPOSITION OF t-BuOOH AT 42°C AND 60°C

[Co x 10 ⁵] ₀ M		[t-BuOOH] ₀ M	[PVA] ₀ g/dl	E _a kcal/mole		$\Delta H^\ddagger$ kcal/mole		$\Delta S^\ddagger$ cal/deg-mole	
II	III			DMSO	H ₂ O	DMSO	H ₂ O	DMSO	H ₂ O
A. Autoxidation of PVA									
17.5		.016	1.06	7.8	7.4	6.5	6.1	-44	-49
	10.6	.016	1.06	10.1	8.7	8.8	7.4	-35	-37
B. Decomposition of t-BuOOH									
17.5		.016	1.06	27.1	28.2	25.8	26.9	82.7	93.7
	10.6	.016	1.06	27.3	28.5	26.0	27.2	82.4	103
C. Cleavage of PVA									
17.5		.016	1.06	28.7	28.1	27.4	26.8	101	68.8
	10.6	.016	1.06	24.8	29.8	23.5	28.5	100	68.5

TABLE VIII

EMPIRICAL RATE EQUATIONS AND THE EVALUATION OF EXPONENTS FOR THE
 AUTOXIDATION OF PVA IN DMSO SOLUTION AT 42°C

$$-(\Delta O_2/\Delta t) = k[Co]^a[t-BuOOH]^b[PVA]^c$$

[Co x 10 ⁵] ₀ M	[t-BuOOH] ₀ M	[PVA] ₀ g/dl	a		b		c		k ^c x 10 ⁴	
			II ^a	III ^b	II ^a	III ^b	II ^a	III ^b	II ^a	III ^b
6.85-27.4	.16	.53	.47	.67					1.4	1.1
"		1.06	.48	.62					1.4	1.1
"		1.60	.45	.53					1.1	1.1
"	.66	.53	.34	.53					.88	.70
"		1.06	.40	.44					.84	.61
"		1.60	.43	.53					.81	.48
"	.96	.53	.39	.55					.26	.22
"		1.06	.47	.53					.25	.19
"		1.60	.48	.63					.27	.16
6.85	.16	.53-1.6					.57	.54	1.4	.94
"	.66	"					.43	.29	.84	.61
"	.96	"					.50	.25	.26	.18
13.7	.16	.53-1.6					.57	.41	1.4	1.0
"	.66	"					.56	.29	1.1	.84
"	.96	"					.53	.26	.73	.65
27.4	.16	.53-1.6					.50	.38	1.4	1.1
"	.66	"					.52	.28	1.0	.69
"	.96	"					.50	.26	.81	.62

			a		b		c		k x 10⁴	
			II	III	II	III	II	III	II	III
6.85	.16-.96	.53			.40	.56			.85	.70
"	"	1.06			.42	.46			.83	.63
"	"	1.60			.35	.27			.73	.58
13.7	"	.53			.33	.48			1.2	.83
"	"	1.06			.34	.41			1.1	.77
"	"	1.60			.23	.32			1.0	.72
27.4	"	.53			.38	.37			1.1	.81
"	"	1.06			.30	.29			1.0	.79
"	"	1.60			.25	.29			1.0	.75

a Catalyzed by $\text{Co}(\text{acac})_2$

b Catalyzed by $\text{Co}(\text{acac})_3$

c. Units of $[\text{PVA}]_0$ are grams of polymer/(GMW of monomer unit x liters)
for the calculation of k.

TABLE IX

EMPIRICAL RATE EQUATIONS AND THE EVALUATION OF EXPONENTS FOR THE
 AUTOXIDATION OF PVA IN AQUEOUS SOLUTION AT 42°C

$$-(\Delta O_2 / \Delta t) = k [Co]^a [t-BuOOH]^b [PVA]^c$$

[Co(III) x 10 ⁵]	t-BuOOH	PVA	a	b	c	k x 10 ⁴
6.85-27.4	.16-.66	.53	.50	.50		2.1
"	"	1.06	.38	.51		2.0
"	"	1.60	.50	.47		2.1
6.85	.16-.66	.53-1.6			.39	2.2
13.7	"	"			.37	2.5
27.4	"	"			.39	2.7

TABLE X

INITIAL RATES OF OXYGEN UPTAKE FOR PVA IN THE PRESENCE OF COBALT (II)
AND (III) ACETYLACETONATE AND t-BuOOH IN DMSO SOLUTION AT 42°C

$[\text{Co} \times 10^5]_0$ M	$[\text{t-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	$-(\Delta O_2 / \Delta t) \times 10^7$ M/sec	
			II ^b	III ^c
6.85	.16	.53	1.64	1.08
6.85	.66	.53	2.92	2.32
6.85	.96	.53	2.24	1.88
13.7	.16	.53	2.16	1.60
13.7	.66	.53	3.40	3.12
13.7	.96	.53	3.10	3.05
27.4	.16	.53	3.31	2.72
27.4	.66	.53	4.48	4.48
27.4	.96	.53	4.00	4.20
6.85	.16	1.06	2.24	1.52
6.85	.66	1.06	3.92	2.84
6.85	.96	1.06	3.03	2.28
13.7	.16	1.06	3.12	2.24
13.7	.66	1.06	5.00	3.92
13.7	.96	1.06	4.00	3.56
27.4	.16	1.06	4.48	3.56
27.4	.66	1.06	6.80	5.20
27.4	.96	1.06	5.36	4.84
6.85	.16	1.60	3.44	2.16
6.85	.66	1.60	5.36	3.12
6.85	.96	1.60	4.68	2.68

TABLE X (cont)

13.7	.16	1.60	4.92	2.88
13.7	.66	1.60	6.80	4.48
13.7	.96	1.60	6.24	4.00
27.4	.16	1.60	6.80	4.48
27.4	.66	1.60	9.64	6.68
27.4	.96	1.60	8.40	6.68
202	.66	1.06	8.50	7.50
404	.66	1.06	9.20	9.40
1010	.66	1.06	8.40	9.10
6.85	.016	1.06	1.06	.92
6.85	.016	n	.30	.20

a Under oxygen atmosphere

b Catalyzed by $\text{Co}(\text{acac})_2$

c Catalyzed by $\text{Co}(\text{acac})_3$

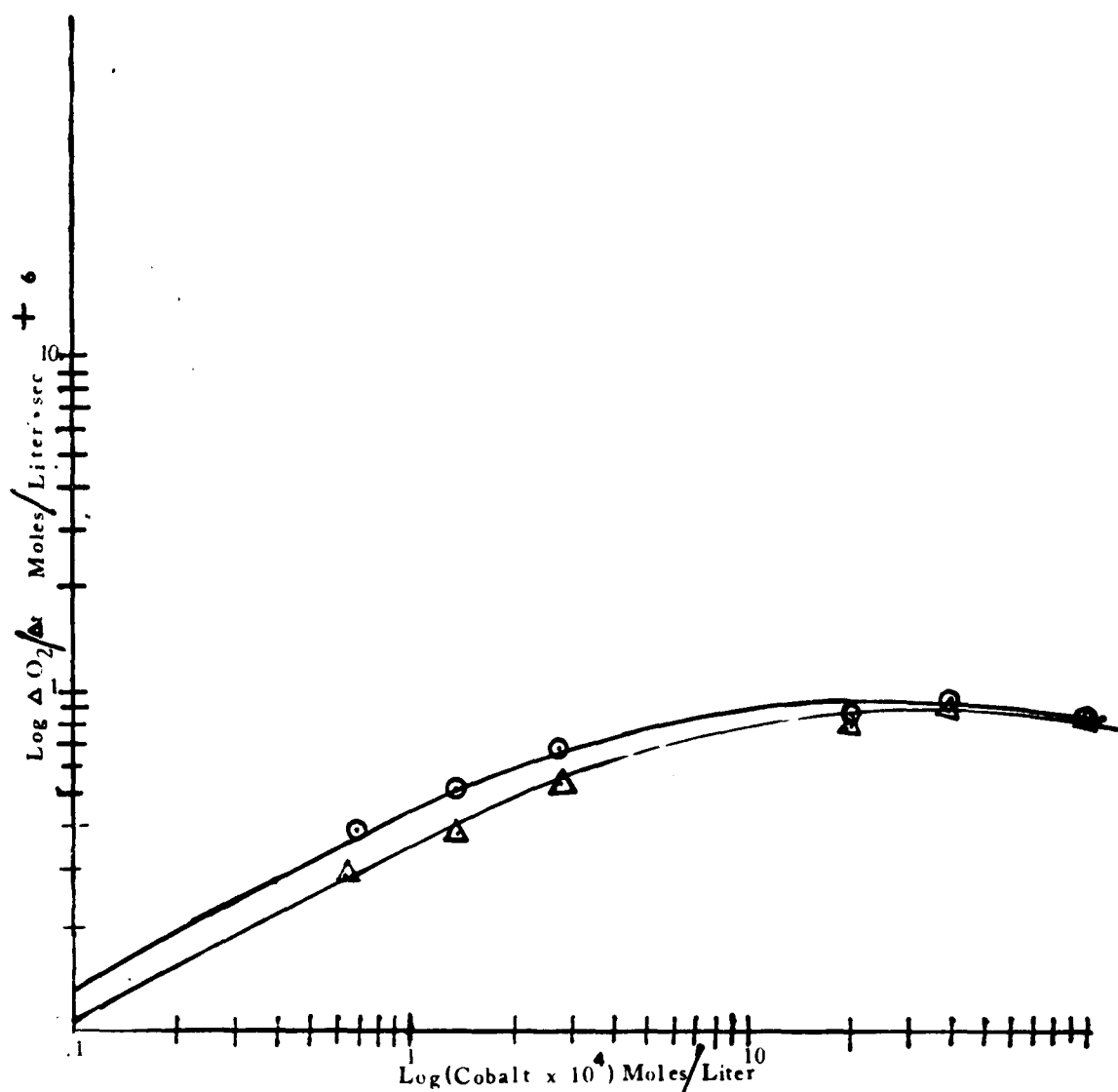


Figure (3) : The initial rate of oxygen uptake with increasing cobalt acetylacetonate concentration in DMSO solution in the presence of .66 M t -BuOOH, and 1.06 g/ dl PVA and $\odot$ cobalt (II) and $\triangle$ cobalt(III) acetylacetonate at 42°C .

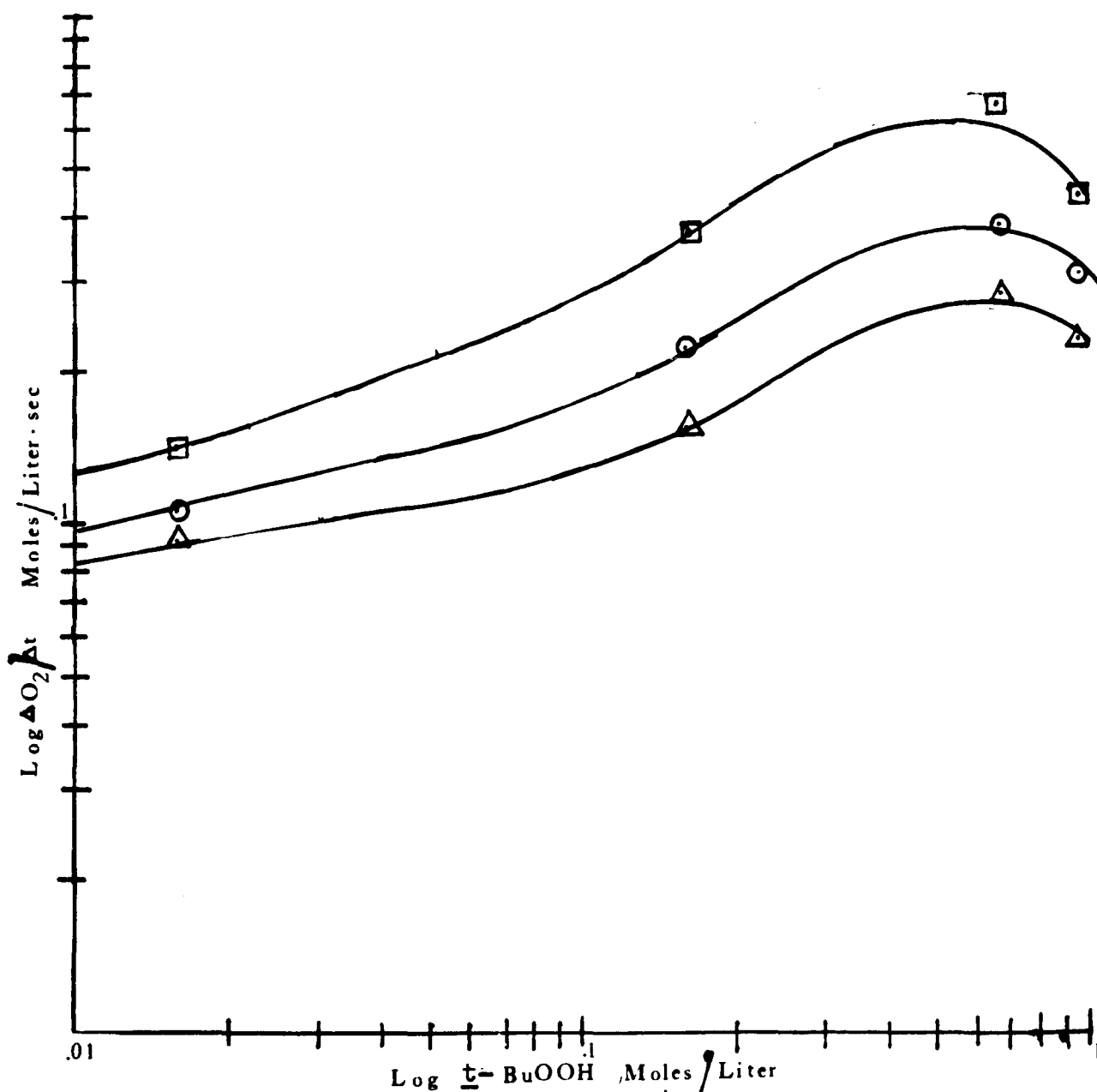


Figure (4) : The initial rate of oxygen uptake in the presence of $6.85 \times 10^{-5} \text{ M}$ $\odot$ cobalt (II) and $\triangle$ cobalt (III) acetylacetonate and 1.06 g/dl PVA as a function of $t\text{-BuOOH}$ concentration in DMSO solution and in the presence of $6.85 \times 10^{-5} \text{ M}$ $\square$ cobalt (II) acetylacetonate and 1.06 g/dl PVA as a function of $t\text{-BuOOH}$ concentration in aqueous solution at 42°C .

TABLE XI

INITIAL RATES OF OXYGEN UPTAKE^b FOR PVA IN THE PRESENCE OF COBALT (II)
ACETYLACETONATES AND t-BuOOH IN AQUEOUS SOLUTION AT 42°C

$[\text{Co(II)} \times 10^5]_0$ M	$[\text{t-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	$-(\Delta O_2/\Delta t) \times 10^7$ M/sec
6.85	.16	.53	3.00
6.85	.66	.53	6.08
6.85	.96	.53	3.60
13.7	.16	.53	4.20
13.7	.66	.53	8.51
27.4	.16	.53	5.92
27.4	.66	.53	12.0
6.85	.16	1.06	3.72
6.85	.66	1.06	6.44(6.72) ^a
6.85	.96	1.06	4.40
13.7	.16	1.06	5.35
13.7	.66	1.06	9.21(9.60) ^a
27.4	.16	1.06	7.50
27.4	.66	1.06	12.9(13.5) ^a
6.85	.16	1.60	4.48
6.85	.66	1.60	8.80
6.85	.96	1.60	6.24
13.7	.16	1.60	6.30
13.7	.66	1.60	12.3
27.4	.16	1.60	8.81
27.4	.66	1.60	17.5

6.85	.016	1.06	1.40
6.85	.016	n	.25

a Catalyzed by Co(III)(acac)₃

b Under oxygen atmosphere

TABLE XII

KINETIC CHAIN LENGTHS FOR THE AUTOXIDATION OF PVA IN THE PRESENCE OF
 COBALT (II) ACETYLACETONATE AND t -BuOOH IN DMSO AND WATER AT 42°C

$[\text{Co} \times 10^5]_0$ M	$[t\text{-BuOOH}]_0$ M	DMSO $[\text{PVA}]_0$ g/dl	C_1^a
6.85	.16	.53	4.0
6.85	.66	.53	3.6
6.85	.96	.53	2.9
13.7	.16	.53	4.3
13.7	.66	.53	4.0
13.7	.96	.53	3.2
27.4	.16	.53	5.1
27.4	.66	.53	4.1
27.4	.96	.53	4.0
6.85	.16	1.06	4.3
6.85	.66	1.06	4.0
6.85	.96	1.06	3.2
13.7	.16	1.06	3.8
13.7	.66	1.06	3.1
13.7	.96	1.06	2.7
27.4	.16	1.06	3.9
27.4	.66	1.06	2.9
27.4	.96	1.06	2.6
6.85	.16	1.60	5.1
6.85	.66	1.60	4.1

6.85	.96	1.60	4.0
13.7	.16	1.60	4.9
13.7	.66	1.60	3.4
13.7	.96	1.60	3.4
27.4	.16	1.60	4.7
27.4	.66	1.60	3.4
27.4	.96	1.60	3.3

a $C_1 = \frac{\text{Initial rate of autoxidation}}{\text{Initial rate of peroxide decomposition}}$

TABLE XIII

KINETIC CHAIN LENGTHS FOR THE AUTOXIDATION OF PVA IN THE PRESENCE
OF COBALT (II) AND (III) ACETYLACETONATES AND t -BuOOH IN AQUEOUS
SOLUTION AT 42°C

$[\text{Co} \times 10^5]_0$ M	$[t\text{-BuOOH}]_0$ M	$[\text{PVA}]_0$ g/dl	C_1^a
6.85	.16	.53	24.0
6.85	.66	.53	15.1
13.7	.16	.53	23.7
13.7	.66	.53	14.9
27.4	.16	.53	23.7
27.4	.66	.53	14.9
6.85	.16	1.06	21.0
6.85	.66	1.06	11.3
13.7	.16	1.06	21.3
13.7	.66	1.06	11.4
27.4	.16	1.06	21.2
27.4	.66	1.06	11.3
6.85	.16	1.60	20.4
6.85	.66	1.60	12.4
13.7	.16	1.60	20.3
13.7	.66	1.60	12.2
27.4	.16	1.60	20.4
27.4	.66	1.60	12.3

^a $C_1 = \frac{\text{Initial rate of autoxidation}}{\text{Initial rate of peroxide decomposition}}$

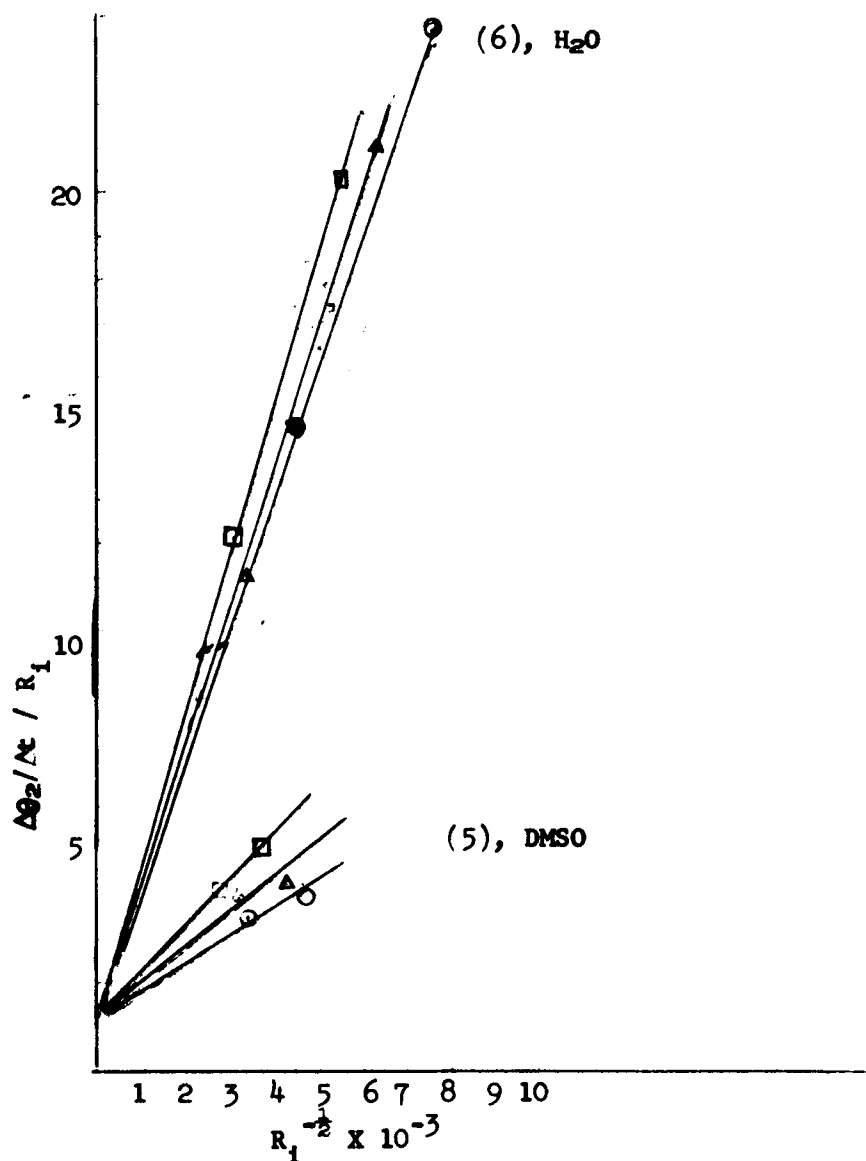


Figure (5, 6) : The kinetic chain length for the autoxidation of poly(vinyl alcohol)- vs R_1^{-1} in the presence of 1.3×10^{-4} M cobalt (II) acetylacetonate, .16-.66M t-BuOOH, and o .53 g/dl, Δ 1.06 g/dl $\square$ 1.60 g/dl poly(vinyl alcohol) in water and dimethyl sulfoxide solution at 42°C.

TABLE XIV

INITIAL CLEAVAGE RATES OF POLY(VINYL ALCOHOL)^a IN THE PRESENCE OF
COBALT (II) AND COBALT (III) ACETYLACETONATES AND t-BUTYL
HYDROPEROXIDE^b IN WATER AND DIMETHYL SULFOXIDE

[Co(acac) ₂] ₀ x 10 ⁵ M	[Co(acac) ₃] ₀ x 10 ⁵ M	[-Δ $\bar{M}_v$ /Δt] ₀ x 10 ² g/mole-sec	
		H ₂ O	DMSO
42°C			
0.00	0.00	0.00	1.90
0.00	0.402	n ^c	2.53
0.00	1.48	0.656, 0.943 ^{d, e}	n
0.00	1.71	n	7.22, ^e 4.84
0.00	1.79	n	1.56 ^{d, f}
0.00	4.02	n	5.09
0.00	6.44	n	6.53
0.00	13.6	n	7.50
0.00	14.2	1.39 ^e	n
0.622	0.0	n	2.53
1.97	0.0	1.33 ^e	n
2.06	0.0	0.578	n
2.12	0.0	n	8.67, 0.348 ^{d, f}
2.12	1.79	n	19.4
2.49	0.0	n	8.67
6.22	0.0	n	18.5
9.96	0.0	n	20.2
30.3	0.0	0.522, ^{e, f} 0.00 ^f	n
30.3	0.0	1.75	n
30.3	1.58	1.24, ^{e, f} 0.00 ^f	n

30.3	1.58	1.31, 2.39 ^e	n
30.3	1.58	1.60 ^g	n
135	0.0	0.0 ^f , 1.39 ^{e, f}	n
135	0.0	3.98 ^e	n
0.0	192	n	18.6
117	0.0	n	34.7

100°C

0.00	0.00	2.88 ^f , 43.6	n
0.00	1.58	47.0	n
30.3	0.00	47.2	n
30.3	1.58	0.00 ^f , 50.0	n

a 1.06 g/dl = [PVA], in air atmosphere

b .66M = [t-BuOOH]

c n = no data

d after induction period

e under N₂ atmosphere

f [t-BuOOH] = 0.00

g [t-BuOOH] = 1.44M

TABLE XIV (con't)

THE EFFECT OF PEROXIDE CONCENTRATION ON CLEAVAGE RATES OF PVA^a
IN DMSO AND AQUEOUS SOLUTION AT 42°C

$[\text{Co}(\text{acac})_2]_0$ $\times 10^5 \text{M}$	$[\text{Co}(\text{acac})_3]_0$ $\times 10^5 \text{M}$	$[\text{t-BuOOH}]_0$	$-\Delta M_v / \Delta t \times 10^3$ g/mole-sec
<u>DMSO SOLUTION</u>			
4.00		.66	1.50
		.066	1.22
		.033	1.16
		.016	1.11
	20.0	.66	1.00
		.016	.65
<u>AQUEOUS SOLUTION</u>			
17.5		.66	.16
		.016	.055
	10.6	.66	.14
		.016	.033

a 1.06 g/dl

b In air atmosphere

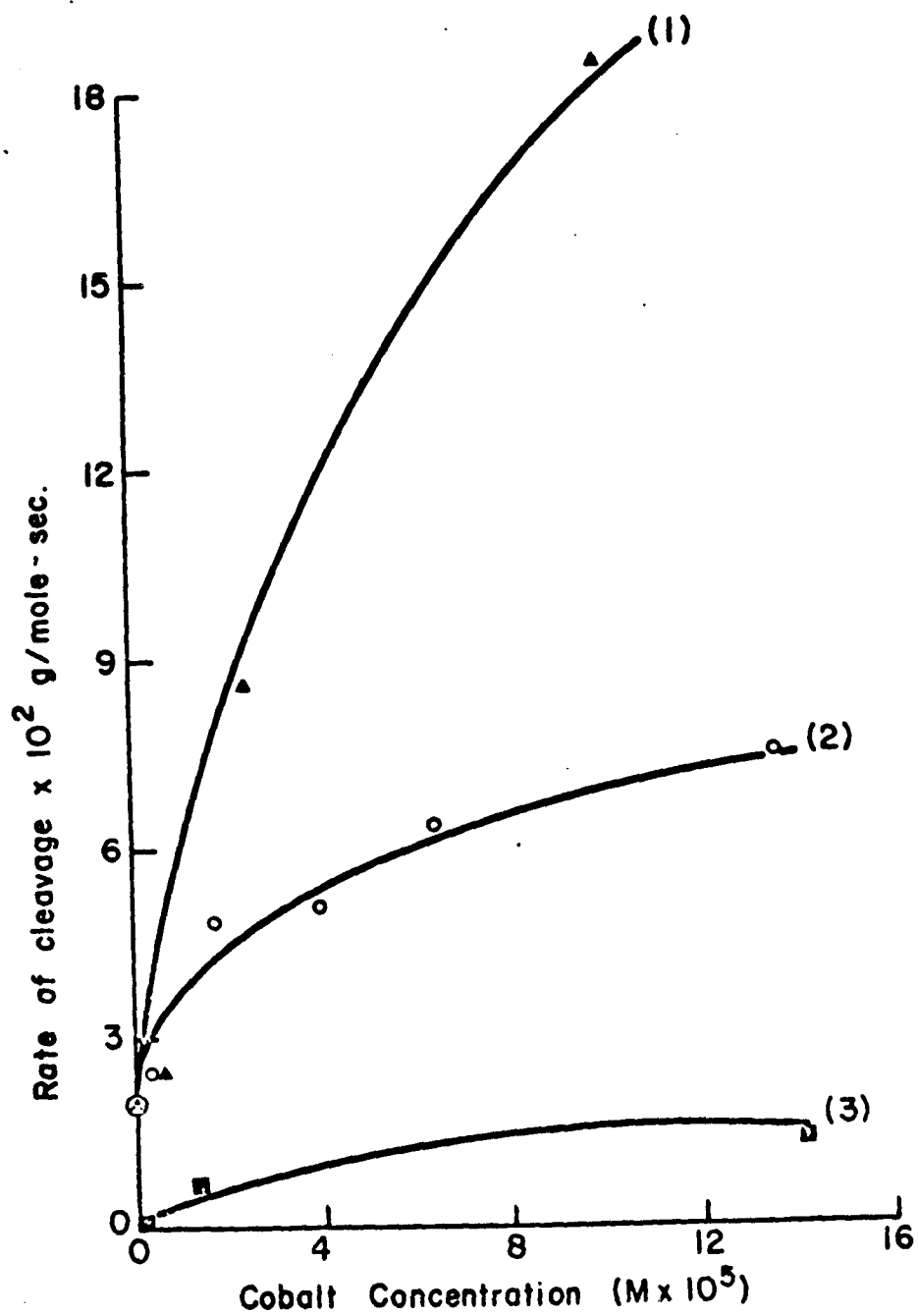


Figure 7. The effect of cobalt concentration on the rate of cleavage under different conditions: (1) $\text{Co}(\text{acac})_2$ in DMSO; (2) $\text{Co}(\text{acac})_3$ in DMSO; (3) $\text{Co}(\text{acac})_2$ in water at 42°C .

TABLE XV

EMPIRICAL RATE EQUATIONS AND THE EVALUATION OF EXPONENTS FOR THE
 CLEAVAGE OF PVA IN DMSO AND AQUEOUS SOLUTION AT 42°C

$$-\Delta M_V / \Delta t = k[Co]^a[t-BuOOH]^b[PVA]^c$$

DMSO SOLUTION

$[Co \times 10^5]$ M	$[t-BuOOH]_0$ M	$[PVA]_0$ g/dl	a	b
<u>Co(acac)₂</u>				
2.12-9.96	.66	1.06	.64	
9-130	.66	1.06	.14	
4.00	.016-.66	1.06		.090

Co(acac)₃

1.97-192	.66	1.06	.30	
20	.016-.66	1.06		.11

AQUEOUS SOLUTIONCo(acac)₂

2.12-135	.66	1.06	.46	
17.5	.016-.66	1.06		.27

Co(acac)₃

1.48-14.2	.66	1.06	.32	
10.6	.016-.66	1.06		.36

TABLE XVI

RELATIVE SHIFT OF THE METHINYL PROTON OF PVA IN THE PRESENCE OF
COBALT (II) CHLORIDE IN DMSO SOLUTION AT 40°C

$[\text{Co} \times 10^6]_0$	Shift in herz
2.00	7.50
3.70	12.0
5.2	13.0
8.7	14.2
11.5	15.1

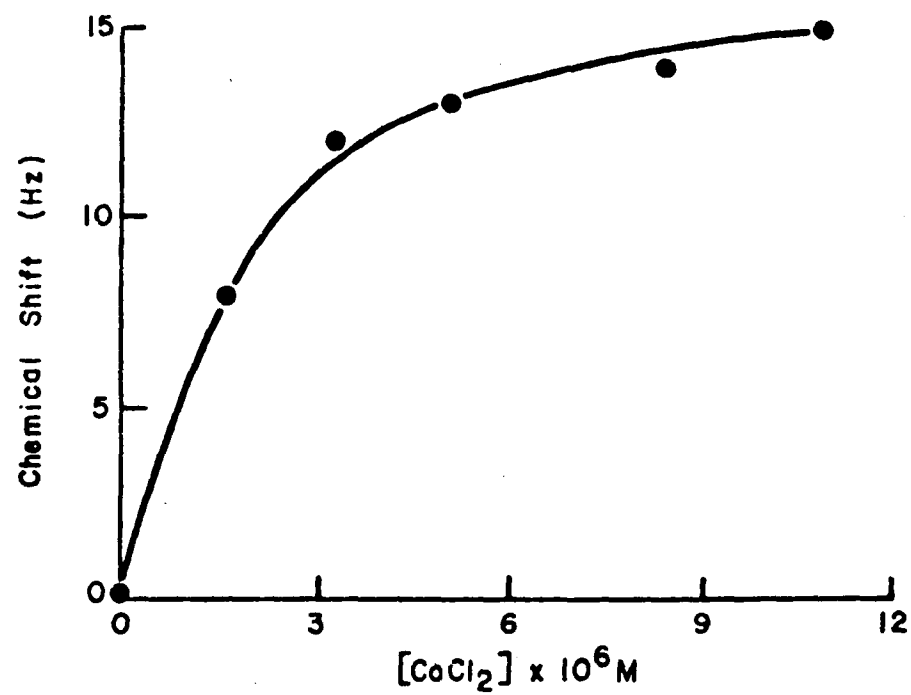


Figure 8. The effect of cobalt concentration on the chemical shift of the methinyl proton of poly(vinyl alcohol).

TABLE XVII

EFFECT OF WATER ON CLEAVAGE RATES IN DIMETHYL SULFOXIDE^a

$[\text{Co}(\text{acac})_2]_0$ $\times 10^5 \text{M}$	$[\text{Co}(\text{acac})_3]_0$ $\times 10^5 \text{M}$	$[\text{H}_2\text{O}]_0$ M	$[-\bar{M}_v/\Delta t]_0$ $\times 10^2 \text{ g/mole-sec}$
0.00	4.00	0.00 ^b	5.25
2.24	0.00	0.00 ^b	11.1
0.00	4.00	0.044	5.25
2.24	0.00	0.044	8.04
0.00	4.00	0.88	3.20
2.24	0.00	0.88	6.94
0.00	1.61	0.11	3.33
2.49	0.00	0.11	7.36
2.49	0.00	0.22	7.12
0.00	1.48	~50	0.656 ^c
2.06	0.00	~50	0.578 ^c

a $[\text{PVA}] = 1.06 \text{ g/dl}$, $[\text{t-BuOOH}] = 0.66 \text{ M}$, $t = 42^\circ\text{C}$

b Molecular sieve (Fischer Type 4A) included in reaction mixture

c Rates in pure water

TABLE XVIII

THIN LAYER CHROMATOGRAPHIC R_f VALUES^a FOR DNPH DERIVATIVES OF
 OXIDATION PRODUCTS OF 1,2 PROPANEDIOL IN THE PRESENCE OF COBALT
 (II) AND (III) ACETYLACETONATE AND t -BuOOH IN DMSO^{b,c,d} AND
 AQUEOUS SOLUTION^{b,c,d} AT 42°C

Band	R_f	Color (Yellow)		NMR of band in d_6 -Benzene
		DMSO	H ₂ O	
1	.16	Dark	Dark	Matches Lactic Aldehyde
2	.23	Light	Dark	Matches Pyruvic Aldehyde
3	.51	Light	Light	Too dilute
4	.60	Very Light	Very Light	Too dilute

AUTHENTIC SAMPLES OF POSSIBLE PRODUCTS WITH R_f VALUES

<u>Product</u>	R_f
Acetaldehyde	.55
Formaldehyde	.50
Acetone	.50
Pyruvic Aldehyde	.23
Lactic Aldehyde	.10

a Silica G plate with benzene as a developing solvent

b $[Co(acac)_2]_0 = 5.0 \times 10^{-4}M$, $[t-BuOOH]_0 = .0066M$, $[1,2 \text{ propanediol}]_0 = 1.05M$

c $[Co(acac)_3]_0 = 5.0 \times 10^{-4}M$, $[t-BuOOH]_0 = .0066M$, $[1,2 \text{ propanediol}]_0 = 1.05M$

d Reacted for 1×10^6 sec

TABLE XIX

COMPARISON OF THE CLEAVAGE NUMBER, ACID EQUIVALENT, AND OXYGEN UPTAKE FOR PVA, AND t-BuOOH DECOMPOSITION IN THE PRESENCE OF PVA, t-BuOOH, AND COBALT (II) AND (III) ACETYLACETONATE IN DMSO^c AND AQUEOUS^c SOLUTION AT 42°C

Cleavage Number(s)	Δ Moles O ₂ Macromole PVA ^d	Δ Moles <u>t</u> -BuOOH Macromole PVA	Δ Moles-COOH Macromole PVA
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DMSO SOLUTION^e

.50 ^a (Co(II))	386	12.67	1.10
.40 ^a (Co(III))	402	10.97	.70

AQUEOUS SOLUTION^f

.050 ^b (Co(II))	512	8.71	.14
.031 ^b (Co(III))	540	8.51	.034

$$a \quad s = \frac{\text{Viscosity average molecular weight of undergraded PVA}}{\text{Viscosity average molecular weight after } 2 \times 10^5 \text{ sec}} - 1$$

$$b \quad s = \frac{\text{Viscosity average molecular weight of undergraded PVA}}{\text{Viscosity average molecular weight after } 4 \times 10^5 \text{ sec}} - 1$$

$$c \quad [\text{Co}(\text{acac})_2]_0 = [\text{Co}(\text{acac})_3]_0 = 2.0 \times 10^{-5} \text{M}, [\text{PVA}]_0 = 1.06 \text{g/dl}, [\text{t-BuOOH}] = .66 \text{M}$$

$$d \quad \text{Macromole PVA} = 10.6 \text{ g/liter} / 76,500 \text{ g/mole} = 1.39 \times 10^{-4} \text{M}$$

$$e \quad \text{All values after } 2 \times 10^5 \text{ sec}$$

$$f \quad \text{All values after } 4 \times 10^5 \text{ sec}$$

TABLE XX

INITIAL CLEAVAGE RATES^{a, c} OF PVA AND INITIAL OXYGEN ABSORPTION
 RATES^{b, d} IN THE PRESENCE OF METAL ACETYLACETONATES IN WATER AND
 DMSO

	$-(\Delta Mv/\Delta t)_0 \times 10^2$ g/mole sec		$-(\Delta O_2/\Delta t)_0 \times 10^7$ M/sec	
	DMSO	H ₂ O	DMSO	H ₂ O
Co(II)	8.65	0.67	11.1	11.2
Co(III)	4.82	1.34	13.8	11.2
Cr(III)	3.08	N.S. ^e	11.1	N.S.
Cu(II)	6.40	2.60	13.2	7.08
Mn(II)	1.25	N.S.	1.36	N.S.
Mn(III)	2.90	N.S.	8.92	N.S.
Fe(II)	3.95	N.S.	5.60	N.S.
Fe(III)	5.50	1.12	3.68	6.60
Ni(II)	3.00	1.14	11.0	6.60
V(III)	1.86	0.55	10.1	0.72
Ce(III)	2.50	N.S.	N.D. ^f	N.D.
Al(III)	1.14	2.00	1.05	N.D.
No Metal	0.0	0.00	0.0	.00

a Ambient atmospheric conditions at 42°C

b Under 100% oxygen atmosphere at 42°C

c $[M]_0 = 2 \times 10^{-5}M$, $[PVA]_0 = 1.06$ g/dl, $[t\text{-BuOOH}]_0 = .66M$

d $[M]_0 = 2 \times 10^{-5}M$, $[PVA]_0 = .86$ g/dl, $[t\text{-BuOOH}]_0 = .66M$

e N.S. = Not Soluble in water

f N.D. = No Data

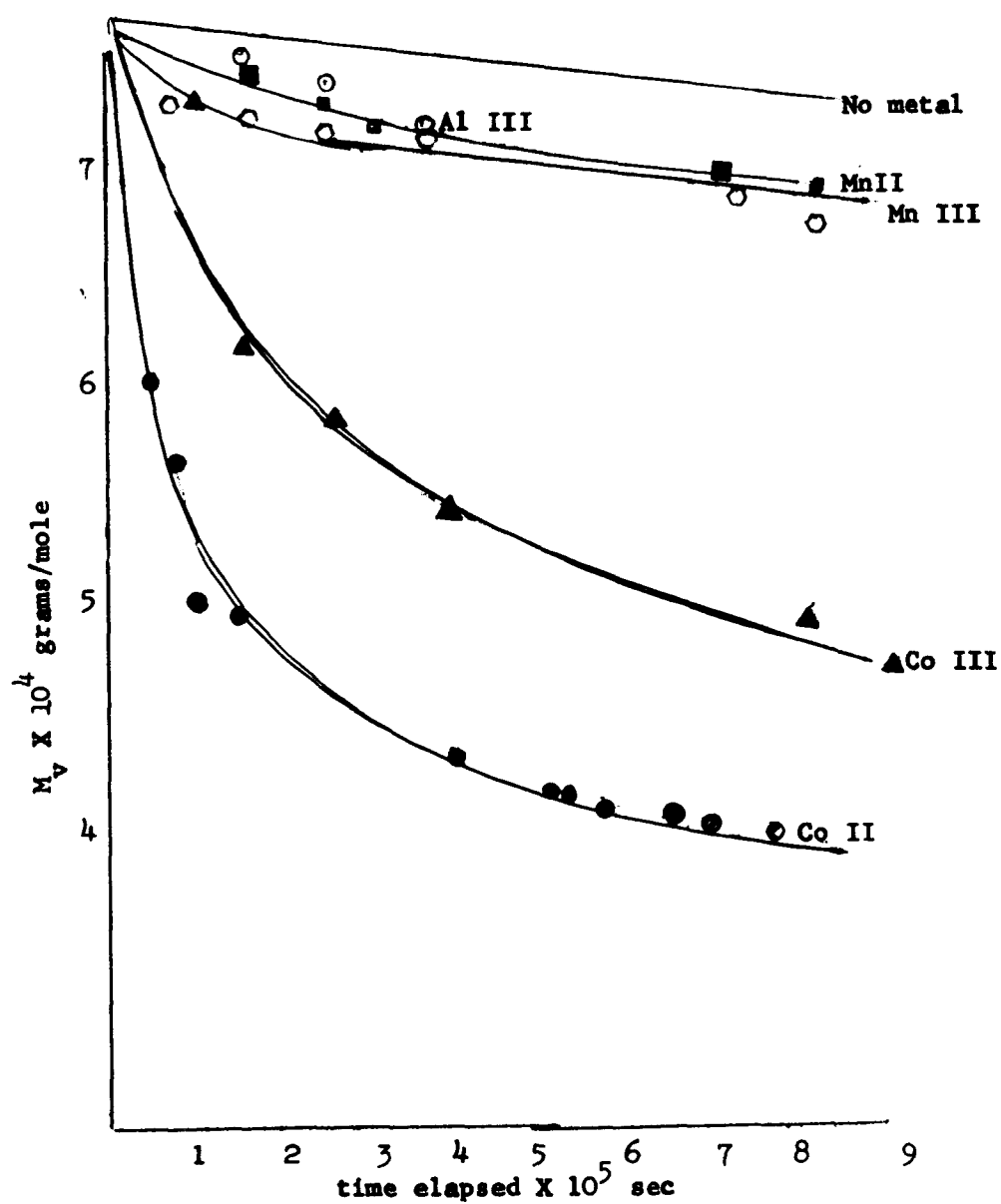


Figure (9a) : The change of the viscosity average molecular weight of PVA in the presence of $2 \times 10^{-5} \text{ M}$ metal acetylacetonates, $.66 \text{ M } t\text{-BuOOH}$ and 1.06 g/dl PVA in DMSO solution at 42°C .

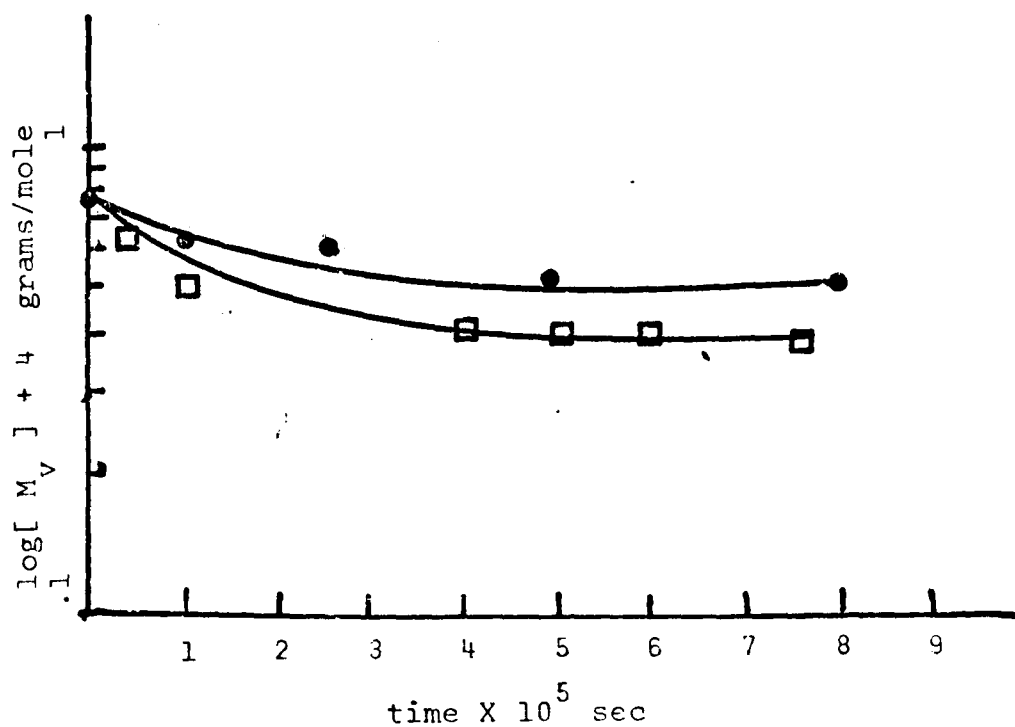


Figure (9b) : The logarithm of the change in the viscosity average molecular weight vs the time elapsed in the reaction for $\square$ cobalt (II) and $\bullet$ (III) acetylacetonate initiated reaction mixtures in DMSO under identical conditions as employed in Figure (9a).

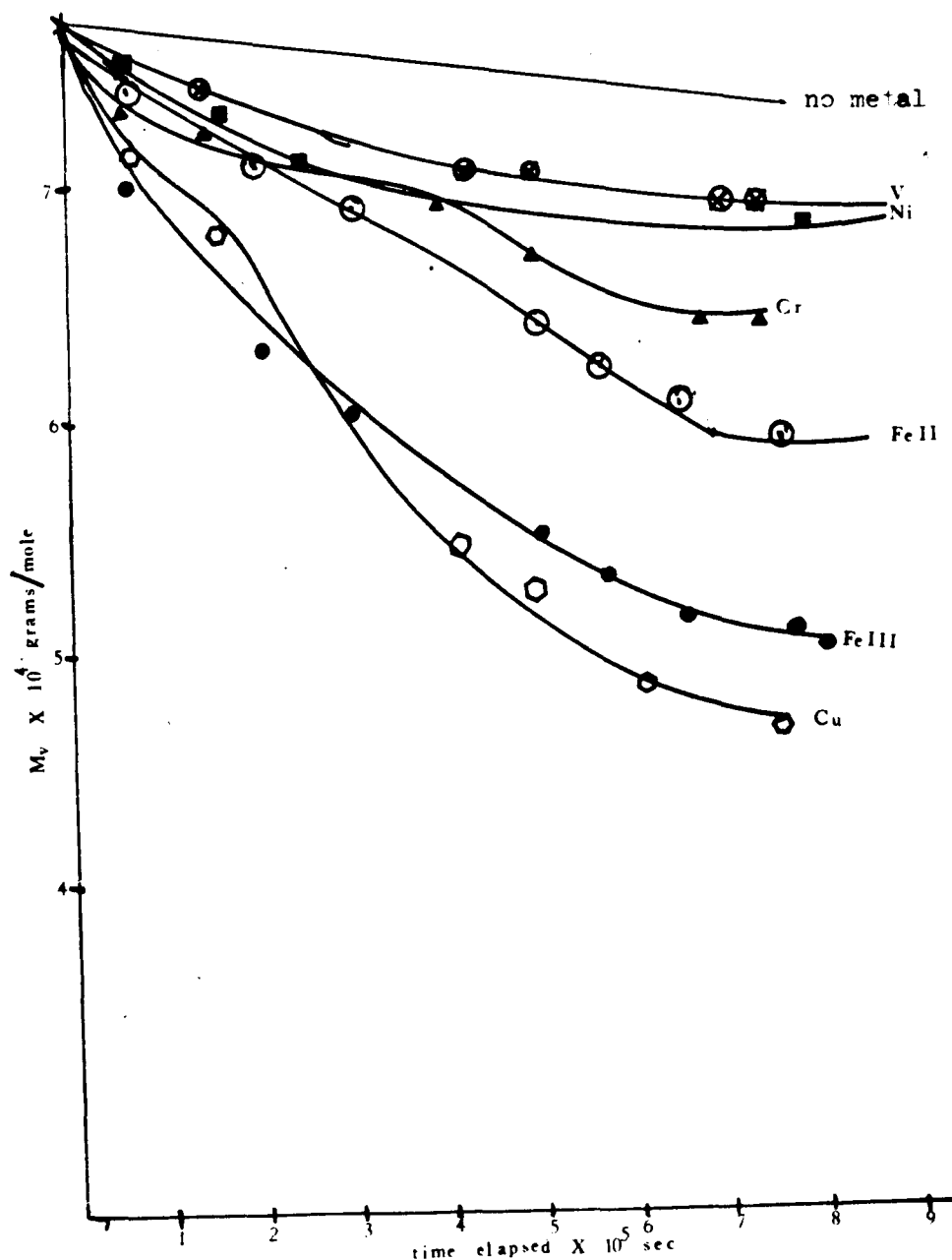


Figure (10) : The change of viscosity average molecular weight of PVA in the presence of 2×10^{-5} M metal acetylacetonates, .66 M *t*-BuOOH and 1.06 g/dl PVA in DMSO solution at 42°C

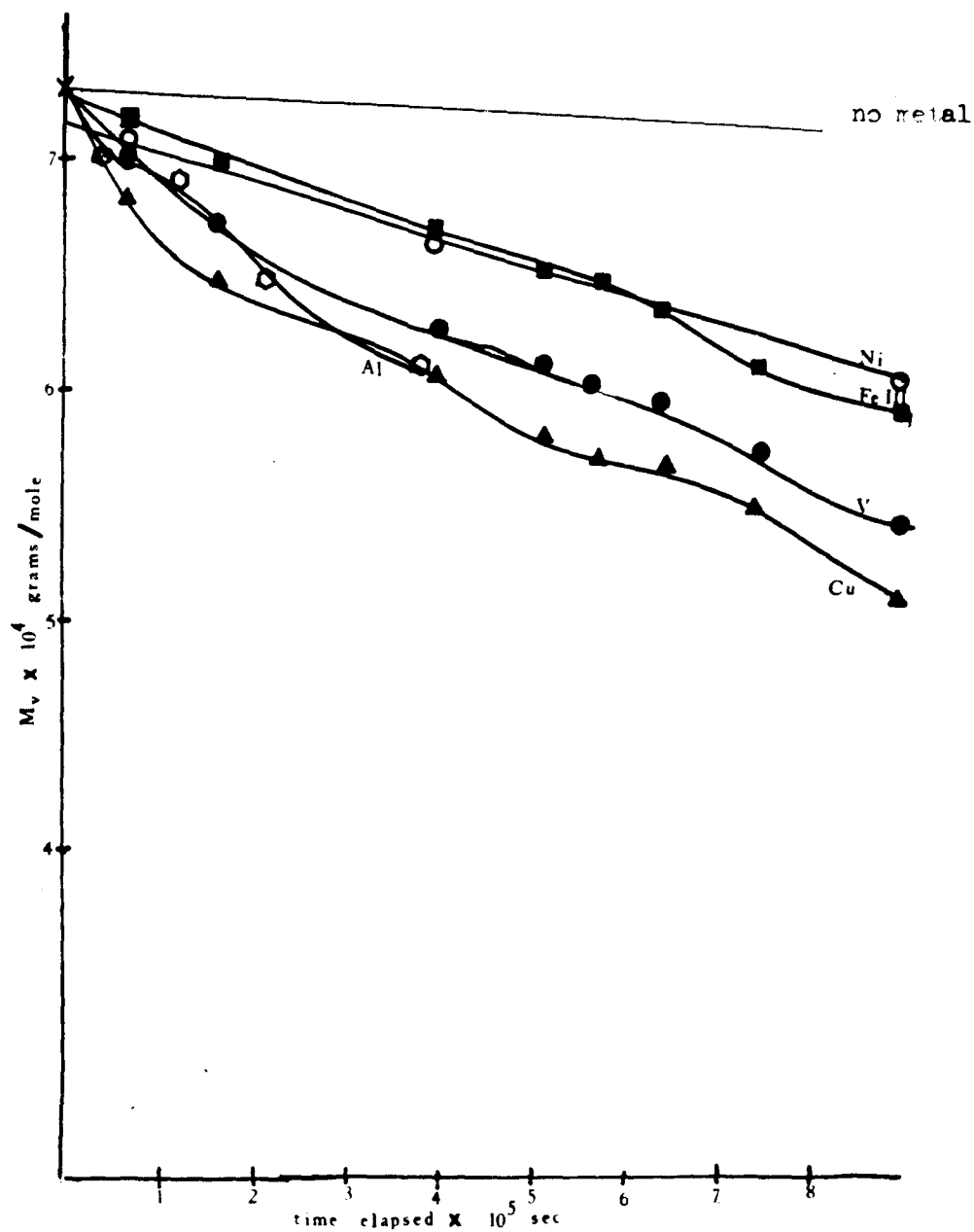


Figure (11) : The change of the viscosity average molecular weight of PVA in the presence of $2 \times 10^{-5} \text{ M}$ metal acetylacetonates, $.66 \text{ M t-BuOOH}$ and 1.06 g/ul PVA in aqueous solution at 42°C

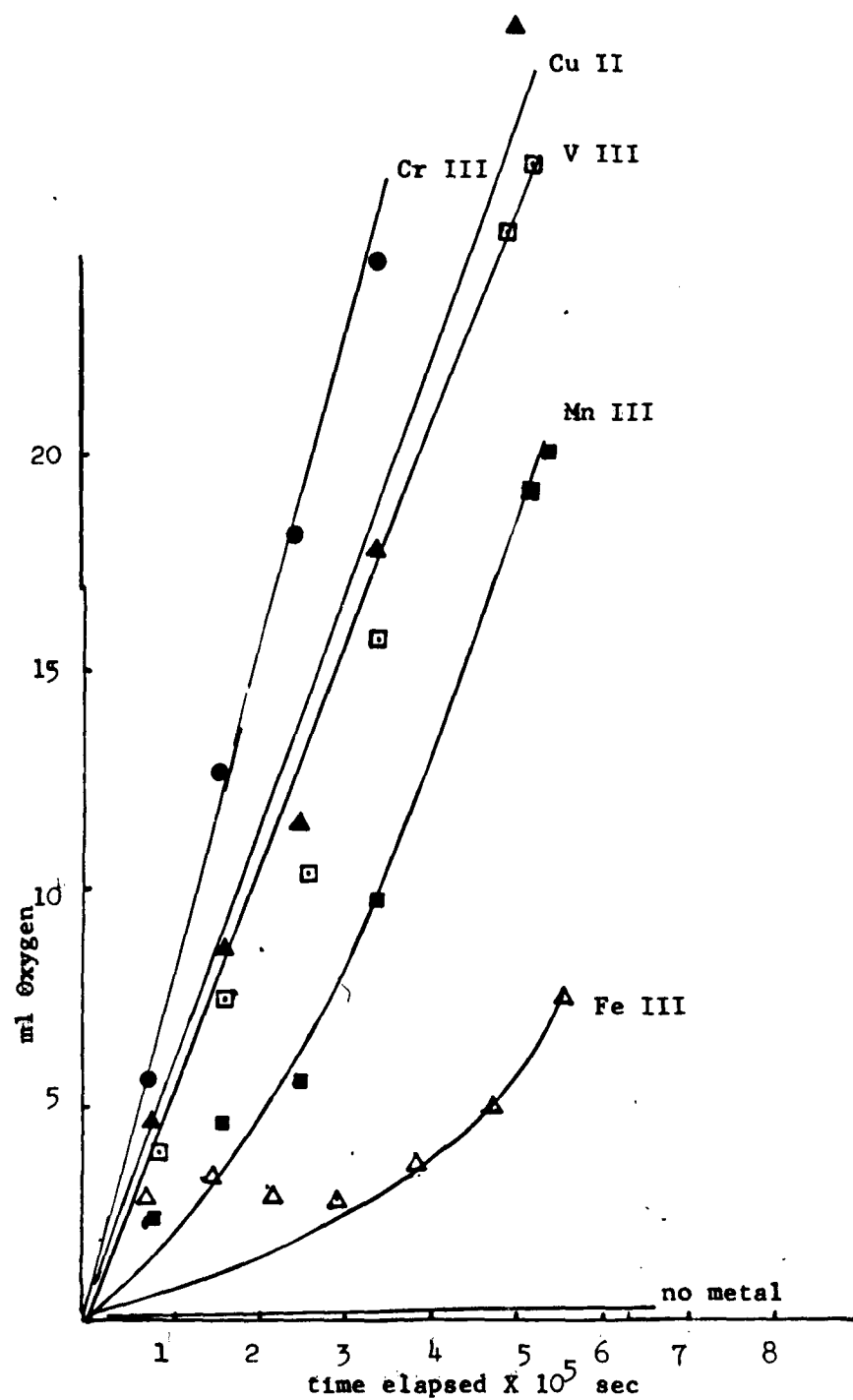


Figure (12) : The amount of oxygen in ml absorbed with time for 2×10^{-5} M solutions of metal acetylacetonates, .66 M *t*-BuOOH and 1.06 g/ dl of PVA in 25 ml of DMSO solution at 42°C .

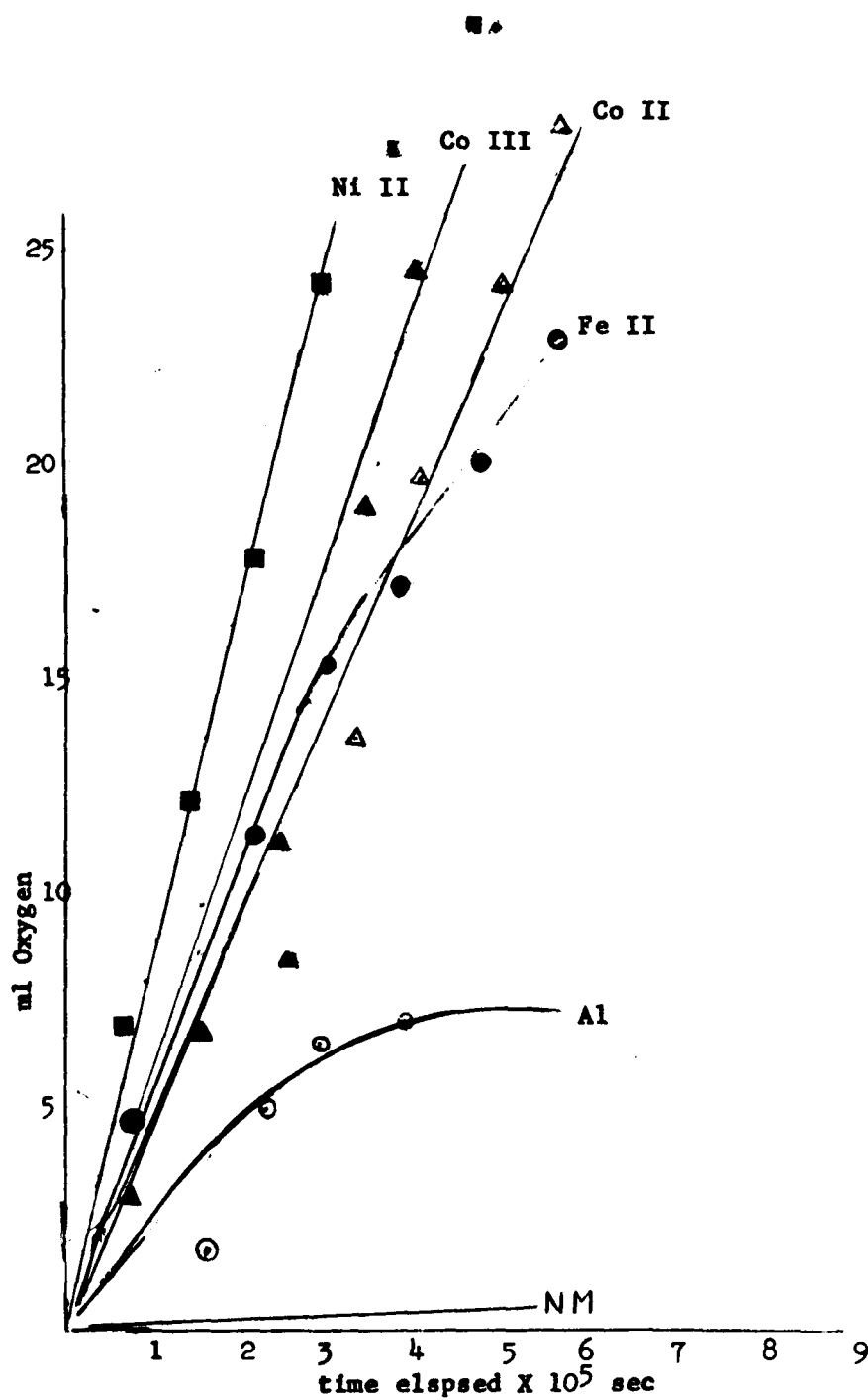


Figure (13) : The amount of oxygen absorbed in ml with time for $2 \times 10^{-5} M$ solutions of metal acetylacetonates, $.66 M$ t -BuOOH and 1.06 g/dl of PVA in 25 ml DMSO solution at $42^\circ C$.

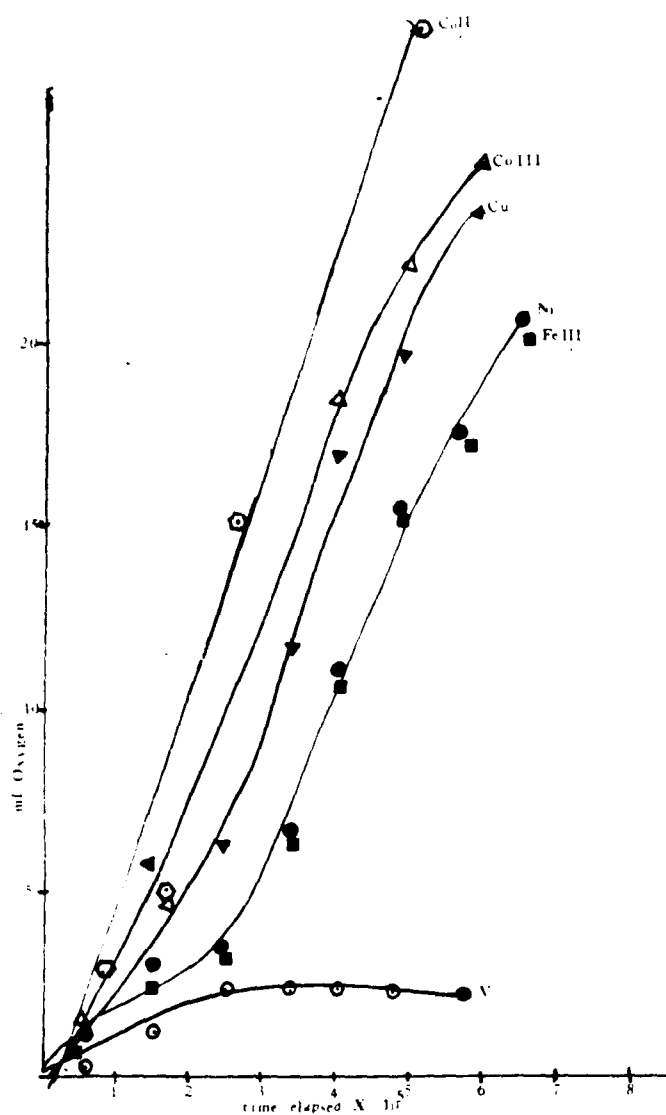


Figure (14) : The amount of oxygen absorbed in ml with time for 2×10^{-3} M solutions of metal acetylacetonates, .66 M t-BuOOH and 1.06 g/dl of PYA in 25 ml of aqueous solution at 42°C.

TABLE XXI

RATES OF t-BuOOH DECOMPOSITION^a AND UV SPECTRAL CHANGES^a FOR
METAL ACETYLACETONATES IN WATER AND DMSO

	-(Δ <u>t</u> -BuOOH/ Δ t) x 10 ³				UV Spectral Changes ^f	
	DMSO $\tau_{\frac{1}{2}}^b$	R ^c	H ₂ O $\tau_{\frac{1}{2}}$	R	DMSO	H ₂ O
Co(II)	9.24	12.0	45.2	2.45	.86 ^g	.95 ^g
Co(III)	9.64	11.5	51.5	2.15	.79 ^g	.96 ^g
Cr(III)	11.7	9.51	N.S. ^e		.58	N.S.
Cu(II)	9.56	11.6	48.6	2.28	2.00	.58
Mn(II)	50.9	2.18	N.S.		1.00	N.S.
Mn(III)	32.6	3.40	N.S.		3.15	N.S.
Fe(II)	16.9	6.58	N.S.		1.00	N.S.
Fe(III)	32.6	3.40	72.5	1.53	.27	.27
Ni(II)	10.9	10.2	110	1.01	2.16	.39
V(III)	13.2	8.40	76.5	1.45	1.26	.64
Al(III)	34.4	3.22	101	1.10	N.D. ^d	N.D.
No metal		0.0		0.0		

a In vacuo, 42°C, [M]₀ = 2.0 x 10⁻⁵M, [PVA]₀ = 1.06 g/dl, [t-BuOOH] = .016M

b $\tau_{\frac{1}{2}}$ = half life for peroxide decomposition (secs x 10⁻⁵)

c R = rate of peroxide decomposition ((.693 [t-BuOOH]₀/ $\tau_{\frac{1}{2}}$) x 10³)

d N.D. = no data

e N.S. = not soluble

f $\frac{\text{Absorbance at } 2 \times 10^5 \text{ sec}}{\text{Absorbance initially at maximum}}$

g [Co(acac)₂ + Co(acac)₃]/[Co(acac)_n]₀ measured at 2 x 10⁵ sec

TABLE XXII

TABLE OF REDOX POTENTIALS OF METAL
ACETYLACETONATES⁷³

<u>Metal</u>	<u>Redox Potential, Volts</u>
Co(III)	1.817
Mn(III)	1.510
Cr(III)	1.300
Fe(III)	0.770
Cu(II)	0.167

TABLE XXIII

RELATIVE BROADENING OF THE OO-H^c SIGNAL IN THE NMR SPECTRA OF t-BuOOH
IN CCl_4 WITH VARIOUS METAL ACETYLACETONATES^{b, 174}

Al(III)	+ ^a
Co(II)	+++
Co(III)	0 ^d
Cr(III)	+++
Cu(II)	++
Fe(III)	+++
Mn(III)	+
Ni(II)	++
VO(II)	++
Zn(II)	+

a + represents approximately 20 cycles of broadening

b Metal acetylacetonates are approximately 10^{-3}M

c $\text{t-BuOOH} = .96 \text{ M}$

d 0 or unperturbed case with 5 cycle line width on a 60 M Hz instrument

TABLE XXIV

RATES OF CLEAVAGE OF PVA^{a, b} AND t-BuOOH DECOMPOSITION^{a, c} IN THE
 PRESENCE OF METAL PHTHALOCYANINES, IRON PORPHYRINS, OR CHLOROPHYLLIN
 AND t-BuOOH IN DMSO SOLUTION

Metal Complex	$-\Delta M_v/\Delta t \times 10^2$	$-\Delta t\text{-BuOOH}/\Delta t \times 10^9$		$-\Delta O_2/\Delta t \times 10^7$
	g/mole	M/sec		M/sec
		R^d	$\tau_{1/2}^e$	
Cu Pht	2.10	15.3	7.24	
Fe Pht	20.5	36.1	3.07	
VO Pht	1.4	8.6	12.9	
Co Pht	18.0	18.1	6.12	14.4
Free Base	.68	.93	119	
Hemin	10.1	1700	.0065	12.6
Hematin	4.6	76.5	1.45	
Hematoporphyrin	.15	1.8	61.6	
Free Base				
Chlorophyllin	.70	25.5	4.35	
Cytochrome c	1.95 ^f	N.D.		

a Under ambient conditions at 42°C

b $[M]_0 = 2.0 \times 10^{-5}M$, $[PVA]_0 = 1.06$ g/dl, $[\underline{t}\text{-BuOOH}]_0 = .66M$

c $[M]_0 = 2.0 \times 10^{-5}M$, $[PVA]_0 = 1.06$ g/dl, $[\underline{t}\text{-BuOOH}]_0 = .016M$

d R = rate of peroxide decomposition ($(.693 [\underline{t}\text{-BuOOH}]_0 / \tau_{1/2}) \times 10^9$)

e $\tau_{1/2}$ = half life for peroxide decomposition (secs $\times 10^{-5}$)

f In water solution

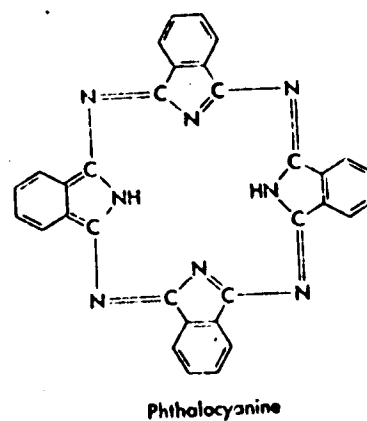
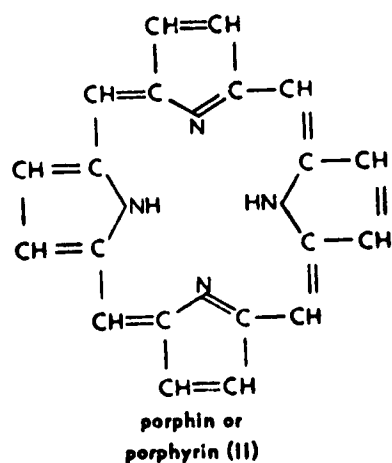
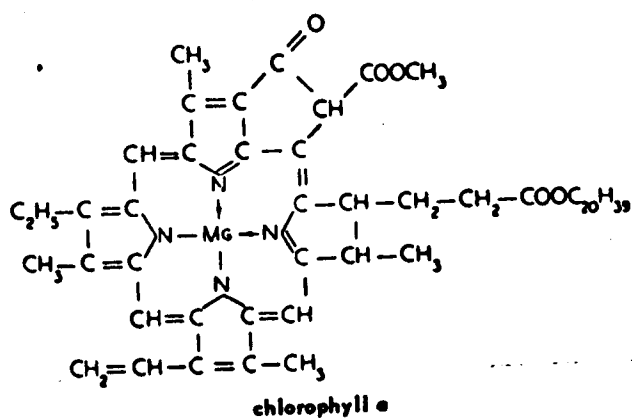
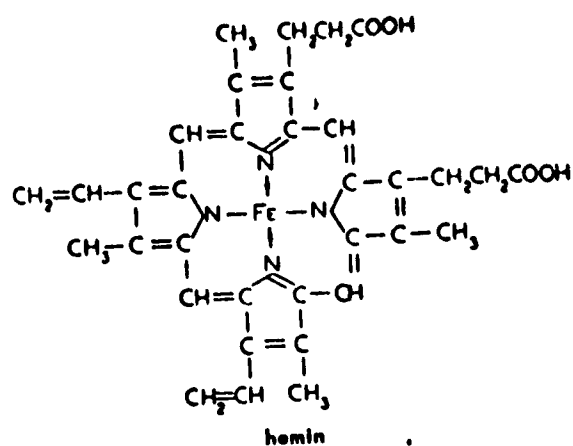


Figure (15a) : Structures of molecules of biological interest used in this study.

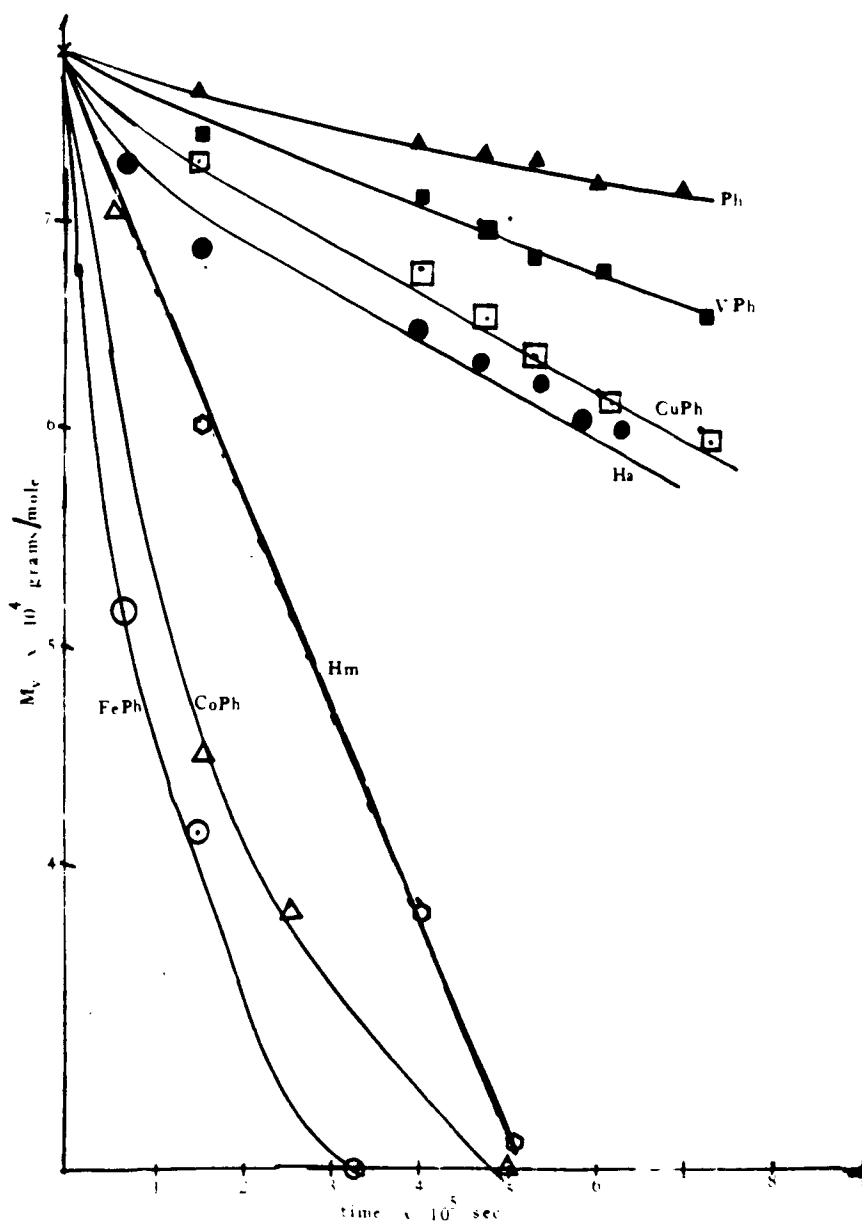


Figure (15) : The change of the viscosity average molecular weight with time of PVA in the presence of 2×10^{-3} M metal phthalocyanines, .66 M t-BuOOH, and 1.06 g/dl PVA in DMSO solution at 42°C .

TABLE XXV

CLEAVAGE RATES OF PVA,^{a,c} OXYGEN UPTAKE,^{b,d} AND t-BuOOH
 DECOMPOSITION^e IN THE PRESENCE OF COBALT SALTS IN WATER AND
 DMSO AT 42°C

Cobalt Salt	$-(\Delta M_v / \Delta t) \times 10^2$ g/mole-sec		$-(\Delta O_2 / \Delta t) \times 10^7$ M/sec		$-(\Delta \underline{t}\text{-BuOOH} / \Delta t) \times 10^9$ M/sec			
	DMSO	H ₂ O	DMSO	H ₂ O	DMSO		H ₂ O	
					$\tau_{\frac{1}{2}}^f$	R ^g	$\tau_{\frac{1}{2}}$	R
CoF ₂	1.50	.72	.64	.36	26.4	4.20	5.84	1.90
CoCl ₂	8.60	.72	5.4	5.7	11.3	9.81	5.38	2.06
CoBr ₂	8.50	2.50	3.2	6.3	10.9	10.2	3.96	2.80
CoI ₂	9.00	.78	3.9	6.4	9.64	11.5	4.42	2.51
CoF ₃	1.70	N.D. ^h	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Co(NO ₃) ₂	8.65	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Co Pht	16.8	N.S. ⁱ	14.4	N.S.	6.16	18.0	N.S.	
Co(acac) ₂	8.65	1.34	11.1	8.8	9.24	12.0	4.53	2.45
Co(acac) ₃	4.82	.67	13.8	11.2	9.64	11.5	5.16	2.15

a under ambient conditions

b under 100% oxygen atmosphere

c $[M]_0 = 2.0 \times 10^{-5} M$, $[PVA]_0 = 1.06$ g/dl, $[\underline{t}\text{-BuOOH}]_0 = .66M$

d $[M]_0 = 2.0 \times 10^{-5} M$, $[PVA]_0 = .86$ g/dl, $[\underline{t}\text{-BuOOH}]_0 = .66M$

e $[M]_0 = 2.0 \times 10^{-5} M$, $[PVA]_0 = 1.06$ g/dl, $[\underline{t}\text{-BuOOH}]_0 = .016M$

f $\tau_{\frac{1}{2}}$ = half life for peroxide decomposition (secs $\times 10^{-5}$)

g R = rate of peroxide decomposition ($(.693 [\underline{t}\text{-BuOOH}]_0 / \tau_{\frac{1}{2}}) \times 10^9$)

h N.D. = no data

i N.S. = not soluble

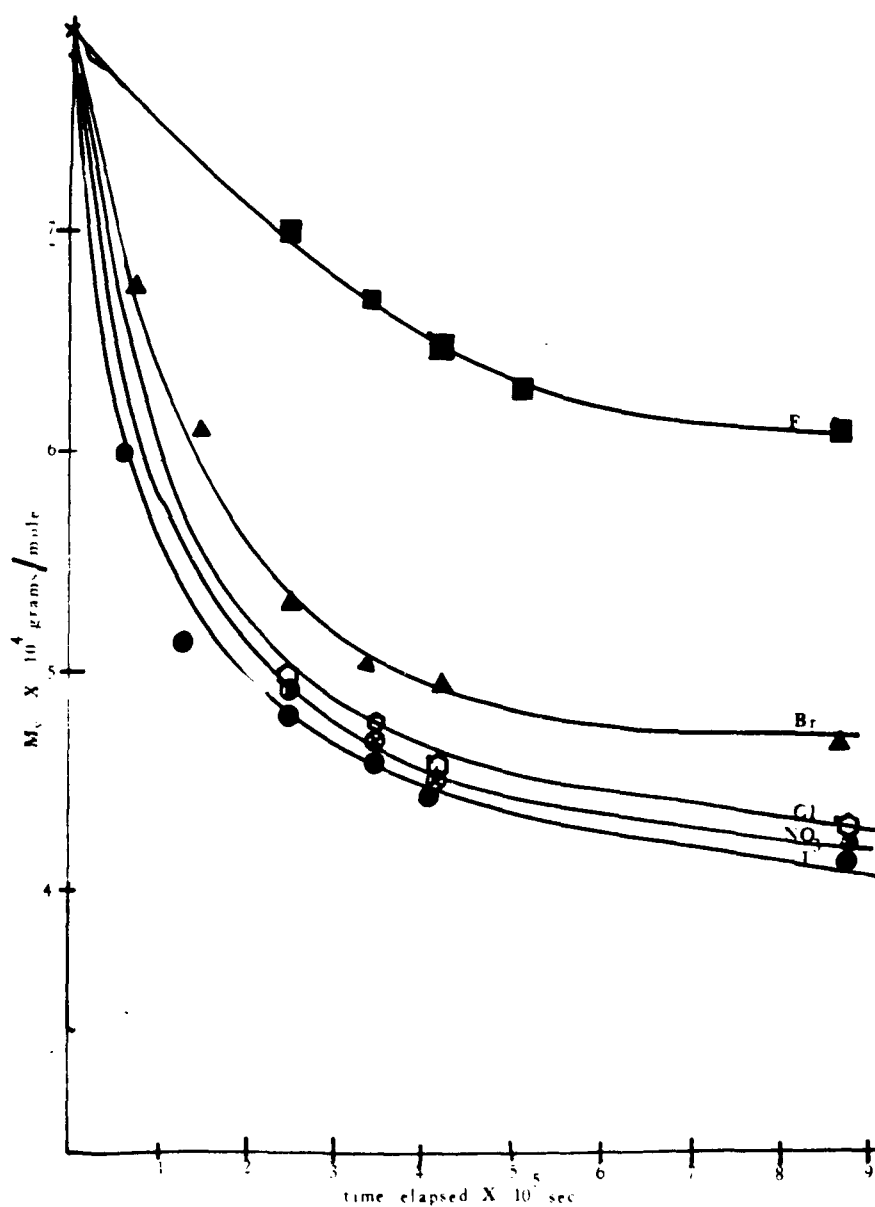


Figure (16) : The change of the viscosity average molecular weight with time of PVA in the presence of 2×10^{-5} M cobalt (II) salts, $.66$ M $t\text{-BuOCH}_3$, and 1.06 g/dl PVA in DMSO solution at 42°C

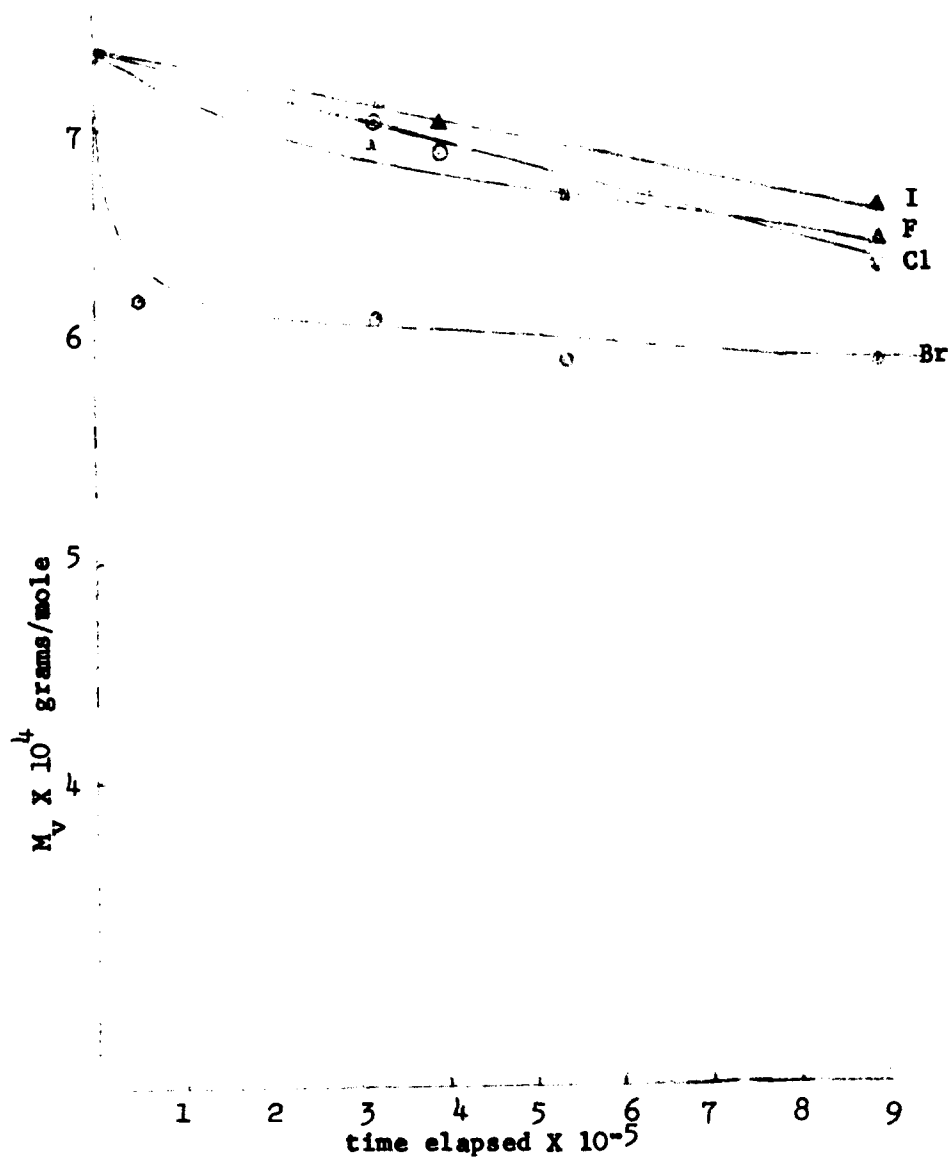


Figure (17a) : The change of the viscosity average molecular weight of PVA in the presence of 2×10^{-5} M cobalt (II) salts, .66M t -BuOOH and 1.06 g/dl PVA in aqueous solution at 42°C .

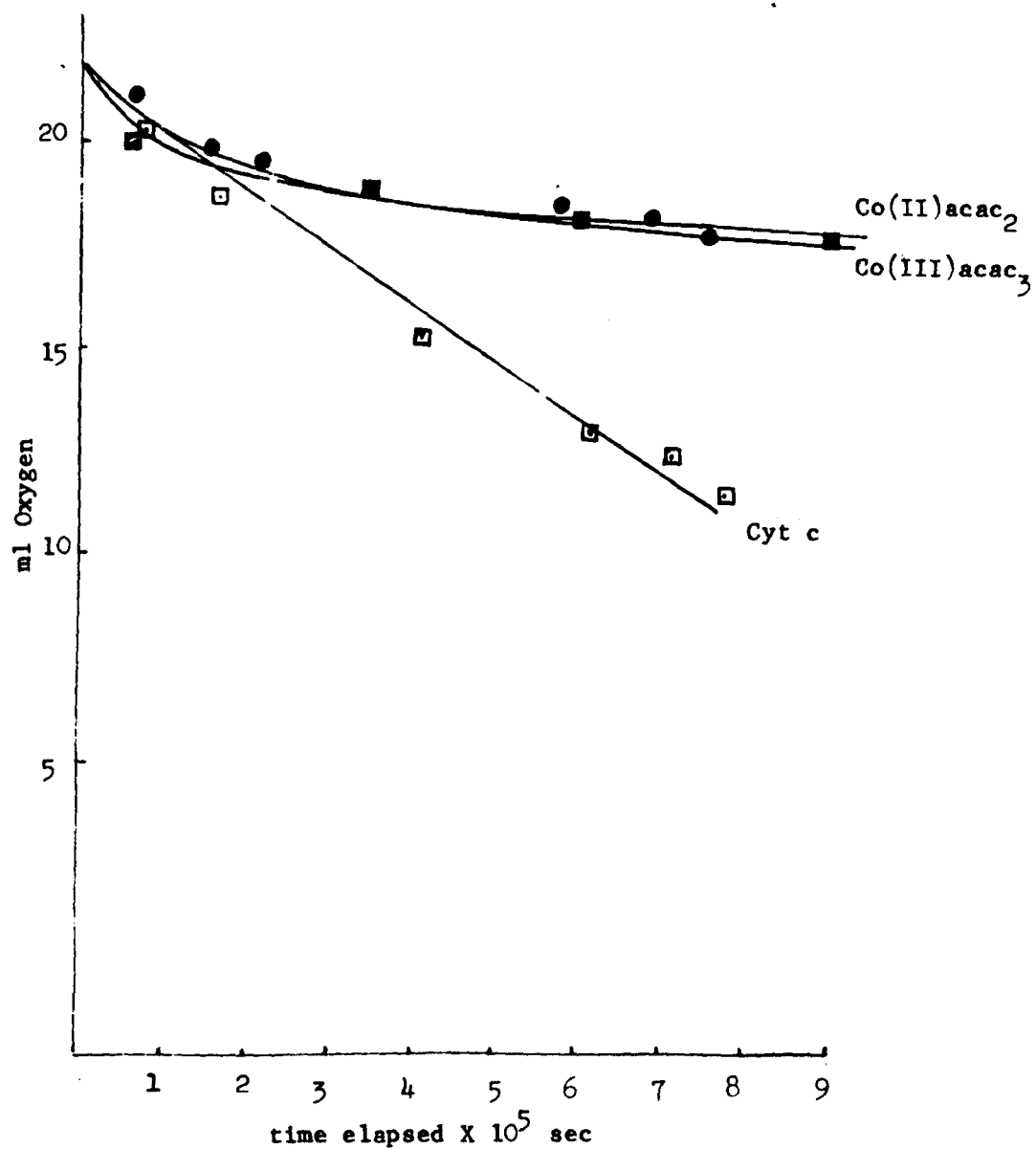


Figure (17b) : The amount of oxygen in ml absorbed with time for 2×10^{-5} M solutions of metal cobalt acetylacetonates and cytochrome c, $.66M$ t -BuOOH and 1.06 g/dl of PMA in 25 ml of aqueous solution at 42°C.

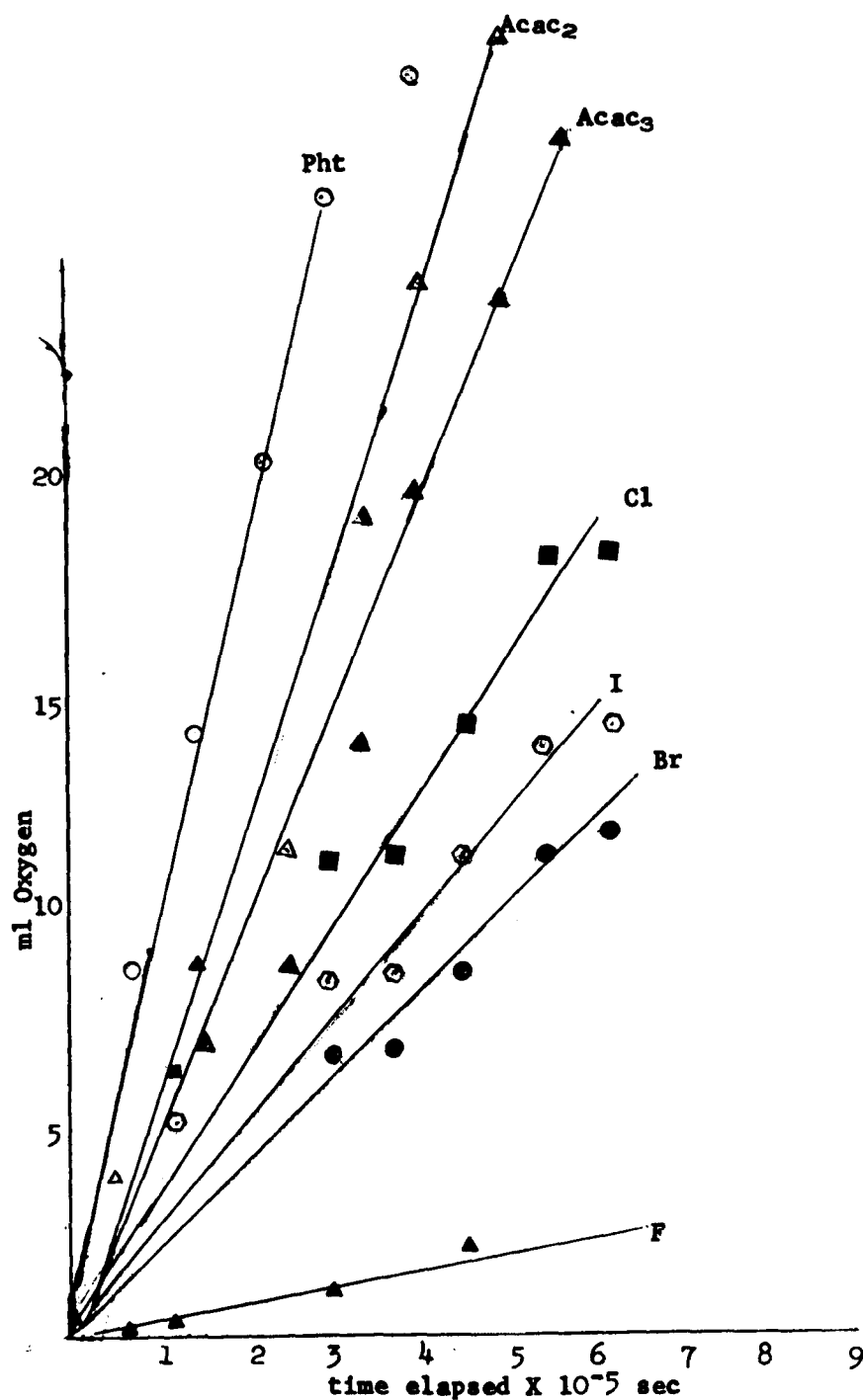


Figure (18) : The amount of oxygen absorbed in ml with time in the presence of 2×10^{-5} M cobalt salts, .66M *t*-BuOOH, and 1.06 g/dl PVA in 25 ml of DMSO solution at 42°C.

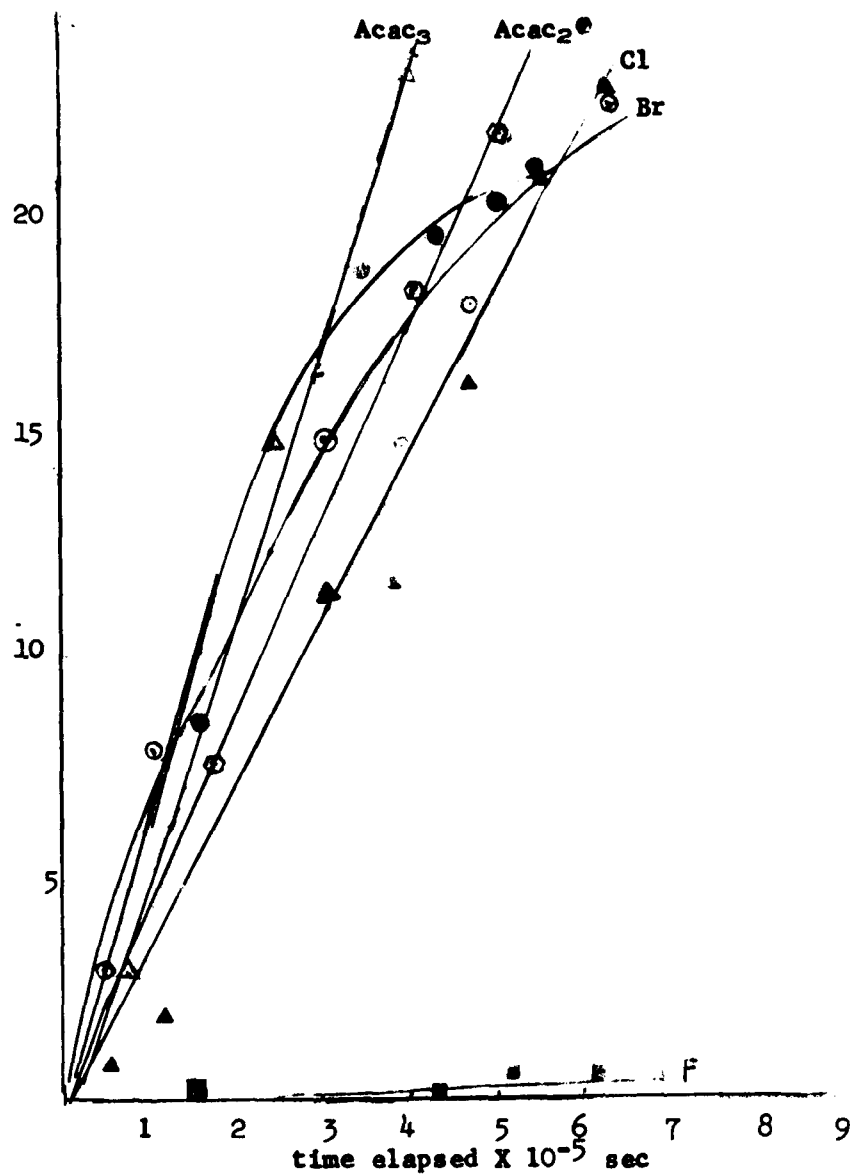


Figure (19) : The amount of oxygen absorbed in ml with time for 2×10^{-5} M solutions of cobalt salts, .66 M $t\text{-BuOOH}$, and 1.06 g/dl of PVA in 25 ml of aqueous solution at 42°C .

TABLE XXVI

EXTINCTION COEFFICIENTS AND WAVELENGTHS OF MAXIMUM ABSORPTION FOR
VARIOUS METAL ACETYLACETONATES IN DMSO AND AQUEOUS SOLUTION

	Extinction Coefficient liter/mole-cm	Maximum Absorption 1/cm (λ_{max})		
	Literature Value ¹⁸²	DMSO	H ₂ O	Literature Value ¹⁸²
Al(III)	42,800	N. D. ^d	N. D.	288
Co(II)	16,200 ^a	292	290	292
Co(III)	34,000 ^b	256	254	258
Cr(III)	15,800	340	N. S. ^e	336
Cu(II)	20,100	295	290	296
Mn(II)	20,500	282	N. S.	276
Mn(III)	24,000	280	N. S.	274
Fe(II)	N. D.	295	N. S.	N. D.
Fe(III)	29,600	283	N. S.	274
Ni(II)	23,700	302	280	294
V(III)	19,600	289	276	280

a A Beer's law plot in aqueous solution yields a value of 16,300 and in DMSO solution a value of 13,100

b A Beer's law plot in aqueous solution yields a value of 20,800 and in DMSO solution a value of 38,100

c All literature values were obtained in chloroform

d N. D. = no data

e N. S. : not soluble in aqueous solution

TABLE XXVII

COMPARISON OF THE RATES OF AUTOXIDATION^a, CLEAVAGE^b, AND t-BuOOH
 DECOMPOSITION^c IN THE PRESENCE OF PVA, COBALT (II) AND (III)
 ACETYLACETONATE, AND t-BuOOH IN DMSO AND AQUEOUS SOLUTION AT 42°C

[Co x 10 ⁵] ₀		[<u>t</u> -BuOOH] ₀	[PVA] ₀	-ΔO ₂ /Δt x 10 ⁷ M/sec		-Δ <u>t</u> -BuOOH/Δt x 10 ⁸ M/sec		-ΔM _V /Δt g/mole-sec	
Co(II)	Co(III)			DMSO	H ₂ O	DMSO	H ₂ O	DMSO	H ₂ O
17.6		.016	1.06	1.50	2.00	4.01	.69	26.0	.55
	10.6	.016	1.06	1.06	1.30	2.80	.47	9.10	.33
17.6		.66	1.06	4.44	10.6	18.5	9.10	28.0	1.75
	10.6	.66	1.06	3.05	8.90	N ^o D.	6.56	7.2	1.2

a Under 100% oxygen atmosphere, 1atm pressure

b Under air atmosphere, 1atm pressure

c In vacuo

Explanation of Tables and Figures

Table (I) and (II) represent U.V. spectral data at various concentrations of PVA, t -BuOOH, and cobalt (II) and (III) acetylacetonate in aqueous and DMSO solution. Two time periods are listed. B_1 represents the initial ratio of cobalt (II) acetylacetonate to cobalt (III) acetylacetonate after 1×10^4 sec and B_2 is the ratio after 2×10^5 sec. After this the ratio is fairly constant with time and this quantity can be regarded as the steady state quantity. U represents a ratio of the loss of overall concentration of cobalt acetylacetonate (cobalt(II) and cobalt (III) acetylacetonate) with time. The major change in overall concentration seems within 2×10^5 sec.

Table (III) and (IV) represent the rate of peroxide decomposition and the half life for peroxide decomposition. Typical plots of initial rates are shown in Figure (1a). Figure (1a) represents the change of $[t\text{-BuOOH}]$ with time in aqueous and DMSO solution. Figure (1b) represents a plot of the logarithm of $[t\text{-BuOOH}]$ with time elapsed in the reaction in DMSO and aqueous solution. If the reaction mechanism is first order, the graph should be linear. The half life for peroxide decomposition ($\tau_{1/2}$) can be found by extrapolating the line obtained in the graph of $\log [t\text{-BuOOH}]$ vs. time to one half the peroxide concentration. The rate of peroxide decomposition can be calculated by using the first order relationship for peroxide decomposition, namely, the rate of peroxide decomposition = $(.693) [t\text{-BuOOH}]_0 / \tau_{1/2}$. Figure (2) represents a log-log plot of the rate of peroxide decomposition as a function of peroxide concentration in DMSO and aqueous solution.

Table (V) and (VI) utilize the empirical relationship $-\frac{d[t\text{-BuOOH}]}{dt} = k[\text{Co}]^a [t\text{-BuOOH}]^b [\text{PVA}]^c$ to describe t -BuOOH decomposition. Values of

a, b, c, and k are listed for aqueous and DMSO solution at various concentrations of reactants. In Table (V) the concentrations of two reactants are held constant and the concentration of the third is varied. The slope of the $\log [\text{reactants}]$ vs. $\log \frac{\Delta [\text{t-BuOOH}]}{\Delta t}$ yields the value of a, b, or c. Values for k are computed on the basis of the exponents that are determined. Table (VII) represents the activation energy, enthalpy, and entropy for various processes studied in autoxidation of PVA, decomposition of t-BuOOH, and cleavage of PVA. The equation employed was $k = Ae^{-E_a/RT}$ (the Arrhenius equation). A plot of $\ln k$ vs. $1/T$ yields $-E_a/R$ as the slope of the line and A as the intercept. This can be related to the enthalpy and entropy of activation.

Table (VIII) and (IX) utilizes the empirical relationship $-(\Delta O_2/\Delta t) = k[Co]^a[BuOOH]^b[PVA]^c$ to describe autoxidation of PVA. Values of a, b, c, and k are listed for aqueous and DMSO solution at various concentrations of two reactants. In Table (VIII) the concentrations of two reactants are held constant and the concentration of the third is varied. The slope of the $\log [\text{reactant}]$ vs. $\log \frac{\Delta O_2}{\Delta t}$ yields the value of a, b, or c on the basis of three or four points. Values for k are computed on the basis of the exponents that were determined. Values for exponents in aqueous solution Table (IX) are essentially constant with concentration conditions and more than one reactant may be varied in this table in order to consolidate values for a, b, c, and k.

Table (X) and (XI) list the initial rate of autoxidation of PVA, initiated by cobalt (II) and cobalt (III) acetylacetonate and t-BuOOH in aqueous and DMSO solution. A higher value for cobalt (II) acetylacetonate than for cobalt (III) acetylacetonate initiated reactions is invariably obtained in DMSO solution.

Figure (3) represents the change of the autoxidation rate with increasing cobalt (II) and (III) acetylacetonate concentration in the presence of .66M t-BuOOH and 1.06g/dl PVA at 42°C in DMSO. Figure (4) is a log-log plot of t-BuOOH concentration vs. the autoxidation rate in DMSO and aqueous solution.

Table (XII) and (XIII) sets forth the calculated kinetic length for autoxidation of PVA in DMSO and aqueous solution. Values for the kinetic chain length are derived from the ratio of the autoxidation rate to the rate of t-BuOOH decomposition under equivalent concentration conditions as the reacting species in autoxidation. Rates of t-BuOOH decomposition were derived from the empirical equation for t-BuOOH decomposition, where data was not available at that concentration of the reactants. Figure (5) and (6) represent the variation of the kinetic chain length for autoxidation with the rate of initiation in DMSO solution and aqueous solution. All lines are drawn through one (1.0) on the y axis in order to make the line conform to Tobolsky's equation for polymer autoxidation (Equation 29).

Table (XIV) represents the initial rate of cleavage for PVA in aqueous and DMSO solution at 42°C. The viscosity of the polymer reaction mixture is converted into the viscosity weight using the empirical equations listed in the experimental section. The maximum rate of the change of the viscosity molecular weight initially (within 2×10^5 sec) is listed as the rate of cleavage. Rates of cleavage at 100°C are listed as well in aqueous solution. Figure (7) represents the effect of cobalt (II) and (III) acetylacetonate concentration on the rate of cleavage at 42°C.

Table (XV) represents the empirical rate for cleavage of PVA

at 42°C. The constants were evaluated from the data in Table (XIV) except for c. Table (XVI) and Figure (8) shows data for the chemical shift in herz for several concentrations of cobalt (II) chloride. This results from a shift in the methinyl proton absorption of PVA in the nmr as a result of the contact shift phenomena.

Table (XVII) provides data for the effect of small amounts of water on the rate of PVA cleavage in DMSO. Table (XVIII) gives the product distribution of the oxidation of 1,2-propanediol in the presence of cobalt (II) and (III) acetylacetonate, and t-BuOOH in DMSO and aqueous solution. R_f values are listed for thin layer analysis of DNPH derivatives of the oxidation products on silica G with benzene as a developing solvent.

Table (XIX) lists values for the cleavage number (s), the number of moles of oxygen taken up and peroxide decomposed per macromole of PVA and the acid equivalent per macromole of PVA. This table allows for the quantitative analysis of the various processes with respect to cleavage.

Table (XX) sets forth the initial rate of cleavage and autoxidation for various metal acetylacetonates.

Figure (9a), and (10) and (11) shows the graphic changes of the viscosity average molecular weight of PVA in the presence of $2 \times 10^{-5}M$ metal acetylacetonate, .66 M t-BuOOH, and 1.06g/dl PVA in DMSO and aqueous solution.

Figure (9b) shows the graphic changes for the logarithm of the viscosity average molecular weight vs. the time elapsed in the reaction for cobalt (II) and (III) acetylacetonate catalyzed reaction mixtures in DMSO solution under the identical concentration conditions as in Figure (9a). If the reaction is first order the graph should be linear.

Figure (12), (13) and (14) represent the amount of oxygen absorbed in ml with time in a 25 ml solution containing $2 \times 10^{-5}M$ metal acetylacetonate, .66 t -BuOOH, and 1.06g/dl of PVA in DMSO and aqueous solution.

Table (XXI) represents the initial and half life for t -BuOOH peroxide decomposition and U.V. spectral changes for various metal acetylacetonates. U.V. spectral changes are tabulated as the ratio of the absorbance of the metal after 2×10^5 sec to the absorbance of initial reaction mixture. This expresses quantitatively the increase or decrease of absorbance of the metal acetylacetonate at the wavelength of maximum absorbance for each metal acetylacetonate.

Table (XXII) lists the redox potentials of various metal acetylacetonates. Table (XXIII) represents relative nmr broadening in chloroform of the ROO-H proton in carbon tetrachloride. The broadening of this peak is representing by + representing 20 cycles of broadening.

Table (XXIV) is the initial rate of cleavage of PVA, t -BuOOH decomposition (and half life), and autoxidation for various metal phthalocyanines, hemin, hematin, hematoporphyrin free base, chlorophyllin, in DMSO solution and cytochrome c in aqueous solution. Figure (15a) represents structures of biological interest. Figure (15b) represents the change of the viscosity average molecular weight with time of PVA in the presence of $2 \times 10^{-5}M$ metal phthalocyanines, .66M t -BuOOH, and 1.06g/dl PVA in DMSO solution.

Table (XXV) gives the rate of cleavage of PVA, rate of autoxidation, and the rate and half life for t -BuOOH decomposition for various cobalt halides in aqueous and DMSO solution. Cobalt (II) phthalocyanine and cobalt (II) and (III) acetylacetonate are included in the table.

Figure (16) and (17) represents the change of viscosity average molecular weight with time of PVA in the presence of $2 \times 10^{-5}M$ cobalt

(II) salts, .66M t-BuOOH, and 1.06g/dl PVA in DMSO and aqueous solution at 42°C. Figures (18) and (19) represent the amount of oxygen absorbed in ml with time in the presence of 2×10^{-5} M cobalt salts, .66M t-BuOOH, and 1.06g/dl PVA in 25 ml of DMSO and aqueous solution at 42°C.

Table (XXVI) is a table of extinction coefficients and wavelengths of maximum absorption for various metal acetylacetonates. This table contrasts literature values for these quantities determined in chloroform with those determined experimentally in this work in DMSO and aqueous solution.

Table (XXVII) lists values for the rate of autoxidation and cleavage of PVA and t-BuOOH decomposition in the presence of PVA, cobalt (II) and (III) acetylacetonate, and t-BuOOH in DMSO and aqueous solution. This table allows for a rapid comparison of these rates in two different solvents and at two different concentrations of t-BuOOH.

III. DISCUSSION OF RESULTS

Introduction

If cobalt (II) or (III) acetylacetonate, *t*-BuOOH and PVA are mixed together in the presence of oxygen several chemical transformations occur. An oxidation-reduction reaction occurs between the cobalt (II) and (III) acetylacetonate and *t*-BuOOH to produce free radicals which initiate chain decomposition of the peroxide. Oxidation of the polymer takes place as well as a cleavage reaction which does not occur as a direct result of autoxidation. This section deals mainly with the mechanistic implications of the kinetic results obtained in both DMSO and aqueous solution at 42°C.

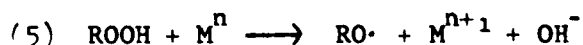
Cobalt (II), cobalt (III), chromium (III), copper (II), manganese (II), manganese (III), iron (II), iron (III), nickel (II), vanadium (III), cerium (III), aluminum (III) acetylacetonates were used to catalyze the autoxidation and cleavage of PVA, *t*-BuOOH decomposition. Spectral changes of each metal acetylacetonate were followed on the U.V. spectrometer in DMSO and aqueous solution, solubility permitting. Cobalt fluoride, chloride, bromide, and iodide were studied in a similar manner. Hemin, hematin, chlorophyllin, and cobalt, copper, iron and vanadyl phthalocyanines were used to catalyze *t*-BuOOH decomposition and PVA cleavage in DMSO and cytochrome c was tested in aqueous solution.

The Disappearance of Cobalt (II) and (III) Acetylacetonate

The original intention of this part of the study was to assess the effect of PVA, *t*-BuOOH, and metal concentration on the overall rate of cobalt (II) or (III) acetylacetonate oxidation and/or reduction. A rate expression such as (81) was used to express this

$$(81) \quad \Delta [\text{Co}] / \Delta t \propto [\text{Co}]^a [\text{t-BuOOH}]^b [\text{PVA}]^c$$

relationship. However, it can be seen from Table (I) and (II) that both cobalt (II) and (III) acetylacetonate reach a steady state concentration during the course of the reaction with t-BuOOH and PVA. This implies that the reactants are going through an oxidation-reduction cycle, such as the reaction (4) and (5) which have been discussed by many authors.⁸⁷



This cycle does not allow quantitatively assessing or correlating the rate of metal ion disappearance with the rate of initiation. However, it can be seen that the positions of the equilibria are different in aqueous and DMSO solution. Cobalt (II) acetylacetonate in the presence of t-BuOOH and PVA in DMSO undergoes an initial color change from pink to green upon addition of peroxide. After approximately 2×10^4 sec a shift back to the pink solution can be seen. Cobalt (III) acetylacetonate gradually shifts to an intermediate green-pink color after peroxide is added. In aqueous solution cobalt (II) acetylacetonate changes from pink to green after peroxide is added and retains the color. Cobalt (III) acetylacetonate in aqueous solution remains green after peroxide addition.

The data in Table (I) and (II) confirms these qualitative observations. In DMSO, cobalt (II) acetylacetonate seems to be approximately 80-90% in the cobalt (II) form and cobalt (III) acetylacetonate approximately 70-80% in the cobalt (II) form. In aqueous solution, approximately 80% of cobalt (II) and (III) acetylacetonate are in the cobalt (III) form. These ratios (cobalt (II)/cobalt (III) and cobalt (II) concentration)

do not appear to vary in any orderly manner with initial cobalt concentration. It can be seen that the cobalt (II)/cobalt (III) and cobalt (II) ratio after 2.0×10^5 sec for cobalt (II) acetylacetonate decreases with increasing PVA concentrations. This change suggests that PVA is participating in the equilibrium.

Z. Osawa, T. Shibamiya, Y. Ogiwara in the cobalt (III) acetylacetonate, *t*-BuOOH system observed that the cobalt (III) form predominates in benzene (green), but that cobalt (II) form predominates in acetic acid (pink).¹⁵⁴ Richardson found a similar dependency of valence form on solvent.⁸⁶ No correlation is made between the predominance of any valence form and its relation to *t*-BuOOH decomposition rates and/or the kinetics involved.

A complication is found to be present in both these solvents. It is noted that the sum of the concentration of cobalt (II) and (III) (as assessed by U.V. measurements) decreased with time (Table (I) and (II)). This indicates that a ligand exchange reaction may be taking place during the reaction causing either precipitation of the catalyst from the solution or the formation of a metal compound in solution which has a lower extinction coefficient than cobalt (II) acetylacetonate.

The greatest loss of total cobalt concentration occurs within 2×10^5 secs in DMSO and H_2O at $42^\circ C$. After this period the rate of total cobalt concentration change seems to slow considerably. Peroxide decomposition is much more rapid within the first 2×10^5 secs indicating that peroxide decomposition may be related to this phenomenon (Figure 1a). It is possible that this nonlinear behavior reflects a first order decomposition process. A graph of the logarithm of the peroxide concentration vs. time (Figure 1b) approximates linear behavior, while a graph of the logarithm of cobalt concentration vs. time does not approach linear

behavior since no loss of intensity occurs after 2×10^5 sec. A relationship between ligand exchange of the catalyst and the catalytic behavior of the metal in peroxide decomposition cannot be quantitatively assessed from these data.

No obvious correlation is seen between the ratio of total cobalt concentration after 2×10^5 secs to the total initial cobalt concentration and PVA concentration or initial concentration in DMSO (Table (I)).

At 60°C the greatest loss of total cobalt concentration occurs within $.5 \times 10^5$ secs. This corresponds to the period of greatest activity in peroxide decomposition at 60°C . The loss is greater in aqueous than in DMSO solution at 60°C , but comparable losses are found in DMSO and aqueous solution at 42°C . Since the rate of peroxide decomposition is lower in aqueous solution at 42°C and 60°C it seems likely that solvent participation in a ligand exchange process is involved. Increasing temperature would seem to favor ligand exchange reaction in aqueous solution to a greater extent than in DMSO solution.

It seems likely that both peroxide decomposition and solvent participation are playing a role in a ligand exchange process. Kamiya has proposed a reaction mechanism for ligand exchange during initiation. (equation (50) - (54)).⁸⁵ Cobalt (II) hydroxide is the end product in Kamiya's ligand exchange mechanism.

Another explanation for deactivation of the catalyst which was put forth by Hiatt, is that formaldehyde or formic acid formed during the initiation process could cause precipitation of the catalyst from solution through complexation.⁸⁷ It would be expected that initiation products would affect peroxide decomposition by blocking metals sites

even if precipitation of the metal does not proceed through this mechanism. This phenomena is known as deactivation. It accounts for the decrease in the rate of t -BuOOH decomposition with time. Deactivation may result from products of the initiation process or of the autoxidation reaction blocking metal sites on the catalyst from reaction with peroxide. Ligand exchange reactions during initiation would also effectively deactivate the catalyst.

An attempt was made to characterize the nature of the precipitation or ligand exchange reaction. Concentrated solutions of cobalt (II) and (III) acetylacetonate ($\sim 10^{-2}M$) in DMSO and aqueous solution were reacted with 0.72M t -BuOOH at $42^{\circ}C$ in the presence of PVA (1.06g/dl). No precipitate was detected. However, if these solutions are titrated with .02N NaOH base to neutralization, a brown precipitate forms in aqueous and DMSO cobalt (II) acetylacetonate solutions. Stock solutions of cobalt (II) and (III) acetylacetonate ($\sim 10^{-2}M$) in DMSO and water which were treated with base show no precipitate within this time period. Stock solutions of cobalt (II) acetylacetonate in water and DMSO which were allowed to air oxidize to cobalt (III) acetylacetonate at $42^{\circ}C$ over two weeks are titrated with .01N base, but no immediate precipitation was noted. This would indicate that it is not the mere change of valence of $Co(II) (acac)_2$ to $Co(III) (acac)_2$ which is responsible for this precipitate.

This precipitate was collected from the product solution and a nujol I.R. run and characteristic -OH bands are seen. An authentic sample of cobalt (II) hydroxide is run and similar bands were seen. This implies that cobalt (II) acetylacetonate had undergone some ligand exchange in the initiation process. In the acidic media which is used for

autoxidation, little precipitation would be expected to take place. In slightly basic solution cobalt (II) acetylacetonate which had reacted with the hydroperoxide precipitated, while unreacted cobalt (II) acetylacetonate does not precipitate under comparable conditions.

It should be noted that the extinction coefficient for cobalt (III) acetylacetonate is more than ten times greater than aquated cobalt complex $\text{Co}(\text{H}_2\text{O})_6^{3+}$ ¹⁵⁵ indicating that if ligand exchange takes place a substantial reduction in the overall cobalt U.V. absorption intensity will take place.

The mechanism of ligand exchange could conceivably be facilitated by solvent participation. The works of K. Saito⁹⁸ on aluminum (III) acetylacetonate in aqueous solution and C. H. Bamford's⁹⁹ work on metal acetylacetonates in DMSO could provide a basis for a mechanism which involved an active role for the solvent in ligand exchange. Saito found that acid may also serve as a catalyst in aqueous solution. *t*-BuOOH, and some initiation and reaction products could possibly act as weak acids and help initiate this process.

Both Kamiya⁹⁵ and Lombard and Knopf⁹⁷ have indicated that initiation reactions play a role in cobalt deactivation and precipitation. A further complication is that organic products formed during the reaction will tend to solubilize the inactivated or undissolved catalyst or solvate and solubilize micelles formed in solution. This will be discussed further for other metal acetylacetonates.

Peroxide Decomposition

The decomposition of *t*-BuOOH in presence of cobalt (II) and (III) acetylacetonate may proceed by either of two paths. When present in high concentration, *t*-BuOOH will decompose via a chain process with kinetic

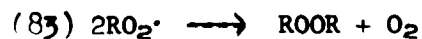
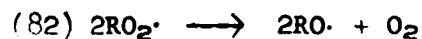
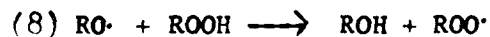
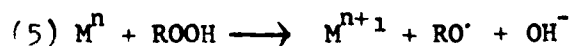
chain lengths >1 . At low peroxide concentrations these chain lengths rapidly approach unity. Chain lengths in protic or polar solvents are low (~ 1) according to Walling and Wagner.¹⁴¹ From product studies it is clear that cleavage of $t\text{-BuO}\cdot$ to $\text{CH}_3\cdot$ and acetone becomes competitive at low $t\text{-BuOOH}$ concentrations or in highly polar solvents. Participation of $\text{CH}_3\cdot$ or $\text{CH}_3\text{OO}\cdot$ in rapid termination reactions reduces chain lengths.

The viscosity and polarity of the solvent may also affect the initiation process. High concentrations of $t\text{-BuOOH}$ and PVA may increase the viscosity of the solvent, thereby increasing cage termination reactions.

Kamiya also found that termination reactions within the cage (production of di- t -butyl peroxide) is suppressed by polar or hydrogen bonding solvents.⁴⁴ The reason for increased cleavage and decreased rate of termination is thought to result from a specific interaction of caged t -butoxy radicals with surrounding solvent molecules in the vicinity of the oxygen. Methyl radicals are found to combine much more rapidly than $t\text{-BuO}\cdot$ radicals as a result a more restrictive orientation of $t\text{-BuO}\cdot$ radicals towards combination. Methyl radicals are much less influenced by solvent due to less interaction of methyl radicals with the solvent.

It is also observed⁹⁰ that protic solvents may block metal binding sites or shift the metal peroxide equilibria, which can significantly lower the rate of initiation. At the low metal concentrations involved in this study metal-radical termination would not be expected to be significant. Metal association in the solvent may be the most important element in the experimental determination of the order of metal ion with respect to decomposition.

In terms of the simplest kinetic scheme we may visualize t-BuOOH decomposition as a radical induced decomposition initiated by metal ion-hydroperoxide interactions.⁸⁰



An expression for the disappearance of peroxide could be written as

$$-d[ROOH] / dt =$$

$$k_5[ROOH] [M(II)] + k_4[ROOH] [M(III)] + k_8[RO\cdot] [ROOH]$$

$$\frac{d[RO\cdot]}{dt} = k_{82}[ROO\cdot]^2 - k_8[RO\cdot] [ROOH] + k_5[M(II)] [ROOH]$$

$$\frac{d[ROO\cdot]}{dt} = k_8[RO\cdot] [ROOH] + k_4[M(III)] [ROOH] - k_{82}[ROO\cdot]^2 - k_{83}[ROO\cdot]^2$$

Assuming a steady state for $ROO\cdot$ and $RO\cdot$ radicals and a rapid cycling of metal ion ($k_5[ROOH] [M(II)] = k_4[ROOH] [M(III)]$) it can be shown that

$$(84) -d [ROOH]/dt = [2k_{82}/k_{83} + 3] [M(II)] [ROOH]$$

Since $M(II) + M(III) = M_T$ or total metal concentration and given the cycling condition we may substitute M_T for $M(II)$.

$$(85) -d[ROOH]/dt = [2k_{82}/k_{83} + 3] \times \frac{(k_4 k_5)}{k_4 + k_5} [M_T] [ROOH]$$

The cobalt (II) and (III) acetylacetonate peroxide decomposition data in DMSO and water exhibit two departures from these kinetics. One departure is that cobalt (II) and (III) acetylacetonate exhibit a reaction order of 1/2 with respect to peroxide decomposition and the second is that

t-BuOOH has an order of less than one with respect to peroxide decomposition. The cobalt (II) and (III) acetylacetonate results are in keeping with Hiatt's work in which a reaction order of 1/2 is found for cobalt (II) and (III) acetylacetonate with respect to decomposition. Hiatt attributed this low order with respect to $[Co_T]$ to aggregation of the cobalt in solution which would mean that cobalt would compete with peroxide for ligand sites. This was also reflected in a non-linear dependence of decomposition on temperature. The high energy of activation of Hiatt's work indicates that temperature may be decreasing aggregate size of the cobalt catalyst as well as increasing the rate of initiation.

Tkac found little radical metal association at ratios of $[t\text{-BuOOH}]/[Co(acac)_2]$ above 15.⁹² This suggests that little radical metal interaction is to be expected in .016M solutions of t-BuOOH with cobalt concentrations of less than $10^{-3}M$. In 0.7M t-BuOOH radical metal reactions would not be important below $10^{-2}M$ metal concentrations. The polarity of solvent would be expected to alter this equilibria. Tkac also found that cobalt (II) acetylacetonate exhibited little esr activity. This suggests a dimeric structure, the existence of which has been independently verified.⁹⁴ Upon addition of a donor ligand (D) the following products are formed: $[Co(acac)_2]_2D$, $[Co(acac)_2D]_2$, $[Co(acac)_2]_2D_2$. $Co(acac)_2OH$ is a more powerful oxidizing agent than $Co(III)(acac)_3$. Some form of dimerization or a dimer monomer equilibrium is likely in DMSO in the system studied here since a $10^{-3}M$ solution of cobalt (II) acetylacetonate did not exhibit any readily detectable metal esr signal in the presence of t-BuOOH.

The presence of a metal hydroperoxide complex between cobalt (II) and (III) acetylacetonate and t -BuOOH has been demonstrated by Jochsberger¹⁷⁴ in chloroform, from the broadening of the $OO-\underline{H}$ line in the nmr. Cobalt (II) acetylacetonate, however, is much more effective at broadening than cobalt (III) (see Table (XXII)). The existence of this complex is much harder to detect in DMSO and water because of the polarity of the solvent. It is assumed that this complex is necessary for initiation on the basis of the kinetic scheme which will now be employed as an alternative to Hiatt's mechanism.

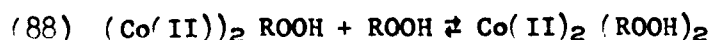
In support of this it is noted that peroxide decomposition is more rapid in DMSO than in water solution at low peroxide concentrations ($<.66M$), but the rate of peroxide decomposition at higher peroxide concentrations ($>.66M$) seems to be similar in both solvents. This may be indicative of the fact that in a very polar solvent such as water the metal peroxide complex equilibria should be shifted to the left towards the uncomplexed form of the metal relative to DMSO. At higher concentrations of peroxide the metal might become saturated with respect to peroxide, masking differences in solvent polarity.

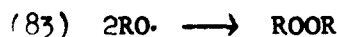
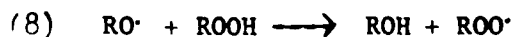
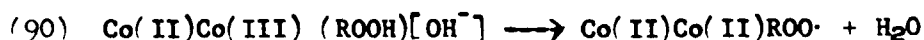
Chain lengths for t -BuOOH decomposition would be equal to the ratio of the total rate of peroxide decomposition to the rate of peroxide decomposition by reactions (4) and (5) (see chain lengths section). This ratio expresses quantitatively the relative amounts of peroxide decomposed by radical induced decomposition of t -BuOOH to that decomposed by a direct reaction with cobalt (II) or (III) acetylacetonate, (reaction (4) and/or (5)). We may assume that peroxide decomposition results totally from cobalt (II) and (III) acetylacetonate-peroxide reactions (reaction (4) and (5)). Chain lengths for peroxide decomposition

would then be equal to one by definition. This assumption is not unreasonable for polar solutions, (e.g. DMSO and H₂O) where chain lengths are expected to be small. Hiatt found that in di-t-butyl-peroxyoxalate initiated t-BuOOH decomposition in acetic acid and t-butyl alcohol that kinetic chain lengths were approximately equal to one for .2M t-BuOOH. Presumably at higher t-BuOOH concentrations kinetic chain lengths would be greater than one, but still short.

Richardson has devised a kinetic scheme for copper 2-ethylhexanoate decomposition of t-BuOOH in chlorobenzene which employs many of the ideas, which have been used in this study.¹² This includes complexation reaction between the metal ion and the hydroperoxide, rapid cycling of the metal ion, a dimeric metal or a monomer dimer equilibrium of the metal, and cage effects with respect to peroxide termination. In addition, the peroxide is assumed to associate with itself in an equilibrium process.

NMR experiments were conducted on the broadening of the hydroperoxide proton absorption in order to demonstrate complexation. This scheme provides less than first order dependence with respect to metal and peroxide in peroxide decomposition. Two possible kinetic schemes are presented. These will be utilized as kinetic models in cobalt acetylacetonate decomposition of t-BuOOH in aqueous and DMSO media. Scheme I does not involve cage effects and the metal is assumed to be in dimeric form. Scheme II involves t-BuOOH cage effects and a monomer dimer equilibrium for the metal ion. Scheme I is represented below.





For the mechanism given by the equations above the rate of disappearance of total hydroperoxide concentration $(\text{ROOH})_T$ is given by eqn. (91), where ROOH is the monomeric hydroperoxide concentration. Rearrangement of the steady state equation for $\text{ROO}\cdot$, $\text{RO}\cdot$ and $\text{Co(II)Co(III)ROOH(OH)}^-$ gives (92). Substitution yields (93) substituting the total, $(\text{Co})_T$ and hydroperoxide ROOH concentration in eqn. (93), and assuming the hydroperoxide exists mainly as a dimer, we obtain equation (94). Equation (94) predicts that order with respect to $(\text{Co})_T$ should be between .5 and 1.0 and ROOH should be between .5 and 1.

$$(91) \quad \frac{d[\text{ROOH}]}{dt} = k_{88}K_{88}K_{87}[\text{Co(II)}_2][\text{ROOH}]^2 + k_{80}[\text{Co(II)Co(III)(ROOH)(OH)}^-] + k_8[\text{RO}\cdot] \text{ROOH}$$

$$(92) \quad [\text{RO}\cdot] = \frac{(k_{88}K_{88}K_{87})^{\frac{1}{2}}[\text{Co(II)}]^{\frac{1}{2}}[\text{ROOH}]}{k_{83}}$$

$$(93) \quad \frac{d[\text{ROOH}]_T}{dt} = 2 k_{88}K_{88}K_{87}[\text{Co(II)}_2] [\text{ROOH}]^2 + k_8 \frac{(k_{88}K_{88}K_{87})^{\frac{1}{2}}}{k_{83}^{\frac{1}{2}}} [\text{Co(II)}_2]^{\frac{1}{2}} [\text{ROOH}]^2$$

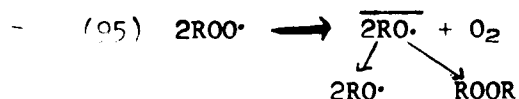
$$(94) \quad \frac{-d[\text{ROOH}]}{dt} = \frac{C_1[\text{Co}_1] [\text{ROOH}]_T}{D} + \frac{C_2[\text{Co}]_T^{\frac{1}{2}} [\text{ROOH}]_T}{D^{\frac{1}{2}}}$$

Where

$$D = C_3 + C_4 [\text{RO}_2\text{H}]_T^{\frac{1}{2}} + C_5[\text{RO}_2\text{H}]$$

$$D^{\frac{1}{2}} = (C_6 + C_7 [\text{ROOH}]_T^{\frac{1}{2}} + C_8[\text{ROOH}]_T)^{\frac{1}{2}}$$

The above mechanism assumes that the cobalt salts remain intact as dimers. Alternatively, a monomer-dimer equilibrium could be assumed (Scheme II). This assumption will change a rate law with first order dependence to half order dependence on total cobalt salt. Such a mechanism requires almost exclusive reaction of the hydroperoxide with the cobalt salt monomer, even though the dimer predominates, to explain .5 order in cobalt salt. Nonetheless, with this assumption, the radical cage reaction (95) can be substituted for reaction (82) without requiring a reaction between two alkoxy radicals to explain the approximate 1/2 order in cobalt (II) salt, where the superscript bar is used to indicate a caged radical. The importance of free t-butoxy



radical combination is subject to reaction conditions. Richard Noyes,^{156, 157}
¹⁵⁸
 and C. Patrick and P. Allen have attempted to treat radical cage recombination in a quantitative manner. Noyes distinguishes between primary recombination processes, in which recombination of radical fragments is fast and occurs quickly (10^{-11} secs) and secondary recombination, which involves escape from the cage and reencounter of the original radical fragments within 10^{-9} secs. A scavenger can only compete with secondary recombination as opposed to primary recombination and can compete only if the scavenger is in sufficiently high concentration. Primary and

secondary recombination combined are commonly referred to as geminate recombination. Radical fragments may combine with each other outside the cage as well. This decrease in radical efficiency results from the combination of fragments from other dissociations. The overall efficiency of initiation will therefore depend on the concentration of the scavenger at very low concentrations, but will approach a constant value at high concentrations. To improve efficiency beyond this point the scavenger must be so reactive as to compete with secondary recombination. The proportion of mutual termination of geminate chains must depend, on one hand, on factor controlling the rate of diffusion of the radicals in the medium, and on the other, the average distances of a radical to its twin and other radicals, and this will depend on the rate of decomposition of the initiating molecule. Patrick and Allen found that if the rate of propagation has a first order dependence on the rate of decomposition of the initiator molecule, geminate recombination will predominate. A half order dependence indicates normal bimolecular termination.

It can be seen that the effect of PVA might be expected to be two-fold in non-metal induced peroxide decompositions. One involves PVA as a chain carrier or scavenger. At higher concentrations, PVA might be expected to compete more effectively for radicals which undergo secondary recombination or bimolecular termination. In this process it must compete with t-BuOOH for propagation reactions. It was observed by Hiatt and Mayo that even though bond strengths for ROO-H and secondary C-H hydrocarbons are approximately the same (~ 90 kcal/mole) the removal of a hydrogen atom from hydroperoxide by an alkoxy radical is much faster than for hydrocarbons.¹⁰⁷ This suggests that activation energies are not

proportional to bond strengths. In fact, secondary alcohols lower chain lengths and retard di-*t*-butylperoxyoxalate induced *t*-BuOOH decomposition. The second effect of PVA concentration is to increase the viscosity of the medium. The viscosity effect of the PVA in increasing cage recombination is expected to be small on the basis of Kamiya's work on di-*t*-butylperoxyoxalate induced decomposition of *t*-BuOOH in polypropylene benzene solutions.⁴⁴ Increases in macroscopic viscosity through increases in the polypropylene concentration did not increase cage termination, since the polymer molecule has little effect on small solvent molecules. Solvent will have an effect on cage recombination, since protic or highly polar molecules seem to diminish cage recombination greatly. Changes in the viscosity of the solvent media by the use of viscous solvents (i.e. *t*-butyl alcohol or *t*-BuOOH) would be expected to have a marked effect on cage recombination as well. This was observed by Kamiya in the DBPO induced decomposition of *t*-BuOOH in solvents of varying viscosity. T. Traylor has also used this effect to explain decreases in chain lengths in *t*-BuOOH peroxide decompositions at high peroxide concentrations ($\approx 1M$).

The viscosity of DMSO is 19.9mp as opposed to 8.94mp for water at 25°C. The viscosity effect of water relative to DMSO is expected to be small. However, the solvent hydrogen bonding effect may be appreciable in aqueous solution as compared to DMSO. This might result in decreased rates of geminate recombination and decreased rates of propagation and termination. This effect could increase overall chain lengths.

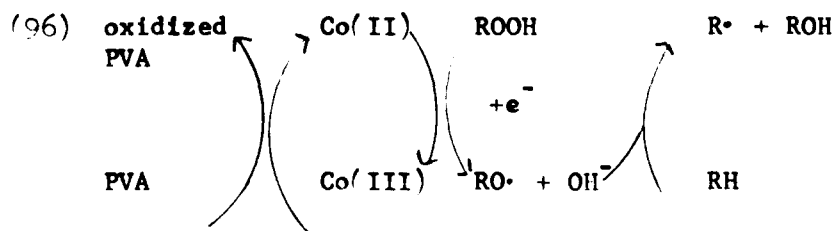
In metal catalyzed PVA autoxidations there are additional possibilities for interaction. For instance, Hiatt and Mayo found that *t*-butyl alcohol (an initiation product) lowered the rate of metal catalyzed decomposition by 100 times in chlorobenzene.⁹⁰ This effect can not be

rationalized by increased cleavage of *t*-butoxy radicals alone, but must represent competition by the alcohol with peroxide for metal sites. Experiments on possible identification of a PVA-cobalt chloride complex have been conducted by observing the shift in the nmr absorbance of the methinyl proton of PVA with increasing cobalt chloride concentration (Table XVI and Figure (8)). It was observed that in DMSO, PVA can complex metal ions. In DMSO solution with small quantities of water added no complex is detected. Presumably *t*-BuOOH would have a similar effect. In these solution PVA might be competing for metal sites with *t*-BuOOH. Another possible PVA effect concerns the ability of α hydroxy ketones in metal catalyzed peroxide decompositions. These reactions have been discussed previously in the historical section (refer to page 52). Possible mechanisms include an increase in metal reduction leading to an increased rate in the metal-peroxide cycling reaction, direct reactions of an intermediate product with peroxide, or direct reaction of an active complex formed between the substrate and the metal.¹⁴⁷ Presumably the cleavage reaction of the PVA would be expected to provide hydroxy ketone groups, which are involved in this reaction. Possible reactions are presented in equations (77) and (79).



Equation (77) and (79) represent a direct reaction of the cobalt species with the substrate and a direct reaction of either a *t*-butylperoxy or alkoxy radical or a polymeric peroxy or alkoxy radical with the metal species. It is possible that a reaction product such as a polymeric aldehyde is the active species in step (77). Using a biological notation the role of PVA and cobalt (II) and (III) acetylacetonate may be represented

as in equation (96). Although experimental evidence exists for these



interactions the kinetic consequences are difficult to predict or verify.

The participation of PVA somehow in the initiation reaction is indicated by the fact that at low peroxide concentrations where chain lengths

are short, PVA exhibits a higher order with respect to peroxide decomposition than at higher peroxide concentrations. A possible initiation

reaction might involve the direct reaction of metal cobalt (II) or (III)

acetylacetonate with the substrate or a cobalt (II) or (III) acetylacetonate substrate complex which undergoes a reaction to form radical products.

Reactions such as these are discussed in numerous articles (Reactions

(6a) and (6b)).¹⁴ It should be noted that hydrocarbons can lower

radical chain lengths by competing for the propagating radical with ROOH.¹⁸⁰

Benson has devised a kinetic scheme for peroxide decomposition in the

presence of a hydrocarbon.¹⁸⁰ The same treatment can be used for t-butoxy

radical cleavage reactions (t-BuO[•] → CH₃ C(=O)CH₃ + CH₃•) where a

different chain carrier, CH₃• is involved. Radical termination reactions

can occur between the two propagating hydrocarbon radicals or between

the t-BuO• or t-BuOO• radical and the hydrocarbon radical. It would be

expected in this system that t-BuOO• radicals would be the primary

chain carriers. The effect of both cleavage and substrate reactions is

to raise the order of t-BuOOH with respect to peroxide decomposition.

At concentrations < .06M PVA might be expected to compete for t-butyl

peroxy radicals more effectively than at higher peroxide concentrations.

Likewise, cleavage reactions of the t-butoxy radical ($\text{t-BuO}\cdot \longrightarrow \text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-CH}_3 + \text{CH}_3\cdot$) are expected to be much more prominent giving rise to a similar increase in order with respect to peroxide decomposition, provided that the $\text{CH}_3\cdot$ takes part in propagation reactions.

Richardson's kinetic treatment seems adequate to explain the reaction orders in DMSO with respect to cobalt (II) (.55) and cobalt (III) (.52) and in aqueous solution where orders with respect to cobalt (II) (.50) and cobalt (III) (.49) are similar. (Table (V) and (VI) and Figure (3)). All of these are approximately half order in cobalt (II) and (III) acetylacetonate and this seems to be a common feature of cobalt (II) and (III) acetylacetonate decompositions in aqueous DMSO, and chlorobenzene solution.⁹⁰ Aqueous solutions of the reaction mixture have orders with respect to t-BuOOH approaching 1.00 (.80) at high peroxide concentrations, where DMSO solutions have a reaction order with respect to t-BuOOH of .50 at high peroxide concentrations. This could mean that a reaction mechanism involving a complex between the metal and hydroperoxide may not be important in aqueous solution. The lower rate at low peroxide concentrations in aqueous solution as compared to DMSO could be explained by the blocking effect of H_2O on the metal sites. At higher peroxide concentrations (.66M) where all the sites (or at least some of them) would be expected to be filled by peroxide molecules the rates of DMSO as compared to aqueous solution are similar.

The cleavage reaction of t-butoxy radical ($\text{t-BuO}\cdot \longrightarrow \text{acetone} + \text{CH}_3\cdot$) is not treated quantitatively. Cleavage reactions would only be important at low peroxide concentrations, since at higher t-BuOOH concentrations t-butyl alcohol will be formed. Deactivation and/or precipitation of the catalyst are not accounted for in either Richardson's

or Hiatt's kinetic scheme. It would not be expected that *t*-butoxy radical cleavage reactions or deactivation of the catalyst would significantly change the kinetic dependancies, since only small changes in kinetic order of cobalt (II) with respect to decomposition occur from .016M *t*-BuOOH to .16M *t*-BuOOH in DMSO (Table (III)). On most cases initial rates were used in *t*-BuOOH decompositions, since auto-retardation occurred before 50% of the peroxide was decomposed (Figure (1)). Deactivation may be fairly serious at high peroxide concentrations, since the rate of decomposition seems to decrease in the concentration range .66 to .96M *t*-BuOOH in DMSO (Figure (2)). Kamiya has attributed a similar effect to deactivation of the catalyst at high peroxide concentrations. Another explanation for this decrease is supplied by Factor, Russell, and Traylor in di-*t*-butylperoxyoxalate initiated decompositions of *t*-BuOOH.¹⁵⁹ They found that at ≈ 1 M *t*-BuOOH chain lengths decreased. They attributed this phenomena to a solvent effect. The peroxide solvent might exert an influence on the solvation of the radical, hydrogen bonding between it and the predominant solvent, or by increasing the viscosity of the solvent which might increase geminate recombination in initiation.

The energy of activation for the decomposition of 0.016M *t*-BuOOH catalyzed by $\approx 2 \times 10^{-4}$ M cobalt (II) and (III) acetylacetonate in DMSO and aqueous solution is 29 Kcal for all processes (Table VII). This value is consistent with Jochsberger's and Indictor's work on metal catalyzed *t*-BuOOH decomposition.¹⁶¹ This value is higher than values reported by Hiatt and Mayo⁹⁰, however. The high value of the energy of activation results from the fact that kinetic chain lengths would be expected to be very short at low peroxide concentrations and in polar

solvents. A chain process would be expected to have a lower energy of activation. Thermal decomposition of t-BuOOH has an energy of activation 43.2 kcal/mole for .02M t-BuOOH in benzene between 170-190°C. This is consistent with (O-O) bond homolysis on the basis of bond energies.¹⁸⁰

It should be noted that the high value for the energy of activation is consistent with Hiatt's data on cobalt (II) acetylacetonate and it was suggested by Hiatt that this was indicative of aggregation of cobalt in solution.⁹⁰ Higher temperatures would reduce the size of aggregates, increasing the rate of decomposition. This was used to explain the half order dependence of cobalt concentration with respect to t-BuOOH decomposition.

The basic difference between Richardson's and Hiatt's scheme for decomposition is that one employs a metal t-BuOOH complex while the latter does not. Richardson's scheme also allows for the possibility of cage termination reactions. Both peroxide decomposition schemes call for a metal cycling reaction in which the metal attains a steady state concentration. A clear distinction cannot be made on the basis of these results between Richardson's and Hiatt's scheme. However, the low reaction orders with respect to cobalt and t-BuOOH in t-BuOOH decomposition seem to favor the more complex kinetics of the Richardson model in DMSO. It is felt that complexation of the metal and the peroxide is an important reaction. This could explain the apparent lower reactivity of cobalt (III) acetylacetonate in the decomposition reaction. Also the cage termination reactions of Richardson provide useful models to explain many features of the reaction. However, in aqueous solution Hiatt's mechanism which involves no metal complexation with t-BuOOH may approximate the kinetic situation observed. On the basis of spectral

data it can be surmised that water is more tightly bound than DMSO to cobalt species in solution.¹⁶² It would seem reasonable that water would compete for metal-peroxide sites on cobalt (II) and (III) acetylacetonate more effectively than DMSO. As a result, metal peroxide complexes in DMSO would be more probable than in aqueous solution. This is supported by the kinetic data in peroxide decomposition, as well as the results obtained in the contact shift experiment with PVA and cobalt (II) chloride (see page 153)

Autoxidation

A standard kinetic treatment for catalyzed autoxidation can be employed to try to explain the results in Tables (VIII), (IX), (X) and (XI). It would be expected that t-BuOOH would be the predominant chain carrier in PVA autoxidation, because of the ease with which the O-O-H can be abstracted in solution. In cumene autoxidation with α,α' azo-bis-isobutyronitrile initiation it was found that t-BuOOH significantly increased the autoxidation rate of cumene. This was attributed to the fact that t-BuOOH was the principal chain carrier and increased the rate of autoxidation by decreasing the rate of termination.¹⁶³

It was found that t-BuOOH solutions which were catalyzed by cobalt (II) and cobalt (III) acetylacetonate in the absence of PVA in DMSO and water absorbed or took up oxygen at a slow rate. Presumably this oxygen is being taken up by $\text{CH}_3\cdot$ radicals, which were being formed from t-BuOOH cleavage. In DMSO, an additional possibility of a t-BuOOH reaction with the solvent is possible.¹⁷¹ This effect is expected to be small.

C. Bawn and E. Chaudhri have pointed out that kinetic dependencies of α, α' azo-bis-isobutyronitrile and the polymer in α, α' azo-bis-isobutyronitrile catalyzed autoxidation of polypropylene are different from 2,6,10,14-tetra-methyl—pentadecane (a low molecular weight model compound).¹⁴² The primary difference is the low chain lengths of the autoxidation process in comparison with high molecular weight compounds. This was attributed to possible increase in geminate recombination which would decrease chain lengths. Also a higher concentration of tertiary hydrogens in solution lowers the chain length (by chain transfer).

In the results presented here the chain lengths for PVA autoxidation appears to be small, as can be seen in Tables (XII) and (XIII) (See section of chain lengths). Because of the variable order of the autoxidation reaction with respect to substrate concentration it is observed that the simple equation of the form $\frac{dO_2}{dt} = [Co]^a [t-BuOOH]^b [PVA]^c$ does not effectively describe the whole autoxidation process. However, values for a, b, and c are tabulated for specific concentrations. It is illustrative to compare the data obtained to the equation derived by Tobolsky for the benzoyl peroxide initiated autoxidation of polypropylene in bulk.²⁴ Two terms are found on the right hand side of the equation. One expresses a dependence on the rate of initiation (R_i) and the other expresses a dependence on $(R_i)^{\frac{1}{2}}$ (RH) $\left[\frac{dO_2}{dt} = R_i + \frac{k_p}{k_t^{\frac{1}{2}}} (R_i)^{\frac{1}{2}} [RH] \right]$.

If both sides are divided by R_i it can be seen that the expression $dO_2/dt/R_i$ (the kinetic chain length) will vary linearly with $(R_i)^{-\frac{1}{2}}$.

In polar solvents where peroxide decomposition chain lengths are low, we may take the chain length for peroxide decomposition as being equal to 1. In other words, all of the peroxide is decomposed by reactions such as (4) and (5), which involve direct cobalt (II) and (III)

acetylacetonate reaction. Using this assumption the rate of initiation is equal to the rate of t -BuOOH decomposition. The kinetic chain length for autoxidation is equal to the ratio of the rate of autoxidation $\frac{dO_2}{dt}$ to the rate of initiation (R_i). We can see that by contrasting Table (XII) and (XIII) that the chain length for autoxidation in DMSO appears to be smaller than in aqueous solution. These chain lengths are based on the assumption that all the hydroperoxide that is decomposed result from reactions (4) and (5). In DMSO it is possible that chain lengths would be greater than one if cobalt (II) acetylacetonate sites were saturated with respect to peroxide. After the saturation point only radical induced decomposition of the peroxide could take place. The rate of peroxide decomposition would then be greater than the rate of initiation. Consequently, the calculated chain length for autoxidation would increase if we assume that saturation of the cobalt (II) acetylacetonate sites is taking place. One explanation for the apparently higher chain lengths in aqueous solution as opposed to DMSO solution is that aqueous solution would be expected to decrease the extent of cage recombination of polymeric alkoxy radicals during the termination reaction of two polymeric peroxy radicals.⁴⁴ As a result, these alkoxy radicals can undergo further propagation reactions. This effect is not significant in hydrocarbon autoxidations where autoxidation rates are generally lower in aqueous solution. Lloyd ascribes this to a specific interaction between the propagating radical and the solvent which lowers the overall rate of propagation.¹⁰⁷ Another explanation for longer kinetic chain lengths in autoxidation in aqueous as compared to DMSO solution is that the polymer conformation in aqueous solution is more tightly coiled than in DMSO solution.¹⁶⁵ The more extended conformation of the PVA molecule in DMSO solution as compared to aqueous solution is exhibited

in the higher viscosity of PVA solutions in DMSO as compared to aqueous solutions. A tightly coiled conformation might result in a lower rate of termination in the more coiled conformation. This would result in longer autoxidation chain lengths in DMSO solution. This explanation is supported by research on the polymerization of methyl methacrylate in aqueous and *t*-butyl alcohol solutions.¹⁷² It was found that in aqueous solution the degree of polymerization was greater than for polymerizations conducted in *t*-butyl alcohol solution. This suggested that the tighter coiling of the polymer chain in aqueous solution lead to a reduced termination rate.

Tobolsky's scheme for autoxidation yields the fact that the kinetic chain length for autoxidation $\left(\frac{dO_2/R_i}{dt}\right)$ varies linearly with $R_i^{-\frac{1}{2}}$.

From the data on cobalt (II) acetylacetonate, *t*-BuOOH initiated autoxidation in DMSO it can be seen from Figure (5) and (6) and Table (XII) and that in the graph of $\frac{dO_2}{dt} / \frac{d\textit{t-BuOOH}}{dt}$ vs. $\left(\frac{d\textit{t-BuOOH}}{dt}\right)^{-\frac{1}{2}}$ the chain length does decrease with $R_i^{-\frac{1}{2}}$ in DMSO and aqueous solution. It is expected from Tobolosky's treatment that the slope of this line will vary with PVA concentration and the intercept will be unity. If the intercent is assumed to be one it can be seen that the slope of the line does increase with PVA concentration. The assumption that peroxide decomposition proceeds exclusively through cobalt (II) and (III) acetylacetonate-peroxide interaction seems to give moderately good fit to Tobolosky's kinetic treatment. It should be noted that this is based on a very limited amount of data and many interpretations can be placed on the data. Values can be computed for $\frac{k_n}{(k_t)^{\frac{1}{2}}}$ from the slone of the line in Figure (5) and (6) for the autoxidation of PVA in aqueous and DMSO

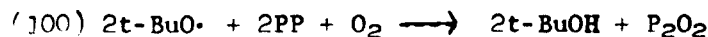
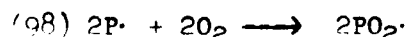
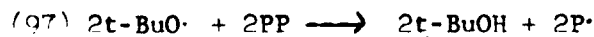
solution under the conditions studied. The values $\frac{k_p}{(k_t)^{1/2}}$ are equal to approximately 1×10^{-2} in aqueous solution and 3×10^{-3} in DMSO solution. These values indicate that PVA is more readily oxidized in aqueous solution than in DMSO solution.

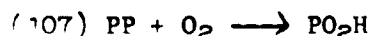
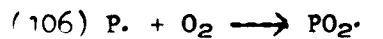
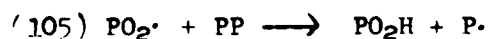
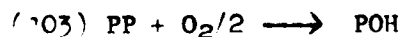
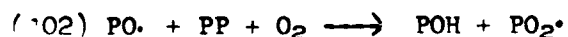
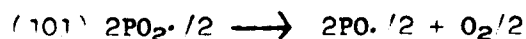
Mayo's kinetic treatment of autoxidation data involves an equation of very similar form $-\frac{dO_2}{dt} = aR_i + \frac{k_p}{(2k_t)^{1/2}} [R_i]^{1/2} (RH)$.⁴³

Mayo found that a took on a value between one half and one in di-*t*-butyl peroxyoxalate initiated polypropylene autoxidation in the bulk phase. The value of a is a complex function of reaction conditions (viscosity, solvent polarity, etc.). This treatment can be utilized to explain the variation of the reaction orders of the reacting species with respect to autoxidation, since the extent of propagating versus non-propagating reactions of polymeric radicals will vary with reaction conditions.

Niki, Decker, and Mayo⁴⁴ concluded that most of the oxidation was taking place within a solvent substrate cage. Termination reactions of polypropylene were much more prevalent than non-terminating reactions. This leads to kinetic dependencies which are different from those found in non-polymeric oxidations.

The following are propagation reactions which were devised by Niki, Decker, and Mayo in which PP is the polymer molecule and *t*-BuO $\cdot$ is the propagating initiator radical.





In this reaction scheme, chain propagation and hydroperoxide formation result only from isolated peroxy radicals outside of the initiating cage. The concentration of isolated $\text{PO}_2\cdot$ radicals are proportional to the square root of their rate of formation, R_i (and disappearance, $R_i = 2k_t [\text{PO}_2\cdot]^2$) and therefore the rate of chain propagation is half order in R_i . It is assumed that all attack is through tertiary C-H bonds. An ordinary tertiary aliphatic C-H bond is about eight times as reactive as a secondary C-H bond toward alkyl peroxy radicals at 145°C, 15-20 times as reactive at 45°C.⁴³

The rate of oxygen absorption by the first order reactions (100) and (103) is $d[\text{O}_2]/dt = a R_i$ where a is a constant depending on the relative proportions of reaction (100) and (103). The rate of oxygen absorption in chain propagation reaction (105) and (98) at any time t during decomposition is $d\text{O}_2/dt = (R_i/2k_t)^{1/2} k_p[\text{PP}]$. R_i is the instantaneous rate of useful $\text{P}\cdot$ radical production and k_p and k_t are defined by reactions (105) and (99). If the rate of the first order reactions is significantly greater than the rate of propagation reactions the equation for the rate of oxygen absorption becomes essentially first order in R_i . If propagation reactions are prevalent (high kinetic chain lengths) then the reaction would be .5 order in R_i and first order in substrate. It

is apparent from the data that apparent chain lengths are not high and that first order reactions will play substantial role in this reaction. Mayo has shown that 84% of the oxygen absorbed in the autoxidation of polypropylene in bulk occurs within the polymer cage. Polymer radicals escaping the cage can be effectively scavenged by any compound with an easily abstractable hydrogen (t -BuOOH or PVA). It has been found by Factor and Traylor in the di- t -butylperoxyoxalate induced decomposition of t -BuOOH that concentration of t -BuOOH which are approximately 1 M, decrease the chain length.¹⁵⁹ This is apparently a solvent effect in which the hydroperoxide is replaced by t -butyl alcohol as a solvent. The viscosity of t -BuOOH is 33mp and a 1:1 mixture of t -BuOOH and t -butyl alcohol is 41 mp and t -butyl alcohol is 46 mp. Viscosity dependant cage recombination of t -butoxy radicals generated in the initiation and termination processes was utilized to explain the decrease in chain length of 1M solution of t -BuOOH.

This same explanation can be utilized as an explanation for the results obtained in PVA autoxidation in the presence of t -BuOOH and cobalt (II) and (III) acetylacetonate (Table (VIII) and (IX)). In DMSO solution, the dependence of the rate of autoxidation on[PVA] seems to decrease with increasing [t -BuOOH]. An increase in the viscosity of the solvent might increase the extent of geminate recombination in both initiating and terminating reactions of PVA autoxidation. The mechanism devised by Mayo can be utilized to investigate the kinetic consequence of this occurrence.

Mayo pictures autoxidation as being a combination of propagating and non-propagating reactions. These two types of reactions define the limits of the reaction orders of PVA, t -BuOOH, and cobalt (II) and (III)

acetylacetonate with respect to autoxidation. An empirical formula of the form $\frac{-dO_2}{dt} = k[Co_T]^a[t-BuOOH]^b[PVA]^c$ can be adopted to represent the autoxidation kinetic behavior of this system. If all reactions were essentially non-propagating then the rate of autoxidation would be proportional to the rate of initiation ($\frac{-dO_2}{dt} = a R_i$). In this case the dependence of the concentration of PVA on the autoxidation rate would be zero. The rate of initiation in DMSO can be taken as equal to the rate of peroxide decomposition of cobalt (II) and (III) acetylacetonate, t-BuOOH, PVA reaction system. In this case it can be seen in Table (III) that $R_i = k [Co_T]^{.5}[t-BuOOH]^{.5}[PVA]^{.35}$. Therefore in non-propagating reactions in DMSO solution the rate of autoxidation is proportional to R_i or $\frac{-dO_2}{dt} = a[Co_T]^{.5}[t-BuOOH]^{.5}[PVA]^{.35}$. In aqueous solution (Table IV) the rate of peroxide decomposition = $k [Co_T]^{.5}[t-BuOOH]^{.6-.80}[PVA]^{.45}$. The above equations define the limits for non-propagating reactions in DMSO and aqueous solutions. If the reactions were exclusively propagating the rate of autoxidation would be proportional to $[R_i]^{\frac{1}{2}}[RH]$. In this case, in DMSO solution $\frac{-dO_2}{dt} = k[Co_T]^{.25}[t-BuOOH]^{.25}[PVA]^{.17+1}$ and in aqueous solution $\frac{-dO_2}{dt} = k[Co_T]^{.25}[t-BuOOH]^{.30-.40}[PVA]^{.22+1}$. The exponents or reaction orders of PVA, t-BuOOH and cobalt (II) and (III) acetylacetonate in the propagating and non-propagating case define the limits of the reaction order values in autoxidation. The limiting values of reaction orders can be compared with the data actually obtained for these constants in Table (VIII) and (IX). In DMSO values are obtained which vary with reaction conditions (Table (VIII)). For cobalt (II) acetylacetonate-t-BuOOH initiated autoxidation of PVA $\frac{-dO_2}{dt} = k[Co_T]^{.45}[t-BuOOH]^{.4-.25}[PVA]^{.53}$. These values fall in

between the limiting values for the propagating and non-propagating reaction mechanism in DMSO solution. In aqueous solution the cobalt (II) acetylacetonate-t-BuOOH initiated autoxidation of PVA it can be seen, $\frac{-dO_2}{dt} = k[Co_T]^{.5}[t-BuOOH]^{.5}[PVA]^{.4}$. These values also fall between the two limiting values for propagating and non-propagating mechanisms.

In DMSO solution it can be seen that the value of the reaction order for PVA with respect to autoxidation decreases with increasing peroxide concentration. One possible explanation for this is that the increased concentration of t-BuOOH increases the viscosity of the solvent increasing the rate of t-butoxy radical and polymer alkoxy radical recombination within the solvent polymer cage. The net effect of this would be to decrease chain lengths in autoxidation thereby favoring non-propagating mechanisms. If we compare non-propagating equations with propagating equations it can be seen that the overall order of PVA with respect to autoxidation will decrease with an increasing proportion of non-propagating reactions. At very high concentrations of t-BuOOH in DMSO (.96M) the autoxidation rate decreases. This could indicate that solution viscosity is playing a role in autoxidation and decreasing the rate of propagation. Similar behavior is exhibited in t-BuOOH initiation reactions as can be seen in Table (III) and Figure (2).

Increasing PVA concentration in DMSO seems to lower the reaction order of t-BuOOH with respect to autoxidation. This may be indicative of an increased likelihood of propagating reactions at higher PVA concentrations. This would decrease the overall dependence of autoxidation on t-BuOOH concentration. The reaction orders do not vary significantly with increasing concentrations of PVA, t-BuOOH, and cobalt (II) and (III) acetylacetonate.

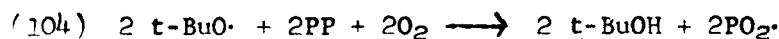
In aqueous solution, dependencies for PVA, *t*-BuOOH and cobalt are similar to those found in DMSO for autoxidation. The reaction order values appear to be less sensitive to concentration effects in DMSO (Table (XIII)). This may reflect the fact that solution viscosity effects are of a much smaller order in aqueous solution as opposed to DMSO ($\eta=0.89\text{cp}$ for water and $\eta=1.99\text{cp}$ for DMSO).

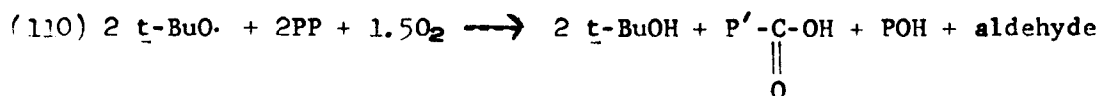
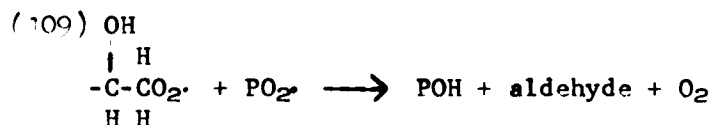
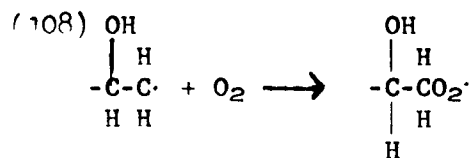
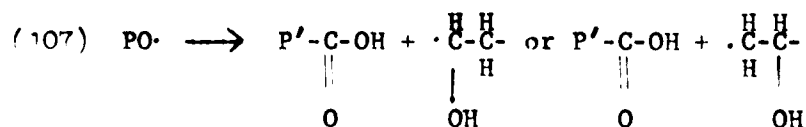
At high cobalt (II) and (III) acetylacetonate concentrations ($>10^{-3}\text{M}$) the rate of autoxidation does not significantly increase and with cobalt solutions of concentration ($>10^{-2}\text{M}$) it decreases. This is consistent with the finding Reich and Stivala.²⁷ It was found that in the cobalt (III) acetylacetonate initiated autoxidation of polypropylene in bulk that autoxidation rate declined in the 10^{-5}M to 10^{-2}M concentration of cobalt (III) acetylacetonate. At higher concentration of metal radical-metal interactions become more important. Tkac indicated that cobalt (II) and (III) acetylacetonates could complex with peroxy radicals at high metal concentrations ($>10^{-3}\text{M}$). Another result found in both aqueous and DMSO solutions is that higher concentrations of peroxide (.72 - .96M) seem to decrease the rate of autoxidation. This is related to a similar phenomenon in the peroxide decomposition reactions. This can be attributed to an increase in the deactivation of the catalyst at higher peroxide concentrations. A more likely explanation is that higher peroxide concentrations alters the nature of the solvent. This leads to a decrease in the chain length for peroxide decomposition. This has been discussed earlier in the section on peroxide decomposition.

The reaction rate appears, as expected⁴³, to have no dependence on oxygen concentration from oxygen atmosphere of 10-100% oxygen (nitrogen

present as a diluent). Cleavage reactions of t-butoxy radicals ($\text{t-BuO}^\cdot \longrightarrow \text{acetone} + \text{CH}_3^\cdot$) at low concentrations would be expected to have some effect on the oxidation rate. Such reactions would increase the rate of termination as well as account for some percentage of oxygen taken up by the reaction. At low concentrations of peroxide cleavage may in fact become the rate controlling reaction for termination. At the concentrations of t-BuOOH employed in this study, cleavage reactions of the t-butoxy radicals would not be expected to be significant. It should be noted that methyl radicals would take part in propagation reactions if cleavage reactions of t-butoxy radicals were significant.

Cleavage reactions of PVA would also have an effect on the autoxidation reaction. Cleavage reactions of PVA could account for only .1% of the oxygen absorbed by the reaction mixture (see cleavage section and Table (XIX)). Presumably polymer termination reactions would be more rapid among polymer cleavage products and therefore polymer cleavage would yield higher rates of termination in the autoxidation reaction. The effect that the cleavage reaction has on the chemical composition of the polymer, thereby altering initiation, propagation and termination reactions cannot be gauged from this data. Oxygen absorption is fairly linear with respect to time in cobalt oxidation reaction. This contrasts sharply with cleavage reaction behavior with time which is not linear with time. This will be discussed further in the cleavage reaction section. Mayo discussed possible cleavage reactions for polypropylene. A typical reaction sequence is represented below for PVA.





This reaction sequence is also proportional to the rate of initiation $\frac{d\text{O}_2}{dt} = a [\text{R}_1]$. The feasibility of this reaction will be discussed in the cleavage section. If the reaction scheme proceeded mainly through 1,2 glycol carbon bond a secondary radical would be obtained as opposed to the formation of a primary radical if 1,3 glycol carbon bond is involved. The primary and secondary radicals formed would be expected to terminate much more rapidly than the tertiary radicals in the reaction. For instance, primary alkyl peroxy radicals are about 10^4 times as reactive as tertiary alkyl peroxy radicals in chain termination of small hydrocarbons.⁴³ The difference can hardly be as large in bulk polymers, but it may still be significant. It is therefore assumed that most of the primary peroxy radicals formed in reactions (107) and (108) terminate by reaction (109) instead of propagating. Cleavage reactions will allow termination to proceed more easily and lower the activation energy of the termination reaction.

Cleavage Reactions

Some of this work has already been published.¹⁸² Cleavage was measured viscometrically and the decrease was expressed in the molecular weight decrease with time. Aqueous solutions are approximately ten times slower within the first 2×10^5 secs than DMSO solutions in terms of cleavage of PVA in the presence of .66M *t*-BuOOH and solutions of cobalt (II) and (III) acetylacetonate (10^{-5} - 10^{-3} M) and 1.06 g/dl of PVA (Table (XIV)). In the presence of a nitrogen atmosphere cleavage proceeds at a similar rate. This indicates that the cleavage rate is not a function of peroxide decomposition. In fact, increasing peroxide and cobalt concentration increases the rate of reaction. After 1×10^5 sec a substantial decrease takes place in the rates of reaction in DMSO. The rate in DMSO approaches the rate in aqueous solution. Under these conditions (42°C, .66 M *t*-BuOOH), the per cent of *t*-BuOOH decomposed relative to the total concentration of *t*-BuOOH is extremely small. As a result, peroxide decomposition data reflects decomposition over the course of several weeks. This data indicates similar decomposition rates in both DMSO and aqueous solution at these concentrations (Table (III) and (IV) and Figure (2)).

The disparity between cleavage rates and *t*-BuOOH decomposition may involve a direct reaction of cobalt with PVA to effect cleavage. It was hypothesized that cobalt could cleave the 1,2 glycol linkage by first forming a complex with PVA, followed by an electron exchange reaction. An alternate explanation is that a cobalt complex might stabilize radicals formed and cause an increase in the rate of cleavage reactions. In fact, the literature is replete with α diol cleavage reactions which are catalyzed by metals.^{51,52} Cobalt (II) and (III) acetylacetonate

cleavage reactions which are run in the absence of peroxide are very slow as compared to reactions in the presence of t -BuOOH and would not be expected to be a major reaction. However, it is found that cobalt (II) acetylacetonate catalyzed reactions in DMSO are much more active in cleavage than cobalt (III) acetylacetonate in spite of small differences in peroxide decomposition rates (Table (XIV) and (XV)). It is also found that the reactions with cobalt (II) acetylacetonate seem to exhibit the most rate acceleration for 10^{-6} - 10^{-5} M cobalt (II) acetylacetonate. In the concentration range of 10^{-4} to 10^{-3} M a much smaller rate increase is seen. Cobalt (III) acetylacetonate seems to exhibit fairly linear behavior in these concentration ranges. The rate enhancement for PVA cleavage as a result of added peroxide is not as great as that in autoxidation or t -BuOOH decomposition.

For these reasons we cannot dismiss the possibility of cobalt taking a part in radical stabilization of an intermediate in the cleavage reaction. Cobalt (II) acetylacetonate is known to stabilize radicals.⁹² Cobalt (II) acetylacetonate will also complex with 1,2 glycols.¹⁶³ The complexing phenomena was investigated by use of contact shifting in the nmr. Szarek and Baird investigated cobalt (II) acetylacetonate complexation with cis and trans 1,2-cyclohexanediols.¹⁶³ These authors showed that a paramagnetic complex between cobalt (II) acetylacetonate and the diols existed. A similar experiment was performed with PVA and cobalt (II) chloride. A plot of chemical shifts observed vs. cobalt chloride concentration (Figure (8) and Table (XVI)) shows an increase in the shift of the methinyl proton of PVA with increasing cobalt chloride concentration up to about 3.5×10^{-6} M, followed by a leveling off. This shifting with PVA is not observed when traces amounts of

water are present in solution. In this case, the cobalt ion is probably preferentially complexed with the water.

Small amounts of water (.04 - .02M) were added to DMSO reaction mixtures and the observed rate of cleavage decreased (Table (XVII)). In all reactions in our study, molecular weight changes corresponded to fewer cleavages than the total number 1,2 glycol linkages present in PVA.

Experimentation indicates that PVA without 1,2-glycol structures (periodate cleaved PVA) exhibit no cleavage activity in DMSO or aqueous solution. This suggests that the cleavage reaction involves 1,2 glycol sites. Other reactions are known which involve 1,2 glycol cleavage in peroxide induced decompositions.⁴⁶ An esr study on this subject has indicated that cleavage seems to take place by a radical reaction pathway. Dixon and Norman studied 1,2-propanediol oxidation in the presence of titanium- H_2O_2 initiating in the esr.¹⁶⁴ The $\dot{C}HOH$ radical was observed which indicates cleavage reaction are taking place. Merz and Waters did an extensive kinetic investigation of alcohol oxidations including α diols and β diols. Merz and Waters indicated that cleavage is not the predominant reaction in Fenton's reagent oxidations of α glycols. Instead, oxidations of ethylene glycol resulted in predominantly glyoxal while 2,3 butylene glycol give mainly diacetyl. Under buffered conditions glycol fission is significantly enhanced.¹⁴⁴

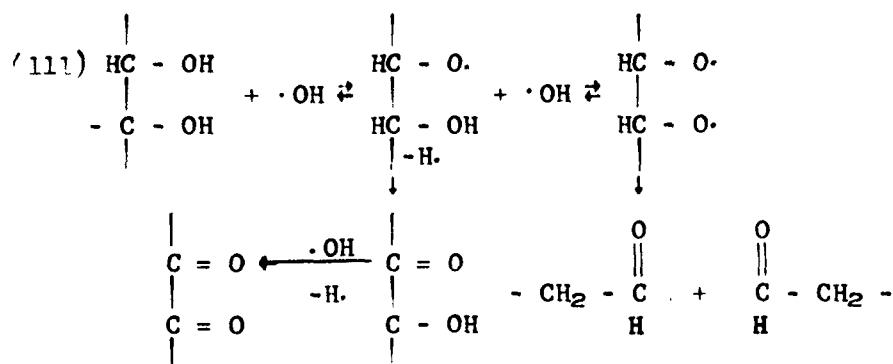
1,2-propanediol can be taken as a model compound in these reactions, since polymer products are extremely difficult to analyze. t -BuOOH and cobalt (II) and (III) acetylacetonate in DMSO and H_2O solution are added in order to initiate the reaction. Analysis is done by precipitating products with DNPH solution and separating DNPH derivatives on TLC plates. These bonds are eluted and analyzed. Similar product

distributions and concentrations are found in both aqueous and DMSO reactions on the basis of nmr analysis of the elution products. Products included pyruvic aldehyde and lactic aldehyde (Table XVIII). On the basis of R_f values of the derivatives only trace amounts of formaldehyde and acetaldehyde could be detected and the quantity of these derivatives was too small to analyze.

The ratio of the number of moles of .66 M t -BuOOH decomposition per macromole of PVA to the cleavage number (s) is 25.3 and 27.4 for 2×10^{-5} M solutions of cobalt (II) and cobalt (III) acetylacetonate in DMSO and 175 and 275 for cobalt (II) and cobalt (III) acetylacetonate in aqueous solution. This ratio is used in order to obtain a quantitative relation between cleavage and peroxide decomposition. Using the notation of Dulog and Kern, s denotes the cleavage number while oxygen uptake and peroxide decomposition are expressed as the number of moles of oxygen taken up or peroxide decomposed per macromole of PVA. A macromole is equal to the number of grams of polymer divided by the molecular weight of the polymer. The cleavage number (s) is calculated from the formula $s = \frac{M_{nd}}{M_d} - 1$. M_{nd} is the number average molecular weight of the sample initially (non-degraded polymer) and M_d is the number average molecular weight after degradation. The difference between the number average molecular weight and the viscosity average molecular weight should not affect the value of the cleavage number, since the relationship between these two quantities should be the same for M_{nd} and M_d .

The data indicates that cleavage of the PVA is a minor side reaction in an oxidation reaction of PVA (Table XIX). Studies with 1,2-propanediol indicate that cleavage products if present are beyond the sensitivity of the TLC plates to detect them (Table XVIII). The major reaction

products would be expected products of the oxidation of the alcohol groups and this is born out in the TLC study, since pyruvic aldehyde is the major product as well as lactaldehyde. It would be expected that α and β glycol groups would be oxidized according to the scheme, which was devised by Merz and Waters for oxidation 1,2 propanediols by Fenton's reagent, namely



Pyruvic aldehyde seems to be a more prominent product in DMSO than in aqueous solution (Table XVIII). This might be related to differing radical stability in the two solvents or to some direct effect of the solvent on the substrate.

Aqueous solutions of .66 M t-BuOOH are approximately 10^{-6}M in hydronium ion and would not be expected to promote cleavage because of the short radical lifetime in solution under these conditions. Merz and Waters found that buffered solutions are much more effective in promoting cleavage. Merz and Waters also found that 1,2 diol oxidation such as these are essentially non chain processes. In support of this the data indicates that cleavage of PVA in 10^{-4}M solutions cobalt (II) and (III) acetylacetonate and .016M t-BuOOH has an energy of activation of 28.8 kcal/mole and 24.8 kcal/mole in water and 28.7 kcal/mole and 29.8 kcal/mole in DMSO in temperature range of 40° to 60°C (Table (VII)).

These values represent high values relative to autoxidation and may be indicative of a non-chain reaction.

One possible explanation for the higher rate of cleavage in DMSO as opposed to aqueous solution is that the dissociation of acids is less in DMSO than it is in water. This will be discussed more fully in the solvent effects section.

ESR experiments were performed, which attempted to detect the radicals formed in this experiment. These experiments proved to be inconclusive, presumably because of the low concentration of the radicals involved. Fast flow techniques might be more successful.

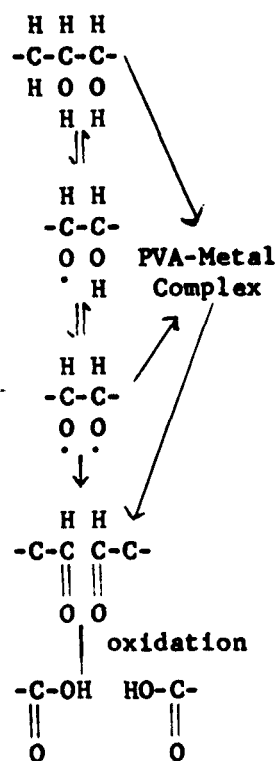
It is noted that molecular weight changes decrease with time and eventually are constant with time (Figure (9)). This behavior cannot be attributed to non-linear t -BuOOH decomposition rates, since substantial activity is retained over a period of time for metals in decomposition and autoxidation. The nonlinear behavior of cleavage with respect to time might reflect a first order reaction process. If the logarithm of the viscosity average molecular weight vs. time elapsed in the reaction is graphed (Figure (9b)) a curved line is still obtained. It is possible that the cleavage process falls between first and second order kinetic treatments. Other explanation can be utilized to explain the nonlinear behavior of the graph of viscosity average molecular weight vs. time. One explanation is that the polymer undergoes a substantial depletion of cleavage sites with time, which would lower the overall rate of cleavage with time. This phenomenon might also be ascribed to coupling reactions of the polymer in solution which would decrease the overall rate of molecular weight change. However, part of this effect might be attributable to deactivation of the catalyst. Quantitative significance cannot be given to the relative contributions of coupling

and deactivation. At high rates of initiation, however, substantial cleavage takes place before the cleavage rate declines.

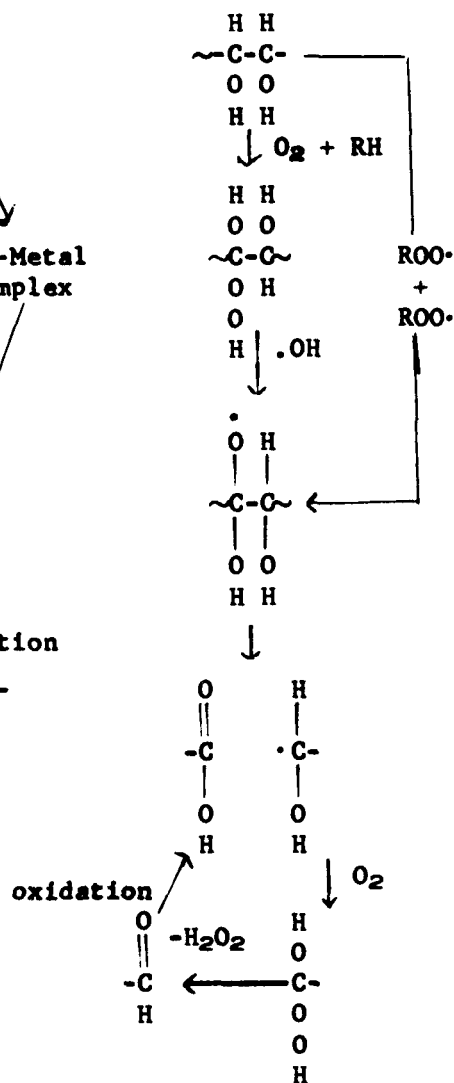
Carboxyl End Groups

In order to elucidate further the mechanism of PVA degradation, NaOH titrations were performed on reaction mixtures which had been autoxidized and on which viscosity measurements had been made. It was found that similar viscosities were obtained, in pure oxygen atmosphere (20% O₂). It was difficult to detect the acidity of the polymer quantitatively in these titrations. The consistency of results on replicate runs was no greater than 20%. Solutions which were initially .016 t-BuOOH and 10⁻⁴M in cobalt (II) and (III) acetylacetonate had negligible influence on the titration results. Data which involved higher peroxide concentrations (.66M) or higher cobalt concentrations, were considered too uncertain because of the appreciable acidity of t-BuOOH and the ability of cobalt (II) and (III) acetylacetonate to undergo basic hydrolysis. The size of this correction was approximately equal to one half the total titration equivalent. It was found in the solutions studied (Table (XIX)) that a 1 to 2 ratio of cleavage number to equivalents of acid per macromole of PVA was present. This result involves an experimental error of 20-30% for replicate runs arising from the large correction necessary for contributions to the titration of t-BuOOH and possible initiation products such as formic acid as well as the significant contamination of carbon dioxide in the titration. There is also the possibility that reaction products such as H₂O₂, resulting from oxidation could affect the acidity of the solution. The mechanism of the formation of this product will be discussed later. The value of 1/2 for the ratio of the cleavage number to number of acid

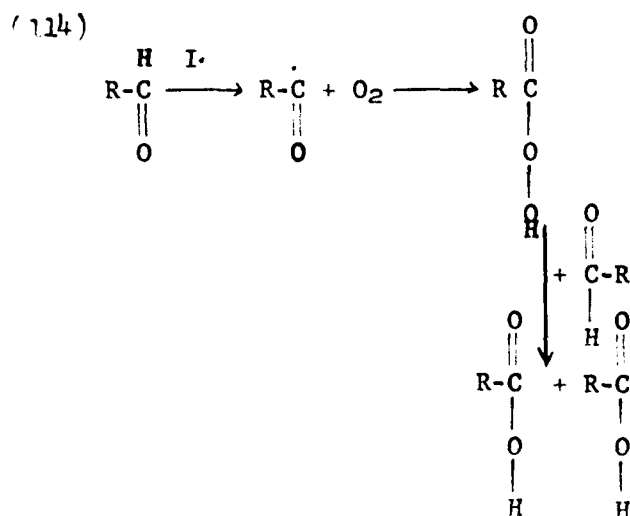
(112)



(113)



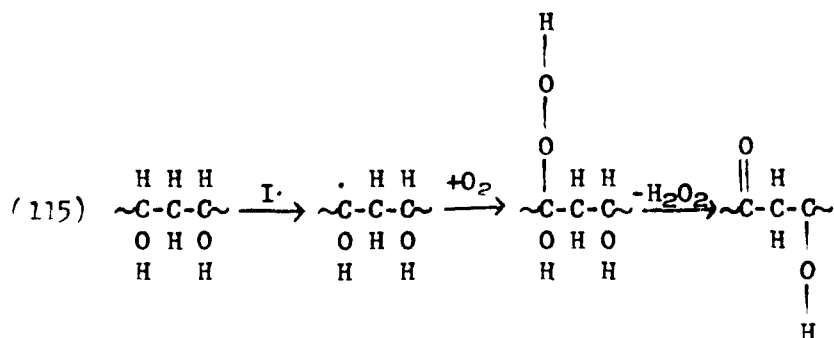
equivalents per macromole is higher than Dulog and Kern's value of 1:1.2 for photosensitized oxidation of PVA. A value of .5 indicates that when cleavage takes place two molecules of acid are produced for every cleavage. This would be consistent with a mechanism which involves either cleavage of the polymer to two terminal aldehydes and then oxidation to an acid or cleavage of the chain by oxidation of the alcohol group to an acid and an aldehyde followed by oxidation, as shown in equation (112) and (113). It should be noted that aldehydes are autoxidized very easily by the following mechanism:



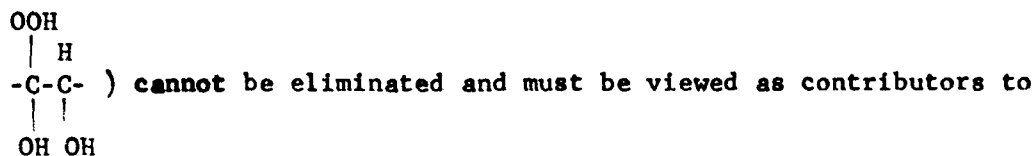
with the production of carboxylic acids as the final product.¹⁰⁷

The ratio of the cleavage number to the number of moles of oxygen absorbed per macromole of PVA is approximately 600 and greater in a typical run in water or DMSO (Table (XIX)). This corresponds to oxidation of approximately 35% of the polymer ($\frac{600}{1738}$) units. In the course of the oxidation, extensive portions of the polymer are being oxidized.

This suggests the oxidation of the chain is the predominant reaction. For instance, by the mechanism of Dulog and Kern, where $I\cdot$ represents initiator radicals. The strong similarity in rates between



cleavage in a nitrogen atmosphere and in an oxygen atmosphere suggests a common mechanism. This is most likely accommodated by chain cleavage similar to that of Merz and Waters followed by oxidation of the aldehyde groups to acids. Contributions from oxidation products of PVA (e.g.



total chain cleavage. However, it should be realized that the cleavage reaction occurs predominately within the first 2×10^5 sec of the reaction, before extensive oxidation has taken place. After this point oxygen may also be taken up in possible coupling reactions of the polymer. Termination reactions between two polymeric peroxy groups are essentially polymeric cross linking reactions. Since chain lengths in this oxidation are not long, a significant amount of oxygen might be going into this process. From a bond energy standpoint 1,2 alcohol carbon bonds are weaker than 1,3 and would be expected to be centers for cleavage.⁵²

Solvent Effects

Autoxidation rates are very similar in DMSO and water (Table (X) and (XI)). This corresponds to similar rates of t-BuOOH decomposition in both solvents at high concentrations of t-BuOOH (Table (III) and (IV)). Cleavage reactions in DMSO are about 10 times more rapid than in water solution (Table (XIV)). From the data available, kinetic dependencies in DMSO and water are similar as far as autoxidation and t-BuOOH decomposition.

Cobalt (II) and (III) acetylacetonate in the presence of DMSO seem to be mainly in the cobalt (II) state in DMSO and in the cobalt (III) state in aqueous solution (Table (I) and (II)). Ligand exchange by the catalyst seems to take place in both solvents.

Differences between the two solvent systems may involve a complex set of factors. DMSO is known to be a better solvent for PVA than aqueous solution.¹⁶⁵ As a result the polymer coil would be expected to be more extended. DMSO is more selective with regard to solvation and hydrogen bonding than water. Recent work on the hydroxyl shift variation produced by DMSO leads to the conclusion that the relative strength of association between alcohol and DMSO depends on steric crowding around the hydroxyl group. As a result, periodic acid degradation of carbohydrates is more selective in DMSO than in aqueous solution because of strong preferential solvation of certain hydroxyl groups by DMSO.¹⁶⁶ Also the hydrogen bonding between DMSO and n-butyl alcohol may be responsible in part for the observed resistance of the latter to oxidation by lead tetra-acetate in DMSO solution.

In terms of association with metal ions it first should be noted that the dipole moment of DMSO is 4.11D at 25°C, while that for water is

1.87D. The dielectric constant for water at 25°C is 78.5 and for DMSO 46.4 at 25°C.¹⁶⁸ Dipolar aprotic solvents, such as DMSO, excel in the solvation of metallic cations. This is true because the negative terminal of the dipolar solvent molecules is exposed, and the cluster around the cation produces a spherical, protective layer of relatively large hydrophobic alkyl groups on the periphery of the solvated ion. Thus, the cation is for all practical purposes "buried" inside the resulting structure and the coulombic forces that normally function between ions of opposite charge tend to be greatly reduced.¹⁶⁹ This situation is apparent among other things from the examination of solubilities, ion pairing equilibria, ionic conductivities, and also from the increased activity of the anions. Generally speaking, the solvation of the anions is more effective with protic solvents because of the formation of hydrogen bonded complexes. However, when hydrogen bonding becomes negligible in the absence of a localized negative charge (either because an electro-negative atom is absent or because the negative charge is delocalized over a large area of the resonance stabilized system), then the dipolar, aprotic solvents exhibit solvating capacity superior to that of protic solvents by virtue of dipole induced dipole interactions. Iodide ions which are highly polarizable have high enthalpies of solvation in DMSO as opposed to water where chloride and bromide do not. DMSO is an excellent ligand and the salts of transition metals readily form DMSO solvates. Aqueous solutions also bind metal ions very tightly as shown by spectral and magnetic properties of cobalt complexes in aqueous solutions.¹⁶⁹ $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is the predominant species in aqueous solution and the water molecules are extremely labile. It would be expected that water would be more effective at blocking metal sites from t-BuOOH than DMSO.

This may account for the greater rates of *t*-BuOOH decomposition in DMSO under conditions of low *t*-BuOOH concentration (Table (III) and (IV) and Figure (2)).

The acid base properties of DMSO are of interest because of the possibility of acidity effecting either the cleavage or autoxidation reaction of PVA. DMSO is a strong proton acceptor, but it can also function as a proton donor under certain conditions. The relative acidity of weak hydrocarbon acids is in good agreement when pKa values determined in DMSO are compared with those in aqueous solution.¹⁷⁰ This is no longer true when one deals with stronger acids. Even though the basicity of DMSO is considerable it is the solvation of the acid anion by the protic solvent that exerts decisive control of the dissociation equilibrium. For all acids studied by Steiner the acidity is greater in water than in DMSO by 2.5 - 6.8 pK units in spite of the fact that the basicity of DMSO is greater than that of water by 1.8 pK units.

In terms of its use in radical reactions DMSO has been found to be an effective medium. Radical transfer with the solvent is relatively low in polymerization reactions.^{99, 171} In aqueous solution it was found that radical transfer reactions in methyl methacrylate polymerization were not detectible.¹⁷² At high temperatures (160°C) DMSO will react with *t*-BuOOH and decompose into inactive products under an inert atmosphere.¹⁷³ Under mild conditions, DMSO is resistant to attack from most neutral, unpaired electron containing species in solution.

It is not clear from this study which factor contributes most to the differing rates of cleavage in DMSO and aqueous solution. However, the different rates of radical production, the acidity of the solvent, and the different degree of solvation of radical species in both solutions could all contribute.

It would be expected that metal sites are blocked more effectively in aqueous solution as far as t-BuOOH complexation with the catalyst or PVA complexation with the catalyst is concerned. Aqueous solvation of the radical would be expected to yield longer chain lengths in oxidation and t-BuOOH decomposition and probably accounts in part for the apparent larger chain lengths in aqueous solution. Cleavage rates are greater in DMSO, which would be consistent with acid-base properties of DMSO. In other words, the DMSO reaction solution would be less acidic and this might favor the cleavage reaction. The influence of the degree of extension of the polymer coil on the reaction was not evaluated. Deactivation and precipitation of the catalyst in these solutions appear to be more rapid in aqueous solution at 60°C, but is approximately equal in DMSO and aqueous solution at 42°C (Table (I) and (II)).

Temperature Effects

The energy of activation for the overall process of autoxidation, t-BuOOH decomposition and cleavage from radical rates in Table (VII). The equation $k = Ae^{-E_a/RT}$ was used to evaluate temperature effects. A plot of the log of the appropriate rate vs. the reciprocal of temperature yields the activation energy ($-E_a/R$) as the slope of the line and the A value as the intercept. As previously discussed the E_a for autoxidation in both solvents is much lower than either peroxide decomposition or the PVA cleavage reaction. This must at least partially reflect the chain character of the autoxidation process while t-BuOOH and PVA cleavage reactions may result primarily from non-chain mechanisms. For instance, t-BuOOH decomposition may result primarily from cobalt-

peroxide interaction and polymer cleavage may proceed by the non-chain mechanism of Merz and Waters. Increasing temperature could affect such diverse factors as catalyst solubility, catalyst deactivation and precipitation, chain termination by catalyst, degree of aggregation of the catalyst in solution as well as the initiation, propagation and termination rates. It is in fact found that increasing the temperature increases the rate of catalyst precipitation. (See page (123)).

Termination in t-BuOOH hydroperoxide decomposition would involve only t-BuO $\cdot$ radicals, where termination in PVA autoxidation would involve a polymer cage mechanism. Termination by t-BuO $\cdot$ radicals is on the order of 2 kcal/mole, where in polymer radical termination E_t might be expected to be considerably higher. This could lower the overall observed energy of activation for autoxidation of the polymer. This assumes that termination does not result from primary cleavage products of polymer autoxidation since the energy of termination for this process would be considerably lower. It is clear from the low chain lengths of autoxidation reactions that cleavage products cannot be contributing extensively to termination since the oxidation reaction is several hundred times more rapid than cleavage.

The $\Delta H^\ddagger$ values are similar in magnitude to the values obtained for Ea. The $\Delta S^\ddagger$ reflect very closely the values obtained by T. Jochsberger and N. Indictor in the decomposition of t-BuOOH in chloroctane in the presence of chromium (III) acetylacetonate and 1-octene.¹⁸¹ A positive $\Delta S^\ddagger$ was obtained for t-BuOOH decomposition in both systems. T. Jochsberger and N. Indictor attributed this to a gain in rotational freedom as a result of a ligand exchange reaction of the acetylacetonate ligand with the substrate or the peroxide, with the corresponding loss of symmetry

of the metal complex. The negative $\Delta S^\ddagger$ values obtained in the autoxidation reaction were also consistent with the values obtained by T. Jochsberger and N. Indictor.

Chain Lengths

The number of substrate molecules that are consumed per radical produced in initiation process is called the chain length. This quantity may be expressed as the ratio of the propagation rate to the initiation rate. In autoxidation, the rate of propagation is simply the rate of oxygen uptake (Table (XII) and (XIII)). The rate of initiation is the rate of radical production by the metal-peroxide reaction. Radical decomposition of peroxide is excluded, since this merely exchanges one propagating radical for another (i.e. $t\text{-BuO}\cdot$ for $t\text{-BuOO}\cdot$). In peroxide decomposition the chain length is simply the ratio of the rate of decomposition of peroxide to the rate of peroxide decomposition from metal catalyzed initiation.

Low kinetic chain lengths for peroxide decomposition would be expected for $t\text{-BuOOH}$ decomposition at low peroxide concentrations (.016M $t\text{-BuOOH}$). At higher concentrations of peroxide (.2M) peroxide molecules will present an abundant source of hydrogen atoms for abstraction by the propagating radical. At higher peroxide concentrations $t\text{-butoxy}$ cleavage reactions ($t\text{-BuO}\cdot \rightarrow \text{acetone} + \text{CH}_3\cdot$) also would not be as prevalent. Cleavage will also vary with solvent polarity. For instance, Hiatt and Mayo found that cobalt catalyzed decomposition of .10M $t\text{-BuOOH}$ yielded approximately no detectable acetone in benzene, 2% acetone in cyclohexane, and 8.7% acetone in a $t\text{-butyl}$ alcohol chlorobenzene solvent. In di- $t\text{-butylperoxyoxalate}$ induced decomposition of .1M $t\text{-BuOOH}$ chain lengths in benzene were ~ 10 in benzene at 100° and 1.5 and 1.11 in acetic acid

and .54 for t-butyl alcohol at 45°C. Higher peroxide concentrations increase chain lengths and decrease the rate of cleavage of t-butoxy radicals. Peroxide decomposition chain lengths are assumed to be approximately one in polar solvents on the basis of these results. Using this assumption the rate of initiation for autoxidation is equal to the rate of peroxide decomposition or that reaction between cobalt (II) and/or cobalt (III) acetylacetonate and t-BuOOH (reactions (4) and (5)) account for all peroxide decomposition. The chain length for autoxidation can then be formulated as the ratio of rate of autoxidation to the rate of t-BuOOH decomposition. This gives chain lengths of 4.3 for .16M t-BuOOH solution, 4.2 for .66M t-BuOOH and 3.2 for .96M t-BuOOH in DMSO for 6.85×10^{-5} M solutions of cobalt (II) acetylacetonate (Table (XII)). In aqueous solution chain lengths of approximately 29 are obtained for .16M t-BuOOH solution and 12 for .66M t-BuOOH solution in the presence of 6×10^{-5} M cobalt (II) acetylacetonate solutions (Table (XIII)). The apparent lower chain lengths for autoxidation in DMSO solution may be explained either by the fact that aqueous solutions decrease the extent of cage termination of polymer alkoxy radicals⁴⁴ or that the lower rate of cleavage reactions in aqueous solution allows for less termination by more mobile cleavage products. Other explanations include the effect of the polymer conformation on termination reactions in aqueous as opposed to DMSO solution. It would be expected that the more tightly coiled PVA molecule conformation in aqueous solution would decrease the rate of termination.¹⁸⁵ Chain transfer reactions to the solvent might also play a role in the autoxidation reaction. It has been found that DMSO undergoes minimal chain transfer to solvent in polymerization reactions,¹⁷¹ while virtually no chain transfer to solvent occurs in polymerizations reactions in water solution.¹⁷² It would not be expected that chain

transfer to the solvent would be the controlling influence in these reactions. It would also not be expected that propagation reactions would be more rapid in aqueous solutions, as opposed to DMSO solutions. It should be noted that these chain lengths were derived from the assumption that the rate of initiation is equal to the rate of peroxide decomposition.

Effects of Metals

Autoxidation and Peroxide Decomposition

The effect of different metals on the autoxidation reaction has been examined in DMSO and water solution at low metal concentrations of $\sim 2 \times 10^{-5}M$ and high peroxide concentrations of .66M (Table XX). It would be expected that the effect of the metal in autoxidation would be related to its ability of decompose t-BuOOH (Table XXI). Factors which affect peroxide decomposition for different metals would be the oxidation potential of the metal (Table XXII), the nature of the peroxide-metal equilibria (Table XXIII), the ease with which the metal is deactivated under experimental conditions, and the ability of the metal to complex with radicals.⁹⁰ During the autoxidation reaction other affects such as metal substrate reactions, metal oxygen reactions, and extensive deactivation of the catalyst could influence autoxidation rates, while not having an affect on t-BuOOH decomposition rates in vacuo.

Peroxide decompositions were carried with .016M t-BuOOH and $2 \times 10^{-5}M$ solutions of the metal ion. Under these conditions, radical induced decomposition of the peroxide would not be extensive and the main effect would be the peroxide metal interaction. Due to the low chain lengths and low metal concentration, radical-metal interactions would not be expected to be significant.

A graph of a log [t-BuOOH] vs. time for metal acetylacetonate catalyzed peroxide decomposition in DMSO (Figure(1)) exhibits deviations form linearity for some metals. This deviation from linearity may be attributed to the possibility of deactivation of the metal catalyst or alternatively solubilization of the metal catalyst by reaction products. Cobalt (II) and (III), chromium (III) and iron

(III) acetylacetonate catalyzed systems exhibit a greater activity initially (within 2×10^5 sec), while manganese (II) and (III), vanadium (III), nickel (II), and copper(II) show a negative deviations suggesting less activity initially. These increases and decreases in activity with time seem to correlate with the increases and decreases of absorbance of the various acetylacetonates with time in the presence of t-BuOOH (Table (XXI)). This suggests that solubilization reactions of the metal catalyst with t-BuOOH decomposition reaction products may play a part in these reactions, while deactivation or ligand exchange reactions may play a part in decreasing the overall U.V. absorbance of the metal complex and possibly decreasing the metal's catalytic activity. This may be related to the behavior of the metal species in promoting the autoxidation reaction, since autoxidation curves of ml oxygen absorbed vs. time appear to have a double maxima in their autoxidation rates in DMSO (Figures (12) and (14)). Kamiya found a similar phenomenon in tetralin oxidation with manganese stearate. Kamiya points out that many catalysts are present in a fine suspension in solution and not truly dissolved. In the beginning of the reaction manganese (III) acetylacetonate is dissolved by peroxide into solution. Manganese is deactivated more rapidly in solution than fresh catalyst can be dissolved in the solution. The rate therefore decreases after the first maximum. Subsequently, the oxidation or initiation products solubilize undissolved catalyst so that the concentration of active catalyst rises and the rate goes through a second maximum. This effect is probably more noticeable in manganese (III), because it is more rapidly deactivated than cobalt (II) and (III) acetylacetonate relative to the initiation rate.

Similar curvature is noted in autoxidation catalyzed by iron (III) acetylacetonate and cobalt (II) and (III) acetylacetonate to a lesser extent in DMSO solution. U.V. data in DMSO tends to bear this hypothesis out (Table (XXI)). Iron (III) goes through a substantial loss of U.V. intensity at 42°C after 2×10^5 secs. Manganese (III) although losing a small amount of intensity initially begins to increase substantially in intensity after 2×10^5 secs. This corresponds to its increased activity in autoxidation within this time interval. This might represent solubilization of manganese (III) by initiation products. The U.V. data does not indicate any effect that autoxidation products might have, since spectral changes were determined in vacuo. Oxidation products could account for the renewed autoxidation activity of cobalt (II) and (III) acetylacetonate as well as iron (III) acetylacetonate. Increased or decreased peroxide activity with time seems to correlate with increases or decreases of U.V. intensity (Table (XXI)). This effect cannot be directly correlated to the autoxidation behavior of PVA in the presence of various metal acetylacetonates, since autoxidation products will also have an effect on autoxidation rates in DMSO, while these products are not present in peroxide decompositions and spectral studies, which were conducted in vacuo. U.V. intensity will also be affected by ligand exchange reactions as well as the concentration of the metal in solution. Manganese (III) acetylacetonate and copper (II) acetylacetonate are known to undergo facile exchange reactions with DMSO. This could account for the marked increase in U.V. intensity found in both these solutions.

Aqueous solutions would be expected to exhibit different

catalytic behaviors. For instance, no increases in U.V. intensities are found. Vanadium (III) acetylacetonate undergoes a sharply reduced U.V. intensity. Its autoxidation rate is also sharply reduced in aqueous solution, as is its rate of peroxide decomposition. Iron (III) appears to be more active in water than DMSO in autoxidation. Changes in redox potential or aggregation might explain this. Metal peroxy interactions could account for observed differences between metal decomposition activity and autoxidation behaviors. For instance, iron salts are known to undergo metal peroxy interactions and they also appear to have a lower activity in autoxidation than would be indicated by the autoxidation data.

Manganese (II) acetylacetonate is not active in promoting autoxidation of t-BuOOH decomposition. This is in line with Kamiya's work.¹²⁴ Manganese (II) is known to inhibit autoxidations by trapping radicals. The lack of true solubility of Manganese (II) in DMSO might also affect the activity of this metal. Radical metal interactions would be expected to be more significant at higher peroxide concentrations (0.66M) as employed in autoxidation.

The apparent lower rates of peroxide decomposition of t-BuOOH in aqueous solution as opposed to DMSO are not necessarily indicative of a lower rate of initiation under autoxidation conditions, since .016 M solutions were used for decomposition reactions and .66M t-BuOOH were used for autoxidation runs. In cobalt (II) and (III) acetylacetonate peroxide decomposition rates were similar at .66M t-BuOOH but not at .016M t-BuOOH. The reaction at .016M would proceed at low chain lengths, where at .66M t-BuOOH higher chain lengths would be expected in decomposition. Higher peroxide concentrations also would shift

the metal peroxide equilibria to more complexation at higher peroxide concentrations. It is clear that aqueous solutions must also be exerting an influence on the chain lengths in autoxidation since at low concentrations of t -BuOOH, autoxidation rates are not markedly different from aqueous solutions to DMSO. This could occur through a decrease in termination reactions in water as a result of the solvation of the peroxy radical which would result in a decrease in the amount of cage termination.

The order of reactivity of the various metals with respect to autoxidation and peroxide decomposition in DMSO and aqueous solutions will be influenced by solubility, changes in oxidation potential, changes in the peroxide-metal equilibria, and degree of deactivation and radical-metal interactions of each metal in these solvents. The order in DMSO of autoxidation (oxygen uptake) is Co (III), Cu (II) > Co(II), Ni(II)>V(III)Mn(III)>Fe(II)>Fe(III)>Mn(II)~Al(III). In aqueous solution the order of autoxidation is Co(III), Co(II)>Cu(II), Fe(III), Ni(II)>V(III). The decomposition of peroxide in DMSO is in the order of Co(II)>Cu(II), Co(II)>Ni(II)>Cr(III)>V(III)>Fe(II)>Fe(III) Mn(III)>Al(III)>Mn(II). The order of catalytic activity with respect to decomposition of t -BuOOH in aqueous solution is Co(II)>Cu(II)>Co(III) >Fe(III)V(III)>Al(III)>N(II). The general trend is the same in both solvents. Namely transition metals with multiple oxidation states such as cobalt and copper are more active than metals such as aluminum. The results are in line with Lombard and Knopf's work on cumene autoxidation and Jochsberger's and Indictor's work on 1-octene autoxidation with metal acetylacetonates. Deactivation and solubilization would be expected to be significant factors at the concentrations

employed in this work.

Factors such as the extent of complexation between the metal and the peroxide were roughly correlated by use of the nmr data (Table XXIII).¹⁷⁴ An attempt was made to quantify the nature of the peroxide metal interaction. Various metal acetylacetonates were run in carbon tetrachloride in the presence of .96M *t*-BuOOH. The broadening of the O-H peak was tabulated for a variety of metal acetylacetonates. Very inactive metals in peroxide decomposition such as aluminum (III) and zinc (II) caused little broadening of the peak. Active metals such as cobalt (II) and chromium (III) caused great broadening of the peak. Interestingly cobalt (II) caused substantial broadening, where cobalt (III) left the peak almost unperturbed. It was noted that after seven days of standing in the nmr tube substantial broadening took place. This is most likely related to the fact that cobalt (III) is transformed into cobalt (II) acetylacetonate during the course of the reaction. Cobalt (II) is the more reactive species in peroxide decomposition.

It was seen by Hiatt and Mayo⁸⁷ that different metal acetylacetonates have no effect on the type of products formed from the decomposition of *t*-BuOOH. A major influence on the metal in peroxide decompositions is the amount of deactivation of the catalyst, and whether the reaction is stoichiometric (1:1 correspondence between peroxide decomposed and metal reacted) or catalytic (greater than 1:1 correspondence).

The phthalocyanines seem least affected by deactivation or autoretardation (Table (XXIV)). It is not clear from the data whether the 10^{-5} M solutions of the metal salts which did not react to any significant extent were non catalytic or were subject to other affects (aggregation, low redox potential, deactivation).

Ligand effects in autoxidation and *t*-BuOOH decomposition are

presented in Table (XXV). It might be expected that the transition from F^- , Cl^- , Br^- , to I^- in cobalt catalyzed reactions with peroxide might affect the nature of the peroxide metal equilibria. The cobalt (II) fluoride bond is considerably stronger than the cobalt iodide bond. As a result, the iodide ligand is the most labile and the one that might be most susceptible to complexation with peroxide. Electron transfer mechanisms might involve both inner (involving a bridging ligand) and outer sphere mechanisms. A normal order of bridging efficiency would be $I^- > Br^- > Cl^- > F^-$.⁸⁴ It should be noted that this order may be reversed, if so called intrinsic forces are active. The ligand may have an effect on propagation reactions in autoxidation reactions as well.

Cobalt (II) fluoride is significantly less active in peroxide decomposition and autoxidation than cobalt (II) chloride, bromide and iodide in DMSO. The rates of *t*-BuOOH decomposition catalyzed by cobalt chloride, bromide, iodide are the same within experimental error in DMSO. Autoxidations rates are similar for cobalt chloride, iodide and bromide in DMSO, but cobalt fluoride is significantly slower. The curves are not linear and exhibit double maxima. Deactivation and solubilization might be employed to explain the double maxima in the autoxidation curves.

Aqueous solutions of cobalt salts exhibit similar behavior to those in DMSO. Similar decomposition rates are found for chloride, iodide and bromide salts, while fluoride salts are slower in autoxidation and *t*-BuOOH decomposition. Both DMSO and water would be expected to strongly solvate these metals. As a result the blocking effect of the solvent would minimize steric effects of ligands. Cobalt

(II) and (III) acetylacetonate and cobalt phthalocyanine promoted t-BuOOH decomposition and autoxidation more effectively than the cobalt (II) halides in DMSO. The nature of the ligand metal bond or the protection the ligand affords the metal from deactivation may account for this effect. Cobalt phthalocyanine might be less susceptible to deactivation, either by oxidation products or by reduction to the hydroxide. Cobalt phthalocyanines bond is extremely strong. One consequence of this is the inability of cobalt phthalocyanine to dissolve in water ($K_{sp}=10^{-8}$) indicating covalent bond character that is extremely resistant to metalligand exchange.¹⁷⁵

Isotopic exchange studies on these compounds point up the difference in ligand stabilities.¹⁷⁶ The rate of isotropic exchange, as indicated by the half life between cobalt phthalocyanine and cobalt acetylacetonate in pyridine is 4.3×10^5 secs while the rate of exchange between cobalt (III) acetylacetonate and cobalt (II) in pyridine is 6.9×10^6 sec at 30°C. Exchange of water with pyridine in cobalt (II) acetylacetonate (aquated vs. non aquated) in pyridine is 50 secs. Reactions of DMSO and water with acetylacetonates' ligand are known and would be expected to cause increased rates of exchange in these solvents.^{98,99} Exchange rates of cobalt (II) halides in aqueous solvents are on the order of 60 sec for chloride ion. The rate of ligand exchange is $F^- < Cl^- < Br^- < I^-$ in aqueous media. Rates in DMSO are rapid as well. The ferrihemoglobin exchange rate is 1×10^5 secs in alcoholic HCl, while ferric protoporphyrin is 5×10^6 sec in the same media.^{98,99}

It appears that those ligands which are not easily exchanged exhibit the highest rates of t-BuOOH decomposition. This indicates

that deactivation of the catalyst through ligand exchange and formation of an inactive product is probably an important reaction in t-BuOOH decomposition.

In aqueous solution cobalt (II) and (III) acetylacetonate exhibit rates of decomposition similar to cobalt halides. This indicates that water has a leveling effect on the ligands influence. This suggests that the solvent may be blocking metal sites or causing similar deactivation of cobalt (II) and (III) acetylacetonate in aqueous solution. The rate of PVA autoxidation is also similar to that of the cobalt halides in water.

Cleavage Reaction

The effect of metal and the ligand were investigated in the cleavage reaction as well. In DMSO solution a marked curvature is seen in the graphs of the viscosity average molecular weight vs. time in Figure (9)-(11) as a result of possible factors such as coupling, depletion of cleavage sites, (first order kinetic effect) and deactivation of the metal catalyst. The most rapid loss of molecular weight occurs within the first 2×10^5 secs. The activity of the metal acetylacetonates in peroxide decomposition closely parallels their activity in PVA cleavage. The order of metal acetylacetonate catalysis with respect to the rates of cleavage in DMSO are $\text{Co(II)} > \text{Cu(II)} > \text{Fe(III)} > \text{Co(III)} > \text{Fe(II)} > \text{Cr(III)} > \text{Mn(III)} \sim \text{Ni(II)} > \text{V(III)} > \text{Mn(II)} > \text{Al(III)}$ (Table XX). In aqueous solution the order with respect to cleavage is $\text{Cu(II)} > \text{V(III)} \sim \text{Al(III)} > \text{Co(III)} > \text{Ni(II)} > \text{Fe(III)} > \text{Co(II)}$ initially. Significantly, cobalt (II) and (III) acetylacetonate cleavage rates are depressed relative to the other metals. Deactivation of the metal in solution may account for this decrease in rate.

Cobalt (II) halides exhibit similar rates of cleavage in DMSO solution except for cobalt (II) fluoride. This is consistent with autoxidation data in DMSO and the *t*-BuOOH decomposition data. In aqueous solution, cobalt (II) iodide, chloride, and fluoride are fairly inactive in cleavage, while cobalt bromide is initially very active in cleavage. The difference in behavior of cobalt bromide might be explained by the influence of the bromide ion in propagation. It is also possible that specific interactions between the metal and the substrate may be operative. The autoxidation rate of PVA in aqueous solution with cobalt (II) bromide seems to be initially more rapid than other salts and then the rate seems to decrease after 1×10^5 secs. Cobalt (II) and (III) acetylacetonates seem to produce similar rates of PVA cleavage as the cobalt halides (except cobalt (II) bromide) with respect to cleavage.

A variety of metal phthalocyanines and porphyrin compounds were tested for their ability to produce PVA cleavage. In terms of ability to decompose *t*-BuOOH and to promote cleavage of PVA in DMSO solution, the order is $\text{Fe} > \text{Co} > \text{Cu} > \text{VO}$ phthalocyanine. Cobalt and iron phthalocyanine are the most active inorganic catalysts. The high activity of iron phthalocyanine is in keeping with work on the decomposition of tetralin hydroperoxide, where iron phthalocyanine proved to be most active in this study, with chromium and cobalt phthalocyanine showing slight activity.¹¹³ Other phthalocyanines showed no activity whatsoever. Kropf's work on cumene autoxidation reflected the same order of metal activity with respect to those phthalocyanines.⁹⁸ Similarly, iron phthalocyanine was found to be by far the most active phthalocyanine in the decomposition of

hydrogen peroxide, in 75% aqueous solution.¹¹³ It was found that metal free phthalocyanine does not catalyze the decomposition. This corresponds with the results on phthalocyanine free base decomposition of t-BuOOH (Table (XXIV)). Therefore, the origin of the catalytic activity stems from the central metal atom.

The similar activity of iron porphyrins and bivalent and trivalent iron phthalocyanine was the first indication that it is the association of the iron atom with the four pyrrole nitrogen atoms that leads to catalytic activity. Hemin was found to also be active in tetralin hydroperoxide decomposition. Hemin, hematin, hematoporphyrin free base, chlorophyllin in DMSO and cytochromes in water were also tested for their ability to promote t-BuOOH decomposition and PVA cleavage. Hemin proved to be an extremely effective catalyst, producing approximately 100 fold increase in decomposing t-BuOOH as compared to iron phthalocyanine. This may be compared with Tappel's work on hematin compounds.¹¹⁹ It should be noted that hematin appears to have significantly less activity than hemin in t-BuOOH decomposition and PVA cleavage reaction. The main difference between hemin and hematin is that hemin central iron binds a chloride, while the hematin central iron binds a hydroxyl group. (Figure (20)). The ease of chloride ligand exchange relative to hydroxide may account for the difference in activity. Hematin is a less stable compound than hemin and this may also account for its lack of activity. This is consistent with the cleavage reaction data for hematin and hemin (Table (XXIV) and Figure (15)). After 2×10^5 secs hematin activity decreased markedly. Hemin activity continues unabated. Hematoporphyrin free

base seemed to have PVA cleavage activity consistent with an uncatalyzed cleavage reaction. Hemin activity in autoxidation was initially high. Its activity as an autoxidation catalyst is not the same order of magnitude as its ability to decompose peroxide, which suggests that it may be deactivated after a short period of time. This is consistent with t-BuOOH decomposition data. Solubility, or steric effects might also play a part in these reactions. Chlorophyllin is the product of careful alkaline hydrolysis of magnesium complex chlorophyll, which replaces the methyl and phytol ester groups with sodium or potassium. Chlorophyllin is somewhat active in peroxide decomposition, but appears to have an inhibitory effect with respect to the PVA cleavage reaction. This suggests that decomposition of peroxide might not be completely free radical in nature in the case of chlorophyllin (refer to Wang's work)¹¹⁸ or that chlorophyllin might also be an inhibitor as well as a catalyst. Cytochrome c catalyzed cleavage of PVA was performed only in aqueous solution, because of its lack of solubility in DMSO. The rate of PVA cleavage seemed to be on the same order as active inorganic salts in that solvent. This is somewhat surprising since Tappel has found that in the catalyzed oxidation of various unsaturated compounds with biological catalysts that cytochrome c and hemin have similar catalytic ability. It is difficult, however, to compare cytochrome c and hemin catalyzed systems directly since two different solvent systems were utilized (DMSO and H₂O). The solvent difference will affect peroxide-metal equilibria, the solvation of intermediates, solubility of the catalyst, and metal deactivation.

The main conclusion that can be drawn is that iron phthalocyanine and porphyrins exhibit a remarkable ability to decompose peroxide.

This ability is greatest for molecules of biological interest. Subtle changes in the metal binding site (chloride to hydroxy) in the iron prophyrin system can yield changes in the behavior of these molecules. These molecules appear to be able to promote PVA cleavage and autoxidation, suggesting that free radical processes are involved. Deactivation of the catalyst may be an important reaction based on U.V. spectral data of various acetylacetonates at various times and its relation to t-BuOOH decomposition data. The hematopotphyrin free base does not exhibit any activity, but the ligand appears to be the primary cause of the unusual activity of this iron complex, since other iron complexes (e.a. iron acetylacetonate) have little activity.

H. Kropf's hypothesis that autoxidation with phthalocyanine catalysis proceeds through an oxy-metal initiation system does not seem to be supported by the fact that phthalocyanines are quite active in t-BuOOH decomposition, in vacuo, and the catalytic order of the phthalocyanines follows their ability to promote cleavage. Cobalt phthalocyanine is active in cleavage and autoxidation compared to other salts and its ability to decompose peroxide reflects this ability. A similar argument could be made for the iron porphyrins. The order of metal phthalocyanine ability in cleavage and peroxide decomposition reflects Kropf's order of catalytic activity. Hemin was found to be less effective than the phthalocyanines in the cleavage reaction, possibly because of partial deactivation after 1×10^4 secs. This is supported by the data on the decomposition of t-BuOOH in DMSO by hemin, which is most rapid within the first $.5 \times 10^4$ secs and falls to a lower rate after 1×10^4 secs. The phthalocyanines also appear to undergo deactivation. On the basis of the data on the rate of peroxide decomposition and cleavage,

deactivation takes place within the first $.8 \times 10^5$ secs.

IV. Conclusion

1. Cobalt (II) and (III) acetylacetonate catalyzes the decomposition of t-BuOOH in both DMSO and aqueous solution in the presence of PVA. Rates of decomposition in aqueous solution are lower than in DMSO solution. The difference in the rate of t-BuOOH decomposition in aqueous and DMSO solutions converges at high peroxide concentration. Decomposition rates are very similar at high concentration of t-BuOOH (.66M) in DMSO and aqueous solution. An empirical rate equation of the form $\frac{\Delta \text{t-BuOOH}}{\Delta t} = k [\text{Co}]^a [\text{t-BuOOH}]^b [\text{PVA}]^c$ was utilized to describe the peroxide decomposition process. Reaction orders were less than or equal to one, but greater than zero. In aqueous solution, $[\text{t-BuOOH}]$ has a reaction order with respect to decomposition approaching one, while the reaction order is closer to one half in DMSO solution. Increasing PVA concentration appears to increase the rate of peroxide decomposition.
2. Cobalt (II) and (III) acetylacetonate appear to go through oxidation and/or reduction in the presence of t-BuOOH and PVA as evaluated by U.V. spectral changes. Cobalt (II) and (III) acetylacetonate in DMSO and aqueous solution appear to reach a steady state concentration, which is predominantly in the cobalt (II) state in DMSO and the cobalt (III) state in aqueous solution. The overall sum of cobalt (II) and cobalt (III) concentration as calculated from their U.V. absorbances decreases as the reaction progresses. The rate of total cobalt (II) and (III) acetylacetonate disappearance seems to be similar in both solvents at 42°C. At 60°C the rate is more rapid in aqueous solution than in DMSO solution.

3. PVA is subject to autoxidation at 42°C in the presence of cobalt (II) and (III) acetylacetonate and t-BuOOH in DMSO aqueous solution. Autoxidation rates seem to be fairly similar in DMSO and aqueous solution. The chain length for the autoxidation ($dO_2/dt/R_1$) of PVA is greater in aqueous solution than in DMSO. An empirical equation of the form $-\frac{dO_2}{dt} = k [Co_T]^a [\underline{t}\text{-BuOOH}]^b [PVA]^c$ was utilized to describe the autoxidation process.

Reaction orders of cobalt (II) and (III) acetylacetonate, PVA, and t-BuOOH with respect to autoxidation were less than one but greater than zero for all reactants in DMSO and aqueous solution for the concentration studied. Reaction orders varied with reaction conditions in DMSO but were fairly constant in aqueous solution. High concentrations of cobalt (II) and (III) acetylacetonates ($10^{-2}M$) decrease the rate of autoxidation in DMSO. High concentration of t-BuOOH (.96M) decrease the rate of autoxidation in DMSO and aqueous solution. Tobolsky's and Mayo's initiated polymer autoxidation mechanism was utilized to explain the results obtained. A reasonable adherence to kinetic consequences of these schemes was obtained.

4. PVA is subject to cleavage (viscometric decrease) at 42°C in the presence of cobalt (II) and (III) acetylacetonate and t-BuOOH in DMSO and aqueous solution. DMSO reaction solutions of PVA cleave ten times faster than aqueous reaction solutions in the presence of .66M t-BuOOH, $10^{-4}M$ cobalt (II) and (III) acetylacetonate and 10.6g/l PVA solution. Rates of peroxide decomposition are similar in DMSO and aqueous solution under these conditions. Base titration of the reaction mixture indicates that each cleavage produces two acid groups. Cleavage is a minor side reaction in relation to autoxidation

and t-BuOOH decomposition reactions. The major changes in viscosity occur within the first 1×10^5 sec of reaction time and then little change in viscosity takes place.

5. Cobalt (II), cobalt (III), chromium (III), copper (II), manganese (II), manganese (III), iron (II), iron (III), nickel (II), vanadium (III), cerium (III), and aluminum (III) acetylacetonate were used to catalyze the autoxidation and cleavage of PVA, t-BuOOH decomposition, and spectral changes of each metal acetylacetonate were followed on the U.V. spectrometer in DMSO and aqueous solution, solubility permitting. The catalytic behavior of various metal acetylacetonates in t-BuOOH decomposition followed the metal's ability to autoxidize PVA and promote cleavage of PVA. Some metal acetylacetonate exhibited increases in absorbance with reaction time. This may reflect a lack of true solubility of some metal acetylacetonates in the solvent studied.

Cobalt fluoride, chloride, bromide, and iodide were studied in a similar manner. Cobalt fluoride was generally least active of the halides in autoxidation, and cleavage of PVA and t-BuOOH decomposition in DMSO and aqueous solution where cobalt, chloride, bromide, and iodide exhibited similar behavior in these processes.

Hemin, hematin, chlorophyllin, and cobalt, copper, iron, and vanadyl phthalocyanines were used to catalyze t-BuOOH decomposition and PVA cleavage in DMSO and cytochrome c was tested in aqueous solution. In general, these metals were more active in t-BuOOH decomposition and PVA cleavage than metal acetylacetonate and halides. Hemin was significantly active as a peroxide decomposer (100 times as active as hematin). Iron phthalocyanine was the most active metal phthalocyanine tested. Cobalt phthalocyanine and hemin were used to

catalyze autoxidation of PVA and found to be more active than metal acetylacetonates and cobalt halides.

V ExperimentalChemicals

DMSO (Fischer Scientific Co.) was vacuum distilled at 50°C and 7 mm Hg pressure and stored over Fischer Type 4A molecular sieve. The water used was distilled and deionized. *t*-BuOOH was obtained from Wallace and Tieran Inc. (Lucidol Division) as "t-butyl hydroperoxide - 90" and further purified by distilling off the lighter impurities under vacuum.⁷⁴ Iodometric titration indicated greater than 95% hydroperoxide. The metal acetylacetonates (McKenzie Chemical Corp.) were recrystallized from acetone, except cobalt (II) acetylacetonate which was recrystallized from benzene. Melting points ($\pm 1^\circ\text{C}$) and crystal structure and color agreed with the published specifications of McKenzie Chemical Corp. Cobalt salt and metal phthalocyanines were obtained from Pfalz and Bauer Chemical Corp. and dried under vacuum at 45°C, 1 mm pressure overnight. Hemin, hematin, cytochrome C, and chlorophyllin were obtained from National Biochemical Co. and used as is. PVA (Baker Chemical Co.) was dried in a vacuum oven (45°C, 1 mm) for four days and stored in a vacuum desiccator. Stock solutions were prepared by stirring the polymer solutions for two days and filtering through glass wool. The viscosity average molecular weight of the polymer is approximately 7.6×10^4 g/mol. The molecular weight was estimated from eqn. (116) and (117) using an Ubbelohde viscometer (Ace Glass) at $42.00 \pm .02^\circ\text{C}$.¹⁷⁷

$$(116) \quad \eta (\text{H}_2\text{O}) = 4.53 \times 10^{-4} M_V^{.84}$$

$$(117) \quad \eta (\text{DMSO}) = 1.58 \times 10^{-4} M_V^{.84}$$

Periodate cleaved PVA was prepared by dissolving potassium metaperiodate in PVA solution, warming, and reprecipitating from acetone.¹⁷⁸ The cleaved polymer had a viscosity average molecular weight of 5.5×10^3 g/mol and a mol % of 1,2 glycol structure ($\Delta \times 100$) of 1.53.¹⁷⁹

Kinetics

Oxygen Absorption-

Oxygen measurements were carried out in jacketed, 50 ml Pyrex cells.¹⁸⁰ The desired temperature was maintained by pumping thermostated water ($\pm 1^\circ\text{C}$) through the jacket using a Precision Scientific 450 watt thermoregulator and circulator.

The flasks were stirred by means of a magnetic stirrer which drove a Teflon coated stirring bar inside the flask. A constant stirring rate was maintained in all flasks.

In a typical run, an appropriate amount of metal salt stock solution ($\approx 10^{-4}$ M) was pipetted into a 25 ml flask volumetrically. The desired amounts of peroxide and PVA solution were added to the flask again using volumetric pipettes. The solutions were brought to volume with solvent (water and DMSO). If the peroxide concentration was high ($> 7\text{M}$) the solution of DMSO, PVA and peroxide had to be heated to 42°C in order to prevent precipitation of the polymer. The metal solution was then added to the thermostated solution. The solution was shaken and poured into the reaction cell. The top of the cell, is fitted with a stopper, a stopcock, and a gas inlet tube which is connected through Tygon tubing to the burette (see Figure 21). All joints and stopcocks were lubricated with Dow Corning silicone stopcock grease. The system was flushed with oxygen by opening stopcock (B) and turning three way stopcock (A) so as to bypass the burette and connect the oxygen tank directly to the reaction cell. After the cell has been flushed for ten to twenty seconds, stopcock (A) is turned so as to connect the cell with burette which had been previously filled with oxygen. When the level of the mercury in the burette has reached that of the mercury in the leveling bulb, the stirrer is turned on and the system is allowed to

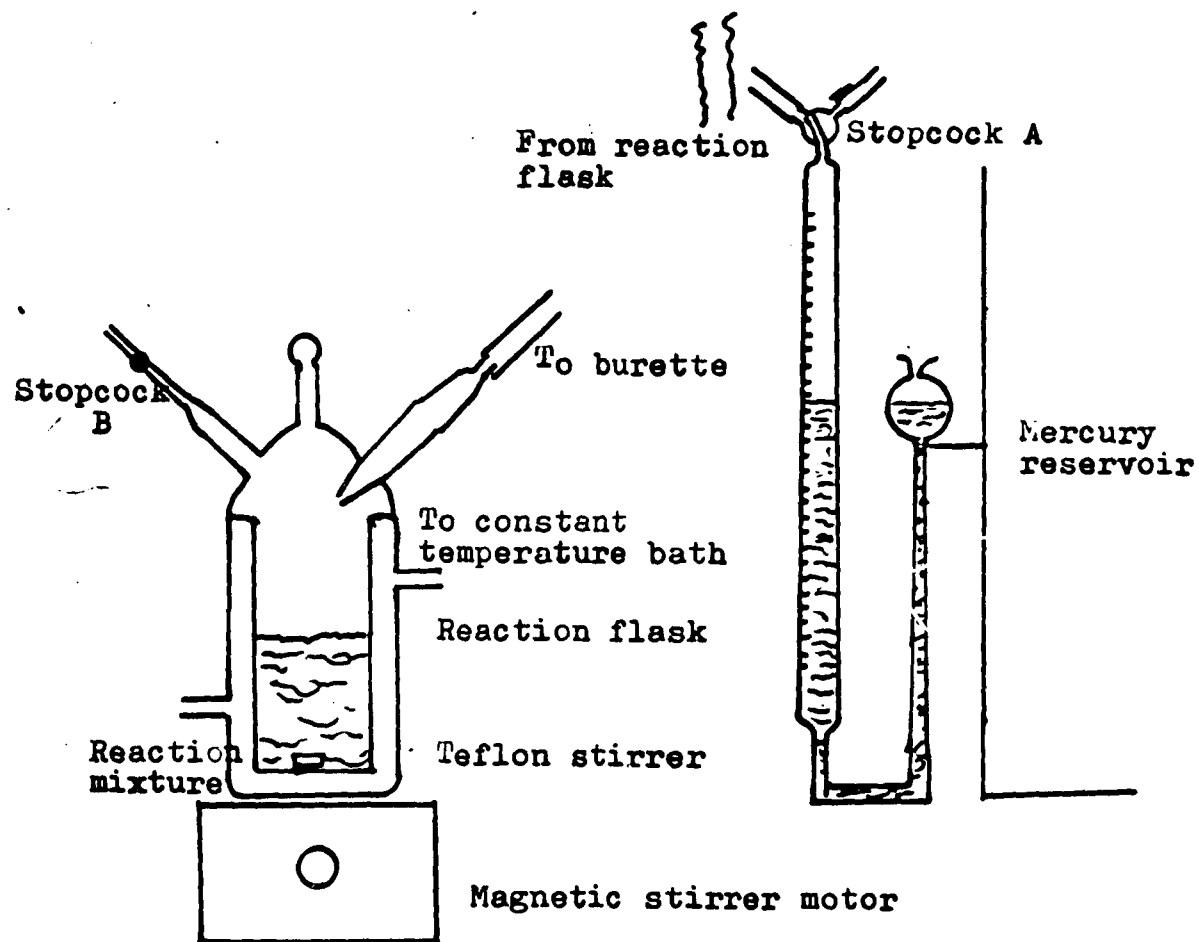


Figure (20) : Manometric apparatus for the measurement of oxygen taken up by the reaction mixture.

equilibrate for five to ten minutes and stopcock (B) is closed.

The gas burette used had a total volume of 50 ml calibrated in tenths of a ml. Before filling it with oxygen, the leveling bulb was raised so that the entire burette was filled with mercury. Stopcock (A) is turned so as to connect the tank directly to the burette. The burette is filled with gas, the leveling bulb is lowered to a point roughly opposite the 10 ml mark on the burette and (A) is turned so as to seal off the burette. (A) is turned so as to connect the burette with the reaction flask. The mercury level rises to the 10 ml mark and can be adjusted by adjusting a set screw on the leveling bulb assembly so as to align the two levels. This method sets the reaction cells to atmospheric pressure ($\pm 2\%$).

Readings are taken every 1×10^5 sec for normal runs. The leveling bulb is brought to a position which is level with that of the burette. In some readings the leveling bulb position was changed and another reading taken. A consistency of .02 ml was found between readings.

The volume of oxygen was plotted versus time and the rates were taken from the initial linear portion of the curve, after readings were corrected to STP and to the number of moles/liter.

t-BuOOH Decomposition

t-BuOOH decomposition studies were performed in vacuo to prevent the formation of other hydroperoxide products, which would have made interpretation of decomposition rates difficult.¹⁸¹ Solutions were prepared in an analagous manner to oxygen uptake studies in 25 ml volumetric flasks. The solution was divided by placing approximately 2.5 ml of solution in each Carius tube (J.H. Berge, 8 x 10 x 200 mm). Approximately three ml of solution were placed in each of four Carius tubes for a spectroscopic determination (U.V.) of cobalt concentration.

The tubes were degassed two to three times and resealed. The degassing process involved attaching the tube to the manifold, freezing the mixture with liquid nitrogen, and then pumping out the tube (pressure < 1 torr) for about 30 seconds. The vacuum line was cut off by means of a stopcock and the tubes were then thawed by means of a heat gun or a hot water bath. This process was then repeated until the sample was degassed.

After the tubes were sealed, they were thermostated at the desired temperature and removed at desired intervals. The bath temperature was controlled by a YSI Model 72 "Proportional Controller" to $\pm .01^{\circ}\text{C}$.

Tubes were opened with a glass cutter for analysis and a 1 ml aliquot of this solution was withdrawn and put into a iodine flask, which had been previously filled with 25 ml of glacial acetic acid, a small amount ($\approx .5\text{g}$) of potassium carbonate, and 1 ml of saturated potassium iodide solution. The mixture was capped and water was placed around the neck for a seal. The appearance of bubbles in the seal indicated that carbon dioxide was being evolved. After about 15 minutes, 25 ml of water was added and the red yellow mixture was titrated to a colorless end point using sodium thiosulfate solution (.005N-.1N). The burette used in most cases was a 10 ml automatic filling burette with graduations .05 ml apart and accuracy of reading $\pm .01$ ml. It was found that titrations were reproducible to better than 5%.

The concentration of hydroperoxide in moles/liters was calculated from equation 118.

$$(118) \quad [\underline{t} - \text{BuOOH}] = \frac{\text{ml titre} \times \text{normality of } \text{S}_2\text{O}_3^{2-}}{2 \times \text{no. ml. aliquot}}$$

This concentration versus time was then plotted and the rates of reaction calculated from the best straight line fit of these points.

$\underline{t}$ -BuOOH was found to be stable without metal catalysis.

Rate of Cobalt (II) or
Cobalt (III) Acetylacetonate
Disappearance and Formation

The rate of cobalt (II) disappearance or formation is measured by observing spectral changes in the range from 400 - 200 μ . In general, samples used were within the amplitude range of the instrument (10^{-5} M) and no dilution was necessary. Aliquots were removed from sealed degassed tubes (as described previously) and placed in a Pyrocell U.V. cell. Measurements were then done on a Carey Model 14 and 17 spectrophotometer. The reference cell contained solvent and a t -BuOOH concentration which approximately corresponded to the t -BuOOH concentration in solution (as determined in the previous part). The t -BuOOH was found to absorb in the region 240 - 300 μ ($\epsilon \approx 10$). This effect of the t -BuOOH can only be corrected for if the t -BuOOH concentration is low ($\sim .01M$). The cobalt solutions were found to obey Beer's law in the range studied. Two consecutive measurements on identical samples agree within $\pm .2\%$.

A Beer's Law plot was constructed using various concentrations of the cobalt (II) and (III) acetylacetonate (10^{-5} - 10^{-4} M) in the desired solvent (water or DMSO). From a curve of concentration vs. absorbance, the extinction coefficient can be found (the slope of this line). Thereafter the concentration of the desired cobalt salt was determined from equation (119).

$$(119) \quad [\text{cobalt acetylacetonate}] = \frac{\text{optical density}}{\epsilon \times \text{path length}}$$

ϵ is the extinction coefficient and the path length is in cm and experimentally is 1.00 cm. If a mixture of cobalt (II) and (III) acetylacetonate is present, an overlap of absorbance between these two peaks takes place. The total absorbance observed is the sum of the absorbances of cobalt (II) and cobalt (III) at that wavelength. Accordingly, it can be seen from equation (120) the relationship between optical density and

concentration of the cobalt species.

$$(120) \quad \text{optical density} = a_1 + a_2 = \epsilon_1 c_1 + \epsilon_2 c_2$$

where a_1 is the absorbance of cobalt (II) at the wavelength and a_2 is absorbance of cobalt (III) at that wavelength and ϵ and c are the respective extinctive coefficients and concentrations of the respective salt at that wavelength. If absorbances at two wavelengths are determined experimentally and the extinction coefficients are known for the two salts at these two wavelengths, a set of two equations can be generated with c_1 and c_2 as the two unknowns.

As a result of this the extinction coefficient was found for each cobalt salt at the place of maximum absorption and at a place corresponding to the maximum absorption of the corresponding cobalt salt. (Table XXVI). In the case of cobalt (II) acetylacetonate in DMSO the maximum absorption was found to be at 290 $m\mu$ and a corresponding extinction coefficient of 13,100. At 255 $m\mu$ (which corresponds to cobalt (III) maximum absorption) the extinction coefficient for cobalt (II) acetylacetonate was 7,500. Likewise the cobalt (III) acetylacetonate maximum was at 254 $m\mu$ in DMSO ($\epsilon = 38,100$) and at 290 $m\mu$ the extinction coefficient was 12,500. In aqueous solution the cobalt (II) acetylacetonate maximum was at 292 $m\mu$ ($\epsilon = 16,300$) and at 256 $m\mu$ the extinction coefficient was 4,000. The cobalt (III) acetylacetonate was at 256 $m\mu$ ($\epsilon = 20,800$) and at 292 $m\mu$ the extinction coefficient was 6,550. It should be noted that in DMSO solution the U.V. absorption of the solvent became very significant below 250 $m\mu$.

During an experimental run the concentrations of cobalt (II) and cobalt (III) acetylacetonate in the solution was calculated using the extinction coefficients indicated, and solving simultaneously. Usually, the tubes were opened over a period of two to three weeks and four

readings were taken. Replicate runs have a 10% margin of error.

Spectral changes for various other metal acetylacetonates were followed in an analogous manner. Extinction coefficients were obtained from a work by R. Holm and F. Cotton,¹⁸² which are listed in Table (XXVI). Metal concentrations were calculated using equation (119). Ratios of the metal acetylacetonate absorbances after 2×10^5 sec to the initial absorbance are listed in Table (XXI).

Viscometry

Solutions were prepared in an identical manner to those employed previously. These were added to an Ubbelohde viscometer, which was suspended in a thermostated bath at $42.00^\circ\text{C} \pm .01^\circ\text{C}$ by a YSI Model 72 "Proportional Controller". The solution was allowed to equilibrate to the temperature for fifteen minutes. Three readings were then obtained by sucking the solution up with a pipette bulb to the mark and clocking the flow time to the lower mark with a precision timer to the nearest tenth of a second. Generally flow times were on the order of 200 seconds and agreed within .2 of a second. The viscometer was then capped with a rubber septum. If the solution was to be run under nitrogen or oxygen, the gas was bubbled through the viscometric solution by means of a needle which passed through the septum. The gas was then passed through the viscometer for ten minutes. Another needle was placed in the septum to serve as a pressure release for the gas in the viscometer. A slight positive pressure was maintained when the needle was removed.

Anhydrous runs were performed with DMSO which was dried by passing it through a molecular sieve column (one and one half meters long with a seven millimeter o.d.) with Fischer Type 4A molecular sieve. The solution was then stored over molecular sieve in the viscometer during the run.

Viscosity readings were taken daily with Ubbelohde viscometers thermostated in a constant temperature bath at the required reaction temperature. Runs performed at 100°C in water solution were heated in a round bottom flask which was fitted with a reflux condenser. Aliquots were taken after 48 hours and introduced to the viscometers thermostated at $42.00^\circ \pm .02^\circ\text{C}$.

The polymer studied was also cleaved using potassium meta periodate and the mole per cent of 1,2 glycol structures ($\Delta \times 100$) was calculated by using the procedure of Flory and Leutner as outlined in Schumaker and Garland. Essentially .25g of periodate is dissolved in 25 ml of stock solution. The solution is warmed to 70°C, and stirred until all the salt dissolved. The viscosity of this solution was obtained at several different dilutions. Essentially all 1,2 glycol head to head structures should be cleaved leaving polymer with 1,3 glycol units only. This polymer was reprecipitated with acetone and used in viscometric runs which employed 1,3 glycol PVA in the presence of *t*-BuOOH and cobalt acetylacetonate. An equal number of grams per liter of polymer was used as in uncleaved polymer runs.

The molecular weight of the polymer was calculated by means of equations which relate viscosity of PVA solutions to molecular weight. Viscometric measurements were made at four different dilutions of the polymer solution in DMSO and aqueous solution (1.06 g/dl, .87 g/dl, 1.79g/dl, and .70g/dl). The intrinsic viscosity was calculated by using the formula (121)

$$(121) \quad (\eta) = \lim_{c \rightarrow 0} \left(\frac{1}{c} \ln \frac{n}{n_0} \right)$$

where n is the polymer solution viscosity and $n_0 = Bt\rho$ where n_0 is the viscosity of the solution, ρ is the density of the solvent, t is the flow time in the viscometer, and B is the viscometer, constant which must be determined through calibration with a liquid of known viscosity.

Determination of the bracketed quantity at infinite dilution ($c \rightarrow 0$) is determined by extrapolation of points at various dilutions to zero concentration. The formulas which were used to determine the molecular weight are

$$(116) \quad \eta_{H_2O} = 4.53 \times 10^{-4} \bar{M}_V^{0.64}$$

$$(117) \quad \eta_{DMSO} = 1.58 \times 10^{-4} \bar{M}_V^{0.84}$$

The mole per cent of 1,2 linkages can be calculated by using the formula (122)

$$(122) \quad \Delta = 83 \left(\frac{1}{\bar{M}_V'} - \frac{1}{\bar{M}_V} \right)$$

where $\bar{M}_V'$ is the uncleaved viscosity molecular weight and $\bar{M}_V$ is the molecular weight of the cleaved polymer.

In the reaction solution studied t - BuOOH was found to alter the viscosity of the solution. Corrections for this were made by applying a constant correction to the viscosities of the solutions. The corrections involved changing the initial viscosity of the reaction mixture to the intrinsic viscosity of a PVA solution in DMSO or water. The ratio of the reaction mixture viscosity to the intrinsic viscosity was applied to all readings. The mole per cent of 1,2 glycol linkages was calculated as 1.53.

This cleaved polymer was precipitated with acetone, collected by filtration, and dried at 60°C and 1 mm pressure. The cleaved polymer was dissolved in dimethyl sulfoxide (1.06g/dl), which had a .66 M concentration of t -BuOOH and 2×10^{-5} M cobalt (II) acetylacetonate. No change of viscosity was observed for 4×10^5 secs.

NMR

The Varian HA-100 was used with tetramethyl silane or 3(trimethylsilyl)-propane sulfonic acid sodium salt used as a reference. PVA was predried in a vacuum oven (1 mm, 60°C) and was dissolved in dimethyl d_6 -sulfoxide (Stohler Isotopes), dried over molecular sieve (Fischer Type 4A) and poured through a molecular sieve column attached via a septum to an NMR tube. Cobalt (II) chloride was dried in a vacuum oven (60°C, 1 mm) and then dissolved in dimethyl d_6 -sulfoxide and stored over molecular sieve. The solution was added with a microliter syringe through a septum. Other cobalt salts were tried such as cobalt (II) and (III) acetylacetonate and cobalt (II) bromide but were found to distort the spectrum. Water peaks were found cases in the nmr spectra. These spectra did not exhibit the shifting phenomena.

Spectra were examined for shifting relative to TMS and shifts were denoted with the use of the frequency counter on the spectrometer. The peak was centered on the nmr frequency counter and the frequency read from the counter. (Table XVI).

NaOH Titrations

All titrations were performed with .001 N NaOH prepared from Titrosol premeasured ampoule (.0400 g/liter). Two milliliters were withdrawn from autoxidation reactions after completion of the run. To this solution 10 mls. of freshly distilled water were added and one drop of phenolphthalein indicator. Only data from autoxidation mixtures with .016 M t -BuOOH were used in this study because of the appreciable acidity of t -BuOOH at higher concentration. An experimental variation for replicate runs of approximately 20-25% was found in these runs as a result of endpoint errors and possible contamination of the solutions

with carbon dioxide.

Reaction of 1,2 propanediol

Solutions were prepared in an analagous manner to those in PVA oxidations. Cobalt (II) and (III) acetylacetonate concentrations were approximately $5 \times 10^{-4}M$ in 25 ml of aqueous and DMSO solution. *t*-BuOOH concentration was $7.2 \times 10^{-3}M$ and 1,2 propanediol concentration was approximately 1.05M. The reaction was run at 42°C for approximately 10^6 seconds. Gas chromatographic analysis of the product mixture proved to be difficult because of the instability of DMSO to temperature. However, 1,2 propanediol (Eastman Organic Co.) was analyzed on a Hewlett Packard Gas Chromatograph 5750 at 180°C on a 15% Carbowax-Chrom W column with an injection port temperature of 100°C, and with a flame detector temperature of 550°C. It was found to be pure and was used as is.

It was decided to isolate the carbonyl products by precipitation of the products with DNPH solution.

After 10^6 secs DNPH solution was added to 2 ml of each solution. The precipitate was collected by simple filtration and dried in a vacuum desiccator under house vacuum. The precipitate was then put on a coverslip and a melting point taken. A wide melting range of from 75° to 85°C was obtained for these crystals. The derivative was thought to be a mixture, since possible products have considerably higher melting points.

Thin layer chromatography was employed to separate the mixture. Silica G plates (Quanta Gram Co.) were employed. A mixture of 50 ml Ethanol. 50 ml Chlorobenzene was allowed to impregnate the TLC plate, while it was in a TLC developing tank. The plate was then dried, DNPH derivative mixtures were dissolved in ethanol and spotted on the plate with 10 μ l applicators. Authentic samples of Formaldehyde, acetaldehyde,

acetone, lactaldehyde, and pyruvic aldehyde DNPH derivatives were also spotted on the plates. Benzene was introduced into another developing tank and the plate was allowed to develop in these tanks. The plate was scored 15 cm from application in order that a uniform solvent front would be obtained. R_f values were calculated by measuring the distance the spot travelled and dividing by the distance the solvent front travelled (Table XVIII).

Preparative TLC was performed by using a preparative applicator (50 μ l) in order to put a broad band of material on the plate. This was developed in the normal manner and the bands were scraped off and put into separate vials. This process was repeated four times. Each fraction was then put into a micro Soxhlet extractor and refluxed for two hours in absolute ethanol. The solution is then evaporated to dryness and stored in a vacuum dessicator under 1 mm vacuum overnight.

D_6 -benzene (SIC) is added to each dried fraction and TMS is added as a reference. Spectrum is taken on the Varian A-60A nmr spectrometer.

ESR Detection of Radicals

ESR analysis of cobalt (II) and (III) acetylacetonate ($\approx 10^{-3}M$), t -BuOOH (.66M), PVA mixtures (1.06g/dl) mixtures was attempted using a Varian (E9) spectrophotometer. DMSO solutions of PVA were run through a 1.5 meter molecular sieve column of Fisher 4A molecular sieve, before use. One half ml of DMSO solution of PVA is put into the esr mixing chamber. The mixture is drawn into the esr tube and is freeze thaw degassed under a .01mm vacuum. On the last evacuation the stopcocks to the two mixing bulbs are opened in order to evacuate the whole system.

DMSO solutions of t -BuOOH and cobalt (II) and (III) acetylacetonate were first degassed by using the freeze thaw method under .01mm of pressure in tubes represented in Figure (16). The tube in which the solution is degassed has a septum fitted to the end of a protruding arm. After the sample is degassed it is removed by means of a vacuum tight syringe through the septum. This degassed sample (0.4 ml) is then injected into one of the mixing bulbs of the esr mixing apparatus. The other degassed solution (either t -BuOOH or cobalt (II) or (III) acetylacetonate) is injected into the other bulb. Then stopcock 3 which connects the mixing chamber to the vacuum line is closed and the esr mixing apparatus may be removed and the apparatus set into the esr cavity. The stopcocks from the two mixing chambers are opened and the sample is scanned. No esr activity was detected. Cobalt (II) and (III) acetylacetonate peaks could also not be detected in this medium.

Another attempt at detection was made by using a tube such as that in Figure (22). One solution (PVA + cobalt (II) acetylacetonate) is put into the bulb and degassed. t -BuOOH is then distilled into this tube by heating a t -BuOOH solution on one end of the vacuum

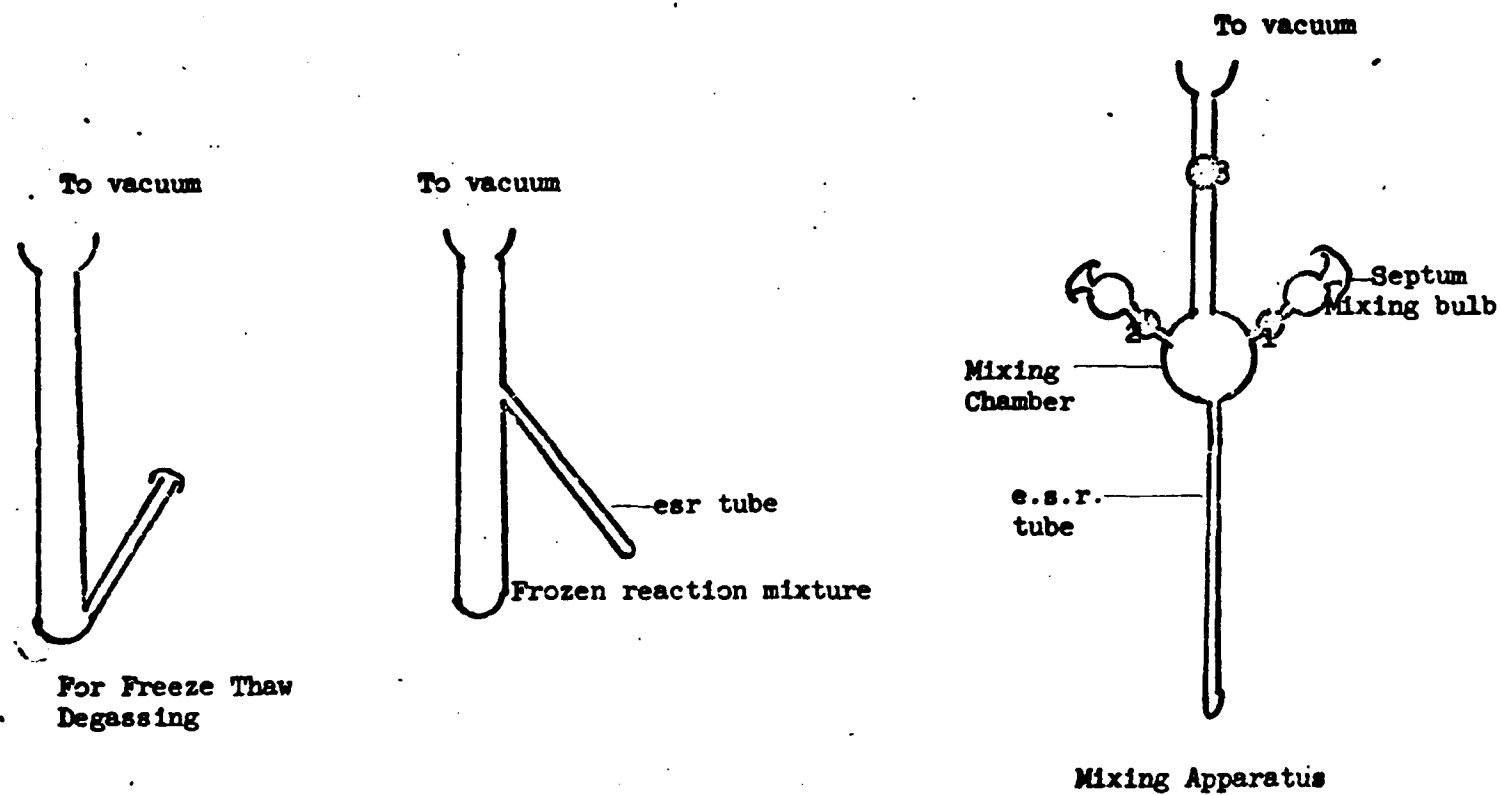


Figure (21): Apparatus used for the detection of radicals in the e.s.r.

line and condensing the solution in the bulb with the use of liquid nitrogen. This tube is then sealed. The bulb is kept in liquid nitrogen. The esr tube is then put into the spectrometer and the bulb is warmed. The solution melts and flows into the esr tube. The esr then scans the region of interest. No peaks were detected at highest sensitivity.

Calculations Of The Rates of Various Processes

In calculating the rate of t -BuOOH decomposition, a graph is constructed of $\log [t\text{-BuOOH}]$ vs. time (Figure 1b). The half life for the decomposition is obtained by extrapolating the line obtained in Figure (1b) to one half the peroxide concentration. The rate of peroxide decomposition is calculated on the basis of the first order relationship, $\text{rate} = .693 [t\text{-BuOOH}] / \tau_{1/2}$. Cleavage rates are taken from the initial linear portion of the curve of viscosity molecular weight vs. time (first 2×10^5 sec). In general, a tangent line is drawn to the initial portion of the curve and the slope of this line is taken as the initial rate of cleavage.

Autoxidation rates were computed by using a least squares computer program on the points of the curve of oxygen absorbed by the reaction mixture vs. time. Rates were computed on the first 4×10^5 sec. If the curve was not linear the maximum rate of autoxidation was obtained by constructing a line through the portion of the curve with the greatest slope. U.V. spectral changes were obtained by obtaining the absorbance of the sample at the maximum absorbance (Table XXVI) for each metal. In the case of cobalt (II) and (III) acetylacetonate maximum absorbances were correlated at the maximum absorptions for both valence states. A computer program was used to solve the simultaneous equations (see experimental section) used to find the concen-

tration of cobalt (II) and (III) acetylacetonate. Extinction coefficients for other metal acetylacetonates were obtained from values obtained in chloroform by R. Holm and F.A. Cotton.^{18 2} (Table XXVI) except for cobalt (II) and (III) acetylacetonate where a Beer's law plot was constructed for absorbance vs. concentration of the metal species.

Errors

The limits of error for each measurement was discussed in the experimental section for each process. Replicate runs were conducted for each process to determine the margin of error for each rate measurement. Rates of autoxidation of PVA were found to agree within 5% on three replicate runs, the rate of cleavage of PVA was found to agree within 8% on four replicate runs, rates of t-BuOOH decomposition were found to agree within 10% on three replicate runs, and U.V. spectral runs yielded ratios of cobalt (II) to cobalt (III) within 5% on three replicate runs. Reaction orders in the empirical equations for each process (cleavage, autoxidation, and t-BuOOH decomposition) represent approximately a 20% margin of error.

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