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POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY t-BUTYL HYDROPEROXIDE IN THE PRESENCE OF METAL ACETYLACETONATES

by

C. J. Shahani

A dissertation submitted to the Graduate Faculty of the City University of New York in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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Abstract

The effect of small catalytic concentrations of acetylacetonates of Cu(II), Co(II), Co(III), Mn(II), Mn(III), Cr(III), Ni(II) and Al(III) on t-butyl hydroperoxide initiated polymerization of methyl methacrylate has been studied in 1-chlorooctane medium. In each of these reaction systems, the progress of the reaction has been followed by a periodical determination of hydroperoxide concentration and polymer content. In order to evaluate initiator efficiencies, the number average molecular weight of the isolated polymer samples has also been determined. While Cu(II), Co(II), Co(III) and Mn(III) acetylacetonates are seen to catalyze the decomposition of t-butyl hydroperoxide, only the Cu(II) complex catalyzes the polymerization of methyl methacrylate. Cobalt(II) acetylacetonate, on the other hand, retards the polymerization reaction.

The Cu(II), Co(II) and Co(III) catalyzed reactions have also been studied in benzene medium. In this solvent too, Co(II) catalyzes the decomposition of t-butyl hydroperoxide but retards the polymerization of methyl methacrylate. In contrast, the catalytic effect of Cu(II) on hydroperoxide decomposition, as well as on methyl methacrylate polymerization, is greatly diminished, while Co(III) does not catalyze hydroperoxide decomposition in the aromatic solvent.

To further investigate the effect of the nature of the solvent, the Cu(II) catalyzed reaction has been studied in DMSO medium. In this reaction system, the rate of hydroperoxide decomposition is appreciably higher than that observed in benzene, but much lower than the rate observed in 1-chlorooctane under identical experimental conditions. However,

for the Cu(II) catalyzed reaction system, the highest rate of polymerization of methyl methacrylate obtains in DMSO. The highest initiator efficiencies are also observed in this solvent.

The catalytic effect of metal acetylacetonates on the decomposition of t-butyl hydroperoxide has also been studied in the absence of methyl methacrylate. In general, the rates observed in 1-chlorooctane and benzene are faster than the corresponding rates in the presence of the monomer. However, the reverse is true in DMSO medium.

For all the reaction systems described thus far, reaction rates have been determined at 40, 60 and 80°C. These data have been used to evaluate activation energies and frequency factors.

The kinetics of the polymerization of methyl methacrylate initiated by t-butyl hydroperoxide in the presence of Cu(II) acetylacetonate have been studied in 1-chlorooctane and DMSO. In each of these solvents, the effect of concentrations of Cu(II), t-butyl hydroperoxide and methyl methacrylate on rates of decomposition of the initiator and polymerization of the monomer has been investigated at 60°C. These data have been used to obtain empirical rate laws, which help to better understand the underlying reaction mechanisms.

Chain transfer constants for acetylacetonates of Cu(II), Co(II), Co(III), Mn(II), Mn(III), Cr(III), Ni(II) and Al(III) have been determined. The polymerization of methyl methacrylate has been initiated with AIBN in the presence of each of these metal complexes in 1-chlorooctane medium. In each case, the metal concentration has been varied over a fairly wide range, while maintaining a constant monomer concentration. The

variation of the number average molecular weight of the polymer with the concentration of the metals has been studied at 60, 70 and 80°C. These data have been used to determine chain transfer constants for each of the metal acetylacetonates mentioned, at these temperatures. Activation parameters for chain transfer have been obtained. An isokinetic plot indicates that although the degree of chain transfer varies greatly with the nature of the metal, the reaction mechanism underlying chain transfer on the different metal acetylacetonates is identical.

I. Introduction

(a) Free radical polymerization:

Free radical polymerization is a chain reaction comprising three major steps: initiation, propagation and termination. In the initiation step, formation of free radicals takes place in the reaction system. During the propagation step, long chain radicals add to monomer units increasing the chain length. Radicals are removed from the system in the termination step. Such a chain process differs from most other radical chain processes in that the final products (inert or 'dead' polymer molecules in this case) are not formed directly in the propagation step, but appear as a result of the termination step.

In many practical systems, a fourth reaction step is encountered, a process in which the center of radical reactivity is transferred from a growing chain to some other species. This is accomplished by the actual transfer of an atom (frequently hydrogen), or a group of atoms, between the two reactants. Such a process, which is aptly known as a 'chain transfer' reaction, results in the formation of inert polymer without any decrease in the radical concentration of the system, and has the general effect of bringing about a decrease in chain length of the product molecules. These basic steps of the radical polymerization process are discussed later in greater detail.

Kinetics of radical polymerization: The whole polymerization process can be represented by the following simplified kinetic schemes in which the chain reaction is initiated by the thermal or photochemical decomposition of a suitable initiator molecule, I:

$$\begin{array}{llcll}
\text{Initiation:} & I & \xrightarrow{k_d} & 2\,R\cdot & (1) \\
 & R\cdot + M & \xrightarrow{k_i} & P\cdot & (2) \\
\text{Propagation:} & P^{\cdot}_{n} + M & \xrightarrow{k_p} & P^{\cdot}_{n+1} & (3) \\
\text{Transfer:} & P^{\cdot}_{n} + S & \xrightarrow{k_s} & P_n + S\cdot & (4) \\
 & S\cdot + M & \longrightarrow & P\cdot & (5) \\
\text{Termination:} & P^{\cdot}_{m} + P^{\cdot}_{n} & \xrightarrow{k_t} & \text{polymer} & (6)
\end{array}$$

Here, M and R• represent a monomer molecule and a primary radical, respectively. Growing polymer molecules are represented by P•, the subscript n being appended when it is required to note the number of monomer units incorporated in the chain. S represents a chain transfer agent, which may be the monomer, initiator, solvent or any other molecule present in the system.

In the above reaction scheme, all the radicals produced in reaction (1) may not necessarily initiate polymerization as in reaction (2). Primary radicals taking part in extraneous 'wastage' reactions (to be described later), are termed 'inefficient'. The fraction of radicals produced in reaction (1) which ultimately initiate a radical chain, is termed the 'efficiency', f, of initiation. The initiator efficiency can be determined by comparing the amount of initiator decomposed with the number of polymer chains formed.

Certain simplified kinetic relationships which are widely applied to free radical polymerization can be derived from the reaction scheme outlined above. If it is assumed that radical reactivity is independent of radical size, and that any transfer derived radicals, S•, rapidly add monomer and are not consumed in any other process, application of the stationary state hypothesis dictates that

$$\text{Rate of initiation} = \text{Rate of termination}$$

$$\text{i.e., } R_i = R_t$$

$$2fk_d[I] = 2k_t[P\cdot]^2 \qquad (7)$$

$$[P\cdot] = (R_i/2k_t)^{\frac{1}{2}} = (k_d[I]/k_t)^{\frac{1}{2}} \qquad (8)$$

Provided that the kinetic chain length is large and transfer to monomer not very efficient, the rate of polymerization is given by:

$$R_p = -\,d[M]/dt = k_p[M][P\cdot] \qquad (9)$$

From (8) and (9):

$$R_p = k_p[M](R_i/2k_t)^{\frac{1}{2}}$$

$$\text{i.e., } R_p = k_p[M](fk_d[I]/k_t)^{\frac{1}{2}} \qquad (10)$$

According to equation (10), the order of monomer concentration and initiator concentration are expected to be 1 and 0.5, respectively. Monomer and initiator rate orders are usually determined from initial polymerization rate measurements. The above kinetic relationships are generally seen to hold. However, deviations have been observed in a significantly large number of cases. Deviations from the expected monomer order are more common, and a number of values greater or less than unity have been reported (1-7). In some cases, the monomer order varies with monomer concentration (1-3). Deviations from the expected initiator exponent of 0.5 are less common, but values below this figure have been reported in the polymerization of methyl methacrylate and higher methacrylate and acrylate esters (7-9). Values greater than 0.5 have also been obtained, particularly for polymerizations taken to high conversions (8, 9). Several explanations have been suggested to account for these anomalies. In general, they involve a modification of the initiation, propagation or termination steps. Any modification of the initiation or termination process would modify equation (7), and consequently the expression for the concentration of polymeric radicals in equation (8), whereas a change in the propagation mechanism would produce a change in equation (9). These mechanisms are briefly described in the following discussion of the individual steps in radical chain polymerization.

Initiation: A great variety of initiating systems is available. Commonly, the initiator molecule I, in reaction (1), may be an organic peroxide, hydroperoxide, azo or diazo compound, which undergoes homolysis thermally or photochemically as in reaction (2), to yield the initiating radical species. Primary radicals may also be generated by high energy electro-magnetic radiation.

In a study of peroxide initiated polymerization of styrene in tolnene solution, the rate of polymerization was found to depend on monomer concentration (1). The normal monomer order of unity was observed at high monomer concentrations, but at lower monomer concentrations a value of 1.5 was obtained. However, the initiator order remained at 0.5 under all conditions. These results were found to satisfy the equation:

$$R_p = K_1[M]^{3/2}[I]^{\frac{1}{2}}/(1 + K_2[M])^{\frac{1}{2}} \qquad (11)$$

where K_1 and K_2 are constants. To account for these results, Schulz (1) suggested a variation in the efficiency of initiation with monomer concentration. He postulated that a complex was formed between monomer and initiator,

$$M + I \rightleftharpoons \text{complex} \longrightarrow 2\,R\cdot$$

and that the unimolecular decomposition of this complex was the true source of primary radicals. No experimental evidence was given, or has been found since, for the existence of such a complex. Matheson (10) suggested that these results could be better explained in terms of a phenomenon known as 'radical caging'. This theory recognizes that primary radical pairs formed by the decomposition of an initiator molecule are surrounded by a "cage" of solvent and monomer molecules. Subsequently, these radicals may undergo many collisions with each other, as well as with the solvent and monomer molecules, which constitute the "cage wall", until one of them adds to a monomer molecule as in reaction (14) in the following kinetic scheme:

$$I \longrightarrow (2R\cdot) \qquad (12)$$

$$(2R\cdot) \longrightarrow Q \qquad \text{Recombination} \qquad (13)$$

$$(2R\cdot) + M \longrightarrow P_1\cdot + R\cdot \qquad \text{Initiation} \qquad (14)$$

$$(2R.) \longrightarrow 2R\cdot \qquad \text{Diffusion} \qquad (15)$$

where $(2R\cdot)$ represents a caged radical pair. It is also possible that the radicals may simply diffuse out of the cage (reaction 15) to initiate polymerization as in reaction (2). Alternatively, one of the caged radicals may undergo further decomposition to give a small molecule, e.g., N_2 or CO_2. If this is followed by recombination (reaction 13), a new molecule, incapable of homolytic decomposition, may be formed. This reaction is one of the leading causes of initiator inefficiency.

If monomer concentration is low enough so that $k_3[M] << k_4$, initiation outside the solvent cage would predominate and a monomer exponent of unity would be observed. But at high monomer concentrations, where $k_3[M] >> k_4$, reactions (8) and (9) would be in direct competition. Under these conditions, the effect of initiation clearly depends on the monomer concentration and it has been shown (10) that

$$R_p = (k_p[M]k_1^{\frac{1}{2}}[I]/k_t^{\frac{1}{2}})\{k_3[M]/(k_2 + k_3[M])\}^{\frac{1}{2}} \qquad (16)$$

The similarity of this equation to that obtained by Schulz (equation 11) is obvious, and his results can be convincingly accounted for by the radical caging theory. In terms of equation (10), the effect of primary radical caging will be to make f monomer dependent. It should be noted that since radical recombination within a solvent cage is a first order process, the order in initiator remains unchanged at 0.5.

Saad and Eirich (11) have considered a reaction scheme similar to equations (12-15), and by the influence of solution viscosity on rates of polymerization were able to show that decomposition rate constants for benzoyl peroxide and azoisobutyronitrite (AIBN) were dependent on the viscosity (although not so much as termination rates, as will be discussed later). They derived from their data average times for recombination of free radicals within the cage and of diffusion out of the cage of the order of 10^{-10} seconds. Considering addition to monomer to require about 10^{-5} sec., they regard the initiation of chain polymerization within the cage as unlikely.

In the cumene hydroperoxide initiated polymerization of styrene unusually high monomer orders and low initiator orders have been explained by Walling and Chang (12) on the basis of monomer participation in the initiation step:

$$ROOH + CH_2{=}CHC_6H_5 \longrightarrow ROO\cdot + CH_3\dot{C}HC_6H_5$$

Tobolsky and Matlack (13) in their study of the same system find that solvent participation in the initiation step is also important. Solvent participation in the initiation step is not restricted to this system. Evidence of such reactions in the polymerization of methyl methacrylate initiated by AIBN (13) and azobisisobutyroamidine (14) has also been obtained.

<u>Propagation</u>: Two major mechanismsof the propagation step have been advanced to account for monomer orders other than unity. Both involve participation by the solvent in the propagation step. The Olivé radical complex theory involves chemical interaction of the solvent with growing radical chains, whereas in the Tudos hot radical theory, a physical interaction is involved. The initiator order remains at 0.5 in both the mechanisms presented below.

Tudos hot radical theory: This theory is based on the premise that the energy released in the propagation step appears in the form of vibrational excitation of the polymeric radicals formed in the reaction (15). If the process of vibrational deexcitation is slow enough, these 'hot radicals' may supply part of the activation energy in subsequent propagation reactions:

$$P_n^{\cdot *} + M \xrightarrow{k_p^*} P_{n+1}^{\cdot *} \qquad (17)$$

Thermalization of these hot radicals also occurs by collision with monomer and solvent, S, molecules, and may be followed by normal propagation:

$$P_n^{\cdot *} + M \xrightarrow{k_c^*} P_n^{\cdot} + M \qquad (18)$$

$$P_n^{\cdot *} + S \xrightarrow{k_c^{\prime *}} P_n^{\cdot} + S \qquad (18a)$$

$$P_n^{\cdot *} + M \xrightarrow{k_p} P_{n+1}^{*} \qquad (19)$$

Thus, two propagation reactions can occur, one involving hot radicals and the other with thermalized radicals. Obviously, the former would add monomer at a much greater rate (i.e., $k_p^* \gg k_p$).

Neglecting the participation of hot radicals in termination reactions because of their low concentration, it has been shown that

$$R_p = K[I]^{\frac{1}{2}}[M] \qquad (20)$$

where,

$$K = k_p(fk_d/k_t)^{\frac{1}{2}}\left[1 + \frac{k_p^*}{k_c^* + k_c'^*[S]/[M]}\right]$$

$$= K_\infty\left[1 + \frac{k_p^*}{k_c^* + k_c'^*[S]/[M]}\right]$$

At high dilutions, $[S]/[M] \longrightarrow \infty$, and $K \longrightarrow K_\infty$

At high $[M]$, $K \longrightarrow K_o$, where

$$K_o = K\ (1 + k_p/k_c^*)$$

Thus, depending on M , K varies between two values irrespective of the nature of the inert solvent. As $[M]$ decreases, the extent of thermalization increases. At sufficiently high dilutions radical thermalization will be complete and only one propagation step will be involved. Under these conditions equation (20) reduces to equation (10), and a monomer order of unity would be expected. At higher monomer concentrations, $K \longrightarrow K_\infty$, resulting in monomer exponents higher than unity. As experimental evidence for hot radical effects in solution, Tudos cites the observation of Bevington and Lewis (16) that 30% of benzoyloxy radicals formed photochemically from benzoyl peroxide are immediately decarboxylated, but in the case of radicals formed by thermal decomposition no such effect occurs. In other work (17), Tudos used ESR to measure the steady state concentration of radicals produced by the addition of cyanopropyl radicals to various inhibitors. The effect of benzene dilution on this concentration was determined for primary radicals generated photochemically and thermally from AIBN. The results were consistent with the photochemical production of vibrationally excited radicals which need some $2x10^6$ collisions before being thermalized.

Olivé radical complex theory: Henrici-Olivé and Olivé (18-21) have pointed out that electron affinities of typical polymer molecules are of the same order as those of such molecules as tetracyanoethylene and chloranil, which are known to form charge-transfer complexes with typical solvents used in vinyl polymerization. These authors suggest that polymer radicals can form complexes with both solvent and monomer molecules, only the latter complex leading to propagation. the concentrations of the complexes are proportional to their lifetimes and to the concentrations of monomer and solvent. Hence, the ratio of concentrations of the monomer complex, PM•, and the solvent complex, PS•, can be shown to be given by the equation:

$$\frac{[PM\cdot]}{[PS\cdot]} = \frac{[M]\tau_m}{[S]\tau_s} \qquad (21)$$

where τ_m and τ_s are the lifetimes of the radical-monomer and the radical--solvent complex, respectively. Since only the polymer-monomer complex can propagate, the rate of polymerization is

$$R_p = k\,[PM\cdot]$$

$$R_p = k\,[P\cdot] \cdot \frac{[M]}{[S]\tau_s/\tau_m + [M]} \qquad (22)$$

where $[P\cdot]$ is the total concentration of complexed radicals. In bulk monomer, all polymer radicals are complexed with monomer. Hence,

$$(R_p)_o = k[P\cdot]$$

$$\text{Or, } (R_p)_o = k_p[P\cdot][M]_B$$

where $[M]_B$ is monomer concentration in bulk. Therefore, in solution,

$$R_p = k_p[P\cdot][M]_B \cdot [M]([S]\tau_s/\tau_m + [M]) \qquad (23)$$

If $[M]_B \simeq [M]+[S]$, then equation (23) shows that a monomer exponent less than unity will be obtained if $\tau_s/\tau_m > 1$, and a value greater than unity if $\tau_s/\tau_m < 1$. When τ_s and τ_m are of the same order, the "normal" monomer order of unity results. Thus, rate enhancement or retardation can be attributed to the nature of the solvent.

Olivé suggested the above mechanism to account for experimental results obtained for the polymerization of styrene and methyl methacrylate in various aromatic solvents. Equation (21) and (22) yield the following relationship:

$$\frac{\tau_s}{\tau_m} = \frac{(R_p)_o - R_p}{R_p} \cdot \frac{[M]}{[S]}$$

The ratio τ_s/τ_m should be characteristic of the monomer solvent system. Styrene gives good agreement with this hypothesis (21). However, the same degree of accord with this theory is not obtained in experiments with methyl methacrylate (22). Bamford and Brumby (23) and Burnett et, al. (24) have demonstrated the importance of the solution viscosity factor in its influence on the overall rate of polymerization. This aspect has not received any consideration in the Olivé analysis. However, another investigation disputes the view that the propagation constant is affected by solution viscosity (25). Both sets of authors have suggested that this might indicate some complexing of polymer radicals with aromatic solvents. Russell (26-29) has presented evidence of complex formation between free radicals and aromatic solvents. It is well known that methyl methacrylate and other radicals form complexes with inorganic molecules such as zinc and aluminium chloride, and that this can result in an increase in the propagation constant (30-33). Burnett et, al. (34) have demonstrated that complex formation occurs between the stable t-butyl mesityl nitroxide radical and π-bonded systems, including certain monomers. In a general sense, polymer radical complexing, either with solvent or monomer can be regarded as an enhanced form of radical solvation. Thus, rate pecularities found in the polymerization of acrylamide and methacrylic acid (35), and methyl methacrylate (36) in dimethyl sulfoxide and other polar solvents, have been attributed to radical solvation effects. Although no charged species are directly involved in propagation, the transition state in certain cases may have some polar characteristics (37-44). Consequently, in some polymerization reactions, propagation energies and entropies of activation would be expected to depend to a certain extent on the overall composition and polarity of the polymerizing medium. Such solvent effects have been demonstrated in nonpolymerizing radical reactions (45), and in the polymerization of methyl acrylate (46) and methacrylic acid (35). Analogous results have been obtained in certain copolymerization systems (47-49).

Chain Transfer: Flory (50) in 1937, first surmised the existence of chain transfer in polymerization and defined the process as one in which 'the active center is transferred from one polymer molecule to another molecule, leaving the former inactive and endowing the latter with the ability to add monomers successively'. Thus, chain transfer is basically a radical transfer reaction in which a growing polymeric radical extracts an atom (frequently H or Cl), or a univalent group of atoms, from a neighbouring molecule to saturate its free valency, with the formation of a new radical:

$$P_n^{\bullet} + SX \longrightarrow P_nX + S^{\bullet} \qquad (24)$$

where P_n is a propagating radical chain and the molecule SX (henceforth referred to as the substrate) may be any molecule present in the system, including monomer, solvent, initiator, or inert polymer. Of these, transfer to monomer or solvent is usually more important. Only at high initiator concentrations or high conversions, do the other two transfer reactions become important. It should be noted here that although the present discussion is confined to free radical systems, chain transfer also takes place in ionic systems.

The immediate effect of chain transfer is to reduce the chain length and therefore the molecular weight of polymer. If the reactant and product radicals in reaction (24) have comparable reactivities, chain growth continues unabated and the rate of polymerization is unaffected. Such chain transfer is termed 'nondegradative'. However, if the reinitiation step is slow, or termination involving the transfer radical, S•, becomes significant, both molecular weight and rate of polymerization are diminished, and the transfer reaction is termed 'degradative'. Recently, an increase in the rate of polymerization of vinyl chloride as a result of chain transfer with carbon tetrachloride (51), and propionic aldehyde (52) has been observed, probably due to an increased rate of reinitiation.

Quantitative formulation: The classic method of investigating chain transfer reaction involves molecular weight measurements and is based upon the relation:

$$\overline{X}_n = \frac{\text{Rate of chain propagation}}{\text{Overall rate of chain termination}}$$

or

$$\frac{1}{\overline{X}_n} = \frac{\text{Sum of rates of formation of chain ends}}{\text{Rate of propagation}}$$

where $\overline{X}_n$ is the number average degree of polymerization (53). Generally, four modes of polymer end formation exist at low monomer conversions: (1) chain termination, (2) chain transfer with initiator, (3) chain transfer with monomer and (4) chain transfer with solvent

$$\text{Hence, } \frac{1}{\overline{X}_n} = \frac{k_M[P_n^\bullet][M] + k_S[P_n^\bullet][S] + k_I[P_n^\bullet] + k_t[P_n^\bullet]^2}{k_p[P_n^\bullet][M]}$$

$$\text{i.e., } \frac{1}{\overline{X}_n} = \frac{k_M}{k_p} + \frac{k_S[S]}{k_p[M]} + \frac{k_I[I]}{k_p[M]} + \frac{k_t[P_n^\bullet]}{k_p[M]}$$

$$\text{Or, } \frac{1}{\overline{X}_n} = \frac{k_M}{k_p} + \frac{k_S[S]}{k_p[M]} + \frac{k_I[I]}{k_p[M]} + \frac{k_t k_p[M][P_n^\bullet]}{k_p^2[M]^2}$$

Therefore,

$$\frac{1}{\overline{X}_n} = C_M + C_s \cdot \frac{[S]}{[M]} + C_I \cdot \frac{[I]}{[M]} + \frac{k_t R_p^2}{k_p^2 [M]^2} \qquad (25)$$

where, C_M, C_S, and C_I are termed chain transfer constants for monomer, solvent and initiator, respectively.

In the derviation of equation (25), it was tacitly assumed that (a) the rate of polymerization remains unaffected by chain transfer, and (b) only a negligible proportion of the substrate radicals formed in the chain transfer reaction (24) participate in termination. In systems in which the latter assumption does not hold, the following termination reactions must also be considered:

$$\text{combination:} \quad P_n^{\bullet} + S^{\bullet} \xrightarrow{k_{tcs}} P_nS$$

$$\text{disproportionation:} \quad P_n^{\bullet} + S^{\bullet} \xrightarrow{k_{tds}} P_x + P_y$$

$$S^{\bullet} + S^{\bullet} \xrightarrow{k_{ts}} \text{products}$$

The kinetic analysis of such a system becomes quite complicated and is most usefully expressed in the form (54):

$$k_S = \frac{\{R_1(2k_{tc}+2k_{td})\}^{\frac{1}{2}} . \lambda\{1+(1-\lambda^2)/\phi^2\lambda^2\}^{\frac{1}{2}} + k_{ps}(k_{tc}+k_{td})[M]k_2)(1-\lambda^2)}{{}^2[S](\ 1+(1-\ {}^2)\phi^2\ {}^2\ {}^{\frac{1}{2}}+1)} \qquad (26)$$

where k_{ps} is the rate constant for reinitiation by transfer radical, $S^{\bullet}$, ϕ is a cross-termination coefficient:

$$\phi = k_2/\{(2k_{tc} + k_{td})2k_{ts}\}^{\frac{1}{2}}$$

where $k_2 = k_{tcs} + k_{tds}$, and λ is a retardation coefficient:

$$\lambda = R_p[M]_o/(R_p)_o[M]$$

The subscript o refers to rate (or monomer concentration) in absence of transfer agent.

Determination of chain transfer constants: Experimental methods for determination of chain transfer constants generally rely on measurement of molecular weights of polymers prepared under suitably varied conditions. This is followed by the application of a suitable equation, usually some form of equation (25). In the determination of the transfer constant for polymer molecules, model molecules having a structural similarity to monomer units make suitable substitutes. Alternately the extent of branching in a polymer can be used to calculate this chain transfer constant (55-59). Experimental details for the determination of chain transfer constants for monomer, initiator and polymer can be obtained from a standard text (53). A discussion of experimental methods available for the determination of C_s, the chain transfer constant for solvent or some other substrate present in the system follows because of the direct relevance of this subject to the present work.

In solvent polymerization, the second term of the general equation (25) usually makes the major contribution. By keeping the initiator concentration low, or preferably, through the choice of an initiator such as an aliphatic azonitrile, which is not susceptible to chain transfer, the third term is rendered negligible. The last term of the general equation may be kept constant by so adjusting the initiator concentration as to keep $R_p/[M]^2$ constant while varying the solvent concentration. Consequently, equation (25) reduces to:

$$1/\bar{X}_n = (1/\bar{X}_n)_o + C_s.[S]/[M] \qquad (27)$$

where $(\bar{X}_n)_o$ is the number average degree of polymerization in absence of the solvent. This is the well-known Mayo equation. A plot of $1/\bar{X}_n$ versus $[S]/[M]$ would give C_s as the slope. It may be noted here that any trend in the degree of polymerization other than expected from equation (27) would indicate some essential change in the mechanism of polymerization. For example, an increase in the degree of polymerization, instead of the expected decrease with increasing concentration of water in the polymerization of methyl methacrylate in mixed solvents has been attributed by Nandi et. al. (60) to a slower termination rate due to increasingly tighter coiling of polymer chains. A similar observation by Jenkins et. al. (61) in the polymerization of acrylonitrile in DMF led them to postulate the formation of a hydrate of DMF, which supposedly had a smaller chain transfer constant than anhydrous DMF.

Mayo's equation (27) has been highly successful in determining C_s by using thermal polymerization data (62,63), but difficulties may be encountered when a catalyst is present (64,65). It is evident from general equation (25) that Mayo's equation can give a correct value for C_s only if R_p is proportional to $[M]^2$, or if R_p is proportional to $[M]^{3/2}$ at constant $[I]/[M]$ (since $R_p = k[M]^n[I]^{\frac{1}{2}}$), provided k does not change considerably with changing $[S]/[M]$. However, the modified method of Palit et. al. (66) overcomes this problem. By plotting $(1/\bar{X}_n - k_tR_p/k_p^2[M]^2)$ against $[S]/[M]$ at constant $[I]/[M]$, or against $[I]/[M]$ at constant $[S]/[M]$, good values of C_s have been obtained from the slope and the intercept, respectively. Using a simpler approach, Allen et. al. (67) plotted $1/\bar{X}_n - 1/(\bar{X}_n)_o$ versus $[S]/[M]$ to obtain C_s in the catalyzed system.

Another method of obtaining C_s consists of measuring the relative rates of consumption of transfer agent (solvent, in this case) and monomer (68):

$$d(\log [S])/d(\log [M]) = C_s \qquad (28)$$

This equation may be further modified by for the consumption of monomer by the transfer reactions.

Yet another method of determining C_s involves the use of isotpically labelled transfer agents (69-72). Radiometric analysis of the polymer sample determines the relative number of molecules of transfer agent incrporated in the polymer. This method avoids the measurement of molecular weights, and has the advantage that it is not affected by retardation.

Structure and reactivity in chain transfer: General patterns of reactivity observed with various substrates are outlined below. The reactivities in various systems are discussed here mainly in relative terms, and no specific data on chain transfer constants is cited here. Such data are readily available in Brandrup and Immergut's Polymer

Handbook (73).

The relative values of the dissociation energies of P_n-X and S-X bonds are important in determining the reactivity of the chain transfer agent SX in:

$$P_n^{\bullet} + S\text{-}X \longrightarrow P_n\text{-}X + S^{\bullet} \qquad (24)$$

These bond energies in turn depend not only on the nature of the atoms concerned, but also on the resonance energies of the radicals $P_n^{\bullet}$ and $S^{\bullet}$. The reaction occurs most readily when radical $P_n^{\bullet}$ is highly reactive as compared to $S^{\bullet}$, and the bond P_n-X is much stronger than the bond S-X.

Gregg and Mayo (62) observed that in styrene polymerization, transfer constants for benzene, toluene, ethylbenzene and tert-butylbenzene increase in that order for the first four members of the series, but the value for tert-butylbenzene is only a little higher than that for benzene. A similar pattern has also been observed in the polymerization of methyl methacrylate (63,64), methyl acrylate (74), vinyl acetate (75) and acrylonitrile (76). These data have been explained on the basis that transfer to toluene, ethylbenzene and isopropy benzene occurs mainly through attack on the benzyl hydrogen. The reactivity increases with increasing substitution at the alpha carbon. This is in accordance with the established influence of substituents in diminishing the strength of the C-H bond. tert-Butylbenzene, having no benzylic hydrogen, is comparatively unreactive inspite of the nine available H atoms in its methyl groups. Saturated alicyclic hydrocarbons, such as cyclohexane, with strong C-H bonds, also have small chain transfer constants.

It was originally suggested by Walling and Mayo and their collaborators (37-39) that the transition states in chain transfer, as well as in the propagation step:

$$P_n^{\cdot} + \overset{|\ \ |}{\underset{|\ \ |}{C{=}C}} \longrightarrow P_n{-}\overset{|\ \ |}{\underset{|\ \ |}{C{-}C\cdot}}$$

may contain polar contributions from $R^{+}S^{-}\cdot X$, and $R^{+}[>\dot{C}-C<]^{-}$, respectively. Later work by Fuhrman and Mesrobian (40), and Bamford and White (41) lent further credence to this view. The importance of the polar character of both substrate and radical was recognized by Alfrey and Price (42-44) in their Q-e scheme, which in its original form was restricted to propagation reaction in copolymerization systems. The Q-e scheme ascribed nonpolar (Q) and polar (e) parameters to both radicals and monomers. Although it is successful in its treatment of copolymer pairs, two fundamental weaknesses are inherent in the Q-e scheme. It has long been realized that the scheme has no firm theoretical basis, the assignments of Q and e being made in an arbitrary manner to give an internally consistent set of figures. Further, the e values for a monomer and its derived radical are assumed to be identical.

Bamford et. al (77,78) have succeeded in placing the separation of the polar and nonpolar facets of radical and substrate character on an experimental basis. A scale of reactivities for a number of radicals is established. The numerical value of the rate constant for chain transfer to toluene (k_{cT}) serves as a measure of the "general reactivity" of a radical. The rate constant k_{cT} is related to the rate constant, k_s, for transfer of the same radical to a substrate:

$$p_{R\cdot} = \log k_s - \log k_{cT} \qquad (29)$$

where $p_{R\cdot}$, the 'polarity parameter' is a measure of the polar contribution to the transition state. Further, it has been shown that $p_{R\cdot}$ is a linear function of the Hammett (para) σ constant (79) for the substituents on the alpha carbon atom of the radical in a linear manner:

$$p_{R\cdot} = \alpha\sigma + \beta \tag{30}$$

where α and β are functions of the intrinsic tendencies of the polar and nonpolar nature of the substrate to react by a polar or nonpolar mechanism, respectively, as compared to toluene. Equations (29) and (30) can be combined to yield:

$$\log k_s = \log k_{cT} + \alpha\sigma + \beta \tag{31}$$

This is the basic equation of Bamford's theory. The values of α and β for a substrate can be estimated by measuring the rate at which it reacts with any two of a series of radicals for which k_{cT} and σ values have been compiled (78). In general, different radicals have different values, so their reactions will be influenced to varying extents by the nature of the substrate. It would therefore be expected that the order of reactivity for a series of radicals will depend on the substrate. The basic difference between Bamford's treatment and the Alfrey-Price Q-e scheme is that the former emphasizes the reactivity of the substrate, while the latter has been used to emphasize the reactivity of the radical.

Another correlationship between substrate structure and its reactivity in chain transfer reaction has been provided by Yamamoto et. al. (80) who find that the relative reactivities of a series of substituted cumene substrates towards chain transfer with polymeric radicals could not be correlated using the conventional Hammett equation (79):

$$\log (k/k_0) = \rho\sigma \text{ or } \rho\sigma^+ \qquad (32)$$

They attribute this to resonance effects in the transition state, which are taken into account in their modified Hammett equation:

$$\log (k/k_0) = \rho\sigma + \gamma E_R \qquad (33)$$

where E_R and σ are constants representing resonance and polar effects, respectively, due to substituents on the substrate, whereas γ and ρ are reaction constants, characteristic of the attacking radical. Thus, $\rho\sigma$ is a polar term and γE_R a resonance term.

Degradative chain transfer: Chain transfer to solvent, or some other substrate present in a system often leads to relatively unreactive radicals, a significant fraction of which may undergo termination rather than propagation reactions. In such a case, chain transfer is termed 'degradative'. In an extreme case when degradative transfer is so facile that it competes even with the addition of primary radicals (from initiator), no growth at all takes place, and the reaction is described as 'inhibition'. When the transfer process is less efficient, the primary radicals initiate chain growth, and the propagating radicals react with the substrate. Under these conditions, the rate and degree of polymerization are reduced, and the process is referred to as 'retardation'. Obviously, retardation and inhibition are just different degrees of the same general process. Whether a particular reagent is a transfer agent, retarder, or inhibitor, depends on the reactivity of the substrate. Thus, isopropylbenzene and dihydromyrcene act as normal transfer agents in the polymerization of methylmethacrylate, but are pronounced retarders in the case of vinyl acetate (81).

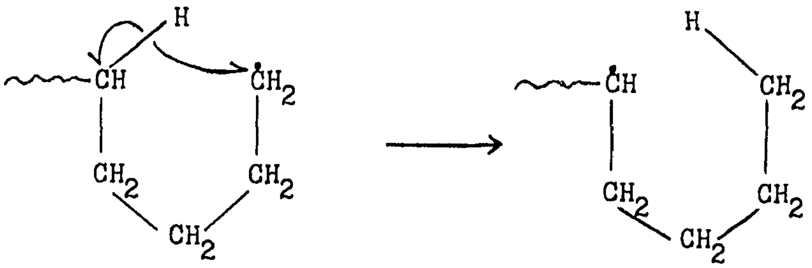
Burnett and Loan (2[illegible]) studied the polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate in benzene solution. Anomalously high monomer orders were found for the latter two monomers. Furthermore, these exponents were dependent on monomer concentration. These results were explained on the basis of degradative chain transfer. It was proposed that the radical produced by transfer to solvent was capable of undergoing propagation, as well as termination with a growing polymer chain, or another solvent radical, thereby bringing about a decrease in the rate of propagation. Making the usual assumptions regarding stationary state and equal reactivity of chains of different lengths, Burnett and Loan derived the following equation:

$$R_p = [M] R_i^{\frac{1}{2}} \{ K_1 [M]^2 + K_2 C_s [M][S] + K_3 C_s^2 [S]^2 \}^{-\frac{1}{2}} \qquad (34)$$

where K_1, K_2 and K_3 are composite constants involving rate constants for propagation and termination reactions, including those involving solvent radicals. This mechanism successfully accounts for high monomer orders, since on dilution the overall rate of termination increases due to the increasing importance of reactions involving solvent radicals. At the same time the initiator order would become less than 0.5. This is not apparent from equation (34), since this conclusion was arrived at by making other assumptions which are not described here. These assumptions are not fully justified in the opinion of Scanlan et. al. (82) who have predicted this increase in initiator exponent from a more sophisticated analysis. However, Atkinson et. al. (83) have shown that under certain conditions an initiator order of 0.5 may in fact result from a mechanism involving degradative chain transfer to solvent.

Sluggish propagation may also be the result of an entirely different reaction. Addition of aromatic solvent molecules to growing radical chains has been observed in the polymerization of vinyl acetate (84) and methyl methacrylate (85). The radicals produced in these reactions may propagate sluggishly. Essentially similar kinetics as those of Burnett and Loan (2) and Scanlan et. al. (82) would prevail, although no degradative chain transfer is involved. Only molecular weight dependencies would distinguish between the two processes.

An alternative mechanism involving degradative chain transfer has been considered by Scott and Senogles (86). This involves an intramolecular transfer process which produces a polymer radical of reduced reactivity toward propagation. Processes involving the establishment of a six-membered ring transition state are more likely to be favored, for example:



This type of back-biting reaction is well-known in the polymerization of ethylene (87, 88), and there is evidence for related reactions occurring in vinyl acetate polymerizations (89). The kinetics of this reaction have been dealt with at length by Scott and Senogles (86) to show that monomer and initiator orders greater than 1 and 0.5, respectively, are obtained. Under certain conditions, the initiator exponent is shown to remain at 0.5, whereas a monomer order higher than unity is obtained.

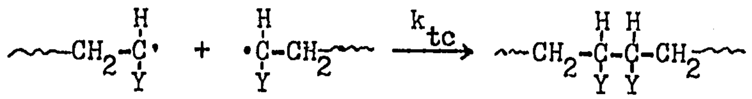
Industrial applications of chain transfer: Most monomers of potential commercial utility, if allowed to polymerize in the absence of chain transfer agents, are converted to polymers of sufficiently high molecular weight, sometimes in the millions, to be intractable in the melt or in solution. This would prevent any further processing, molding, or vacuum devolatilizing in an extruder at a low enough temperature to avoid degradation. Also, addition of various agents, such as stabilizers, plasticizers, slip and anti-block additives could be rendered impossible. Accordingly, extensive use is made of chain transfer agents in the form of so-called modifiers or regulators to control the molecular weight of the polymer. Besides controlling the molecular weight, these modifiers also impart technically desirable properties such as, plasticity, hardness, tensile strength, improved stress-strain behavior, solubility, etc. Chain transfer studies also give us insight into telomerization processes, which are rapidly gaining in industrial importance. Telomers are polymeric molecules of a very small size (degree of polymerization $\simeq$ 2-5).

Termination: The termination step controls the molecular weight and indeed the distribution of molecular weights in the polymer. Of course, it also affects the rate of polymerization. Termination processes have a negligible effect on the chemical nature of the polymer produced, but a pronounced effect on its physical properties. Unimolecular, as well as bimolecular termination are known to occur, although the latter is much more common.

Unimolecular termination: This process is not commonly observed, but may occur through chemical or physical means. Chemical "deactivation" usually involves isomerization to an unreactive species, although in some cases the propagative radical itself becomes unreactive. In the polymerization of vinyl monomers, the most common unimolecular deactivation process is typified by that encountered in vinyl benzoate polymerization (90). It is seen that propagation occurs normally until a growing vinyl radical adds to the aromatic ring to form a resonance stabilized radical. This radical may possibly propagate and add to fresh monomer, ultimately leading to bimolecular termination and a square root dependence on initiator concentration. However, at high enough radical concentrations, the stabilized radical is more likely to be terminated by growing vinyl radicals before such repropagation can occur. At temperatures which lead to moderate rates of initiation, the stabilized radicals have time enough to propagate further, and a normal square root dependence on initiator concentration is observed (91). However, at higher temperatures, the formation of such radicals is effectively a process of termination, and a first order dependence of the rate of polymerization on initiator concentration is observed (92,93).

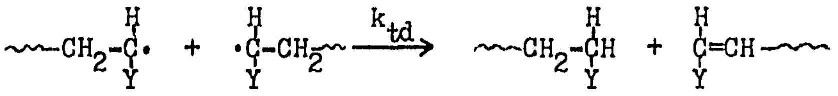
The most common physical process leading to the removal of radicals from an active system is one of entanglement or agglomeration in impermeable polymer. Such a process occurs when the reaction takes place in a poor solvent for the polymer being formed, and the "trapping" may occur in macroscopic aggregates of many polymer molecules, or even in tightly coiled regions of the same polymer chain. The permeability of polymer surrounding the occluded radical is of great importance. When this polymer is swollen with monomer or solvent, diffusion of monomer is possible, so that propagation continues almost unhindered, although bimolecular termination is severely reduced. The net result is an increase in the rate and degree of polymerization. On the other hand, if the precipitating polymer is a solid rather than a gel (as in a very poor solvent), even the propagation step becomes impossible, and the process is effectively one of termination. To discuss the kinetics of such systems, where these two possibilities exist, a knowledge of the rate of occlusion is required. It is not easy to quantify and measure such a rate. Nevertheless, it has been attempted by Bamford and Johnston (94). Durup and Magat have also analyzed a a similar system (95).

Bimolecular termination: The termination process which is most commonly observed is bimolecular, and involves the mutual destruction of two centers of unpaired spin. The two radical chains achieve termination through combination to form a single covalent bond:



$$\sim\!\sim CH_2-\overset{H}{\underset{Y}{C}}\cdot \;+\; \cdot\overset{H}{\underset{Y}{C}}-CH_2\sim\!\sim \xrightarrow{k_{tc}} \sim\!\sim CH_2-\overset{H}{\underset{Y}{C}}-\overset{H}{\underset{Y}{C}}-CH_2\sim\!\sim$$

or through disproportionation when an atom, or a group of atoms, transfers from one radical to another to give two inert molecules, one saturated, and the other unsaturated at the chain end:



$$\sim\sim CH_2-\overset{H}{\underset{Y}{C}}\cdot + \cdot\overset{H}{\underset{Y}{C}}-CH_2\sim\sim \xrightarrow{k_{td}} \sim\sim CH_2-\overset{H}{\underset{Y}{C}}H + \overset{H}{\underset{Y}{C}}=CH\sim\sim$$

Experimental methods for determining the relative probabilities of combination and disproportionation reactions have been reviewed recently by North and Postlethwaite (96). In general, it is seen that disproprotionation is more likely in the polymerization of 1,1-disubstituted olefins because of steric hindrance to a combination reaction, which in turn is more probable for vinyl monomers, unless the monomer contains an especially labile transfer atom. Besides, disproportionation generally requires a larger activation energy than combination, so that the relative importance of the two processes will shift toward combination at low temperatures. Thus, in the polymerization of methyl methacrylate at 60° disproportionation reaction accounts for 60% of termination reactions (97), whereas at 90°C termination takes place almost entirely by disproportionation (98).

Primary radical termination: Bamford, Jenkins and Johnston (99) studied AIBN-initiated polymerization of styrene in DMF solution. At low monomer concentrations and high initiator concentrations, they observed significant departures from the values of 1 and 0.5 expected from simple kinetic theory (equation 10) for monomer and initiator orders, respectively. The observed data were correlated using kinetic equations derived by assuming that primary radicals participate in termination reactions. Allen and Patrick (100) have shown that deviations from equation (10) due to primary radical termination can be expected when relatively low values of k_i, k_t or $[M]$ apply, specially if the rate of initiation is high. Under these conditions, a monomer order greater than unity and less than 0.5 is observed.

Diffusion controlled termination: The mutual termination reaction of two macroradicals in a liquid phase polymerization involves a very rapid chemical conversion of two species present in a rather small concentration. Obviously, before any two radicals can react they must diffuse close enough to each other. It may be that this diffusion step is the slow, rate-determining step of the two-stage (transport and chemical) process. When this is the case, the reaction is referred to as being "diffusion controlled".

Attention was first drawn to the importance of diffusive effects when first Norrish and Smith (101) and later Tromsdorff et.al. (102) suggested that the autoacceleration observed in many free radical polymerizations was due to diffusion control of the termination process at increased viscosities obtainable at high monomer conversions. However, it is now known that many radical-radical, ion-ion, and triplet state reactions (involving species of much greater diffusivity than terminating macroradicals) are diffusion controlled (96). As a consequence, the termination process in polymerization could be diffusion-controlled even in liquids of normal viscosity.

North (103-105) has proposed a three-stage termination process in which polymer molecules first approach each other so that certain segments are in contact (translational diffusion). Rearrangement of the polymer chains (segmental diffusion) can then occur so that the two radical chain ends approach sufficiently close for the third step, chemical reaction, to take place:

1. $P_r^{\bullet} + P_s^{\bullet} \rightleftarrows [P_r^{\bullet}{-}{-}{-}{-}P_s^{\bullet}]$
2. $[P_r^{\bullet}{-}{-}{-}{-}P_s^{\bullet}] \rightleftarrows [P_r{:}P_s]$
3. $[P_r{:}P_s] \longrightarrow$ polymer

Experimental evidence suggests that segmental diffusion is the rate-determining step under most reaction conditions (103). North and co-workers (103-105) have shown theoretically, as well as demonstrated experimentally for the polymerization of methyl methacrylate, that k_t, the rate constant for termination, is proportional to the reciprocal of the viscosity of the system. Therefore, it follows that the magnitude of k_t would depend on monomer concentration, which affects the initial viscosity of a polymerizing system, as well as the conformation and average size of the polymeric radicals. The magnitude of k_t may also depend on initiator concentration, which also controls the size of polymeric radicals and therefore the viscosity of the medium. Consequently monomer orders other than unity, and initiator orders other than 0.5 could arise even if the simple kinetic equation (10) is obeyed.

Yohota and Itoh (106) have modified equation (10) to:

$$R_p = k_p[M]\eta^{\frac{1}{2}}(k_d[I]f/k_t^{o})^{\frac{1}{2}} \qquad (35)$$

where k_t^{o} is the value of k_t at some standard viscosity (e.g., 1 cP). They subsequently measured the polymerization rate of methyl methacrylate at different concentrations in a variety of solvents and found the results to be consistent with equation (35). If no allowance was made for solvent viscosity and the results analyzed using equation (10), monomer orders, both greater and less than unity, were obtained.

There is some evidence that initiator decomposition rates are also dependent on solution viscosity (23,107).

Role of metal catalysts in free radical polymerization: Since this work involves the use of metal catalysts for hydroperoxide decomposition, it is pertinent to examine the general effects of metal ions and complexes on the polymerization process itself. Only homogeneous systems are considered here because of their relevance to the present study. Also metal catalyst systems involving peroxides or hydroperoxide, are discussed later.

In recent years several reports have appeared in the literature on the use of metal salts, complexes and chelates in the initiation of vinyl polymerization (108-125). Bengough *et. al.* (108) have reported the use of ferric chloride as a photoinitiator of acrylonitrile polymerization at 25° in DMF solution. In such photolytic systems, $FeCl_3$ behaves both as an initiator and terminator of polymerization:

$$\text{Initiation:}\quad FeCl_3 + M \longrightarrow Cl\text{-}M\cdot + FeCl_2$$

$$\text{Termination:}\quad P_n\cdot + FeCl_3 \longrightarrow P_n + FeCl_2 + HCl$$

Lingamurthy and Palit (109) have reported the use of ferric laurate as thermal initiator of vinyl polymerization, and the polymerization is considered to be initiated by a free radical mechanism. In aqueous media, ferric salts such as chloride, bromide and perchlorate are good initiators (110,111) of polymerization in the presence of visible or UV light. Initiation is supposed to result from the formation of free radicals by an electron transfer process within the ion-pair complex of the type $Fe^{3+}X^{-}$ present in aqueous solution:

$$(Fe^{3+}X^{-}) \xrightarrow{h\nu} Fe^{2+} + X\cdot (X = Cl, Br, I, OH, etc.)$$

It is possible that water molecules in the inner and outer sphere of the ferric ion may be involved in the polymerization process (110). Cupric salts have been shown to initiate polymerization of basic heterocyclic vinyl monomers such as N-vinylcarbazole and 4-vinyl pyridine (112,113). The presence of a coordination bond between a cupric ion and the nitrogen of the pyridine group seems to be absolutely necessary, since the addition of a chelating agent such as acetylacetone completely inhibits polymerization (113). Polymerization is believed to be initiated by one electron transfer from the nitrogen in the monomer to the Cu^{2+} ion in the complex $Cu(OAc)_2.2$ (4-vinyl pyridine). Salts of Fe(III) and Ce(IV) also initiate polymerization of the same monomers, possibly by similar mechanisms (112). Copper(II) salts have also been shown to initiate the polymerization of acrylonitrile (114,115). Recently, Bamford and co-workers (116-118) have reported the use of several metal carbonyl-halide systems as initiators of vinyl monomers in bulk or in solution. Metal chelates such as acetylacetonates of Ru(III), Fe(III), Pd(II), Ni(II), Rh(IV), Mn(III), Mn(II) and Co(III) have been used as initiators of vinyl polymerization by Kastning and co-workers (119). It was observed that the initiating efficiency of the chelates is a function of both the central metal ion and the ligand. Manganese (III) acetylacetonate was seen to be the most effective initiator. Bamford et.al. (120-122) also reached a similar conclusion regarding Mn(III) acetylacetonate., but failed to initiate polymerization with a number of compounds which Kastning found to be useful initiators. The initiation mechanism has been shown to have a free radical nature. Co(II) acetylacetonate has also been shown to serve as an efficient free radical initiator (123). Copper(II) acetylacetonate and ammonium trichloroacetate have been shown to form a complex which easily takes part in an electron transfer reaction to form the $\dot{C}Cl_3$ radical, which initiates polymerization (124). Otsu et al. (125) have found that Cu(II) acetylacetonate initiates the polymerization of methyl methacrylate, although not as efficiently as Cu(II) ethyl acetoacetate. Thus, a number of metal catalysts have been shown to initiate polymerization through a free radical mechanism, although the exact mechanism may vary from one system to another, and indeed in most of the systems studied, the mechanism through which the free radicals are generated remains obscure.

Several metal complexes have been seen to participate actively in chain transfer reactions. Huff and Perry (126) have studied the reactivity of polystyryl, poly(methyl methacrylyl) and polyacrylonitryl radicals towards several organometallic substrates involving metals (or metalloids) of groups 2b, 3a, 4a and 5a of the periodic table. The chain transfer constants, which vary over an extremely wide range were seen to be sensitive to polar effects. In general, the reactivity is found to depend on the metal as well as the organic portion of the molecule. Although some correlation appears between metals in the same group, wide variations in reactivity for similar compounds from one group to another seem to indicate that depending on the nature of the metal, different reaction mechanisms may be involved. Aoki et.al. (127) have found Co(III) cyclohexanecarboxylate to be fairly receptive to chain transfer in the polymerization of methyl methacrylate.

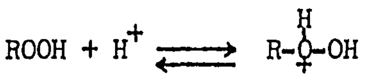
(b) Hydroperoxides:

The chemistry of hydroperoxides has been studied extensively. Several good reviews of the literature on this subject are available (128-135). Hydroperoxides have aroused great interest not only because of their formation in the oxidation of organic molecules, but also because of their use as initiators in polymer chemistry. With the exception of the very lowest molecular weight members of the series, most are remarkably stable thermally. Consequently, they are specially suited for application in those areas of polymer chemistry in which polymerization is to be initiated at relatively high temperatures, such as in certain unsaturated polyester resin systems and in the rubber and silicone field. Despite their thermal stability, the hydroperoxides may initiate free radical polymerizations at room temperature and below in the presence of reducing agents or other 'catalysts'. Indeed many of the so-called 'cold recipes' for the emulsion copolymerization of butadiene with styrene involve hydroperoxides as oxidizing agent in redox systems. Many of the anaerobic polymerization compositions consist of dimethacrylates and hydroperoxides. Presumably, because of the thermal stability of hydroperoxides, such compositions are stable at room temperature for prolonged periods of time, at least as long as oxygen is permitted to diffuse through the liquid phase (136).

Hydroperoxides are capable of undergoing a great variety of reactions because of their ability to react by polar as well as radical mechanisms. Some reactions may even start through a polar route, but end as free radical reactions, and vice versa. A detailed discussion of the chemistry of hydroperoxides is beyond the scope of this discussion. An attempt is made here to project the complexity and the scope of this subject. Homolytic decomposition reactions, however, have been described in detail because of their relevance to the present study.

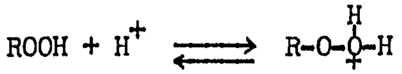
Hydroperoxides are stronger acids than alcohols. Values of pK_a in water at 20° range from 11.5 to 12.8 for several simple alkyl and aralkyl hydroperoxides (137,138). Hydroperoxides and their anions exhibit a number of nucleophilic reactions analogous to those of alcohols. Thus, they form peroxy esters, peroxy acetals and ketals, and dialkyl peroxides. They can be reduced to alcohols by several reducing agents, including iodide ion, and stannous chloride (139), which are commonly used for quantitative analysis of hydroperoxides (140,141). Reactions that cleave the O-O bond are complex mechanistically. Some of the above reductions which occur with a well-defined stoichiometry, for example, the reduction with iodide ion, can be formulated as a nucleophilic attack at the oxygen with the lower electron density, while others such as those involving metal ions of variable valency appear to involve free radicals at some stage.

Hydroperoxides are also attacked by electrophiles, most notably by protons. Electrophilic attack by a proton may occur at either oxygen atom:



$$\mathrm{ROOH} + \mathrm{H}^{+} \rightleftharpoons \mathrm{R{-}\overset{H}{\underset{+}{O}}{-}OH} \qquad (36a)$$

Or,



$$\mathrm{ROOH} + \mathrm{H}^{+} \rightleftarrows \mathrm{R{-}O{-}}\overset{\mathrm{H}}{\underset{+}{\mathrm{O}}}\mathrm{{-}H} \qquad (36b)$$

The net result of the first possibility (36a) may be the loss of hydrogen peroxide from those hydroperoxides whose R groups are sufficiently electron releasing (142). Protonation of the hydroxylic oxygen leads to O-O heterclysis, often accompanied by rearrangement.

Hydroperoxides can epoxidize olefins by a number of different mechanisms (133).

Perhaps, the most significant practical aspect of hydroperoxide chemistry is homolytic decomposition. Homolytic decomposition may be induced (a) thermally (or photochemically) in the presence or absence of a catalyst or (b) by free radicals which may either abstract the hydrogen atom:

$$\mathrm{ROOH} + \mathrm{R'}\!\cdot \longrightarrow \mathrm{R'H} + \mathrm{ROO}\cdot \qquad (37)$$

or displace an oxygen atom:

$$\mathrm{RO{-}OH} + \mathrm{R'}\!\cdot \longrightarrow \mathrm{R'OH} + \mathrm{RO}\cdot \qquad (38)$$

Of these only abstraction by a free radical is unique for hydroperoxides; the other reactions are common to all peroxidic compounds. Both, free radical induced and thermal decompositions (assisted by catalysts or otherwise) are described below. Homolytic decompositions which may well have characteristics of both these types of decompositions, are treated separately and in greater detail.

Free radical induced decomposition:

Decompositions initiated by peroxyesters (143,144) azo compounds (145), or hypochlorites (146) at 20-60° (thus uncomplicated by thermal homolysis) have amply verified earlier views (147-149) that decomposition of tertiary hydroperoxides by a chain reaction is induced by free radical abstraction:

$$\text{Initiator} \xrightarrow{k_1} 2\,X\cdot \qquad (39)$$

where X is any initiator fragment.

$$X\cdot\ (\text{or } RO\cdot) + ROOH \xrightarrow{k_p} XH\ (\text{or } ROH) + ROO\cdot \qquad (37)$$

where R is tertiary. The peroxy radicals may interact in two possible ways:

$$2\,ROO\cdot \xrightarrow{k_c} 2\,RO\cdot + O_2 \qquad (40a)$$

$$2\,ROO\cdot \xrightarrow{k_t} ROOR + O_2 \qquad (40b)$$

Assuming a steady state, it is possible to calculate a rate of hydroperoxide disappearance that corresponds to the experimental results (143,144):

$$-\frac{d[ROOH]}{dt} = k_1[\text{Initiator}](1 + \frac{k_c}{k_t}) \qquad (41)$$

The critical factor is k_c/k_t, which determines the chain length. The products of reaction (40) are most probably formed through a tetroxide intermediate (150). t-Butyl hydroperoxide decomposition initiated by di-t-butylperoxalate in benzene or chlorobenzene at 35-45° yields more than 99% O_2, 88-89% t-BuOH, and 11-12% t-Bu_2O_2; a chain length of about 10 is observed (150).

This simple picture of radical induced decomposition may be complicated by the ability of alkoxy radicals to cleave:

$$R_3CO\cdot \longrightarrow R_2C{=}O + R\cdot \qquad (42)$$

Under some circumstances this reaction competes with hydrogen abstraction (135,151-153). The alkyl radical formed in this reaction is capable of absracting a hydrogen atom from a hydroperoxide molecule and thus continuing the chain. But, in the presence of high concentrations of peroxy radicals, or oxygen (produced from hydroperoxide decomposition), this alkyl radical would be more likely to undergo rapid termination. (151-153):

$$\cdot CH_3 + ROO\cdot \longrightarrow ROOCH_3 \qquad (43)$$

$$\cdot CH_3 \xrightarrow{O_2} CH_3OO\cdot \xrightarrow{ROO\cdot} ROH + CH_2O + O_2 \qquad (44)$$

The consequences of alkoxy cleavage are, thus, lower chain lengths and more complex kinetics since hydroperoxide concentration now becomes a factor (151,153). In the limiting case in which all termination occurs via the cleavage route, the rate expression becomes:

$$- d[ROOH]/dt = k[Initiator]^{\frac{1}{2}}[ROOH] \qquad (45)$$

which is in fact the observed rate dependence for high temperature thermal decompositions where ROOH is the initiator (147,154,155). Similar results are found for low temperature radical induced decomposition of _t_-BuOOH in solvents such as _t_-BuOH or acetic acid (151) which promote alkoxy cleavage and make hydrogen abstraction more difficult by hydrogen bonding with the hydroperoxides (156).

Radical displacements on oxygen-oxygen: Thermodynamically it would seem preferable for alkyl radicals to effect a displacement on the relatively weak O-O bond, rather than abstract hydrogen:

$$R^{'}\cdot + RO\text{-}OH \longrightarrow RO\cdot + R^{'}OH \qquad (46)$$

However, this reaction is not facile as shown by Pryor's measurements of chain transfer constants for dialkyl peroxides in polymerizing styrene (157).

Thermal Decomposition:

Hydroperoxides are among the most stable peroxides towards heat. At elevated temperatures they decompose in a rather complex manner.

Unimolecular decomposition: In unimolecular decomposition:

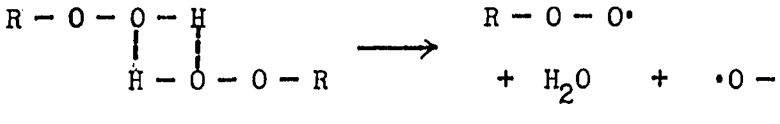
$$RO{-}OH \xrightarrow{\Delta \text{ or } h\nu} RO\cdot + \cdot OH \qquad (47)$$

since the reverse reaction would be expected to have zero activation energy, the dissociation energy of the RO-OH bond should approximately equal the activation energy for equation (47). The most widely accepted value for D_{RO-OH} is 43-44 kcal/mole for R=Me, Et, i-Pr and t-Bu, as reported by Benson et.al. (158,159) who have, incidentally, assigned a value of 90±2 kcal/mole for D_{ROO-H}. Thermal decomposition of t-BuO_2H either neat at 100° (160), or in chlorobenzene solution at 140° (147) or photolytic decomposition at lower temperatures (148) yields t-BuOH and oxygen in nearly quantitative amounts. Cumene hydroperoxide behaves somewhat similarly (149,161), though substantial amounts of dicumyl peroxide and acetophenone are formed as well and yields of oxygen are lower. The kinetics of thermal decomposition of both t-butyl hydroperoxide (147,154) and -cumyl hydroperoxide (155,161) have shown 1 to 3/2 order dependence on hydroperoxide concentration, indicating a combination of unimolecular and radical-induced decomposition (162). In solution, however, the initial rate of decomposition is generally first order in hydroperoxide at low concentrations (133). Hiatt et.al. (135) have attempted to measure the true rate of thermal decomposition of t-butyl hydroperoxide in several solvents. The nature of the solvent was seen to exert a strong influence on the mode, as well as the rate of decomposition. Thus, in cumene the rate of decomposition is four times as fast as in benzene or toluene. On the other hand, in alkanes and alkylbenzenes the decomposition appeared to be largely induced, even at the lowest concentrations of t-butyl hydroperoxide. In both alkylbenzenes and alkanes, RO• and HO• radicals from homolysis of the peroxide readily produced solvent radicals. Other investigators have also concluded that the rates of thermal decomposition vary substantially with the solvent (163-165). Thomas (166) noted that decomposition rates roughly paralleled the ease of autoxidation of the solvent and suggested that concerted C-H and O-O bond breaking might be responsible:

$$RH + R'OOH \longrightarrow R\cdot + R'O\cdot + H_2O \qquad (48)$$

<u>Thermal decomposition in presence of catalysts</u>: Homolysis of RO_2H can be assisted by olefins, aldehydes and ketones, carboxylic acids, alcohols, amines and amine salts, sulfur compounds, bromide ions, aralkanes, or another molecule of hydroperoxide (133). A few of these systems are mentioned below:

Bimolecular homolysis: Rates of hydroperoxide disappearance often show a second-order dependence on hydroperoxide concentration if the concentration is high or the solvent nonpolar, conditions that promote dimerization (155,167-169). The reaction may be supposed to proceed via the dimer:



$$\begin{array}{ccc} R-O-O-H & & R-O-O\cdot \\ \vert \quad \vert & \longrightarrow & \\ H-O-O-R & & + H_2O \quad + \quad \cdot O-R \end{array} \qquad (49)$$

Olefin assisted homolysis: In the discussion of the initiation step in polymerization, mention was made of the interactions of hydroperoxides with styrene (12,13) and methyl methacrylate (13) deduced from the observed kinetics in these systems. Walling and Heaton (170) have even measured the stability constants of the styrene-hydroperoxide complex. They also showed that such complexes are involved in the initiation reaction. The mechanism of radical formation probably (171) involves 0-0 homolysis:

$$\mathrm{ROOH} + {>}\mathrm{C{=}C}{<} \longrightarrow \mathrm{RO\cdot} + {>}\dot{\mathrm{C}}{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\mathrm{OH} \qquad (50)$$

However, hydroperoxides are not efficient initiators in these systems. Walling and Heaton (169) calculated that in styrene at 70°, only 1.6% of the decomposing $\underline{t}$-BuO_2H yields radicals by interaction with styrene, 7.9% is destroyed by radical-induced decomposition, and the remainder is converted by an apparently non-radical route to $\underline{t}$-BuOH and styrene oxide. Brill and Indictor (172) have found activation energies of about 20 kcal/mole for the decomposition of $\underline{t}$-BuO_2H in several olefins.

Homolysis assisted by other compounds: Compounds capable of forming hydrogen-bonded intermediates with hydroperoxides are seen to lead to higher rates of decomposition. Hydrogen bonding is supposed to weaken the 0-0 bond, but it makes the terminal hydrogen less readily available (173). Such hydrogen-bonded 'complexes' are formed by alcohols, ethers, amines and amine salts, ketones, sulfoxides, carboxylic acids, etc. Equilibrium constants have been calculated for a number of such complexes (174). Complexes, presumably of a π-type are also formed with aromatic rings and probably also with carbon-carbon double bonds (175). Association constants for complexes with benzene and styrene have been determined (175). Such complexes probably contribute to the olefin assisted homolysis described earlier. Complexes with aldehydes, however, are not usually hydrogen bonded, but results from addition to the C=O bond (176):

$$\mathrm{ROOH} + \mathrm{>C{=}O} \longrightarrow \mathrm{ROO} - \overset{|}{\underset{|}{\mathrm{C}}} - \mathrm{OH} \qquad (51)$$

Hydrogen bonded carbonyl hydroperoxide complexes are possible if addition is sterically unfavorable (177).

Decomposition of hydroperoxides catalysed homogeneously by transition metals of variable valence

Catalysis of autoxidation and hydroperoxide decomposition processes by metal ions and complexes has been the subject of numerous investigations. The literature on such reactions has been surveyed a few times (135,178,179). In spite of the volume of literature on this subject, there is no general consensus regarding the kinetics and mechanism of metal-hydroperoxide reactions, and a number of apparent contradictions seem to emerge from the available experimental data. This is understandable in view of the sensitivity of metal-hydroperoxide reaction to the experimental conditions. The kinetics and mechanism seem to vary with the nature of the solvent, metal ion, gegen ion or ligand, as well as the reactant concentration and temperature. Indeed, it seems that a 'general' mechanism for metal-hydroperoxide reactions does not exist (180). In the following discussion, some possible reaction mechanism are briefly described and the effects of various reaction conditions are surveyed.

Although a great amount of work has been done with metal catalyzed decomposition of organic hydroperoxides, studies with H_2O_2 have received much greater attention, probably because of its biological significance. Almost all of the mechanisms that will be described here, were suggested in their original form to describe the decomposition of H_2O_2 in the presence of metal catalyst.

Haber and Weiss (181) in their study of Fenton's reagent suggested the following sequence of one-electron transfer reactions to explain the oxidation of Fe(II) by H_2O_2:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\cdot + OH^- \tag{52}$$

$$Fe^{2+} + OH\cdot \longrightarrow Fe^{3+} + OH^- \tag{53}$$

$$OH\cdot + H_2O_2 \longrightarrow HOO\cdot + H_2O \tag{54}$$

$$HOO\cdot + H_2O_2 \longrightarrow O_2 + H_2O + OH\cdot \tag{55}$$

Barb <u>et</u>. <u>al</u>. studied this reaction in the presence of Fe(III) ion, and suggested a modification of the above mechanism for the reduction of Fe(III) by H_2O_2 (182,183):

$$Fe^{3+} + HO_2^- \longrightarrow Fe^{2+} + HOO\cdot \tag{56}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\cdot + OH^- \tag{52}$$

$$OH\cdot + H_2O_2 \longrightarrow HOO\cdot + H_2O \tag{54}$$

$$HOO\cdot + Fe^{2+} \longrightarrow Fe^{3+} + HOO^- \tag{57}$$

$$Fe^{3+} + HOO\cdot \longrightarrow Fe^{2+} + O_2 + H^+ \tag{58}$$

Kharasch <u>et</u>.<u>al</u>. (184) in their early work on the decomposition of cumene hydroperoxide by cobalt ions suggested the following reaction scheme:

$$ROOH + Co^{2+} \longrightarrow RO\cdot + Co^{3+} + OH^- \tag{59}$$

$$ROOH + Co^{3+} \longrightarrow ROO\cdot + Co^{2+} + O_2 \tag{60}$$

$$RO\cdot + Co^{2+} \longrightarrow RO^- + Co^{3+} \tag{61}$$

$$RO\cdot + ROOH \longrightarrow \begin{array}{c}\text{ketone + alcohol} + RO\cdot \\ \text{(induced decomposition)}\end{array} \tag{62}$$

$$ROO\cdot + Co^{3+} \longrightarrow R^+ + Co^{2+} + O_2 \tag{63}$$

This mechanism was mainly based on product studies under a wide variety of conditions. Later work by Kharasch and co-workers (185,186) has led to some modifications of this mechanism, especially with regard to reaction (63), since no evidence of carbonium ion formation could be obtained.

Instead the following reactions were suggested as probable causes of oxygen formation:

$$2\ ROO\cdot \longrightarrow 2\ RO\cdot + O_2 \qquad (64)$$

$$ROO\cdot + ROOH \longrightarrow ROH + O_2 + RO\cdot \qquad (65)$$

In metal-catalyzed decomposition of organic hydroperoxides, several workers have introduced their own modification of this basic one-electron transfer mechanism to suit the products obtained or the kinetics observed, but most of them are agreed on reactions (58) and (59) for the reduction and oxidation of the metal ion accompanied by free radical formation. When these reactions complement each other to work in a cycle, catalytic decomposition of hydroperoxide takes place and a small metal concentration efficiently decomposes a much larger amount of hydroperoxide. When only reaction (58) or (59) is feasible, stoichiometric concentrations of metal and hydroperoxide react (187).

Bray and Gorin (188) have proposed a two-electron oxidation of Fe(II) to Fe(IV) in the reaction of Fe(II) and H_2O_2:

$$Fe^{2+} + H_2O_2 \longrightarrow FeO^{2+} + H_2O \qquad (66)$$

$$FeO^{2+} + H_2O_2 \longrightarrow Fe^{2+} + H_2O + O_2 \qquad (67)$$

$$Fe^{3+} + OH\cdot \longrightarrow FeO^{2+} + H^+ \longrightarrow FeOH^{3+} \qquad (68)$$

$$Fe(OH)^{3+} + Fe^{2+} \longrightarrow 2\ Fe^{3+} + OH^- \qquad (69)$$

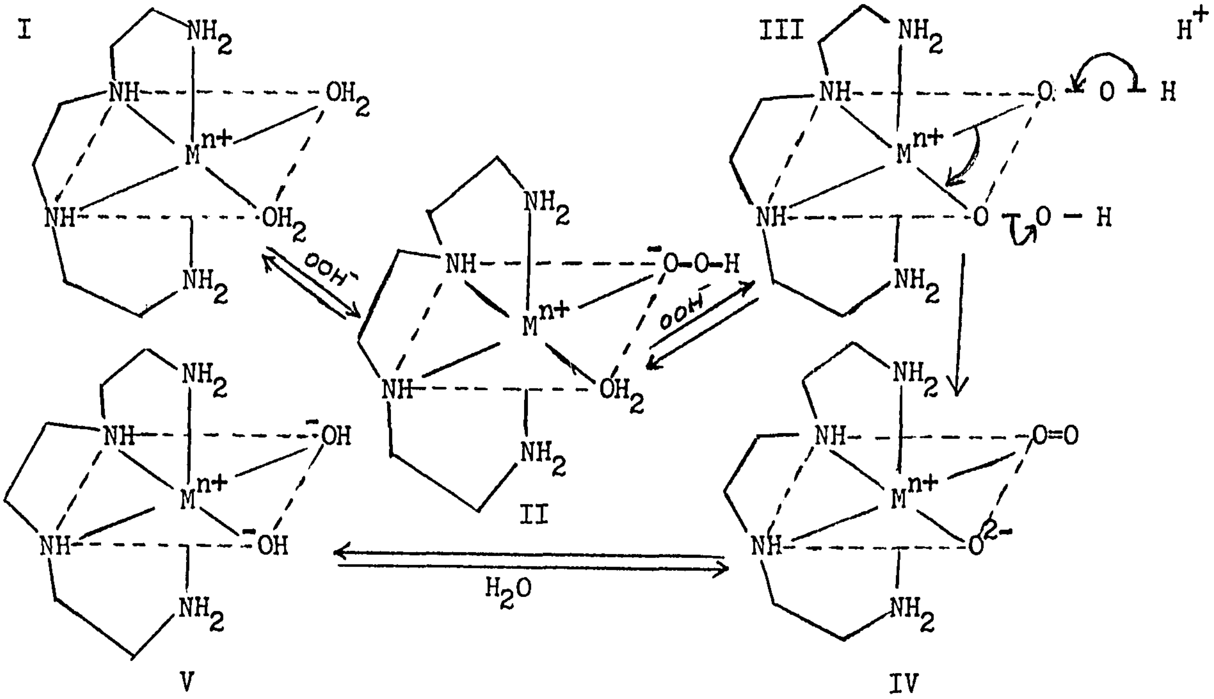
The ferryl ion FeO^{2+} formed in reaction (65) or (68) reacts in subsequent steps with either H_2O_2 or iron(II). The oxidation of Fe(II) to Fe(IV) by a two electron reduction of H_2O_2 has also been proposed by Cahill and Taube (189). On the other hand, Conocchioli et. al. (190) have disputed the presence of iron(IV) in Fe(II)-H_2O_2 systems. King and Winfield (191) reported the two-electron oxidation of ruthenium(II) to ruthenium(IV).

in the catalytic reduction of H_2O_2 by ruthenium(II) in aqueous solution.

Both, the one-electron and the two-electron transfer redox mechanisms suppose that the acts of oxidation and reduction of hydroperoxide occur separately and therefore must involve participation by oxidixed and reduced forms of the metal catalyst in these reactions. Yet another type of mechanism involves a concerted reduction and oxidation reaction between two hydroperoxide molecules or peroxy anions,while they are co-ordinated to the metal catalyst. The metal itself does not undergo a redox reaction but may assist in electron transfer between the reacting hydroperoxide ligands, or possibly it may just act as a template on which the hydroperoxide molecules bind and react. Here the catalytic activity is attributed to the stabilization of the transition state achieved through coordination. Such reaction mechanisms have mainly been proposed in work on the disproportionation of hydrogen peroxide by the enzyme catalase (which is the best known catalyst for this reaction) or its model compounds.

Goudot(192,193) has shown that tetracoordinate complex compounds of Fe(III) and Cu(II) function as efficient models of catalase. He has proposed that coordination of two H_2O_2 molecules to the two available coordination sites on the metal leads to the disproportionation of H_2O_2 to water and oxygen. Extensive molecular orbital calculations have been worked out to describe the nature and shape of this complex. Peroxidase type reactions in which one molecule of H_2O_2 oxidizes a molecule of another compound have also been treated in this manner. From the molecular shape of the complex and its effect on bond energies, values of expected activation energies have been calculated and found to correspond favourably with experiment. Kovats (194) has further confirmed this mechanism by his observation of the catalytic effect of several tetraordinate Cu(II) complexes on the disproportionation of hydrogen peroxide.

The concept of the requirement of two free coordination positions about the metal ions is strengthened by the observation of Wang *et. al.* (195,196). It is seen that Mn(II) and Fe(III), both of which have coordination numbers of 6, when complexed with tetradentate triethylene tetramine actively catalyze the decomposition of hydrogen peroxide. These authors proposed that the reaction takes place through metal coordination such that one peroxide anion is bidentate and occupies two in positions of the metal ion. In view of the fact that the Mn(II) catalyzed reaction is second order in peroxide concentration, Hamilton (197) suggested the mechanism described in the figure shown below:



Here two hydroperoxide groups are simultaneously coordinated to the two available sites on the metal (III). In this complex, electron transfer takes place smoothly through the metal ion to give oxygen and water, the protons being transferred through the aqueous solvent. The first order dependence of the Fe(III)-trien reaction rate on peroxide concentration was considered due to the fact that the higher coordinating ability of the iron(III) ion resulted in one of the peroxide anions being bound to the ferric ion at the beginning of the reaction, leaving only one more to be added prior to the rate determining step.

Berger and Bickel (198) found that in the presence of copper(II) phenanthroline acetate, t-BuOOH in benzene solution decomposed to yield stoichiometric amounts of t-BuOH and oxygen. To account for this observation they proposed a mechanism involving the complexation of one or two peroxy anions with the metal. These complexes further react with the hydroperoxide to give radical intermediates which lead to the observed products. In their mechanism outlined below only reactions involving the monoperoxy anion complex are shown, but similar reactions involving the dianion complex are also proposed. Here Cp = $[\mathrm{Cu(phenanthroline)}_2]^{2+}$, $\mathrm{OAc}^- = \mathrm{CH_3COO}^-$, and R = t-butyl:

$$\mathrm{Cp(OAc)_2 + ROO^- \rightleftharpoons OAc^- + Cp(OAc)(OOR)} \qquad (70)$$

$$\mathrm{Cp(OAc)(OOR) + ROOH \rightleftharpoons Cp(OAc)(O\cdot) + RO\cdot{-}HOOR} \qquad (71)$$

$$\mathrm{RO\cdot{-}HOOR \longrightarrow ROH + ROO\cdot} \qquad (72)$$

$$\mathrm{ROO\cdot + Cp(OAc)(O\cdot) \longrightarrow O_2 + Cp(OAc)(OR)} \qquad (73)$$

$$\mathrm{Cp(OAc)(OR) \longrightarrow Cp(OAc)(OOR) + ROH} \qquad (74)$$

This mechanism stresses the importance of ionic complexes of the catalyst with both substrate and product, while no valence change of the cupric ion is assumed. Instead a cupryl form, Cp(O•), represents the oxidized form of the catalyst. The authors acknowledge that oxygen could alternatively be produced by the reactions suggested by Kharasch <u>et. al.</u> (185,186):

$$2\ \mathrm{ROO}\bullet \longrightarrow 2\ \mathrm{RO}\bullet + \mathrm{O_2} \qquad (64)$$

$$\mathrm{ROO}\bullet + \mathrm{ROOH} \longrightarrow \mathrm{ROH} + \mathrm{O_2} + \mathrm{RO}\bullet \qquad (65)$$

In such a case, they suggest that their reaction mechanism would apply to the initiation step only, and O_2 would be evolved as a result of chain reactions (72) ⟶ (64) or (65) ⟶ (72). However, the fact the addition of a phenolic inhibitor accelerates the decomposition of the hydroperoxide would seem to indicate the catalyst is involved in the formation of the peroxy adduct, since an acceleration of reactions (64) or (65) by a phenol is improbable.

Kochi (198a) has suggested the following mechanism for the conversion of tertiary hydroperoxides to peroxides in the presence of copper salts:

$$\mathrm{ROOH} + \mathrm{Cu^{I}} \longrightarrow \mathrm{RO}\bullet + \mathrm{Cu^{II}OH} \qquad (76)$$

$$\mathrm{Cu^{II}OH} + \mathrm{ROOH} \rightleftharpoons \mathrm{Cu^{II}OOR} + \mathrm{H_2O} \qquad (77)$$

$$\mathrm{RO}\bullet + \mathrm{R'H} \longrightarrow \mathrm{ROH} + \mathrm{R'}\bullet \qquad (78)$$

$$\mathrm{R'}\bullet + \mathrm{Cu^{II}OOR} \longrightarrow \mathrm{R'OOR} + \mathrm{Cu^{I}} \qquad (79)$$

This mechanism is operative only in the presence of a substrate, R'H, which can act as a hydrogen donor towards oxy radicals. In order to maintain copper salt catalysis, it is necessary to form intermediates which are oxidized by cupric salts, as in reaction (78). Although this mechanism is based on the cuprous salt reduction of the peroxide (reaction 75), it is not necessary for the cuprous salt to be present initially. Since any thermal dissociation of the hydroperoxide will generate oxy radicals, cuprous salts are readily formed from cupric salts by the subsequent reactions (77) and (78).

In the homogeneously catalyzed decomposition of organic hydroperoxides by metals, the mechanism which seems to have found the widest support is the one-electron transfer mechanism, originally cited by Kharasch et. al. (184):

$$ROOH + M^{n+} \longrightarrow RO\cdot + M^{n+1+} + OH^- \qquad (59)$$

$$ROOH + M^{n+1+} \longrightarrow ROO\cdot + M^{n+} + H^+ \qquad (60)$$

followed in turn by radical induced chain decomposition in competition with:

$$RO\cdot + M^{n+} \longrightarrow RO^- + M^{n+1+} \qquad (79)$$

$$ROO\cdot + M^{n+} \longrightarrow ROO^- + M^{n+1+} \qquad (80)$$

When reactions (59) and (60) follow each other, the net reaction is:

$$2\ ROOH \longrightarrow RO\cdot + ROO\cdot + H_2O \qquad (81)$$

The wide acceptance of this single electron transfer mechanism stems from the similarity of product compositions from metal catalyzed decomposition of hydroperoxides to those obtainable in radical induced decompositions (135).

Product studies: The catalytic decomposition of a hydroperoxide, ROOH, in the presence of transition metals of variable valence generally results in the formation of oxygen (90%, based on $\frac{1}{2}$ O_2 from each ROOH), along with substantial amounts of alcohol, ROH, and peroxide, ROOR, (133). Thus, t-BuO_2H with catalytic amounts of Co^{2+} or Mn^{2+} at 25°, yields 86% t-BuOH 12% t-Bu_2O_2, and 93% O_2 along with 0.5% acetone (135). Evidence of formaldehyde formation has also been reported by a few workers. Dean and Skirrow (199) found 3.8% formaldehyde under conditions similar to those cited above. Several secondary reactions have been seen to lead to small fractions of other products. Thus, the products are often influenced by dimerization of hydroperoxide or abstraction of hydrogen (200,201), reaction with anions in the system (202-204), or telomerization with added olefins (204). Decomposition by metal ions in solvents that readily undergo hydrogen abstraction can produce good yields of dialkyl peroxides:

$$RH + R'OOH \xrightarrow{M^{n+}} ROOR'$$

where RH = cumene (185,205), alkenes (205,206), THF (207), nitriles (186), or even cyclohexane (135).

Kinetics: Assuming a one-electron transfer mechanism:

$$ROOH + M^{n+} \xrightarrow{k_A} RO\cdot + M^{n+1+} + OH^- \qquad (64)$$

$$ROOH + M^{n+1+} \xrightarrow{k_B} ROO\cdot + M^{n+} + H^+ \qquad (65)$$

followed by an induced chain:

$$RO\cdot + ROOH \xrightarrow{k_1} ROH + ROO\cdot \qquad (37)$$

$$2\ ROO\cdot \xrightarrow{k_2} 2\ RO\cdot + O_2 \qquad (40a)$$

$$2\ ROO\cdot \xrightarrow{k_3} ROOR + O_2 \qquad (40b)$$

a simple kinetic treatment has been worked out by Hiatt et. al. (135). When a steady state concentration of RO• prevails the rate of hydroperoxide disappearance is given by:

$$- d[ROOH]/dt = k_A[ROOH][M^{n+}] + k_B[ROOH][M^{n+1+}] + k_1[RO\cdot][ROOH]$$

With rapid cycling of the metal ion the following equations apply:

$$k_A[ROOH][M^{n+}] = k_B[ROOH][M^{n+1+}]$$

and, $- d[ROOH]/dt = (2\ k_2/k_3 + 3)[M^{n+}][ROOH]$

Since $[M^{n+}] + [M^{n+1+}] = [M]_0$, the initial metal ion concentration:

$$- d[ROOH]/dt = (2\ k_2/k_3 + 3)[k_A k_B/(k_A + k_B)][M]_0[ROOH]$$

i.e., $-d[ROOH]/dt = k[M]_0[ROOH]$ (82)

Thus, one would expect the rate of hydroperoxide disappearance to be first order in metal as well as in hydroperoxide concentration. However, in practice, the kinetics of metal ion catalyzed hydroperoxide decomposition are often more complex than indicated by equation (82). This complexity can arise from several possible factors.

An almost consistent feature of these reactions is autoretardation, which may be more or less extreme, depending on the temperature, the nature of the metal catalyst, the hydroperoxide and the solvent.(135). Apparently, the reaction products complex with the the metal ion, deactivating it, and often eventually causing its precipitation. The precise nature of the reaction products which are responsiblle for the deactivation of the metal catalyst is not known with any certainty. Some workers suspect formic acid (133), although the nature of the products which cause deactivation may well vary from one reaction system to another. Several authors (179, 208-210) have been led to postulate that the formation of a metal-hydroperoxide complex precedes reactions (64) and (65). Retardation by millimolar quantities of compounds which strongly complex metal ions, e.g., carboxylic acids, 1-10 phenanthroline, acetylacetone, etc., seems to confirm this view.(135). The formation of a metal-hydroperoxide complex is also an essential feature of some mechanisms discussed earlier. Products of hydroperoxide decomposition may well compete with hydroperoxide for coordination sites on the metal, thereby exerting a blocking effect.(208), consequently retarding further decomposition of hydroperoxide. Deactivation of a metal complex catalyst may also result from the autoxidation of the ligands (239).

The initial rates of hydroperoxide decomposition in most instances are first order or nearly so, although Dyer (211) in his study of Co(II) 2-ethyl hexanoate catalyzed decomposition of tetralin hydroperoxide in cyclohexane observed a second order dependence on hydroperoxide concentration. Hiatt et. al. (135) suspect that Dyer's system may have suffered from autoretardation at an early stage in the reaction. However, initial rates of hydroperoxide decomposition show considerable variation in dependence on metal ion concentration. The rate order in metal catalyst is seen to vary from 0 to 3, depending on the reaction system and conditions (135, 198, 199,209). Some authors have rationalized these results by means of complex kinetics based on the nature of the metal-hydroperoxide complex and suitably modified reaction mechanisms.(198,199,209). However, Hiatt et. al. (135) point out that the metal ion exponent is sensitive to catalyst concentration, solvent and temperature. Hence, it may reflect the solubility of the metal catalyst, as well as its degree of association in a particular system. These authors suggest that complex formation between metal and hydroperoxide may have no important consequence other than retardation in the presence of other compounds which also form strong complexes with the metal catalyst. Furthermore, Hiatt et. al. (op. cit.) have shown that reactions which are first order in metal ion have activation energies of 9 to 12 kcal/mole, but those with higher orders in the metal catalyst have activation energies of 17 to 22 kcal/mole. Hence, in the latter case the catalysts may exist in the form of fairly large aggregates which decrease in size as the temperature increases, giving rise to a faster rate of reaction.

In general, it is seen that the kinetics observed for one reaction system, may not hold true for even a related but slightly different system. The slightest change in a reaction system, often exerts a strong influence.

Some factors which influence metal-hydroperoxide reactions are discussed below:

Effect of metal: It is certainly to be expected that some metals would be more reactive than others. However, different reaction systems may lead to different orders of metal reactivity (212,213). No satisfactory relation seems to exist between the activity of a metal catalyst and other seemingly relevant properties, such as its redox potential (133, 214). This may well be due to a lack of knowledge of the true redox potentials, which are expected to be influenced by the ligands and the solvent (215). On the other hand, observed reactivities may result from several factors which affect each metal ion in a characteristic manner.

Effect of ligand: Several workers have noticed that metal reactivity is strongly influenced by the nature of the gegen ion or the complexing ligand (132,214-216). Thus, in acetic acid solution Co(III) complex with EDTA does not influence hydroperoxide decomposition, while the Co(II) complex does.(187). However, under the same experimental conditions Co(III) acetate is much more reactive than Co(II) acetate (199). Most ferric salts do not decompose hydroperoxides readily, although the phthalocyanine complex does (135). Wallace and Skomoroski (217), who have observed a wide variation in the reactivity of Fe(III) with the nature of the ligand, believe that the effect of the ligand on the redox potential of the metal may be responsible. Any change in ligand, which brings about a change in the shape of the catalyst molecule may also affect its reactivity (216,239). Siegel (218) has shown that a 1:1 complex of Cu(II) with ethylenediamine (bidentate) is highly reactive towards H_2O_2 decomposition, while a complex of Cu(II) with triethylenetetramine (tetradentate) is relatively unreactive. This is believed to indicate that the former complex has two free coordination sites, which enables it to bond simultaneously to two molecules of H_2O_2 and thereby catalyze its decomposition, whereas the latter complex is coordinatively saturated. However, several other 4-coordinate complexes of Cu(II) have been found to be very efficient catalysts for H_2O_2 decomposition (193,194,219). Moreover, their catalytic activity has been ascribed to the ability of these compounds to coordinate with two H_2O_2 molecules (193,194).

Concentration effects: Scott (220) has shown that at high hydroperoxide concentrations, radical induced decomposition may become the preferred reaction and high radical concentrations may lead to termination reactions with the metal ions:

$$M^{n+} + RCH_2OO\cdot \longrightarrow M^{n+1+} + OH^- + RCHO \qquad (83)$$

$$M^{n+1+} + RCH_2O\cdot \longrightarrow M^{n+} + H^+ + RCHO \qquad (84)$$

besides reactions (40a) and (40b). It was shown that a greater than first order dependence on the metal concentration prevailed under these conditions. High metal ion concentrations also tend to retard hydroperoxide decomposition due to reactions (79) and (80) which reduce radical concentration and retard radical induced decomposition (178). Hence, low catalytic concentrations of metal ions or complexes are more efficient.

Solvent effects: If the solvent molecule possesses a donor atom, it can conceivably enter the coordination sphere of the metal and thereby alter its pattern of reactivity (135,221). Dean and Skirrow (199) observed that water inhibits the Co(II) acetate catalyzed decomposition of t-BuOOH in acetic acid, apparently by hydrating the catalyst. These authors also report that in acetic acid Co(III) catalyzes the decomposition of t-BuOOH much more actively than Co(II). The reverse is seen to be true in nonpolar solvents (222). Such changes in reactivity with solvent polarity can be due to several causes, such as a decrease in the degree of aggregation or an increase in ionic character of the catalyst with increasing polarity of solvent, or a change in the tendency of the solvent to coordinate with the metal. Other possibilities are a shift in the equilibrium of the metal-hydroperoxide complex or a change in the redox potential. Because of so many variables it is not surprising that any change in reaction conditions affects each metal catalyst differently.

In most of the studies cited above no effort has been made to determine the fraction of hydroperoxide which decomposes to give nonradical products, and it seems to have been presumed that in the presence of metal catalysts of variable valence, all decomposition takes place either through reactions (59) and (60), or is induced by the radicals obtained from these reactions. Nevertheless, evidence exists (223,224) to indicate that a significant fraction of hydroperoxide decomposition catalyzed by metals may lead to nonradical products.

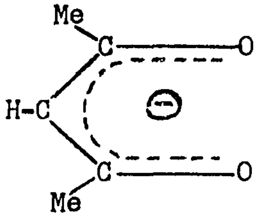
Decomposition of hydroperoxides catalyzed by metals of nonvariable valence:

Stearates of Mg(II), Zn(II), Ca(II) and Sr(II) (225) have been reported to catalyze the decomposition of hydroperoxides. A mechanism involving one-electron oxidation or reduction of these ions is unlikely. It has been conjectured that Zn(II) acts as a Lewis acid and that Mg(II) in some way facilitates radical chain decomposition without initiating chains by itself (225). It is possible that one of the mechanisms mentioned earlier, in which no valence change of the metal is involved, may be operative. Lead(II) stearate (135) and lead tetracetate (226-228) are also known to catalyze hydroperoxide decomposition. Although a two-electron transfer mechanism is feasible in these systems, the nature of the actual mechanism involved is little understood. Ionic (226,227) and free radical (228) intermediates have both been suggested.

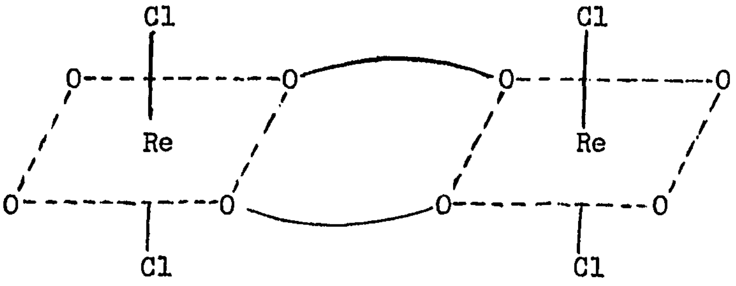
(c) Bonding and structure of metal acetylacetonates:

Since the present work involves homogeneous catalysis with metal acetylacetonates, it is necessary to understand the nature of these complexes.

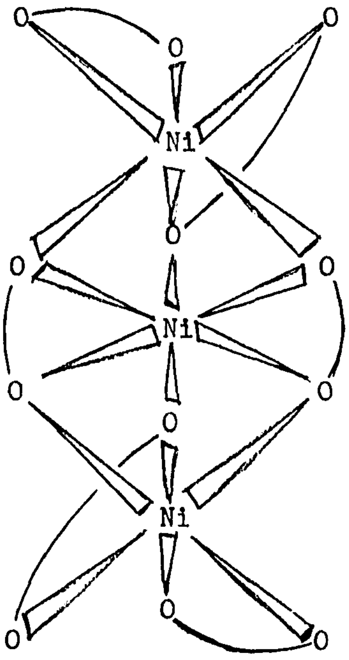
Acetylacetone is a weak acid and the 3-proton can be lost easily to give the enolate anion:



This enolate anion has a five-atom network extending over the two oxygen and three non-terminal carbon atoms. Six electrons occupy the resulting π type molecular orbitals. Numerous derivatives of this anion can be formed giving rise to a variety of metal-to-ligand bonding structures (229). For the present purpose we shall concern ourselves only with the derivative in which the enolate anion is coordinated to a central metal atom through both oxygen atoms. This is by far the most frequent form of association with metals. A second type of oxygen-chelated complex that can be formed involves the neutral acetylacetone molecule which is a difunctional Lewis base and can coordinate to acceptor (Lewis acid) metal atoms, in the keto tautomeric form. Such donor-acceptor complexes are often reactive with respect to loss of the acidic ring proton to give the chelated acetylacetonate complex. Some of these acetylacetonate complexes exist in an oligomeric or polymeric form which is achieved through bridging enolate anions. Such bridge bonding may occur when one of the enolate ions has the two oxygen atoms chelated to two metal atoms as in



Another form of bridge bonding occurs when the terminal oxygen atoms in the enolate anion serve as donor atoms to two metal atoms:



Thus, in nickel acetylacetonate, $Ni(AA)_2$, nickel actually exists in an octahedrally coordinated form, and the molecule in the solid state is actually a trimer (230,231). Cotton and Fackler (232) found that $Ni(AA)_2$ exists in a monomer-trimer equilibrium in diphenylmethane over a 80-200°C range, with the monomer predominating at higher temperatures. The green color of $Ni(AA)_2$ normally observed was seen to be due to the octahedrally coordinated trimeric species, whereas the square planar monomeric form gave a red solution. Other complexes which polymerize via chelated oxygen bridges are $Zn(AA)_2$ which is trimeric (233), and $Co(AA)_2$ (234) and $Mn(AA)_2$ (235) which are tetrameric in the solid state.

It is interesting to note that metal acetylacetonates are capable of reacting on Lewis acids (236). Complexes of the type $M(AA)_2$ react with basic ligands such as pyridine and water to give six coordinate adducts. Indeed, the self-association of $M(AA)_2$ molecules such as $Ni(AA)_2$ can be thought of in terms of inter-molecular Lewis type donor-acceptor interactions.

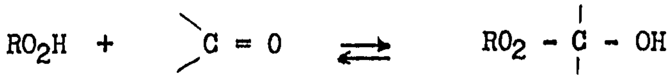
II. Discussion of Results

Part I: Polymerization of methyl methacrylate in the presence of t-butyl hydroperoxide and metal acetylacetonates: Effect of nature of metal and solvent.

The decomposition of hydroperoxides in the presence of metal catalysts in solution has been studied extensively (178). Among the large variety of metal compounds studied in this respect, metal acetylacetonates have received considerable attention (135,178). Metal acetylacetonates have also been used to catalyze the autoxidation of several substrates (239-242) and hydroperoxide initiated polymerization of styrene (243) and methyl methacrylate (244,245).

The present study was undertaken to obtain a better understanding of the metal acetylacetonate-hydroperoxide reaction system. The effect of the nature of (a) the metal catalyst, and (b) the solvent system on the extent and the rate of radical formation in hydroperoxide initiated polymerization of methyl methacrylate has been studied.

In the first phase of this work, the polymerization of methyl methacrylate (MMA) initiated by _t_-butyl hydroperoxide (TBHP) has been studied in the presence of several metal acetylacetonates, $M(AA)_n$, in 1-chloroctane medium. The choice of an aliphatic solvent was prompted by an earlier study (240) from this laboratory in which it was observed that the rate of hydroperoxide initiated autoxidation of 1-octene was appreciably faster in an aliphatic than in an aromatic medium. Other workers (246) have also observed a similar solvent effect. The use of a tertiary alkyl hydroperoxide prevents complicating reactions such as hydration and rearrangement. Moreover, since TBHP has also been employed in most related studies in published literature, a direct comparison with this work is facilitated. Metal catalysts investigated include some species of potentially variable valence, viz., Co(II), Co(III), Mn(II), Mn(III), Cu(II), Cr(III) and Ni(II), as well as Al(III) which is unlikely to participate in redox reactions. The concentrations of metal acetylacetonates were so small ($\sim 10^{-4}$M) as to preclude any possibility of direct initiation by the metal acetyl acetonates. Moreover, a relatively large concentration of TBHP (~ 0.02 $\underline{M}$) was used so that any acceleration observed in the rate of initiation would be due to catalytic rather than stoichiometric metal-hydroperoxide interactions. The effect of the nature of the metal catalyst on the rate, as well as efficiency of initiation has been studied. The rates of polymerization of MMA monomer, R_p, and of TBHP decomposition, R_d, were determined in the presence of each of the metal catalysts, as well as in their absence. Number average molecular weights of the polymer formed were also obtained. Initiator efficiencies in the presence of the metal catalysts were then calculated. These data obtained at 40, 60 and 80° are presented in Tables I, II and III respectively. Some general trends in reactivity emerge from these data. It is seen that the decomposition of TBHP is catalyzed most effectively by Cu(II) and Co(II) acetylacetonates. While Mn(III) and Co(III) display intermediate activity, Cr(III), Ni(II) and Al(III) do not significantly affect the reaction. Representative plots of the progress of hydroperoxide decomposition with time are shown in Figure 1 for Cu(II), Co(II) and Co(III) catalyzed reactions at 60°. Although in the early stage of the reaction hydroperoxide decomposition seems to follow a first order pattern, retardation sets in as the reaction progresses. A continuous decrease in the rate of hydroperoxide decomposition, or 'autoretardation' in the presence of metal catalysts has also been observed by other workers (135,208,210). Autoretardation of the rate of hydroperoxide decomposition may result from (a) the approach of steady state conditions as an increasing number of peroxy radicals abstract hydrogen atoms to reform hydroperoxide, (b) a stabilization of hydroperoxide molecules through complexation with the products of decomposition (247); for example:



$$RO_2H + \gt C = O \rightleftarrows RO_2 - \overset{|}{\underset{|}{C}} - OH$$

or (c) deactivation of the metal catalyst. Deactivation of the metal catalyst may result from the autoxidation of organic ligands or an interaction of the catalyst with the products of decomposition (mainly alcohols and ketones). In the last case, the decomposition products may precipitate the catalyst (210), or block the active sites on the metal through coordination (208) and thereby prevent the formation of a metal-hydroperoxide complex (135,178,179). The formation of such a complex is generally believed (178) to precede catalytic decomposition of the hydroperoxide. Evidence for the formation of metal-hydroperoxide complexes is overwhelming. It has been seen that in the presence of free ligands, metal catalysts are rendered ineffective (135). Other evidence for the formation of such complexes comes from NMR, ESR, UV and visible spectra (179).

A decrease in the rate of hydroperoxide decomposition with the progress of the reaction would result in a decreasing rate of initiation. This explains the observed trend of increase in the molecular weight of the polymer with reaction time. A comparison of the polymer molecular weight data in Tables I, II and III indicates that in most of the reaction systems a decrease in molecular weight accompanies an increase in temperature due to an increasing rate of initiation. In the Cu(II) catalyzed system in 1-chlorooctane, however, the molecular weight is seen to increase with increasing temperature. In these experiments, a large fraction of TBHP is consumed in the early stage of the reaction. The higher the temperature, the larger the initial decomposition, and therefore, slower the rate of initiation which leads to the observed trend. The presence of metal catalysts generally tends to lower the molecular weight of the polymer formed due to an increased rate of initiation, as well as chain transfer to the metal complexes. Work in this laboratory has shown that several of the metal acetylacetonates have appreciably high chain transfer constants (part III of this work). Other workers have concluded that metal-hydroperoxide complex intermediates lend themselves to chain transfer reaction (248).

Most of the metal acetylacetonates studied do not significantly affect the rate of polymerization of MMA in 1-chlorooctane medium. However, $Cu(AA)_2$, which best catalyzes hydroperoxide decomposition, also catalyzes polymerization. However, in the presence of $Co(AA)_2$, although the rate of decomposition of TBHP is enhanced, the rate of polymerization is actually less than that observed in the uncatalyzed system. In Figure 2 are shown some representative monomer conversion versus time plots obtained at 60°. In most cases percent conversion increases linearly with time, but the retardation in the Co(II) catalyzed system is obvious. Possibly, oxygen produced in the Co(II) catalyzed decomposition of hydroperoxide is responsible for the observed retardation. The production of irrecoverably low molecular weight polymer due to an initially high rate of initiation may also be responsible for the observed results. The fact that the rate of initiation decreases with the progress of the reaction is indicated clearly by the increasing molecular weight of the polymer. A slight curvature is also observed in the percent conversion versus time plot (Figure 2) for the Cu(II) catalyzed reaction in the initial stage of the reaction, beyond which, however, a recovery of catalytic activity is observed. The lack of a prolonged period of retardation in this system can be ascribed to the early onset of autoretardation in the decomposition of the hydroperoxide. The acetylacetonates of Co(III) and Mn(III) neither catalyze nor retard the polymerization of MMA, although they do promote hydroperoxide decomposition. The rate of polymerization of MMA also remains unaffected in the presence of Mn(II), Cr(III), Ni(II) and Al(III) acetylacetonates.

The initiator efficiencies (f=number of polymer chains initiated per initiator molecule decomposed) shown in Tables I to III, represent effective, rather than true initiator efficiencies, since any wastage of the initiator due to radical induced decomposition has not been taken into account in computing these f values. Smaller initiator efficiencies are observed in the presence of metals which catalyze hydroperoxide decomposition. Initiator efficiency is seen to increase in the order: Cu(II) $<$ Co(II) $<$ Co(III) $<$ (Mn(III) $<$ Al(III), Ni(II), Mn(II) $<$ Cr(III). The smaller initiator efficiencies in the presence of metals which facilitate hydroperoxide decomposition may be due to the greater probability of radical-radical termination reactions in these systems, in which relatively higher radical concentration would be expected to exist. It is possible that a significant fraction of metal catalyzed hydroperoxide decomposition leads to nonradical products, as will be discussed later. Such a phenomenon may also account for the observed order of initiator efficiencies. Furthermore, low molecular weights of the polymers obtained in the presence of Cu(II) and Co(II) catalysts suggest that it is possible that some polymer of small molecular weight may not have been recovered. Although the effect of such an eventuality on the observed values of the rate of polymerization would be minimal, the molecular weight of the polymer and therefore the calculated values of initiator efficiency may be influenced appreciably.

Osawa et. al. (244,245) have studied the polymerization of MMA initiated by TBHP in the presence of Co(II) and Co(III) acetylacetonates in benzene medium. The authors have employed metal concentrations about fifteen times higher than those used in the present work. For the Co(II) catalyzed reaction at 60°C, Osawa et. al. (244) observed a rate of polymerization about five times as fast as that observed here. On the other hand, the Co(III) catalyzed reaction in benzene at 60° is reported to proceed at only a third of the rate observed in 1-chlorooctane at the same temperature. A confirmation of the data reported in benzene medium led to the conclusion that the change in metal concentrations, or the nature of the solvent, or both must be responsible for the observed differences in the rate of polymerization of MMA.

To be able to view the present data in proper perspective with reference to that of Osawa et. al. (op. cit.), a study of the Co(II) and Co(III) catalyzed systems in benzene medium was undertaken. The solvent was changed, but all concentrations were maintained constant at the values shown in Tables I to III. In an earlier work of Osawa et. al. (213), which was also carried out in benzene medium, it was reported that $Cu(AA)_2$ had a much smaller effect on TBHP decomposition than the Co(II) and Co(III) complexes. However, it has been seen that Cu(AA)$_2$ is the most effective catalyst in 1-chlorooctane. Therefore, it was of interest to investigate the effect of benzene medium on the Cu(AA)$_2$ catalyzed system. The data obtained in the TBHP initiated polymerization of MMA in benzene medium in the presence of Co(II), Co(III),and Cu(II) catalysts, as well as in their absence, are presented in Tables IV, V and VI. It is observed that the catalytic effect of Cu(AA)$_2$ on the rates of decomposition of TBHP and the polymerization of MMA diminishes greatly in benzene. The catalytic affect of Co(III) acetylacetonates on hydroperoxide decomposition also decreases to such an extent that it is barely noticable at 80°, and not at all at lower temperatures. The Co(III) complex also does not exhibit any effect on the rate of polymerization of MMA monomer. On the other hand, Co(II) acetylacetonate catalyzes the decomposition of TBHP and retards the polymerization of MMA as it did in 1-chlorooctane.

The reduced catalytic effect of Cu(II) and Co(III) species on hydroperoxide decomposition observed in the aromatic medium may be due to different redox potentials in 1-chlorooctane and benzene (215). Osawa et. al. (244), who observed that in benzene medium Co(III) acetylacetonate retards the polymerization of MMA, obtained a polymer of much lower molecular weight than that obtained in the present experiments at a relatively lower concentration of the metal catalyst. This observation suggests that the larger metal catalyst concentration must have resulted in a significant increase in chain transfer events. Possibly, a substantial fraction of the low molecular weight polymer might have remained in solution in the presence of methanol, thereby escaping detection, and hence the observed apparent retardation. It is also possible that at high Co(III) concentrations termination reactions involving the metal become significant (252). For example,

$$Co^{3+} + R\cdot \longrightarrow Co^{2+} + R^{+} \qquad (I-1)$$

In such a case too a lower molecular weight polymer may result.

Chalk and Smith (208) in their study of autoxidation of simple hydrocarbons in the presence of metal catalysts observed that with increasing hydroperoxide concentration the rate of autoxidation increased at first and then decreased continuously. These results have been explained on the basis that at low hydroperoxide concentrations a 1:1 metal-hydroperoxide complex is formed which leads to hydroperoxide decomposition and consequent initiation of autoxidation of the substrate. As the hydroperoxide concentration increases, the rate of formation of the metal-hydroperoxide complex increases to a maximum, beyond which a second complex is formed. The latter complex consists of more than one hydroperoxide molecule coordinated to the metal at the same time. This complex has a lower initiation efficiency than the 1:1 metal-hydroperoxide complex. Therefore a decrease in the rate of autoxidation is observed at higher hydroperoxide concentrations. The formation of a metal-hydroperoxide complex of higher initiating efficiency at a relatively low ratio of hydroperoxide concentration to metal concentration serves to account for the increased catalytic effect of Co(II) acetylacetonate on the rate of polymerization of MMA at higher metal concentrations observed by Osawa et. al. (244). The retardation observed in the presence of a relatively low Co(II) concentration in the present experiments, is probably due to the lower initiation efficiency of TBHP under these conditions due to an increase in the formation of a 1:2 metal-hydroperoxide complex.

Several workers have arrived at the conclusion that radicals are stabilized in the presence of metal species as a result of the formation of metal-radical complexes (250). Increasing metal concentration must increase the extent of such complex formation, and therefore the stability of radicals. Hence, at high metal concentrations radical species may be expected to display greater selectivity. The extent of addition may increase at the expense of other reactions which result in a wastage of initiator molecules. Such an explanation also accounts for the higher rate of polymerization and longer polymer chains observed by Osawa _et_. _al_. at relatively high concentrations of Co(II) acetylacetonate.

In view of the observed sensitivity of the metal-hydroperoxide reaction system to the nature of the solvent, it was of interest to study the effect of a polar solvent on a representative reaction system. Such a study is specially interesting because widely differing phenomena have been reported for related reaction systems in polar media. Some workers have observed that polar solvents enhance the catalytic effect of metal compounds on the decomposition of hydroperoxides (251). Such observations are generally ascribed to an increase in the solubility of the metal catalyst (252). However, in other studies it has been noticed that increased solvent polarity leads to deactivation of the metal catalyst (224). Such deactivation is believed to be a result of the coordination of the solvent to the metal and the consequent blockage of active sites where the hydroperoxide molecules must coordinate before decomposition can occur. In a study of TBHP decomposition catalyzed by Co(II) and Co(III) acetylacetonates, it has been observed that in the presence of both the catalysts, the reaction is faster in benzene than in acetic acid (222). However, the rates of decomposition observed in acetic acid are large enough to suggest that the metal catalysts in these systems do not exist in a deactivated state. To gain further insight into metal acetylacetonate-hydroperoxide interactions in polar media, TBHP decomposition catalyzed by $Cu(AA)_2$ in the presence of MMA monomer has been studied in dimethyl sulfoxide (DMSO). These experiments were carried out at 40, 60 and 80°C. The data obtained are presented in Tables VII to IX. Similar data were obtained in the presence of Co(II) and Co(III) acetylacetonates by a coworker in this laboratory, whose data are presented in Table X. The solvent DMSO was used in these experiments since it offers the advantage of a low chain transfer constant (36).

It is seen from Tables VIIto IX that the catalytic effect of $Cu(AA)_2$ on the rate of hydroperoxide decomposition in DMSO is significant. However, the rate of hydrperoxide decomposition observed in the presence of Cu(II) is appreciably smaller in DMSO than in 1-chlorooctane (Tables I to III). The progress of hydroperoxide decomposition in the presence of $Cu(AA)_2$ with reaction time at 60° is shown in Figure 3 for all the three solvents. The progress of monomer conversion with time is shown in Figure 4 for the $Cu(AA)_2$ catalyzed reaction in 1-chlorooctane, benzene and DMSO at 60°C. This figure shows that the rate of polymerization, however, is the fastest in in the Cu(II) catalyzed system in DMSO. This is understandable when it is considered that the initiator efficiency in DMSO is appreciably larger than that observed in 1-chlorooctane. The rates of hydroperoxide decomposition and the polymerization of MMA are smallest in the benzene system, possibly because of the stabilization of radical-aromatic complexes in the presence of copper species (185, 246). The high initiator efficiency for the Cu(II) catalyzed reaction in bezene supports this view.

An examination of the data in Table X indicates that both Co(II) and Co(III) catalyze the polymerization of MMA monomer. It was seen earlier that Co(II) acetylacetonate retards the polymerization of MMA in 1-chlorooctane (Tables I to III), as well as in benzene (Tables IV to VI). Unfortunately, at present reliable quantitative data on hydroperoxide decompostion and polymer molecular weights in Co(II) and Co(III) catalyzed systems in DMSO are not available. However, it can be said with certainty that the rates of hydroperoxide decomposition in the presence of both Co(II) and Co(III) are appreciably slower in DMSO than in 1-chlorooctane. Furthermore, in the Co(II) catalyzed reaction, substantially longer polymer chains were formed in DMSO than in 1-chlorooctane or benzene. Thus, in the presence of Co(II), the initiator efficiency observed in DMSO is clearly larger than that observed in 1-chlorooctane or benzene. A similar increase in initiator efficiency in DMSO has already been observed for the Cu(II) catalyzed reaction system.

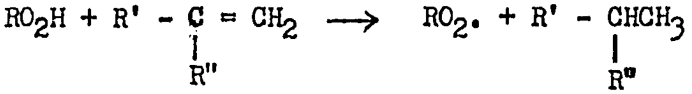
It is possible that DMSO molecules, which are good donors, compete with hydroperoxide molecules for coordination to the metal and thereby prevent the formation of metal-hydroperoxide complexes in which two hydroperoxide molecules are coordinated to the metal at the same time. The prevention of formation of such a complex, which is believed to lead to a smaller initiator efficiency than the 1:1 metal-hydroperoxide complex, may account for the increase in initiator efficiency and the consequent catalytic effect on the rate of polymerization of MMA observed in the presence of Co(II) in DMSO. This explanation also accounts for the higher initiator efficiency observed in DMSO for the Cu(II) catalyzed system. It may be noticed that both Co(II) and Cu(II) acetylacetonates can coordinate with two more molecules by assuming an octahedral configuration.

In all the metal catalyzed systems studied here, UV spectra were taken as each reaction progressed to observe if any change in the oxidation state of the metal catalysts could be detected. In most of the reaction systems no significant change in the spectrum was observed with the progress of the reaction. In the Co(II) catalyzed system, in 1-chlorooctane as well as in benzene, it was visually observed that the pink color of Co(II) acetylacetonate changed to the deep green color characteristic of Co(III) acetylacetonate immediately upon the addition of TBHP solution. Spectra of freshly prepared reaction mixtures containing Co(II) acetylacetonate in 1-chlorooctane, or in benzene, showed no evidence of the presence of Co(II) species. In fact, as long as the 'Co(II) catalyzed' reaction was followed, no spectral evidence of the presence of Co(II) was observed in both the nonpolar solvents; at the same time, no change in the Co(III) concentration was observed. Similarly, in the Co(III) catalyzed reaction in 1-chlorooctane, and also in benzene, no Co(II) species could be detected, while the Co(III) concentration remained unaffected throughout the course of the reaction. In DMSO, on the other hand, it has been seen that whether the initial catalyst is Co(II) or Co(III) acetylacetonate, as the reaction progresses, a steady state concentration of the two species is gradually approached (241).

A comparison of the polymerization data in absence of the metal catalysts in the three solvents shows that although comparable rates of polymerization are obtained in 1-chlorooctane and DMSO, the rate observed in benzene is substantially smaller. A decrease in autoxidation rates in aromatic solvents has been observed earlier and attributed to possible formation of phenols (240,246). Another factor which could contribute to the decrease in polymerization and autoxidation rates in stabilization of the radicals through π complex formation with the aromatic solvent (26-29). On the other hand, the observed trend may be a consequence of hydroperoxide decomposition induced by the aliphatic solvents (186):

$$RO_2H + SH \longrightarrow RO\cdot + S\cdot + H_2O \qquad (84)$$

Osawa et. al (244) in their study of the effect of metal acetylacetonates on hydroperoxide initiated polymerization of methyl methacrylate, have measured rates of hydroperoxide decomposition in absence of the monomer. However, it seems from their data that polymerization of MMA proceeds monotonically long after almost all hydroperoxide seems to have been consumed. It is possible, therefore, that hydroperoxide decomposition proceeds at a slower pace in the presence of MMA. One would expect a faster rate of hydroperoxide decomposition in the presence of MMA, since alkenes, in general, are known to induce hydroperoxide decomposition (12,13,170-172):



$$RO_2H + R' - \underset{\substack{|\\ R''}}{C} = CH_2 \longrightarrow RO_2\cdot + R' - \underset{\substack{|\\ R''}}{C}HCH_3 \qquad (I\text{-}2)$$

Besides, the sensitivity of metal acetylacetonate catalyzed hydroperoxide decomposition to the reaction medium has already been demonstrated. It is therefore of interest to determine in what manner the data of Tables I-X has been influenced by the presence of the monomer. The decomposition of TBHP catalyzed by Co(II) Co(III) and Cu(II) acetylacetonates has been studied in the absence of MMA. The Co(II) and Co(III) catalyzed systems have been studied in 1-chlorooctane and in benzene. These data are presented in Table XI along with data on the Cu(II) catalyzed system in DMSO. Decomposition of TBHP in the presence of $Cu(AA)_2$ was much too fast to obtain reproducible data. The Co(II) and Co(III) systems were being studied in DMSO by a coworker (253). Although, presentable data on these systems are not available at this time, the general trend of these data is described in the foregoing discussion.

A comparison of the data in Table XI with those in Tables I to IX shows that in both 1-chlorooctane and benzene the rates of Co(II) and Co(III) catalyzed hydroperoxide decomposition are appreciably faster in the absence of MMA. The Cu(II) catalyzed reaction too is undoubtedly faster in pure 1-chlorooctane or pure benzene than in a mixture of either of these solvents with MMA. However, the rate of hydroperoxide decomposition catalyzed by $Cu(AA)_2$ in pure DMSO is seen to be slower than the rate observed in the presence of MMA monomer. A similar decrease in the rate of decomposition of TBHP was observed in this laboratory for the Co(II) and Co(III) catalyzed systems in DMSO in the absence of MMA (253). Thus, it is seen that Co(II) Co(III) or Cu(II) catalyzed decomposition of TBHP is slowest in pure DMSO and fastest in pure 1-chlorooctane or benzene, while an intermediate rate is observed in mixtures of these solvents with MMA.

It is generally believed (178) that the decomposition of hydroperoxides is catalyzed by metals of variable valence as a result of Haber-Weiss redox reactions:

$$RO_2H + M^{+n} \longrightarrow RO_2\cdot + H^+ + M^{+n-1} \qquad \text{(I-3)}$$

$$RO_2H + M^{+n-1} \longrightarrow RO\cdot + OH^- + M^{+n} \qquad \text{(1-4)}$$

These reactions would obviously be facilitated by an increase in solvent polarity. But, in fact, as the polarity of the reaction medium increases from 1-chlorooctane or benzene to MMA, to DMSO, the rate of hydroperoxide decomposition actually decreases. It is possible that MMA competes with the hydroperoxide for coordination to the metal in nonpolar solvent systems. Therefore, in 1-chlorooctane and benzene, the rate of formation of metal-hydroperoxide complexes would decrease in the presence of MMA, and so would the rate of hydroperoxide decomposition. In DMSO, which would be expected to be a better donor than MMA, the presence of the monomer would increase the rate of formation of metal-hydroperoxide complexes, and therefore the rate of hydroperoxide decomposition.

Rates of hydroperoxide decomposition from Tables I to XI have been presented in Table XIIA, along with the resective rate constants. Rate constants for hydroperoxide decomposition have been calculated by assuming the reaction to be first order in both, metal and hydroperoxide. Such an assumption is supported by the work of Hiatt et. al. (135). In the case of the Cu(II) catalyzed decomposition of TBHP in 1-chlorooctane and DMSO media in the presence of MMA, rate constants calculated on the basis of empirical rate expressions obtained elsewhere in this work (see Part III) are also presented. The order in MMA has been excluded from these rate laws since it is believed that this order only reflects the effect of the composition of the reaction medium on the rate of hydroperoxide decomposition.

The data on rates of polymerization of MMA and the corresponding rate constants are presented in Table XIIB. These rate constants have been calculated with the help of rate expressions obtained by considering that the rate expressions for hydroperoxide decomposition in Table XIIA represent the respective rates of initiation. Furthermore, all polymerization reactions have been assumed to be first order in the monomer. Even in the case of experimentally determined rate expressions, any deviations from a first order dependence on monomer concentration have been disregarded. It is believed that such deviations occur because of a medium effect. However, in the experiments under consideration here, the composition of the reaction medium remains essentially unchanged with the progress of the reaction. It has been seen that Co(II) retards the polymerization of methyl methacrylate. In this reaction the role of the metal complex is not clear enough to warrant any assumption regarding a rate expression. Therefore, no rate constants can be calculated for the polymerization of MMA in the presence of Co(II) acetylacetonate. Cobalt(III) and Mn(III) catalyze the decomposition of TBHP in 1-chloro-octane medium. But in the same reaction system, these catalysts do not exert a discernible catalytic effect on the polymerization of MMA. It is therefore assumed that Co(III) and Mn(III) catalysts do not take part in the initiation reaction under the present experimental conditions. In the case of reactions carried out in the presence of Al(III), Ni(II), Cr(III) and Mn(II) acetylacetonates, which catalyze neither hydroperoxide decomposition nor the polymerization of MMA, there is no doubt that the rate of polymerization must be independent of metal concentration.

Variation of the logarithms of rate constants for hydroperoxide decomposition, k_d, and for the polymerization of MMA, k_p, with reciprocal temperature has been utilized to obtain activation energies and preexponential factors for hydroperoxide decomposition (E_d, A_d) and for the polymerization reaction (E_a, A). These data are shown in Table XIIC along with E_a values calculated from E_d by using the relation (254):

$$E_a = E_p + (E_d - E_t)/2 \qquad \text{(I-5)}$$

where the activation energy for propagation (E_p) and that for termination (E_t) are considered to have values of 4.7 and 0 kcal/mole, respectively (255). The correspondence between the observed and calculated values of E_a for the metal catalyzed systems is not good. A similar trend has been observed by Osawa <u>et</u>. <u>al</u>. (244). They suggest that E_p and E_t values may be different in these systems from the accepted literature values. the observed discrepancy may also be due to an increase in initiator efficiency with temperature. It is seen from Tables I to VIII that in most of the reaction systems , the initiator efficiency indeed tends to increase with temperature. It has been mentioned earlier that Chalk and Smith (208) have considered the formation of two kinds of metal-hydroperoxide complexes which lead to different initiator efficiencies. If indeed hydroperoxide decomposition takes place through two different mechanisms leading to different initiator efficiencies, an increase in the overall initiator efficiency with increasing temperature may occur if the mechanism which leads to a higher initiator efficiency also has a higher activation energy.

The data in Tables XIIA to XIIC have been used to calculate values of enthalpy and entropy of activation at 40°C by using the following relationships:

$$\Delta H^{\ddagger} = E_a - RT$$

$$\text{and, } k = (\kappa e/h)T.e^{\Delta S^{\ddagger}/R}.e^{-\Delta H^{\ddagger}/RT}$$

where κ is the Boltzman constant and h is Planck's constant. The calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are presented in Table XIID.

The possibility of a change in the reaction mechanism with a change in the relative concentration of the metal catalyst and hydroperoxide has already been discussed. It seems, furthermore that the dominant reaction mechanism may depend on the nature of the metal catalyst, as well as that of the reaction medium. This view is supported by the following attempt to find an isokinetic relationship between the enthalpy and entropy of activation for hydroperoxide decomposition. The nature of an isokinetic relationship, and the inferences which can be drawn from it, are described in the succeeding paragraph.

A linear relationship between corresponding changes in the enthalpy and entropy of activation is known as an isokinetic relationship (256):

$$\Delta H^{\ddagger} = \beta \Delta S^{\ddagger} \qquad \text{(I-6)}$$

where β is positive or zero. The coefficient β is known as the isokinetic temperature. It is the temperature at which the variable being studied has no effect on the rate of reaction. Reaction systems involving a common mechanism share an isokinetic relationship. However, reaction systems related isokinetically need not have identical mechanisms. A plot of $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ (or E_a versus log A) may also give a straight line relationship if the reaction systems involved have equal β values, even if they react by different mechanisms.

Figure 5 shows an isokinetic plot for the decomposition of TBHP in the presence of different metal catalysts. Data obtained in 1-chlorooctane, benzene and DMSO are presented in this figure. The data obtained in the absence of MMA are also included. Furthermore, only activation parameters corresponding to a first order reaction in both metal and hydroperoxide, that is , those based on a common reaction mechanism, are represented here. It is obvious that no isokinetic relationship exists between these reaction systems. Therefore, it appears that a change in the nature of the reaction medium, or that of the metal catalyst affects the reaction mechanism. However, it must be mentioned that a failure to observe an isokinetic relationship may also result if the experimental data have been obtained at temperatures close to the isokinetic temperature. It is also possible that the lack of an isokinetic relationship in the present circumstance may be due to a deviation from the first order rate dependance on metal and hydroperoxide concentrations assumed here.

It was described earlier that UV spectra showed that redox reactions with metal catalysts probably do not occur to a detectable extent in nonpolar solvents. In DMSO, on the other hand, the occurance of a redox reaction with Co(II) and Co(III) catalysts has been observed (241). In the case of reactions catalyzed by $Cu(AA)_2$, however, no redox reaction could be detected in DMSO either, although a significantly larger initiator efficiency was obtained in DMSO than in 1-chlorooctane or benzene. Thus, different reaction mechanisms may prevail in polar and nonpolar solvents. It is possible that in DMSO hydroperoxide decomposition takes place mainly through reactions (I-3) and (I-4), while in the nonpolar solvents a large fraction of the hydroperoxide decomposes through a mechanism which does not involve the metal in redox reactions and probably leads to nonradical products. The possibility that an appreciable fraction of metal catalyzed hydroperoxide decomposition in nonpolar solvents leads to nonradical products should not be ignored in view of the fact that relatively poor initiator efficiencies obtain in these reaction systems. Brown _et_. _al_. (257) in their fine review of peroxide chemistry have suggested that redox reactions with peroxides are much more subtle than has been thought. To quote these authors '...the case for free radical interpretations of these processes has too often been overstated. That is not to say that free radical processes are in general unimportant in peroxide redox reactions - there is considerable evidence to the contrary - but the elevation of a concept to a dogma is not a scientific advance'.

Berger and Bickel (198) have investigated the decomposition of TBHP catalyzed by the phenanthroline acetate complex of Cu(II) in benzene. They have proposed a mechanism which does not involve the metal in any redox reaction. It was observed that the decomposition of TBHP leads to the formation of _t_-butyl alcohol and oxygen in stoichiometric amounts:

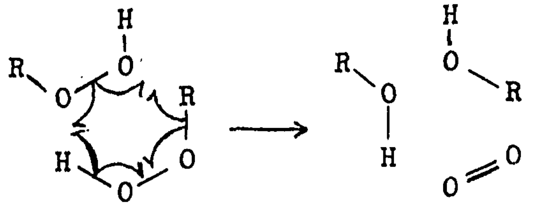
$$2\ ROOH \longrightarrow 2\ ROH + O_2 \qquad (I-7)$$

The mechanism proposed by these authors involves the initial complexation of the metal with peroxy anions which displace the acetate ion ligands from the metal. This complex leads through radical intermediates to the observed products. Such a mechanism would be possible in the present reaction system only if the peroxy anions can displace the acetylacetonate ligands, which must also act as proton acceptors. Such a prospect, although not impossible, would appear at least improbable in view of the high stabilities of acetylacetonate complexes of the metals (258).

A suitable mechanism for metal acetylacetonate catalyzed hydrperoxide decomposition in nonpolar solvents must account for the fact that an increase in the rate of TBHP decomposition in the presence of more active catalysts is accompanied by a decrease in the initiator efficiency in these solvents. Thus, the fastest rate of hydroperoxide decomposition and at the same time the poorest initiator efficiency is observed in the Cu(II) catalyzed reaction in 1-chlorooctane. Goudot (192,193) has made a theoretical study of the decomposition of hydrogen peroxide catalyzed by tetracoordinate metal complexes which are capable of assuming a hexacoordinate configuration. A mechanism has been propsoed, in which the metal assumes an octahedral configuration by accepting two H_2O_2 ligands, which then react to give non-radical products:

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad \text{(I-8)}$$

Other authors have suggested similar mechanisms (257). Here the metal serves to increase the probability of reaction by bringing the two reacting species together and also assists in electron transfer between the two ligands. An alternative explanation can also account for heterolytic decomposition of hydroperoxides in the presence of metal catalysts. The catalytic mechanism may consist of a template like reaction between two coordinated hydroperoxide molecules:



(I-9)

Besides accounting for the decreased initiator efficiency in the presence of the active metals, and the fact that no change is observed in the oxidation state of the metal, a mechanism of this type would also explain the pronounced catalytic effect of Co(II) and Cu(II) acetylacetonates. Among all the acetylacetonate complexes studied in 1-chlorooctane, those of Cu(II) and Co(II) are the only ones which are tetracoordinate but are capable of bonding to two more ligands. As has already been mentioned, Co(II) is immediately oxidized to Co(III) in the presence of TBHP and therfore must assume an octahedral configuration by bonding to two TBHP ligands. In the case of the Cu(II) complex, the driving force for the attainment of an octahedral configuration may be the stabilization obtained in this configuration from a Jahn-Teller distortion. A study by Kovats (194) of the decomposition of hydrogen peroxide in the presence of $Cu(AA)_2$ among other tetracoordinate complexes of Cu(II) lends support to a mechanism of the type suggested by Goudot (op. cit.) in which two H_2O_2 coordinated to the same metal atom react to yield nonradical products.

The observed data in nonpolar solvents can also be explained by a mechanism, which would involve the coordination of two TBHP ligands to Cu(II) or Co(II) acetylacetonate, as suggested by Goudot (op. cit.), with the differnce that these ligands may also react to give free radical products:

$$2\ \mathrm{ROOH} \longrightarrow \mathrm{ROO\cdot} + \mathrm{RO\cdot} + \mathrm{H_2O} \qquad \text{(I-10)}$$

The decrease in initiator efficiency in the presence of active metal catalysts may result from the reactions:

$$2\ \mathrm{ROO\cdot} \longrightarrow 2\ \mathrm{RO\cdot} + \mathrm{O_2} \qquad \text{(I-11)}$$

$$\mathrm{RO\cdot} + \mathrm{ROOH} \longrightarrow \mathrm{ROH} + \mathrm{ROO\cdot} \qquad \text{(I-12)}$$

$$\mathrm{ROO\cdot} + \mathrm{ROOH} \longrightarrow \mathrm{ROH} + \mathrm{RO\cdot} + \mathrm{O_2} \qquad \text{(I-13)}$$

Reaction (I-11) is known to proceed slowly for tertiary peroxy radicals due primarily to the fact that the decomposition of the tetroxide intermediate to alkoxy radicals and oxygen requires an appreciably high activation energy (259). However, all these reactions may be catalyzed by the simultaneous coordination of the reactants to the metal. Credibility is lent to such a view by the observation of a Co(III)-peroxy radical complex by Tkac *et. al.* (260) in their ESR study of the $Co(AA)_2$-TBHP system in benzene.

In DMSO, however, the simultaneous coordination of two hydroperoxide molecules to Cu(II) or Co(II) acetylacetonates would be unlikely because of the competition by DMSO molecules for coordination to the metal. Most of the hydroperoxide decomposition in DMSO would therefore be expected to proceed through reactions (I-3) and (I-4). In DMSO, although the rate of decomposition of the hydroperoxide is not as fast as in the nonpolar solvents, the initiator efficiency is relatively higher because of the preponderance of radical products.

Part II: Kinetics of decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate catalyzed by copper(II) acetylacetonate.

The kinetics and mechanism of the decomposition of hydroperoxides in the presence of metal catalysts has received increasing attention over the past twenty years or so. A substantial volume of literature has evolved on this subject (135,178). The catalytic effect of compounds of copper was noted by Kharasch et. al. (246) almost twenty years ago. Since then only a few detailed studies of the copper catalyzed decomposition of hydroperoxides have been reported (180, 198, 198a). However, these studies fail to consider the possibility of a mechanism of hydroperoxide decomposition which may lead to nonradical products. Earlier work in this laboratory on the decomposition of TBHP catalyzed by $Cu(AA)_2$ has shown that at high rates of hydroperoxide decomposition relatively poor rates of radical formation obtain, especially in nonpolar solvents (261,262).

In the present work, kinetics of the decomposition of TBHP have been studied in the presence of $Cu(AA)_2$ and MMA monomer, which serves as a radical trap. The sensitivity of this reaction system to the nature of the solvent has already been observed (261,262). Moreover, some workers have discussed the possibility that in polar media the reaction between hydroperoxide and metal catalysts may take place without initial metal--hydroperoxide complex formation (231,268-271). It would be of interest to see if a change in the mechanism of metal catalyzed decomposition of hydroperoxide can be discerned by changing the polarity of the reaction medium. Identical experiments have, therefore, been carried out in nonpolar 1-chlorootane and polar dimethyl sulfoxide.

The data obtained in 1-chlorooctane medium at 60°C are presented in Tables XIII to XV. These data show the effect of variation of concentrations of $Cu(AA)_2$, TBHP and MMA on the rate of hydroperoxide decomposition (R_d), the overall rate of polymerization of MMA (R_p), and the rate of polymerization catalyzed by the metal ($R_p - R_p^o$), which is the overall rate of polymerization corrected for the rate of polymerization in absence of the metal (R_p^o). The effect of reactant concentrations on the molecular weight of the polymer formed has also been studied. Initiator efficiencies, f, calculated from the values for percent conversion of monomer, percent decomposition of hydroperoxide and the number average molecular weight of the polymer, are also presented. A summary of the data in Tables XIII to XV appears in Table XVI.

It is seen from Tables XIII and XIV that an increase in the concentrations of $Cu(AA)_2$ and TBHP produces a corresponding increase in the rate of hydroperoxide decomposition. As would be expected, this increase in the rate of initiation is translated into an increase in the extent of monomer conversion. However, Table XV shows that increasing concentration of MMA has a deleterious effect on the rate of decomposition of TBHP, although the rate of polymerization continues to increase.

The data in Tables XIII to XV have been used to obtain empirical rate laws of the form:

$$R_d = k[Cu(AA)_2]^a[TBHP]^b[MMA]^c$$

$$R_p - R_p^o = k'[Cu(AA)_2]^p[TBHP]^q[MMA]^r$$

In order to evaluate the exponents, log-log plots of the rate of hydroperoxide decomposition (R_d) and the rate of metal catalyzed polymerization

$(R_p-R_p^o)$ versus each reactant concentration have been obtained. These plots are shown in Figures 6 to 11. The slopes of these straight line plots give the order in the respective reactant. Thus, it is seen that in 1-chlorooctane at 60°C:

$$R_d = k[Cu(AA)_2]^{0.32}[TBHP]^{0.60}[MMA]^{-0.53} \tag{II-1}$$

$$R_p - R_p^o = k'[Cu(AA)_2]^{0.18}[TBHP]^{0.29}[MMA]^{0.81} \tag{II-2}$$

Richardson.(180), who studied the copper-2 ethyl hexanoate catalyzed decomposition of TBHP in 1-chlorobenzene, has proposed the following reaction mechanism:

$$2\ ROOH \rightleftharpoons (ROOH)_2 \tag{II-3}$$

$$Cu_2^{II} + ROOH \rightleftharpoons Cu_2^{II}(ROOH) \tag{II-4}$$

$$Cu_2^{II}(ROOH) + ROOH \rightleftharpoons Cu_2^{II}(ROOH)_2 \tag{II-5}$$

$$Cu_2^{II}(ROOH)_2 \longrightarrow Cu^{II}Cu^{I}(ROOH)(H^+) + ROO\cdot \tag{II-6}$$

$$Cu^{II}Cu^{I}(ROOH)(H^+) \longrightarrow Cu_2^{II} + H_2O + RO\cdot \tag{II-7}$$

$$2\ ROO\cdot \longrightarrow 2\ RO\cdot + O_2 \tag{II-8}$$

$$RO\cdot + ROOH \longrightarrow ROH + ROO\cdot \tag{II-9}$$

$$2\ RO\cdot \longrightarrow ROOR \tag{II-10}$$

This free radical mechanism involves a dimeric copper salt and includes the concept of association of the hydroperoxide with itself and with the copper salt. The catalytic nature of the copper salt is explained by redox reactions between metal species and the hydrperoxide in equations (II-6) and (II-7). Richardson was led to believe that a substantial concentration of the copper salt existed in a reduced state since an oxygen purge reduced the rate of reaction by a factor close to two. In the present work no evidence of the existence of Cu(I) could be found from UV spectra. However, this does not rule out the possibility of a redox mechanism of catalysis, since it is possible that Cu(I) could not be detected only because of its high reactivity.

Berger and Bickel (198) have investigated the decomposition of TBHP catalysed by the phenanthroline acetate complex of Cu(II) in benzene. These authors have proposed a mechanism in which the metal is not involved in redox reactions. However, the empirical rate equations (II-1) and (II-2) obtained for the present system are not compatible with the kinetic expression derived from this mechanism, which has been presented in the Introduction (p. 46).

Richardson (op. cit.) has derived the following rate equation for hydroperoxide decomposition from the mechanism described by equations (II-3) to (II-10):

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{2k_6K_4K_5[\mathrm{Cu}][\mathrm{ROOH}]}{(K_3 + K_3^{\frac{1}{2}}K_4[\mathrm{ROOH}]^{\frac{1}{2}} + K_4K_5[\mathrm{ROOH}])} + \frac{k_9(k_6K_4K_5/k_{10})^{\frac{1}{2}}[\mathrm{Cu}]^{\frac{1}{2}}[\mathrm{ROOH}]}{K_3(1 + K_3^{-\frac{1}{2}}K_4[\mathrm{ROOH}] + K_3^{-1}K_4K_5[\mathrm{ROOH}])^{\frac{1}{2}}} \quad \ldots\ldots\ldots(\mathrm{II}\text{-}11)$$

Between one half and first order dependence on the copper salt concentration is expected from this expression. The order in hydroperoxide is expected to be between zero and one.

In the present experiments in 1-chlorooctane, the decomposition of TBHP is seen to be 0,60 order in TBHP (equation II-1). This value is well within the range expected from equation (II-11). However, the order of 0.32 in $Cu(AA)_2$ is appreciably smaller than the expected order. In the mechanism in equations (II-3) to (II-10), it was assumed that the copper salt remains intact as the dimer. Richardson (op. cit.) has also considered the possibility of the existence of an equilibrium between monomeric and dimeric copper salt:

$$2Cu^{II} \rightleftarrows Cu_2^{II} \qquad \text{(II-12)}$$

In such a case the order in monomeric copper will be half of that expected from equation (II-11). In such a case an order of 0.25 to 0.5 in copper would be expected. However, no evidence of the existence of copper acetylacetonate in a dimeric form has been reported (266), although dimers, trimers and tetramers of some other metal acetyl acetonates have been reported (224,267). On the other hand, it is possible that $Cu(AA)_2$ exists in an aggregated state in 1-chlorooctane medium. In such a case, any increase in the total concentration of copper would result in a smaller increase in the effective concentration of the metal, leading to a lower order in copper. The aggregation of metal compounds into a micellar form in nonpolar organic media is a well known phenomenon (135,210).

Since copper(II) acetyl acetonate is not known to exist in dimeric form (266,267), it would be more accurate to rewrite equations (II-4) to (II-7) in the following form:

$$Cu^{II} + ROOH \rightleftarrows Cu^{II}(ROOH) \qquad \text{(II-4a)}$$

$$Cu^{II}(ROOH) + ROOH \rightleftarrows Cu^{II}(ROOH)_2 \qquad \text{(II-5a)}$$

$$Cu^{II}(ROOH)_2 \longrightarrow Cu^{I}(ROOH)(H^+) + ROO\cdot \qquad \text{(II-6a)}$$

$$Cu^{I}(ROOH)(H^+) \longrightarrow Cu^{II} + H_2O + RO\cdot \qquad \text{(II-7a)}$$

These equations have been substituted for equations (II-4) to (II-7) and a rate equation has been derived for the modified mechanism in Appendix I.1. This rate equation is seen to be identical to equation (II-11). Thus, this rate equation holds if copper is assumed to be consistently in the monomeric or dimeric form. It has already been pointed out that the order in copper would be halved if an equilibrium exists between monomeric and dimeric copper species.

It has been suggested earlier (261,262) that the small initiator efficiency observed in metal catalyzed hydroperoxide decomposition may be due to the decomposition of metal-hydroperoxide complexes to nonradical products. For example,

$$\mathrm{Cu_2^{II}(ROOH)_2} \longrightarrow \mathrm{Cu^{II}} + 2\ \mathrm{ROH} + \mathrm{O_2} \qquad \text{(II-13)}$$

If it is assumed that hydroperoxide decomposition takes place through reactions II-6a, II-7a and II-13, the following kinetic expression can be obtained (see Appendix 1.2):

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{(2k_{6a}K_{4a}K_{5a} + k_{13}K_{4a}K_{5a})[\mathrm{Cu}][\mathrm{ROOH}]}{(K_3 + K_3^{\frac{1}{2}}K_{4a}[\mathrm{ROOH}]^{\frac{1}{2}} + K_{4a}K_{5a}[\mathrm{ROOH}])}$$

$$+ \frac{k_9(k_{6a}K_{4a}K_{5a}/k_{10})^{\frac{1}{2}}[\mathrm{Cu}]^{\frac{1}{2}}[\mathrm{ROOH}]}{K_3(1 + K_3^{-\frac{1}{2}}K_{4a}[\mathrm{ROOH}]^{\frac{1}{2}} + K_3^{-1}K_{4a}K_{5a}[\mathrm{ROOH}])^{\frac{1}{2}}} \qquad \text{(II-14)}$$

A comparison of equations II-11 and II-14 shows no significant difference between the two equations. Hence, it is not possible to infer from kinetic data whether reaction II-13 takes place or not.

In Richardson's mechanism (equations II-3 to II-10), only the complex in which two hydroperoxide molecules are associated with the metal leads to hydroperoxide decomposition. Other authors (208) have suggested that a complex in which a single hydroperoxide molecule is coordinated to the metal center (as in the complex formed in reaction II-4) may provide another route to decomposition. Thus,

$$\mathrm{Cu^{II}(ROOH)} \longrightarrow \mathrm{Cu^{I}(H^+)} + \mathrm{ROO\cdot} \qquad \text{(II-15)}$$

$$\mathrm{Cu^{I}(H^+)} \longrightarrow \mathrm{Cu^{II}} + \mathrm{H_2O} + \mathrm{RO\cdot} \qquad \text{(II-16)}$$

Complexation of reduced copper with hydroperoxide is neglected since Cu(I) is believed to be highly reactive (198a). If reactions (II-15) and (II-16) are substituted for reactions (II-6a) and (II-7a), the followng rate equations can be derived (Appendix I.3):

$$-\frac{d[ROOH]}{dt} = \frac{2K_{4a}K_{5a}[Cu][ROOH]^{\frac{1}{2}}}{(K_3^{\frac{1}{2}} + K_{4a}[ROOH]^{\frac{1}{2}})} + \frac{k_9(K_{4a}k_{15}/k_{10})^{\frac{1}{2}}[Cu]^{\frac{1}{2}}[ROOH]^{3/4}}{(K_3^{3/4} + K_3^{\frac{1}{2}}K_{4a}[ROOH]^{\frac{1}{4}})} \qquad \text{(II-17)}$$

In such a case, orders of one half to one in copper, and zero to three fourths in hydroperoxide would be expected. In view of the rate data obtained for for copper(II) acetylacetonate catalyzed decomposition of TBHP in 1-chlorooctane (equation II-1), the formation of neither of the two metal-hydroperoxide complexes can be precluded.

It has already been noticed that an increasing MMA concentration results in a decreasing rate of hydroperoxide decomposition. An order of -0.53 in MMA is observed. One would expect that redox reactions (II-6a) and (II-7a) would be facilitated in the presence of MMA, which is more polar than 1-chlorooctane. Therefore, one would have expected faster rates of hydroperoxide decomposition at higher concentrations of MMA. Pssibly, the observed decrease in the catalytic effect of $Cu(AA)_2$ at higher monomer concentrations is an indication of less favorable redox potentials in MMA than in 1-chlorooctane. It is also possible that MMA molecules exert a blocking effect (208) and thereby decrease the probability of formation of metal-hydroperoxide complexes as in reactions (II-4a) and (II-5a). The equilibrium constants K_4 and K_5 would therefore decrease continuously with increasing MMA concentration, leading to an increasingly slower rate of hydroperoxide decomposition.

It is seen from equation (II-2) that for the metal catalyzed polymerization of MMA, the rate orders in copper and TBHP are close to half of those observed in the decomposition of hydroperoxide in equation (II-1). This is to be expected for reaction systems involving a biradical termination process. The order of 0.81 in MMA monomer is appreciably below the order of unity expected for most radical chain polymerization reactions. However, this disparity is understandable since an increasing concentration of MMA besides increasing the rate of propagation, also reduces the rate of hydroperoxide decomposition, and therefore the rate of initiation.

In Tables XIII and XIV, the initiator efficiencies do not show a significant variation over the range of $Cu(AA)_2$ and TBHP concentrations studied here. In Table XV, however, increasing MMA concentration is accompanied by an unmistakable increase in initiator efficiency. Higher monomer concentrations would be expected to increase the probability of the occurance of propagation reactions, and at the same time decrease the probability of initiator molecules and radicals engaging in wastage reactions. Also, since increasing MMA concentration is accompanied by a decreasing rate of initiation, a simultaneous increase in the efficiency of initiation is only to be expected.

The effects of the variation of concentrations of $Cu(AA)_2$, TBHP and MMA on the rates of hydroperoxide decomposition and metal catalyzed polymerization of MMA have also been studied in DMSO medium. The data obtained in these experiments are presented in Tables XVII to XIX. The kinetic data in these Tables are presented in a summarized form in Table XX. In conformation with data presented in Part I of this work, it is seen that, in general, at comparable reactant concentration, the rate of hydroperoxide decomposition is slower while the rate of polymerization of MMA is faster in DMSO than in 1-chlorooctane. Consequently, higher initiator efficiencies obtain in the polar solvent. To obtain empirical rate laws for TBHP decomposition and metal catalyzed polymerization of MMA, logarithm of rate of reaction has been plotted against logarithms of each reactant concentration. These plots are shown in Figures 12 to 17. The slopes of these straight line plots were evaluated and the following rate laws were thereby obtained:

$$R_d = k[Cu(AA)_2]^{0.69}[TBHP]^{1.0}[MMA]^{1.0} \qquad \text{(II-18)}$$

$$R_p - R_p^o = k'[Cu(AA)\ ]^{0.20-0.36}[TBHP]^{0.50}[MMA]^{1.5} \qquad \text{(II-19)}$$

The rate orders of 0.69 and 1.0 in $Cu(AA)_2$ and TBHP, respectively, for the decomposition of hydroperoxide, are appreciably higher than the respective orders observed in 1-chlorooctane medium, but are still within the range of values expected on the basis of equation (II-11). Nevertheless, it is unlikely that the mechanism proposed in equations (II-3) to (II-10), from which equation (II-11) has been derived, holds in polar media. In this mechanism, the hydroperoxide molecules are assumed to exist essentially as dimers. However, hydroperoxides do not dimerize to a significant extent in polar media (133). Some authors have suggested that hydroperoxides react directly with metals in polar media, without the intermediate formation of metal-hydroperoxide complexes as in reactions (II-4) and (II-5) (223,263-265). More recently, spectral evidence for the formation of metal-hyuroperoxide complexes in DMSO has been reported from this laboratory (241). Even so, it is unlikely that in the presence of a preponderance of donor solvent molecules, more than one hydroperoxide molecule can associate with the metal center at the same time. Even if a reaction akin to (II-4) does take place, the formation of the metal-hydroperoxide complex product may or may not be of kinetic significance (210). Two mechanisms are considered below. One of these involves the formation of a metal-hydroperoxide complex, while no such complex formation precedes the reaction of metal and hydroperoxide in the other mechanism. In both mechanisms hydroperoxide molecules do not dimerize.

Mechanism A:

$$Cu^{II} + ROOH \rightleftarrows Cu^{II}(ROOH) \qquad (II\text{-}4a)$$

$$Cu^{II}(ROOH) \longrightarrow Cu^{I}(H^{+}) + ROO\cdot \qquad (II\text{-}15)$$

$$Cu^{I}(H^{+}) + ROOH \longrightarrow Cu^{II} + H_2O + RO\cdot \qquad (II\text{-}16)$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2 \qquad (II\text{-}8)$$

$$RO\cdot + ROOH \longrightarrow ROH + ROO\cdot \qquad (II\text{-}9)$$

$$2RO\cdot \longrightarrow ROOR \qquad (II\text{-}10)$$

The following rate expression has been derived for this mechanism (see Appendix I.3a):

$$-\frac{d[ROOH]}{dt} = \frac{2K_{4a}k_{15}[Cu][ROOH]}{1 + K_{4a}[ROOH]} + \frac{K_9(K_{4a}k_{15}/k_{10})^{\frac{1}{2}}[Cu]^{\frac{1}{2}}[ROOH]^{3/2}}{(1 + K_{4a}[ROOH])^{\frac{1}{2}}} \qquad (II\text{-}20)$$

From this equation one would expect an order in copper of one half to one, and a maximum order of 3/2 in hydroperoxide. However, this mechanism has any significance only if the equilibrium constant K_{4a} has a large enough value. In such a case, the order in hydroperoxide would be no more than unity. Since the observed rate order in hydroperoxide is 1.0 (equation II-19), it may be that the metal catalyzed hydroperoxide decomposition in DMSO medium takes place through mechanism A.

Mechanism B:

$$Cu^{II} + ROOH \longrightarrow Cu^{I}(H^{+}) + ROO\cdot \qquad (II\text{-}21)$$

$$Cu^{I}(H^{+}) + ROOH \longrightarrow Cu^{II} + H_2O + RO\cdot \qquad (II\text{-}22)$$

$$2\ ROO\cdot \longrightarrow 2\ RO\cdot + O_2 \qquad (II\text{-}8)$$

$$RO\cdot + ROOH \longrightarrow ROH + ROO\cdot \qquad (II\text{-}9)$$

$$2\ RO\cdot \longrightarrow ROOR \qquad (II\text{-}10)$$

Based on this reaction mechanism, the following rate expression has been derived (refer to Appendix 1.4):

$$-\,d[ROOH]/dt = 2k_{21}[Cu][ROOH] + k_9(k_{21}/k_{10})^{\frac{1}{2}}[Cu]^{\frac{1}{2}}[ROOH]^{3/2} \qquad (II\text{-}23)$$

If indeed hydroperoxide decomposition takes place through mechanism B, the observed order of 1.0 in TBHP would indicate that in equation (II-23) the first term on the right hand side predominates. In such a case an order of unity in $Cu(AA)_2$ would be expected. However, the observed order of 0.69 in the metal catalyst is appreciably smaller. This mechanism may still be acceptable if it were assumed that $Cu(AA)_2$ forms aggregates or micelles in DMSO. If micelle formation does take place under the present experimental conditions, one would expect to see a slower increase in the rate of hydroperoxide decomposition with increasing $Cu(AA)_2$ concentration, since the size of the micelles, rather than their number, would continue to increase, and a limiting rate of hydroperoxide decomposition would be approached. Therefore, it may be instructive to study the effect of even higher concentrations of $Cu(AA)_2$ on the rate of hydroperoxide decomposition. However, a decrease in the rate of reaction at higher concentrations of the metal due to its participation in termination reactions (249) or deactivation of the catalyst (208,210).

The higher initiator efficiencies observed in DMSO may well be due to smaller rates for reactions (II-9) and (II-10) in DMSO. In 1-chlorooctane, these reactions are probably catalyzed by the simultaneous coordination of the reactants to the metal and the consequent stabilization of the transition state. In the presence of DMSO molecules, such coordination would be much less probable.

It is seen from equation (II-18) that the rate of hydroperoxide decomposition shows a first order dependence on MMA concentration. The increasing hydroperoxide decomposition with increasing MMA concentration may be attributed to more favorable redox potentials in MMA medium.

Equation (II-19) is the empirical rate equation for the metal catalyzed polymerization of MMA. For this reaction an order of 0.50 in TBHP is observed. This value, as expected, is exactly one half of the order in TBHP observed for the initiation reaction (equation II-18). However, for the metal catalyzed polymerization reaction, the order in $Cu(AA)_2$ varies from 0.36 at lower metal concentrations to 0.20 at higher concentrations. It can be seen from Figure 16 that at higher copper concentrations, the rate of polymerization increases more slowly. However, hydroperoxide decomposition is not affected in a similar manner at comparable copper concentrations as seen from Figure 13. Therefore, the decrease in the rate order in copper with increasing copper concentration observed for the polymerization reaction cannot be attributed to a decrease in catalyst efficiency due to the formation of aggregates or micelles at higher catalyst concentrations.

George and Robertson (268,269) have observed evidence of redox reactions of copper stearate with alkoxy and peroxy radicals in the oxidation of tetralin:

$$RO_2\cdot + Cu(II) \longrightarrow Cu(I) + R^+ + O_2 \qquad (II\text{-}24)$$

$$RO\cdot + Cu(I) \longrightarrow Cu(II) + RO^- \qquad (II\text{-}25)$$

$$RO_2\cdot + Cu(I) \longrightarrow Cu(II) + RO_2^- \qquad (II\text{-}26)$$

Several other workers (270-272) have reported similar termination reactions with metal catalysts. Such reactions may be expected to be favored in polar solvents. It is also possible that the redox potentials in DMSO may be more favorable than in 1-chlorooctane.

It has been known for some time that radical species are not completely free in the presence of copper compounds. Kharasch et. al. (273) observed that copper salts are capable of deactivating some radicals. Thus, chloride was suggested to 'trap' a benzoyloxy radical:

$$C_6H_5CO\cdot + CuCl \rightleftharpoons C_6H_5COCuCl \qquad (II-27)$$

Other authors (249,274-276) have also concluded that the formation of radical-copper complexes is responsible for a reduction in the reactivity of radicals in the presence of compounds of copper. Such stabilization of radicals through complex formation with copper is known to lead to lower rates of propagation and higher rates of termination (210,250). However, one would expect that the probability of formations of copper-radical complexes would be higher in 1-chlorooctane than in DMSO. It has been seen that in 1-chlorooctane medium the rate order in $Cu(AA)_2$ for the polymerization reaction is close to half of the order in the catalyst for the initiation reactions. Thus, there appears to be no evidence for the formation of copper-radical complexes in 1-chlorooctane medium. Therefore, it is doubtful if the formation of such complexes is responsible for the observed decrease in the rate order in copper for the polymerization reaction with increasing copper concentration in DMSO. Redox reactions with the metal leading to chain termination are the more likely cause. Evidence of wastage reactions such as (II-24) to (II-26) appears in the form of a decrease in initiator efficiency which accompanies an increase in the concentration of the copper catalyst, as shown in Table XVII.

For the metal catalyzed polymerization reaction in DMSO, an order of 1.5 in the monomer is observed (Equation 2-19). This value is much higher than the order of unity in monomer that is generally expected for a radical chain polymerization reaction. In the present reaction system, however, the rate of initiation has itself been seen to have a first order dependence on MMA concentration. Hence, the order of 1.5 is to be expected as a sum of half of the order in MMA for the initiation reaction and the expected order of 1.0 in monomer for the polymerization reaction.

Part III. Determination of chain transfer constants of metal acetylacetonates in the polymerization of methyl methacrylate.

In hydroperoxide initiated polymerization of MMA in the presence of metal acetylacetonates it has been seen that the molecular weight of the polymer is influenced by the nature of the metal catalyst (261,262). In the presence of metals which catalyze hydroperoxide decomposition, and therefore the initiation process, more effectively, smaller molecular weights would be expected. However, even in the presence of metals which influence the rate of hydroperoxide decomposition to a comparable extent, significant differences in molecular weights of the polymer products were observed. A variable degree of chain transfer with different metal catalysts would account for this observation. A kowledge of chain transfer constants of these complexes is therefore necessary for a better understanding of this system.

Metal acetylacetonates have been utilized as homogeneous catalysts in free radical initiated polymerization (243-245), hydroperoxide decompositon (213), autoxidation processes (239-245), epoxidation of olefins (172,277), as well as to initiate polymerization (120-124). Inspite of the wide applicability of metal acetylacetonates, there are no data available on chain transfer with these complexes, except for an investigation by Gritter et. al. (278), who studied hydrogen atom abstraction from several acetylacetonates. by t-butoxy radicals. In this reaction system t-butoxy radicals must either abstract a hydrogen atom to form t-butanol, or decompose to give acetone and a methyl radical. It has been reported that the ratio of the rate of formation of alcohol to that of acetone varies widely with the nature of the metal acetylacetonate.

In the present work, chain transfer constants of acetylacetonates of Co(II), Co(III), Mn(II), Mn(III), Cu(II), Cr(III), Ni(II) and Al(III) have been determined in the polymerization of MMA in 1-chlorooctane medium. The polymerization reaction was initiated by 2-azoisobutyronitrile, which itself has a very small chain transfer constant (279). In these experiments, a 4,16 M solution of MMA in 1-chlorooctane was reacted with 0.0011 M AIBN in the presence of each of the metal acetylacetonates mentioned above. The concentration of the metal was varied from 1.8×10^{-4} to 1.8×10^{-3} M, except in the case of Mn(II) and Mn(III) complexes where reproducible data could not be obtained at the higher concentrations. In these cases, data obtained at concentrations higher than 5.4×10^{-4} M has not been reported. The polymer obtained in the presence of varying concentrations of each of the metals, as well as in their absence was isolated, weighed and its number average molecular weight determined. These experiments have been carried out at 60, 70 and 80°C. At all temperatures, the rate of polymerization was seen to be independent of the nature and concentration of the metal, indicating that the chelates neither catalyzed the decomposition of AIBN, nor directly initiated polymerization under present experimental conditions. Rates of polymerization of 3.70×10^{-5}, 9.36×10^{-5} and 22.5×10^{-5} moles l^{-1} sec^{-1} were observed at 60 70 and 80°, respectively. It should be mentioned here that the polymerization reaction was never allowed to proceed beyond a monomer conversion of 5.0 percent, in order to minimize chain transfer to the polymer. For each metal acetylacetonate studied here, the variation of the degree of polymerization with metal concentration has been used to obtain chain transfer constants at 60, 70 and 80° by the conventional application of Mayo's equation (68):

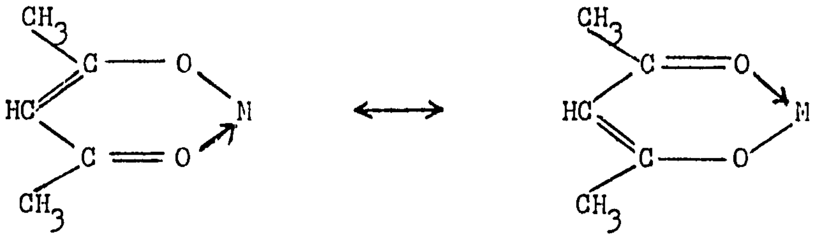
$$1/\bar{X}_n = 1/(\bar{X}_n)_o + C_s[M(AA)_n]/[MMA] \qquad \text{(III-1)}$$

where $\overline{X}_n$ and $(\overline{X}_n)_o$ represent the degree of polymerization of poly(MMA) obtained in the presence and absence of the metal complex, respectively, and C_s is the chain transfer constant of the metal complex, while square brackets denote molar concentrations. To evaluate the chain transfer constant of a metal acetylacetonate, the reciprocal of the degree of polymerization is plotted against the molar concentration of the metal. A linear correlation would be expected. The slope of this straight line is, obviously, $C_s/[MMA]$, or $C_s/4.16$ in these experiments. Such plots for data obtained at 60, 70 and 80°C are shown in Figures 18-23. The experimental point shown in these Figures at zero metal concentration corresponds to the reciprocal of the degree of polymerization of the polymer obtained in the absence of any metal acetylacetonate. These experimental values of the intercept have also been used to obtain the the straight lines in Figures 18-23 through a least squares fit of the data. The slopes of these straight lines gave the chain transfer constants listed in Table XXI. The order in which the rate of chain transfer decreases is: Co(III) > Mn(II) > Cr(III) > Cu(II) > Mn(III) > Co(II) > Ni(II) > Al(III). This order of decreasing rate of chain transfer is not in total agreement with that observed by Gritter (278), which is: Co(III) > Cu(II) > Mn(II) > Mn(III) > Ni(II) > Cr(III) > Al(III) > Co(II). However, both these orders of reactivity have been arrived at through computations in which concentrations of the metal complexes have been used, rather than concentrations of the acetylacetonate ligands which are potentially involved in chain transfer. The data in Table XXI has been suitably modified to arrive at chain transfer constants per ligand. These data are also presented in Table XXI. The order of decreasing rate, in this case, is seen to be Mn(II) > Co(III) > Cu(II) > Cr(III) > Co(II) > Mn(III) > Ni(II) > Al(III). This order of reactivity is compared in the following table with the order in which some physical and chemical properties of these metals decrease:

Property	Order of decreasing numerical value	Reference
Chain transfer constant, C_s	Co(III) > Mn(II) > Cr(III) > Cu(II) > Mn(III) > Co(II) > Ni(II) > Al(III)	
Chain transfer const. per ligand	Mn(II) > Co(III) > Cu(II) > Cr(III) > Co(II) > Mn(III) > Ni(II) > Al(III)	
Stability constant	Al(III) > Co(III) > Cr(III) > Cu(II) > Ni(II) > Co(II) > Mn(II)	(262)
M-O bond strength	Al(III) > Co(III) > Cr(III) > Cu(II) > Ni(II) > Co(II) > Mn(II)	(285)
Ionic radius	Cu(II), Mn(II) > Co(II) > Ni(II) > Co(III), Cr(III) > Al(III)	(284)
$M^{n+} + ne^- \rightleftarrows M$, E^o	Co(III) > Mn(III) > Cu(II) > Ni(II) > Co(II) > Cr(III) > Al(III)	(284)

It appears that no meaningful relationship exists between the chain transfer data and the physical constants in the above table. This is not altogether surprising, since perhaps the only thing that the metal acetylacetonates have in common is the nature of the ligand. Significant differences in their structure, bonding and other properties exist, to make each one behave as an individual compound, rather than as a member of a family of compounds (229,235).

Coordination of an organic molecule to a metal can bring about a significant electronic distortion within the molecule (287). Such electronic changes are known to decrease the strength of C-H and even C-C bonds within the coordinated molecule (283). The unexpectedly high chain transfer constants observed for some organometallic compounds (126,127) also point towards a labilization of C-H bonds in these compounds. Although chain transfer constants obtained for metal acetylacetonates in this work are not as large as those observed with some organometallic compounds (126), they are nevertheless appreciably larger than that observed for acetylacetone itself (284). Another factor which may facilitate chain transfer on acetylacetonate ligands is their benzenoid character (235):



A number of studies on the chemistry of the coordinated acetylacetonate anion have unambiguously established the fact that the chelate ring is at least aromatic in nature with regard to the chemical reactivity of the coordinated ligand (235). Moreover, Gritter <u>et. al.</u> (278) have established that chain transfer with metal acetylacetonates takes place by abstraction of a hydrogen atom from the 1-position of the chelate (from a methyl group), while with acetylacetone the hydrogen atom at the 3 position is abstracted. Thus, coordination changes the site of radical attack. It would seem that the methyl hydrogens behave as benzylic hydrogen. The ensuing resonance in the radical formed after abstraction of a methyl hydrogen probably provides the driving force for chain transfer.

The chain transfer constants per acetylacetonate ligand in Table XXI have been used to obtain Arrhenius plots (log C_s versus 1/T). From the slopes of these plots the difference in activation energies between chain transfer and propagation processes (E_{tr}-E_p) has been calculated (since $C_s = k_{tr}/k_p$). The corresponding frequency factors (A_{tr}/A_p) have also been calculated. These activation parameters which are presented in Table XXII., have been used to obtain an isokinetic plot (E_a versus log A) which is shown in Figure 24. The straight line in this figure represents the best fit obtained by a least squares analysis of the data. The slope of this straight line leads to an isokinetic temperature of 487°K. It is seen that all the points fall well within a deviation of ten percent in the activation energy. According to conventionally accepted standards, this fact does not warrant the presumption of a change in reaction mechanism for any of the metal acetylacetonate reaction systems.

TABLE I

Effect of presence of metal acetylacetonates on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in 1-chlorooctane.

$[\mathrm{MMA}] = 4.\ 16\ \underline{M}$, $[\mathrm{TBHP}] = 0.022\ \underline{M}$, $[\mathrm{M(AA)}_n] = 1.8\mathrm{x}10^{-4}\mathrm{M}$, temperature = 40°C

Metal acetylacetonate	Time (hours)	TBHP decomposition (%)	$R_d\mathrm{x}10^7$ (moles $l^{-1}\mathrm{sec}^{-1}$)	Monomer conversion (%)	$R_p\mathrm{x}10^5$ (moles $l^{-1}\mathrm{sec}^{-1}$)	$\bar{M}_n\mathrm{x}10^{-5}$	f
None	8	< 5.0	-	2.2	0.32	2.98	-
	12	< 5.0		3.3		3.31	-
	15	< 5.0		4.1		3.37	-
Co(II)	5	16	2.1	-	0.22	-	-
	8	22		1.1		-	-
	12	25		2.0		-	-
	15	32		2.8		0.634	0.026
Co(III)	8	5.5	0.38	2.1	0.29	1.85	0.039
	15	9.0		3.8		1.92	0.042
Mn(II)	8	<5.0	-	1.9	0.29	-	-
	12	<5.0		3.0		2.67	-
	15	<5.0		3.8		2.65	-
Mn(III)	8	7.7	0.61	2.4	0.35	0.922	0.064
	12	10		3.7		0.983	0.071
	15	11		4.5		1.10	0.070
Cu(II)	0.33	52	140	-	1.6	-	-
	1.0	76		-		-	-
	1.5	84		1.3		-	-
	2.5	88		2.7		0.234	0.025
	3.5	92		4.5		0.452	0.021
	4.5	94		6.4		0.626	0.021
Cr(III)	8	< 5.0	-	2.0	0.31	2.48	-
	15	< 5.0		4.0		2.71	-
Al(III)	15	< 5.0	-	4.0	0.31	3.12	-
Ni(II)	15	<5.0	-	3.8	0.29	3.06	-

TABLE II

Effect of presence of metal acetylacetonates on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in 1-chlorooctane.

$[\mathrm{MMA}] = 4.16\ \underline{M}$, $[\mathrm{TBHP}] = 0.022\ \underline{M}$, $[\mathrm{M(AA)}_n] = 1.8\mathrm{x}10^{-4}\underline{M}$, temperature = 60°C

Metal acetylacetonate	Time (hours)	TBHP decomposition (%)	$R_d\mathrm{x}10^7$ (moles $l^{-1}\mathrm{sec}^{-1}$)	Monomer conversion (%)	$R_p\mathrm{x}10^5$ (moles $l^{-1}\mathrm{sec}^{-1}$)	$\overline{M}_n\mathrm{x}10^{-5}$	f
None	2.5	<5.0	-	4.0	1.8	2.98	-
	3.5	<5.0		5.1		2.70	-
	4.5	<5.0		7.1		2.85	-
Co(II)	1.0	20	14	-	1.2	-	-
	2.0	30		1.5		-	-
	3.0	35		2.5		0.482	0.028
	4.5	40		4.7		0.551	0.040
Co(III)	1.0	<5.0	2.6	-	1.8	-	-
	2.0	7.8		2.9		1.28	0.055
	3.0	12		4.6		1.35	0.054
	4.5	18		6.8		1.41	0.051
Mn(II)	2.5	< 5.0	-	4.1	1.8	-	-
	4.0	< 5.0		6.3		2.14	-
	5.0	<5.0		7.5		2.35	-
Mn(III)	2.5	12	3.1	3.9	1.9	0.668	0.093
	4.0	18		6.6		0.779	0.089
	5.0	21		8.3		0.872	0.086
Cu(II)	0.083	45	440	-	6.0	-	-
	0.167	74		-		-	-
	0.33	80		1.1		-	-
	0.83	86		4.6		0.438	0.023
	1.25	92		6.5		0.895	0.015
	1.67	95		8.5		1.12	0.015
Cr(III)	2.5	<5.0	-	3.9	1.9	1.65	-
	3.5	<5.0		5.6		1.69	-
	4.5	<5.0		7.7		1.87	-
Al(III)	4.5	<5.0	-	7.2	1.9	2.52	-
Ni(II)	4.5	<5.0	-	7.5	1.9	2.38	-

TABLE III

Effect of presence of metal acetylacetonates on decomposition of $\underline{t}$-butyl hydroperoxide and polymerization of methyl methacrylate in 1-chlorooctane.

$[MMA] = 4.16\ \underline{M}$, $[TBHP] = 0.022\ \underline{M}$, $[M(AA)_n] = 1.8\text{x}10^{-4}\ \underline{M}$, temperature = 80°C

Metal acetylacetonate	Time (hours)	TBHP decomposition (%)	R_dx10^7 (moles l^{-1} sec^{-1})	Monomer conversion (%)	R_px10^5 (moles l^{-1} sec^{-1})	$\bar{M}_n$x10^{-5}	f
None	0.75	<5.0	1.9	6.4	9.7	2.31	-
	1.17	<5.0		9.9		2.39	-
	1.5	5.2		13		2.32	0.20
Co(II)	0.22	20	61	-	3.8	-	-
	0.58	44		1.1		-	-
	1.08	54		2.4		0.414	0.021
	1.5	59		4.2		0.427	0.031
	2.0	62		5.7		0.474	0.037
Co(III)	0.50	10	13	4.5	9.2	0.961	0.089
	1.08	16		8.4		1.08	0.092
	1.5	21		12		1.16	0.093
Mn(II)	0.75	<5.0	2.0	6.7	9.5	1.75	-
	1.25	<5.0		10		1.75	-
	1.75	6.4		14		1.82	0.22
Mn(III)	0.75	17	15	6.4	9.2	0.466	0.15
	1.25	26		10		0.458	0.16
	1.75	35		14		0.483	0.16
Cu(II)	0.083	90	1700	-	15.3	-	-
	0.17	95		3.3		-	-
	0.45	94		6.1		1.04	0.011
	0.58	95		7.4		1.69	0.0087
	0.83	95		11		2.62	0.0084
Cr(III)	1.0	<5.0	2.0	8.4	9.9	1.35	-
	1.5	5.4		13		1.57	0.29
Al(III)	1.5	5.9	2.2	12	9.2	1.92	0.20
Ni(II)	1.5	5.7	2.0	12	9.5	2.13	0.19

TABLE IV

Effect of presence of metal acetylacetonates on decomposition of *t*-butyl hydroperoxide and polymerization of methyl methacrylate in benzene.

$[MMA] = 4.16\ \underline{M}$, $[TBHP] = 0.022\ \underline{M}$, $[M(AA)_n] = 1.8\times10^{-4}\ \underline{M}$, temperature = 40°C

Metal acetylacetonate	Time (hours)	TBHP decomposition (%)	$R_d\times10^{7}$ (moles $l^{-1}sec^{-1}$)	Monomer conversion	$R_p\times10^{5}$ (moles $l^{-1}sec^{-1}$)	$\bar{M}_n\times10^{-5}$	f
None	8.0	<5.0	-	0.60	0.10	-	-
	12	<5.0		1.1		14.5	-
	15	<5.0		1.3		14.3	-
Co(III)	5.0	<5.0	-	0.64	0.15	-	-
	10	<5.0		1.4		-	-
	15	<5.0		2.0		3.68	-
Co(II)	5.0	31	4.5	-	0.042	-	-
	10	45		-		-	-
	15	52		0.40		-	-
	20	57		0.72		0.654	0.0036
Cu(II)	10	<5.0	-	1.5	0.18	2.15	-
	15	<5.0		2.3		2.33	-

TABLE V

Effect of presence of metal acetylacetonates on decomposition of *t*-butyl hydroperoxide and polymerization of methyl methacrylate in benzene.

$[\mathrm{MMA}] = 4.16\ \underline{M}$, $[\mathrm{TBHP}] = 0.022\ \underline{M}$, $[\mathrm{M(AA)}_n] = 1.8\times10^{-4}\ \underline{M}$, temperature = 60°C

Metal acetylacetonate	Time (hours)	TBHP decomposition (%)	$R_d \times 10^7$ (moles $l^{-1}sec^{-1}$)	Monomer conversion (%)	$R_p \times 10^5$ (moles $l^{-1}sec^{-1}$)	$\bar{M}_n \times 10^{-5}$	f
None	2.0	< 5.0	-	1.2	0.70	-	-
	3.5	< 5.0		1.8		8.78	-
	4.5	< 5.0		2.7		9.07	-
Co(III)	2.0	< 5.0	-	1.4	0.82	-	-
	3.0	< 5.0		2.0		-	-
	3.75	< 5.0		2.7		-	-
	4.5	< 5.0		3.4		2.88	-
Co(II)	0.75	30	29	-	0.17	-	-
	1.5	52		-		-	-
	3.0	65		0.38		-	-
	4.5	72		0.65		0.519	0.0033
Cu(II)	2.0	-	0.78	2.3	1.2	1.43	-
	3.0	<5.0		3.7		1.55	-
	4.5	5.6		4.5		1.69	0.14

TABLE VI

Effect of presence of metal acetylacetonates on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in benzene.

$[\text{MMA}] = 4.16\ \underline{M}$, $[\text{TBHP}] = 0.022\ \underline{M}$, $[\text{M(AA)}_n] = 1.8\text{x}10^{-4}\ \underline{M}$, temperature = 80°C

Metal acetylacetonate	Time (hours)	TBHP decomposition (%)	$R_d\text{x}10^7$ (moles $l^{-1}\text{sec}^{-1}$)	Monomer conversion (%)	$R_p\text{x}10^5$ (moles $l^{-1}\text{sec}^{-1}$)	$\bar{M}_n\text{x}10^{-5}$	f
None	0.75	<5.0	-	2.2	3.7	-	-
	1.25	<5.0		4.3		5.87	-
	1.75	<5.0		5.7		6.08	-
Co(III)	0.75	<5.0	2.1	2.3	3.5	-	-
	1.25	<5.0		3.8		-	-
	1.75	5.8		5.3		2.30	0.075
Co(II)	0.17	20	82	-	1.2	-	-
	0.33	38		-			
	0.67	55		-			
	1.0	60		0.85			
	1.75	66		1.84		0.476	0.011
Cu(II)	1.0	5.3	3.3	4.3	5.0	0.814	0.19
	1.5	7.3		6.5		0.895	0.19

TABLE VII

Effect of presence of copper(II) acetylacetonate on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in DMSO.

[MMA] = 4.16 M, [TBHP] = 0.022 M, temperature = 40°C

[Cu(AA)$_2$] (moles l^{-1})x10^4	Time (hours)	TBHP decomposition (%)	R$_d$x10^7 (moles l^{-1}sec^{-1})	Monomer conversion (%)	R$_p$x10^5 (moles l^{-1}sec^{-1})	$\overline{M}_n$x10^{-5}	f
0	10	< 5.0	-	2.6	0.30	16.4	-
	12	< 5.0		3.1		15.9	-
	15	< 5.0		3.7		18.4	-
	18	< 5.0		4.8		19.8	-
1.8	1.0	5.1	3.0	-	3.3	-	-
	2.0	8.8		5.7		1.73	0.0708
	3.0	13		8.5		1.85	0.0668
	4.0	17		11		1.98	0.0629

TABLE VIII

Effect of presence of copper(II) acetylacetonate on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in DMSO.

[MMA] = 4.16 M, [TBHP] = 0.022 M, temperature = 60°C

[Cu(AA)$_2$] (moles l^{-1})x10^4	Time (hours)	TBHP decompOsition (%)	R$_d$x10^7 (moles l^{-1}sec^{-1})	Monomer conversion (%)	R$_p$x10^5 (moles l^{-1}sec^{-1})	$\overline{M}_n$x10^{-5}	f
0	2.0	5.0	-	3.3	1.9	9.67	-
	3.0	5.0		4.9		9.81	-
	4.0	5.0		6.5		10.8	-
1.8	0.33	6.9	13.1	3.9	13	1.16	0.091
	0.50	10		5.7		1.25	0.087
	0.75	15		8.5		1.31	0.082
	1.0	19		11		1.36	0.080

TABLE IX

Effect of presence of copper(II) acetylacetonate on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in DMSO.

[MMA] = 4.16 M, [TBHP] = 0.022 M, temperature = 80°C

$[Cu(AA)_2]$ (moles l^{-1})$\times 10^4$	Time (hours)	TBHP decomposition (%)	$R_d \times 10^7$ (moles $l^{-1}sec^{-1}$)	Monomer conversion (%)	$R_p \times 10^5$ (moles $l^{-1}sec^{-1}$)	$M_n \times 10^{-5}$	f
0	0.5	<5.0	-	4.5	10	3.75	-
	1.0	<5.0		8.6		4.08	-
	1.5	-		13		3.95	-
1.8	0.083	15	66	-	39	-	-
	0.167	28		5.5		0.341	0.109
	0.25	35		8.4		0.333	0.136
	0.50	45		18		0.452	0.167
	0.60	48		22		0.515	0.168

TABLE X

Effect of presence of cobalt(II) and cobalt(III) acetylacetonates on t-butyl hydroperoxide initiated polymerization of methyl methacrylate in DMSO.

[MMA] = 4.16 M, [TBHP] = 0.022 M, $[M(AA)_n] = 1.8 \times 10^{-4}$ M

Metal acetylacetonate	Temperature = 40°C			Temperature = 60°C			Temperature = 80°C		
	Time (hours)	Monomer conversion(%)	$R_p \times 10^5$ $\left(\frac{\text{moles}}{\text{l sec}}\right)$	Time (hours)	Monomer conversion(%)	$R_p \times 10^5$ $\left(\frac{\text{moles}}{\text{l sec}}\right)$	Time (hours)	Monomer conversion(%)	$R_p \times 10^5$ $\left(\frac{\text{moles}}{\text{l sec}}\right)$
None*			0.30			1.9			10
Co(II)**	9.0	7.0	0.85	1.0	3.8	5.3	0.33	6.5	17
	15	11		2.0	11		0.67	9.9	
	21	15		2.5	12		1.0	13	
				3.0	14				
Co(III)**	15	7.0	0.51	0.47	0.93	3.2	0.33	3.3	12.5
	17	7.4		0.67	2.2		1.0	11	
	19	8.4		1.0	3.2		2.0	22	
	21	9.4		3.0	8.2				

* Data from Tables VII - IX.

** Unpublished data of H. J. Yan (253)

TABLE XI

Effect of presence of metal acetylacetonates on decomposition of t-butyl hydroperoxide.

$[\text{TBHP}] = 0.022\ \underline{M}$, $[\text{M(AA)}_n] = 1.8\text{x}10^{-4}$

Metal acetylacetonate	Solvent	Temperature = 40°C			Temperature = 60°C			Temperature = 80°C		
		Time (hours)	TBHP decomposition (%)	$R_d\text{x}10^7$ (moles $l^{-1}\ sec^{-1}$)	Time (hours)	TBHP decomposition (%)	$R_d\text{x}10^7$ (moles $l^{-1}\ sec^{-1}$)	Time (hours)	TBHP decomposition (%)	$R_d\text{x}10^7$ (moles $l^{-1}\ sec^{-1}$)
Co(II)	a	1.0	25	18	0.17	33	150	0.083	49	500
		3.0	48		0.50	43		0.167	78	
		6.0	60		1.0	50		0.50	92	
Co(III)	a	5.0	25	3.5	0.75	23	21	0.25	33	98
		8.0	35		1.5	40		1.0	77	
Co(II)	b	1.0	46	38	0.10	44	350	0.083	74	990
		3.0	80		0.17	62		0.17	87	
		5.0	85		0.33	76		0.50	95	
					0.67	86				
					1.0	90				
					1.7	95				
Co(III)	b	15	5.2	0.22	1.5	<5.0	0.65	1.33	<5.0	1.3
					3.0	5.2		2.17	5.2	
Cu(II)	c	5.0	<5.0	0.51	0.50	5.1	5.5	0.25	15	41.
		7.0	5.7		1.0	9.0		0.5	29	
		10	8.0		1.5	13		0.75	38	
		14	11		2.0	16		1.0	48	
					3.0	19				

a: 1-chlorooctane, b: benzene, c: DMSO

TABLE XIIA

Rates of hydroperoxide decomposition and rate constants

$[M(AA)_n] = 1.8\times10^{-4}$ M, $[TBHP] = 0.022$ M

Metal	Solvent	$[MMA]$ (moles/l)	$R_d\times10^7$ (moles l^{-1} sec^{-1})			Rate law	k_d^* (l $mole^{-1}$ sec^{-1})		
			40°	60°	80°		40°	60°	80°
Co(II)	a	4.16	2.1	14	61	p	0.053	0.35	1.5
Co(III)	a	4.16	0.38	2.6	13	p	0.0096	0.066	0.33
Mn(III)	a	4.16	0.61	3.1	15	p	0.015	0.078	0.38
Cu(II)	a	4.16	140	440	1700	p	3.5	11	43
Cu(II)	a	4.16	140	440	1700	q	0.0022	0.0069	0.027
Co(II)	a	0	18	150	990	p	0.45	3.8	12
Co(III)	a	0	3.5	21	98	p	0.088	0.53	2.5
Co(II)	b	4.16	4.5	29	82	p	0.11	0.73	2.1
Cu(II)	b	4.16	0.18	1.2	3.3	p	0.0045	0.30	0.083
Co(II)	b	0	38	350	990	p	0.96	8.8	25
Cu(II)	c	4.16	3	13	66	p	0.078	0.33	1.7
Cu(II)	c	4.16	3	13	66	r	0.0052	0.023	0.12
Cu(II)	c	0	0.51	5.5	41	p	0.013	0.14	1.0

a: 1-chlorooctane

b: benzene

c: DMSO

p: $R_d = k_d[Metal][TBHP]$

q: $R_d = k_d[Metal]^{0.32}[TBHP]^{0.60}$

r: $R_d = k_d[Metal]^{0.69}[TBHP]$

* Units shown correspond to rate expression 'p'. For expressions 'q' and 'r', units are $moles^{0.08}l^{-0.08}sec^{-1}$ and $l^{0.69}mole^{-0.69}sec^{-1}$, respectively.

TABLE XIIB

Rates of polymerization of methyl methacrylate and rate constants

$[M(AA)_n] = 1.8\times10^{-4}$ $\underline{M}$, $[TBHP] = 0.022$ $\underline{M}$, $[MMA] = 4.16$ $\underline{M}$

Metal	Solvent	$R_p\times10^5$ (moles l^{-1} sec^{-1})			Rate law	$k_p^*\times10^5$ (l $mole^{-1}$ sec^{-1})		
		40°	60°	80°		40°	60°	80°
None	a	0.32	1.8	9.7	v	0.52	2.9	16
Co(II)	a	0.22	1.2	3.8	z	—	—	—
Co(III)	a	0.29	1.8	9.2	v	0.47	2.9	15
Mn(II)	a	0.29	1.8	9.5	v	0.47	2.9	15
Mn(III)	a	0.35	1.9	9.2	v	0.57	3.1	15
Cu(II)	a	1.6	6.0	15	w	190	730	1800
Cu(II)	a	1.6	6.0	15	x	10	39	97
Al(III)	a	0.31	1.9	9.2	v	0.50	3.1	15
Cr(III)	a	0.31	1.9	9.9	v	0.50	3.1	16
Ni(II)	a	0.29	1.9	9.5	v	0.47	3.1	15
None	b	0.11	0.75	3.7	v	0.18	1.2	6.0
Co(II)	b	0.042	0.17	1.2	z	—	—	—
Co(III)	b	0.14	0.82	3.5	v	0.23	1.3	5.7
Cu(II)	b	0.18	1.2	5.0	w	22	150	600
None	c	0.30	1.9	10	v	0.49	3.1	16
Co(II)	c	0.85	5.3	17	w	100	640	2100
Co(III)	c	0.51	3.2	13	w	62	390	1600
Cu(II)	c	3.3	13	39	w	400	1600	4700
Cu(II)	c	3.3	13	39	y	110	430	1300

a: 1-chlorooctane, b: benzene, c: DMSO,

v: $R_p = k_p[TBHP]^{\frac{1}{2}}[MMA]$, w: $R_p = k_p[Metal]^{\frac{1}{2}}[TBHP]^{\frac{1}{2}}[MMA]$,

x: $R_p = k_p[Metal]^{0.18}[TBHP]^{0.29}[MMA]$, y: $R_p = k_p[Metal]^{0.36}[TBHP]^{0.50}[MMA]$

z: Because of the observed retardation, any assumption regarding a rate law would be unwarranted.

* Units shown correspond to rate expression 'w'. For expressions 'v', 'x' and 'y' units are $l^{0.5}mole^{-0.5}sec^{-1}$, $l^{0.47}mole^{-0.47}sec^{-1}$, and $l^{0.86}mole^{-0.86}sec^{-1}$, respectively.

TABLE XIIC

Activation parameters for decomposition of hydroperoxide and polymerization of methyl methacrylate

$[M(AA)_n] = 1.8x10^{-4}$ M, $[TBHP] = 0.022$ M, $[MMA] = 4.16$ M

Metal	Solvent	E_d (kcal $mole^{-1}$)	Log A_d	$(E_a)_{calc}$ (kcal $mole^{-1}$)	$(E_a)_{obs}$ (kcal $mole^{-1}$)	Log A
None	a	$(39.0)^e$	-	24.2	19.5	8.183
Co(II)	a	18.8	11.808	14.1	18.8	–
Co(III)	a	19.6	11.605	14.5	19.2	7.987
Mn(II)	a	-	-	-	19.4	8.117
Mn(III)	a	18.1	10.699	13.8	18.1	7.298
Cu(II)	a	11.8	8.739	10.6	12.1	5.753
Cr(III)	a	-	-	-	19.6	7.294
Al(III)	a	-	-	-	19.2	8.016
Ni(II)	a	-	-	-	19.6	7.294
$Co(II)^d$	a	16.6	11.408			
$Co(III)^d$	a	15.4	9.770			
None	b	$(40.8)^f$	-	25.1	19.5	7.799
Co(II)	b	17.4	11.214	13.4	18.4	-
Co(III)	b	-	-	-	17.7	6.655
Cu(II)	b	17.7	10.023	13.6	18.1	8.968
$Co(II)^d$	b	18.4	12.947			
None	c	-	-	-	19.0	7.885
$Co(II)^g$	c	-	-	-	15.4	7.852
$Co(III)^g$	c	-	-	-	16.8	8.547
Cu(II)	c	16.3	11.747	12.9	13.8	7.198
$Cu(II)^d$	c	21.0	12.845			

a: 1-chlorooctane, b: benzene, c: DMSO, d: in absence of monomer, e: data from reference (237), f: data from reference (238), g: data from reference (253).

TABLE XIID

Enthalpy and entropy of activation for decomposition of hydroperoxide and polymerization of methyl methacrylate at 40°C.

$[M(AA)_n] = 1.8x10^{-4}\ \underline{M}$, $[TBHP] = 0.022\ \underline{M}$, $[MMA] = 4.16\ \underline{M}$

Metal	Solvent	$\Delta H_d^{\ddagger}$ (kcal mole^{-1})	$\Delta S_d^{\ddagger}$ (cal deg^{-1} mole^{-1})	$\Delta H_p^{\ddagger}$ (kcal mole^{-1})	$\Delta S_p^{\ddagger}$ (cal deg^{-1} mole^{-1})
None	a	-	-	18.9	-24.5
Co(II)	a	18.2	-8.40	18.2	-
Co(III)	a	19.0	-9.24	18.6	-25.7
Mn(II)	a	-	-	18.6	-25.7
Mn(III)	a	17.5	-13.1	17.5	-28.8
Cu(II)[e]	a	11.2	-22.4	11.6	-13.2
Cu(II)[f]	a	11.2	-37.1	11.6	-19.1
Cr(III)	a	-	-	19.0	-24.3
Al(III)	a	-	-	18.6	-25.6
Ni(II)	a	-	-	19.0	-24.4
Co(II)[d]	a	16.0	-11.8	-	-
Co(III)[d]	a	14.8	-18.3	-	-
None	b	-	-	18.9	-26.6
Co(II)	b	16.8	-11.4	17.8	-
Co(III)	b	-	-	17.1	-31.9
Cu(II)	b	17.1	-16.8	17.5	-26.1
Co(II)[d]	b	17.8	-3.91	-	-
None	c	-	-	18.4	-26.2
Co(II)	c	-	-	14.8	-27.1
Co(III)	c	-	-	16.2	-23.6
Cu(II)[e]	c	15.7	-15.6	13.2	-29.5
Cu(II)[g]	c	15.7	-21.0	13.2	-32.1
Cu(II)[d]	c	20.4	-4.17	-	-

a: 1-chlorooctane, b: benzene, c: DMSO, d: in absence of monomer, e: calculation based on rate expressions p and w in Tables XII A and B, respectively; f: calculation based on rate expressions q and x in Tables XII A and B, respectively; g: calculation based on rate expressions r and y in Tables XII A and B, respectively.

TABLE XIII

Effect of concentration of copper(II) acetylacetonate on decomposition of <u>t</u>-butyl hydroperoxide and polymerization of methyl methacrylate in 1-chlorooctane at 60°C

$[MMA] = 4.16\ \underline{M}$, $[TBHP] = 0.022\ \underline{M}$

$[Cu(II)]$ (moles l^{-1})$\times10^4$	Time (hours)	TBHP decomposition (%)	$R_d\times10^6$ (moles l^{-1} sec^{-1})	Monomer conversion (%)	$R_p\times10^5$ (moles l^{-1} sec^{-1})	$\bar{M}_n\times10^{-5}$	f
0	2.5	< 5.0	-	4.0	1.8	2.61	-
	3.5	< 5.0		5.1		2.70	-
	4.5	< 5.0		7.1		2.85	-
0.90	0.083	40	37	-	5.5	-	-
	0.167	62		-		-	-
	1.0	84		4.8		0.425	0.025
	1.5	90		7.1		0.934	0.016
	2.0	94		9.5		1.17	0.016
1.80	0.083	45	44	-	6.0	-	-
	0.17	74		-		-	-
	0.33	80		1.1		-	-
	0.83	86		4.6		0.438	0.023
	1.25	92		6.5		0.895	0.015
	1.67	95		8.5		1.12	0.015
3.60	0.083	51	52	-	6.5	-	-
	0.17	73		-		-	-
	1.0	89		5.6		0.629	0.019
	1.5	94		8.4		1.22	0.014
	2.0	-		11		1.85	-
7.20	0.083	60	67	-	7.2	-	-
	0.17	73		-		-	-
	0.25	82		1.6		0.327	0.011
	1.0	92		6.3		0.834	0.015
	1.5	95		9.0		1.40	0.013

TABLE XIV

Effect of concentration of t-butyl hydroperoxide on its decomposition and polymerization of methyl methacrylate in 1-chlorooctane at 60°C.

[MMA] = 4.16 M

[Cu(II)] (moles l^{-1})x10^4	Time (hours)	TBHP decomposition (%)	R_dx10^6 (moles l^{-1} sec^{-1})	Monomer conversion (%)	R_px10^5 (moles l^{-1} sec^{-1})	$\bar{M}_n$x10^{-5}	f
[TBHP] = 0.011 M							
0	3.0	< 5.0	-	3.1	1.2	-	-
	4.0	< 5.0		4.3		-	-
	6.0	< 5.0		5.8		-	-
1.80	0.083	55	29	-	4.6	-	-
	0.17	78		-		-	-
	0.33	84		1.4		0.551	0.011
	1.0	90		4.0		1.36	0.012
	1.5	95		5.8		1.91	0.012
[TBHP] = 0.022 M							
0			-		1.8		
1.80			44		6.0		
(Detailed data at these concentrations shown in Table XIII)							
[TBHP] = 0.044 M							
0	2.0	<5.0	-	4.3	2.5	-	-
	3.0	<5.0		6.3		-	-
	4.0	<5.0		8.5		-	-
1.80	0.083	37	66	-	7.6	-	-
	0.17	59		-		-	-
	0.25	70		-		-	-
	0.50	84		3.3		0.329	0.011
	1.0	90		6.6		0.447	0.015
	1.5	92		10		0.586	0.018

TABLE XV

Effect of concentration of methyl methacrylate on its polymerization and decomposition of *t*-butyl hydroperoxide in 1-chlorooctane at 60°C.

[TBHP] = 0.022 M

[Cu(II)] (moles l^{-1})x10^4	Time (hours)	TBHP decomposition (%)	R_dx10^6 (moles $l^{-1}sec^{-1}$)	Monomer conversion (%)	R_px10^5 (moles $l^{-1}sec^{-1}$)	$\overline{M}_n$x10^{-5}	f
			[MMA] = 3.12 M				
0	3.0	<5.0	-	4.7	1.4	-	-
	4.0	<5.0		6.5		-	-
	6.0	<5.0		9.9		-	-
1.80	0.083	50	51	-	4.7	-	-
	0.17	65		-		-	-
	0.25	74		-		-	-
	0.50	82		2.8		0.518	0.0092
	1.0	90		5.4		0.957	0.0089
	1.5	-		8.0		-	-
			[MMA] = 4.16 M				
0			-		1.8		
1.80			44		6.0		
(Detailed data at these concentrations shown in Table XIII)							
			[MMA] = 5.20 M				
0	2.0	<5.0	-	3.2	2.3	-	-
	3.0	<5.0		4.8		-	-
	4.0	<5.0		6.4		-	-
1.80	0.083	41	39	-	7.3	-	-
	0.17	62		-		-	-
	0.25	73		1.3		0.328	0.013
	0.50	89		2.5		0.417	0.016
	1.0	93		5.1		0.605	0.021
	1.5	-		7.7		-	-

TABLE XVI

Rates of polymerization of methyl methacrylate and decomposition of t-butyl hydroperoxide in 1-chlorooctane at 60°C.

[Cu(II)] (moles/l) $\times 10^4$	[TBHP] (moles/l)	[MMA] (moles/l)	$R_d \times 10^6$ (moles l^{-1} sec^{-1})	$R_p \times 10^5$ (moles l^{-1} sec^{-1})	$R_p^o \times 10^5$ (moles l^{-1} sec^{-1})	$(R_p - R_p^o) \times 10^5$ (moles l^{-1} sec^{-1})
0	0.022	4.16	-		1.8	
0.90	0.022	4.16	37	5.5		3.7
1.8	0.022	4.16	44	6.0		4.2
3.6	0.022	4.16	52	6.5		4.7
7.2	0.022	4.16	67	7.2		5.4
0	0.011	4.16	-		1.2	
1.8	0.011	4.16	29	4.6		3.4
0	0.022	4.16	-		1.8	
1.8	0.022	4.16	44	6.0		4.2
0	0.044	4.16	-		2.5	
1.8	0.044	4.16	66	7.6		5.1
0	0.022	3.12	-		1.4	
1.8	0.022	3.12	51	4.7		3.3
0	0.022	4.16	-		1.8	
1.8	0.022	4.16	44	6.0		4.2
0	0.022	5.20	-		2.3	
1.8	0.022	5.20	39	7.3		5.0

TABLE XVII

Effect of concentration of copper(II) acetylacetonate on decomposition of t-butyl hydroperoxide and polymerization of methyl methacrylate in DMSO at 60°C.

$[\mathrm{MMA}] = 4.16\ \underline{M}$, $[\mathrm{TBHP}] = 0.022\ \underline{M}$

$[\mathrm{Cu(II)}]$ (moles/l) $\mathrm{x}10^4$	Time (hours)	TBHP decomposition (%)	$R_d\mathrm{x}10^6$ (moles $l^{-1}\mathrm{sec}^{-1}$)	Monomer conversion (%)	$R_p\mathrm{x}10^5$ (moles $l^{-1}\mathrm{sec}^{-1}$)	$M_n\mathrm{x}10^{-5}$	f
0	2.0	<5.0	-	3.3	1.9	9.67	-
	3.0	<5.0		4.9		9.81	-
	4.0	<5.0		6.5		10.8	-
0.018	1.0	<5.0	-	3.6	4.1	5.51	-
	2.0	<5.0		7.0		6.87	-
	3.0	<5.0		11		6.33	-
0.18	0.50	-	0.27	2.8	6.7	3.88	-
	1.0	<5.0		5.8		4.22	-
	1.5	6.6		9.0		4.78	0.054
	2.0	8.1		12		4.63	0.061
0.54	0.50	4.7	0.59	4.1		2.17	0.076
	1.0	9.2		8.8		2.29	0.079
	1.5	13		13		2.38	0.080
1.8	0.33	6.9	1.3	3.9	13	1.16	0.091
	0.50	10		5.7		1.25	0.087
	0.75	15		8.5		1.31	0.082
	1.0	19		11		1.36	0.080
9.0	0.25	14	4.1	3.6	17	-	-
	0.33	20		5.0		0.628	0.070
	0.50	26		7.3		0.682	0.079
	0.75	37		11		0.720	0.079
18	0.17	16	6.6	-	19	-	-
	0.25	24		4.3		0.452	0.076
	0.50	41		8.1		0.534	0.070
	0.75	51		12		0.589	0.076

TABLE XVIII

Effect of concentration of t-butyl hydroperoxide on its decomposition and polymerization of methyl methacrylate in DMSO at 60°C.

[MMA] = 4.16 M

[Cu(II)] (moles l^{-1})x10^4	Time (hours)	TBHP decomposition (%)	R_dx10^6 (moles $l^{-1}sec^{-1}$)	Monomer conversion (%)	R_px10^5 (moles $l^{-1}sec^{-1}$)	M_nx10^{-5}	f
			[TBHP] = 0.0044 M				
0	4.0	-	-	2.9	0.83	14.4	-
	5.0	-		3.6		16.0	-
	6.0	-		4.3		16.5	-
1.8	0.5	-	-	2.5	5.8	2.22	-
	1.0	-		5.1		2.39	-
	1.5	-		7.4		2.57	-
	2.0	-		11		2.65	-
			[TBHP] = 0.011 M				
0	3.0	< 5.0	-	3.4	1.3	-	-
	5.0	< 5.0		5.5		-	-
	7.0	< 5.0		8.4		-	-
1.8	0.50	9.6	0.62	4.4	8.9	1.63	0.11
	0.75	14		6.7		1.77	0.10
	1.0	18		9.5		1.81	0.11
			[TBHP] = 0.022 M				
0	-	-	-	-	1.9	-	-
1.8	-	-	1.3	-	13	-	-
	(Detailed data at these concentrations shown in Table XVII)						
			[TBHP] = 0.044 M				
0	2.0	-	-	4.5	2.6	-	-
	3.0	-		6.4		-	-
	4.0	-		9.0		-	-
1.8	0.17	3.7	2.7	-	19	-	-
	0.50	11		8.0		0.691	0.10
	0.75	15		12		0.796	0.10
	1.0	18		16		0.747	0.10

TABLE XIX

Effect of concentration of methyl methacrylate on its polymerization and decomposition of $\underline{t}$-butyl hydroperoxide in DMSO at 60°C.

$[\mathrm{TBHP}] = 0.022\ \underline{M}$

$[\mathrm{Cu(II)}]$ (moles l^{-1})x10^4	Time (hours)	TBHP decomposition (%)	R_dx10^6 (moles l^{-1} sec^{-1})	Monomer conversion (%)	R_px10^5 (moles l^{-1} sec^{-1})	$\overline{M}_n$x10^{-5}	f
			$[\mathrm{MMA}] = 2.08\ \underline{M}$				
0	4.0	< 5.0	-	6.9	1.0	-	-
	6.0	< 5.0		11		-	-
	8.0	< 5.0		14		-	-
1.8	0.5	5.2	0.63	4.3	5.1	-	-
	1.0	9.9		8.9		1.53	0.055
	1.5	15		14		1.66	0.052
			$[\mathrm{MMA}] = 4.16\ \underline{M}$				
0	-	-	-	-	1.9	-	-
1.8	-	-	1.3	-	13	-	-
	(Detailed data at these concentrations shown in Table XVII)						
			$[\mathrm{MMA}] = 6.24\ \underline{M}$				
0	2.0	-	-	3.3	2.9	-	-
	3.0	-		5.0		-	-
	4.0	-		6.7		-	-
1.8	0.25	8.0	2.0	3.0	23	0.747	0.14
	0.50	15		6.5		0.812	0.13
	0.75	21		10		0.825	0.14

TABLE XX

Rates of polymerization of methyl methacrylate and decomposition of t-butyl hydroperoxide in DMSO at 60°C.

$[Cu(II)]$ (moles/l) x10^4	$[TBHP]$ (moles/l)	$[MMA]$ (moles/l)	R_dx10^6 (moles $l^{-1}sec^{-1}$)	R_px10^5 (moles $l^{-1}sec^{-1}$)	R_p^ox10^5 (moles $l^{-1}sec^{-1}$)	$(R_p - R_p^o)$x10^5 (moles $l^{-1}sec^{-1}$)
0	0.022	4.16	-		1.9	
0.018	0.022	4.16	-	4.1		2.2
0.18	0.022	4.16	0.27	6.7		4.8
0.54	0.022	4.16	0.59	9.9		8.0
1.8	0.022	4.16	1.3	13		11
9.0	0.022	4.16	4.1	17		15
18	0.022	4.16	6.6	19		17
0	0.0044	4.16	-		0.83	
1.8	0.0044	4.16	-	5.8		5.0
0	0.011	4.16	-		1.3	
1.8	0.011	4.16	0.62	8.9		7.6
0	0.022	4.16	-		1.9	
1.8	0.022	4.16	1.3	13		11
0	0.044	4.16	-		2.6	
1.8	0.044	4.16	2.7	19		16
0	0.022	2.08	-		1.0	
1.8	0.022	2.08	0.63	5.1		4.1
0	0.022	4.16	-		1.9	
1.8	0.022	4.16	1.3	13		11
0	0.022	6.24	-		2.9	
1.8	0.022	6.24	2.0	23		20

TABLE XXI

Chain transfer constants of some metal acetylacetonates in the polymerization of methyl methacrylate

Metal	Chain transfer constant, C_s, at			Chain transfer constant per ligand, C_s', at		
	60°	70°	80°	60°	70°	80°
Co(II)	0.162	0.210	0.264	0.0810	0.105	0.132
Co(III)	0.621	0.699	0.810	0.207	0.233	0.270
Mn(II)	0.510	0.610	0.705	0.255	0.305	0.353
Mn(III)	0.211	0.261	0.322	0.0703	0.0870	0.107
Cu(II)	0.288	0.358	0.426	0.144	0.179	0.213
Cr(III)	0.369	0.448	0.549	0.123	0.149	0.183
Al(III)	0.0292	0.0401	0.0549	0.0097	0.0133	0.0183
Ni(II)	0.109	0.150	0.200	0.055	0.075	0.100

TABLE XXII

Activation parameters for chain transfer to metal acetylacetonates in polymerization of methyl methacrylate

Metal	$E_{tr} - E_p$ (kcal/mole)	$\log(A_{tr}/A_p)$
Co(II)	5.96	2.789
Co(III)	2.96	1.245
Mn(II)	3.53	1.715
Mn(III)	4.99	2.097
Cu(II)	4.79	2.284
Cr(III)	4.76	2.191
Al(III)	7.43	3.189
Ni(II)	7.06	3.343

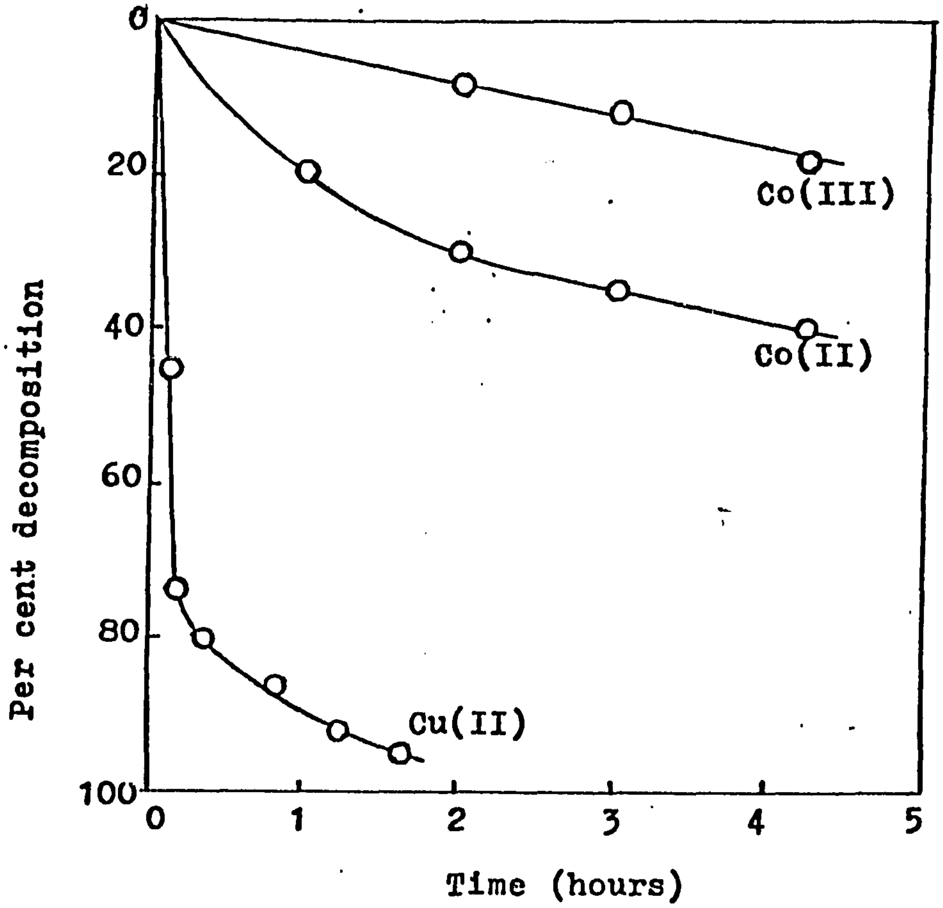


Figure 1: t-Butyl hydroperoxide decomposition in metal catalyzed polymerization of methyl methacrylate in 1-chlorooctane at 60°

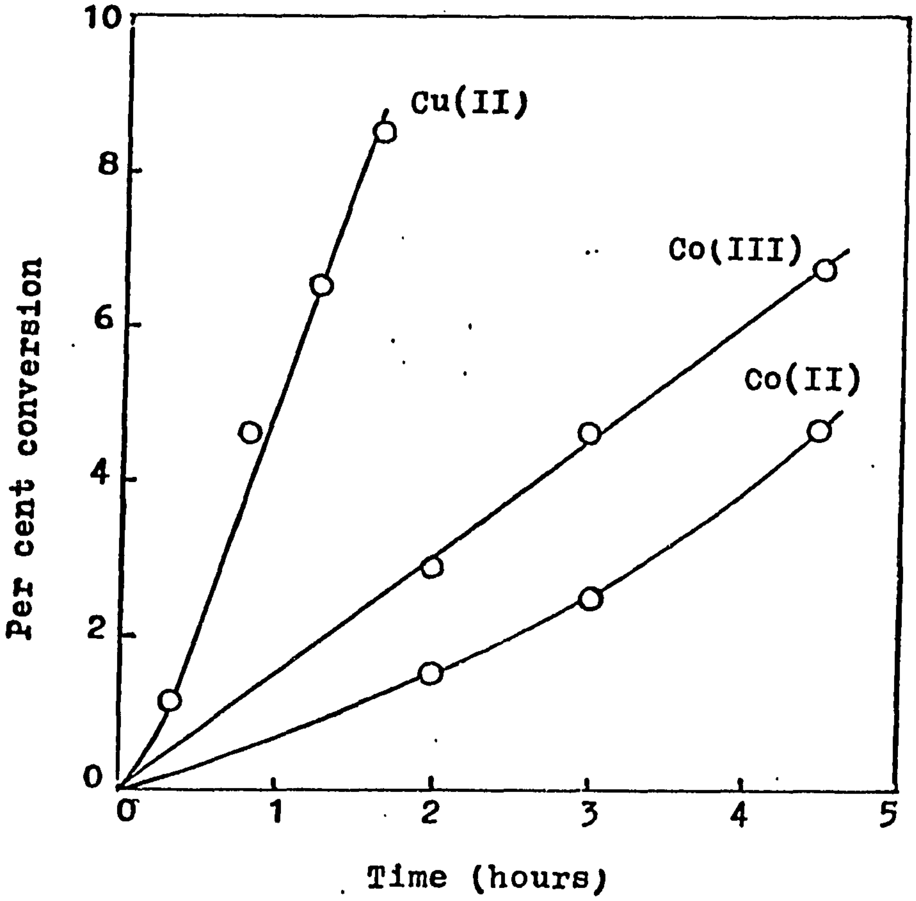


Figure 2: Polymerization of methyl methacrylate in 1-chlorooctane at 60°.

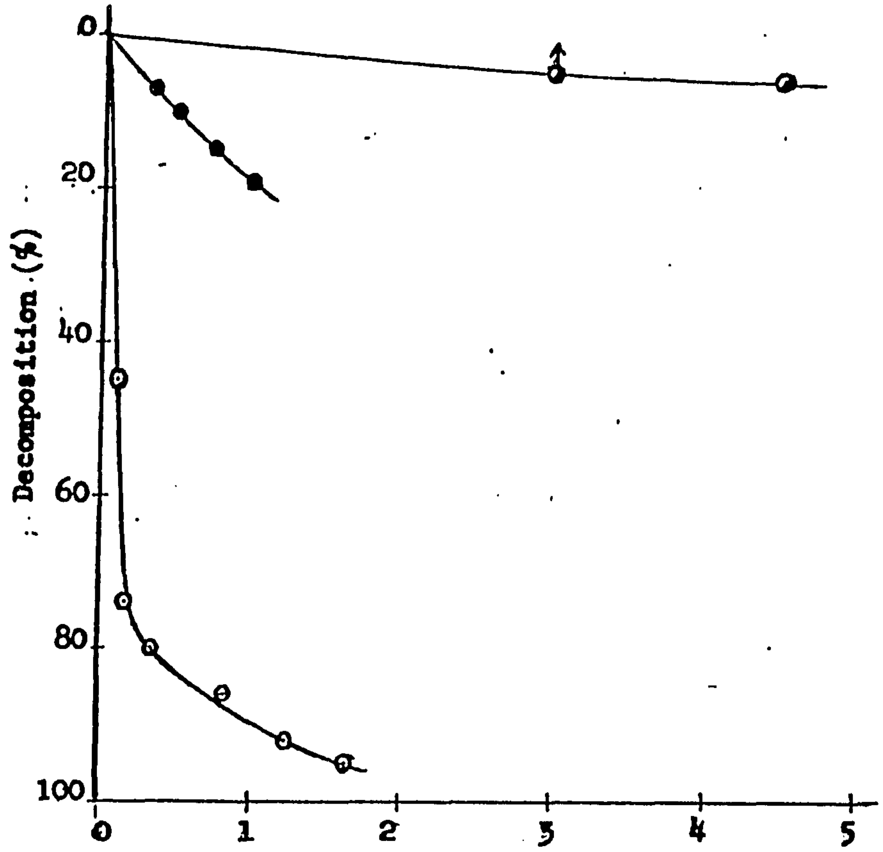


Figure 3: Decomposition of TBHP catalyzed by Cu(AA)$_2$ at 60°

$[\mathrm{Cu(AA)_2}] = 1.8\times10^{-4}$ M, [TBHP] = 0.022 M, [MMA] = 4.16 M

○ : 1-chlorooctane, ⊘ : benzene, ● : DMSO

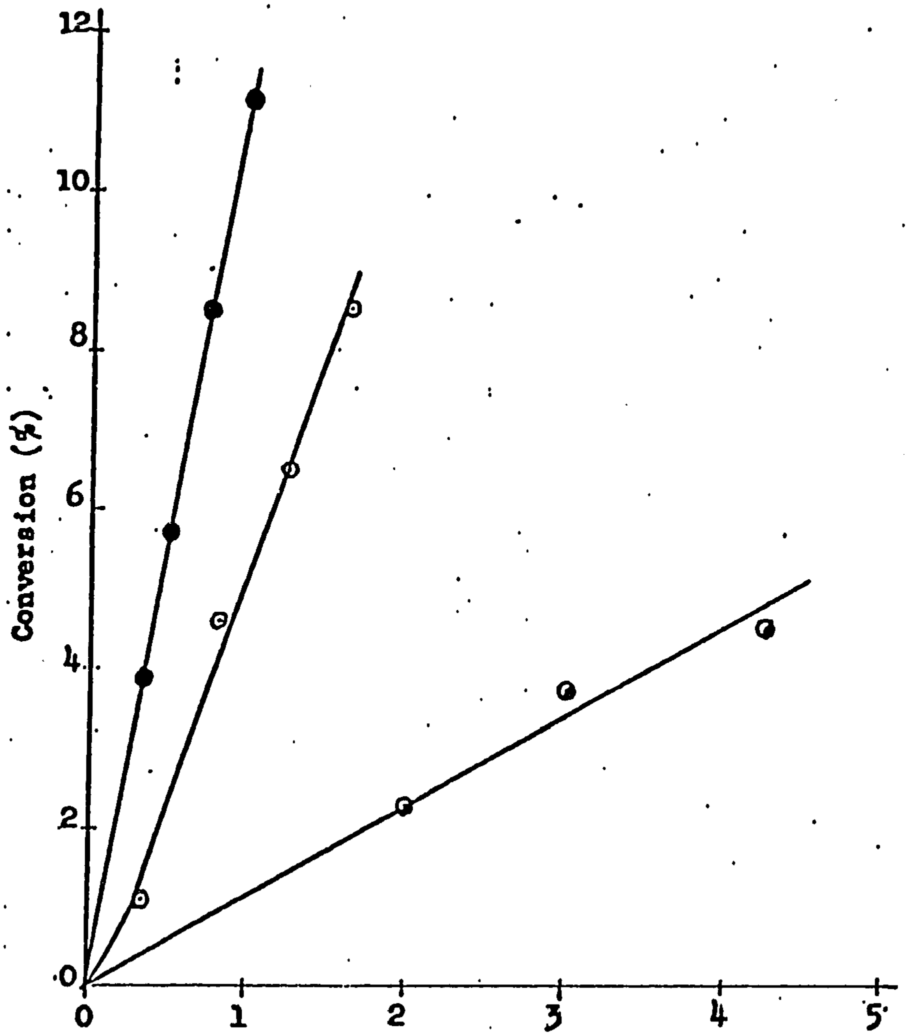


Figure 4: Polymerization of MMA initiated by TBHP in presence of $Cu(AA)_2$ at 60°.

$[Cu(AA)_2]$ = 1.8x10^{-4} M, [TBHP] = 0.022 M, [MMA] = 4.16 M

○: 1-chlorooctane, ◐: benzene, ●:DMSO

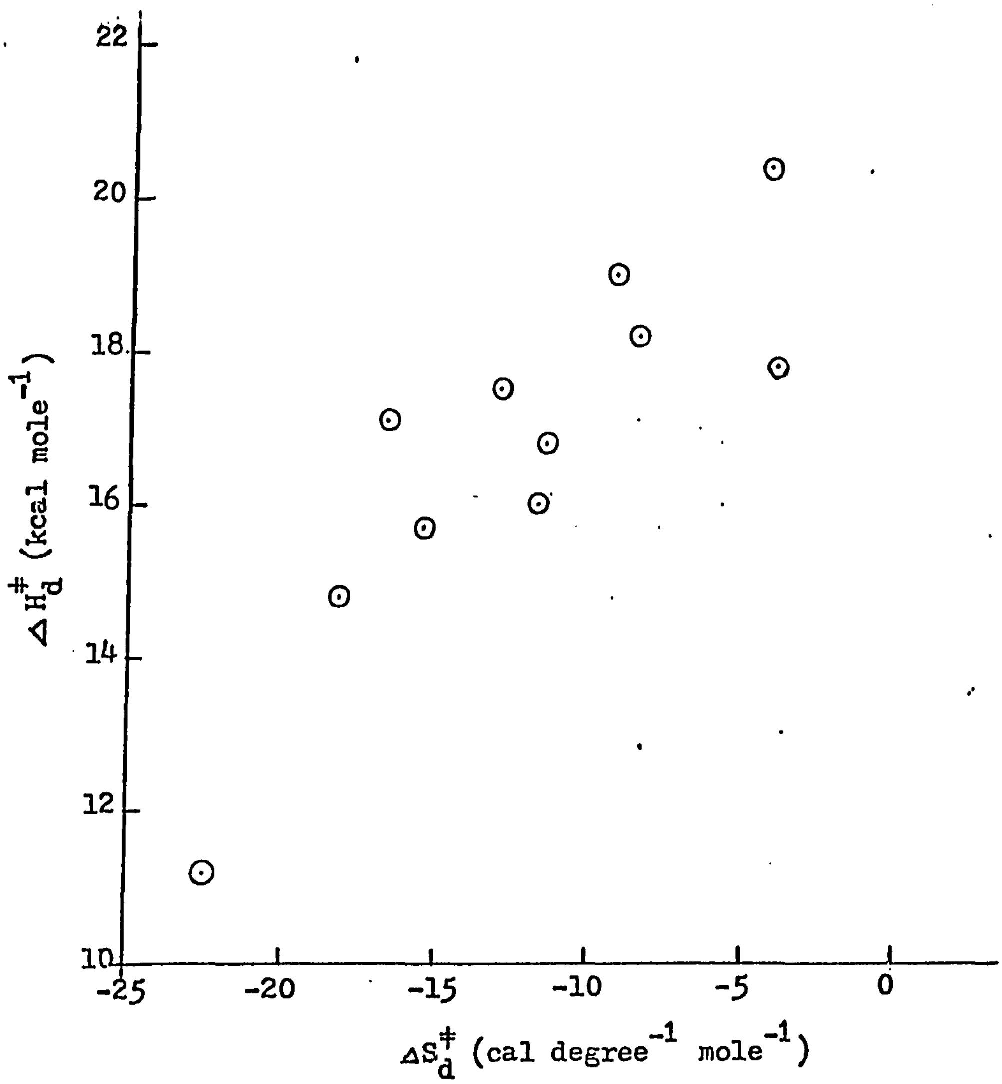


Figure 5: Isokinetic plot for decomposition of t-butyl hydroperoxide

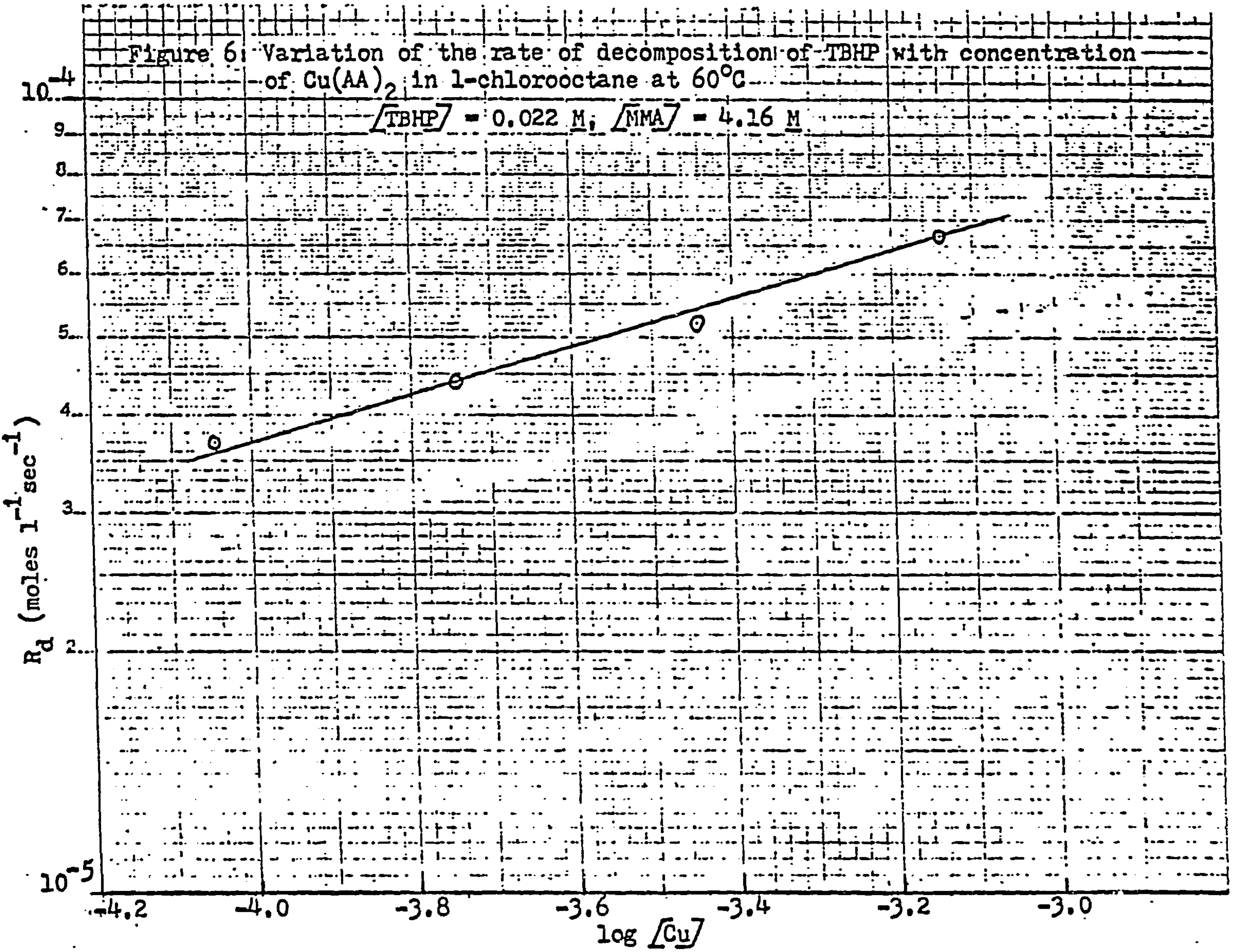


Figure 6: Variation of the rate of decomposition of TBHP with concentration of $Cu(AA)_2$ in 1-chlorooctane at 60°C

[TBHP] = 0.022 M; [MMA] = 4.16 M

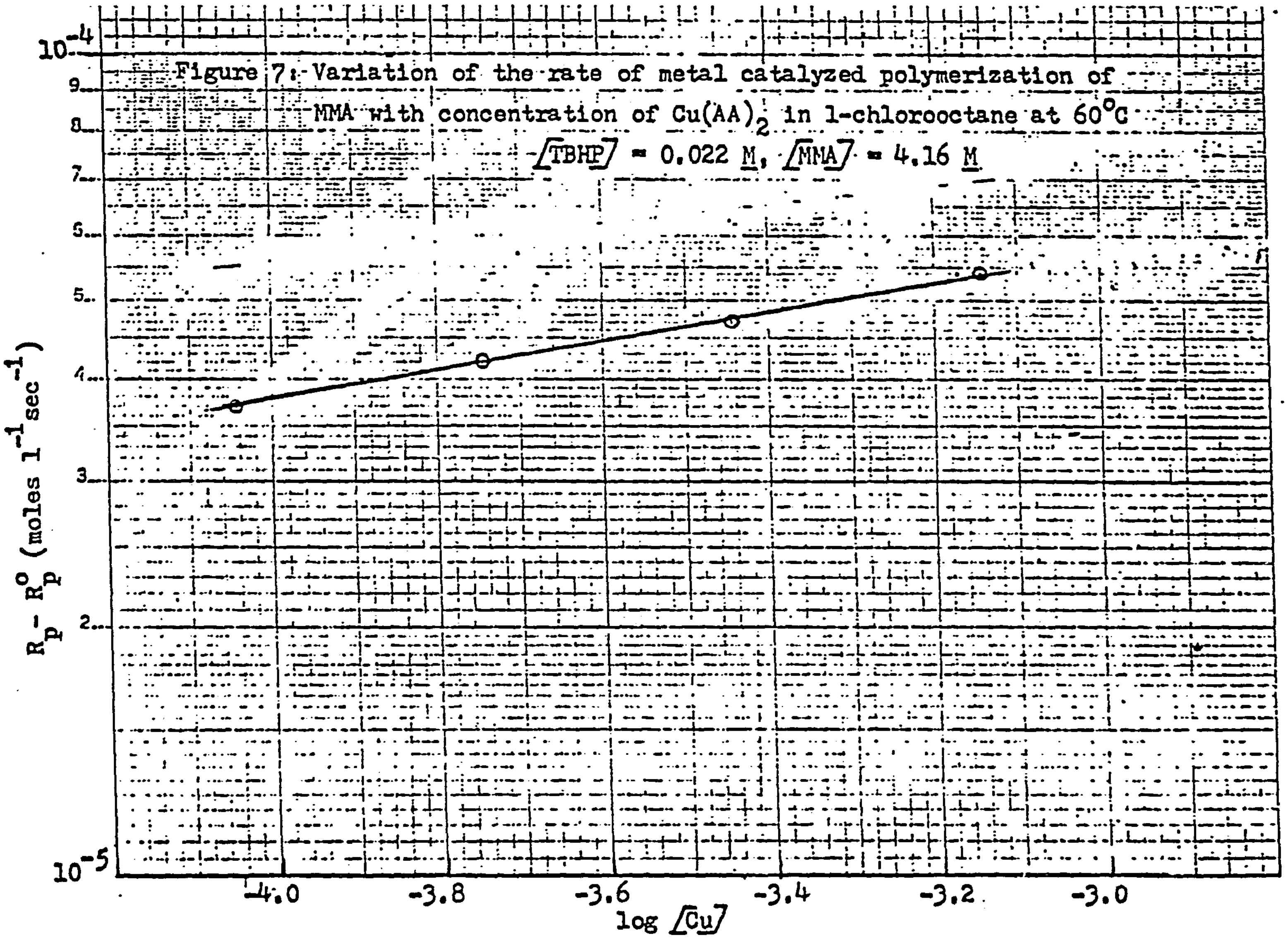


Figure 7: Variation of the rate of metal catalyzed polymerization of MMA with concentration of $Cu(AA)_2$ in 1-chloroooctane at 60°C

$[TBHP] = 0.022$ M, $[MMA] = 4.16$ M

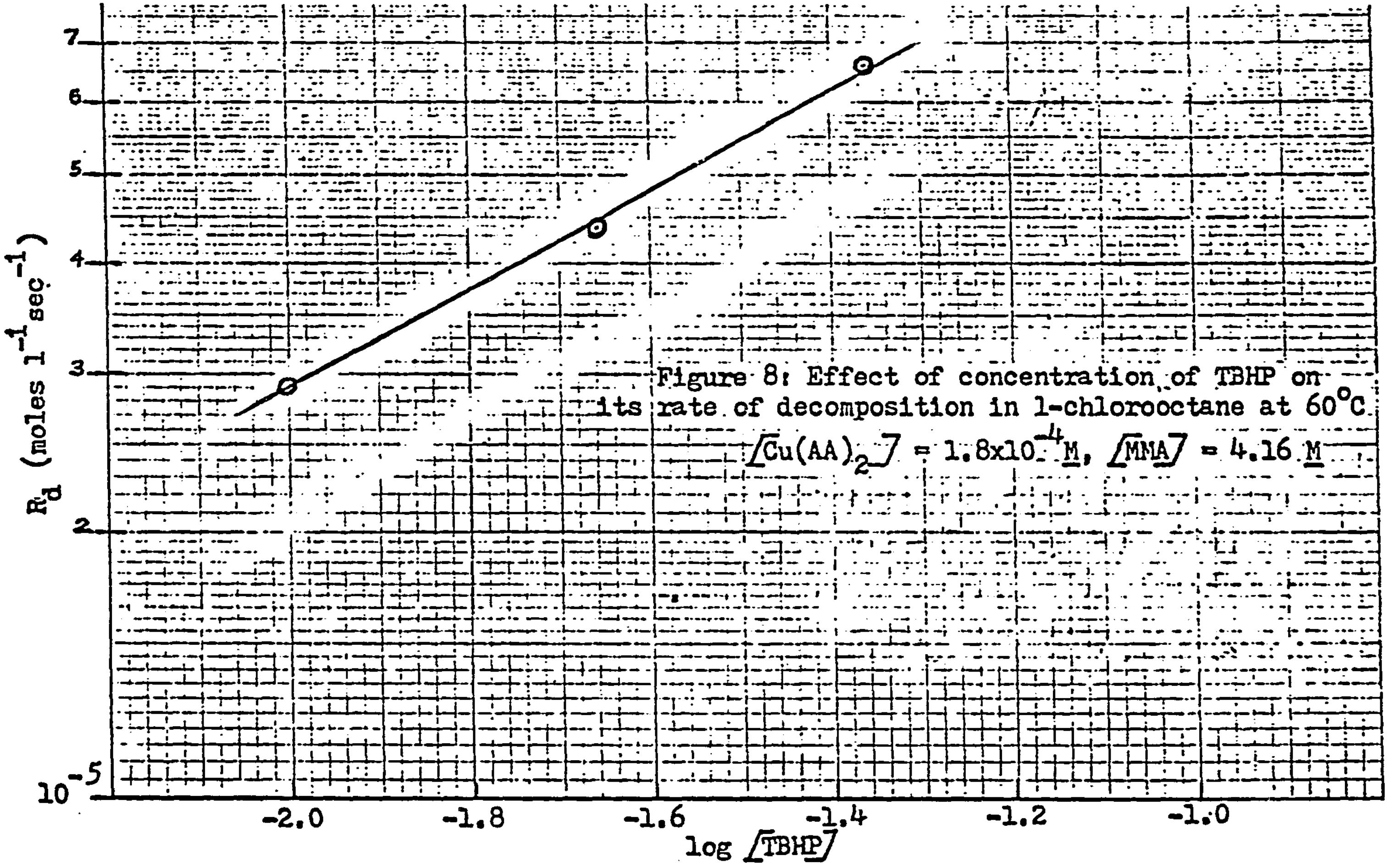


Figure 8: Effect of concentration of TBHP on its rate of decomposition in 1-chlorooctane at 60°C. $[Cu(AA)_2] = 1.8\times10^{-4}$ M, [MMA] = 4.16 M

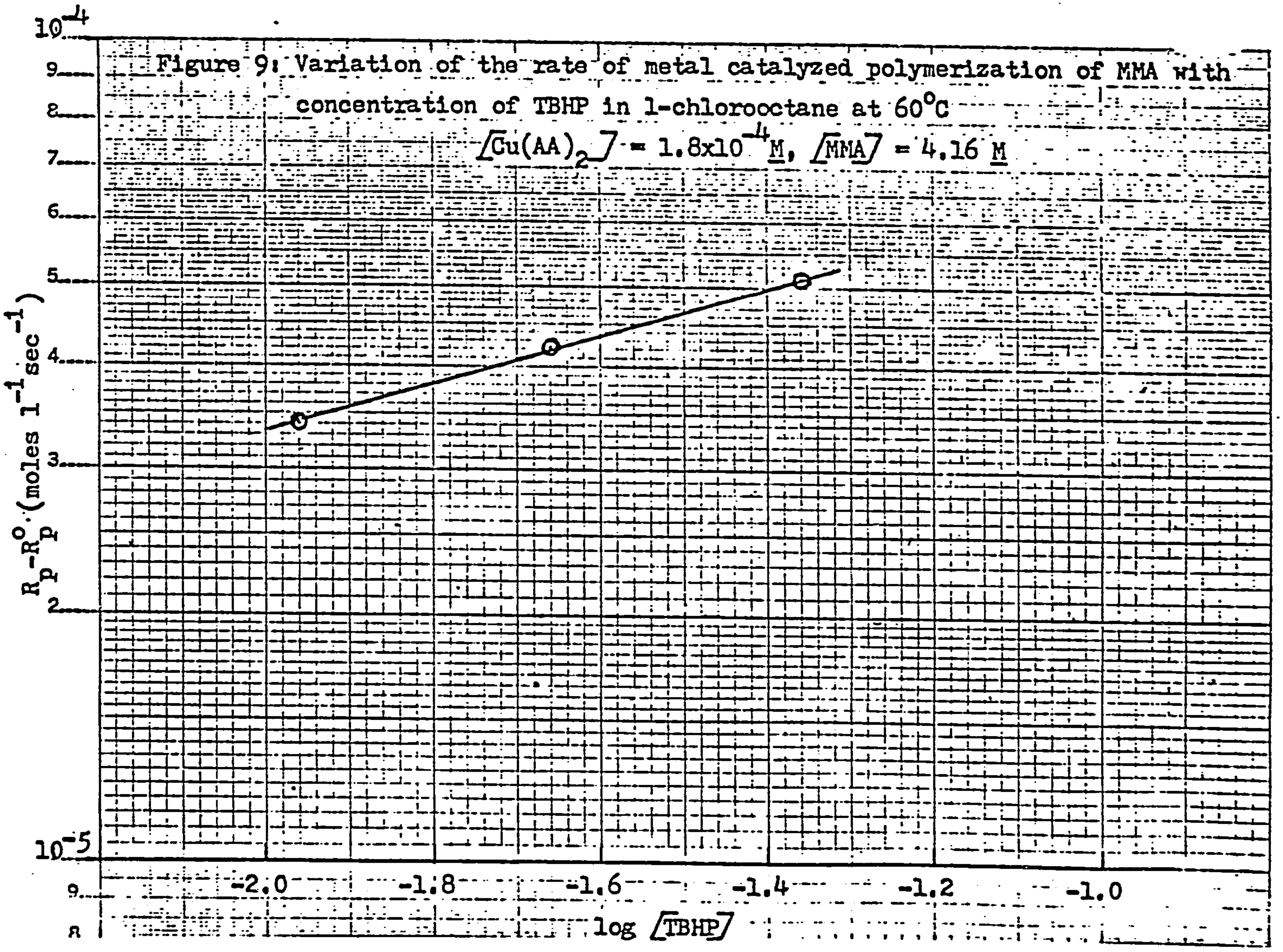


Figure 9: Variation of the rate of metal catalyzed polymerization of MMA with concentration of TBHP in 1-chlorooctane at 60°C

$[Cu(AA)_2] = 1.8 \times 10^{-4}$ M, $[MMA] = 4.16$ M

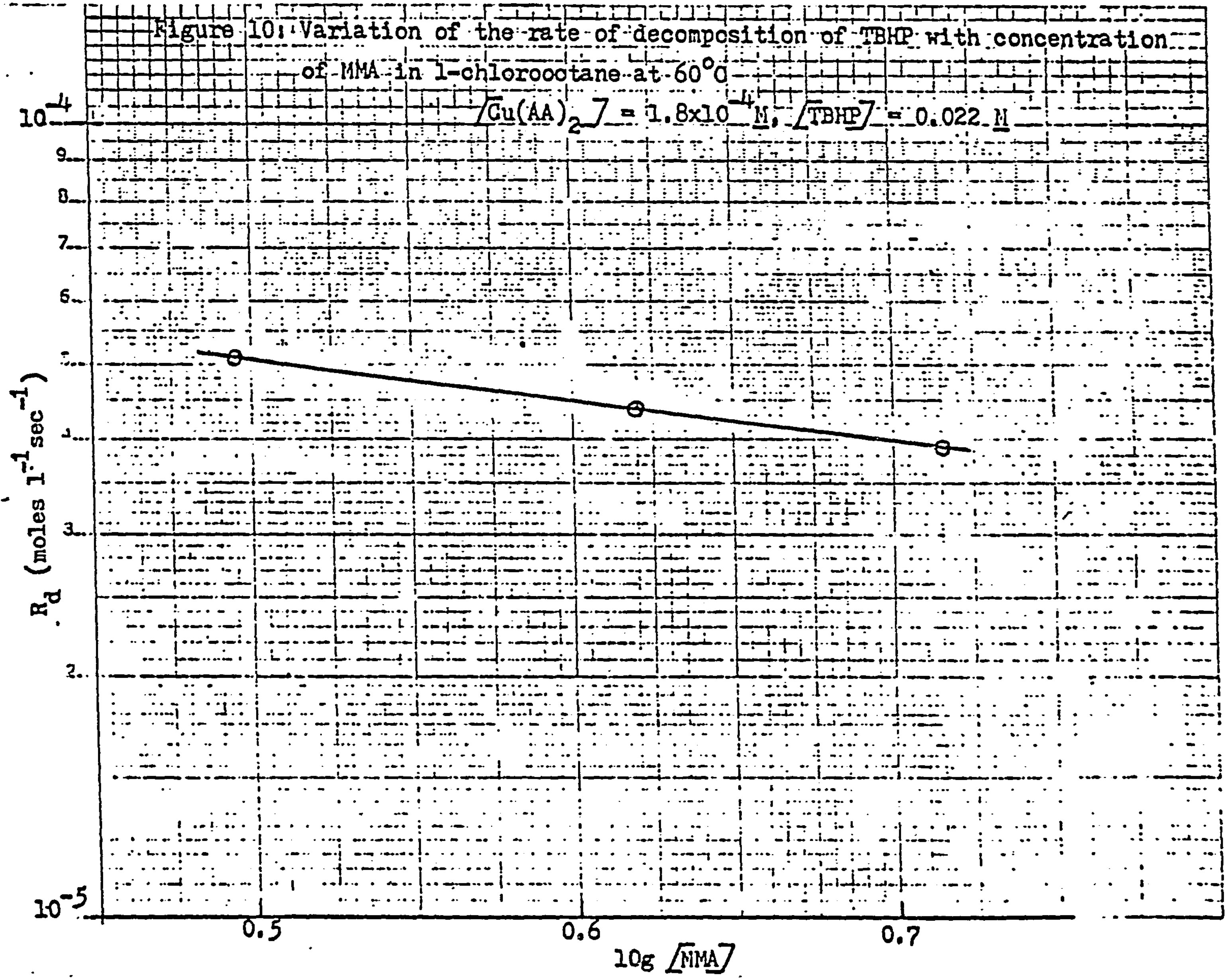


Figure 10: Variation of the rate of decomposition of TBHP with concentration of MMA in 1-chlorooctane at 60°C

[Cu(AA)$_2$] = 1.8x10^{-4} M, [TBHP] = 0.022 M

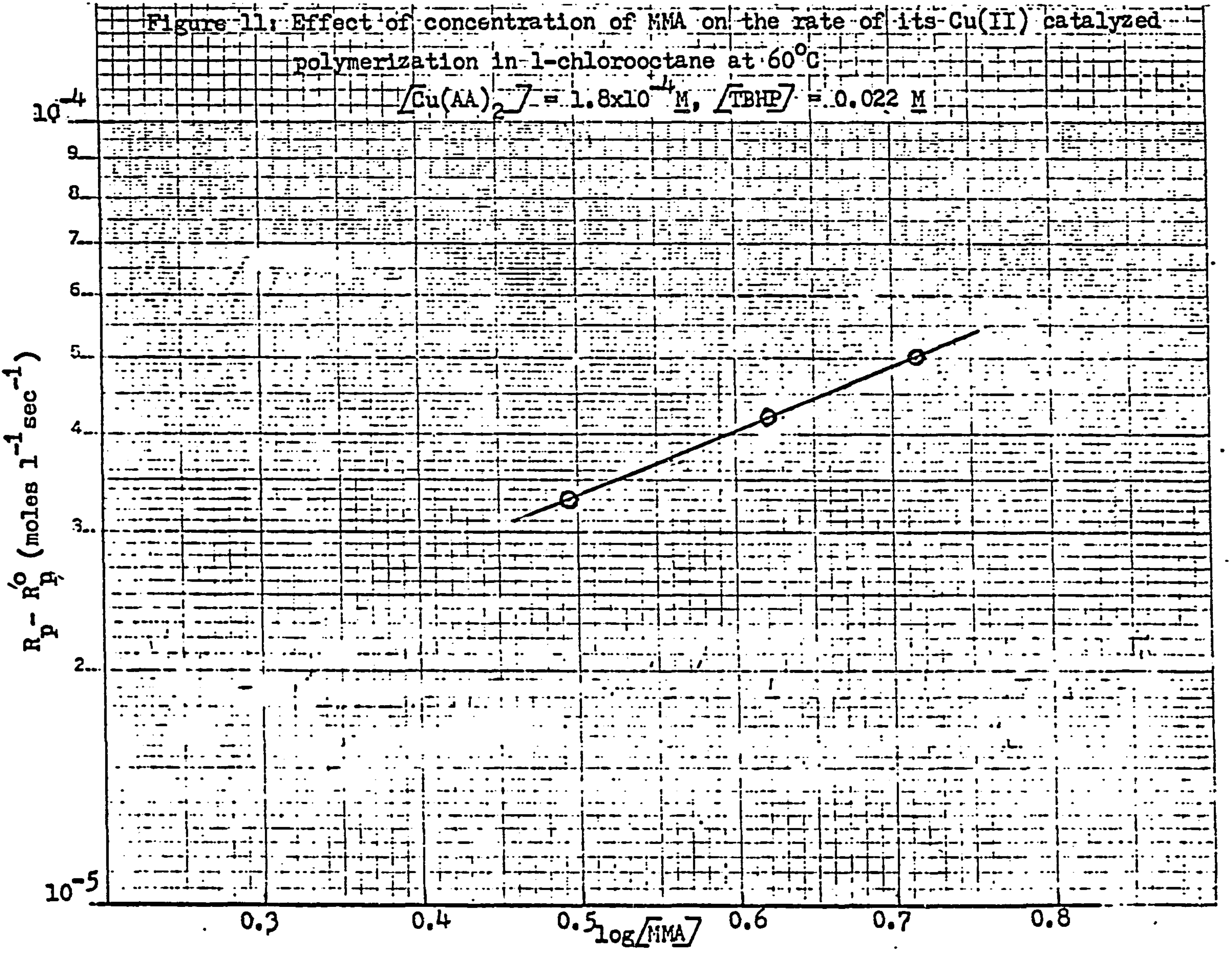


Figure 11: Effect of concentration of MMA on the rate of its Cu(II) catalyzed polymerization in 1-chlorooctane at 60°C

$[Cu(AA)_2] = 1.8 \times 10^{-4}$ M, $[TBHP] = 0.022$ M

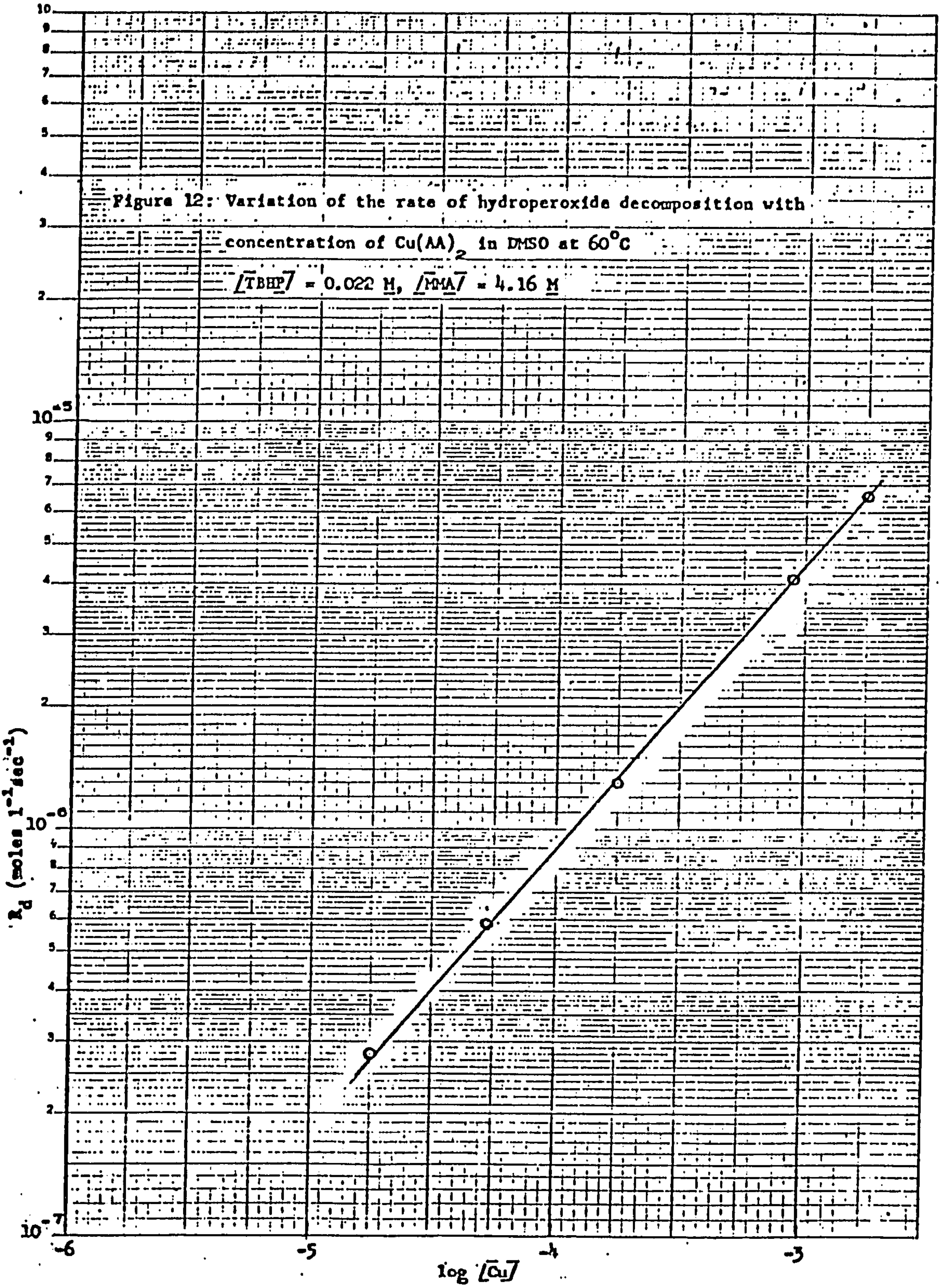


Figure 12: Variation of the rate of hydroperoxide decomposition with concentration of $Cu(AA)_2$ in DMSO at 60°C

[TBHP] = 0.022 M, [MMA] = 4.16 M

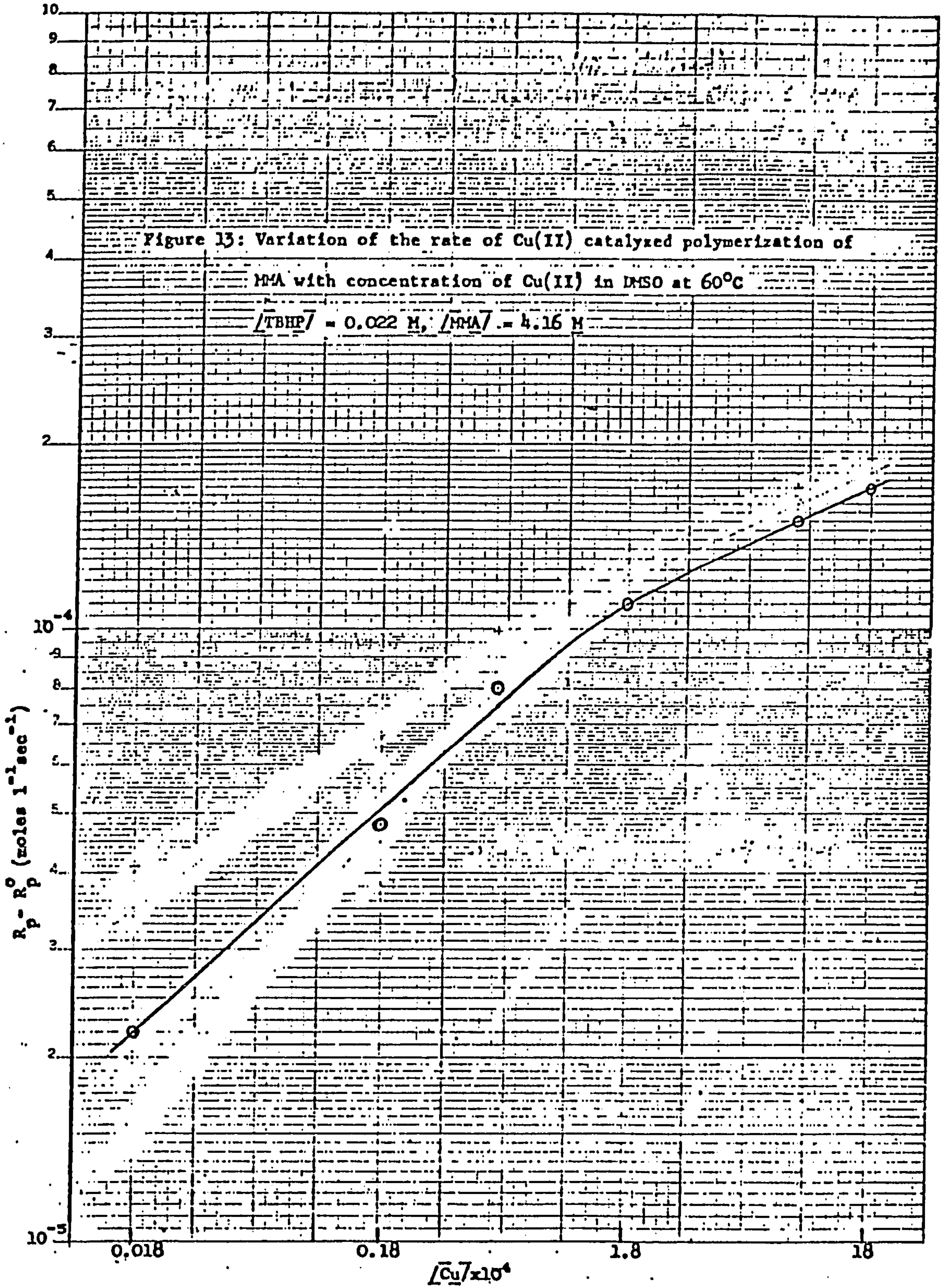


Figure 13: Variation of the rate of Cu(II) catalyzed polymerization of MMA with concentration of Cu(II) in DMSO at 60°C

$[TBHP] = 0.022$ M, $[MMA] = 4.16$ M

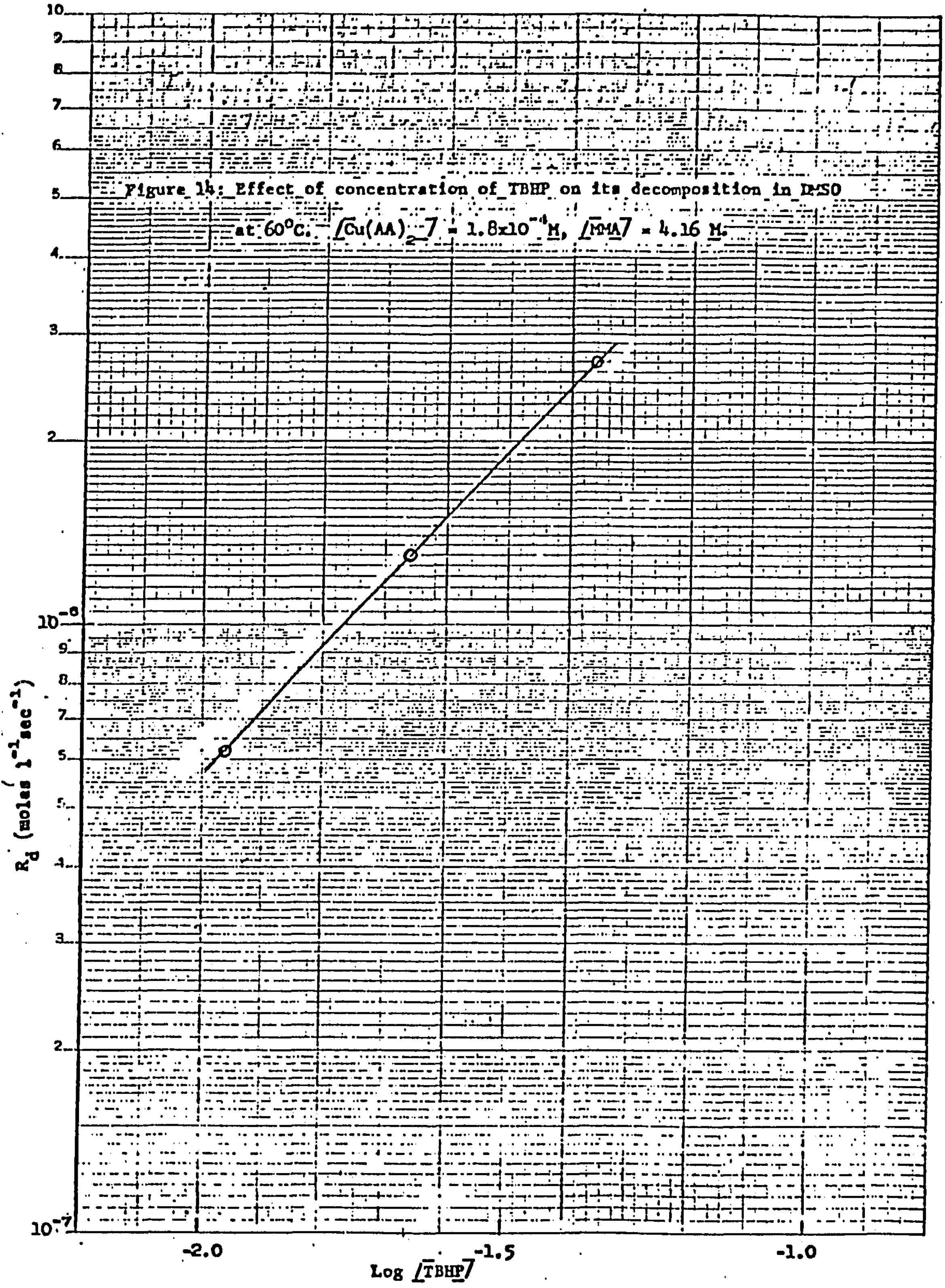


Figure 14: Effect of concentration of TBHP on its decomposition in DMSO at 60°C. $[Cu(AA)_2] = 1.8 \times 10^{-4}$ M, $[MMA] = 4.16$ M.

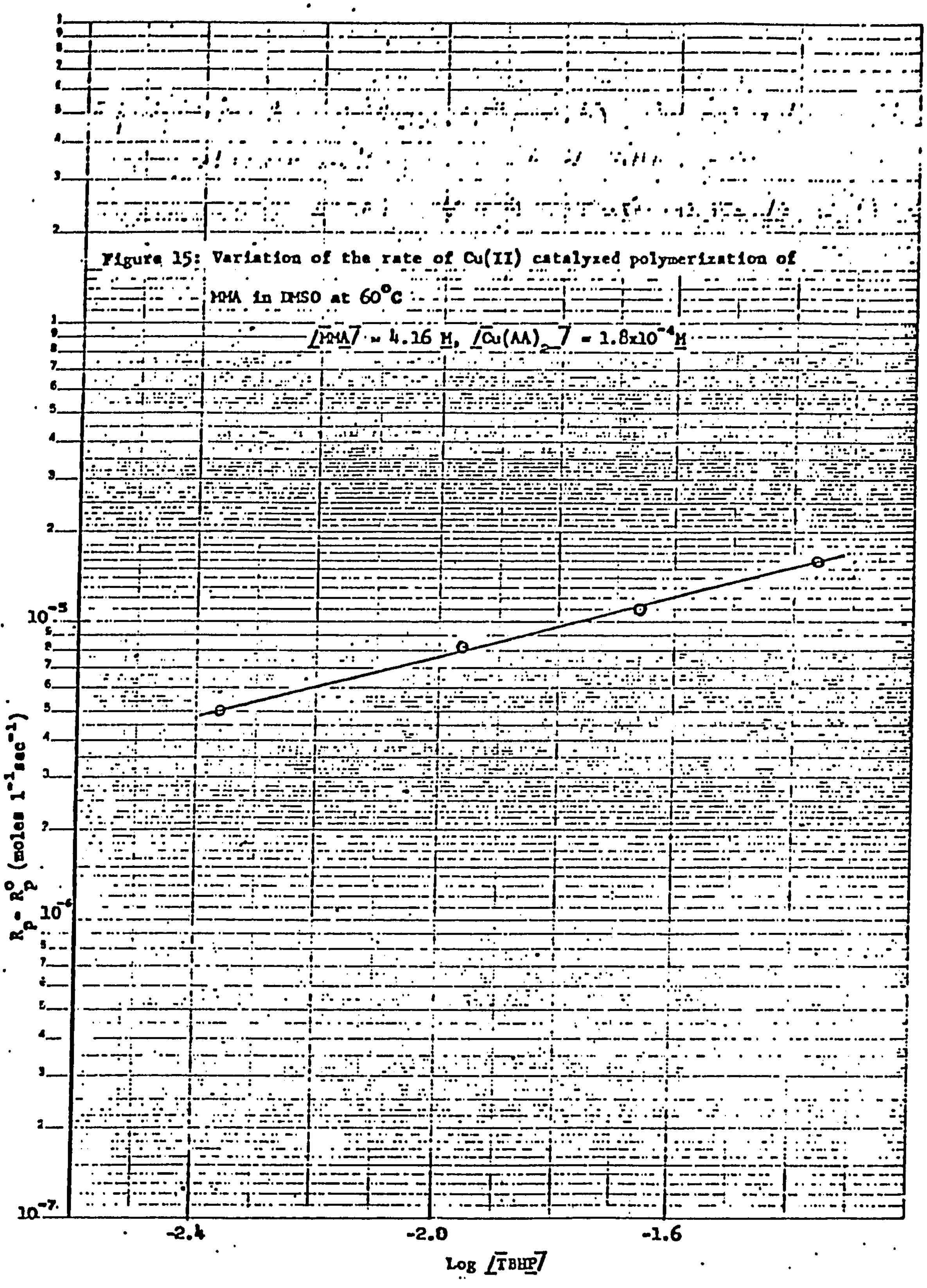


Figure 15: Variation of the rate of Cu(II) catalyzed polymerization of MMA in DMSO at 60°C

$[MMA] = 4.16$ M, $[Cu(AA)_2] = 1.8 \times 10^{-4}$ M

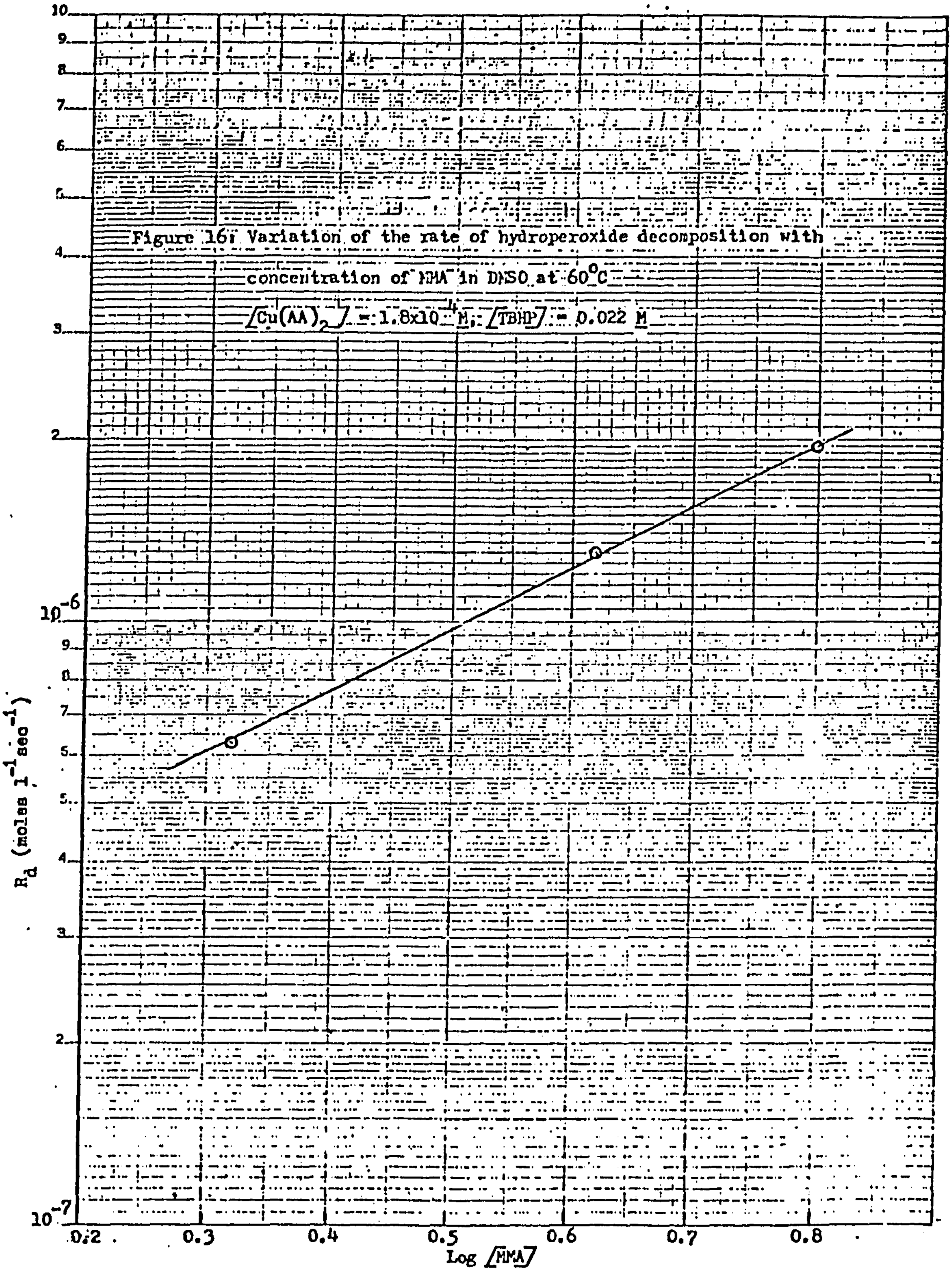


Figure 16: Variation of the rate of hydroperoxide decomposition with concentration of MMA in DMSO at 60°C

[Cu(AA)$_2$] = 1.8x10^{-4} M; [TBHP] = 0.022 M

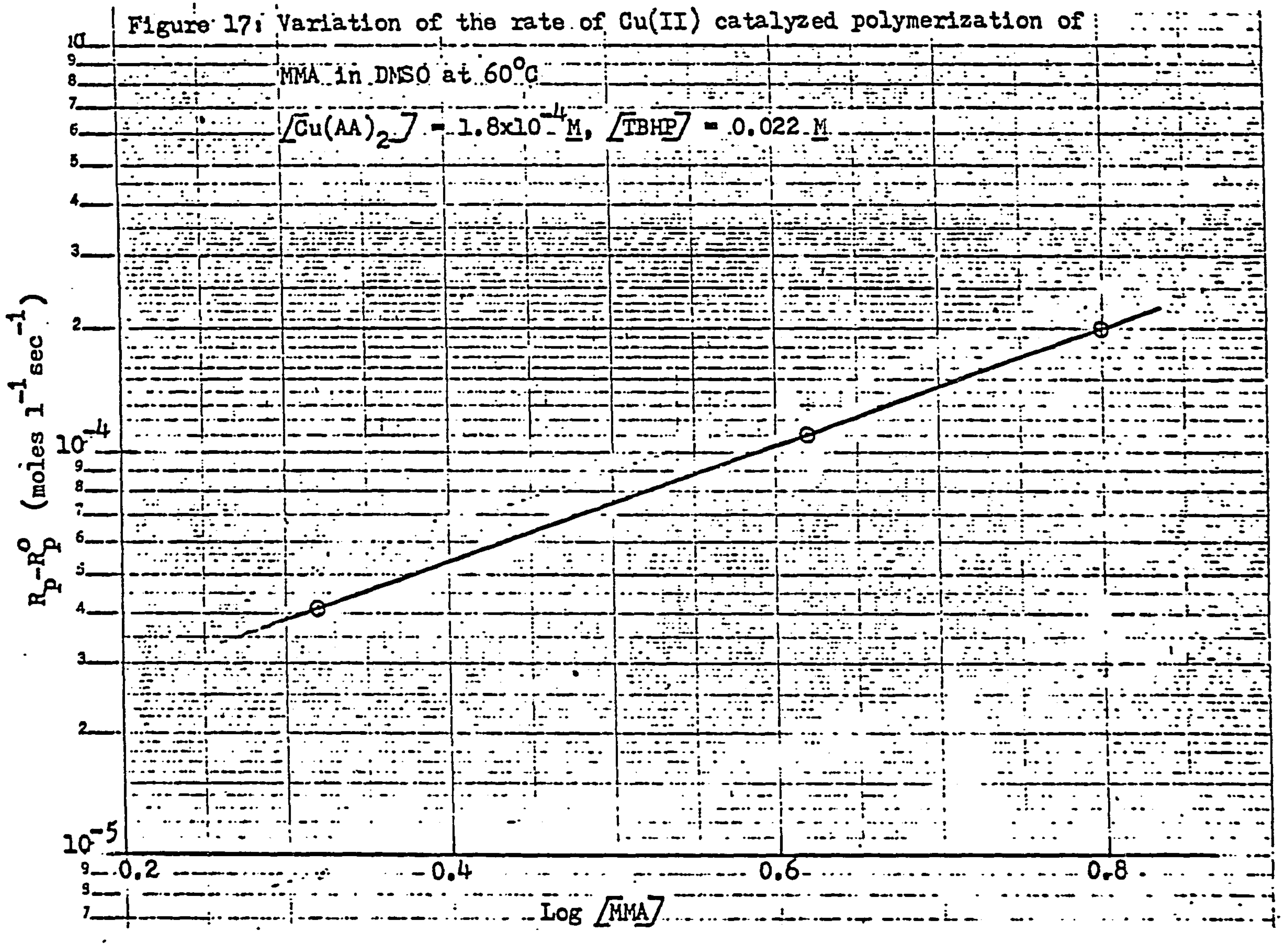


Figure 17: Variation of the rate of Cu(II) catalyzed polymerization of MMA in DMSO at 60°C

[$Cu(AA)_2$] = 1.8×10^{-4} M, [TBHP] = 0.022 M

Figure 18: Variation of $1/\bar{X}_n$ with metal concentration in 1-chlorooctane at 60°C

$[MMA] = 4.16\ \underline{M}$, $[AIBN] = 0.0011\ \underline{M}$

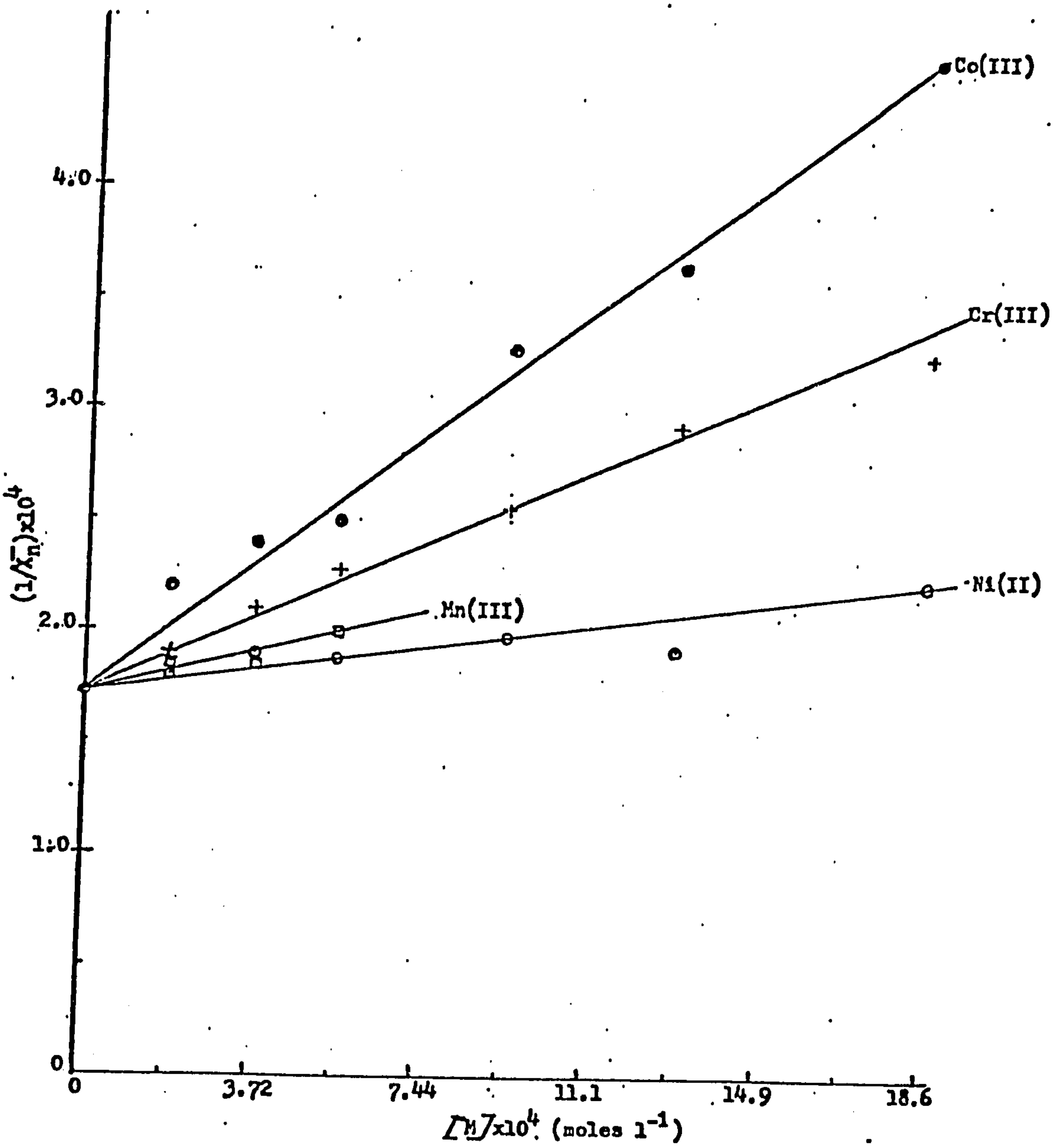
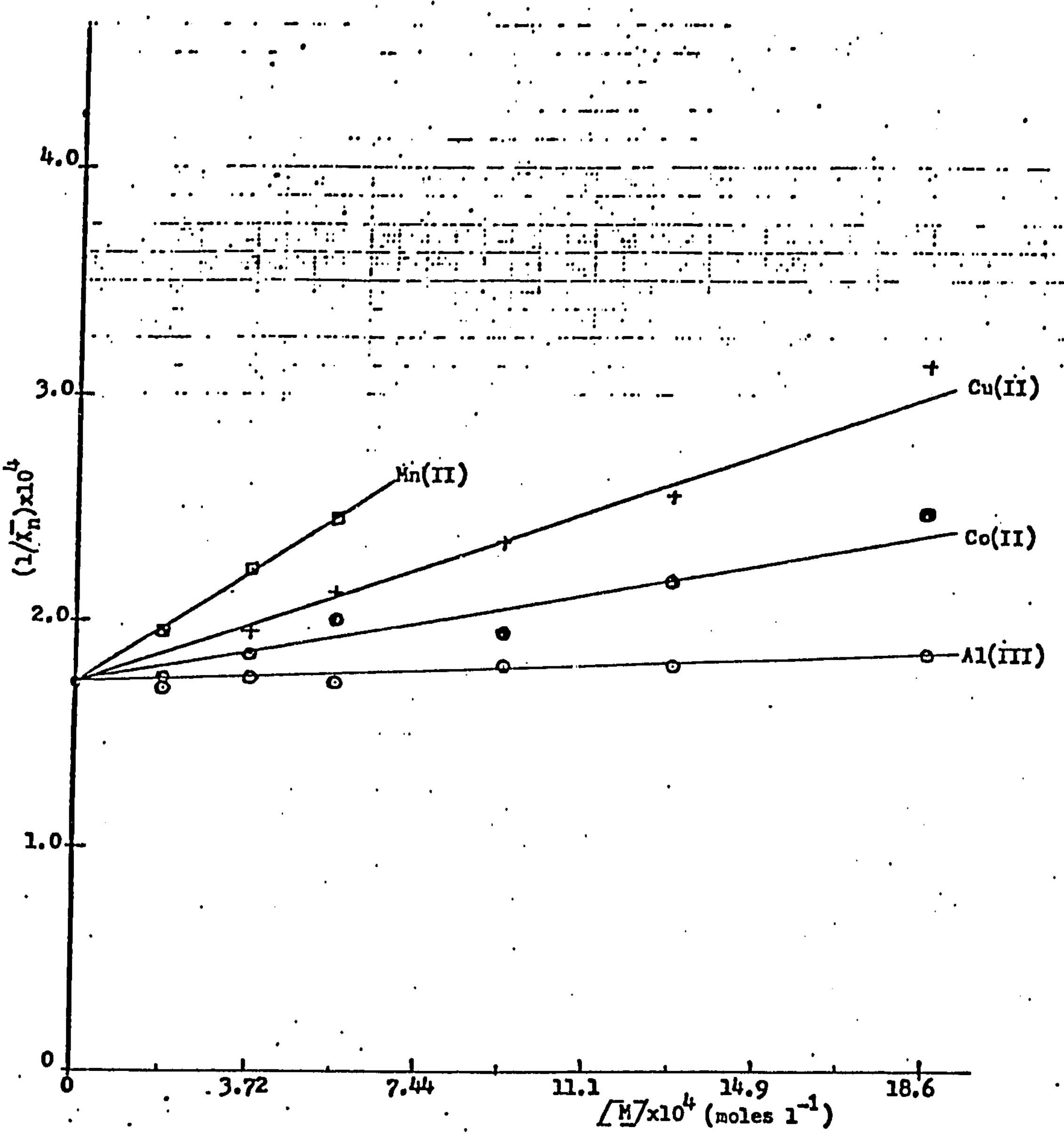


Figure 19: Variation of $1/\bar{X}_n$ with metal concentration in 1-chlorooctane at 60°C

$[MMA] = 4.16$ M, $[AIBN] = 0.0011$ M



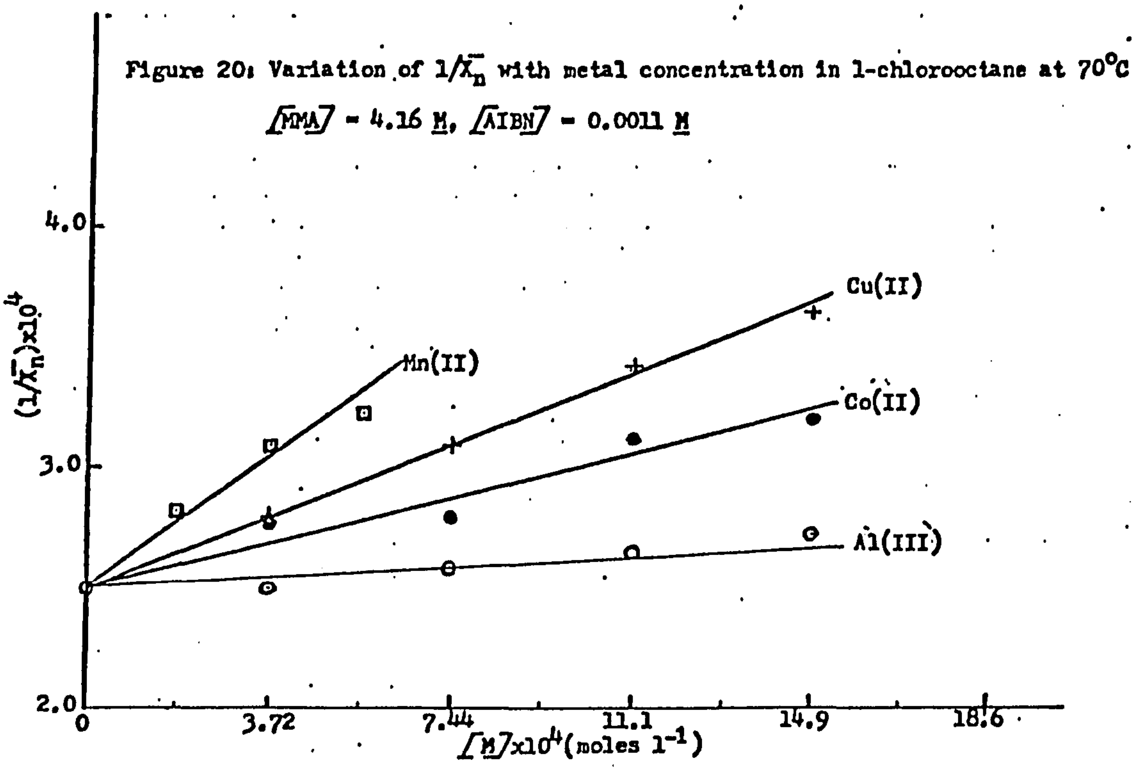


Figure 20: Variation of $1/\bar{X}_n$ with metal concentration in 1-chlorooctane at 70°C

$[MMA] = 4.16\ \underline{M}$, $[AIBN] = 0.0011\ \underline{M}$

Figure 21: Variation of $1/\bar{X}_n$ with metal concentration in 1-chlorooctane at 70°C

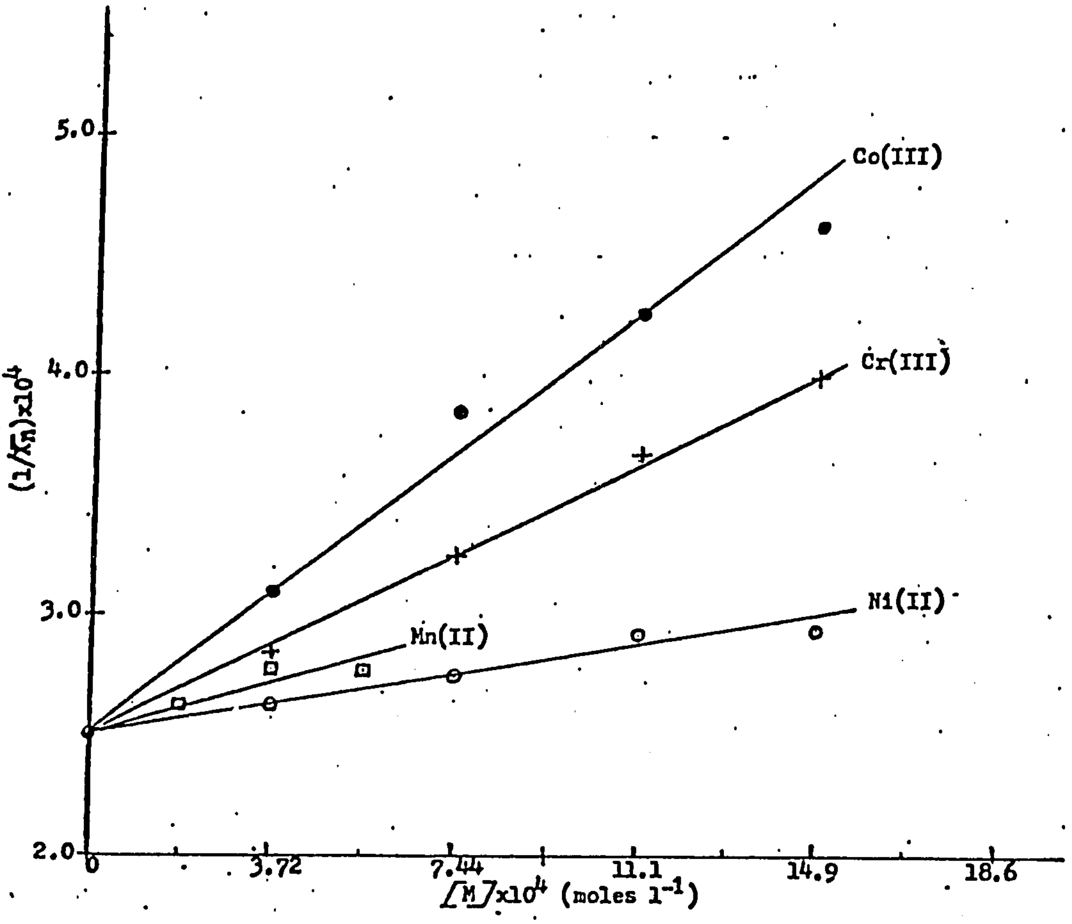
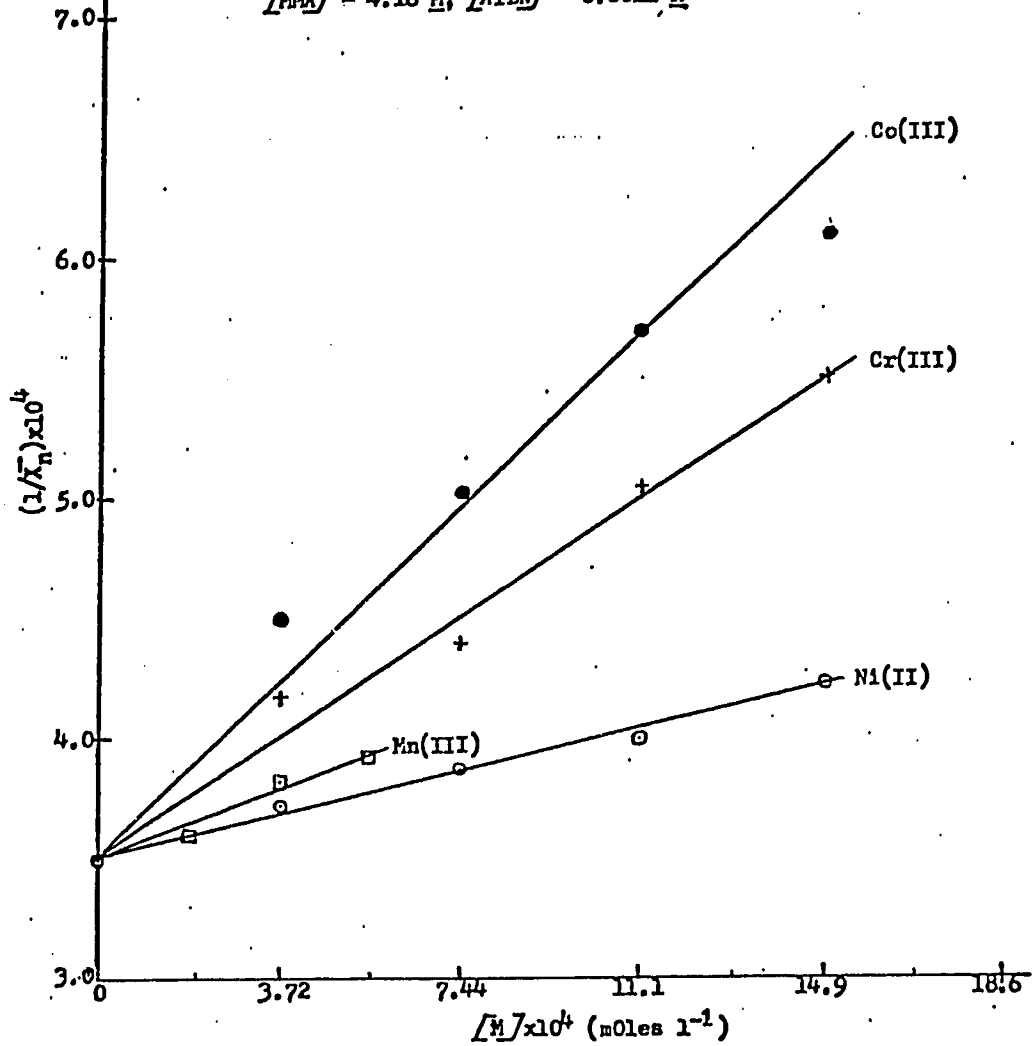


Figure 22: Variation of $1/\bar{X}_n$ with metal concentration in 1-chlorooctane at 80°C

$[MMA] = 4.16\ \underline{M}$, $[AIBN] = 0.0011\ \underline{M}$



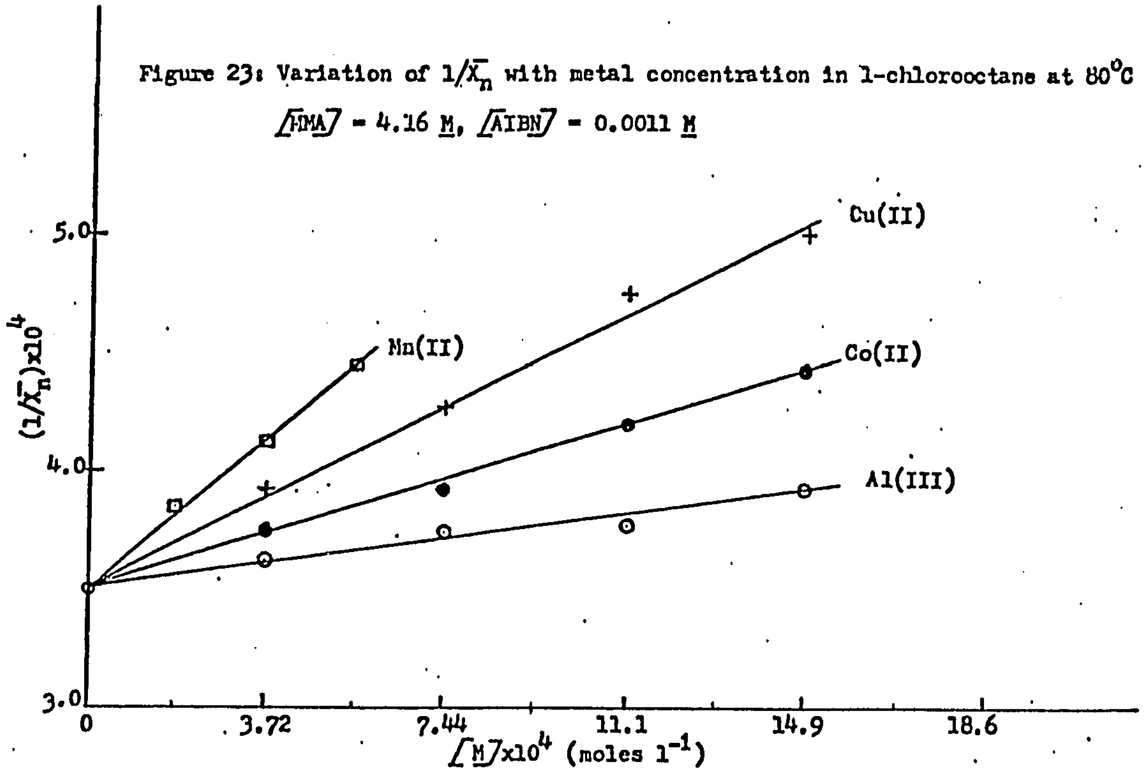


Figure 23: Variation of $1/\bar{X}_n$ with metal concentration in 1-chlorooctane at 80°C

[MMA] = 4.16 M, [AIBN] = 0.0011 M

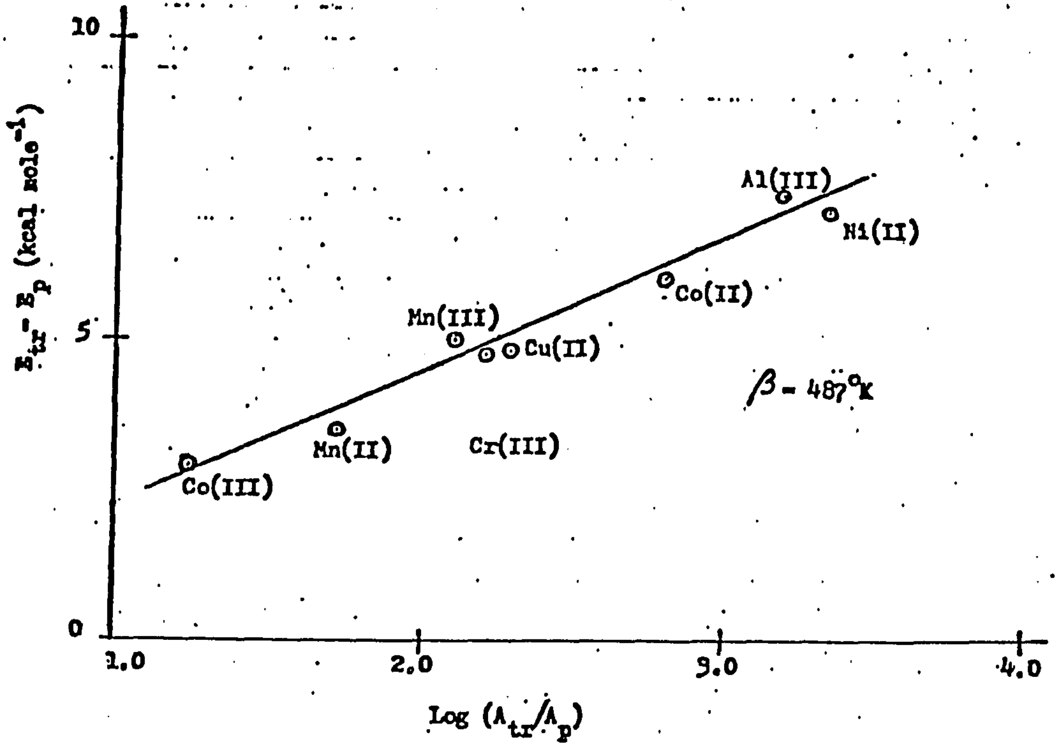


Figure 24: Isokinetic plot for chain transfer on acetylacetonate ligands

Experimental

Chemicals:

Methyl **methacrylate** (Eastman Organic Chemicals) was allowed to stand over anhydrous sodium sulfate for at least 24 hours with intermittent shaking and then distilled under vacuum. tert-Butyl hydroperoxide 90 (Pennwalt Corporation, Lucidol Division) was purified by distilling away the lower boiling products of decomposition and was found to be at least 95 percent pure by iodomedric titration. 1-Chlorooctane (Aldrich Chemicals, Inc.) was purified by gas chromatography. Metal acetylacetonates obtained from McKenzie Chemical Corporation were recrystallized from chloroform and their purity ascertained from their UV spectra. Spectroanalyzed chloroform and benzene (Fisher Scientific Co.), and reagent grade dimethyl sulfoxide, acetic acid and potassium iodide (J.T. Baker Chemical Co.), were used without further purification. 2,2'-Azoisobutyronitrile (Baker Chemical Co.) was purified just before use by repeated recrystallization from anhydrous ethanol. Standard solutions of $Na_2S_2O_3$ were obtained from J. T. Baker Chemical Co. and diluted to a suitable volume with distilled water.

Preparation of solutions of metal acetylacetonates:

Since solutions containing very small concentrations of metal acetylacetonates ($\sim 10^{-4}$ M) were required, it was necessary to prepare more concentrated stock solutions ($\sim 10^{-2}$ M) and then dilute to the desired concentrations. Such stock solutions were always prepared in benzene. When reaction systems in 1-chlorooctane or DMSO were under study, aliquots of stock solutions in benzene were first evaporated to dryness under vacuum at 50°C and then dissolved in an appropriate volume of the desired solvent.

Ultraviolet spectra of solutions prepared in this manner from stock solutions in benzene were exactly the same as those obtained for solutions prepared by dissolving metal acetyl acetonates directly in 1-chlorooctane. Also for the most active catalysts, viz., Cu(II), Co(II), Co(III) and Mn(III), experiments carried out with solutions prepared by directly dissolving the metal acetylacetonates in 1-chlorooctane gave results comparable to those obtained from identical experiments in which 1-chlorooctane solutions of metal acetylacetonates prepared from a benzene concentrate were used.

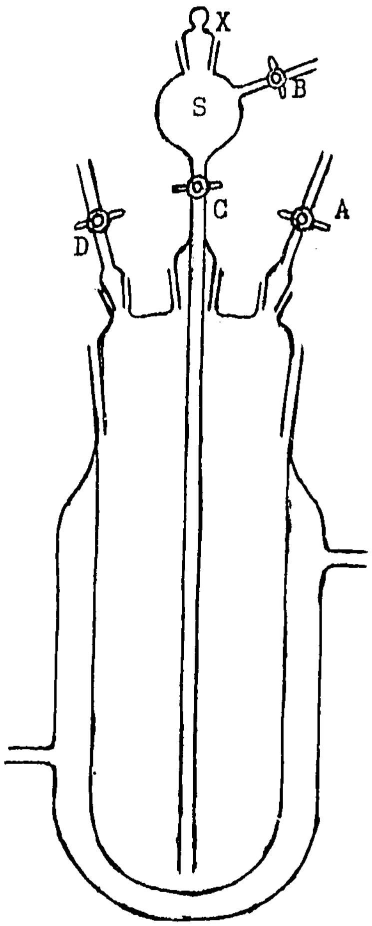
Solutions of metal acetylacetonates were refrigerated after preparation. However, these solutions were never stored for periods longer than one week. There are indications that solutions of metal acetylacetonates undergo a change in their composition on aging, especially those in 1-chlorooctane. Pink solutions of the Co(II) compound develop a green tint due to the oxidation of Co(II) to Co(III). In the case of other metals, no visual, or even spectral change may be observed for solutions kept over a few weeks. Nevertheless, the catalytic activity of metal acetylacetonate solutions towards hydroperoxide decomposition often decreases as the solutions age. In solutions stored for longer periods changes in color are sometimes observed. Several months after their preparation, yellow solutions of $Fe(AA)_3$ in 1-chlorooctane lose their color, while blue solutions of $Cu(AA)_2$ in the same solvent turn yellow. Incidentally, the aged, colorless solution of $Fe(AA)_3$ in 1-chlorooctane was seen to be a good initiator of MMA polymerization. In a 1-chlorooctane solution containing 4.16 $\underline{M}$ MMA, and 1.8×10^{-4} $\underline{M}$ $Fe(AA)_3$, a rate of polymerization of 3.2×10^{-5} moles l^{-1} sec^{-1} was observed at 60°C. A freshly prepared $Fe(AA)_3$ solution in 1-chlorooctane does not initiate polymerization under the same conditions.

While preparing solutions of metal acetylacetonates one must not apply heat to hasten dissolution. It has been seen that solutions of $Cu(AA)_2$ in 1-chlorooctane prepared by the application of heat do not catalyze the decomposition of TBHP. On the other hand, $Cu(AA)_2$ in 1-chlorooctane solutions prepared at room temperature strongly catalyzes the same reaction.

Kinetics:

Reactions were studied using either of two techniques. In one, reactants were introduced into Carius tubes which had been previously cleaned with chromic acid, washed thoroughly with water, and rinsed with distilled water before drying under vacuum at 100°C. While introducing desired aliquots of solutions of reactants, the initiator (TBHP or AIBN) solution was added last. The Carius tubes containing the frozen mixture of reactants were evacuated under an atmosphere of mercury vapor to a pressure of less than 1 mm of Hg. The vacuum was then shut off and the reactant mixture allowed to thaw by removing the liquid nitrogen bath. In this fashion, the Carius tubes were put through two more freeze-thaw cycles, and finally frozen before sealing under vacuum. The sealed Carius tubes were kept under liquid nitrogen until the reaction was to be started. Storage of sealed Carius tubes in the freezer compartment of a refrigerator was found to lead to some polymer formation (when MMA was present) after three to five days. To start a reaction, the sealed Carius tube containing the frozen reactant mixture was warmed to let the reactant solution thaw, shaken to obtain a homogeneous solution and then immersed in a thermostatic bath at a desired temperature. The reaction was arrested at a suitable time by transferring the Carius tube to a freezing mixture of dry ice and acetone. The Carius tube was then broken open and its contents analyzed.

In the method of reaction described above, dissolved oxygen was removed by decreasing the pressure above the reaction mixture. In another experimental method dissolved O_2 was removed by flushig the reaction mixture with nitrogen first and then maintaining a nitrogen atmosphere throughout the course of the reaction. The reaction mixture was kept in a jacketed vessel maintained at a constant temperature as in the figure shown below:



This apparatus was insulated by wrapping asbestos tape around it. The reactant solutions were individually saturated with nitrogen gas and brought to the reaction temperature before introduction into the reaction vessel. The reaction mixture in this vessel is stirred constantly but gently by means of a magnetic stirrer. The reaction starts at the instant the initiator solution is added to the rest of the reactants. A nitrogen atmosphere was maintained throughout the course of the reaction. Nitrogen enters the reaction vessel through stopcock A or stopcocks B and C, while it leaves through stopcock D. For the first 2 to 3 minutes of the reaction period stopcock A was closed and stopcocks B and C were opened to let N_2 gas bubble through the reaction mixture to ensure saturation. Stopcock D was, of course, kept open to provide an outlet. Stopcocks B and C were then closed, and stopcock A opened to maintain a nitrogen atmosphere.

Samples of the reaction mixture were withdrawn for analysis at regular intervals of time. To withdraw a sample, stopcock D was closed and stopcocks B and C, and stopper X opened at the same time. The reaction mixture was forced up into the sampling bulb S. When a suitable volume was collected in this bulb, it was withdrawn by means of a transfer pipet and immediately cooled to arrest the reaction. The stopper X was then replaced, stopcocks B and C opened and stopcock A closed. As soon as any remaining solution in the bulb S and the tube below it was forced back into the reaction vessel, stopcocks B and C were closed and stopcock A opened till the next sample was to be withdrawn.

This method was used only when the reaction mixtures did not contain MMA monomer.

Analysis: To analyze a solution in a sealed Carius tube it was broken open and the contents transferred quantitatively to a volumetric flask and diluted to the mark with chloroform. This solvent helps to thin viscous solutions containing dissolved polymer. Dilution with chloroform is specially helpful in the case of reaction mixtures in 1-chlorooctane media, since the polymer often precipitates out on cooling the Carius tubes at the end of the reaction period. Aliquots were then withdrawn from the diluted solution for UV spectral analysis, and for the determination of hydroperoxide content and polymer content. When reaction mixtures did not contain poly(MMA), aliquots were withdrawn directly from the reaction mixtures. Also, when only the polymer content of a reaction mixture was to be determined, the solution in the Carius tube was transferred quantitatively to a beaker for precipitation.

Determination of hydroperoxide concentration: The concentration of TBHP was determined by iodometric titration. Solution of TBHP in benzene and 1-chlorooctane media were analyzed by the method of Wibaut et.al. (285):

In this method 25 ml of glacial acetic acid are introduced into a 150 or 250 ml iodine flask. Several chips of dry ice are introduced and the flask swirled so as to saturate the acid with carbon dioxide. A small volume (~1 ml) of a saturated solution of KI is added to the deaerated acetic acid. The exact volume of the KI solution must be added in each of a series of related titrations. An aliquot of the solution to be analyzed is then introduced. The iodine flask is stoppered, swirled and set aside. Until the hydroperoxide solution is introduced, the solution in the flask must be kept frothing by the intermittent addition of dry ice. The stoppered iodine flask is allowed to stand for 15 minutes after the introduction of the hydroperoxide sample. It is then opened and 50 ml of water introduced. The solution is then titrated against a standard $Na_2S_2O_3$ solution. In these experiments a 0.01 N $Na_2S_2O_3$ solution was employed. Use of starch indicator is not necessary as a sharp end point can be obtained without it.

The titre volume must be corrected by subtracting from it the titre volume of a 'blank' titration which is run in an exactly analogous manner except that instead of an aliquot of hydroperoxide solution, an equivalent volume of only the solvent is introduced.

In the analysis of hydroperoxide solutions in DMSO the method described above gave erratic results. At present, the reason for this irreproducibility is not clear. However, the following modification of the method described above yields most satisfactory results. The following changes are made: (a) glacial acetic acid was deaerated by introducing about 0.5 grams of Na_2CO_3 (anhydrous) in several installments with constant swirling of the flask and (b) after the addition of 50 ml of distilled water, 5 ml of chloroform is added before titration against standard $Na_2S_2O_3$ solution.

In both of the techniques described above, glacial acetic acid may be deaerated alternatively by passing a constant current of N_2 gas through it while stirring constantly by means of a magnetic stirrer. Both, N_2 gas and stirring are discontinued after the sample of hydroperoxide solution is introduced, and the iodine flask is stoppered and allowed to stand as described earlier.

Each percent hydroperoxide decomposition value reported here is an average of three determinations from three separate reaction mixtures. A reproducibility of ± 10 percent was observed. Because of this uncertainty, small changes in hydroperoxide concentrations could not be determined accurately enough. In such cases only an upper limit for percent decomposition could be established. For the same reason only a lower limit for percent decomposition could be established for solutions in which very small concentrations of hydroperoxide remained undecomposed. Rates of hydroperoxide decomposition (R_d) have been calculated by extrapolating the observed rates to zero time assuming a first order decomposition.

Determination of polymer content: An excess of methanol (150 ml) was added to 5 to 10 ml aliquots of the solution containing the polymer in a 250 ml beaker. A small quantity of quinhydrone inhibitor (50 to 100 mg) was also added, the solution stirred and allowed to stand overnight. The precipitated polymer was then transferred to a weighed sintered glass funnel, and washed with methanol. The polymer was then dried to constant weight under vacuum at 40°C.

Each percent conversion figure reported here is an average of three determinations from three separate reaction mixtures. A reproducibility of ± 10 percent was observed.

Ultraviolet spectra of metal acetylacetonates: Aliquots of reaction mixtures diluted with chloroform were withdrawn and diluted five times with the same solvent. UV spectra of these solutions were obtained on a Cary 14 Spectrophotometer. The regions where characteristic peaks were observed for the metals studied in Part I of this work are tabulated in Appendix II. No significant change in the spectra of any of the metal catalysts was observed with the progress of the reactions studied in Part I.

Determination of number average molecular weight of polymer: Number average molecular weights ($\overline{M}_n$) were determined viscometrically. Viscocities were measured in benzene at 30°C using Ubbelohde viscometers. The flow time was never smaller than 100 seconds. Intrinsic viscocities, $[\eta]$, were obtained (286) and the following correlation (287) used to calculate the number average molecular weights of poly(MMA) samples:

$$[\eta] = 7.24 \times 10^{-5}\,\overline{M}_n^{\,-0.76}$$

<u>Calculation of initiator efficiency</u>: The initiator efficiency, f, is defined as the number of radicals produced which initiate polymer chains. In parts I and II of the present work, metal catalyzed decomposition of TBHP is the major source of radical production. Each TBHP molecule which decomposes as a result of a redox reaction with a metal species is expected to lead to the formation of one free radical:

$$RO_2H + M^{+n} \longrightarrow ROO\cdot + H^+ + M^{+n-1}$$

$$RO_2H + M^{+n-1} \longrightarrow RO\cdot + OH^- + M^{+n}$$

Hence, the number of radicals produced per liter of the reaction mixture

$$= \text{the number of TBHP molecules decomposed per liter}$$

$$= \frac{\text{percent decomposition}}{100} \times [\text{TBHP}] \times N$$

where N is Avogadvo's number.

While the number of polymer chains formed per liter of the reaction mixture

$$= \frac{\text{percent conversion} \times [\text{MMA}] \times N}{100 \times \overline{DP}_n}$$

where $\overline{DP}_n$ is the number average degree of polymerization.

Therefore, initiator efficiency, f

$$= \frac{\text{number of polymer chains formed}}{\text{number of radicals produced}}$$

Hence, $f = (\text{percent conversion} \times [MMA])/(\text{percent decomposition} \times [TBHP] \times \overline{DP}_n)$ Obviously, the percent conversion and percent decomposition data must be obtained at the same reaction time.

Since this calculation of initiator efficiency does not correct for any wastage of the initiator due to radical induced decomposition, the f values calculated here may be regarded as 'effective' or 'practical' values of initiator efficiency.

Determination of chain transfer constants of metal acetylacetonates: For each of the metal acetylacetonates studied, a series of experiments were performed in which the concentration of the metal was varied over a fairly wide range while the concentrations of MMA and AIBN, the initiator, were maintained constant. In each experiment, 2.0 ml of a solution of a metal acetyl acetonate in 1-chlorooctane was mixed in a Carius tube with 2.0 ml of MMA monomer and 0.50 ml of 0.010 M AIBN solution in 1-chlorooctane. Carius tubes were deaerated and sealed under vacuum as already described, and then immersed in a bath maintained at the desired temperature for a suitable time. Reactions carried out at 60, 70 and 80°C were allowed to proceed for 70, 30 and 15 minutes, respectively. At the end of the reaction period, Carius tubes were broken open and their contents transferred to suitably labeled beakers using a few ml of chloroform. The polymer was precipitated with methanol and filtered, washed and dried in the usual manner. Weighed samples of the polymer were dissolved in benzene and the viscocities of the solutions were determined to obtain the degree of polymerication.

It was of interest to determine the fate of radicals created on the as a result of chain transfer on metal acetylacetonate molecules. Such radicals may either initiate new chains, or abstract an atom to terminate. To investigate this aspect the polymer samples obtained in the presence of metal acetylacetonates were analyzed for their metal content by atomic absorption. In this analysis all polymer solutions were prepared in acetone. Standard solutions of metals were also prepared in acetone. These solutions also contained poly(MMA) in a concentration comparable to that present in the solutions to be analyzed. A control experiment was run for each of the metals analyzed, in which samples of poly(MMA) prepared in absence of the metal acetylacetonates, but precipitated in their presence were also analyzed. It was seen that even these control samples contained appreciable but irreproducible quantities of coprecipitated or occluded metals inspite of repeated washings with methanol or dilute acids. As a result, no conclusive inference could be drawn from this analysis.

APPENDIX I

Kinetics and mechanism of the decomposition of hydroperoxides catalyzed by copper(II) species

I.1 A mechanism for the catalytic decomposition of alkyl hydroperoxides is described below. This mechanism is similar in all respects to that suggested by Richardson (180), except that instead of a dimeric copper(II) catalyst, the monomeric form has been employed:

$$\begin{array}{rcll}
2\,\mathrm{ROOH} & \rightleftharpoons & (\mathrm{ROOH})_2 & (1)\\
\mathrm{Cu^{II}} + \mathrm{ROOH} & \rightleftharpoons & \mathrm{Cu^{II}(ROOH)} & (2)\\
\mathrm{Cu^{II}(ROOH)} + \mathrm{ROOH} & \rightleftharpoons & \mathrm{Cu^{II}(ROOH)_2} & (3)\\
\mathrm{Cu^{II}(ROOH)_2} & \longrightarrow & \mathrm{Cu^{I}(ROOH)(H^+)} + \mathrm{ROO.} & (4)\\
\mathrm{Cu^{I}(ROOH)(H^+)} & \longrightarrow & \mathrm{Cu^{II}} + \mathrm{H_2O} + \mathrm{RO\cdot} & (5)\\
2\,\mathrm{ROO\cdot} & \longrightarrow & 2\,\mathrm{RO\cdot} + \mathrm{O_2} & (6)\\
\mathrm{RO\cdot} + \mathrm{ROOH} & \longrightarrow & \mathrm{ROH} + \mathrm{ROO\cdot} & (7)\\
2\,\mathrm{RO\cdot} & \longrightarrow & \mathrm{ROOR} & (8)
\end{array}$$

This mechanism leads to the following kinetic expression:

$$-d[\mathrm{ROOH}]/dt = k_4[\mathrm{Cu^{II}(ROOH)_2}] + k_5[\mathrm{Cu^{I}(ROOH)(H^+)}] + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] \quad (9)$$

Application of steady state conditions for $\mathrm{Cu^{I}(ROOH)(H^+)}$ yields:

$$k_4[\mathrm{Cu^{II}(ROOH)_2}] = k_5[\mathrm{Cu^{I}(ROOH)(H^+)}]$$

Therefore, $-d[\mathrm{ROOH}]/dt = 2k_4[\mathrm{Cu^{II}(ROOH)_2}] + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}]$

$$= 2K_2K_3k_4[\mathrm{Cu^{II}}][\mathrm{ROOH}]^2 + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] \quad (10)$$

By assuming steady state conditions for RO· and ROO· radicals, the following expressions are obtained:

$$K_2K_3k_4[\mathrm{Cu^{II}}][\mathrm{ROOH}]^2 + 2k_6[\mathrm{ROO\cdot}]^2 - k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] - 2k_8[\mathrm{RO\cdot}]^2 = 0 \quad (11)$$

$$K_2K_3k_4[\mathrm{Cu^{II}}][\mathrm{ROOH}]^2 - 2k_6[\mathrm{ROO\cdot}]^2 + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] = 0 \quad (12)$$

Combination of equations (11) and (12) yields:

$$2K_2K_3k_4[\mathrm{Cu^{II}}][\mathrm{ROOH}]^2 - 2k_8[\mathrm{RO\cdot}]^2 = 0$$

Therefore, $[\mathrm{RO\cdot}] = (K_2K_3k_4/k_8)^{\frac{1}{2}}[\mathrm{Cu^{II}}]^{\frac{1}{2}}[\mathrm{ROOH}]$ (13)

Substitution of the right hand side of equation (13) for $[\mathrm{RO\cdot}]$ in equation (12) yields:

$$-d[\mathrm{ROOH}]/dt = 2K_2K_3k_4[\mathrm{Cu^{II}}][\mathrm{ROOH}]^2 + k_5(K_2K_3k_4/k_8)^{\frac{1}{2}}[\mathrm{Cu^{II}}]^{\frac{1}{2}}[\mathrm{ROOH}]^2 \quad (14)$$

The total concentration of copper species in the system

$$\begin{aligned} = [\mathrm{Cu}]_T &= [\mathrm{Cu^{II}}] + [\mathrm{Cu^{II}(ROOH)}] + [\mathrm{Cu^{II}(ROOH)_2}] \\ &= [\mathrm{Cu^{II}}] + K_2[\mathrm{Cu^{II}}][\mathrm{ROOH}] + K_2K_3[\mathrm{Cu^{II}}][\mathrm{ROOH}]^2 \\ &= [\mathrm{Cu^{II}}](1 + K_2[\mathrm{ROOH}] + K_2K_3[\mathrm{ROOH}]^2) \end{aligned}$$

Or, $[\mathrm{Cu^{II}}] = [\mathrm{Cu}]_T/(1 + K_2[\mathrm{ROOH}] + K_2K_3[\mathrm{ROOH}]^2)$ (15)

Substitution of this expression for $[\mathrm{Cu^{II}}]$ in equation (14) yields:

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{2K_2K_3k_4[\mathrm{Cu}]_T[\mathrm{ROOH}]^2}{(1 + K_2[\mathrm{ROOH}] + K_2K_3[\mathrm{ROOH}]^2)} + \frac{k_5(K_2K_3k_4/k_8)^{\frac{1}{2}}[\mathrm{Cu}]_T^{\frac{1}{2}}[\mathrm{ROOH}]^2}{(1 + K_2[\mathrm{ROOH}] + K_2K_3[\mathrm{ROOH}]^2)^{\frac{1}{2}}} \quad (16)$$

It is assumed here that although the hydroperoxide molecules react in the monomeric form, they exist mainly as dimers. Furthermore, since copper(II) is present only in catalytic amounts, the concentration of hydroperoxide coordinated to the metal is expected to be negligibly small.

Therefore, $[\mathrm{ROOH}]_T = [\mathrm{(ROOH)_2}] = [\mathrm{ROOH}]^2/K_1$

Or, $[\mathrm{ROOH}] = [\mathrm{ROOH}]_T^{\frac{1}{2}}/K_1$ (17)

Substitution of this expression for $[\mathrm{ROOH}]$ in equation (16) gives:

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{2K_2K_3k_4[\mathrm{Cu}]_T[\mathrm{ROOH}]_T}{K_1 + K_1^{\frac{1}{2}}K_2[\mathrm{ROOH}]_T^{\frac{1}{2}} + K_2K_3[\mathrm{ROOH}]_T} + \frac{k_5(K_2K_3k_4/k_8)^{\frac{1}{2}}[\mathrm{Cu}]_T^{\frac{1}{2}}[\mathrm{ROOH}]_T}{K_1(1 + K_1^{\frac{1}{2}}K_2[\mathrm{ROOH}]_T^{\frac{1}{2}}+K_1^{-1}K_2K_3[\mathrm{ROOH}]_T)^{\frac{1}{2}}} \quad (18)$$

I.2 In the mechanism described above hydroperoxide molecules decompose through redox reactions (4) and (5) giving free radical products. It is suggested here that in addition to these reactions, decomposition to nonradical products may take place:

$$\mathrm{Cu^{II}(ROOH)_2 \longrightarrow Cu^{II} + O_2 + 2\ ROH} \tag{19}$$

In such a case,

$$\begin{aligned}-d[\mathrm{ROOH}]/dt = {} & k_4[\mathrm{Cu^{II}(ROOH)_2}] + k_5[\mathrm{Cu^{I}(ROOH)(H^+)}] + k_7[\mathrm{RO\bullet}][\mathrm{ROOH}] \\ & + k_{19}[\mathrm{Cu^{II}(ROOH)_2}]\end{aligned}$$

$$\begin{aligned}-d[\mathrm{ROOH}]/dt = {} & (k_4 + k_{19})[\mathrm{Cu^{II}(ROOH)_2}] + k_5[\mathrm{Cu^{I}(ROOH)(H^+)}] \\ & + k_7[\mathrm{RO\bullet}][\mathrm{ROOH}]\end{aligned} \tag{20}$$

This equation differs from equation (9) only in the value of the constant in the first term on the right hand side. Equation (20) will therefore lead to exactly the same orders in reactants as equation (18).

I.3a The following mechanism involves the decomposition of the first Cu(II)-ROOH complex formed in reaction (2) into radical products:

$$\mathrm{Cu^{II} + ROOH \rightleftharpoons Cu^{II}(ROOH)} \tag{2}$$

$$\mathrm{Cu^{II}(ROOH) \longrightarrow Cu^{I}(H^+) + ROO\bullet} \tag{21}$$

$$\mathrm{Cu^{I}(H^+) + ROOH \longrightarrow Cu^{II} + H_2O + RO\bullet} \tag{22}$$

$$\mathrm{2\ ROO\bullet \longrightarrow 2\ RO\bullet + O_2} \tag{6}$$

$$\mathrm{ROOH + RO\bullet \longrightarrow ROO\bullet + ROH} \tag{7}$$

$$\mathrm{2\ RO\bullet \longrightarrow ROOR} \tag{8}$$

Here, $-d[\mathrm{ROOH}]/dt = k_{21}[\mathrm{Cu^{II}(ROOH)}] + k_{22}[\mathrm{Cu^{I}(H^+)}][\mathrm{ROOH}] + k_7[\mathrm{RO\bullet}][\mathrm{ROOH}]$

Application of the steady state approximation for $\mathrm{Cu^{I}(H^+)}$ gives:

$$-d[\mathrm{ROOH}]/dt = 2k_{21}[\mathrm{Cu^{II}(ROOH)}] + k_7[\mathrm{RO\bullet}][\mathrm{ROOH}]$$

$$-d[\mathrm{ROOH}]/dt = 2k_{21}K_2[\mathrm{Cu^{II}}][\mathrm{ROOH}] + k_7[\mathrm{RO\bullet}][\mathrm{ROOH}] \tag{23}$$

Assumption of steady state conditions for RO• and ROO• leads to:

$$k_{22}[\mathrm{Cu}^{\mathrm{I}}][\mathrm{ROOH}] + 2k_6[\mathrm{ROO}\cdot] - k_7[\mathrm{RO}\cdot][\mathrm{ROOH}] - 2k_8[\mathrm{RO}\cdot] = 0$$

$$\text{Or, } k_{21}K_2[\mathrm{Cu}^{\mathrm{II}}][\mathrm{ROOH}] + 2k_6[\mathrm{ROO}\cdot]^2 - k_7[\mathrm{RO}\cdot][\mathrm{ROOH}] - 2k_8[\mathrm{RO}\cdot]^2 = 0 \qquad (24)$$

$$\text{Also, } k_{21}K_2[\mathrm{Cu}^{\mathrm{II}}(\mathrm{ROOH})] + k_7[\mathrm{RO}\cdot][\mathrm{ROOH}] - 2k_6[\mathrm{ROO}\cdot]^2 = 0$$

$$\text{Or, } k_{21}K_2[\mathrm{Cu}^{\mathrm{II}}][\mathrm{ROOH}] + k_7[\mathrm{RO}\cdot][\mathrm{ROOH}] - 2k_7[\mathrm{ROO}\cdot]^2 = 0 \qquad (25)$$

Combination of equations (24) and (25) yields:

$$2k_{21}K_2[\mathrm{Cu}^{\mathrm{II}}][\mathrm{ROOH}] - 2k_8[\mathrm{RO}\cdot]^2 = 0$$

$$\text{i.e., } [\mathrm{RO}\cdot] = (k_{21}K_2/k_8)^{\frac{1}{2}}[\mathrm{Cu}^{\mathrm{II}}]^{\frac{1}{2}}[\mathrm{ROOH}]^{\frac{1}{2}}$$

Substitution of this expression for $[\mathrm{RO}\cdot]$ in (23) yields:

$$-\,d[\mathrm{ROOH}]/dt = 2k_{21}K_2[\mathrm{Cu}^{\mathrm{II}}][\mathrm{ROOH}] + k_7(k_{21}K_2/k_8)[\mathrm{Cu}^{\mathrm{II}}]^{\frac{1}{2}}[\mathrm{ROOH}]^{3/2} \qquad (26)$$

$$\text{Total concentration of copper} = [\mathrm{Cu}]_T = [\mathrm{Cu}^{\mathrm{II}}] + [\mathrm{Cu}^{\mathrm{II}}(\mathrm{ROOH})]$$

$$= [\mathrm{Cu}^{\mathrm{II}}] + K_2[\mathrm{Cu}^{\mathrm{II}}][\mathrm{ROOH}]$$

$$\text{Or, } [\mathrm{Cu}^{\mathrm{II}}] = [\mathrm{Cu}]_T/(1 + K_2[\mathrm{ROOH}]) \qquad (27)$$

Substitution of the expression on the right hand side for $[\mathrm{Cu}^{\mathrm{II}}]$ in equation (26) yields:

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{2k_{21}K_2[\mathrm{Cu}]_T[\mathrm{ROOH}]}{(1 + K_2[\mathrm{ROOH}])} + \frac{k_7(k_{21}K_2/k_8)^{\frac{1}{2}}[\mathrm{Cu}]_T^{\frac{1}{2}}[\mathrm{ROOH}]^{3/2}}{(1 + K_2[\mathrm{ROOH}])^{\frac{1}{2}}} \qquad (28)$$

<u>I.3b</u> If, furthermore, it is assumed that the hydroperoxide exists mainly in the dimeric form,

$$[\mathrm{ROOH}] = [\mathrm{ROOH}]_T^{\frac{1}{2}}/K_1^{\frac{1}{2}} \qquad (17)$$

Substitution of this expression for $[\mathrm{ROOH}]$ in (28) yields:

$$-\frac{d[\mathrm{ROOH}]}{dt} = \frac{2k_1K_2[\mathrm{Cu}]_T[\mathrm{ROOH}]^{\frac{1}{2}}}{K_1^{\frac{1}{2}} + K_2[\mathrm{ROOH}]_T^{\frac{1}{2}}} + \frac{k_7(k_{21}K_2/k_8)^{\frac{1}{2}}[\mathrm{Cu}]_T^{\frac{1}{2}}[\mathrm{ROOH}]_T^{3/4}}{K_1^{3/4}(1 + K_1^{-\frac{1}{2}}K_2/\mathrm{ROOH}/_T^{\frac{1}{2}})^{\frac{1}{2}}} \qquad (29)$$

<u>I.4</u> In this mechanism, copper(II) and hydroperoxide react without any intermediate complex formation to yield radical products:

$$\mathrm{Cu^{II} + ROOH \longrightarrow Cu^{I} + H^{+} + ROO\cdot} \tag{30}$$

$$\mathrm{Cu^{I} + ROOH \longrightarrow Cu^{II} + OH^{-} + RO\cdot} \tag{31}$$

$$\mathrm{2\ ROO\cdot \longrightarrow 2\ RO\cdot + O_2} \tag{6}$$

$$\mathrm{RO\cdot + ROOH \longrightarrow ROH + ROO\cdot} \tag{7}$$

$$\mathrm{2\ RO\cdot \longrightarrow ROOR} \tag{8}$$

In this case,

$$- d[\mathrm{ROOH}]/dt = k_{30}[\mathrm{Cu^{II}}][\mathrm{ROOH}] + k_{31}[\mathrm{Cu^{I}}][\mathrm{ROOH}] + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}]$$

Application of the steady state approximation for Cu(I) gives:

$$- d[\mathrm{ROOH}]/dt = 2k_{30}[\mathrm{Cu^{II}}][\mathrm{ROOH}] + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] \tag{32}$$

If steady state conditions are also assumed for RO• and ROO• radicals, the following expressions are obtained:

$$k_{31}[\mathrm{Cu^{I}}][\mathrm{ROOH}] + 2k_6[\mathrm{ROO\cdot}]^2 - k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] - 2k_8[\mathrm{RO\cdot}]^2 = 0$$

$$\text{Or, } k_{30}[\mathrm{Cu^{II}}][\mathrm{ROOH}] + 2k_6[\mathrm{ROO\cdot}]^2 - k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] - 2k_8[\mathrm{RO\cdot}]^2 = 0 \tag{33}$$

$$\text{Also, } k_{30}[\mathrm{Cu^{II}}][\mathrm{ROOH}] + k_7[\mathrm{RO\cdot}][\mathrm{ROOH}] - 2k_6[\mathrm{ROO.}]^2 = 0 \tag{34}$$

Combination of equations (33) and (34) gives:

$$2k_{30}[\mathrm{Cu^{II}}][\mathrm{ROOH}] - 2k_8[\mathrm{RO\cdot}]^2 = 0$$

$$\text{i.e., } [\mathrm{RO\cdot}] = (k_{30}/k_8)^{\frac{1}{2}}[\mathrm{Cu^{II}}]^{\frac{1}{2}}[\mathrm{ROOH}]^{\frac{1}{2}} \tag{35}$$

Substitution of this expression for $[\mathrm{RO\cdot}]$ in equation (32) yields:

$$- d[\mathrm{ROOH}]/dt = 2k_{30}[\mathrm{Cu^{II}}][\mathrm{ROOH}] + k_7(k_{30}/k_8)^{\frac{1}{2}}[\mathrm{Cu^{II}}]^{\frac{1}{2}}[\mathrm{ROOH}]^{3/2}$$

APPENDIX II

UV Absorption peaks for metal acetylacetonates in chloroform solution

Metal	λ_{max}	
	cm^{-1}	$m\mu$
Al(III)	34,700	288
Mn(II)	36,200	276
Mn(III)	36,500	274
Co(II)	34,200	292
Co(III)	38,800	258
Cu(II)	40,800 33,800	245 296
Cr(III)	29,800	336
Ni(II)	37,700 33,800	265 296
Fe(III)	36,500	274

References

1. G. V. Schulz and E. Husemann, Z. Phys. Chem., B39, 246 (1938).
2. G. M. Burnett and L. D. Loan, Trans. Faraday Soc., 51, 219 (1955).
3. D. B. Anderson, G. M. Burnett and A. C. Gowan, J. Polymer Sci., Part A, 1, 1465 (1963).
4. W. M. Thomas, E. H. Gleason and J. J. Pellon, ibid, 17, 275 (1955).
5. M. Devaleriola, Bull. Roy. Soc. Liege, 30, 367 (1961).
6. G. M. Burnett and W. W. Wright, Proc. Roy. Soc., Series A, 221, 28 (1954).
7. G. E. Scott and E. Senogles, J. Macromol. Sci.-Chem., A4, 1105 (1970).
8. P. Hayden and H. Melville, J. Polymer Sci., 43, 201 (1960).
9. G. M. Burnett and G. L. Duncan, Makromol. Chem., 51, 154, 171 (1962).
10. M. S. Matheson, J. Chem. Phys., 13, 584 (1945).
11. I. A. Saad and F. R. Eirich, Polymer Preprints, 1, 276 (1960).
12. C. Walling and Y. Chang, J. Amer. Chem. Soc., 76, 4878 (1954).
13. A. V. Tobolsky and L. R. Matlack, J. Polymer Sci., 55, 49 (1961).
14. S. N. Gupta and U. S. Nandi, ibid, Part A-1, 8, 3019 (1970).
15. F. Tudos, Acta Chim. Hung., 43, 397 (1965); ibid, 44, 403 (1965).
16. J. C. Bevington and T. D. Lewis, Trans. Faraday Soc., 54, 1340 (1958).
17. F. Tudos, J. Polymer Sci., Part C, 16, 3461 (1968).
18. G. Henrici-Olive and S. Olive, Makromol. Chem., 68, 219 (1963).
19. G. Henrici-Olive and S. Olive, Z. Phys. Chem. (Frankfurt am Main), 47, 286 (1965).
20. G. Henrici-Olive and S. Olive, ibid, 48, 35 , 51 (1966).
21. G. Henrici-Olive and S. Olive, Makromol. Chem., 96, 221 (1966).
22. G. M. Burnett, Chem. Soc. Symposium on "Growth and Termination in Polymerization Processes, Aberdeen University, 1970.

23. C. H. Bamford and S. Brumby, Makromol. Chem., 105, 122 (1967).

24. G. M. Burnett, G. G. Cameron and M. M. Zafar, Eur. Polymer J., 6, 823 (1970).

25. W. I. Bengough and N. K. Henderson, Chem. Ind., 1969, 657.

26. G. A. Russell, J. Amer. Chem. Soc., 79, 2977 (1957).

27. G. A. Russell, ibid, 80, 4987, 4997, 5002 (1958).

28. G. A. Russell, J. Organ. Chem., 24, 300 (1959).

29. G. A. Russell, Tetrahedron, 8, 101 (1960).

30. C. H. Bamford, S. Brumby and R. P. Wayne, Nature, 209, 292 (1966).

31. V. P. Zubov, M. B. Lachinov, V. B. Golubev, V. F. Kulikova, V. A. Kabanov, L. S. Polak and V. A. Kargin, J. Polymer Sci., Part C, 23, 147 (1968).

32. C. H. Bamford and S. Brumby, Makromol. Chem., 134, 159 (1970).

33. S. Brumby, Chem. Soc. Symposium on "Growth and Termination in Polymerization Processes", Aberdeen University, 1970.

34. L. Batt, G. M. Burnett, G. G. Cameron and J. Cameron, Chem. Commun. 1, 29 (1971).

35. F. C. DeSchryver, G. Smets and J. Van Thielen, J. Polymer Sci., Part B, 6, 547 (1968).

36. S. N. Gupta and U. S. Nandi, ibid, Part A-1, 8, 1493 (1970).

37. C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, J. Amer. Chem. Soc., 70, 1537, 1544 (1948).

38. C. Walling, D. Seymour and K. B. Wolfstirn, ibid, 70, 2559 (1948).

39. C. Walling, ibid, 70, 2561 (1948).

40. N. Fuhrman and R. B. Mesrobian, ibid, 76, 3281 (1954).

41. C. H. Bamford and F. C. White, Trans. Faraday Soc., 52, 716 (1956).

42. T. Alfrey, Jr. and C. C. Price, J. Polymer Sci., 2, 101 (1947).

43. C. C. Price, ibid, 3, 772 (1948).

44. T. Alfrey, Jr., J. J. Bohrer and H. Mark, Copolymerization, Interscience, New York, 1957.

45. C. Walling, J. Amer. Chem. Soc., 86, 3368 (1964).

46. B. E. Lopez Madriga, J. M. Barrales- Rienda and G. M. Guzman, Preprints, Intern. Symp. Macromol. Chem., Hungary, 111P.5/10, 37 (1969).

47. G. Saini, A. Leoni and S. Franco, Macromol. Chem., 147, 213 (1971).

48. W. K. Busfield and R. B. Low, Chem. Soc. Symp. on "Growth and Termination in Polymerization Processes", Aberdeen University, 1970.

49. J. Ito and T. Otsu, J. Macromol. Sci., A3, 197 (1969).

50. P. J. Flory, J. Amer. Chem. Soc., 59, 241 (1937).

51. J. M. Liegeois, Seventh IUPAC Microsymposium on Macromolecules, 1970, cited by S. R. Singh, Colourage, 19, 67 (1972).

52. M. Ryska, M. Kolinsky and D. Lim, ibid.

53. (a) P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York., 1953.
(b) G. Odian, Principles of Polymerization, McGraw-Hill, Inc., New York, 1970.

54. A. D. Jenkins, Trans. Faraday Soc., 54, 1885 (1958).

55. D. Lim and O. Wichterle, J. Polymer Sci., 29, 579 (1958).

56. M. S. Gluckman, M. J. Kampf, J. L. O'Brien, T. G. Fox and R. K. Graham, ibid, 37, 411 (1959).

57. R. B. Carlin and N. E. Shakespeare, J. Amer. Chem. Soc., 68, 876 (1946).

58. J. C. Bevington, G. M. Guzman and H. W. Melville, Proc. Roy. Soc., London, Series A, 221, 437, 453 (1954).

59. E. H. Gleason, M. L. Miller and G. F. Sheats, J. Polymer Sci., 38, 133 (1959).

60. U. S. Nandi, P. R. GhOsh and S. R. Palit, Nature, 195, 1197 (1962).

61. A. D. Jenkins and R. Johnston, J. Polymer Sci., 39, 81 (1959).

62. R. A. Gregg and F. R. Mayo, Disc. Faraday Soc., 2, 328 (1947).

63. S. Basu, J. N. Sen and S. R. Palit, Proc. Roy. Soc. London, Ser. A, 202, 485 (1950).

64. S. Basu, J. N. Sen and S. R. Palit, ibid, 214, 247 (1952).

65. G. Smets and P. Rieske, Bull. Soc. Chim. Belges, 56, 159 (1947).

66. S. R. Palit and U. S. Nandi, J. Polymer Sci., 14, 295 (1954).

67. P. W. Allen, F. M. Merrett and J. Scanlan, Trans. Faraday Soc., 51, 95 (1955).

68. F. R. Mayo, J. Amer. Chem. Soc., 65, 2324 (1943).

69. C. Walling, ibid, 70, 2561 (1948).

70. L. A. Wall and D. W. Brown, J. Polymer Sci., 14, 513 (1954).

71. J. C. Bevington and H. G. Troth, Trans. Faraday Soc., 58, 2005 (1962).

72. J. C. Bevington and H. G. Troth, ibid, 59, 127 (1963).

73. J. Brandrup and E. H. Immergut, Polymer Handbook, Wiley-Interscience, New York, 1966.

74. J. N. Sen, U. S. Nandi and S. R. Palt, J. Indian Chem. Soc., 40, 729 (1963).

75. S. R. Palit and S. Das, Proc. Roy. Soc. Lond., Ser. A, 226, 82 (1954).

76. S. K. Das, S. R. Chatterjee and S. R. Palit, ibid, 227, 252 (1955).

77. C. H. Bamford, A. D. Jenkins and R. Johnston, Trans. Faraday Soc., 55, 418 (1959).

78. C. H. Bamford and A. D. Jenkins, J. Polymer Sci., 53, 149 (1961).

79. H. Jaffe, Chem. Rev., 53, 191 (1953).

80. T. Yamamoto and T. Otsu, J. Polymer Sci., Part A-1, 6, 49 (1968).

81. U. S. Nandi, "Studies on reaction kinetics of vinyl polymerization", Ph.D. Thesis, Calcutta University, India, 1956.

82. J. Scanlan, .F H. Merrett and P.W. Allen, Trans. Faraday Soc., 51, 95 (1955).

83. W. H. Atkinson, C. H. Bamford and G. C. Eastmond, ibid, 66, 1446 (1970).

84. L. H. Peebles and W. H. Stockmayer, J. Amer. Chem. Soc., 75, 2278 91953).

85. D. B. Anderson and G. M. Burnett, unpublished results, cited in reference 3.

86. G. E. Scott and E. Senogles, unpublished data, cited in Macromol. Chem., C9, 49 (1973).

87. M. J. Roedel, J. Amer. Chem. Soc., 75, 6110 (1953).

88. A. G. Morrell, Discussions Faraday Soc., 22, 152 (1956).

89. H. W. Melville and P. R. Sewell, Makromol. Chem., 32, 139 (1959).

90. M. Litt and V. Stannett, ibid, 37, 19 (1960).

91. A. Vrancken and G. Smets, ibid, 30, 197 (1959).

92. E. D. Morrison, E. H. Gleason and V. Stannett, J. Polymer Sci., 36, 267 (1959).

93. G. M. Burnett and W. W. Wright, Trans. Faraday Soc., 49, 1108 (1953).

94. C. H. Bamford, A. D. Jenkins and R. Johnston, Proc. Roy. Soc. Lond., A241, 354 (1957).

95. M. Durup and M. Magat, J. Polymer Sci., 18, 586 (1955).

96. A. M. North and D. Postlethwaite, "The Termination Mechanism in Radical Polymerization", Chapter 4 in Y. Tsuruta and K. F. O'Driscoll (Eds.), Structure and Mechanism in Vinyl Polymerization, Marcel Dekker, New York, 1969.

97. J. C. Bevington et. al., J. Polymer Sci., 12, 449 (1954); ibid, 14, 463 (1954).

98. C. H. Bamford, A. D. Jenkins and R. Johnston, Trans. Faraday Soc., 55, 179 (1959).

99. C. H. Bamford, A. D. Jenkins and R. Johnston, ibid, 55, 1451 (1959).

100. P. E. M. Allen and C. R. Patrick, Makromol. Chem., 48, 89 (1961).

101. R. G. W. Norrish and R. R. Smith, Nature, 150, 566 (1942).

102. E. Tromsdorff, H. Kohle and P. Lagally, Makromol. Chem., 1, 169 (1947).

103. S. W. Benson and A. M. North, J. Amer. Chem. Soc., 81, 1339 (1959).

104. A. M. North and G. A. Reed, Trans. Faraday Soc., 57, 859 (1961).

105. A. M. North and G. A. Reed, J. Polymer Sci., Part A, 1, 1311 (1963).

106. K. Yohota and M. Itoh, ibid, Part B, 6, 825 (1968).

107. S. R. Rafikov, P. E. Masserle, G. P. Gladyshev and I. B. Shafranskaya, ibid, Part B, 5, 715 (1967).

108. W. I. Bengough, S. A. MacIntosh and I. C. Ross, Nature, 200, 567 (1963).

109. V. Lingamurty and S. R. Palit, J. Sci. Ind. Res. (India), 18B, 140 (1959).

110. M. K. Saha, A. R. Mukerjee, P. Ghosh and S. R. Palit, Proc. Intern. Symp. Macromol. Chem., Prague, 1965.

111. (a) M. G. Evans and N. Uri, Nature, 164, 404 (1949); (b) N. Uri, Chem. Rev., 50, 375 (1952).

112. C. H. Wang, Chem. Ind. (London), 1964, 751.

113. S. Tazuke and S. Okamura, J. Polymer Sci., A4, 141 (1966).

114. E. H. Cornish, Makromol. Chem., 64, 210 (1963).

115. M. Watanabe and H. Kiuchi, J. Polymer Sci., 58, 103 (1962).

116. C. H. Bamford and C. A. Finch, Proc. Roy. Soc. London, A268, 553 (1962).

117. C. H. Bamford, R. Denyer and G. C. Eastmond, Trans. Faraday Soc., 62, 688 (1966).

118. C. H. Bamford, G. C. Eastmond and V. J. Roleinson, ibid, 60, 751 (1964).

119. E. G. Kastning, H. Naarman, H. Reis and Ch. Berding, Angew. Chem., Intern. Edn., 4, 322 (1965).

120. C. H. Bamford and K. Hargreaves, Trans. Faraday Soc., 63, 392 (1967).

121. C. H. Bamford and D. J. Lind, Proc. Roy. Soc. London, A302, 145 (1968).

122. C. H. Bamford and A. N. Ferrar, ibid, A321, 425 (1971).

123. M. M. Zafar, A. H. K. Yousafzai and R. Mahmud, Makromol. Chem., 167, 243 (1973).

124. C. H. Bamford, G. C. Eastmond and J. A. Rippon, Trans. Faraday Soc., 59, 2548 (1963).

125. T. Otsu, Y. Nishikawa and S. Aoki, Kogyo Kagaku Zasshi, 71, 1067 (1968).

126. T. Huff and E. Perry, J. Polymer Sci., Part A, 1, 1553 (1963).

127. S. Aoki, S. Matsumara and T. Otsu, Bull. Chem. Soc. Japan, 42, 2574 (1969).

128. A. G. Davies, Organic Peroxides, Butterworth, London, 1961.

129. E. G. E. Hawkins, Organic Peroxides, Van Nostrand-Reinhold, Princeton, New Jersey, 1961.

130. W. O. Lundberg, Ed., Autoxidation and Antioxidants, Vol. 1, Wiley-Interscience, New York, 1961.

131. G. Sosnovsky and J. H. Brown, Chem. Rev., 66, 529 (1966).

132. E. T. Denisov and N. M. Emanuel, Russian Chem. Rev., 29, 645 (1960).

133. R. Hiatt, "Hydroperoxides", Chapter 1, in D. Swern (Ed.), Organic Peroxides, Vol. II, Wiley-Interscience, New York, 1971.

134. G. Sosnovsky and D. J. Rawlinson, Chapter 2 in D. Swern (ed.), Organic Peroxides, Vol. II, Wiley-Interscience, New York, 1971.

135. (a) R. Hiatt, T. Mill and F. R. Mayo, J. Organ. Chem., 1416 (1968),
(b) R. Hiatt, K. C. Irwin and C. W. Gould, ibid, 1430 (1968).

136. J. Dickstein, E. Blommers and W. Karo, J. Appl. Polymer Sci., 6, 193 (1962).

137. I. M. Kolthoff and A. I. Medalia, J. Amer. Chem. Soc., 71, 3789 (1949).

138. A. J. Everett and G. J. Minkoff, Trans. Faraday Soc., 49, 410 (1953).

139. D. Barnard and K. R. Hargrave, Anal. Chim. Acta, 5, 476 (1951).

140. A. J. Martin, Organic Analysis, Vol. IV, Interscience, New York, 1960, pp. 1-64.

141. S. Siggia, Quantitative Organic Analysis, Wiley, New York, 1963, pp. 255-295.

142. A. J. Davies, R. V. Foster and R. Nery, J. Chem. Soc., 1954, 2204.

143. R. Hiatt, J. R. Clipsham and T. Visser, Can. J. Chem., 42, 2754 (1964).

144. A. Factor, C. A. Russell and T. G. Taylor, J. Amer. Chem. Soc., 87, 3692 (1965).

145. J. R. Thomas and K. U. Ingold, Oxidation of Organic Compounds, Vol. I, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D.C., 1968, p. 258.

146. D. B. Denny and J. D. Rosen, Tetrahedron, 20, 271 (1964).

147. E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, Discussions Faraday Soc., 10, 246 (1951).

148. J. T. Martin and R. G. W. Norrish, Proc. Roy. Soc. London, A220, 322 (1953).

149. M. S. Kharasch, A. Fono and W. Nudenberg, J. Organ. Chem., 16, 113 (1951)

150. Reference 133, p. 88.

151. R. Hiatt, T. Mill, K. C. Irwin and J. K. Castleman, J. Organ. Chem., 1421 (1968).

152. J. R. Thomas, J. Amer. Chem. Soc., 89, 4872 (1967).

153. T. G. Taylor and C. A. Russell, ibid, 87, 3698 (1965).

154. R. Hiatt and K. C. Irwin, J. Organ. Chem., 33, 1436 (1968).

155. G. H. Twigg, Discussions Faraday Soc., 14, 240 (1953).

156. I. V. Berezin, N. F. Kazanskaya and N. N. Ugarova, Zh. Fiz. Khim., 40, 766 (1966).

157. W. M. Pryor, D. M. Huston, T. R. Fike, T. L. Pickering and E. Ciuffarin, J. Amer. Chem. Soc., 86, 4237 (1964).

158. S. W. Benson, J. Chem. Phys., 40, 1007 (1964).

159. S. W. Benson and J. Buss, ibid, 29, 546 (1958).

160. N. A. Milas and D. M. Surgenor, J. Amer. Chem. Soc., 68, 205, 643 (1946).

161. G. H. Twigg, G. W. Godin, H. C. Bailey and J. Holden, Erdol und Kohle, 15, 74 (1962).

162. P. D. Bartlett and K. Nozaki, J. Amer. Chem. Soc., 69, 2299 (1947).

163. A. Robertson and W. A. Waters, J. Chem. Soc., 1948, 1578.

164. V. Stannett and R. B. Mesrobian, J. Amer. Chem. Soc., 72, 4125 (1950).

165. E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, ibid, 73, 18 (1951).

166. J. R. Thomas and O. Harle, J. Phys. Chem., 63, 1027 (1959).

167. L. Bateman and H. Hughes, J. Chem. Soc., 1952, 4594.

168. V. L. Antonovskii, E. T. Denisov and L. V. Solntseva, Kinetika i Kataliz, 6, 815 (1965).

169. V. Stannett and R. B. Mesrobian, Discussions Faraday Soc., 14, 242 (1953).

170. C. Walling and L. Heaton, J. Amer. Chem. Soc., 87, 38 (1965).

171. E. T. Denisov and L. N. Denisova, Doklady Akad. Nauk SSSR, 157, 907 (1964).

172. W. F. Brill and N. Indictor, J. Organ. Chem., 29, 710 (1964).

173. A. L. Buchachenko and O? P. Sukhanova, Usp. Khim., 36, 475 (1967).

174. Reference 133, p. 47.

175. C. Walling and L. Heaton, J. Amer. Chem. Soc., 87, 48 (1965).

176. V. L. Antonovskii V. A. Ternt'ev, Zh. Organ. Khim., 3, 1011 (1967).

177. W. H. Richardson and R. F. Steed, J. Organ. Chem., 32, 771 (1967).

178. Reference 133, pp. 102-105.

179. L. Reich and S. S. Stivala, Autoxidation of Hydrocarbons and Polyolefins: Kinetics and Mechanism, Marcel Dekker, Inc., New York, 1969, pp. 247-342.

180. W. H. Richardson, J. Amer. Chem. Soc., 88, 975 (1966).

181. F. Haber and J. Weiss, Proc. Roy. Soc. London, A147, 332 (1934).

182. W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, Nature, 163, 692 (1949).

183. W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, Trans. Faraday Soc., 47, 462 (1951).

184. M. S. Kharasch, P.Pauson and W. Nudenberg, J. Organ. Chem., 18, 322 (1943).

185. M. S. Kharasch and A. Fono, ibid, 24, 72 (1959).

186. M. S. Kharasch and G. Sosnovsky, Tetrahedron, 3, 105 (1958).

187. W. H. Richardson, J. Amer. Chem. Soc., 87, 247 (1965).

188. W. C. Bray and M. H. Gorin, ibid, 54, 2124 (1932).

189. A. E. Cahill and H. J. Taube, ibid, 74, 2313 (1952).

190. T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, ibid, 87, 926 (1965).

191. N. K. King and M. E. Winfield, Austr. J. Chem., 12, 138, 147 (1959).

192. A. Goudot, Compt. Rend., 250, 346 (1960).

193. A. Goudot, ibid, 250, 712 (1960).

194. Z. Kovats, Magy. Folyoirat. 69, 98 (1963).

195. J. H. Wang, J. Amer. Chem. Soc., 77, 4715 (1955).

196. R. C. Jarnigan and J. H. Wang, ibid, 80, 6477 (1958).

197. G. A. Hamilton, Advan. Enzymol., 24, 54 (1969).

198. H. Berger and A. F. Bickel, Trans. Faraday Soc., 57, 1325 (1961).

198a. J. K. Kochi, Tetrahedron, 18, 483 (1962).

199. M. H. Dean and G. Skirrow, Trans. Faraday Soc., 54, 849 (1958).

200. J. B. Braunworth, and G. W. Crosby, J. Org. Chem., 27, 2064 (1962).

201. S. Murai, N. Sonoda and S. Tsutsumi, Bull. Chem. Soc. Japan, 36, 527 (1963).

202. F. Minisci and G. Belvedere, Gazz. Chim. Ital., 90, 1299 (1960).

203. J. K. Kochi and F. F. Rust, J. Amer. Chem. Soc., 84, 3946 (1962).

204. J. Kumamoto, H. E. De La Mare and F. F. Rust, ibid, 82, 1935 (1960).

205. V. L. Antonovskii and Yu. D. Emelin, Zh. Vses. Khim. Obshecestva im D. I. Mendeleeva, 9, 471 (1964); through Chem. Abstr., 61, 13222 (1964).

206. F. Minisci and R. Galli, Tetrahedron Lett., 1963, 357.

207. J. A. Bigot, Rec. Trav. Chim., 80, 825 (1961).

208. A. J. Chalk and J. F. Smith, Trans. Faraday Soc., 53, 1214, 1235 (1957).

209. W. H. Richardson, J. Amer. Chem. Soc., 87, 1096 (1965).

210. Y. Kamiya, S. Beaton, A. LaFortune and K. U. Ingold, Can. J. Chem., 2020, 2034 (1963).

211. E. Dyer, K. R. Carle and D. Weiman, J. Org. Chem., 23, 1464 (1958).

212. N. Indictor and T. Jochsberger, ibid, 4271 (1966).

213. Z. Osawa and T. Shibamiya, J. Polymer Sci., Part B, 6, 721 (1968).

214. J. K. Kochi. J. Amer. Chem. Soc., 84, 1193 (1962).

215. H. Taube in Advances in Inorganic and Radiochemistry, Vol. I, edited by H. J. Emeleus and A. G. Sharpe, Academic Press, New York, 1959, p. 1.

216. K. Onuma K. Wada, J. Yamashita and H. Hashimoto, Bull. Chem. Soc. Japan, 40, 290 (1967).

217. T. Wallace and R. M. Skomoroski, Chem. Ind. (London), 1965, 348.

218. H. Siegel. Angew. Chem., Intern. Edn.,Engl., 8, 167 (1969).

219. H. Knopf, Ann., 637, 73-111 (1960).

220. E. Y. Scott, J. Phys. Chem., 74, 1174 (1970).

221. N. Uri, Chem. Ind. (London), 1956, 515; Nature, 177, 1177 (1956).

222. Z. Osawa, T. Shibamiya, Y. Ogiwara and M. Kei, Kogyo Kagaku Zasshi, 73, 115 (1970).

223. Z. G. Kozlova, V. F. Tsepalov and V. Y. Shlyapintokh, Kinetika i Kataliz, 5, 868 (1964).

224. Y. Kamiya, Bull. Chem. Soc. Japan, 38, 2156 (1965).

225. H. B. Van Leeuwen, J. P. Wibaut, A. F. Bickel and E. C. Kooyman, Rec. Trav. Chim., 77, 17 (1958); ibid, 78, 667 (1959).

226. R. Hiatt, C. W. Gould and F. R. Mayo, J. Org. Chem., 29, 3461 (1964).

227. G. Dobson and G. Hughes, J. Phys. Chem., 69, 1814 (1965).

228. G. Wagner, J. Prakt. Chem., 27, 297 (1965).

229. D. W. Thompson, "Structure and Bonding in Inorganic Derivatives of β-Diketones", Chapter 2 in P. Hemmerich *et. al.* (Eds.), *Structure and Bonding*, Vol. 9, Springer-Verlag, New York, 1971, p. 27.

230. J. P. Fackler and F. A. Cotton, J. Amer. Chem. Soc., 83, 2818 (1961).

231. (a) G. J. Bullen, Nature, 177, 537 (1956).
     (b) G. J. Bullen, R. Mason and P. Pauling, ibid, 189, 291 (1961)
     (c) G. J. Bullen, R. Mason and P. Pauling, Inorg. Chem., 4, 456 (1965).

232. J. P. Fackler, and F. A. Cotton, J. Amer. Chem. Soc., 83, 3775 (1961).

233. M. J. Bennett, F. A. Cotton, R. Eiss and R. C. Elder, Nature, 213, 174 (1967).

234. F. A. Cotton and R. C. Elder, J. Amer. Chem. Soc., 86, 2294 (1964).

235. J. P. Fackler, "Metal β-ketoenolate complexes" in F. A. Cotton (Ed.), *Progress in Inorganic Chemistry*, Vol. 17, Wiley-Interscience, New York, 1966, p. 411.

236. D. P. Graddon, Coordination Chem. Rev., 4, 1 (1969).

237. E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, Discussions Faraday Soc., 10, 242 (1951).

238. R. Hiatt and W. M. J. Strachan, J. Org. Chem., 28, 1893 (1963).

239. R. Lombard and J. Knopf, Bull. Soc. Chim. Fr., 1966, 3926, 3930.

240. N. Indictor, T. Jochsberger and D. Kurnit, J. Org. Chem., 34, 2855, 2861 (1969).

241. (a) A. Auerbach, T. Jochsberger and N. Indictor, Macromolecules, 6, 143 (1973); (b) A. Auerbach, N. Indictor and A. Kruger, ibid, 8, 262 (1975).

242. Z. Osawa, M. Suzuki, Y. Ogiwara and K. Matsuzaki, Kogyo Kagaku Zasshi, 73, 110 (1970).

243. N. Indictor and C. Linder, J. Polymer Sci., A3, 3668 (1965).

244. Z. Osawa, T. Shibamiya and T. Kawamata, ibid, Part A-1, 8, 262 (1970).

245. Z. Osawa, K. Kabayashi and Y. Ogiwara, J. Macromol. Sci., A6, 1665 (1972).

246. M. S. Kharasch and A. Fono, J. Org. Chem., 23, 324 (1958).

247. E. T. Denisov, Russ. J. Phys. Chem., 37, 1029 (1963).

248. M. D. Goldfein, A. D. Stepukhovich and E. I. Cheptsov, Vysokomol. Soedin., Ser. A, 9, 2641 (1967); ibid, 13, 1484 (1971).

249. Y. Kamiya and K. U. Ingold, Can. J. Chem., 42, 2424 (1964).

250. K. U. Ingold, Chem. Rev., 61, 563 (1961).

251. Y. Kamiya and K. U. Ingold, Can. J. Chem., 42, 1027 (1964).

252. R. Hiatt, unpublished work, cited in reference 135.

253. H. J. Yan, unpublished data obtained for Master's thesis at Brooklyn College of CUNY, 1975.

254. Reference 53(b), pp. 240-245.

255. Z. A. Sinitsyna and Kh. S. Bagdasarayan, Zh. Fiz. Khim., 32, 1319 (1958).

256. J. E. Leffler and E. Grunwald, Rates and Equilibia of Organic Reactions, John Wiley & Sons, Inc., New York, 1963.

257. S. B. Brown, P. Jones and A. Suggett, "Recent Developments in Redox Chemistry of Peroxides", in J. O. Edwards (Ed.), Inorganic Reaction Mechanisms, Vol. 13, Interscience, New York, 1970, p. 159.

258. Chemical Society, Special Publication No. 6, p. 29 (1957).

259. J. R. Thomas and K. U. Ingold, Advances in Chemistry Series, No. 75, Amer. Chem. Soc., Washington, D.C., 1968, p. 258;
P. D. Bartlett and G. Guaraldi, J. Amer. Chem. Soc., 89, 4799 (1967).

260. A. Tkac, K. Vesely and L. Omelka, J. Phys. Chem., 75, 2575, 2580 (1971).

261. This thesis, part I.

262. C. J. Shahani and N. Indictor, Macromolecules, 8, 935 (1975).

263. (a) J. W. L. Fordham and H. C. Williams, J. Amer. Chem. Soc., 72, 4465 (1950); ibid, 73, 1634 (1951); (b) R. J. Orr and H. C. Williams, Can. J. Chem., 30, 985 (1952).

264. A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, J. Amer. Chem. Soc., 72, 1942 (1950).

265. A. E. Woodward and R. B. Mesrobian, ibid, 75, 6189 (1953).

266. R. H. Holm, "The stereochemistry of bis-chelate metal(II) complexes", in S. J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. 14, Wiley-Interscience, New York, 1971, p. 241.

267. Reference 235, p. 361.

268. P. George and A. Robertson, J. Inst. Petrol., 32, 383, 400 (1946).

269. P. George and A. Robertson, Trans. Faraday Soc., 42, 217 (1946).

270. N. K. Chakravarty, J. Inst. Petrol., 48, 196 (1962).

271. A. T. Betts and N. Uri, Makromol. Chem., 95, 22 (1966).

272. C. E. H. Bawn, A. A. Pennington and C. F. H. Tipper, Discussions Faraday Soc., 10, 282 (1951).

273. M. S. Kharasch, A. Fono, W. Nudenberg and A. C. Poshkus, J. Org. Chem., 17, 207 (1952).

274. M. S. Kharasch and A. Fono, ibid, 24, 606 (1959).

275. E. T. Denisov, Zhur. Fiz. Khim., 32, 2074 (1965).

276. S. O. Lawesson and C. Berglund, Tetrahedron Lett., 2, 4 (1960).

277. N. Indictor and W. F. Brill, J. Org. Chem., 32, 2074 (1965).

278. R. J. Gritter and E. L. Patmore, Proc. Chem. Soc., 328 (1962).

279. G. Ayrey, Makromol. Chem., 175, 1463 (1974).

280. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, Wiley & Sons, Inc., New York, 1967, p. 81.

281. K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, J. Amer. Chem. Soc., 1066 (1961).

282. M. L. Bender, Mechanisms of Homogeneous Catalysis from Protons to Proteins, Wiley- Interscience, New York, 1971, pp. 232-235.

283. M. L. Bender, ibid, pp. 215-221.

284. Reference 73, p. 134.

285. J. P. Wibaut, H. B. van Leeuwen, and B. van der Wal, Rec. Trav. Chim., 73, 1033 (1954).

286. E. A. Collins and F. W. Billmeyer, Jr., *Experiments in Polymer Science*, Wiley-Interscience, New York, 1973.

287. P. Ghosh and F. W. Billmeyer, Jr., Advances in Chemistry Series, No. 91, American Chemical Society, Washington, D.C., 1969, pp. 75-93.