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# THE REACTIONS OF t-BUTYL HYDROPEROXIDE AND 1-OCTENE IN THE PRESENCE OF METAL ACETYLACETONATES

by

THEODORE JOCHSBERGER

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

1968

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# Abstract

The reaction of t-butyl hydroperoxide with metal acetylacetonates in the presence of 1-octene has been studied. It has been shown that some of the metals catalyze the decomposition of t-butyl hydroperoxide and, in the presence of oxygen, act with the peroxide to initiate the autoxidation of 1-octene. Other metals are found to have no effect upon t-butyl hydroperoxide decomposition but act in combination with the peroxide to initiate olefin autoxidation. A third group of metals initiated the decomposition of t-butyl hydroperoxide but were ineffective as initiators of the autoxidation. Finally, some metals were observed to have no effect either upon the peroxide decomposition or the autoxidation of 1-octene.

Chromium (III) acetylacetonate was found to initiate the decomposition of t-butyl hydroperoxide and catalyze the autoxidation of 1-octene both in the presence and absence of peroxide. This metal was the only one studied that initiated the autoxidation in the absence of t-butyl hydroperoxide. Temperature and concentration effects on the kinetics of the chromium (III) acetylacetonate-initiated decomposition of t-butyl hydroperoxide and the chromium (III) acetylacetonate-t-butyl hydroperoxide-induced autoxidation of 1-octene have been studied. Although the kinetics are complex, they fit a multistep mechanistic scheme which is not fundamentally different from that usually proposed for chain reactions.

The effect of usual free radical inhibitors on both the decomposition and the autoxidation has been investigated. Again, although complexities are evident, the data can be explained on the basis of fundamental free radical inhibitor theories.

An interesting solvent effect on the autoxidation has been observed in both aromatic and oxygen-containing compounds. These results have been explained in terms of the proposed mechanism. Products of the autoxidation of 1-octene initiated by _t_-butyl hydroperoxide and chromium (III) acetylacetonate have been identified and compared to other systems in which olefins have been oxidized.

# Acknowledgments

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Finally I wish to thank the members of my advisory committee and other members of the faculty whose helpful suggestions contributed largely to the writing of this dissertation.

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# I. Introduction

A. Autoxidations.--The autoxidation of an olefin proceeds by a self-perpetuating chain mechanism involving free radicals.[1] As for any chain reaction, there are three main processes involved: initiation, propagation, and termination.

## (1) Initiation

a. Decomposition of free radical sources.--In general, initiation may take place through the decomposition of an initiator (small amount of a substance capable of producing free radicals under mild conditions) or in the absence of initiator through some external energy source such as light, heat, or ionizing radiation, or a combination of these.

The two major types of compounds used as initiators are organic peroxides and azo-compounds. Peroxides can be destroyed in a variety of ways, including thermally,[2] photolytically,[2] and by metal catalysis.[2] The thermal decomposition of peroxides has received a good deal of attention[2] and in many cases it has been shown that the decomposition is itself a chain reaction. Decomposition can proceed by either a unimolecular scission (Reaction 1) or at high peroxide concentrations by a bimolecular reaction (Reaction 2).[3]

$$(1) \quad ROOH \longrightarrow RO\cdot + \cdot OH$$

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

(3) $RO\cdot + ROOH \longrightarrow ROO\cdot + ROH$

It is usually suggested[3] that the unimolecular reaction involves O-O bond scission since this is by far the weakest bond in the system ($D_{RO-OH}$ = 36 kcal, $D_{ROO-H}$ = 84 kcal, $D_{R-OOH}$ = 80 kcal).[4] Although the bimolecular reaction involves breaking the O-H bond as well as steric problems not involved in the unimolecular reaction, it may be shown[5] that Reaction 2 is some 20 kcal/mole more exothermic than Reaction 1. Reaction 3 indicates induced decomposition of a hydroperoxide, a step which must be considered part of the initiation process in peroxide catalyzed chain reactions.

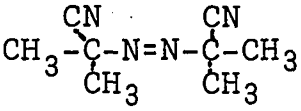
Among the more common peroxides and hydroperoxides employed as free radical initiators are benzoyl peroxide,[6] di-t-butyl peroxide,[6] and t-butyl hydroperoxide.[6] In many cases the free radical produced in the decomposition reaction is not the sole initiating species. For example, the benzoyl peroxy radical decomposes readily to a phenyl radical and carbon dioxide,[7] while the t-butoxy radical may decompose to acetone and a methyl radical.[8]

Since hydroperoxides are the primary intermediates or end products in olefin autoxidations, it is very often observed that these reactions are autocatalytic since the hydroperoxide formed also decomposes, sometimes more rapidly than the one used to initiate the reaction. This occurs when a primary or secondary hydroperoxide is formed (i.e., $RCH_2OOH$ or $R_2CHOOH$) since these are in general less stable than tertiary hydroperoxides.[9]

Azo-compounds (i.e., RN=NR) may be decomposed thermally[10] or photolytically[11] to form nitrogen and two alkyl radicals (Reaction 3). Two such compounds employed commonly are azobisisobutyronitrile [AIBN (I)][11] and azobiscyclohexane 1-carbonitrile [ABC (II)].[12]

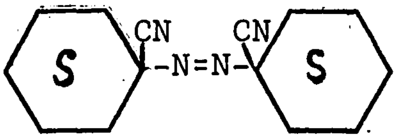
(4) $$R\text{-}N{=}N\text{-}R \xrightarrow[\text{or }\Delta]{h\nu} 2\,R\cdot + N_2$$

Figure 1: Some Azo-compounds Used as Free Radical Initiators



$$CH_3\text{-}\overset{CN}{\underset{CH_3}{C}}\text{-}N{=}N\text{-}\overset{CN}{\underset{CH_3}{C}}\text{-}CH_3$$

(I) AIBN



(II)ABC

In an autoxidation system the initiating radical is generally a peroxy radical produced by the rapid interaction of the radical produced in Reaction 4 with molecular oxygen[12] (Reaction 5).

(5) $$R\cdot + O_2 \longrightarrow RO_2\cdot$$

b. Initiation by application of an external energy source.--Another way of initiating free radical chains is by applying heat, light, or ionizing radiation. The latter two methods generally involve unimolecular decomposition of the substrate[3] (RH) (Reaction 6).

(6) $$RH \xrightarrow{h\nu} R\cdot + H\cdot$$

On the other hand, thermal initiation may involve a substrate-oxygen interaction (Reaction 7).

(7) $RH + O_2 \longrightarrow R\cdot + HO_2\cdot$

The activation energy for Reaction 7 involves 30-45 kcal/mole while simple scission of the R-H bond (Reaction 6) involves 70-100 kcal/mole.[3] Under photolytic conditions, the supply of energy is usually in excess so that the unimolecular reaction may take place readily (This is a more likely initiation pathway in the case of gas-phase or high dilution liquid phase systems).

Another reaction which has been proposed[3] as a possible initiation step in thermal autoxidations is Reaction 8.

(8) $2\ RH + O_2 \longrightarrow 2\ R\cdot + H_2O_2$

The enthalpy of formation of hydrogen peroxide (137 kcal/mole) is much greater than that of the hydroperoxy (HOO·) radical (37 kcal/mole),[13] so that for substrate molecules with C-H bond strengths of less than 100 kcal/mole, the heat of reaction for Reaction 8 is less than for Reaction 7. However, the termolecular reaction (Reaction 8) probably requires a much more ordered transition state than the bimolecular reaction (Reaction 7). The probability of a termolecular reaction occurring is much less than a bimolecular one. Consequently, the entropy of activation for Reaction 8 should be much less favorable than that of Reaction 7.

It may be shown that, in general, the rate of oxygen uptake ($-d[O_2]/dt$) under high (usually > 100 mm Hg) pressures of oxygen is related to the initiation rate ($R_i$) and the substrate concentration ([RH]) as follows[1] (see Kinetics Section, p. 79):

(9) $$-d[O_2]/dt = kR_i^{0.5}[RH]$$

where k = a complex composite rate constant. If Reaction 7 is the primary initiation process in an autoxidation then Equation 9 becomes:

(10) $$-d[O_2]/dt = k'[RH]^{1.5}[O_2]^{0.5}$$

whereas if Reaction 8 is important, Equation 9 becomes:

(11) $$-d[O_2]/dt = k''[RH]^{2}[O_2]^{0.5}$$

The usual observation[3] is that thermal autoxidations obey Equation 10.

Another mode of initiation is via interaction with metal ions.[3] Although this usually involves metal-hydroperoxide reactions, initiation can be accomplished via a direct reaction between the substrate and the metal,[3] followed by subsequent reaction of metal and hydroperoxide once the chain is started.

(12) $$RH + M^{n+1} \longrightarrow R\cdot + M^{n} + H^{+}$$

or

(13) $$RH + M^{n} \xrightarrow{O_2} RO\cdot + M^{n+1} + OH^{-}$$

The metals involved are usually multivalent and initiation in these systems involves oxidation-reduction reactions. It has been shown in many cases[14] that metal catalysis is much more efficient in the presence of hydroperoxides. Metal-hydroperoxide interactions (Reactions 14 and 15) will be discussed in more detail below (see p. 13).

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

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

The catalytic activity of metals is in many instances confined to very low concentrations and indeed some metals have been observed to inhibit autoxidations as their concentration is increased.[3] Woodward and Mesrobian[15] have observed that the catalysis of the oxidation of tetralin by a cobalt salt-tetralyl hydroperoxide system reaches a constant value as the metal concentration is increased. These authors attribute this effect to the attainment of a steady-state concentration of hydroperoxide (i.e., the rate of $RO_2H$ formation equal to the rate of decomposition) which leads to a rate law which is independent of cobalt concentration. An alternate explanation[16] involves the following chain terminating steps (Reactions 16-18).

(16) $RO_2\cdot + M^n \longrightarrow R^+ + M^{n-1} + O_2$

(17) $RO_2\cdot + M^n \longrightarrow RO_2^- + M^{n+1}$

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

Reactions 16-18 would require appreciable concentrations of metal to compete with Reactions 12-15 since the steady-state concentrations of the radicals are extremely low (ca. $10^{-5}$ M).

Radical-metal complexes also have been postulated to account for the reduced catalytic activity in certain systems.[3] For example, it has been shown that the ferric stearate and cobalt stearate initiated oxidations of several hydrocarbons are retarded by the presence of copper stearates.[17] The fact that the retarded rate is that which is observed with the copper salts alone suggests that a more stable radical-metal complex is formed with copper ions than with ferric or cobalt ions (Reaction 19).

(19) $\mathrm{Fe{-}R + Cu \longrightarrow Cu{-}R + Fe}$

Chalk and Smith[16] have observed that the catalytic activity of some metals is markedly affected by complexing agents. These effects may be due to interference with the formation of metal-substrate, metal-hydroperoxide, or metal-radical complexes or modification of the redox potential[18] of the metal so as to retard or accelerate Reactions 12-18.

In the present work[19] we have attempted to explain the metal acetylacetonate-*t*-butyl hydroperoxide-catalyzed autoxidation of 1-octene in terms of some of the ideas discussed above. It has been observed that complexing, oxidation-reduction reactions, and metal concentrations all have a marked effect on the *t*-butyl hydroperoxide-chromium (III) acetylacetonate autoxidation of 1-octene.

### (2) Propagation

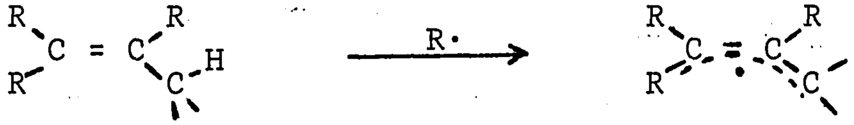
The propagation steps of a chain reaction involve attack by a radical on a substrate molecule to produce a new radical. This attack may either involve addition to a double-bond (Reaction 20) as is the case in many olefin autoxidations[12] or abstraction of a hydrogen atom (Reaction 21). In the case of "non-polymerizable" olefins with readily available allylic hydrogens, abstraction is almost always favored over addition.

(20) $\mathrm{R^{\cdot} + R'_2C{=}CR'_2 \longrightarrow R'_2\underset{R}{C}{-}\underset{\cdot}{C}R'_2}$ (III)

(21) $\mathrm{R^{\cdot} + R'CH_2CH{=}CR'_2 \longrightarrow R'\underset{\cdot}{C}HCH{=}CR'_2}$ (IV) $+$ RH

Although the activation energies for Reactions 20 and 21 are similar,[20] it will be noted that Radical III is an alkyl radical whereas Radical IV is an allylic radical. Therefore resonance stabilization is possible with Radical IV which is not available to Radical III. Furthermore, the steric effect in going from the 120° bond angle in the olefin to the 109° angle in Radical III is also unfavorable, while a more favorable transition takes place in Reaction 21 as the tetrahedral arrangement around the allylic carbon changes to a trigonal one (see Figure 2).

Figure 2: Rearrangement of the Allylic Carbon due to Hydrogen Abstraction



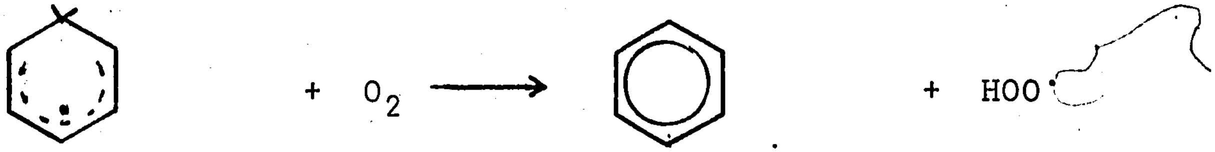
In both cases a positive entropy change would be expected, since there is less order in the alkyl radical (III) than in the olefin and less order around the allylic carbon (see Figure 2) after abstraction than before. Since addition does play a significant role in the autoxidation of many olefins it might be expected that the entropy change for Reaction 20 is more important than for Reaction 21.

Recently, Mayo et al.[12] have published some work in which they have calculated the relative amounts of addition and abstraction (Reactions 20 and 21 respectively) in the propagation steps of a variety of olefin autoxidations. By assuming that certain products arise from the addition reaction and others from the abstraction, similar results are observed here for 1-octene.

Although propagation in an autoxidation chain usually involves peroxy radical attack on the substrate to form hydroperoxide and an alkyl radical, with subsequent oxidation of the latter (Reactions 22, 23), K.U. Ingold[21] has shown that for certain compounds, (e.g., 1,4-cyclohexadiene and 9,10-dihydronaphthalene) the hydroperoxy radical (HOO$^\cdot$) is the chain-carrying species (Reaction 24).

(22) $ROO\cdot + RH \longrightarrow ROOH + R^\cdot$

(23) $R^\cdot + O_2 \longrightarrow RO_2\cdot$

(24)


Although Reaction 24 is not a "true" propagation step it does indicate a type of chain-transfer in which the chain-carrying species is not derived from the substrate molecule. In the autoxidation of 1-octene initiated by chromium (III) acetylacetonate and _t_-butyl hydroperoxide, the metal reacts with the allylic hydroperoxide in a more rapid reaction than with _t_-butyl hydroperoxide, thereby producing a chain-carrying radical ($C_5H_{11}\underset{\text{O}\cdot}{C}HCH{=}CH_2$) which is not a peroxy radical (see Kinetics Section, p. 36). Peroxy radicals, especially on a tertiary carbon,[4] may participate in non-terminating reactions (25) in which new radicals are produced.

(25) $2\ ROO^\cdot \longrightarrow 2\ RO^\cdot + O_2$

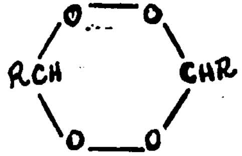
Again the chain-carrying species is converted from a peroxy radical to an alkoxy radical.

The above discussion points out reactions which play important roles in the propagation steps of some autoxidations and have a marked effect on the product distribution.

### (3) Termination

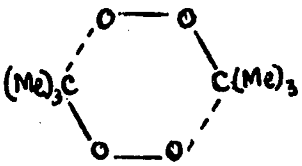
While propagation involves interaction of a radical with a substrate to form a new radical, termination involves interaction between two radicals to form an inactive product. Another type of termination which involves oxidation or reduction of the radical to a cation or an anion has been discussed above (p. 6). In general, termination of autoxidation chains involves two peroxy radicals. Although in most systems it is not possible to separate the propagation rate constant from the termination rate constant, Howard and Ingold[22] have recently reported the termination rate constants for a number of olefin autoxidations obtained by the rotating sector method. These authors have observed that primary peroxy radicals terminate faster than secondary which in turn terminate faster than tertiary. Termination of the latter type of peroxy radical has received considerable attention in recent years.[22,23,24] While primary and secondary radicals terminate mainly by disproportionation, i.e., hydrogen transfer, this pathway is not available to tertiary radicals and therefore it is of much interest to determine their exact mode of termination. The intermediacy of a tetroxide (see Figure 3) has been proposed by Russell[25] and confirmed by Howard and Ingold[26] for the termination of secondary peroxy radicals.

Figure 3: Tetroxide Intermediate
in Peroxy Radical Termination[25]

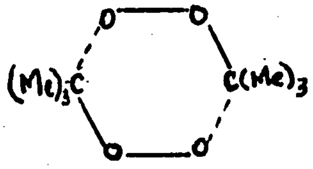


Attempts have been made[23,27] to apply a similar mechanism to tertiary radical termination. However there are many inconsistencies in the literature concerning tertiary radicals. For example, Thomas[23] has shown that t-butyl peroxy radicals terminate with an activation energy of 10 kcal/mole while cumyl peroxy radicals terminate with about zero activation energy. It is difficult to understand why there should be such a large difference in activation energy between two very similar reactions. However polar effects are known to be important in tertiary alkoxy radical reactions[28] and it is possible that the phenyl group α to the peroxy carbon in the cumyl peroxy radical has an important influence in this respect. Concerning the formation of a tetroxide in tertiary peroxy radical termination, Thomas has given some data which can be used to calculate the entropy of activation for the decomposition of the tetroxide (Reaction 27) produced by t-butyl peroxy radicals (Reaction 26). ($k_{27}$ at 22° = 30 $sec^{-1}$, $E_{27}$ = ca. 0).

(26) $2\ Me_3COO\cdot \rightleftharpoons$



(27)



$\longrightarrow\ 2\ Me_3CO\cdot\ +\ O_2$

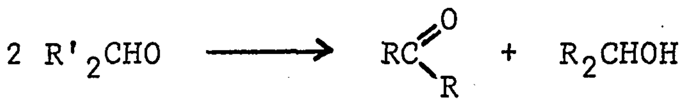
Although the entropy of activation for the decomposition of the complex into smaller products would be expected to have a large positive value,[29] due to a high degree of order in the tetroxide, the data actually yield a high negative value (ca. -60 cal/deg-mole).

Since termination of peroxy radicals of any type generally produces oxygen, in those systems where the kinetic chains are short ( $\leq$ 10) the rate of oxygen production becomes comparable ( $\geq$ 10%) to the rate of oxygen uptake. Tobolsky and Mesrobian[14] have pointed out that under certain conditions, where the rate of hydroperoxide decompositions, and hence oxygen production, becomes appreciable, a steady state rate of autoxidation is attained.

Although disproportionation is the primary mode of peroxy radical termination, in those systems involving alkoxy radicals as chain carriers coupling reactions (Reaction 28) may play an important role.

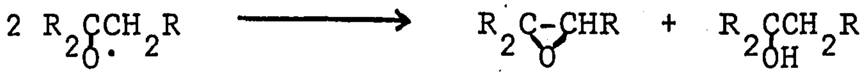
(28) $2\ RO\cdot \longrightarrow ROOR$

Although the O-O bond in the resulting peroxide is weak, no bond-breaking is involved so that the activation energy for Reaction 28 should be comparable to the disproportionation reaction of the same radicals (Reaction 29).

(29) 

$$2\ R'_2CHO \longrightarrow RC(=O)R + R_2CHOH$$

Again it is noted that for tertiary alkoxy radicals the same disproportionation is not available although reactions such as Reaction 30 are possible.[30]

(30) 

However, these radicals decompose under most conditions to alkyl radicals and ketones.[31]

(4) Chain lengths.

The chain length of a free radical reaction is defined[32] as the number of molecules of substrate consumed per radical produced in the initiation process. The chain length may be calculated by dividing the propagation rate by either the rate of initiation or the rate of termination, since the latter two quantities are equal in chain processes.

Two distinct chain processes, the autoxidation of 1-octene and the decomposition of _t_-butyl hydroperoxide, are observed in this study and hence two distinct chain lengths have been estimated. Alternate definitions of chain lengths[27] are discussed in Appendix IV (see p.159).

B. Metal-peroxide reactions.--The reaction of metal ions and organo-metallic compounds with hydroperoxides is well known.[2,33,34,35] The susceptibility of peroxides to oxidation-reduction reactions[36] facilitates electron transfer reactions especially with transition metals (Reactions 31, 32).

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

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

The above reactions which have been extensively studied especially with hydrogen peroxide,[37] cumyl hydroperoxide,[38] and _t_-butyl hydroperoxide[39] may be used to initiate a variety of free radical reactions, such as polymerizations,[40] epoxidations,[41] decomposition of the peroxide,[42] hydroxylations,[43] and autoxidations[19] (cf. Part A of this section, pp. 1-13).

The presence of trace metals has been shown to be responsible for many anomalies in peroxide decompositions.[44] These anomalies are found to vanish when the decompositions are run in the presence of strong chelating agents (e.g., ethylenediamine tetraacetic acid, EDTA).[44] It has been observed, however, that complexing of metal ions does not always reduce their effectiveness in peroxide decompositions. Indeed, in an extensive survey of the effect of complexing agents on the catalytic efficiency of metals, Chalk and Smith[16] observed that some compounds had an accelerating effect, while others had either a retarding effect or none at all.

The effect of any complexing agent in metal-catalyzed peroxide decomposition may be two-fold. If peroxide-metal complexes play an important role in initiating radical formation[39a] then ligands which are strongly bonded with the metal will retard the formation of such a complex and hence the decomposition (Reaction 33).

(33) $\mathrm{M\,(L)_n + m\,ROOH \longrightarrow M\,(L)_{n-m}\,(ROOH)_m + mL}$

where M is a metal atom and L is a ligand. If initiation of the decomposition depends on the oxidation-potential of the metal (i.e., if $\mathrm{M + ROOH \longrightarrow}$ radicals and $\mathrm{ML + ROOH \longrightarrow}$ no radicals) then modification of this potential via complexing will have a marked effect on the reaction.[18]

Large differences may be found in the mechanisms of various metal-peroxide reactions as one changes the system. For example, a series of metal acetylacetonates were reacted with t-butyl hydroperoxide in a variety of reactions including the polymerization of styrene,[45] the epoxidation of a series of olefins,[41] the decomposition of the hydroperoxide,[19] the autoxidation of 1-octene,[19] and the autoxidation of the acetylacetonates themselves.[46] The data for the various reactions are presented in Table I. Although, in general, the same metals are active or inactive in the various systems, a different order of reactivity is observed as one changes the system. This work is described in this section as it has already been published.[19] (see Appendix V)

Although many metal-peroxide reactions clearly involve free radicals, several cases have been cited in the literature in which polar intermediates are suggested.[47] It has been shown[48] that the cobalt (II) acetate-induced decomposition of t-butyl hydroperoxide in acetic acid at 60° is retarded by the presence of water, a fact which indicates inhibition via some sort of polar intermediate. It has also been observed[19] that the cobalt (II) acetylacetonate-catalyzed decomposition of t-butyl hydroperoxide is retarded in glacial acetic acid. On the other hand, although Dean and Skirrow[48] have observed that t-butyl hydroperoxide reacts several hundred times faster with cobalt (III) acetate than the cobalt (II) salt in glacial acetic acid, Richardson[39a] observed no reaction between the hydroperoxide and cobalt

Table I: Reactivities of Metal Acetylacetonates in Several Reactions with *t*-Butyl Hydroperoxide

| Metal | Hydroperoxide[a,b] Decomposition | Olefin[b] Epoxidation | Styrene[c] Polymerization | Olefin[a] Autoxidation | Chelate[d] Autoxidation |
|---|---|---|---|---|---|
| Cr(III) | ++ | ++ | ++(-) | ++(-) | (-) |
| V(III) | + | ++ | (-) | n.d. | ++ |
| VO(II) | + | ++ | (-) | ++ | n.d. |
| Co(III) | + | + | ++(-) | ++ | + |
| Co(II) | ++(-) | + | (-) | ++(-) | ++ |
| Cu(II) | + | + | ++ | + | + |
| Fe(III) | (-) | (-) | + | + | ++ |
| Mn(III) | + | + | n.d. | ++ | ++ |
| Mn(II) | + | + | (-) | ++ | n.d. |
| Ni(II) | (-) | (-) | (-) | (-) | ++ |
| Al(III) | (-) | (-) | (-) | (-) | (-) |
| TiO(II) | (-) | (-) | (-) | n.d. | n.d. |
| Zn(II) | (-) | (-) | (-) | (-) | n.d. |
| Zr(IV) | (-) | (-) | (-) | (-) | (-) |

a This work (Ref. 19)
b Reference 41
c Reference 45
d Reference 46

++ Very reactive
\+ Reactive
(-) Not reactive
++(-) Reactivity is concentration dependent
n.d. No data available

(III) ethylenediamine tetraacetate in 50% acetic acid and in the present work[19] only a slow reaction was observed between t-butyl hydroperoxide and cobalt (III) acetylacetonate in 1-octene. The preceding discussion points up the importance of the ligand in metal-peroxide reactions.

Striking color changes in many of these reactions[19] indicate either ligand exchange[39a,49] or alteration in the oxidation state of the metal[16] or the ligand.[50]

The present study has dealt with the reaction between t-butyl hydroperoxide and metal acetylacetonates.[19] The main part of this work however, has been concerned with the kinetics and mechanism of the chromium (III) acetylacetonate-t-butyl hydroperoxide reaction. Temperature and concentration studies have been used to elucidate the mechanism not only of chromium (III) acetylacetonate disappearance and peroxide decomposition, but also of the autoxidation of 1-octene, initiated by this metal-peroxide system. A detailed discussion of the results of these studies is given in the Kinetics Section (p. 36). In addition to the reactions mentioned above, it has been shown that the chromium (III) acetylacetonate-t-butyl hydroperoxide interaction will catalyze the autoxidation of substrates other than 1-octene, the polymerization of styrene,[45] the epoxidation of a variety of olefins,[41,47a] and the oxidation of tertiary amines.[47b]

C. Solvent effects in free radical reactions.-- Although solvent effects in free radical reactions are not as marked as in heterolytic systems, there are many cases where changes in product distribution and reaction rates are directly attributable to changes in solvent.[51]

In many instances the effect is due to the formation of a radical-solvent complex. Russell[52] has shown that the distribution of alkyl chlorides in the chain chlorination of 2,3-dimethylbutane is solvent dependent. The chain steps in the chlorination are as follows.

(34) $Cl_2 \longrightarrow 2\ Cl\cdot$

(35) $Cl\cdot + Me_2CHCHMe_2 \longrightarrow Me_2\underset{\cdot}{C}CHMe_2$

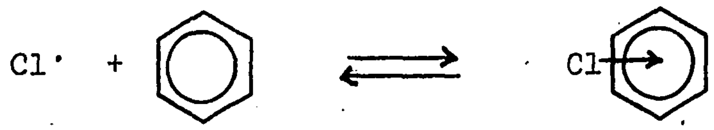
(36) $Cl\cdot + Me_2CHCHMe_2 \longrightarrow \cdot CH_2MeCHCHMe_2$

(37) $Me_2\underset{\cdot}{C}CHMe_2 + Cl_2 \longrightarrow Me_2CClCHMe_2 + Cl\cdot$

(38) $\cdot CH_2MeCHCHMe_2 + Cl_2 \longrightarrow ClCH_2MeCHCHMe_2 + Cl\cdot$

The ratio of tertiary hydrogen abstraction to primary hydrogen abstraction is given by $k_{35}/k_{36}$, and this ratio is in turn given by the ratio of 2-chloro-2,3-dimethylbutane/1-chloro-2,3-dimethylbutane in the products. After correcting for the statistical factor (12 primary hydrogens/2 tertiary) this ratio is ca. 3.6 in most aliphatic solvents and $>$ 10 in most aromatic solvents, sulphur monochloride and carbon disulphide. Russell[53] attributes this dramatic change to stabilization of the chlorine atom via a radical-solvent $\pi$-complex in the case of the aromatic compounds (Reaction 39).

(39)



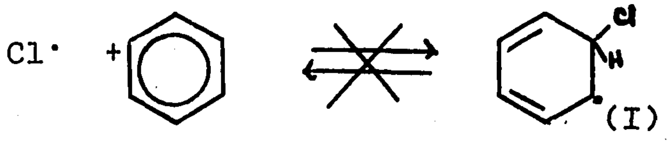
and a $\sigma$-complexed radical in the case of the sulphur compounds (Reactions 40, 41).

(40) $Cl^{\cdot} + ClSSCl \rightleftharpoons Cl_2\dot{S}SCl$

(41) $Cl^{\cdot} + S{=}C{=}S \rightleftharpoons Cl{-}\dot{S}{=}C{=}S$

A sigma complex (Reaction 42) has been discounted[54] for aromatic-chlorine atom systems since no addition or substitution products arising from the chloro-phenyl radical (I) are observed.

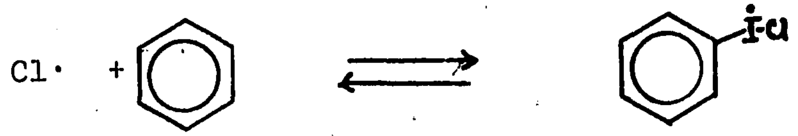
(42)



Furthermore the ability of a series of aromatic compounds to increase the selectivity of chlorine atoms cannot be correlated with the susceptibility of the compounds towards addition of phenyl radicals.

On the other hand the formation of a $\pi$-complex would be facilitated by electron-donating substituents and retarded by electron-withdrawing substituents. Thus, Russell[53] has shown that nitro-, carbonyl-, and halogen groups (with the exception of iodine) decrease the selectivity of the chlorine atom relative to benzene, while alkyl and ether groups increase the selectivity. In the case of iodobenzene, the iodine atom acts much like the sulphur atoms in that there is an expansion of the valence shell to form a $\sigma$-complex between the iodine atom and the chlorine atom (Reaction 43).

(43)



Bromine atoms as well as chlorine atoms are subject to complexing effects. Thus Mayo and Hardy[55] have observed that the photobromination of toluene is retarded by the presence of naphthalene. Although these authors have attributed this effect to preferential attack on the naphthalene, Huyser[56] has shown that the intermediacy of either a $\pi$ or $\sigma$ bromine-naphthalene complex in the propagation sequence could be responsible for the observed effect.

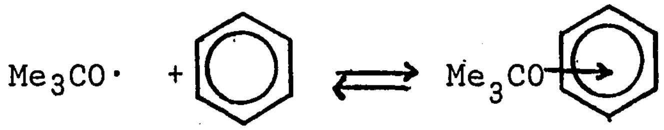
Solvent effects have also been shown to affect alkoxy and peroxy radical reactions. As far as alkoxy radicals are concerned most recent investigations have been limited to tertiary systems. Tertiary alkoxy radicals can, under most conditions, undergo one of two reactions: abstraction of a hydrogen atom to form an alcohol or loss of an alkyl group to form a ketone (Reactions 44, 45).

(44) $R_3CO\cdot + R'H \longrightarrow R_3COH + R'\cdot$

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

The "R" groups are not necessarily identical. The ratio $k_{45}/k_{44}$ is given by the ratio of ketone/alcohol multiplied by the substrate concentration $[R'H]$. It was observed by Russell[57] that the ratio of $k_{11}/k_{10}$ (for t-butoxy radicals derived from the thermal decomposition of di-t-butyl peroxide) was solvent dependent. For example, while the ratio was 0.46-0.47 in aliphatic solvents it increased to $\geq$ 0.55 in aromatic systems. Although the change is small compared to the chlorine-atom reactions, a similar intermediate (i.e., a $\pi$-complex) may be responsible for the observed effect.[58]

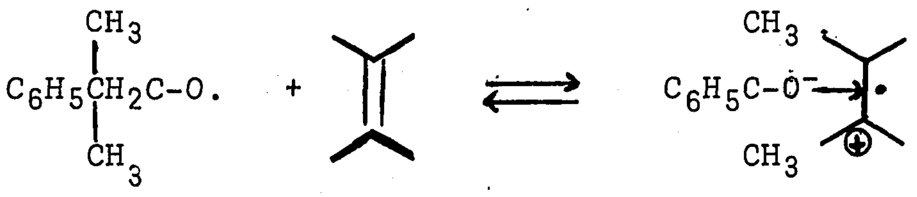
(46)



It is suggested[58] that complexing may reduce the rate of hydrogen abstraction and therefore enhance the decomposition rate.

This is in part confirmed by the observation[59] that aromatic solvents and carbon disulphide increase the selectivity of the t-butoxy radical in hydrogen abstraction reactions. Complexing with olefins has also been observed[60] in reactions using benzyldimethyl methoxy radicals from the corresponding hypochlorite ($C_6H_5CH_2C(Me)_2O\cdot$). The effect of this complexing is the almost complete suppression of hydrogen abstraction relative to the decomposition of the radical to acetone and a benzyl radical. It has been suggested[60] that the olefin-radical complex is of the charge-transfer type (see Figure 4). This suggestion is somewhat supported by the observation that electron-withdrawing groups near the double bond apparently reduce the complexing ability of the olefin.

Figure 4: Charge Transfer Complex between Benzyl-Dimethyl Methoxy Radical and an Olefin



Although the effect of olefins on the reactions of benzyldimethyl methoxy radicals is quite dramatic there is a much smaller effect on t-butoxy radicals. For example, the rate of decomposition is 9-14 times the rate of hydrogen abstraction in the reaction of t-butyl hypochlorite with cyclohexane in cis or trans dichloroethylene. However in trichloro, trifluoro ethane, a saturated hydrocarbon, the decomposition rate is 53 times the abstraction rate.[28] It has been suggested that in the case of the benzyldimethyl methoxy radical, complexing might produce steric effects which favor decomposition over abstraction and furthermore may lower the activation energy requirement of the decomposition reaction but raise it in the case of the abstraction.[61] However, the same arguments could be applied to the t-butoxy radical which clearly does not show the same effect as the benzyldimethyl methoxy radical. Any explanations for this phenomenon must involve the benzyl group. One possible explanation is that the presence of the benzyl group helps to stabilize the olefin-radical complex via resonance effects and thus complex formation is much easier with the benzyldimethyl methoxy radical than with the t-butoxy radical. Alternatively, the formation of the benzyl radical in the decomposition of the former as opposed to the methyl radical in the latter, would make decomposition of the benzyldimethyl methoxy radical easier than the decomposition of the t-butoxy radical. Hence anything that would favor the decomposition relative to abstraction would have a greater effect on reactions of the former radical than on those of the latter.

It is observed that the decomposition/abstraction ratios of t-butoxy radicals from different sources are somewhat different using the same substrate. Thus $k_{45}/k_{44}$ (see p. 20) is 0.55 for t-butoxy radicals produced by the thermal decomposition of di-t-butyl peroxide at 130°[57] whereas the same ratio is 1.26 for the t-butoxy radical produced by the photodecomposition of t-butyl hypochlorite at 130°[62] (Both cases using cyclohexane as the substrate in benzene). It is suggested that the production of a more energetic radical, i.e., an "excited" t-butoxy radical in the photolysis is the cause of the higher decomposition/abstraction ratio.

Reactions involving peroxy radicals are also subject to solvent effects. As with the other radicals discussed above, these effects are probably due to the formation of radical-solvent complexes.[63] As stated above (see Part A of this section, p. 1 ), chain autoxidations consist of three general steps: initiation, propagation, and termination. The rate law for most autoxidations is given by:

(47) $-d[O_2]/dt = (k_p/k_t^{0.5})\ R_i^{0.5}\ [RH]$

where $k_p$ and $k_t$ are the rate constants for the propagation and termination steps respectively, $R_i$ is the rate of initiation, and [RH] is the substrate concentration.

Since the rate of initiation is in many cases solvent independent or may be corrected for solvent effects, much of the work done involves the effect of solvent on the propagation/termination ratio. It has been observed that for such varied substrates as styrene,[64] cumene and cyclohexane[65] (all initiated by AIBN at 60-65°) the ratio of the propagation/termination rate constants ($k_p/k_t^{0.5}$) increases with increasing solvent polarity.

Although the effects are small (A four-fold increase is observed in going from decane to acetonitrile, using styrene as the substrate.), they are clearly an effect of the polarity of the solvent and there is apparently little or no π-complexing, such as that observed with chlorine atoms or alkoxy radicals. (There are only slight increases in the ratio ($k_p/k_t^{0.5}$) in going from no solvent to an aromatic solvent using cyclohexane as a substrate and no effect using styrene as a substrate).

Two explanations[65] have been offered for the observed polar effect. The first of these involves the transition state of the propagation step (see Figure 5).

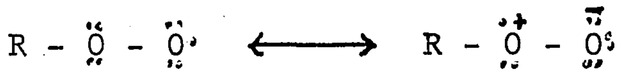
Figure 5: Transition State for Hydrogen Abstraction by a Peroxy Radical

$$R'O\overset{\delta-}{O}\text{--}H\text{--}\overset{\delta+}{R}$$

The formation of this polar transition state is facilitated by the electrophilic character of the peroxy radical.[66] Clearly, solvation of this species would be most extensive in polar solvents. Furthermore, in the same solvent, solvation would increase with the ability of the substrate to donate electrons. As an example, Hendry and Russell[65] have observed that the oxidation of cycloheptatriene is affected much more by increasing the solvent polarity (i.e., in going from chlorobenzene to nitromethane) than oxidation of cycloheptene, a poorer electron donor. However, the same authors have observed that the oxidation of p-nitro cumene is more affected by the same change in solvent than that of cumene. Huyser[67] has stated that this observation tends to negate the explanation of transition state solvation, since cumene is a better electron donor than p-nitro cumene. By the same token, however, the p-nitrocumyl radical is more electrophilic than the cumyl radical. Since the polarity of the transition state and hence the degree of solvation, depends not only on the electron donor ability of the substrate but on the electrophilicity of the peroxy radical, the above results are not at all inconsistent with transition state solvation.

An alternate explanation offered by Hendry and Russell[65] suggests that the ground state of the peroxy radical has some polar character due to the following type of resonance.

Figure 6: Resonance Structures for the Peroxy Radical



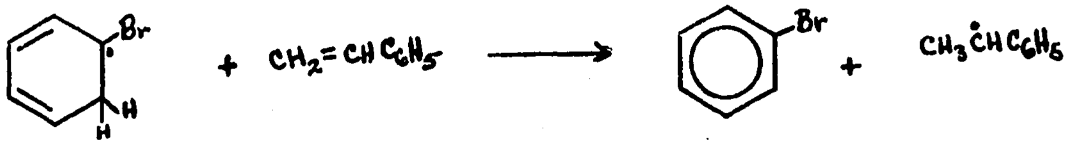
$$R-\ddot{O}-\dot{O}\cdot \longleftrightarrow R-\overset{+}{O}-O^{-}$$

If termination of peroxy radicals involves the formation of a non-polar intermediate (e.g., a tetroxide[25]) then there will be little solvation of the termination transition state. Furthermore energy will be required to desolvate the radicals if there is a good deal of polar character involved. Assuming the amount of desolvation required for both the propagation and the termination processes to be about the same, there will be a greater effect on the activation energy of the latter, since termination generally requires a much smaller activation energy than propagation. Therefore increasing the polarity of the solvent decreases the termination rate more than the propagation rate and hence increases the overall rate of autoxidation. It should be noted that for some tertiary peroxy radicals activation energies of termination greater than 10 kcal have been observed.[46] Since activation energies of propagation are not usually greater than about 8 kcal,[68] the arguments given above are not applicable to these tertiary systems.

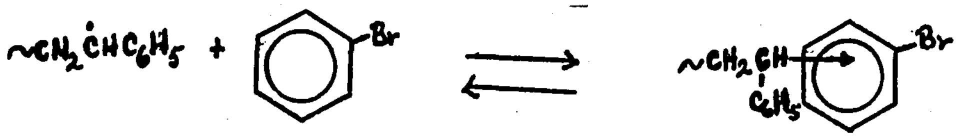
Complexing of carbon radicals has also been suggested. For example, Mayo[69] has observed a decrease in the degree of styrene polymerization by running the reaction in bromobenzene. Although retardation of polymerizations have been observed[70] in the presence of aromatic solvents, these are usually due to involvement of the solvent as a reactant and the subsequent incorporation of solvent molecules in the polymer. In the styrene-bromobenzene case, however, no solvent was observed in the product. It was therefore suggested[69] that the polymer chain might be terminated by hydrogen transfer to a solvent molecule which then initiated a new chain by hydrogen transfer to a monomer (Reactions 48, 49).

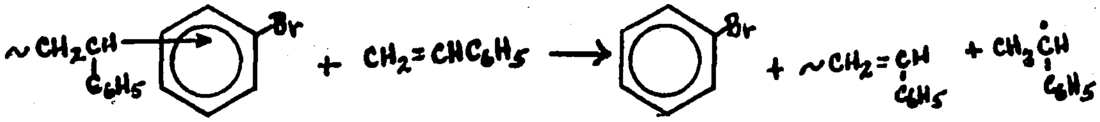
(48)

(49)



As an alternative, a radical-solvent complex was suggested[69] which then terminated the chain via a transfer reaction (Reactions 50, 51).

(50) 

(51) 

Indictor and Linder[45] have investigated the polymerization of styrene initiated by metal acetylacetonates and <u>t</u>-butyl hydroperoxide in order to contrast various metals in the initiating system. It would be of interest to study this reaction in terms of a solvent effect to ascertain the importance, if any, of a radical-solvent complex. However, any such investigation must take into account the possibility of solvent-hydroperoxide interactions.[71]

Aside from the example of Mayo given above, complexing of carbon radicals is relatively uncommon. Martin and Gleicher[72] have suggested complex formation in the reactions of trichloromethyl radicals and the ratio of coupling/disproportionation of photolytically produced methyl and ethyl radicals[73] appears to be solvent dependent. This latter observation has been suggested[73] to be a consequence of "cage" effects (i.e., the recombination of radicals within solvent "cages")[74] rather than solvent-radical complexing. It is perhaps significant that most cases in which radical-solvent complexing is postulated involve electrophilic radicals, i.e., chlorine atoms, alkoxy radical, peroxy radicals, and among the few carbon radical cases, the trichloromethyl radical. The situation clearly calls for an investigation in which the effect of a particular solvent is studied as a function of the electrophilicity of the radical.

Although all of the above discussion is concerned with solvent effects on radical-substrate or radical-radical reactions, a few cases have been observed in which the radical-forming reaction is affected by the solvent. As noted in Part A of this section (p. 1 ), the primary sources of radicals are peroxides and azo-compounds. Most observed solvent effects on peroxide decompositions involve peroxide-solvent interactions in which the solvent is actually a reactant and therefore these are not true solvent effects in the sense that they have been discussed thus far.[75]

On the other hand, polar solvents have been observed to have a marked effect on the decomposition of azo-compounds. Many of these effects involve selective solvation of either the ground state or the transition state and thus have a large effect on the activation parameters[76] (i.e., $\Delta H^{\pm}$ and $\Delta S^{\ddagger}$).

The autoxidation of 1-octene in the presence of chromium (III) acetylacetonate and t-butyl hydroperoxide also exhibits a marked solvent effect. Experiments were done on the autoxidation, the disappearance of chromium (III) acetylacetonate and the decomposition of t-butyl hydroperoxide in a variety of solvents (see Table VI ). The results of these experiments are discussed and interpreted according to some of the ideas described above (see p. 93).

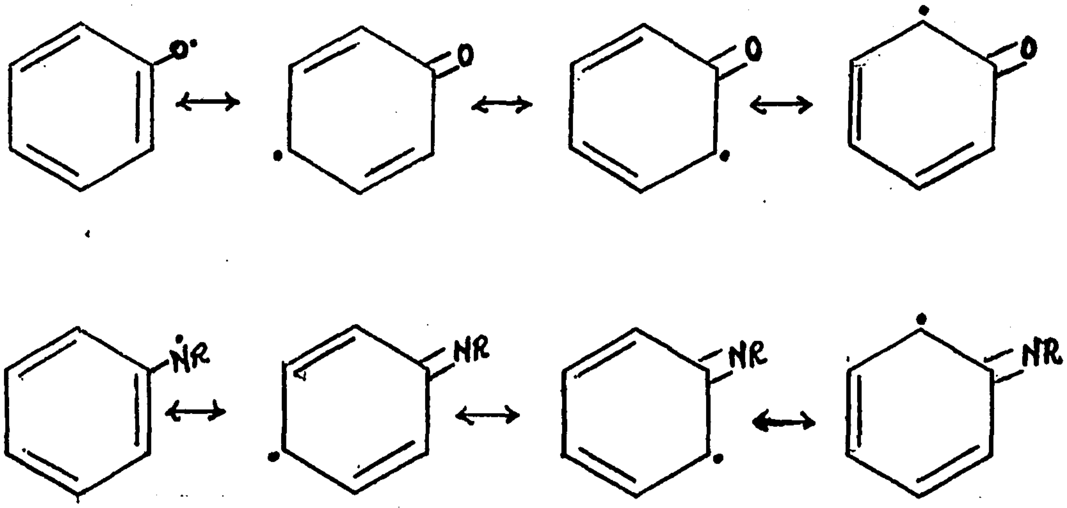
D. Inhibition of Free Radical Reactions.--The inhibition of free radical reactions, particularly autoxidations, has received a good deal of attention.[77,78] The usual compounds used as inhibitors are phenols, aromatic amines, and aromatic nitro compounds. Inhibition involves interaction of the growing chain (in the case of polymerizations) or the chain-carrying radical (e.g., the peroxy radical in autoxidations) with an inhibitor molecule to produce a more stable radical. This latter species, because of its longer life-time, may interact with another radical to terminate the chain before it reacts with the substrate in a propagation step. The relevant reactions for inhibition of an autoxidation are given below:

(52) $ROO\cdot + C_6H_5OH \longrightarrow ROOH + C_6H_5O\cdot$

(53) $2\ C_6H_5O\cdot \longrightarrow$ inactive products

The inhibitor radicals generally owe their greater stability to resonance (see Figure 7) and therefore phenols and aromatic amines make excellent inhibitors.

Figure 7: Resonance Structures of Some Inhibitor Radicals



Although Reaction 53 indicates termination between two phenoxy radicals, often termination occurs between a chain-carrying radical and an inhibitor radical (Reaction 54).

(54) $$ROO\cdot + C_6H_5O\cdot \longrightarrow \text{inactive products}$$

In this case it is observed that one inhibitor molecule has stopped two chains. The number of chains stopped per inhibitor molecule is called the stoichiometric factor (n) (cf. Inhibitor Section, p.112). Stoichiometric factors for a large number of inhibitors in a variety of reactions have been determined.[79,80] For many phenols and amines it is observed that n = 2.

Although inhibition usually involves the propagation step of a chain reaction, inhibition of the initiation process is also possible. This type of inhibition may involve complex formation with the initiator (in many cases a metal)[81] which retards radical formation. For this type of inhibition, known chelating agents have been shown to be very useful. In other systems direct reaction of the initiator with an additive (e.g., the reaction of phenol and di-t-butyl peroxide)[82] can inhibit the reaction.

The structure of the inhibitor often plays an important role in determining the efficiency of the inhibition. For example, bulky substituents ortho to the OH group in phenols or the amino group in anilines can retard inhibition.[83] This retardation may either be via steric interference with hydrogen abstraction[83] or with the proper orbital alignment for resonance.[84]

On the other hand, it has been shown[85] that phenoxy radicals, which are unsubstituted in the 2,6 positions can react with hydroperoxides to form peroxy radicals (i.e., the reverse of Reaction 52). Clearly, this type of reaction reduces the efficiency of the inhibitor particularly in those reactions which are initiated by hydroperoxides.

Since the efficiency of an inhibitor depends primarily on the ease of hydrogen abstraction, many attempts have been made to correlate the efficiency with such properties as oxidation potentials,[86] the O-H stretching frequency from infra-red spectra,[86] and resonance energies of the inhibitor radicals from molecular orbital calculations.[85]

As was mentioned above the stoichiometric factor for many inhibitor molecules is 2. However, variation from this value is known.[79,80] If the products of Reactions 53 or 54 are themselves good inhibitors (e.g., quinones or hydroquinones) then n will be greater than 2. On the other hand, if the inhibitor radical is extremely stable, it may be inert to further attack by a chain-carrying radical. Inhibition of the initiation step via complexing can lead to fractional values of n, if several molecules of inhibitor are required to complex with the initiator.

A variety of known free radical inhibitors and other compounds including known complexing agents were investigated in the chromium (III) acetylacetonate-<u>t</u>-butyl hydroperoxide-initiated autoxidation of 1-octene. These same compounds were used in the chromium (III) acetylacetonate-catalyzed decomposition of t-butyl hydroperoxide. The results obtained are set forth and discussed in terms of the foregoing ideas (see Inhibitor Section, p.112 ).

Finally, although metals are often used as free radical initiators (cf. p. 5), it has been observed that some metals may act as inhibitors.[16] The general mechanism for this inhibition is via oxidation or reduction of free radicals to ionic species, therefore essentially terminating the chain (Reactions 55, 56).

(55) $M^{n} + R\cdot \longrightarrow M^{n-1} + R^{+}$

(56) $M^{n} + R\cdot \longrightarrow M^{n+1} + R^{-}$

Alternatively, the presence of one metal may often interfere with complex formation of another and therefore retard the rate of radical formation.[17] Although the rate of autoxidation of 1-octene initiated by chromium (III) acetylacetonate and t-butyl hydroperoxide is proportional to the metal concentration at low concentrations ( $< 10^{-3}$ M), at higher concentrations ( $> 10^{-2}$ M) the rate is observed to decrease.

E. Products of Autoxidations, Metal-Peroxide Reactions, and Peroxide-Olefin Reactions.--

(1) Autoxidations

The primary products of most autoxidations are hydroperoxides.[87] However, other oxygenated compounds derived either from the hydroperoxide or via side reactions of the peroxy radical (e.g., decomposition, addition to a double bond, etc.) are also observed. In general, in those systems where chain lengths (see p. 13) are large, products resulting from termination processes are small compared to those formed in the propagation step.[88] Among these other products are carbonyl compounds, alcohols, epoxides, ethers, and polyperoxides.

Much work has been done on the products of autoxidation.[87] Some of the most comprehensive data have been obtained recently by Mayo et al.[12] An indication of the type of products and relative yields for the autoxidation of 1-hexene initiated by 1,1'-azobiscyclohexane-1-carbonitrile (at 90°) is given in Table XII. A comparison of the products obtained in this work and by Mayo et al. is given in Tables XII and XV.

### (2) Metal-Peroxide Reactions

Since metal-induced peroxide decompositions usually involve O-O bond scission,[34] the products obtained reflect the intermediacy of alkoxy radicals. With hydroperoxides, abstraction of the peroxidic hydrogen is usually the primary propagation step in induced decompositions, and therefore alcohols are a major product of the reaction. Peroxy radicals, resulting from the abstraction of the peroxidic hydrogen, usually react with each other or with a parent molecule to produce alkoxy radicals and oxygen, which is usually the other major product of peroxide decompositions.[89] Peroxy radicals or alkoxy radicals may terminate to form dialkyl peroxides. However, again it should be noted that in chain decompositions, where the chains are long, products produced in the termination step are negligible compared to those produced in the propagation step.[88] Thus the major products of the thermal decomposition of t-butyl hydroperoxide are t-butanol and oxygen.

In some cases, the alkoxy radical, particularly tertiary alkoxy radicals, decompose to form carbonyl compounds and simpler radicals. In the case of acyl or aroyl peroxides, carbon dioxide is obtained (Reactions 57, 58)

(57)

(58)

In the presence of olefins, the reaction products are generally oxidation products of the olefin.[2] For example, Kharasch and Fono[90] have investigated a number of metal-catalyzed olefin-hydroperoxide reactions and generally have obtained dialkyl peroxides and carbonyl compounds derived from the olefin. Due to the similarity of the work of these authors and our own system, it was of interest to compare the products obtained in both cases. This is done in Table XIV.

### (3) Peroxide-Olefin Reactions

Even in the absence of metals, hydroperoxides are known to undergo reactions with olefins. The products of these reactions are generally dialkyl peroxides or epoxides arising from the olefin. Brill and Indictor[91] have investigated the reaction of t-butyl hydroperoxide and a variety of olefins under varying conditions. These authors observed that epoxide yields from these reactions are dependent on olefin structure (1-olefins give lowest epoxide yields). Olefins and hydroperoxides are also known to undergo reaction in the presence of acid catalysts[92] and organic hypochlorites.[92]

Peroxidic compounds other than hydroperoxides also are known to react with olefins. The reaction of peracids with olefins yields epoxides and glycol esters,[93] although Hawkins[93] has pointed out that occasionally carbonyl compounds and acetals are produced. However, it is possible that these are secondary products arising from further reactions of the epoxides or glycol esters.

The decomposition of peroxides in the presence of polymerizable olefins usually results in polymerization.[94] On the other hand, with non-polymerizable olefins, products arising from addition to the double bond or abstraction of allylic hydrogens are observed. Thus the decomposition of dibenzoyl peroxide in cyclohexene produces mainly cyclohexyl benzoate (an addition product)[95] while the reaction of phthaloyl peroxide with the same olefin yields products arising from allylic attack (i.e., cyclohex-2-enyl hydrogen phthalate and phthalic acid.[95]

## II. Results and Discussion

### i. Kinetics and Temperature Effects:

A. Introduction.--If chromium (III) acetylacetonate, t-butyl hydroperoxide, and 1-octene are mixed together in the presence of oxygen, several chemical transformations occur. An oxidation-reduction reaction occurs between the chromium (III) acetylacetonate and t-butyl hydroperoxide to produce free radicals which initiate chain decomposition of the peroxide. In the presence of oxygen, the olefin is autoxidized, also by a chain process. The purpose of this study was to determine the mechanisms of these transformations. Part of this study involves an investigation of the kinetics of the chromium (III) acetylacetonate disappearance, peroxide decomposition and autoxidation under various temperature and concentration conditions. This section deals with this investigation and its mechanistic implications.

B. The Disappearance of Chromium (III) Acetylacetonate.--The rate law for the disappearance of chromium (III) acetylacetonate in the absence of oxygen is given in Equation 59 where Cr = chromium (III) acetylacetonate.

$$(59) \qquad -d[Cr]/dt \propto [Cr]_0^{a}\ [\underline{t}\text{-BuOOH}]_0^{b}\ [C_8H_{16}]_0^{c}$$

The values of a, b, and c are temperature dependent, and c is also dependent on the concentration of 1-octene at 30° (see Figures 8, 9, 10 and Table II). At -1.0°, a = 1.0, while at

Figure 8: Dependence of Rates on [Cr (acac)$_3$] (30°)

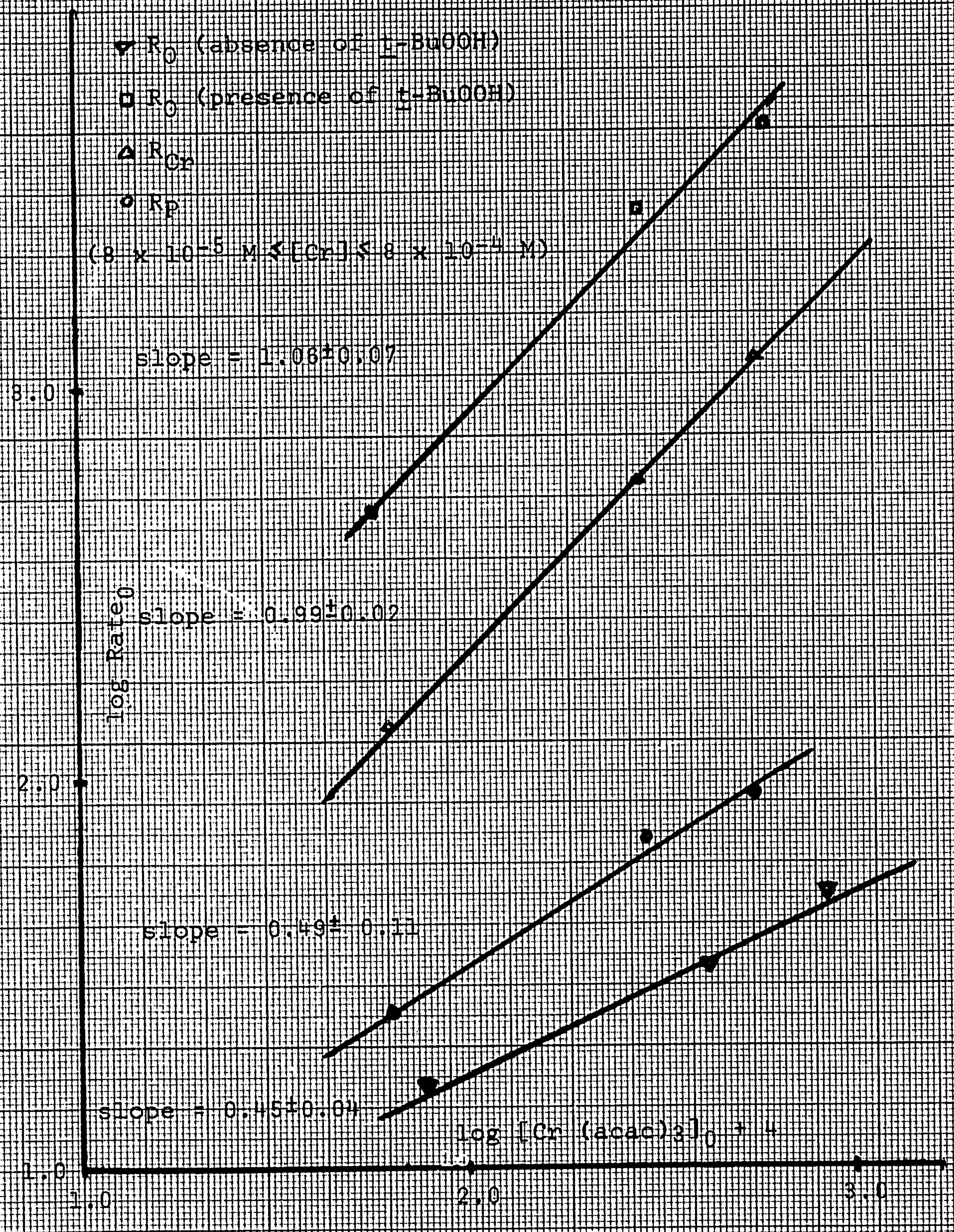


Figure 9: Dependence of Rates on [t-BuOOH] (30°)

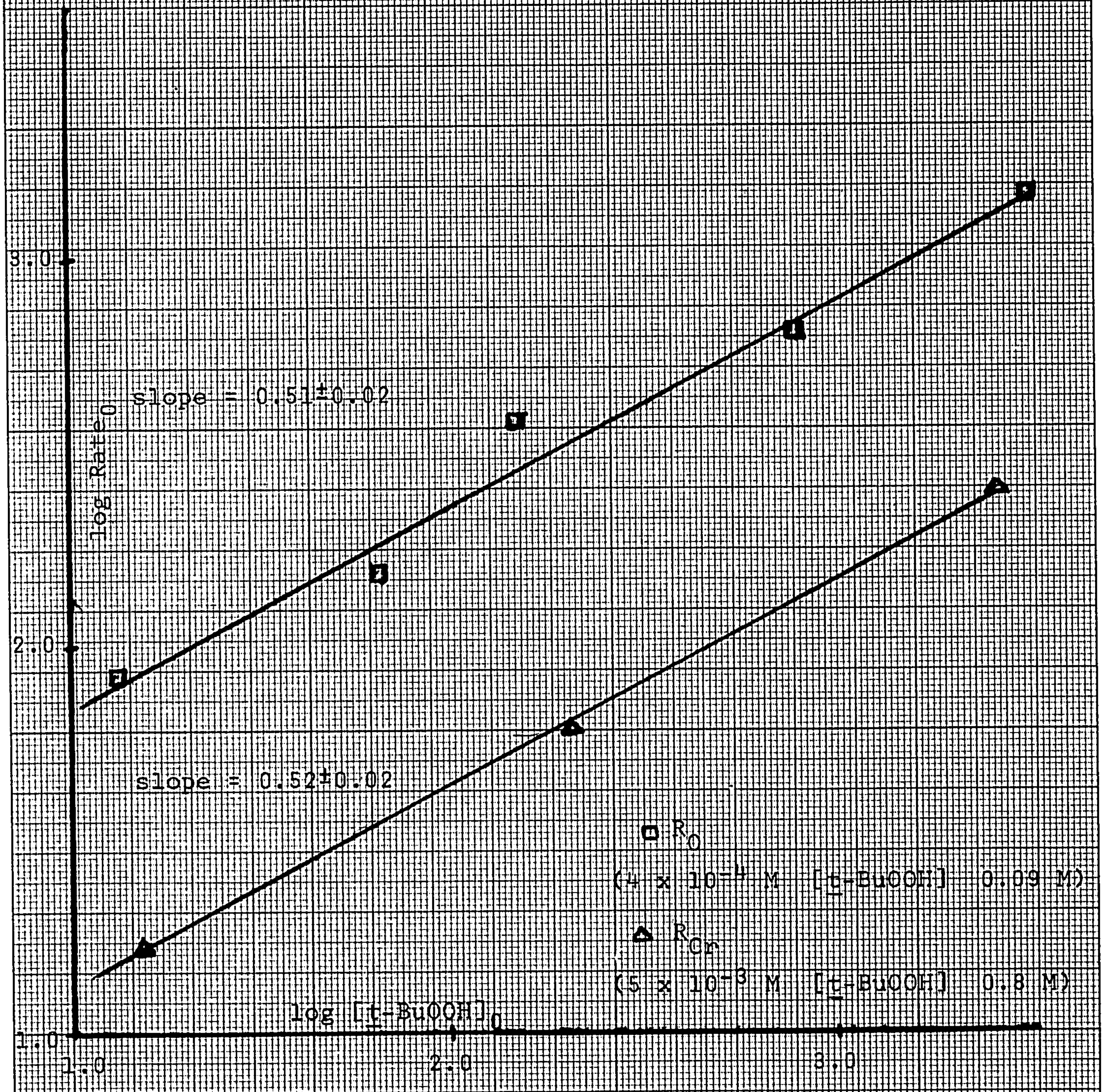


Figure 10: Dependence of Rates on [1-Octene] (30°)

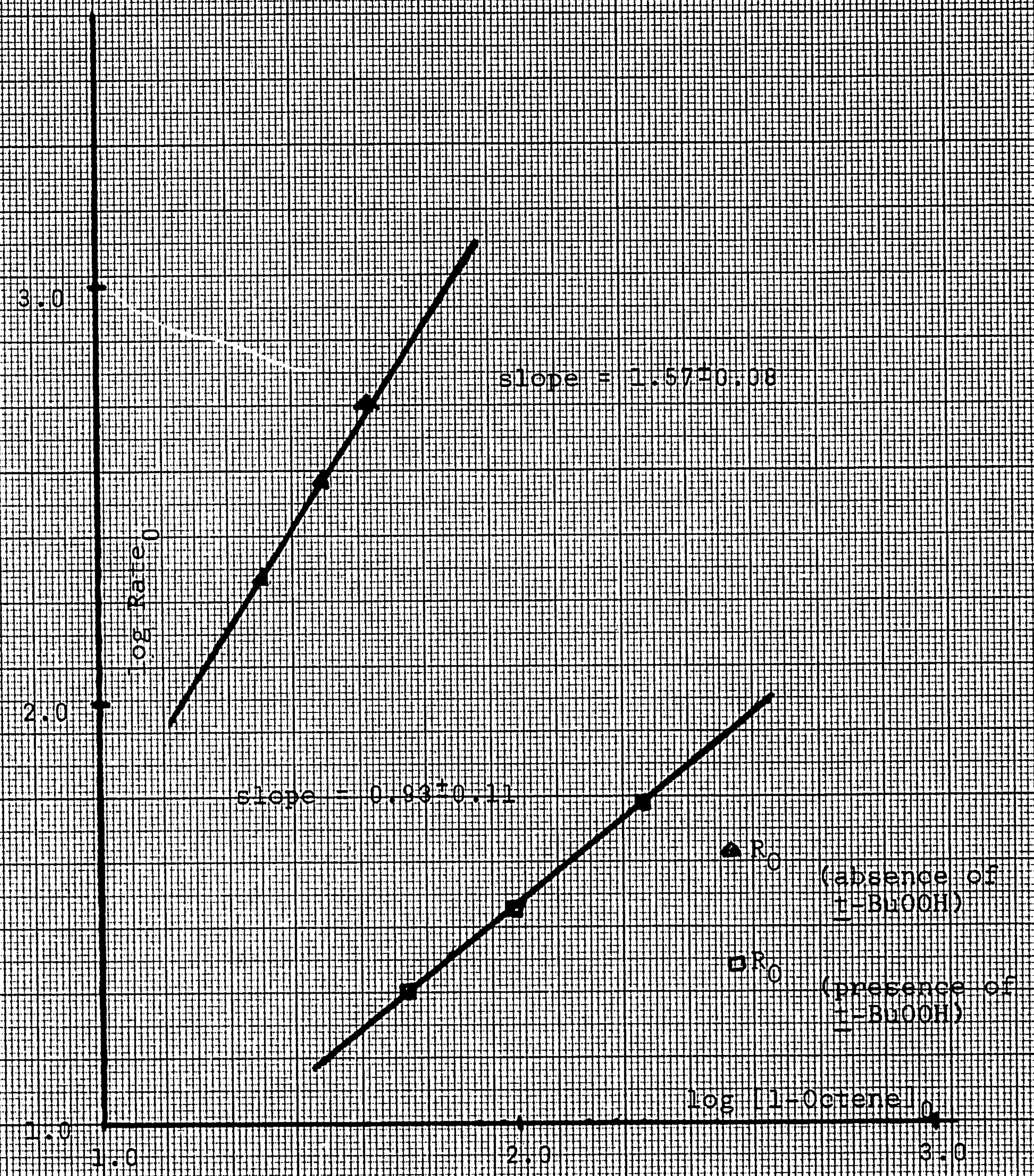


Table II: Rate Equations Under Various Concentration and Temperature Conditions

| $[\text{Cr}]_0$* x $10^4$ M | $[\underline{t}\text{-BuOOH}]_0$ M | $[\text{1-Octene}]_0$ M | Temp. °C | k x $10^4$ | a | b | c |
|---|---|---|---|---|---|---|---|
| A. $-\frac{\Delta[\text{Cr}]}{\Delta t}_0 = k[\text{Cr}]_0^a\,[\underline{t}\text{-BuOOH}]_0^b\,[\text{1-Octene}]_0^c$ | | | | | | | |
| 4.0-16.0 | 0.8 | 2.56 | -1.0 | 0.0005 | 1.0 | n** | n |
| 4.0 | 0.8 | 0.6 | 30 | 0.067 | n | n | 0.0 |
| 0.8-8.0 | 0.005-0.8 | 0.6-2.6 | " | 0.072 | 1.0 | 0.52 | 1 |
| 0.6-4.0 | 0.1-0.8 | " | 40 | 0.282 | 1.4 | 0.13 | 0.0 |
| " | " | " | 50 | 1.12 | 1.7 | " | " |
| B. $-\frac{\Delta[\underline{t}\text{-BuOOH}]}{\Delta t}_0 = k[\text{Cr}]_0^a\,[\underline{t}\text{-BuOOH}]_0^b\,[\text{1-Octene}]_0^c$ | | | | | | | |
| 4.0 | 0.005-0.8 | 2.6 | 30 | 1.59 | n | 1 b 4 | n |
| 0.9-4.0 | 0.8-1.6 | 0.13-2.6 | " | 50.1 | 0.49 | 1.0 | 0.0 |
| 0.6-4.0 | 0.1-8.0 | 0-2.6 | 40 | 138 | 0.71 | 2.9 | 0.0 |
| " | " | " | 50 | 407 | 0.50 | 2.3 | 0.0 |
| C. $-\frac{\Delta[\text{O}_2]}{\Delta t}_0 = k[\text{Cr}]_0^a\,[\underline{t}\text{-BuOOH}]_0^b\,[\text{1-Octene}]_0^c$ | | | | | | | |
| 4.0 | .09-0.8 | 2.6 | 2 | 6.03 | n | -0.7 | n |
| 4.0-12.0 | .0004-.02 | 0.13-4.5 | 30 | 40.1 | 0.85 | 0.49 | 0.23 |
| 4.0 | 0.8 | 0.07-2.6 | " | 146 | n | n | 0.93 |
| 0.8-8.0 | 0.1-0.8 | 2.6 | " | 41.3 | 1.1 | 0.0 | 0.26 |
| 4.0 | 0.1-4.5 | 0.13 | " | 22.5 | n | -0.2 | n |
| 0.8-8.0 | 0.0 | 2.6-6.0 | " | .049 | 0.45 | - | 1.57 |
| 4.0 | 0.02-0.09 | 2.6 | 40 | 42.4 | n | 0.16 | n |
| 0.8-4.0 | 0.8 | " | " | 97.0 | 1.0 | n | n |

Table II (continued)

| $[Cr]_0$* x $10^4$ M | [t-BuOOH]$_0$ M | [1-Octene]$_0$ M | Temp. °C | k x $10^4$ | a | b | c |
|---|---|---|---|---|---|---|---|
| C. $\left(\frac{-\Delta[O_2]}{\Delta t}\right)_0 = k[Cr]_0^a\,[t\text{-BuOOH}]_0^b\,[1\text{-Octene}]_0^c$ | | | | | | | |
| 4.0 | 0.8 | 0.07-0.26 | 40 | 214 | n | n | 0.95 |
| " | " | " | 50 | 324 | n | n | 0.76 |
| 2.0-4.0 | 0.1-0.8 | 2.6 | " | 180 | 1.1 | 0.51 | n |
| 4.0 | " | " | 59 | 326 | n | 0.77 | n |

* Cr = Chromium (III) Acetylacetonate

** n = no data

50°, a = 1.7. An attempt was made to measure b and c at -1.0°, but no reliable results were obtained because of the low rate of reaction under these conditions. However, the value of b varies from 0.5 at 30° to 0.13 at 50°, and c varies from 0.0 - 1.0 at 30° to zero at 50°. Below 0.6 M 1-octene, c = 0 at 30° and only increases to about 1.0 at higher concentrations. The data clearly indicate that the rate law for the disappearance of chromium (III) acetylacetonate involves a multi-term process. The following mechanism, similar to that suggested for the cobalt (II) catalyzed decomposition of *t*-butyl hydroperoxide,[39a] and consistent with the observed data, is proposed.

(60) $\mathrm{Cr(III)} + \nu\, \underline{t}\text{-BuOOH} \rightleftharpoons \text{Complex I}$

(61) $\text{Complex I} \longrightarrow \mathrm{Cr(III} + \mu) + \mu\, \underline{t}\text{-BuO}^{\cdot} + \mu\, \mathrm{OH}^{-}$

(62) $\mathrm{Cr(III} + \mu) + \mathrm{Cr(III)} \longrightarrow \mathrm{Cr(VI)} + \mathrm{Cr}(\mu)$

(63) $\mathrm{Cr(III)} + \lambda\, \mathrm{C_8H_{16}} \rightleftharpoons \text{Complex II}$

(64) $\text{Complex II} + x\mathrm{Z} \longrightarrow \mathrm{Cr(III} + \mu) + \mathrm{Z'}$

where Z is any reactive species in the system (e.g., a radical or oxygen) and Z' represents a species derived from Z and olefin. From the above scheme, the rate equation for the disappearance of chromium (III) acetylacetonate becomes:

$$-d[\mathrm{Cr}]/dt = k_{61}[\text{Complex I}] + k_{62}[\mathrm{Cr(III)}][\mathrm{Cr(III} + \mu)] + k_{64}[\text{Complex II}][\mathrm{Z}]^{x} \tag{65}$$

$$-d[\mathrm{Cr}]/dt = \frac{k_{61}k_{60}}{k_{-60}}[\mathrm{Cr(III)}][\underline{t}\text{-BuOOH}]^{\nu} + k_{62}[\mathrm{Cr(III)}][\mathrm{Cr(III} + \mu)] + \frac{k_{64}k_{63}}{k_{-63}}[\mathrm{Cr(III)}][\mathrm{C_8H_{16}}]^{\lambda}[\mathrm{Z}]^{x} \tag{66}$$

Equation 66 predicts that the rate of chromium (III) acetylacetonate disappearance should be between first and second order in chromium (III) acetylacetonate, between 0 and $\nu$ th order in *t*-butyl hydroperoxide and between 0 and $\lambda$ th order in olefin. Reaction 60 involves complex formation between a chromium (III) acetylacetonate molecule and $\nu$ *t*-butyl hydroperoxide molecules. From a study of *t*-butyl hydroperoxide decomposition using very small amounts ( $\lesssim$ .06 M) of peroxide (so that decomposition is primarily via Reaction 60), a value of $\nu = 4$ is indicated. It is observed, however, that the value of b (see Table II) is never more than 0.5-0.6, even when relatively high ( $\gtrsim$ 1.5 M) concentrations of *t*-butyl hydroperoxide are used. This indicates one of two things. Either the first term on the right in Equation 66 is very much smaller than the other two or Cr(III) is oxidized by just one molecule of *t*-butyl hydroperoxide even though it complexes with $\nu$ molecules (i.e., a one-electron transfer). Therefore Equation 60 might be written as a multistep reaction in which Cr(III) is oxidized in one of the steps by one molecule of *t*-butyl hydroperoxide.

(60a) $\mathrm{Cr(III)} + 3\ t\text{-BuOOH} \rightleftarrows \mathrm{Cr(III)}(t\text{-BuOOH})_3$

$= \text{Complex III}$

(60b) $\text{Complex III} + t\text{-BuOOH} \longrightarrow \mathrm{Cr(IV)}(t\text{-BuOOH})_3$

$+\ \mathrm{OH^-}\ +\ t\text{-BuO}\cdot$

In the first step, three *t*-butyl hydroperoxide molecules replace three of the chromium-acetylacetonate bonds (see Figure 11). In the second step a fourth molecule is reduced by reaction with Complex III. If $k_{60a} > k_{60b}$, then 60b is the rate determining step of the sequence. Furthermore, if the complexed t-butyl hydroperoxide molecules are non-titratable (and essentially "destroyed" therefore), then the rate of t-butyl hydroperoxide decomposition for this process becomes:

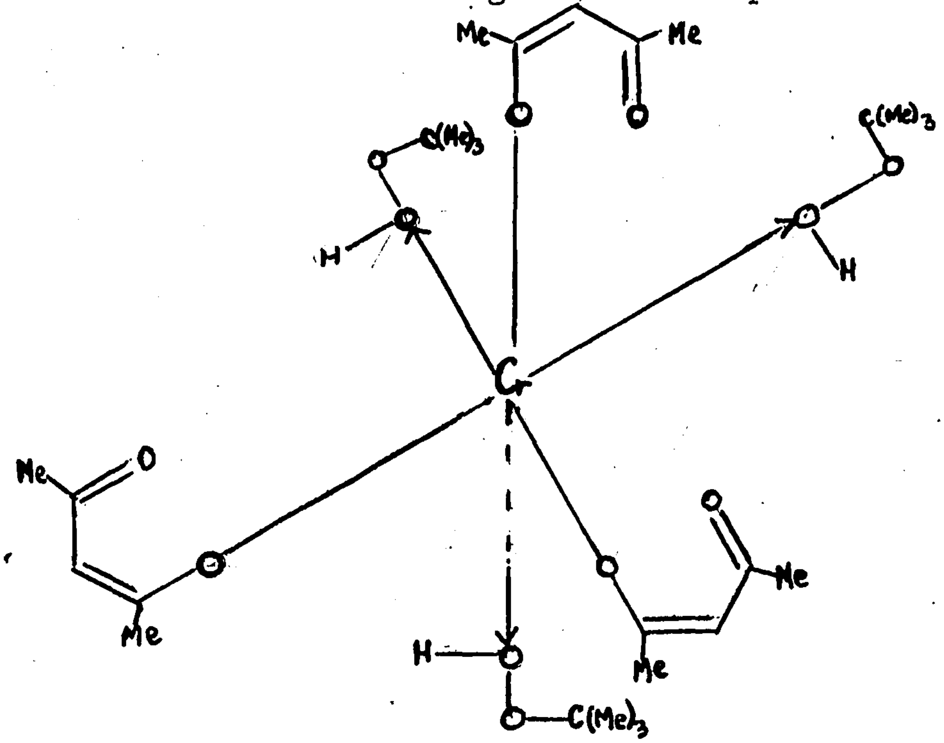
(67) $-d[\underline{t}\text{-BuOOH}]/dt = k_{60}[\text{Cr(III)}][\underline{t}\text{-BuOOH}]^4$

and the rate of chromium (III) acetylacetonate disappearance becomes:

(68) $-d[\text{Cr}]/dt = k_{60b}[\text{Cr(III)}][\underline{t}\text{-BuOOH}]$

since complexing does not affect the oxidation state of the metal. The involvement of three molecules of hydroperoxide in Reaction 60a is suggested since the chelation by the acetylacetonate groups leaves three "open" coordination sites on the metal.

Figure 11: Complex III



The Cr(IV) species produced in Reaction 60b can be oxidized to Cr(VI), probably by a two-step reaction involving two Cr(III) molecules. Reactions[96] between Cr (IV) and Cr(V) may be neglected due to the extremely low concentration of these species.[97] The intervention of Cr(IV) and Cr(V) in the Cr(VI) oxidation of organic compounds is well known.[96] It is also known that these species are particularly stable in complexing media,[99] Cr(V) being especially stable in the presence of $OH^-$.[2] Furthermore, the formation of a relatively stable complex, tetra-t-butoxy Cr(IV), is known to occur in the presence of di-t-butyl peroxide.[100] Therefore there is ample precedent for the existence of these species in a system of the type under study. Cr(IV) is known to be a good reducing agent[96] and therefore oxidation of this species should be especially facile. Support for the suggestion of a 2-electron oxidation of Cr(IV) by two molecules of Cr(III) (see Reaction 69) comes from the fact that oxidation of Cr(IV) to Cr(V) by Cr(III) is a highly endothermic reaction, but oxidation of Cr(V) by Cr(III) is exothermic to almost the same extent.[97]

$$(69) \qquad \mathrm{Cr(IV)} + 2\ \mathrm{Cr(III)} \longrightarrow \mathrm{Cr(VI)} + 2\ \mathrm{Cr(II)}$$

The energy of activation for Reaction 69 is about zero.[97] Evidence for the formation of Cr(VI) comes from the observation that an absorption peak appears in the visible region (438 mμ) as the reaction proceeds. Dichromate ion absorbs at 440 mμ.[101] The rate of appearance of this peak is some 5 times faster in the presence of oxygen than in its absence at 40° under the conditions of Table III and it has been reported[102] that Cr(III) is oxidized to Cr(VI) in the presence of peroxides and molecular oxygen. It is also observed that as the reaction proceeds, the solution takes on a yellow-orange color suggestive of chromate ion. In the presence of methanol a blue color[103] develops in the solution instead of the yellow-orange (possibly due to a methanol-chromium complex). When a small amount of potassium dichromate and glacial acetic acid is added to a solution of _t_-butyl hydroperoxide and 1-octene in methanol, an identical blue color appears. Under the conditions of Table III the appearance of the color and the absorption peak at 438 $m\mu$ takes about 0.5-3 hours to develop. Where oxidation was rapid (e.g., high temperature, high metal concentration, etc.), the rate of appearance was greater.

In the absence of oxygen or peroxide there is no detectable change in the ultra violet spectrum of a chromium (III) acetylacetonate solution in 1-octene (see Table III). However, this same solution is found to absorb oxygen at an appreciable rate at 30° (see Table III). It has been reported[46] that there is no chromium (III) acetylacetonate-oxygen reaction at 100° in diphenyl ether, although it has been shown in this laboratory that there is a slow pick-up of oxygen if 1-chloroöctane is used as a solvent instead of diphenyl ether (see Appendix I). Since this latter reaction should be negligible at 30°, the absorption of oxygen by the chromium (III) acetylacetonate-1-octene solution is due to

Table III: Dependence of the Rate of Disappearance[a] of t-Butyl Hydroperoxide and Chromium (III) Acetylacetonate and the Rate of Autoxidation[b] of 1-Octene on Reactant Concentrations[c] and Temperature.

| $[Cr(acac)_3]_0$ x $10^4$ M | $[t\text{-BuOOH}]_0$ M | $[1\text{-Octene}]_0$ M | Temp. °C | $R_{Cr}$[d] | $R_P$[d] | $R_0$[d] |
|---|---|---|---|---|---|---|
| 4.00 | 0.094 | 2.56 | -1.0[e] | 0.0[f] | 0.0[f] | 2.03 |
| " | 0.76 | 0.64 | " | 0.13 | 0.0025 | n[g] |
| " | " | 2.56 | " | 0.31 | .0018 | 0.40 |
| 16.00 | " | " | " | 1.23 | 0.0013 | n |
| 0.00 | " | 5.97 | 30 | - | n | 0.0[h] |
| 0.762 | 0.00 | 2.56 | " | 0.0[i] | - | 0.17 |
| 0.800 | 0.76 | 5.97 | " | n | n | 0.53 |
| 0.904 | " | 2.56 | " | 1.47 | 0.257 | n |
| 4.00 | 0.00 | " | " | 0.0[i] | - | 0.34 |
| " | " | 3.25 | " | n | - | 0.48 |
| " | " | 4.50 | " | 0.0[i] | - | 0.85 |
| " | " | 5.80 | " | 0.0[i] | - | 1.25 |
| " | 0.0004 | 2.56 | " | n | n | 0.46 |
| " | 0.0019 | " | " | n | n | 0.83 |
| " | 0.0045 | " | " | 0.39 | 0.0[j] | 1.29 |
| " | 0.023 | " | " | n | n | 1.85 |
| " | 0.064 | " | " | 1.42 | 0.0002 | n |
| " | 0.094 | 0.128 | " | n | n | 1.21 |
| " | " | 0.637 | " | n | n | 1.77 |
| " | " | 1.27 | " | n | n | 2.09 |

(continued)

Table III (continued)

| $[Cr(acac)_3]_0$ x $10^4$ M | [t-BuOOH]$_0$ M | [1-Octene]$_0$ M | Temp. °C | $R_{Cr}$[d] | $R_P$[d] | $R_O$[d] |
|---|---|---|---|---|---|---|
| 4.00 | 0.094 | 2.56 | 30 | n | 0.003 | 2.31 |
| " | " | 4.46 | " | n | n | 2.85 |
| " | 0.168 | 2.56 | " | n | n | 2.24 |
| " | 0.183 | 0.128 | " | n | n | 0.90 |
| " | 0.76 | 0.00 | " | 2.52 | 1.77 | 0.0[k] |
| " | " | 0.072 | " | n | n | 0.46 |
| " | " | 0.128 | " | 2.33 | 0.533 | 0.74 |
| " | " | 0.256 | " | n | n | 1.34 |
| " | " | 0.637 | " | 2.18 | n | n |
| " | " | 2.56 | " | 6.43 | 0.761 | 2.25 |
| " | " | " | " | n | n | 1.61[l] |
| " | " | " | " | n | n | 1.43[m] |
| " | " | 5.97 | " | n | n | 3.12 |
| " | 1.52 | 0.128 | " | n | 1.52 | n |
| " | " | 2.56 | " | n | 1.67 | n |
| " | 4.50 | 0.128 | " | n | n | 0.52 |
| 8.00 | 0.00 | 2.56 | " | 0.0[i] | - | 0.57 |
| " | 0.76 | " | " | 13.4 | 0.967 | n |
| 8.46 | " | 5.97 | " | n | n | 5.36 |
| 12.00 | 0.094 | 2.56 | " | n | n | 5.85 |
| 0.762 | 0.00 | " | 34 | n | - | 0.25 |
| 8.00 | " | " | " | n | - | 0.95 |
| 0.574 | 0.76 | " | 40 | 4.27 | 0.565 | 1.15[n] |

(continued)

Table III (continued)

| [Cr(acac)$_3$]$_0$ x $10^4$ M | [$\underline{t}$-BuOOH]$_0$ M | [1-Octene]$_0$ M | Temp. °C | $R_{Cr}^d$ | $R_P^d$ | $R_0^d$ |
|---|---|---|---|---|---|---|
| 4.00 | 0.018 | 2.56 | 40 | n | n | 1.93 |
| " | 0.094 | " | " | 47.6 | 0.006 | 2.52 |
| " | 0.76 | 0.00 | " | 63.9 | 2.75 | n |
| " | " | 0.077 | " | n | n | 0.70 |
| " | " | 0.256 | " | n | n | 2.18 |
| " | " | 0.640 | " | 65.5 | 1.91 | n |
| " | " | 2.56 | " | 66.6 | 2.25 | 4.84 |
| 0.574 | " | " | 46 | 8.94 | n | n |
| 4.00 | 0.094 | " | " | 99.2 | n | n |
| " | 0.76 | 0.00 | " | 133 | n | n |
| " | " | 0.64 | " | 136 | n | n |
| " | " | 2.56 | " | 137 | n | n |
| 0.574 | " | " | 50 | 12.1 | 2.24 | n |
| 2.00 | 0.094 | " | " | n | n | 1.47 |
| " | 0.76 | " | " | n | n | 4.04 |
| 4.00 | 0.094 | " | " | 206 | 0.049 | 2.94 |
| " | 0.76 | 0.00 | " | 278 | 4.97 | n |
| " | " | 0.077 | " | n | n | 1.09 |
| " | " | 0.256 | " | n | n | 2.72 |
| " | " | 0.640 | " | 268 | 4.82 | n |
| " | " | 2.56 | " | 286 | 5.91 | 8.61 |
| " | 0.094 | " | $60^o$ | n | 0.666 | 3.10 |
| " | 0.76 | 0.256 | " | n | n | 4.22 |

(continued)

Table III (continued)

| $[Cr(acac)_3]_0$ x $10^4$ M | [$\underline{t}$-BuOOH]$_0$ M | [1-Octene]$_0$ M | Temp. °C | $R_{Cr}$[d] | $R_P$[d] | $R_0$[d] |
|---|---|---|---|---|---|---|
| 4.00 | 0.76 | 0.64 | 60 | 537 | 8.92 | n |
| " | " | 2.56 | " | 859 | 8.29 | 14.7 |
| 8.00 | 0.00 | " | " | n | - | 7.50 |

---

a *in vacuo*

b oxygen pressure = 1 atmosphere except where noted

c reactions run in 1-chloroöctane

d $R_{Cr} = (-\Delta[Cr(acac)_3]/\Delta t)_0 \times 10^{-9}$ M/sec

$R_P = (-\Delta[\underline{t}\text{-BuOOH}]/\Delta t)_0 \times 10^{-4}$ M/sec

$R_0 = (-\Delta[O_2]/\Delta t)_0 \times 10^{-6}$ M/sec

e autoxidations run at 2° C.

f no detectable change after 15 days

g n = no data

h no oxygen picked up for 5.5 hours

i no detectable change after 18 hours

j " " " " 71 "

k negligible oxygen pick-up ( 1 ml) after 7 hours

l oxygen pressure = 0.5 atmospheres

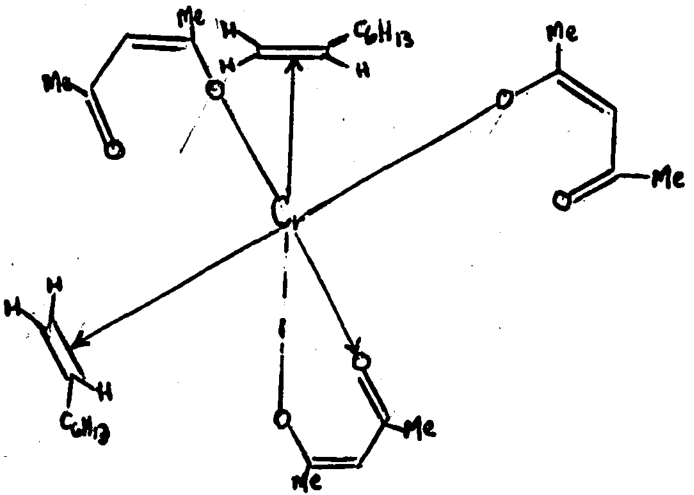
m " " = 0.2 "

n $[Cr(acac)_3]_0 = 8.0 \times 10^{-5}$ M

o autoxidations run at 59° C.

some metal-olefin interaction. Metal-olefin complexes are well known,[104-106] and it has been observed that there is a dramatic effect of 1-octene on the rate of chromium (III) acetylacetonate disappearance if the olefin concentration is high enough ( $\geqslant$ 0.6 M). It is therefore proposed that a chromium-1-octene complex is formed (see Reaction 63), in which the ratio of olefin molecules to chromium (III) acetylacetonate molecules is $\lambda$ . The presence of alkyl chromium species has been observed in the Cr(II) reduction of alkyl halides.[107] It is suggested that a similar species is formed, perhaps in very small concentrations, via Reaction 63, i.e., Complex II (see Figure 12). In the absence of an active species (e.g., a free radical or even oxygen), this complex reverts to chromium (III) acetylacetonate and 1-octene ($k_{-63} > k_{63}$). However, in the presence of an active species, Z, the complex reacts to form free radicals, and in the process changes the oxidation state of the metal (see Reaction 64). Evidence for the participation of oxygen in Reaction 64 comes from the observation that chromium (III)

Figure 12: Complex II



acetylacetonate disappears 1.5-2 times faster in its presence. The free radical species formed in Reaction 64 can then initiate a chain-reaction and therefore accounts for the autoxidation of 1-octene in the presence of chromium (III) acetylacetonate and the absence of t-butyl hydroperoxide. There is some evidence that Reaction 64 plays a role in the initiation process even in the presence of t-butyl hydroperoxide from the observation that there is a slight dependence of the autoxidation rate on the pressure of oxygen (see Table III).

At low olefin concentrations or high temperatures, the concentration of Complex II should be greatly diminished and therefore the contribution of Reaction 64 to the disappearance of chromium (III) acetylacetonate should be negligible. This accounts for the observed negligible dependence of the chromium (III) acetylacetonate disappearance rate upon 1-octene concentration. Olefins which would show large values of $k_{63}$ would behave differently.

Since the Cr(III +$\mu$) species (Cr(IV) and Cr(V)) originally derives from Cr(III), the second term in Equation 66 is essentially second order in Cr(III). The concentration of these species (i.e., Cr(IV) and Cr(V)) should increase with increasing temperature (the formation of these species being highly endothermic). Clearly then, the second-order term in Equation 66 will become more important at higher temperatures. We did indeed observe that the rate of chromium (III) acetylacetonate disappearance increases from first order in chelate at −1.0° to an order of 1.7 at 50° (see Table II). At lower temperatures where Reaction 62 is relatively unimportant, it is observed that the order in t-butyl hydroperoxide and the order in 1-octene (b and c respectively in Equation 59) are slightly greater than 0.5. If $\nu = \lambda = 1$, then $(b + c)/2 \lesssim 0.5$ (depending on the importance of Reaction 62). It is clear therefore that either $\nu$ or $\lambda$ or both are greater than 1. It was pointed out above that at least 4 molecules of t-butyl hydroperoxide can complex with one molecule of chromium (III) acetylacetonate, although it is suggested that only one of these partakes in an oxidation-reduction reaction. It is altogether possible however that more than one peroxide molecule is involved in the disappearance of a chromium (III) acetylacetonate molecule, and therefore $\nu > 1$. The possibility of more than one olefin molecule participating in Reaction 63 also exists and would account for the relatively high concentrations of 1-octene required before there is an observed effect on the rate of chromium (III) acetylacetonate disappearance. However, it is observed that in the autoxidation in the presence of chromium (III) acetylacetonate but the absence of t-butyl hydroperoxide (where Reaction 64 is the suggested initiation step), the rate of oxygen uptake is 3/2 order in olefin. Assuming a rate law similar to Equation 9 (p. 5), this would indicate that the initiation process is first order in 1-octene, i.e., $\lambda = 1$. The rate law could show $\geqslant$ 0.5 dependence on t-butyl hydroperoxide if the concentration of the active species Z is dependent on the peroxide concentration (e.g., if Z = t-BuO· or even $O_2$) (see Reactions 74, 77, 78 below). Therefore, even if the third term in the rate equation (66) is more important than the first, the overall rate could show $\geqslant$ 0.5 dependence on both 1-octene and t-butyl hydroperoxide.

Although it is not possible to estimate individual rate constants, the relative importance of the various terms of Equation 66 may be indicated from the study of the effect of temperature on the rate of chromium (III) acetylacetonate disappearance under various concentration conditions. It is observed that the enthalpy of activation ( $\Delta H^{\ddagger}$) (see Table IV) decreases with increasing olefin concentration. The contribution of Reaction 62 to the overall enthalpy should be small[97] and therefore the difference in enthalpy between the reaction in the absence of olefin and that in its presence reflects the enthalpy difference of Reactions 61 and 64.

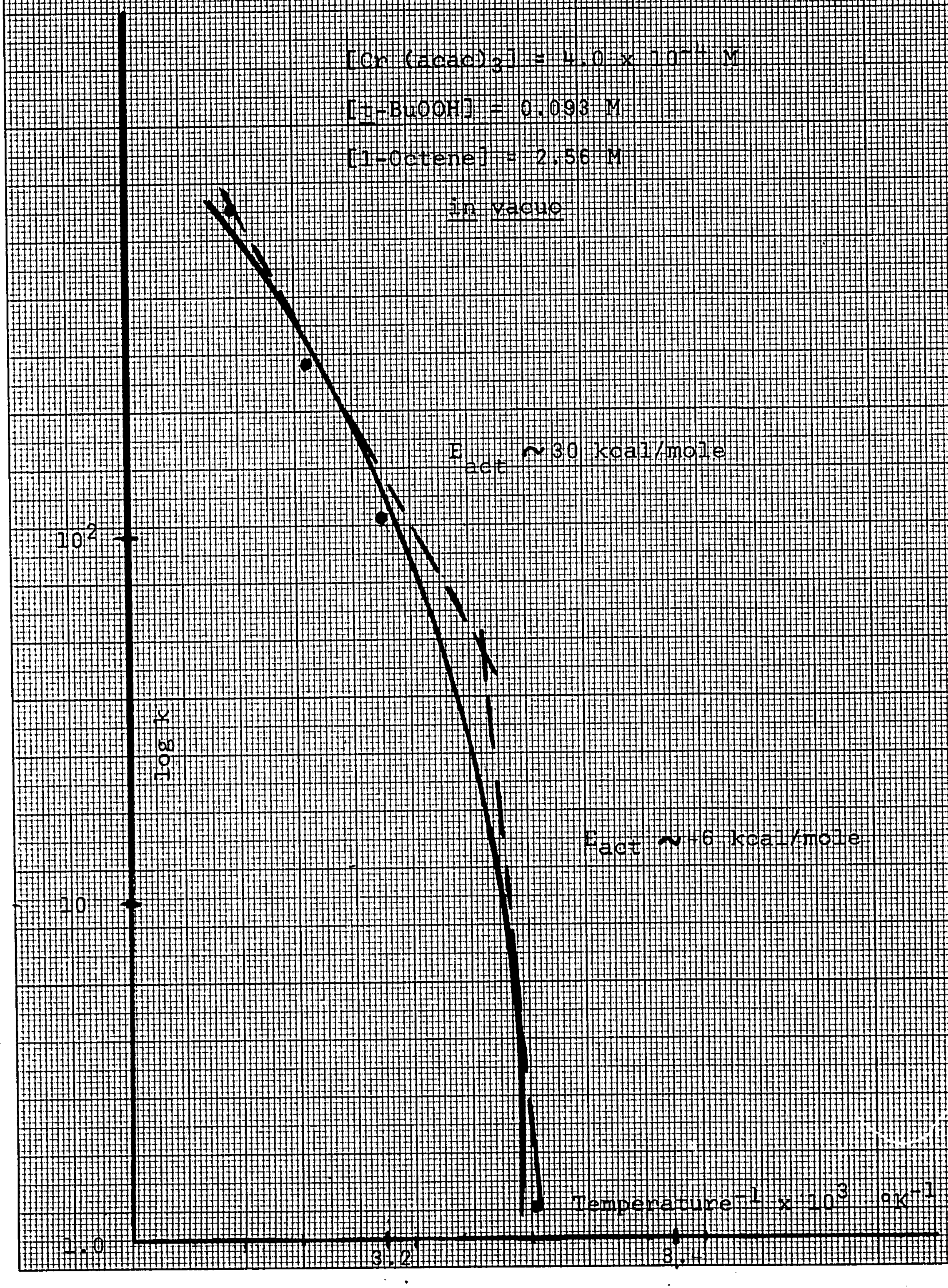
The important difference between Reaction 61 and 64 is the formation of a t-butoxy radical in the former and an allylic radical in the latter. The difference in the enthalpies of the two reactions should be largely due to the difference in the stabilities of the radicals formed in each reaction. If it is assumed that the difference in stability between the t-butoxy radical and the allylic radical (assuming this is the radical formed in Reaction 64) is due to resonance[108] then the latter species should be some 15 kcal/mole[108] more stable than the former. It is in fact observed that the

Table IV: Activation Parameters[a]

| $[Cr]_0$[b] x $10^4$ M | $[\underline{t}\text{-BuOOH}]_0$ M | $[1\text{-Oct.}]_0$ M | $E_{act}$ kcal/mole | $\Delta S^{*}$ cal/deg-mole | $\Delta H^{*}$ kcal/mole |
|---|---|---|---|---|---|
| A. Disappearance of Cr[b,c] | | | | | |
| 4.00 | 0.76 | 2.56 | 26.6±3.5 | +3.32 | 26.0 |
| " | 0.093 | " | (30-46)[d] | +41.8[d] | 37.8[d] |
| " | 0.76 | 0.00 | 39.3±2.8 | +45.2 | 38.7 |
| " | " | 0.64 | 29.1±5.6 | +11.1 | 28.5 |
| B. Decomposition of t-BuOOH[c] | | | | | |
| 4.00 | 0.76 | 2.56 | 19.9±4.1 | -5.72 | 19.3 |
| " | 0.093 | " | 41.7±8.4 | +66.5 | 41.1 |
| " | 0.76 | 0.00 | 10.1±1.7 | -36.4 | 9.5 |
| " | " | 0.64 | 20.2±4.0 | -5.04 | 19.6 |
| C. Autoxidation of 1-Octene[e] | | | | | |
| 4.00 | 0.76 | 2.56 | 12.1±0.7 | -31.8 | 11.5 |
| " | 0.093 | " | 1.3±0.1 | -67.8 | 0.66 |
| " | 0.76 | 0.256 | 7.66±0.43 | -44.2 | 7.05 |
| " | " | 0.077 | 7.54±0.16 | -44.2 | 6.93 |
| " | 0.00 | 2.56 | 18.2±0.3 | -11.4 | 17.3 |

[a] Temperature range = -1.0° to 60° for A and B and 2° to 59° for C
[b] Cr = Chromium (III) Acetylacetonate
[c] in vacuo, 1-chloroöctane solvent
[d] non-linear Arrhenius plot, See text- Figure 13.
[e] 1-chloroöctane solvent, oxygen pressure = 1 atmosphere

Figure 13: Arrhenius Plot for the Rate of Chromium (III) Acetylacetonate Disappearance in the Presence of t-Butyl Hydroperoxide and 1-Octene. Plot (1)



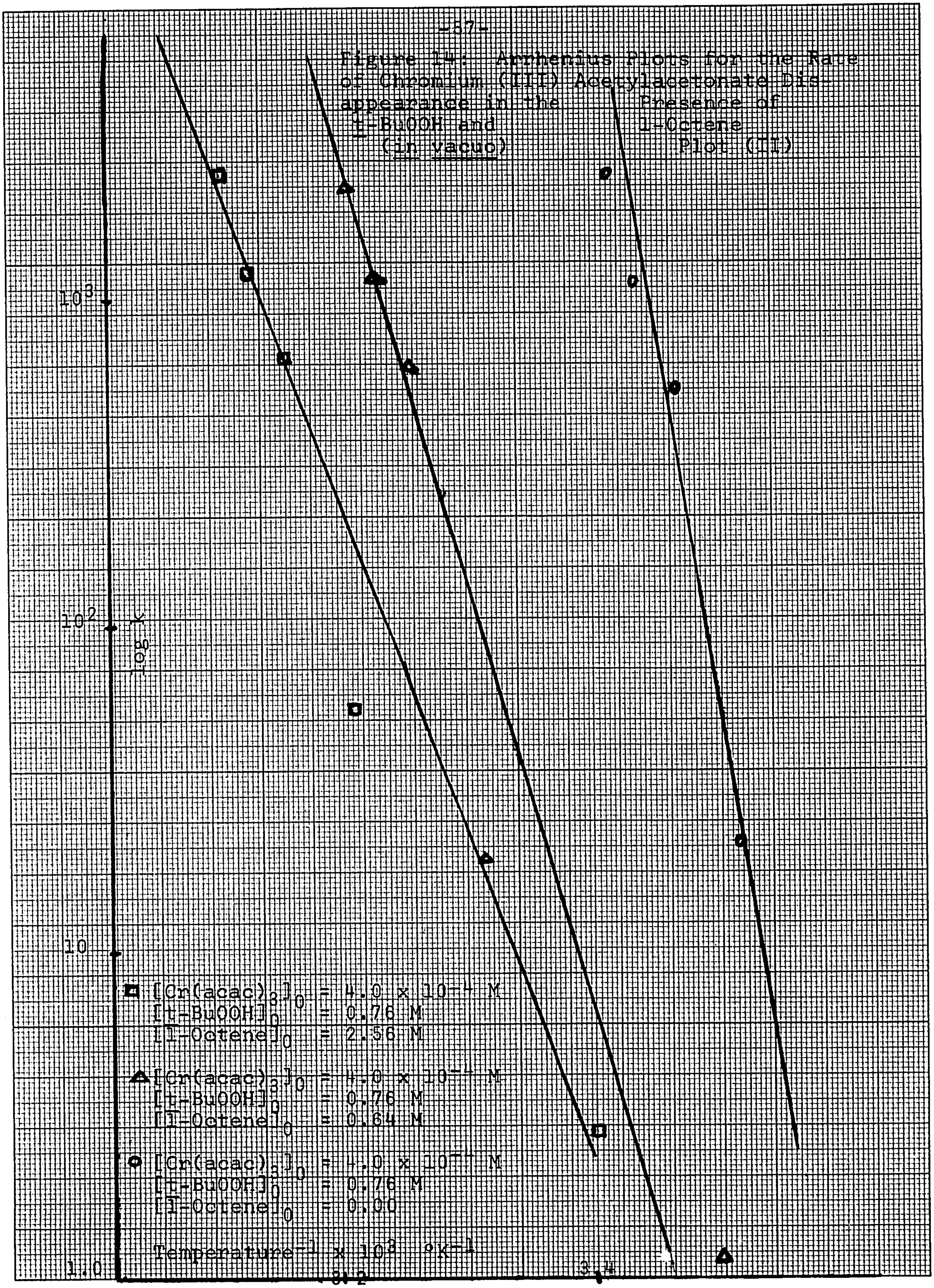


Figure 14: Arrhenius Plots for the Rate of Chromium (III) Acetylacetonate Disappearance in the Presence of t-BuOOH and 1-Octene (*in vacuo*) Plot (II)

Figure 18: Arrhenius Plots for the Rate of t-Butyl Hydroperoxide Decomposition In the Presence of Chromium (III) Acetylacetonate and 1-Octene (*in vacuo*) Plot I

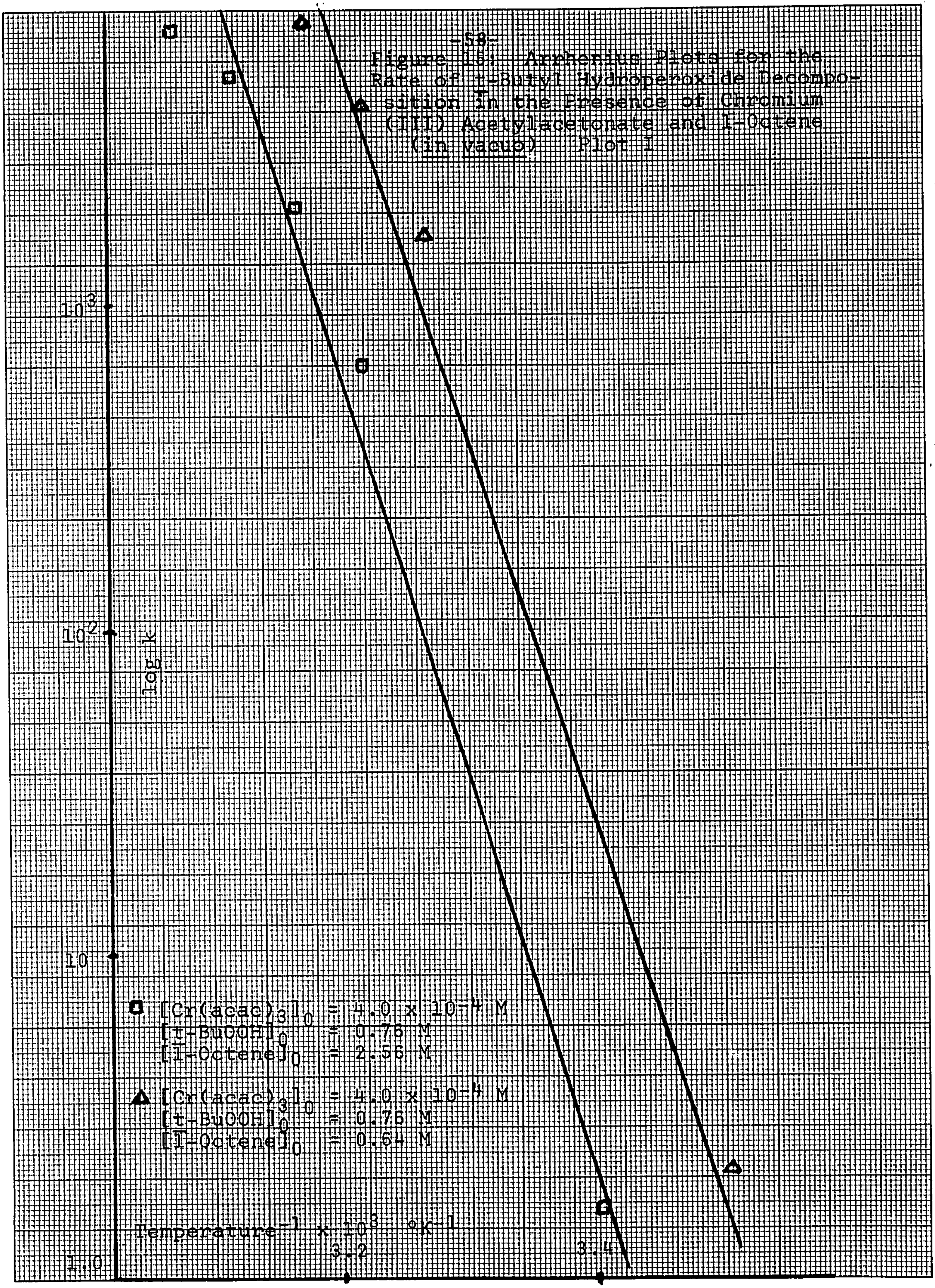
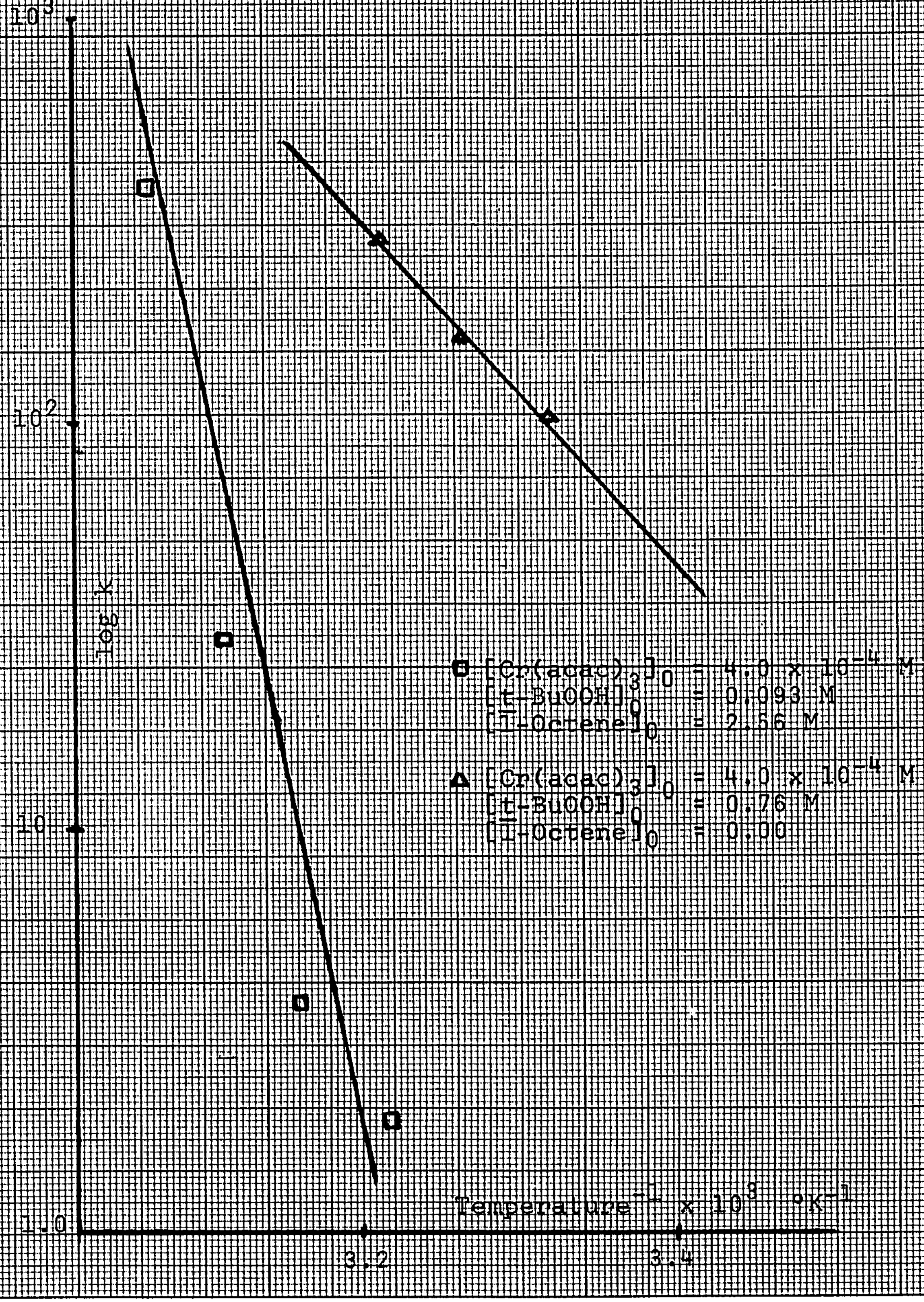


Figure 16: Arrhenius Plots for the Rate of t-Butyl Hydroperoxide Decomposition in the Presence of Chromium (III) Acetylacetonate and 1-Octene (*in vacuo*) Plot (II)



disappearance of chromium (III) acetylacetonate is some 10-13 kcal/mole more endothermic in the absence of 1-octene than in its presence (see Table IV).

The enthalpy of activation for the disappearance of chromium (III) acetylacetonate cannot be strictly related to the olefin/_t_-butyl hydroperoxide ratio. It is observed that in the presence of small amounts of _t_-butyl hydroperoxide ( $\leqslant$ 0.09 M) the overall enthalpy of activation is actually greater than with larger ( $\geqslant$ 0.8 M) peroxide concentrations. This appears contradictory to the discussion given above, however the situation becomes clearer in the light of the following observations.

Although Table IV presents a value of 38.4 kcal/mole for the activation energy for the disappearance of chromium (III) acetylacetonate in the presence of a small amount of _t_-butyl hydroperoxide, it is noted that this is an average value as the Arrhenius plot for this system is non-linear. At higher temperatures the slope (and hence the activation energy) is actually smaller than at lower temperatures. This observation is readily explained if one studies the temperature effect on the decomposition of _t_-butyl hydroperoxide under the same conditions (see p. 64 ). It is noted that the hydroperoxide decomposition, under these conditions, has an activation energy of 42 kcal/mole (see Table IV), which means that at high temperatures the peroxide disappears at a much faster rate than at low temperatures. As a consequence, Reaction 64 soon becomes much more important relative to Reaction 61 at high temperatures, even though it has a lower activation energy, due to the rapid depletion of t-butyl hydroperoxide. It is therefore observed that the high temperature chromium (III) acetylacetonate disappearance reaction has an activation energy of about 30 kcal/mole, which is similar to those systems in which Reaction 64 is relatively more important than Reaction 61. At lower temperatures the activation energy of the chromium (III) acetylacetonate disappearance is about 46 kcal/mole. It is observed that over the whole temperature range (20° to 60°) the activation energy for the low peroxide system is greater than for the high peroxide system. There are two possible explanations for this. First, it is noted that Reactions 61, 62, and 64 involve electron-exchange. Clearly, these reactions are facilitated in a more polar medium. The polarity of the system increases with the concentration of t-butyl hydroperoxide and therefore it is expected that these electron-transfer reactions will have a lower activation energy in the presence of large amounts of peroxide.

An alternate explanation arises from the fact that t-butyl hydroperoxide is known to be an excellent hydrogen-bonding species.[109] Hydrogen-bonding may play an important role in the transition states of the various reactions involved in the disappearance of chromium (III) acetylacetonate (e.g., in stabilizing the intermediate species). Therefore in a good hydrogen-bonding medium, i.e., in the presence of large concentrations of t-butyl hydroperoxide, the activation energies for these various reactions are lowered. The same effect, as manifested by an increase in the rate of chromium (III) acetylacetonate disappearance, is observed in other hydrogen bonding solvents such as methanol, t-butanol, and acetic acid (see p. 93 ).

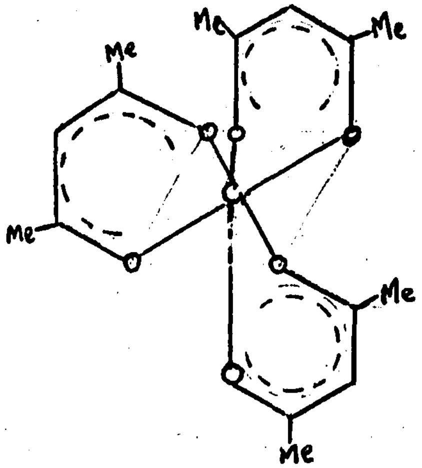
The enthalpy ( $\Delta H^{\ddagger}$) of the chromium (III) acetylacetonate disappearance reaction in the absence of 1-octene is 39 kcal/mole. This value is essentially the enthalpy of Reaction 61, again assuming negligible contribution from Reaction 62, and indicates that O-O bond scission is the primary mode of t-butyl hydroperoxide dissociation (The bond strength of the O-O bond in t-butyl hydroperoxide is 35-37 kcal/mole[4,110]). The fact that the O-H bond strength in t-butyl hydroperoxide is about 84 kcal/mole[4] essentially precludes decomposition via Reaction 70:

(70) $$Cr(III) + \underline{t}\text{-BuOOH} \longrightarrow Cr(II) + \underline{t}\text{-BuOO}\cdot + H^{+}$$

although similar reactions have been suggested for other metal-peroxide systems.[15,90,111,112,113] The energy involved in oxidizing or reducing the metal, although appreciable, should have little effect on the overall enthalpy since electron transfer should be very fast compared to bond-breaking. The bond-breaking step should therefore control the rate and the enthalpy of the overall reaction. Furthermore, the presence of t-butanol among the products suggests the formation of t-butoxy radicals although these could arise via Reaction 74 below.[23]

The overall entropy of activation ($\Delta S^{\ddagger}$) for the disappearance of chromium (III) acetylacetonate is a function of the entropies of Reactions 60-64. It has been shown[114] that acetylacetonates are highly rigid molecules with a good deal of symmetry insofar as the ligand structure around the central atom is concerned (see Figure 17).[115] Since the above reactions involve some departure from this symmetry, e.g., via ligand exchange ( cf. Figures 11 and 12), one would expect the entropy of the transition state to be greater than that of the original reactants and hence to observe a positive $\Delta S^{\ddagger}$ value.[29] It is this positive entropy value that helps to offset the energy loss due to destruction of the "aromaticity"[114] of the acetylacetonate structure.

Figure 17: The Structure of Chromium (III) Acetylacetonate



It is noted that in the transition state there is more rotational freedom for the ligands than in the original molecule, regardless of whether exchange is with _t_-butyl hydroperoxide or 1-octene. In the latter case, however, the effect is not as great. It is suggested that this is due to the formation of resonance stabilized species (e.g., an allylic radical) in this process. In these species only certain conformations are permitted, to allow for maximum orbital overlap, thus restricting rotation about certain bonds and resulting in a more negative entropy of activation.[116] It is observed that as the olefin concentration increases, the entropy of activation becomes less positive, indicating increased participation of Reaction 64. The entropy of activation for the disappearance of chromium (III) acetylacetonate in the presence of small amounts of t-butyl hydroperoxide ($\lesssim$ 0.09 M) appears unusually high. This is probably due to the lack of ion-solvent interactions or hydrogen-bonding effects, either of which would restrict motion and result in a more negative entropy.[117] The entropy of activation for Reaction 62 should be small since the products and the reactants resemble each other very closely. A negative $\Delta S^{\ddagger}$ value would also be expected if there were an increase in the coordination number of the metal, i.e., from 6 to 8. Although coordination numbers of 8 are rare, the acetylacetonates of many +4 ions are believed to involve eight-coordination.[118] On the other hand, the formation of +2 species might reduce the coordination number to 4,[119] resulting in a more positive $\Delta S^{\ddagger}$ value.

C. The Decomposition of t-Butyl Hydroperoxide in the Absence of Oxygen.--The decomposition of t-butyl hydroperoxide in the presence of chromium (III) acetylacetonate may proceed by either of two paths. When present in large concentrations

( $\gtrsim$ 0.8 M) t-butyl hydroperoxide will decompose via a chain process[110,120] with chain lengths of $10^3$-$10^4$ (see Table V). As the concentration of t-butyl hydroperoxide decreases, the chain length rapidly approaches unity (see Table V) and at low concentrations ( $\lesssim$ .09 M), t-butyl hydroperoxide decomposes via a non-chain process. This mechanism is supported by temperature studies which indicate that the activation energy for the decomposition increases from 20 kcal/mole under conditions of high peroxide concentrations where the chain process is predominant to 42 kcal/mole under low peroxide concentration and hence non-chain conditions. The value of 42 kcal/mole is consistent with the rupture of the O-O bond in t-butyl hydroperoxide and with observed activation energy for the disappearance of chromium (III) acetylacetonate under the same conditions (46 kcal/mole), suggesting that both compounds disappear via the same process under these conditions, namely Reactions 60 and 61 (<u>vide supra</u>, p.42). As the chain process becomes more important, the overall activation energy becomes a function of the activation energies of the initiation, propagation, and termination processes[121] (see Equation 95 below).

The rate equation for the decomposition in the absence of oxygen is given by:

(71) $-d[\underline{t}\text{-BuOOH}]/dt = k_{obs}[Cr]^a\ [\underline{t}\text{-BuOOH}]^b\ [C_8H_{16}]^c$

where Cr = chromium (III) acetylacetonate and $k_{obs}$ = the experimental rate constant. The value of a is 0.5-0.7 under all conditions studied (see Tables II and III).

Table V: Dependence of Chain Length on Concentration and Temperature Conditions

| $[Cr(acac)_3]_0$ | [*t*-BuOOH]$_0$ | [1-Octene]$_0$ | Temp. °C | $v_0 \times 10^{-3}$ | $v_p \times 10^{-4}$ |
|---|---|---|---|---|---|
| 4.00 | 0.76 | 2.56 | 0.0±2.0 | 1.3 | .058 |
| 0.904 | " | " | 30 | 0.35 | 1.8 |
| 4.00 | 0.0047 | " | " | 2.7 | 0.0[a] |
| " | 0.064 | " | " | n[b] | 0.0014 |
| " | 0.094 | " | " | 1.0 | 0.013 |
| " | 0.76 | 0.128 | " | 0.32 | 2.3 |
| " | " | 0.640 | " | 0.60 | n |
| " | " | 2.56 | " | 0.35 | 1.2 |
| 8.00 | " | " | " | 0.34 | 0.72 |
| 0.574 | " | " | 40 | 0.19 | 1.3 |
| 4.00 | 0.094 | " | " | 0.053 | 0.0013 |
| " | 0.76 | 0.64 | " | n | 0.29 |
| " | " | 2.56 | " | 0.073 | 0.34 |
| 0.574 | " | " | 50 | n | 1.9 |
| 4.00 | 0.094 | " | " | 0.014 | .0024 |
| " | 0.76 | 0.64 | " | n | 0.18 |
| " | " | 2.56 | " | 0.030 | 0.21 |
| " | " | 0.64 | 60±1.0 | n | 0.17 |
| " | " | 2.56 | " | 0.017 | 0.097 |

[a] No detectable *t*-BuOOH decomposition after 71 hours. However, the rate is probably not zero; a rate of *t*-BuOOH of $10^{-9}$ M/sec would be beyond the limits of detection but would result in a value of about one for the chain length.

[b] n = no data

The value of b is dependent on both temperature and peroxide concentration, decreasing with both an increase in temperature and an increase in concentration. The decomposition of t-butyl hydroperoxide shows a slight dependence on olefin concentration (i.e., $c > 0$). This observation may be attributed to chain transfer effects. The effect of the presence of olefin is also temperature dependent and will be discussed below.

At low concentrations of t-butyl hydroperoxide, decomposition is primarily via a non-chain process (Reactions 60 and 61). As discussed above (see p. 44) the rate law for the decomposition of t-butyl hydroperoxide by this process is given by Equation 67 above (see p. 44). The rate law for the chain decomposition of t-butyl hydroperoxide (cf. Equation 93 below) is given by Equation 72:

$$(72)\quad -d[\underline{t}\text{-BuOOH}]/dt = k_{obs}[Cr]^{0.5}\,[\underline{t}\text{-BuOOH}]^{1.25}\,[C_8H_{16}]^{0.25}$$

Clearly then the values of a, b, and c (Equation 71) depend on experimental conditions and upon which rate law (Equation 67 or 72) predominates. As the concentration of t-butyl hydroperoxide increases, the chain process becomes more important and therefore the value of a should decrease from 1 to 0.5, the value of b should decrease from 4 to 1.25, and the value of c should increase from 0 to 0.25. In the presence of large amounts of t-butyl hydroperoxide the value of a is observed to be 0.5 to 0.7 and the value of c is about 0.1. It was not possible to obtain accurate data under conditions of low peroxide concentrations because of the very low rate of decomposition. The values of a and c could not be calculated under these conditions. However, the rate of t-butyl hydroperoxide decomposition was studied over a twenty-fold range of peroxide concentrations and it was observed that the value of b was about 4 (within experimental error) in the low peroxide region (0.06-0.09M) and decreased to a value of about 1.1 at high concentrations (0.8-1.6 M). The data are given in Table III (see p.47 ) and the dependence of the decomposition rate on t-butyl hydroperoxide concentration is described in Table III. The strong dependence of the decomposition rate in the low peroxide region might be attributed to polar effects,[122] e.g., via solvolysis of the intermediates involved in the initiation process. However several observations were made which tend to refute this suggestion. Solvent studies indicate that polar media have little effect on the decompositions, the reaction actually being slightly slower in methanol and acetic acid (see p. 93). Furthermore, a 4-fold change in concentration from 0.094 M to 0.37 M, which should produce a large change in the dielectric constant of the medium- produces only a 5-fold change in rate, while a 1.5-fold change in concentration from 0.064 M to 0.094 M produces a 15-fold change in rate. Furthermore, an increase in concentration from 0.37 M to 0.76 M, which should have little effect on the polarity of the medium, increases the rate some 20 times. Finally, the effect of known free radical inhibitors suggests that the decomposition is primarily free radical in nature and therefore polar effects should not be significant.

The chain process for the decomposition of *t*-butyl hydroperoxide in the absence of added oxygen may be described by the following scheme:

(73) $\underline{t}\text{-BuOOH} + \text{I}\cdot \longrightarrow \underline{t}\text{-BuOO}\cdot + \text{IH}$

(74) $2\ \underline{t}\text{-BuOO}\cdot \longrightarrow 2\ \underline{t}\text{-BuO}\cdot + O_2$

(75) $\underline{t}\text{-BuOOH} + \underline{t}\text{-BuO}\cdot \longrightarrow \underline{t}\text{-BuOO}\cdot + \underline{t}\text{-BuOH}$

(76) $2\ \underline{t}\text{-BuO}\cdot \longrightarrow \underline{t}\text{-Bu}_2O_2$

(77) $2\ \underline{t}\text{-BuOO}\cdot \longrightarrow \underline{t}\text{-Bu}_2O_2 + O_2$

(78) $\underline{t}\text{-BuO}\cdot + \underline{t}\text{-BuOO}\cdot \longrightarrow \underline{t}\text{-Bu}_2O + O_2$

where I is the initiating radical from Reaction 61 or 64. Reactions 73 and 75 represent the propagation steps and Reactions 76-78 represent the termination process. In the Presence of 1-octene, additional propagation steps (79-80) and termination steps (81-83) must be included.[4]

(79) $\underline{t}\text{-BuO}\cdot + C_8H_{16} \longrightarrow C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + \underline{t}\text{-BuOH}$

(80) $C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + \underline{t}\text{-BuOOH} \longrightarrow \underline{t}\text{-BuOO}\cdot + C_8H_{16}$

(81) $C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + \underline{t}\text{-BuO}\cdot \longrightarrow$ inactive products

(82) $C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + \underline{t}\text{-BuOO}\cdot \longrightarrow$ inactive products

(83) $2\ C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 \longrightarrow$ inactive products

Reactions involving oxygenated alkenyl radicals have not been included, even though there may be some oxygen present (from Reactions 74, 77, and 78) because the concentration of these radicals should be small compared to the others represented in the above scheme. The involvement of radical-peroxide complexes may play a significant role in this system and will be discussed below (see p. 154).

In the absence of olefin the primary propagation step is Reaction 75. Assuming steady state conditions, the rate of production of t-butoxy radicals is equal to their rate of disappearance. Assuming further that t-butoxy radicals are produced mainly by Reaction 74 and disappear primarily by Reaction 75, then

(84) $k_{74}[\underline{t}\text{-BuOO}\cdot]^2 = k_{75}[\underline{t}\text{-BuO}\cdot]\,[\underline{t}\text{-BuOOH}]$

or

(85) $[\underline{t}\text{-BuO}\cdot] = k_{74}[\underline{t}\text{-BuOO}\cdot]^2/k_{75}[\underline{t}\text{-BuOOH}]$

where $[\underline{t}\text{-BuOO}\cdot]$ and $[\underline{t}\text{-BuO}\cdot]$ are the steady state concentrations of the $\underline{t}$-BuOO· radical and the $\underline{t}$-BuO· radical, respectively. Under conditions where the chains are long the rate of initiation is equal to the rate of termination. Therefore if $R_i$ = the rate of initiation,

(86) $R_i = k_{76}[\underline{t}\text{-BuO}\cdot]^2 + k_{78}[\underline{t}\text{-BuO}\cdot][\underline{t}\text{-BuOO}\cdot] + k_{77}[\underline{t}\text{-BuOO}\cdot]^2$

Upon substitution of (85) into (86), one obtains:

(87) $$R_i = \frac{k_{76}k_{74}{}^2[\underline{t}\text{-BuOO}\cdot]^4}{k_{75}{}^2[\underline{t}\text{-BuOOH}]^2} + \frac{k_{78}k_{74}[\underline{t}\text{-BuOO}\cdot]^3}{k_{75}[\underline{t}\text{-BuOOH}]} + k_{77}[\underline{t}\text{-BuOO}\cdot]^2$$

From the literature[23,123] one may estimate the values of the rate constants in Equation 87. Substituting these values into Equation 87 and rearranging terms one obtains:

(88) $10^{11}[\underline{t}\text{-BuOO}\cdot]^4 + 10^6[\underline{t}\text{-BuOO}\cdot]^3 + 10^2[\underline{t}\text{-BuOO}\cdot]^2 - R_i = 0$

The value of $R_i$ may be obtained from the chromium (III) acetylacetonate disappearance data (see Table III) and under most conditions equals $10^{-8}$-$10^{-9}$. Equation 88 can be solved then for $[\underline{t}\text{-BuOO}\cdot]$ and one obtains a value of $\sim 10^{-5}$ M. This is seen to be a reasonable value when compared with that measured by Thomas[23] for the azobisisobutyronitrile (AIBN) initiated chain-decomposition of t-butyl hydroperoxide at 22° C.

In the presence of 1-octene the primary chain-carrying species is the octenyl radical ($C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2$) due to the weakness of the allylic carbon-hydrogen bond and the greater stability of the allylic radical. Therefore the predominant propagation step is Reaction 80 and the predominant termination step is Reaction 83. In the presence of olefin the rate of decomposition of t-butyl hydroperoxide is given by:

(89) $$-d[\underline{t}\text{-BuOOH}]/dt = k_{80}[C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2][\underline{t}\text{-BuOOH}]$$

The concentration of the octenyl radical may be obtained by assuming equality of the termination and initiation rates. Therefore

(90) $$R_i = k_{83}[C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2]^2$$

where $[C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2]$ is the steady-state concentration of the octenyl radical. Solving for $[C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2]$ and substituting into Equation 89, one obtains:

(91) $$-d[\underline{t}\text{-BuOOH}]/dt = \frac{k_{80}}{k_{83}^{0.5}} R_i^{0.5}[\underline{t}\text{-BuOOH}]$$

The rate of initiation is essentially given by the rates of Reactions 61 and 64. The combined rate law for this process is given by Equation 92:

(92) $$R_i = k_i[Cr][\underline{t}\text{-BuOOH}]^{0.5}[C_8H_{16}]^{0.5}$$

Substituting Equation 92 into Equation 91 one obtains the rate law for the decomposition of t-butyl hydroperoxide in the presence of 1-octene:

$$(93)\quad -d[\underline{t}\text{-BuOOH}]/dt = \frac{k_{80}k_i^{0.5}}{k_{83}^{0.5}}[\text{Cr}]^{0.5}[\underline{t}\text{-BuOOH}]^{1.25}[C_8H_{16}]^{0.25}$$

The overall activation energy ($E_{obs}$) is proportional to the logarithm of the observed rate constant ($k_{obs}$), and

$$(94)\quad k_{obs} = \frac{k_{80}k_i^{0.5}}{k_{83}^{0.5}}$$

Therefore

$$(95)\quad E_{obs} = 0.5\ E_i + E_{80} - 0.5\ E_{83}$$

where $E_i$, $E_{80}$, and $E_{83}$ are the activation energies for the initiation process, Reaction 80, and Reaction 83 respectively.

Termination via Reaction 83 should have an activation energy of 0-2 kcal/mole.[124] If the value of $E_i$ (26.6 kcal/mole) is taken from the chromium (III) acetylacetonate disappearance data (see Table III) then from the value of $E_{obs}$ (19.9 kcal/mole) (see Table IV), $E_{80}$ equals 6.6-7.6 kcal/mole. This value is similar to the value suggested by Benson[4] (i.e., 7.5 kcal/mole) for the reaction of alkoxy radicals with t-butyl hydroperoxide and with the value estimated from bond strengths[4,125] for Reaction 80 (7.0 kcal/mole). In the absence of olefin, termination occurs via Reactions 76-78, and propagation primarily *via* Reaction 75. Assuming steady state kinetics, the rate law for the decomposition of t-butyl hydroperoxide in the absence of olefin becomes:

$$(96)\quad -d[\underline{t}\text{-BuOOH}]/dt = \frac{k_{18}}{k_t^{0.5}} R_i^{0.5}\ [\underline{t}\text{-BuOOH}]$$

where $k_t$ is a function of the rate constants involved in the overall termination process. The activation energy ($E_{obs}^{\cdot}$) under these conditions becomes:

(97) $E_{obs} = 0.5\ E_i + E_{75} - 0.5\ E_t$

In the absence of olefin, the initial production of radicals is primarily via Reaction 61, which has an activation energy of 39 kcal/mole (see Table IV). Furthermore, in the absence of 1-octene, the probability of reaction between two t-butyl peroxy radicals is greatly increased. This reaction may either terminate a chain (77) or form new radicals (74). It has been observed[23] that the latter reaction proceeds some five times faster than the former at 22° and has an activation energy of 15 kcal/mole. Since Reaction 74 has a much lower activation than Reaction 61, this reaction becomes the predominant source of radicals. $E_t$ may be estimated as 4-10 kcal/mole[23,123] depending on the relative importance of the various termination reactions. Assuming a value of $E_i$ of 15 kcal/mole (vide supra, p. 73 ), from $E_{obs}$ = 10.1 kcal/mole (see Table IV), $E_p$ is estimated as 4.5-7.5 kcal/mole. The latter value is in good agreement with Benson's[4] estimate (7.5 kcal/mole) for the reaction of alkoxy radicals with t-butyl hydroperoxide, and is the value one obtains by assuming termination primarily via Reaction 77. This termination process is the one usually assumed for the chain decomposition of t-butyl hydroperoxide.[23,110] The similarity of the activation energies for the attack of various radicals [alkoxy,[4] t-butoxy, and octenyl (vide supra, p. 72 )] on the peroxide hydrogen of t-butyl hydroperoxide, suggests that bond-breaking in the transition state is more important than bond-making.

It is interesting at this point to consider the effect of olefin on the rate of t-butyl hydroperoxide decomposition as a function of temperature. At 30°, the presence of 2.6 M 1-octene causes a two-fold decrease in the rate. This effect diminishes with increasing temperature, until at 50° the presence of olefin has a slight accelerating effect. There are two ways in which the olefin can affect the decomposition. The first is by competing with t-butyl hydroperoxide for radicals (Reaction 79) and thus diminishing the rate (like a weak inhibitor). The second is by attack of the octenyl radical on the peroxide, therefore inducing decomposition (Reaction 80). In any chain process, attack of the chain-carrying radical on the substrate must compete with termination. In the decomposition of t-butyl hydroperoxide in the absence of 1-octene, the chain-carrying species is either the t-butoxy or the t-butyl peroxy radical. Termination by these radicals requires an activation energy of about 4-10 kcal/mole[23,123] while the propagation step requires 4.5-7.5 kcal/mole (vide supra, p.72 ). Hence propagation can compete successfully with termination regardless of conditions. In the presence of 1-octene the chain-carrying species is the octenyl radical and although the activation energy for propagation is still about 7 kcal/mole, termination by two octenyl radicals only requires

0-2 kcal/mole.[124] Therefore at lower temperatures the propagation step cannot compete as well with the termination step, and 1-octene has a retarding effect on the decomposition due to chain transfer (Reaction 79). However, as the temperature increases the propagation/termination ratio increases due to the difference in activation energy and the retarding effect is reduced. Certain other compounds exhibit the same effect as 1-octene on the decomposition of t-butyl hydroperoxide (see Solvent section, p. 93 ).

An alternative explanation for the effect of olefin arises from a reaction suggested for the induced decomposition of t-butyl hydroperoxide by styrene.[128]

(98) $\underline{t}\text{-BuOOH} + C_6H_5CH{=}CH_2 \longrightarrow \underline{t}\text{-BuOO}\cdot + C_6H_5\dot{C}HCH_3$

However the energetics involved and the probable importance of the styrene structure make the intervention of Reaction 98 unlikely under the conditions of the present study.

The entropy data (see Table IV) are consistent with the proposed mechanisms for t-butyl hydroperoxide decomposition. In the presence of small amounts ( $\leq$ 0.09 M) of t-butyl hydroperoxide, the entropy of activation is +66.5 cal/deg-mole. This is consistent with the value obtained for the disappearance of chromium (III) acetylacetonate under the same conditions and can be attributed to the non-chain process of t-butyl hydroperoxide decomposition. The high positive entropy value is indicative of an increase in rotational freedom in the transition state. This is due to a lack of hydrogen bonding and solvent-ion interactions under low peroxide concentration conditions. At higher concentrations the overall entropy of activation can be related to the entropies of the various steps in the chain process.

(99) $\Delta S^{\ddagger}_{obs} = 0.5\ \Delta S^{\ddagger}_{i} + \Delta S^{\ddagger}_{p} + 0.5\ \Delta S^{\ddagger}_{t}$

Applying the same arguments as in the analysis of the activation energies, the values for the various entropy terms may be estimated. From data in the literature,[23,123,127] and experimental values in the present study, a value of $\Delta S^{\ddagger}_{p}$ of -43.6 cal/deg-mole is estimated for the decomposition of t-butyl hydroperoxide in the absence of 1-octene. In the presence of olefin this value is -25.4 cal/deg-mole. Assuming Reactions 75 and 80 to be the major propagation steps in the absence and presence of 1-octene respectively, the corresponding $\Delta S^{\ddagger}$ values can be estimated[123,128] as $\Delta S^{\ddagger}_{75}$ = -36.6 cal/deg-mole and $\Delta S^{\ddagger}_{80}$ = -18.0 cal/deg-mole. The consistency of the experimental values with these estimated values lends strong support to the proposed mechanisms.

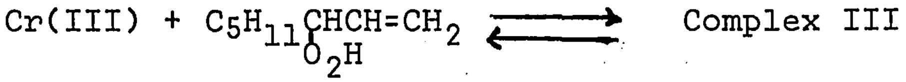
D. Autoxidation of 1-Octene.--1-Octene is autoxidized in the presence of chromium (III) acetylacetonate and t-butyl hydroperoxide or in the presence of chromium (III) acetylacetonate alone. In general, the reaction in the presence of t-butyl hydroperoxide is faster than in its absence. The autoxidation proceeds by a chain process (chain length ca. $10^3$) (see Table V), which is relatively unaffected by the concentration of peroxide (cf. the decomposition of t-butyl hydroperoxide).

The kinetics of the reaction are quite complex, but fit a general mechanistic scheme. [The symbols used in the following reactions are those employed previously, and Reactions 61 and 64 are reproduced here (in part) for clarification (see p. 42)] The initiation reactions are:

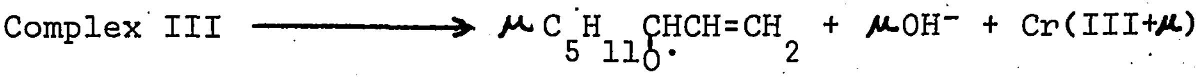
(61) Complex I $\longrightarrow$ $\underline{t}$-BuO·

(64) Complex II $\longrightarrow$ Z'·

where Z'· is a radical produced from the decomposition of Complex II. In addition to these reactions a third process must be included, which substitutes octenyl hydroperoxide for $\underline{t}$-butyl hydroperoxide in Reactions 60 and 61 (q.v.).

(100) 

$$\mathrm{Cr(III)} + C_5H_{11}\underset{O_2H}{CH}CH{=}CH_2 \rightleftarrows \text{Complex III}$$

(101) 

$$\text{Complex III} \longrightarrow \mu\, C_5H_{11}\underset{O\cdot}{CH}CH{=}CH_2 + \mu OH^- + \mathrm{Cr(III}+\mu)$$

The intervention of Reaction 101 in the initiation process is inferred in several ways. First, it has been observed that the amount of octenyl hydroperoxide formed in the autoxidation corresponds to only about 2% of the oxygen absorbed. It is clear therefore that either the hydroperoxide is being destroyed in a rapid reaction (e.g., Reaction 101) or that the octenyl peroxy radical is destroyed before it has a chance to abstract a hydrogen atom (e.g., via Reaction 102).

(102) ROO· + $\underline{t}$-BuOO· $\longrightarrow$ RO· + $\underline{t}$-BuO· + $O_2$

where R = $C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2$

However, although there is much precedent for reactions such as (102),[4,23] in the presence of a good hydrogen donor such as 1-octene, it is unlikely that this reactions could compete

Figure 18: Arrhenius Plot for the Autoxidation of 1-Octene in the Presence of Chromium (III) Acetylacetonate and the Absence of t-Butyl Hydroperoxide ($Press_{O_2}$ = 1 atm).

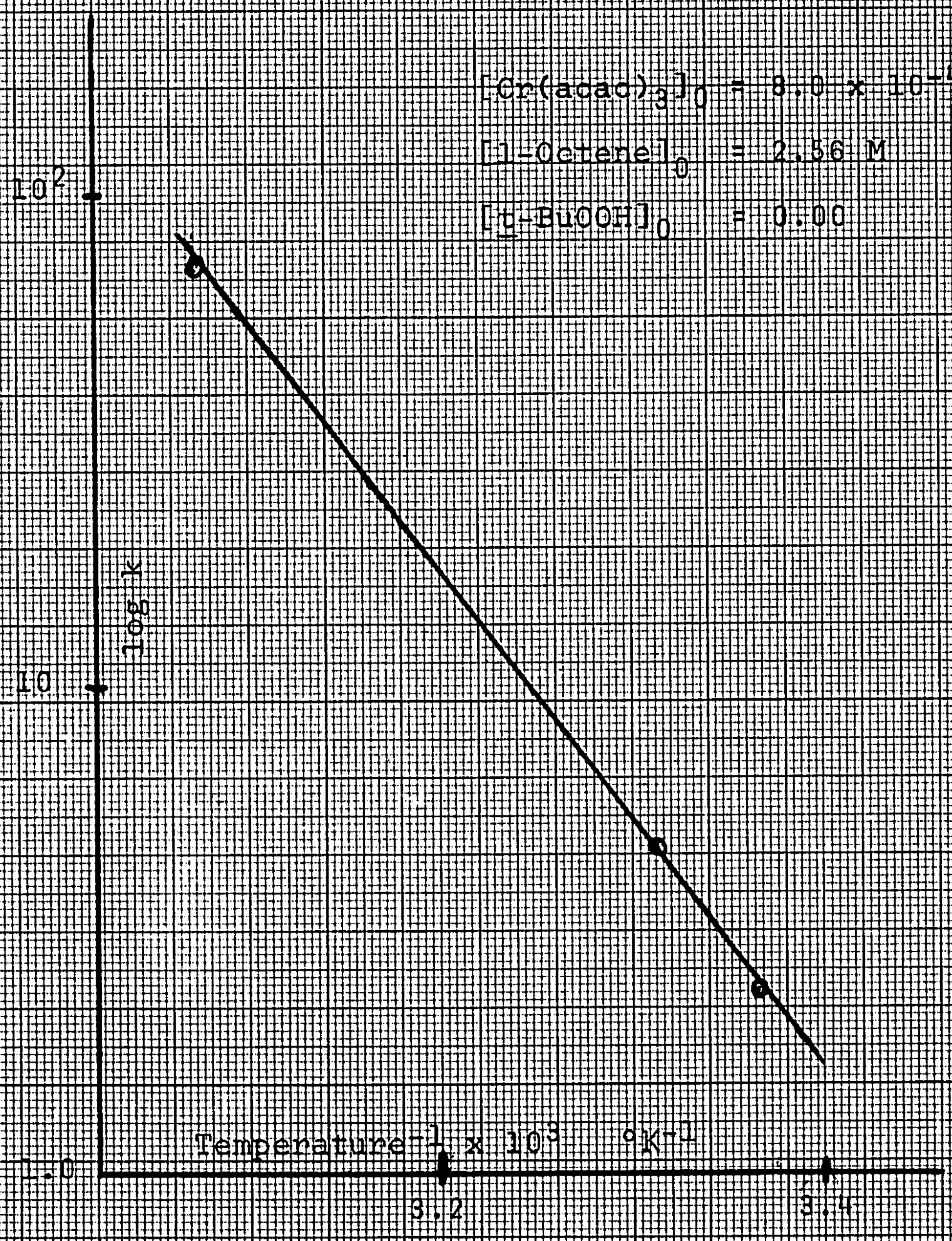
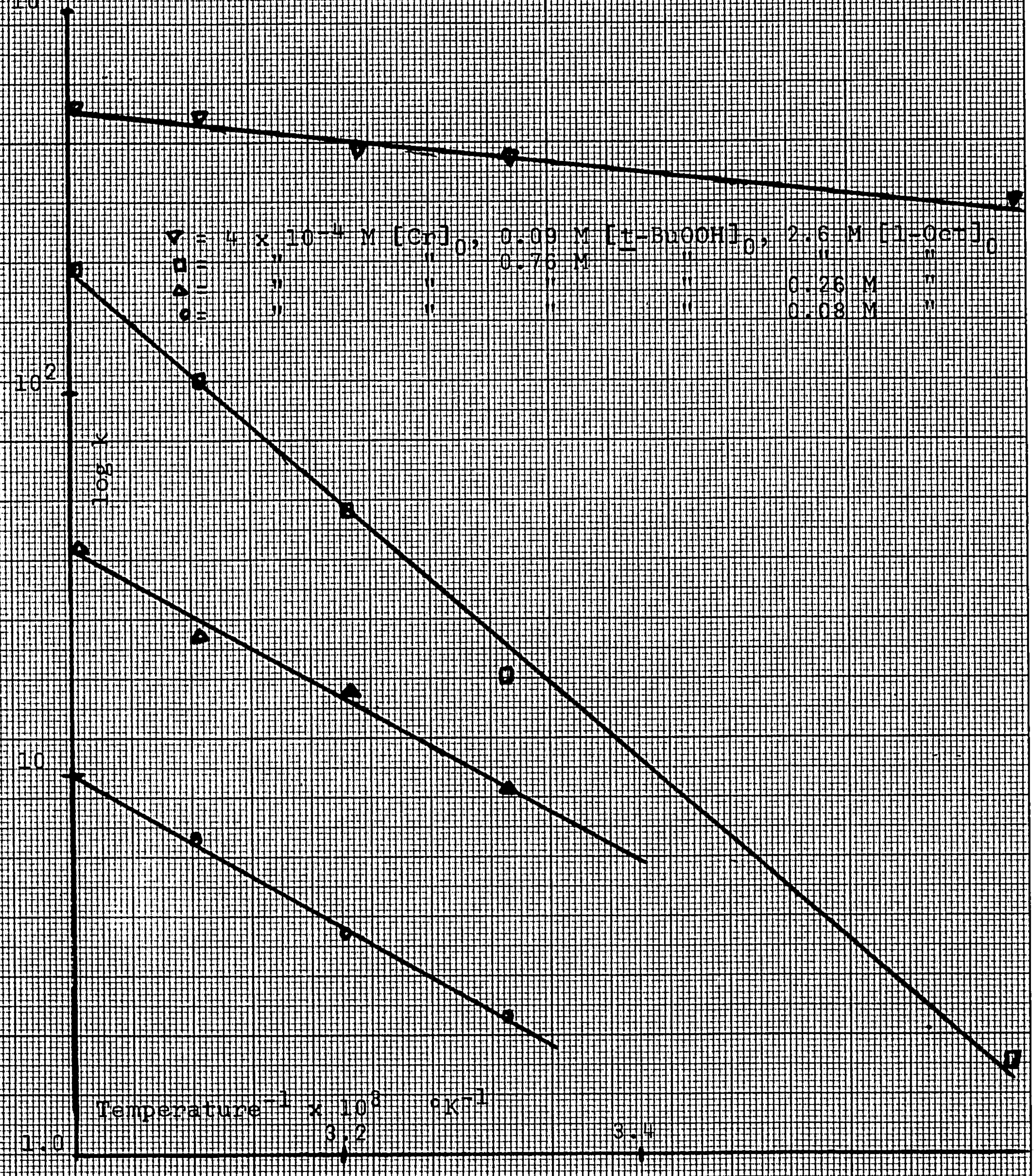
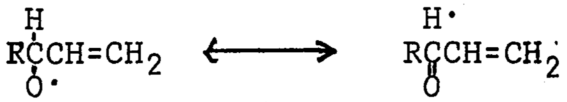


Figure 19: Arrhenius Plots for the Autoxidation of 1-Octene in the Presence of t-Butyl Hydroperoxide and Chromium (III) Acetylacetonate (Press$_{O_2}$ = 1 atm).



to any large extent with the abstraction reaction. Furthermore, one of the major products of the reaction is 1-octen-3-one which suggests the formation of the octenoxy radical:  $C_5H_{11}\underset{O\cdot}{\dot{C}}HCH{=}CH_2$. Ingold[22] has shown that secondary peroxy radicals are more selective and hence more stable than the t-butoxy radical. One reason for this difference in stability is the possibility of hyperconjugation in the secondary case where none is possible in the tertiary radical (see Figure 20). Therefore, in a system where Reaction 101 is more important in the initiating process relative to Reaction 61, a decrease in activation energy should be observed. Indeed, when the ratio of 1-octene to t-butyl hydroperoxide is increased from 3.4 to 27, thereby favoring Reaction 101 over Reaction 61, the overall activation energy is decreased by some 11 kcal/mole. If this were completely attributable to the initiation process, which is unlikely, it would mean that the activation energy for this process decreased 22 kcal/mole ($E_{overall} = 0.5\ E_i + E_p - 0.5\ E_t$).[121]

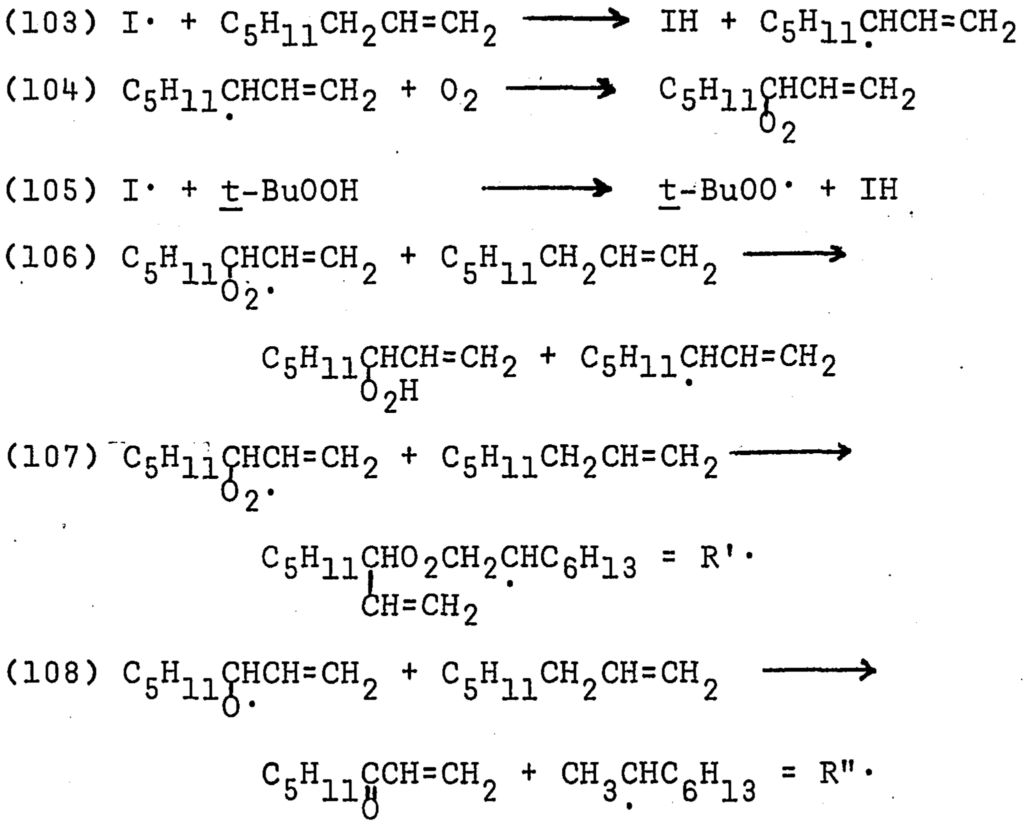
Figure 20: Hyperconjugation Structures for an Alkenoxy Radical



(I) (II)

The hyperconjugation structures shown in Figure 18 demand that there be some loss in entropy due to the restricted rotation required by conjugation.[116] Therefore a change in the initiation process from Reaction 61 to 101 should be accompanied by a shift to a more negative entropy. It is in fact observed that the entropy of activation in the presence of a 21/1 ratio of olefin to t-butyl hydroperoxide is some 41 cal/deg more negative than when the ratio is 3.4/1 (see Table IV). Another piece of evidence in support of Reaction 101 is the observation that the autoxidation is slightly dependent on the partial pressure of oxygen. This dependence is small, but indicates the intervention of oxygen in a step other than the propagation sequence. It has been noted previously (see p. 42 ), however, that oxygen may be involved in Reaction 64 as the species "Z".

The propagation steps in the autoxidation are given in Reactions 103-112. [I· = any radical formed in an initiation step (i.e., t-BuO·, RO·, Z'·)]



$$(103)\quad I\cdot + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow IH + C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2$$

$$(104)\quad C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + O_2 \longrightarrow C_5H_{11}\underset{\substack{|\\O_2}}{C}HCH{=}CH_2$$

$$(105)\quad I\cdot + \underline{t}\text{-}BuOOH \longrightarrow \underline{t}\text{-}BuOO\cdot + IH$$

$$(106)\quad C_5H_{11}\underset{\substack{|\\O_2\cdot}}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow$$

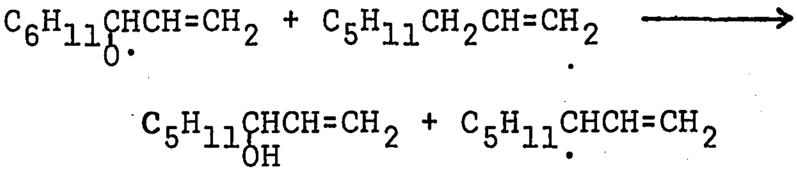
$$C_5H_{11}\underset{\substack{|\\O_2H}}{C}HCH{=}CH_2 + C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2$$

$$(107)\quad C_5H_{11}\underset{\substack{|\\O_2\cdot}}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow$$

$$C_5H_{11}\underset{\substack{|\\CH=CH_2}}{C}HO_2CH_2\underset{\cdot}{C}HC_6H_{13} = R'\cdot$$

$$(108)\quad C_5H_{11}\underset{\substack{|\\O\cdot}}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow$$

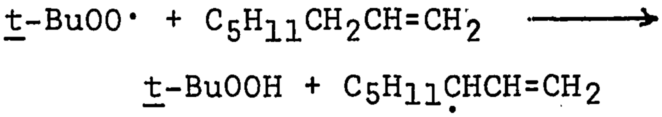
$$C_5H_{11}\underset{\substack{\|\\O}}{C}CH{=}CH_2 + CH_3\underset{\cdot}{C}HC_6H_{13} = R''\cdot$$

(109) 

$$C_6H_{11}\underset{O\cdot}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow C_5H_{11}\underset{OH}{C}HCH{=}CH_2 + C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2$$

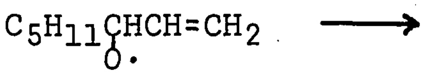
(110) $R'\cdot + O_2 \longrightarrow R'O_2\cdot$

(111) $R''\cdot + O_2 \longrightarrow R''O_2\cdot$

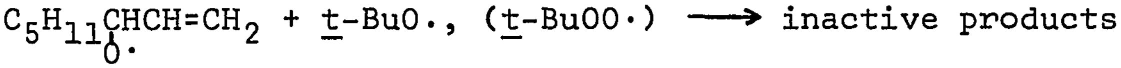
(112) 

$$\underline{t}\text{-BuOO}\cdot + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow \underline{t}\text{-BuOOH} + C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2$$

Under conditions where the olefin/t-butyl hydroperoxide ratio is high, Reaction 103 receives little competition from Reaction 105, considering that the O-H bond strength in t-butyl hydroperoxide is some 7 kcal/mole[4,125] greater than the allylic C-H bond in 1-octene. However, as the peroxide concentration increases, Reaction 105 takes on added importance and has a profound effect on both the rate of oxygen uptake and the kinetic rate law. The termination reactions are given below (113-115).

(113) 

$$2\ C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2 \longrightarrow \text{inactive products}$$

(114) 

$$C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2 + \underline{t}\text{-BuO}\cdot,\ (\underline{t}\text{-BuOO}\cdot) \longrightarrow \text{inactive products}$$

(115) $2\ \underline{t}\text{-BuO}\cdot,\ (\underline{t}\text{-BuOO}\cdot) \longrightarrow$ inactive products

It will be noted that the radical in Reactions 113 and 114 is designated as an alkoxy rather than a peroxy radical. It seems likely that in the presence of a good hydrogen donor such as 1-octene, the peroxy radicals would quickly abstract a hydrogen atom and form hydroperoxide. However, since little octenyl hydroperoxide is found under the conditions of these experiments it is probably rapidly decomposed to octenoxy radicals. If abstraction of hydrogen by the peroxy radical is rapid compared to termination (as is indicated by the long chain lengths) then even though propagation is via the peroxy radical, the chains are terminated via the alkoxy radical. The same arguments applied to octenyl hydroperoxide can, of course, be applied to t-butyl hydroperoxide. However, the t-butyl peroxy radicals must be in greater concentration than the octenyl-peroxy radical and therefore should be more important at least initially in both the propagation and termination processes. It is probable that Reaction 115 becomes important only in the presence of substantial amounts of t-butyl hydroperoxide. Indeed, increasing the concentration of t-butyl hydroperoxide has a dramatic effect on the rate expression, which is directly attributable to Reaction 115.

In the presence of small amounts of t-butyl hydroperoxide the primary propagation steps are Reactions 106-109. Applying the steady state approximation to the concentration of the various radicals, one obtains:

$$(116)\quad (k_{104}[C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2] + k_{110}[R'\cdot] + k_{111}[R''\cdot])[O_2]$$

$$= [C_5H_{11}CH_2CH{=}CH_2][(k_{106} + k_{107})[C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2]$$

$$+ (k_{108} + k_{109})[C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2]]$$

Therefore the rate of oxygen uptake is given by:

$$(117)\quad -d[O_2]/dt = [C_5H_{11}CH_2CH{=}CH_2][(k_{106} + k_{107})[C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2]$$

$$+ (k_{108} + k_{109})[C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2]]$$

In a chain process, where the chain lengths are long, the rate of initiation approximates the rate of termination. Designating the former as $R_i$, and assuming termination primarily via Reaction 113 (low t-butyl hydroperoxide concentrations) we may write:

$$(118) \quad k_{113}[C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2]^2 = R_i$$

Since it has been shown that the amount of hydroperoxide formed in the autoxidation is small compared to the amount of oxygen taken up, the rate of decomposition of the peroxide must be compatable to its rate of formation. As a first approximation, we may assume these two rates to be equal and we may then write:

$$(119) \quad k_{100}[Cr][C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2]$$
$$= k_{106}[C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2][C_5H_{11}CH_2CH{=}CH_2]$$

The left hand expression in Equation 119 is just the rate of formation of the octenoxy radical $[C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2]$.

Under steady state conditions this expression equals the rate of disappearance of the octenoxy radical and therefore:

$$(120) \quad k_{100}[Cr][C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2]$$
$$= (k_{108} + k_{109})[C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2][C_5H_{11}CH_2CH{=}CH_2]$$
$$+ k_{113}[C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2]^2$$

Under conditions where chains are long the termination steps (e.g., Reaction 113) are insignificant compared to the propagation steps (e.g., Reactions 108 and 109). Therefore

Equation 120 simplifies to:

(121) $$k_{100}[\mathrm{Cr}][\mathrm{C_5H_{11}}\underset{\mathrm{O_2H}}{\mathrm{C}}\mathrm{HCH{=}CH_2}]$$

$$= (k_{108} + k_{109})[\mathrm{C_5H_{11}}\underset{\mathrm{O\cdot}}{\mathrm{C}}\mathrm{HCH{=}CH_2}][\mathrm{C_5H_{11}CH_2CH{=}CH_2}]$$

or substituting into Equation 119:

(122) $$k_{106}[\mathrm{C_5H_{11}}\underset{\mathrm{O_2\cdot}}{\mathrm{C}}\mathrm{HCH{=}CH_2}][\mathrm{C_5H_{11}CH_2CH{=}CH_2}]$$

$$= (k_{108} + k_{109})[\mathrm{C_5H_{11}}\underset{\mathrm{O\cdot}}{\mathrm{C}}\mathrm{HCH{=}CH_2}][\mathrm{C_5H_{11}CH_2CH{=}CH_2}]$$

Substituting Equation 122 into Equation 117 one obtains:

(123) $$-d[\mathrm{O_2}]/dt$$

$$= [k_{107} + 2(k_{108} + k_{109})][\mathrm{C_5H_{11}}\underset{\mathrm{O\cdot}}{\mathrm{C}}\mathrm{HCH{=}CH_2}][\mathrm{C_5H_{11}CH_2CH{=}CH_2}]$$

or from Equation 118:

(124) $$-d[\mathrm{O_2}]/dt$$

$$= [k_{107} + 2(k_{108} + k_{109})]\ R_i^{0.5}\ [\mathrm{C_5H_{11}CH_2CH{=}CH_2}]/k_{113}^{0.5}$$

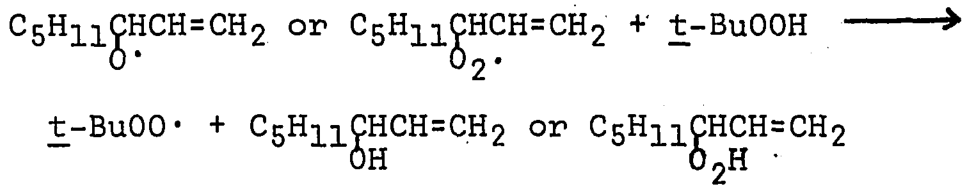
The initiation process is a multistep procedure consisting of Reactions 61, 64, and 101. From studies of chromium (III) acetylacetonate disappearance and the assumption that decomposition of octenyl hydroperoxide to produce radicals proceeds in the same fashion as the chromium (III) acetylacetonate-t-butyl hydroperoxide reaction the rate of initiation can be written:

(125) $$R_i = k_{61}[\mathrm{Cr}][\underline{t}\text{-}\mathrm{BuOOH}] + k_{64}[\mathrm{Cr}][\mathrm{C_5H_{11}CH_2CH{=}CH_2}][\mathrm{Z}]$$

$$+ k_{101}[\mathrm{Cr}][\mathrm{C_5H_{11}}\underset{\mathrm{O_2H}}{\mathrm{C}}\mathrm{HCH{=}CH_2}]$$

The rate law therefore becomes very comples, and it is observed that the kinetic "orders" of the various reactants are extremely dependent on experimental conditions. The next part of this section attempts to deal with these "orders" as a function of reactant concentration and reaction temperature.

As the $\underline{t}$-butyl hydroperoxide-1-octene ratio increases abstraction of the peroxide hydrogen becomes important:

(126) 

$$C_5H_{11}\underset{O\cdot}{C}HCH{=}CH_2 \text{ or } C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 + \underline{t}\text{-BuOOH} \longrightarrow$$

$$\underline{t}\text{-BuOO}\cdot + C_5H_{11}\underset{OH}{C}HCH{=}CH_2 \text{ or } C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2$$

The increased importance of Reaction 126, and hence increased importance of the $\underline{t}$-butyl peroxy radical in the termination process (e.g., Reactions 114 and 115) introduce a term into the rate law which is inversely proportional to the concentration of $\underline{t}$-butyl hydroperoxide. It is indeed observed that as the $\underline{t}$-butyl hydroperoxide/1-octene ratio increases from 0.71 to 35, the rate of oxygen uptake <u>decreases</u> by a factor of almost 2.5. Since no evolution was noted when chromium (III) acetylacetonate was mixed with $\underline{t}$-butyl hydroperoxide in the absence of 1-octene, this effect cannot be attributed to an increased production of oxygen via peroxide decomposition.[39a] When present in low concentrations, participation by $\underline{t}$-butyl hydroperoxide is probably confined to the initiation process. Under these conditions the rate of oxygen uptake is given by Equation 124, and the rate of initiation by Equation 125. If all three terms in the latter equation are of equal importance then the "order" in $\underline{t}$-butyl hydroperoxide should be about 1/3. The observed order under conditions of extremely low $\underline{t}$-butyl hydroperoxide concentrations ($10^{-3}$-$10^{-4}$ M) is about 0.45. It may therefore be comcluded that in the initiation process Reaction 61 is as important as the other steps combined. It has been noted that the overall activation energy of the autoxidation is markedly dependent on the concentration of peroxide. Since at high concentrations of t-butyl hydroperoxide the activation energy is almost independent of the t-butyl hydroperoxide/1-octene ratio, it is probable that the change in activation energy arises from a change in the relative important of $k_{61}$, $k_{64}$, and $k_{101}$ in the initiation process as one changes the absolute concentration of t-butyl hydroperoxide.

The greater bond strength of the O-H bond in t-butyl hydroperoxide as compared to the allylic C-H bond in 1-octene, should produce an increase in the ratio of t-butyl peroxy radicals to allylic radicals as the temperature increases. This increased importance of the former should manifest itself as a decrease in the importance of t-butyl hydroperoxide in the rate equation. This effect can only be observed, however, at low concentrations of t-butyl hydroperoxide. It is observed that in the presence of $<$ 0.1 M t-butyl hydroperoxide the kinetic "order" in peroxide is 0.49 at 30° and 0.16 at 40°.

Since the mechanism and the activation parameters are so strongly dependent on peroxide concentration, one can study the autoxidation under various t-butyl hydroperoxide concentrations and determine the "isokinetic" temperature[129] of different systems. For example, the reaction was run in the presence of 0.76 M *t*-butyl hydroperoxide and 0.093 M *t*-butyl hydroperoxide. The overall activation energy for the former is 12.1 ± 0.7 kcal/mole while that of the latter is 1.27 ± 0.1 kcal/mole (-1.0 to 59°). The isokinetic temperature of these two systems, i.e., the point at which their respective Arrhenius plots intersect, is determined to be -23° C. This means that the two reactions should have the same observed *rate constant* at this temperature. However, due to the fact that they do not obey the same rate law, the two reactions should proceed at different *rates* at -23°. They have the same rate at 30° C. This means that above 30° the rate of oxygen uptake increases with increasing *t*-butyl hydroperoxide concentration, while just the reverse is observed below 30° (see Table III).

The isokinetic point is that temperature at which changes in the enthalpy of activation in comparing one system to another are exactly offset by entropy changes and hence the free energy of activation is unchanged (i.e., $\delta \Delta F = 0$).[129] In the neighborhood of the isokinetic temperature, such things as substituent effects,[130] solvent effects,[131] etc. may have very little effect on a given set of reactions. The effect of *t*-butyl hydroperoxide, if considered a medium effect, should be small in the neighborhood of the isokinetic temperature.

The rate of autoxidation is first order in 1-octene up to concentrations of about 1 M, after which it appears to be less dependent on olefin. It is suggested that as the concentration increases, termination via octenyl radicals begins to compete with the octenyl-oxygen reaction. Since termination via two octenyl radicals should have a very low activation energy[124] and a more negative entropy of activation[116] than termination by peroxy radicals, the overall activation energy should increase and overall entropy of activation should become more positive as the concentration of 1-octene increases. These predictions are consistent with experimental observations (see Table IV).

A small rate of oxygen uptake by a solution of 1-octene and chromium (III) acetylacetonate is observed in the absence of t-butyl hydroperoxide. It is suggested that a metal-olefin complex is formed which is attacked by a third species (perhaps oxygen) to form a free radical (cf. Reaction 64). Attempts to discover if the reaction was dependent on oxygen were unsuccessful because of the low rate of reactions. However, by using relatively high 1-octene concentrations it was observed that the rate law, under the conditions studied, is:

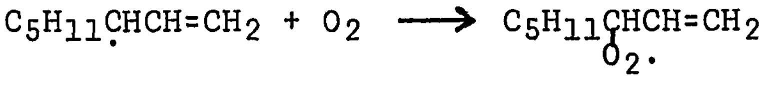
(127) $-d[O_2]/dt = k_{obs}[Cr]^{0.5}[C_5H_{11}CH_2CH{=}CH_2]^{1.5}$

This equation is consistent with the following mechanism:

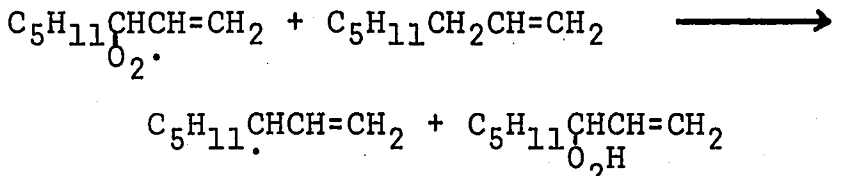
(128) $Cr(III) + C_5H_{11}CH_2CH{=}CH_2 \xrightarrow{Z} I\cdot$

where Z = any active species in the system (see p. 42 )

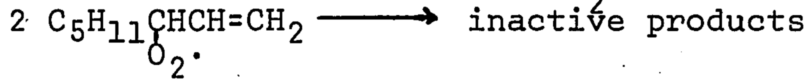
(129) $I\cdot + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + IH$

(130) 

$C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + O_2 \longrightarrow C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2$

(131) 

$$C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2$$

(132) 

$$2\ C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 \longrightarrow \text{inactive products}$$

The overall activation energy for the "non-t-butyl hydroperoxide" reaction is 18.2 kcal/mole or about 6 kcal/mole more than the reaction involving t-butyl hydroperoxide (see Table IV). Since the propagation and termination steps in both systems should be similar, the extra 6 kcal/mole can be attributed to the difference in the initiation process. Since a difference in the overall activation energy of 6 kcal/mole would mean a difference of about 12 kcal/mole in the activation energy of the initiation process ($E_{overall} = 0.5\ E_i + E_p - 0.5\ E_t$)[121] then Reaction 128 should play a relatively small role in initiating the autoxidation in the presence of t-butyl hydroperoxide.

E. Chain Lengths.--The number of substrate molecules that are consumed in a chain process per radical produced in the initiation process is called the chain length.[132] This quantity may be expressed as the ratio of the propagation rate to the initiation rate (or the termination rate).

If it is assumed that all the initiation processes in the systems studied here involve the disappearance of chromium (III) acetylacetonate then the rate of chromium (III) acetylacetonate disappearance is a measure of the initiation rate. This rate should be corrected for non-radical producing reactions involving chromium (III) acetylacetonate (e.g., Reaction 62). However, these probably do not become important until high metal concentrations or high temperatures are reached. For the autoxidation of 1-octene in the presence of chromium (III) acetylacetonate and t-butyl hydroperoxide, the rate of propagation is simply the rate of oxygen uptake and therefore the initial chain length for the autoxidation ($\nu_o$) is given by:

(133) $\nu_o = (-d[O_2]/dt)_0/(-d[Cr]/dt)_0$

The propagation rate for the chain decomposition of t-butyl hydroperoxide is given by the observed rate of peroxide disappearance. This rate should be corrected for the t-butyl hydroperoxide that disappears via a direct interaction with metal in the initiation process (Reaction 60). Again, however, under conditions where a chain process is occurring this correction is extremely small. Therefore the initial chain length for t-butyl hydroperoxide decomposition ($\nu_p$) is given by:

(134) $\nu_p = (-d[\underline{t}\text{-BuOOH}]/dt)_0/(-d[Cr]/dt)_0$

Values for $\nu_o$ and $\nu_p$ under various conditions are given in Table V. Although $\nu_o$ is fairly independent of concentration conditions $\nu_p$ rapidly approaches unity and the chain disappears. As mentioned above (see p. 64) the disappearance of the chain is accompanied by a marked change in the rate law for t-butyl hydroperoxide decomposition - from first order in peroxide to fourth order - as the metal-peroxide reaction becomes the primary mode of decomposition.

Mesrobian and Tobolsky[14] observed that in autoxidations which produced hydropeoxides, it was possible to attain conditions in which the rate of decomposition of the hydroperoxide became equal to its rate of production. These authors showed that as this steady state concentration of hydroperoxide is approached the chain length approaches unity.

In the chromium (III) acetaylacetonate-*t*-butyl hydroperoxide initiated autoxidation of 1-octene it is not possible to achieve such conditions due to the presence of *t*-butyl hydroperoxide. According to Mesrobian and Tobolsky's model, the hydroperoxide formed from the substrate is responsible for the initiation of the autoxidation. In the system under study here, the autoxidation is initiated primarily via the chromium (III) acetylacetonate-*t-butyl hydroperoxide* reaction. Thus even under conditions where metal-*octenyl* *hydroperoxide* initiation is appreciable (i.e., low *t*-butyl hydroperoxide concentrations) the only observed effect is a slight *increase* in chain length. This increase is possibly due to a relative increase in the propagation rate since fewer radicals are intercepted by *t*-butyl hydroperoxide molecules.

It would have been of interest to study the non-peroxide induced autoxidation in terms of Mesrobian and Tobolsky's model, but it was difficult to obtain a reliable initiation rate under these conditions, because the rate of chromium (III) acetylacetonate disappearance under these conditions is too slow.

In general both $\nu_o$ and $\nu_p$ are found to decrease with increasing temperature. This reflects the larger activation energies required for the initiation steps relative to those required for the propagation steps.

## ii. Solvent Effect

### Results

Table VI presents data on the disappearance rates of t-butyl hydroperoxide and chromium (III) acetylacetonate and the rate of autoxidation of 1-octene in various solvents. It is found that there is very little variation with solvent in the rates of the disappearance of chromium (III) acetylacetonate and t-butyl hydroperoxide under equivalent concentration conditions. The oxidation rate shows a larger dependence on the solvent. The fastest rates are observed in normal or chlorinated aliphatic hydrocarbons. Cumeme and tetralin also show appreciable autoxidation rates, however neither is as fast as would be expected on the basis of previously observed oxidation rates for these two compounds.[22] N,N-dimethylformamide and glacial acetic acid give very rapid rates but both of these compounds undergo rapid autoxidation themselves under these conditions. Hence the significance of the solvent effect in these experiments cannot be estimated, but the generality of the initiator system is indicated.

Aromatic solvents and solvents containing oxygen atoms invariably reduce the autoxidation rate (see Table VI). In a series of runs varying the ratio of benzene to 1-chlorooctane it was found that as the benzene concentration

Table VI: Solvent Effects on the Rate of Autoxidation of 1-Octene and the Rate of t-Butyl Hydroperoxide and Chromium (III) Acetylacetonate Disappearance[a] (30°)

| Solvent | Solvent Conc.[b] M | $(-\Delta O_2/\Delta t)_0$ x $10^6$ M/sec | $(-\Delta[t\text{-BuOOH}]/\Delta t)_0$ x $10^4$ M/sec | $(-\Delta[Cr]/\Delta t)_0$ x $10^9$ M/sec |
|---|---|---|---|---|
| 1-Octene | 5.97 | 3.12 | n[e] | n |
| 1-Chloro-octane[c] | 6.75 | 0.0 | 1.77 | n |
| " | 3.06 | 2.25 | 0.76 | 6.46 |
| n-Heptane | 2.73 | 2.40 | 1.01 | 8.24 |
| sym-Tetrachloro-ethane | 3.81 | 2.08 | 0.68 | n |
| $CCl_4$ | 4.15 | 3.08 | 0.51 | n |
| Benzene[d] | 6.31 | 0.0 | n | n |
| " | 4.51 | n | 0.91 | 7.22 |
| " | 0.68 | 1.38 | n | n |
| " | 1.36 | 0.95 | n | n |
| Naphthalene | 0.57 | 0.71 | n | n |
| " | 0.37 | n | 0.30 | n |
| Phenyl Ether | 3.28 | 0.82 | n | n |
| " | 2.52 | n | 0.31 | n |
| Chloro-benzene | 3.90 | 0.36 | 0.88 | n |
| Cumene | 2.88 | n | 0.32 | 7.61 |
| " | 1.44 | 2.56 | n | n |
| Tetralin | 2.94 | n | 0.41 | n |
| " | 1.47 | 1.42 | n | n |
| Pyridine | 4.98 | 0.50 | 1.15 | 5.92 |
| t-Butanol | 5.56 | 0.23 | n | n |
| " | 4.28 | 0.19 | 0.83 | 10.4 |
| Ethanol | 6.84 | 0.24 | n | n |
| Methanol | 9.96 | 0.0 | 0.56 | 8.85, 9.92[f] |
| Acetic Acid | 5.25 | 3.30 | n | n |
| " | 7.00 | n | 0.27 | 9.00 |
| " | 9.10 | 7.09 | n | n |
| Ethyl Acetate | 3.07 | 0.71 | n | n |
| " | 4.08 | n | 0.35 | n |
| N,N-dimethyl-formamide | 4.96 | n | 0.66 | 8.00 |
|  | 3.71 | 2.11 | n | n |
| p-Dioxane | 4.71 | 0.27 | 0.59 | n |

---

[a] in vacuo [b] All runs cited contain 4.00 x $10^{-4}$ M $Cr(acac)_3$; 0.76 M t-BuOOH (except where noted); 2.56 M 1-Octene (except in first two cases).

[c] no 1-octene present [d] t-BuOOH concentration 0.37 M

[e] n = no data [f] oxygen not excluded from this run

increased the oxidation rate decreased, until at a concentration of 6.31 M (56%) benzene, there was no perceptible oxygen pick-up for 72 hours.

In a series of alcohols it was found that t-butanol and ethanol retarded the autoxidation to the same extent (ca. 90%), while in methanol, a gas was evolved for about one hour after the reaction had started. It was shown that this gas is formaldehyde.

Induction periods were observed in diphenyl ether, ethanol, ethyl acetate, and p-dioxane. In the first case this may have been due in part to a phenolic impurity as it was observed that the induction period was reduced to 40 minutes from 150 minutes after washing the ether with alkali followed by distillation and drying.

The induction periods observed for ethanol, ethyl acetate, and p-dioxane may be due to the formation of volatile products (as in the case of methanol) which lower the apparent rate of oxidation (in the case of methanol there is more solvent per mole of 1-octene than in the other systems). The production of low molecular weight compounds indicates that the solvent is being oxidized in preference to the olefin.

## Discussion

A. Oxygen-bearing Solvents.--The results of Table VI indicate that the rates of chromium (III) acetylacetonate disappearance and t-butyl hydroperoxide decomposition are essentially solvent independent while the rate of autoxidation shows a strong solvent dependence.

Although the rate of chromium (III) acetylacetonate disappearance varies by less than a factor of two over the whole range of solvents studied, it appears to be slightly greater in t-butanol, methanol, and acetic acid than in other solvents. This apparent increase in rate may be due to the complexing ability of these solvents,[47a] and the resulting ligand exchange (see Equation 135) which facilitates the change in oxidation state of the chromium, thus removing the observed species (chromium (III) acetylacetonate)[114] from the system.

(135) $Cr(acac)_3 + nL \longrightarrow Cr(acac)_{3-n}L_n + n(acac)$

where L = any ligand. The same effect is observed in the presence of some phenols and other compounds used to inhibit the free radical reactions (see p.112 ). Aromatic solvents, although known to complex with chromium (III) acetylacetonate[133] apparently have no effect on the disappearance rate.

t-Butyl hydroperoxide is known to undergo a chain decomposition in the presence of free radicals.[134] It may be shown that in the presence of chromium (III) acetylacetonate the decomposition of the peroxide preceeds via such a process with chain lengths of $10^3$-$10^4$. The following reaction scheme is consistent with the observed data (see Kinetics Section, p. 42 ) ($I\cdot$ = any initiating radical).

Initiation

(136) $Cr(acac)_3 + \underline{t}\text{-}BuOOH \longrightarrow I\cdot$

(137) $I\cdot + \underline{t}\text{-}BuOOH \longrightarrow \underline{t}\text{-}BuOO\cdot + IH$

(138) $I\cdot + \underline{t}\text{-BuOOH} \longrightarrow \underline{t}\text{-BuO}\cdot + \text{IOH}$

Propagation

(139) $2\ \underline{t}\text{-BuOO}\cdot \longrightarrow 2\ \underline{t}\text{-BuO}\cdot + O_2$

(140) $\underline{t}\text{-BuO}\cdot + \underline{t}\text{-BuOOH} \longrightarrow \underline{t}\text{-BuOO}\cdot + \underline{t}\text{-BuOH}$

Termination

(141) $2\ \underline{t}\text{-BuO}\cdot \longrightarrow$ inactive products

(142) $\underline{t}\text{-BuO}\cdot + \underline{t}\text{-BuOO}\cdot \longrightarrow$ inactive products

(143) $2\ \underline{t}\text{-BuOO}\cdot \longrightarrow$ inactive products

In the presence of olefins, an additional reaction can compete with attack on the peroxide:

(144) $R\cdot + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2 + RH$

where R· is any radical in the system. Evidence for Reaction 144 comes from the fact that at 30° in 1-chlorooctane the rate of decomposition is more than twice as fast in the absence of 1-octene as in its presence. Furthermore, it is observed that as the temperature increases the importance of Reaction 144 is diminished. Based on bond dissociation energies ($D_{ROO-H}$ = 84 kcal, $D_{allyl-H}$ = 77 kcal)[4,125] the attack on an allylic hydrogen should require a lower activation energy than attack on the peroxide hydrogen. Therefore as the temperature increases, the relative importance of attack on the olefin compared to attack on the hydroperoxide diminished (see Table III). A possible alternate explanation for this temperature effect is the intervention of Reaction 145 at higher temperatures. A similar reaction has been suggested for the styrene induced decomposition of t-butyl hydroperoxide at 70°.[126]

(145) $\underline{t}\text{-BuOOH} + \text{RCH=CH}_2 \longrightarrow \underline{t}\text{-BuOO}\cdot + \text{R}\dot{\text{C}}\text{HCH}_3$

However, considering the energetics involved and the effect of the olefin structure, it seems unlikely that Reaction 145 plays a significant role in the present system.

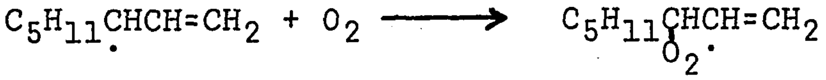
Any active hydrogen atom donor can participate in a reaction analogous to Reaction 144. Thus in the presence of cumene or tetralin, two demonstrated sources of hydrogen atoms, the rate of t-butyl hydroperoxide decomposition is reduced by a factor of two to three compared to solvents with no abstractable hydrogen (e.g., 1-chlorooctane or benzene). Alcohols or other compounds having hydrogen atoms alpha to an oxygen atom also react readily with free radicals (see Reaction 146).[135]

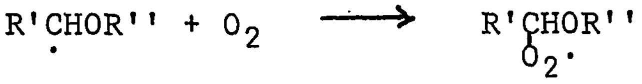
(146) $\text{R}\cdot + \text{R'CH}_2\text{OR''} \longrightarrow \text{R'}\dot{\text{C}}\text{HOR''} + \text{RH}$

For example, it has been shown that t-butoxy radicals attack the hydrogen atoms alpha to the oxygen atom in diethyl ether some six times faster than the carbon-hydrogen bonds in cyclohexane.[136] It is also observed in this work that at 30° there is a small but definite retardation of the t-butyl hydroperoxide decomposition rate in methanol, ethyl acetate, acetic acid, and p-dioxane. A rate reduction of the same magnitude in carbon tetrachloride, a well-known chain transfer agent,[137] and, as mentioned above, in tetralin and cumene, is also observed. Furthermore, it is noted that this effect is absent in t-butanol, consistent with the absence of a hydrogen atom alpha to the hydroxyl group.[135] From consideration of bond dissociation energies,[4,125] Reactions 144 and

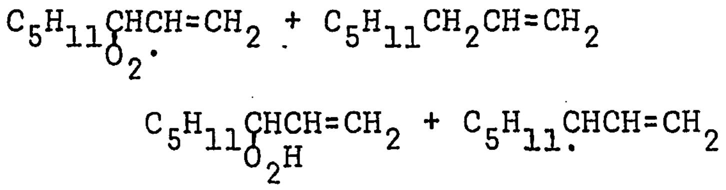
146 should have a lower activation energy than reactions involving attack on the peroxide oxygen. Therefore, as the temperature is increased, these latter reactions begin to compete favorably with reactions such as 144 and 146. Indeed, the presence of substances which retard the reaction at low temperatures due to their ease of forming radicals, can actually promote the reaction via induced decomposition[134] at higher temperatures. Thus, Stannett and Mesrobian[138] have shown that the decomposition of t-butyl hydroperoxide at 73.5° proceeds at a faster rate in certain alcohols, dioxane, and di-n-butyl ether than in benzene or cyclohexane. As mentioned above, in the present work it is observed that at 30° the rate of t-butyl hydroperoxide decomposition is more than twice as fast in the absence of 1-octene than in its presence, while at 50° the presence of olefin causes a 20% increase in the rate.

In the presence of oxygen, the radicals formed in Reactions 144 and 146 will be scavenged rapidly to form peroxy radicals:[68]

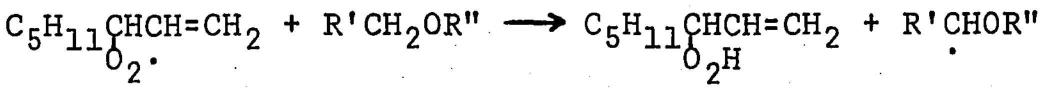
(147) 
$C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + O_2 \longrightarrow C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2$

(148) 
$R'\underset{\cdot}{C}HOR'' + O_2 \longrightarrow R'\underset{O_2\cdot}{C}HOR''$

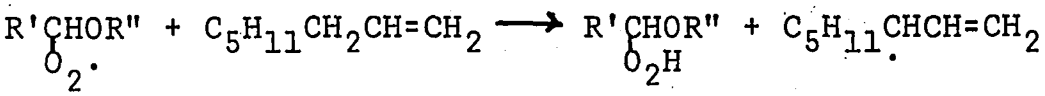
These peroxy radicals are the primary chain-carrying species in the autoxidation via Reactions 149-152.

(149) 
$C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2$

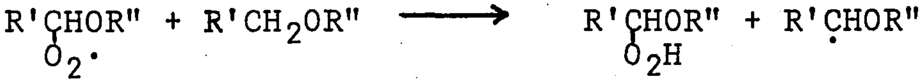
$C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2 + C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2$

(150) 

$$C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 + R'CH_2OR'' \longrightarrow C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2 + R'\underset{\cdot}{C}HOR''$$

(151) 

$$R'\underset{O_2\cdot}{C}HOR'' + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow R'\underset{O_2H}{C}HOR'' + C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2$$

(152) 

$$R'\underset{O_2\cdot}{C}HOR'' + R'CH_2OR'' \longrightarrow R'\underset{O_2H}{C}HOR'' + R'\underset{\cdot}{C}HOR''$$

There should be little difference in the rates of Reactions 147 and 148, or in those in the sequence 149-152 (which are the rate-determining steps of the propagation sequence) so that the presence of oxygen-bearing solvents should have little effect on the propagation steps of the autoxidation. It has been shown, furthermore, that there is little effect of solvent on the rate of chromium (III) acetylacetonate disappearance or the rate of _t_-butyl hydroperoxide decomposition . Since the latter reaction is essentially initiated by the same reaction that initiates the autoxidation, i.e., Reaction 60, and since the rate of reaction is primarily the rate of chromium (III) acetylacetonate disappearance, it is clear that solvents which retard the autoxidation cannot do so via the initiation step.

Since primary and secondary peroxy radicals terminate mainly via transfer of an alpha hydrogen atom,[22] i.e., disproportionation (Reaction 153), the rate of termination depends to a large extent on strength of the bondbetween this hydrogen atom and the carbon atom to which it is attached.

(153) $2\ R_2CHO_2\cdot \longrightarrow R_2C{=}O + R_2CHOH + O_2$

It is clear that this bond will be weaker when it is alpha to an oxygen atom[139] and therefore radicals of the type

$R'\underset{O_2\cdot}{C}HOR''$ will terminate faster than $R_2CHO_2\cdot$ radicals (e.g., $C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2$). Indeed, it has been observed that the peroxy radicals derived from decanal terminate at least 700 times faster than octenyl peroxy radicals.[68] It should be noted that in this system one also has t-butyl peroxy and t-butoxy radicals. However, tertiary radicals are known to terminate at a much slower rate than primary or secondary radicals.[22] It is suggested than lower overall autoxidation rates are the result of increased termination rates by radicals derived from oxygen-bearing solvents.

In the absence of oxygen, the chain-carrying radicals are in general substituted alkyl radicals (The concentration of alkoxy radicals must be neglgible in the presence of 1-octene or active hydrogen-donor solvents). Alkyl radicals generally terminate more by combination (see Reaction 154) than by disproportionation,[140] especially at low temperatures.

(154) $2\ R\cdot \longrightarrow R{-}R$

Although this is not as certain for allylic radicals as for saturated radicals, it is probably safe to assume a good deal of combination in the termination process. Since the combining of radicals usually requires a very small activation energy,[124] the structure of the terminating radical has little effect on the overall rate except in very special cases. It will be observed from the following analysis that hydrogen transfer cannot play a significant role in alkyl radical termination in the absence of oxygen. The two competing termination steps (via disproportionation) in the absence of oxygen are given by Reactions 155 and 156:

(155) $2\ C_5H_{11}\underset{\bullet}{C}HCH{=}CH_2 \longrightarrow C_4H_9CH{=}CH{-}CH{=}CH_2 + C_6H_{13}CH{=}CH_2$

(156) $2\ R'CH_2\underset{\bullet}{C}HOR'' \longrightarrow R'CH{=}CHOR'' + R'CH_2CH_2OR''$

It may be calculated[13] that Reaction 156 is some 28 kcal/mole more exothermic than Reaction 155. Therefore, if Reactions 155 and 156 played a significant role in this system, one would expect that oxygenated solvents would retard the rate of <u>t</u>-butyl hydroperoxide decomposition (in the presence of 1-octene), to the same extent that they retard the autoxidation. Since this does not occur, it is concluded that the termination step does not involve a significant amount of disproportionation.

B. <u>Aromatic</u> <u>Solvents</u>.--While the effect of aromatic solvents on the rate of <u>t</u>-butyl hydroperoxide decomposition or chromium (III) acetylacetonate disappearance is nil, there is a marked effect on the autoxidation (see Table VI). In the presence of 6 M benzene, no oxygen pick-up is observed for 72 hours. At lower concentrations of benzene, there is a complex inverse relationship between the rate of oxidation ands the concentration of benzene. Even with compounds which are easily autoxidized, such as tetralin and cumene, the retardation effect of the aromatic nucleus is obvious (see Table VII). Under ordinary conditions, tetralin would be expected to undergo autoxidation at a rate which is some 40 times faster than 1-octene, while cumene would be expected to be 25 times faster at 30°.[22] Using the chromium (III)

Table VII: The Autoxidation of Solvents with Chromium (III) Acetylacetonate[a] and t-Butyl Hydroperoxide[b] at 30° in 1-Chlorooctane

| Compound | Concentration of Compound [M] | $-[dO_2/dt] \times 10^6$ M/sec |
|---|---|---|
| 1-Octene | 1.27 | 2.09 |
| Cumene | 1.44 | 1.88 |
| Tetralin | 1.47 | 2.03 |
| Acetic Acid | 12.20 | 2.08 |
| N,N-dimethyl Formamide | 8.68 | 1.27 |

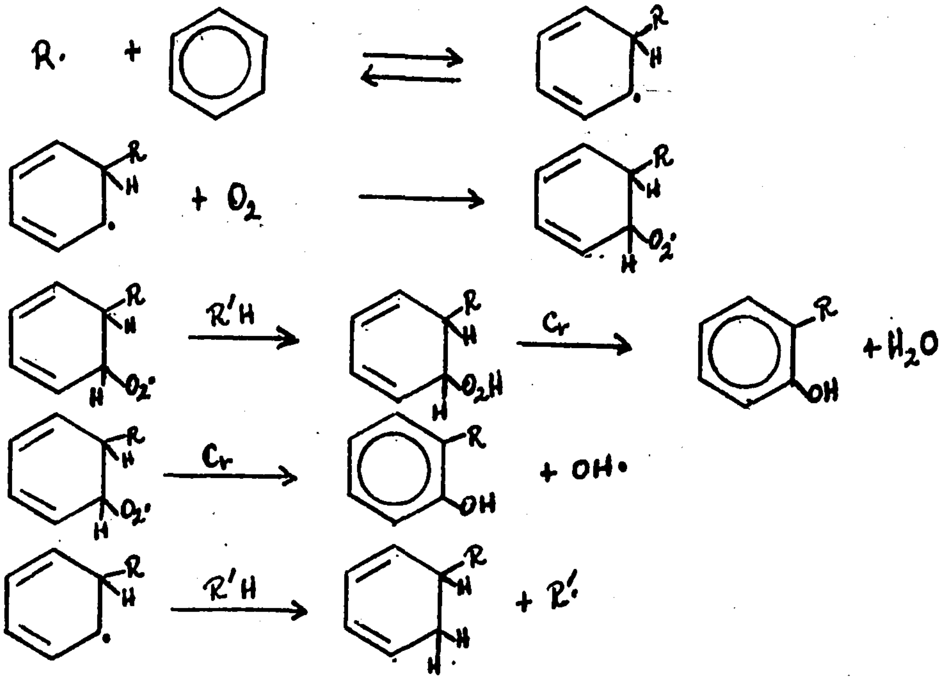
[a] $4.00 \times 10^{-4}$ M

[b] 0.74 M

acetylacetonate-t-butyl hydroperoxide system as an initiator, tetralin is autoxidized at about the same rate as 1-octene, while cumene is slightly slower (see Table VII).

Since aromatic solvents have no effect on either the disappearance rate of chromium (III) acetylacetonate or the decomposition rate of t-butyl hydroperoxide, it is clear that retardation of the autoxidation is not through interference with the initiation step. Furthermore, the complete lack of effect upon the radical reactions in the absence of oxygen suggests that perhaps the presence of oxygen is essential to the retarding effect of the aromatic solvents. Since the presence of an aromatic nucleus does not apparently affect the oxidation of aromatic compounds initiated by other systems,[22] even those systems employing peroxides,[141] it may be assumed that chromium (III) acetylacetonate is also essential to the observed effect. Ingold has observed[3] that some autoxidations are retarded when run in aromatic solvents and suggests that this is due to oxidation of the solvent to a phenol.

The complexing of radicals[122] and even oxygen itself[142] with aromatic systems is well known. It is suggested that this complexing reaction competes favorably with attack on the substrate (e.g., olefin or hydroperoxide). In the presence of oxygen this complex is quickly oxidized to a peroxy radical and thence to a substituted phenol.[143] In the absence of oxygen the complex may either dissociate or react with the substrate; but no retarding species (i.e., a phenol) is formed. The sequence may be described by Reactions 157-161.[144,145]



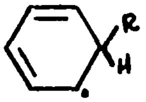
(157)

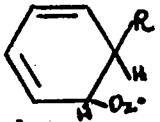
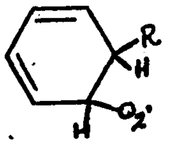
(158)

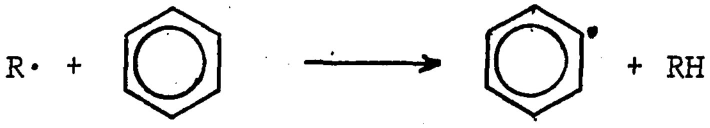
(159)

(160)

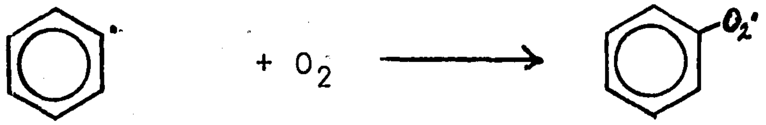
(161)

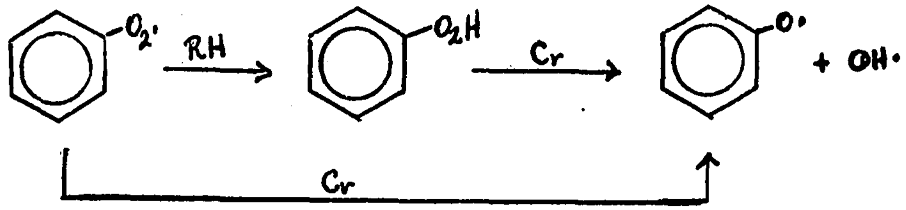
Since Reaction 158 must be much faster than any of the other reactions involving the radical formed in Reaction 157 (  ),[68] it is clear that oxygen is necessary to produce the retarding effect of the aromatic compounds.

However, if the peroxy radical (  ) or the corresponding hydroperoxide does not decompose to a phenol or does so only slowly, the retarding effect will be greatly diminished. Indeed, one explanation for the lack of such an effect in most other aromatic systems is that at the higher temperatures generally employed in autoxidations, either the complex formed in Reaction 157 dissociates rapidly or attacks a substrate molecule (161). It is clear that this reaction (161) would compete favorably with Reaction 158 only as the temperature increased, assuming a difference in activation energy. Furthermore, the peroxy radical (  ) or its corresponding hydroperoxide could yield non-aromatic products which would not necessarily be effective radical chain inhibitors. A reaction of this type might require more energy than the formation of an aromatic compound and thus would be favored only at elevated temperatures. In low temperature autoxidations, initiated by other systems, the decomposition of peroxy radical or hydroperoxide might be very slow. However, in the presence of chromium (III) acetylacetonate, which has been shown in this system to decompose t-butyl hydroperoxide, it would be expected that the decomposition of the hydroperoxide indicated in Reaction 159 would be greatly facilitated. The chromium (III) acetylacetonate also may act on the system in another way. It is known[133] that the chelate complexes readily with aromatic solvents. This complexing might facilitate radical attack on the aromatic nucleus (Reaction 157). The radical ($R\cdot$) depicted in Reaction 157 is either a peroxy radical or an alkoxy radical; in either case, the radical has electrophilic properties. Complexing may therefore accomplish any or all of the following. If the electron density on the aromatic system is increased, attack by electrophilic species would be enhanced. Furthermore, the radical complex formed could be stabilized by delocalization into the 3d orbital of chromium, this orbital being energetically between the lowest empty molecular orbital and the highest occupied molecular orbital of the aromatics.[133] Alternatively, complexing may enhance abstraction of an aromatic hydrogen (Reaction 162), normally an extremely endothermic process.

(162) 

Again, in the presence of oxygen the phenyl radical is readily transformed to a phenylperoxy radical and thence, perhaps through the intervention of chromium (III) acetylacetonate, to a phenol (Reactions 163-164).

(163) 

(164) 

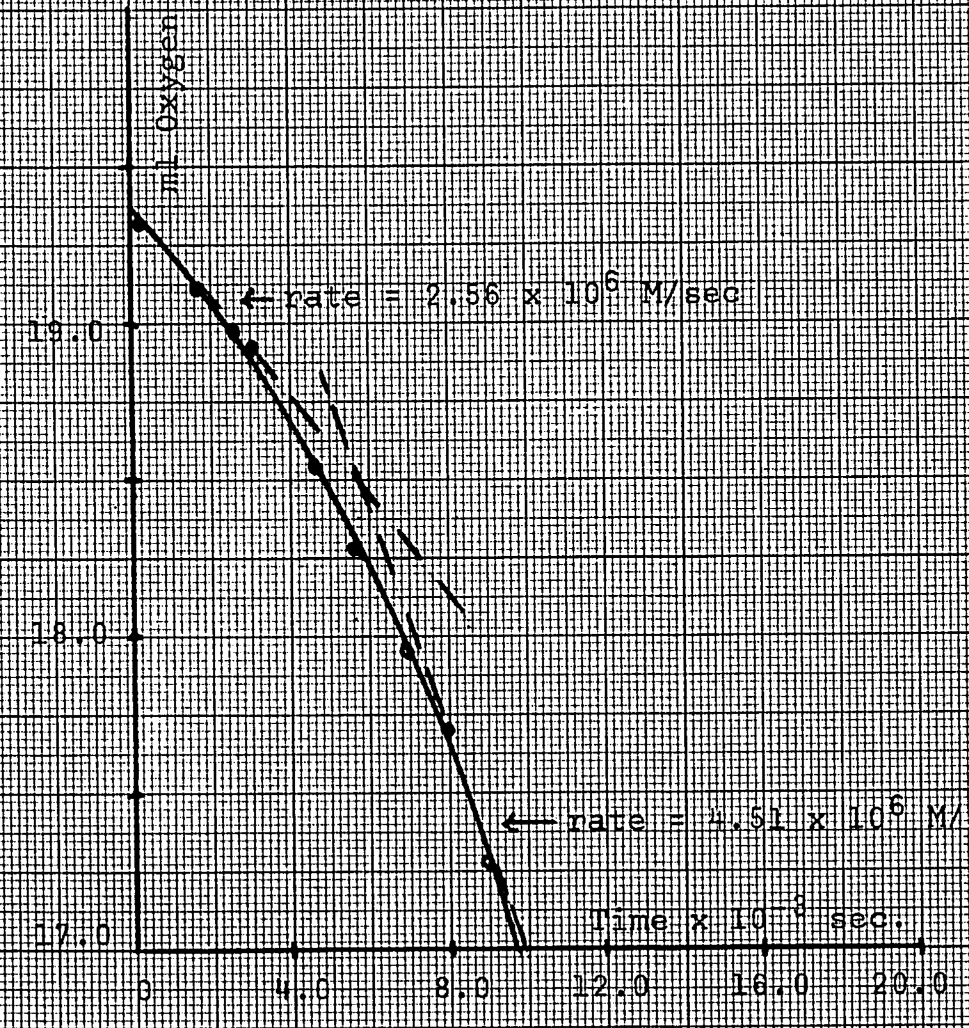
It has been demonstrated that in the presence of oxygen and chromium (III) acetylacetonate, aromatic compounds become effective retarders of free radical reactions probably through production of phenols. This reaction system might prove useful as an oxidation inhibitor or retarder or even for the synthesis of phenols. In any case it is a system worth further investigation.[146]

Retardation in some systems has been attributed to increased viscosity of the medium.[27] Other workers[21] have failed to find a marked effect of viscosity. Two systems which clearly were more viscous than most (diphenyl ether and 0.4 M naphthalene) also showed retardation of the autoxidation. The explanations favored here for this retardation are those discussed above indicating phenol formation.

C. Mixed Autoxidations.--Before leaving this subject it would be interesting to consider the effect of tetralin and cumene on the autoxidation of 1-octene. Although the unexpected slowness of the autoxidation of either tetralin or cumene alone may be explained by the considerations given above (i.e., the fornation of phenolic compounds) there is an alternate explanation for the behavior of the mixed autoxidations of either tetralin or cumene with octene. It will be noted that the autoxidation of a tetralin-1-octene mixture proceeds at a slower rate than that of either compound alone (see Tables VI and VII). This phenomenon cannot be attributed to the same factors which cause the retardation of cumene autoxidation by tetralin,[147] i.e., via chain transfer to tetralin. Tetralyl-peroxy radicals terminate some 35 times slower than octenyl peroxy radicals at 30°[22] and this decrease in the termination rate would tend to increase the rate of oxidation. However, the present situation is not entirely analogous to the cumene-tetralin system. The ratio of tetralin to cumene was much smaller[147] than the tetralin-1-octene ratio employed here. Secondly, tetralyl-peroxy radicals terminate more than 500 times faster than cumyl-peroxy radicals and propagate 40 times faster, whereas they propagate only 6.5 times faster than octenyl-peroxy radicals.[22] Therefore, it is suggested that much of the effect observed in the tetralin-1-octene autoxidation is due to the retardation effect of aromatic compounds observed in this system. On the other hand, chain transfer seems to play a slightly more important role in the mixed autoxidation of cumene and 1-octene. It was observed that cumene caused a slight accelerating effect on the rate of oxygen uptake relative to 1-octene alone (see Table VI). Furthermore, it was observed that the reaction was autocatalytic, the rate almost doubling as the reaction proceeded (see Figure 21). Chain transfer to the cumene results in the formation of cumyl-peroxy radicals which terminate 20,000 times slower and propagate five times slower than octenyl peroxy radicals at 30°[22] and are therefore responsible for the observed rate enhancement. This rate enhancement is slight, probably because of the retarding effect of the aromatic nucleus. It is interesting to note that cumene does not, according to this assumption, complex as well with chromium (III) acetylacetonate as do some other aromatic compounds, perhaps for steric reasons.[133] If aromatic-chromium (III) acetylacetonate complexing plays an important role in the retarding effect of the aromatic compounds, this effect would be expected to be less with cumene.

It is suggested that chain transfer to the cumene is from the octenyl or the octenyl-peroxy radical and not directly from the initiating radical, since no autocatalysis is observed in the absence of the olefin. The autocatalysis may be due to the slow build up of a more reactive hydro-

Figure 21: Rate of Oxygen Uptake by Cumene and 1-Octene in the Presence of t-Butyl Hydroperoxide and Chromium (III) Acetylacetonate (30°)

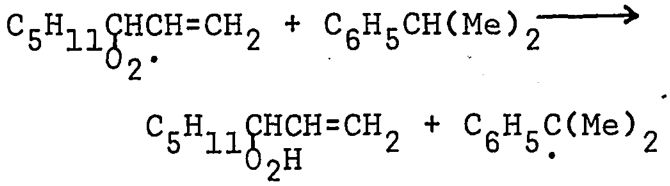


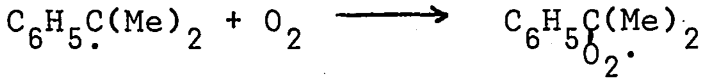
peroxide ($C_6H_5\underset{O_2H}{C}(Me)_2$). The initiating radicals which are probably for the most part t-butoxy radicals attack the less hindered allylic hydrogen of 1-octene in preference to the tertiary hydrogen of cumene,[148] forming the less hindered octenyl (or octenyl peroxy) radical. Since steric effects are not as important with this latter radical as with the t-butoxy radical, it attacks the cumene rather than another olefin molecule, this being the more energetically favored reaction (see Reactions 165-168).

(165) $t\text{-BuO}\cdot + C_6H_{13}CH{=}CH_2 \longrightarrow C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + t\text{-BuOH}$

(166)

$$C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + O_2 \longrightarrow C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2$$

(167)

$$C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 + C_6H_5CH(Me)_2 \longrightarrow C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2 + C_6H_5\underset{\cdot}{C}(Me)_2$$

(168)

$$C_6H_5\underset{\cdot}{C}(Me)_2 + O_2 \longrightarrow C_6H_5\underset{O_2\cdot}{C}(Me)_2$$

The suggestion that aromatics and other solvents reduce the apparent oxygen uptake by enhancing the decomposition of peroxide and thus the production of oxygen obviously has no basis in fact in this system. The effect of solvent on the decomposition rate is only slight. It has been shown that the evolution of oxygen from mixtures of chromium (III) acetylacetonate and t-butyl hydroperoxide are negligible at 30° ( $<$ 5%) (see Experimental Section, p. 137 ). In the case of methanol, a good deal of evolution was noted but it has been shown that this is due to the oxidation of methanol to formaldehyde.[149] When the evolved gas was trapped in a solution of 2,4-dinitrophenylhydrazine a yellow precipitate was obtained. The substance was recrystallized from chloroform. Upon mixing with a sample of formaldehyde 2,4-dinitrophenylhydrazone the melting point (164-166°) was undepressed (lit. m.p. for 2,4-dinitrophenylhydrazone of formaldehyde = 166°).[150]

## iii. Inhibitor Study

### Results

The data of Table VIII indicate that small amounts of known free radical inhibitors will inhibit the autoxidation of 1-octene initiated by chromium (III) acetylacetonate and *t*-butyl hydroperoxide, and the decomposition of *t*-butyl hydroperoxide catalyzed by chromium (III) acetylacetonate. The effect of these compounds on the rate of chromium (III) disappearance is small. The data also indicate that the stoichiometric factor for many of these inhibitors is 2, which is consistent with a mechanism in which one inhibitor molecule intercepts two chains. There is evidence, furthermore, that the efficiency of the inhibitors in the peroxide decomposition chain is sensitive to the structure of the phenols. Inhibition of autoxidation chains appears to be less sensitive to inhibitor structure. This suggests that the chain-carrying species is different in the two reactions. Finally, there is indication of a reaction between phenoxy radicals and hydroperoxide to form radicals capable of

Table VIII: The Effect of Some Free Radical Inhibitors on the Rate of Autoxidation[a] of 1-Octene and the Rate of Disappearance[b] of Chromium (III) Acetylacetonate and t-Butyl Hydroperoxide (30° in 1-chloroöctane)

| Inhibitor | Inhibitor Conc M x $10^4$ | Induction Period[c] sec x $10^{-3}$ | $R_{O_i}$[d] | $R_{O}$[e] | $n$[f] | $\alpha$[f] M x $10^5$ | $R_{Cr}$[g] | $R_P$[h] |
|---|---|---|---|---|---|---|---|---|
| Nitrobenzene | 1.63 | 5.2 | 0.165 | 1.08 | 0.77 | 6.7 | 2.43 | 5.89 |
| Aniline | 1.08 | 8.5 | 0.500 | 1.94 | 2.14 | -0.5 | 2.72 | 4.03 |
| Ethylene diamine | 1.83 | 3.0 | 0.130 | 0.851 | 0.34 | 10.1 | 2.06 | 7.10 |
| Pyridine | 2.03 | 4.0 | 0.073 | 2.11 | 0.28 | 11.6 | 1.43 | 5.21 |
| $\alpha$-Tocopherol | 1.12 | 6.8 | 0.500 | 1.85 | 1.65 | 1.3 | 2.72 | 2.07 |
| BHA[i] | 1.28 | 8.3 | 0.408[n] | 1.59 | 2.32 | -1.4 | 3.58 | 4.24 |
| DOP[j] | 0.75 | 5.0 | 0.113 | 1.22 | 2.86 | -2.2 | 4.29 | 8.95 |
| Phenol | 0.44 | 3.5 | 0.114 | 1.01 | 2.99 | -1.4 | 3.72 | 1.59 |
| Phenol | 1.74 | 8.7 | 0.491 | 1.52 | 2.00 | 0.0 | 4.00 | 2.26 |
| NDGA[k] | --[l] | n[m] | n | n | n | n | 1.71 | 2.07 |
| None | -- | -- | 9.00[o] | 2.44[p] | -- | -- | 2.68 | 13.7 |

(continued)

Table VIII: continued

a oxygen pressure = 1 atmosphere, [1-octene] = 2.56 M,
[Cr (acac)$_3$] = 1.6 x $10^{-3}$ M, [*t*-BuOOH] = 0.76 M.

b *in vacuo*, [1-octene] = 2.56 M, [Cr (acac)$_3$] = 1.6 x $10^{-3}$ M,
[*t*-BuOOH] = 0.76 M.

c for autoxidation

d rate of oxygen uptake during induction period x $10^6$ M/sec

e " " " " after " " " " "

f see text

g $R_{Cr}$ = rate of Cr (acac)$_3$ disappearance x $10^8$ M/sec

h $R_P$ = rate of *t*-BuOOH disappearance x $10^5$ M/sec

i mixture of 2- and 3-*t*-butyl-4-hydroxyanisole

j 2,6-dioctadecylphenol

k nordihydroguaiaretic acid

l saturated solution (ca. $10^{-3}$-$10^{-4}$ M)

m n = no data

n some evolution noted during induction period

o rate for first 1000 seconds

p rate after 5000 seconds

initiating chains. This reaction is sensitive to groups in the ortho position of the phenoxy radical.

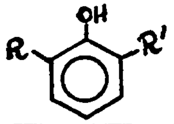
## Discussion

A. Phenols.--Phenols have long been known to inhibit free radical reactions.[151] The usual mechanism described for this inhibition is abstraction of the phenolic hydrogen to form the highly stable phenoxy radical[152] (see Reaction 169).

(169) $R\cdot + C_6H_5OH \longrightarrow RH + C_6H_5O\cdot$

It has been observed that large groups ortho to the hydroxy group reduce the inhibiting efficiency of the phenol.[79] In this work several phenols were used to inhibit both the autoxidation of 1-octene and the decomposition of t-butyl hydroperoxide. In the latter case, where the chain-carrying species is the t-butoxy radical, the efficiency of the inhibitor is more sensitive to its structure than in the autoxidation where the less hindered octenyl-peroxy radical is the chain-carrying species (see Table IX). It is also observed that the inhibitors studied are in general about three times more efficient in the autoxidation than in the decomposition reaction. The explanation for this may lie in the fact that t-butoxy radicals are in general less selective than secondary peroxy radicals[22] and therefore more readily undergo an energetically more difficult reaction[153] than the octenyl-peroxy radicals. For example, note the following reaction sequence (Reactions 171-174).

Table IX: Dependence of Inhibiting Efficiency on Structure of Phenol (30°)



| Phenol | R | R' | $[\mathrm{Conc}]_0$ of Phenol M x $10^4$ | Relative Molar Efficiency[a] Autoxidation[b] | Peroxide Decomposition[c] |
|---|---|---|---|---|---|
| Phenol | H | H | 1.74 | 1.00 | 1.00 |
| DOP[d] | n-$C_{18}H_{37}$ | n-$C_{18}H_{37}$ | 0.75 | 2.43 | 0.96 |
| -Tocopherol | $CH_3$ | $CH_3$ | 1.12 | 1.55 | 1.58 |
| BHA[e] | H | t-$C_4H_9$ | 1.28 | 1.37 | 1.12 |
| NDGA[f] | H | OH | g | h | 0.09 |

a Molar Efficiency = percent decrease in rate per mole of initiator

$$= \frac{\text{(uninhibited rate) - (inhibited rate)}}{\text{(uninhibited rate)(moles of inhibitor)}}$$

(Above efficiencies reported relative to phenol)

b Autoxidation of 1-octene (2.56 M) initiated by chromium (III) acetylacetonate (1.6 x $10^{-3}$ M) and t-butyl hydroperoxide (0.76 M) in 1-chloroöctane at 30°.

c Decomposition of t-butyl hydroperoxide (0.76 M) initiated by chromium (III) acetylacetonate (1.6 x $10^{-3}$M) in the presence of 1-octene (2.56 M) in 1-chloroöctane at 30°

d 2,6-dioctadecylphenol

e mixture of 2- and 3-t-butyl-4-hydroxy anisole

f nordihydroguaiaretic acid

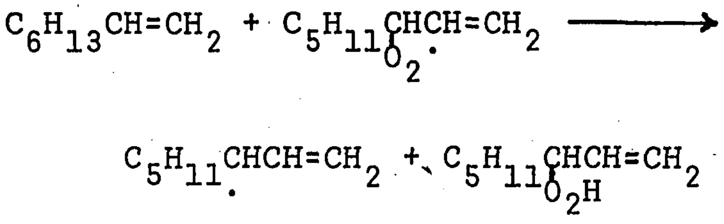
g saturated solution - estimated concentration 5 x $10^{-4}$ M

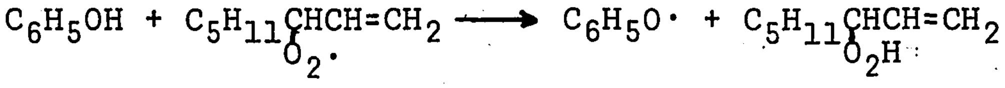
h no data

(170) $$\frac{k_{171}[\underline{t}\text{-BuOOH}]}{k_{172}[C_6H_5OH]} > \frac{k_{173}[C_6H_{13}CH{=}CH_2]}{k_{174}[C_6H_5OH]}$$

(171) $\underline{t}\text{-BuOOH} + \underline{t}\text{-BuO}\cdot \longrightarrow \underline{t}\text{-BuOO}\cdot + \underline{t}\text{-BuOH}$

(172) $C_6H_5OH + \underline{t}\text{-BuO}\cdot \longrightarrow C_6H_5O\cdot + \underline{t}\text{-BuOH}$

(173)

$$C_6H_{13}CH{=}CH_2 + C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 \longrightarrow C_5H_{11}\underset{\cdot}{C}HCH{=}CH_2 + C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2$$

(174)

$$C_6H_5OH + C_5H_{11}\underset{O_2\cdot}{C}HCH{=}CH_2 \longrightarrow C_6H_5O\cdot + C_5H_{11}\underset{O_2H}{C}HCH{=}CH_2$$

It is also indicated in Table IX that steric effects play a more important role in the hydroperoxide decomposition reaction than in the autoxidation.

It is observed (see Table VIII) that as the concentration of phenol increases the induction period of the oxidation also increases, but the rate of oxygen uptake during this period is greater with the greater concentration of phenol. It is suggested that this phenomenon is due to the following. It is known[85] that phenoxy radicals, not hindered in the 2,6 positions, can attack hydroperoxides and hydrocarbons to produce chain-initiating free radicals (Reactions 175 and 176).

(175) $C_6H_5O\cdot + RO_2H \longrightarrow C_6H_5OH + RO_2\cdot$

(176) $C_6H_5O\cdot + RH \longrightarrow C_6H_5OH + R\cdot$

As the concentration of phenol increases, the relative importance of Reactions 175 and 176 also increases. Hence, although the length of the induction period is proportional to the phenol concentration (which is the normal observation in autoxidations), the rate of oxidation during this period is also proportional to phenol concentration. This latter observation which is contrary to the usual findings,[79] is mainly due to the presence of a large excess of t-butyl hydroperoxide in the present system which increases the importance of Reaction 175. It is observed (see Table IX) that 2,6-dioctadecylphenol (DOP) is the most efficient inhibitor for the autoxidation but the least efficient for the t-butyl hydroperoxide decomposition. The first observation is consistent with participation by the less hindered phenols[79] in chain starting reactions such as 175 or 176. However, in the decomposition of the peroxide, steric effects are much more important, either through t-butoxy radical-phenol interactions or direct decomposition of the peroxide by the phenols (Reaction 175). In either case, it is expected that the more hindered phenols will be the least efficient, which is consistent with the observed data. The rate constant for attack of a non-hindered phenoxy radical on a hydroperoxide (i.e., $k_{175}$) is very similar to the rate constant for alkoxy radical attack on a hydroperoxide (e.g., $k_{171}$).[4,154] Therefore it is noted that there is some induced decomposition due to the phenoxy radical and there is a slight accelerating effect on the hydroperoxide decomposition rate when the phenol concentration is increased (see Table VIII).

It is of interest to determine the number of radical chains stopped per molecule of inhibitor (i.e., the stoichiometric factor).[79] It is possible to calculate this from the rate of the initiation step by calculating the number of radicals produced during the induction period.[79] The stoichiometric factor (n) is given by Equation 177.

(177) $n = Z/N$

where Z = the number of radicals produced during the induction period = rate of initiation x induction period and N = the number of molecules of inhibitor originally present. The rate of initiation is taken as the rate of chromium (III) acetylacetonate disappearance, since it is clear that this reaction is primarily responsible for the initiation of the chain reactions (see Kinetics Section, p. 36 ). One further assumption made in calculating n is that each initiation reaction produces only one radical (i.e., a one-electron change between the chromium (III) acetylacetonate and the peroxide is involved) (see Reaction 178 and Kinetics Section, p. 42 ).

(178) $Cr(III) + \underline{t}\text{-BuOOH} \longrightarrow Cr(IV) + \underline{t}\text{-BuO}^{\cdot} + OH^{-}$

(Oxidation of the metal and scission of the O-O bond in the peroxide are implied from temperature and chromium (III) acetylacetonate disappearance rate studies)

The reasonableness of this assumption is indicated by the observation that many of the n values are approximately 2 (see Table VIII). Values in the neighborhood of 2 have been observed previously.[79,80] The usual inhibition mechanism involves reaction similar to Reactions 179 and 180. It is observed from this sequence that two chains are stopped per inhibitor molecule:

(179) $ROO\cdot + C_6H_5OH \longrightarrow ROOH + C_6H_5O\cdot$

(180) $ROO\cdot + C_6H_5O\cdot \longrightarrow$ inactive products

Hammond[80] has suggested an alternate mechanism based on isotope and kinetic studies,[155] which also accounts for a stoichiometric factor of 2.

(181) $ROO\cdot$ + Inhibitor $\rightleftarrows$ Complex

(182) $ROO\cdot$ + Complex $\longrightarrow$ inactive products

If the products of Reaction 180 or Reaction 182 are also good inhibitors, then the stoichiometric factor will be greater than 2. This has been observed in several cases.[79,80] A factor of less than 2 could mean that participation in reactions such as 175, 176, or 183[156] (below) is important or that inhibition involves a different mechanism than those indicated above (see Reaction 184). In Reaction 184 the products of the radical-inhibitor interaction either are self-terminating or are unusually stable.

(183) $InH + O_2 \longrightarrow In\cdot$ (InH = inhibitor molecule)

(184) $InH + R\cdot \longrightarrow$ inactive products

If it is assumed that deviation from the stoichiometric factor of 2 arises from participation of inhibitor molecules in chain initiating processes (e.g., Reactions 175, 176, and 183), then the number of molecules participating in these reactions may be calculated. Let $\alpha$ = this number, then $N - \alpha$ = the total number of inhibitor molecules which terminate chains, and $Z + \alpha$ = the number of radicals produced during the induction period. Assuming that each inhibitor molecule will end two chains, then:

$$(185) \quad \frac{Z + \alpha}{N - \alpha} = 2$$

or

$$(186) \quad \alpha = (2N-Z)/3$$

Values of $\alpha$ for various phenols, aniline, and nitrobenzene are given in Table VIII. The value of $\alpha$ (as well as n) may be taken to be a measure of the efficiency of the inhibitor. A negative value of $\alpha$ indicates a greater inhibitor efficiency, i.e., more radicals are intercepted per inhibitor molecule. It is noted that as the concentration of phenol increases $\alpha$ becomes more positive, indicating lowered efficiency. It is also observed that both 2,6-dioctadecylphenol and butylated hydroxy anisole (BHA) gave lower $\alpha$ values than phenol (in the same concentration range). Both of these observations are consistent with the idea of participation by unhindered phenols in chain-initiating reactions. The observation that $\alpha$-tocopherol has a more positive $\alpha$ value than phenol may be more a consequence of the stability of this molecule towards attack by peroxy radicals[157] than of participation in chain-initiating reactions. The large positive $\alpha$ value of nitrobenzene is consistent with the stability of the peroxo-nitrophenyl radical towards further radical attack (see below).

Another method of determining inhibitor efficiency is to assume that some inhibitor molecules do not terminate chains but also do not initiate new chains. For example, a molecule might react with a radical to produce a new but equally active radical. If this number is equal to $\beta$, then by again assuming n = 2:

(187) $Z/(N - \beta) = 2$

(188) $\beta = (2N - Z)/2 = 1.5\alpha$

While the effect of the inhibitors on the rate of chromium (III) acetylacetonate disappearance is small, some of the phenols appear to have a slight accelerating effect (see Table VIII). It is possible that this effect is due to a ligand exchange reaction which facilitates a change in the oxidation state of the metal.[16] This suggestion is supported somewhat by the fact that two of the largest phenols ($\alpha$-tocopherol and nordihydroguaiaretic acid) have no effect on the reaction, although 2,6-dioctadecylphenol does. It may be pointed out, however, that complexing could be with the aromatic ring (see Solvent Section, p.102 ) and therefore 2,6-dioctadecylphenol which has its bulk "compressed" into one part of the molecule may participate in complexing while the tocopherol and nordihydroguaiaretic acid, being more "spread out," cannot. The extent of this exchange is apparently not too large, judging from the lack of a significant dependence on phenol concentration. It is also noted that this effect is observed to the same extent with much larger phenol/chromium (III) acetylacetonate ratios as well as with oxygen-containing solvents (e.g., <u>t</u>-butanol, methanol, and acetic acid (see Table X).

B. <u>Nitrogen Compounds.</u>--Inhibition of free radical reactions by amines is well known.[151] As with phenols, the

Table X: The Effect of Various Compounds on the Rate of Chromium (III) Acetylacetonate Disappearance[a] (30°)

| Additive | $\frac{\text{Moles of Additive}}{\text{Mole of Cr III (acac)}} \times 10^2$ | $\Theta$[b] |
|---|---|---|
| Phenol | 2.7 | 1.4 |
| " | 10.9 | 1.5 |
| " | 545 | 1.1 |
| " | 2,180 | 1.1 |
| DOP[c] | 4.7 | 1.6 |
| BHA[d] | 8.0 | 1.3 |
| *t*-Butanol | $1.07 \times 10^6$ | 1.6 |
| Methanol | $2.49 \times 10^6$ | 1.4 |
| Acetic Acid | $1.75 \times 10^6$ | 1.4 |

[a] In the presence of *t*-butyl hydroperoxide (0.76 M) and 1-octene (2.56 M) in 1-chlorooctane *in vacuo*. [Cr] = $1.6 \times 10^{-3}$ M for first six values and $4.0 \times 10^{-4}$ M for last three.

[b] $\Theta$ = -d[Cr]/dt in the presence of additive/-d[Cr]/dt in the absence of additive

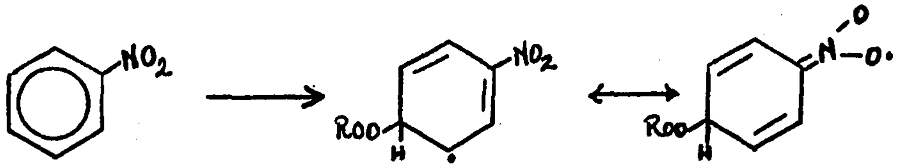
[c] 2,6-dioctadecyl phenol

[d] mixture of 2- and 3-*t*-butyl-4-hydroxy anisole

suggested mechanism for inhibition involves abstraction of an N-hydrogen to form a more stable free radical. Again, however, Hammond[80] has suggested that complex formation is a more important mechanistic route, and in fact has noted an unstable intermediate in the N,N,N',N'-tetramethyl-p-phenylene-diamine-inhibited autoxidation of cumene. In the present work it was noted that aniline, ethylene diamine (EDA) and pyridine inhibit both the autoxidation of 1-octene and the decomposition of t-butyl hydroperoxide. It is also observed that N,N'-diphenyl-p-phenylenediamine acts as an inhibitor for both reactions (in experiments using much larger concentrations of inhibitor, however). Although aniline has a stoichiometric factor af about 2, both pyridine and EDA have factors of less than 0.5 (see Table VIII). This behavior suggests that, although aniline behaves in a normal fashion, EDA and pyridine interfere with the initiation process, i.e., retard the chromium (III) acetylacetonate-t-butyl hydroperoxide reaction. This could be accomplished in one of two ways. Either the inhibitor competes with the hydroperoxide for a complexing site on the metal or there is an interaction between the inhibitor and a chromium (III) acetylacetonate-t-butyl hydroperoxide complex which prevents the latter from decomposing into a free radical. In either case, these observations strongly suggest the intervention of a peroxide-metal complex in the initiating step. The value of about 0.3 for the stoichiometric factor suggests that ~ 3 molecules of inhibitor are required to stop one chain. Although pyridine inhibits the decomposition of t-butyl hydroperoxide at low concentrations (ca. $10^{-4}$ M), when it is used as a solvent (ca. 5 M) it actually enhances the rate (see Table VI). This apparent anomaly is explained by the work of Sheng and Zajacek[47b] who have recently shown that pyridine reacts slowly with t-butyl hydroperoxide in the presence of chromium (III) acetylacetonate to produce pyridine oxide. At low concentrations of pyridine this reaction would be insignificant, but under conditions where pyridine is the solvent it should play an important role in the decomposition of the peroxide. The suggestion that EDA and pyridine inhibit the initiation step is further supported by the observation that the rate of chromium (III) acetylacetonate disappearance is somewhat retarded in the presence of either compound.

It is observed that nitrobenzene acts as an inhibitor in both the autoxidation of 1-octene and in the peroxide decomposition. The fact that trinitrobenzene was found to be ineffective as an inhibitor in the autoxidation of cumene[80] and that in the present work a stoichiometric factor of about 1 (see Table VIII) is observed for nitrobenzene suggests that inhibition by nitrobenzene might be in the initiation process rather than the propagation steps. For example, as was suggested for EDA and pyridine, an interaction with either the chromium (III) acetylacetonate or a metal-peroxide complex might take place. There is some retardation of the chromium (III) acetylacetonate disappearance rate which increases with increasing nitrobenzene concentration. It should be noted, however, that there is much data[158] which indicate that inhibition (at least of radical polymerizations) by aromatic nitro compounds is in the propagation step. The primary mechanistic path for this inhibition is through attack on the ring, although attack on the nitro group has also been suggested.[158] While attack on the ring by the electrophilic[159] peroxy might be retarded by the presence of the nitro group,[160] the resulting radical (see Reaction 189) would be highly stable due to resonance effects.[161]

(189) ROO· +



The resulting peroxo-nitrophenyl radical undoubtedly would be inert to further radical attack and thus one expects the stoichiometric factor to approach unity for nitrobenzene.

The effect of known free radical inhibitors on the chromium (III) acetylacetonate-t-butyl hydroperoxide initiated autoxidation of 1-octene and the chromium (III) acetylacetonate catalyzed decomposition of t-butyl hydroperoxide has been studied. It has been clearly demonstrated that these are free radical chain reactions.

Certain of these inhibitors act through the initation process which is essentially the same for both the autoxidation and the hydroperoxide decomposition. Other inhibitors act through the propagation or termination steps. Therefore their efficiency is strongly dependent on the chain-carrying radical and hence the type of reaction (i.e., the autoxidation or the decomposition) involved. Stoichiometric factors have been calculated which are used to explain the mode of inhibition exhibited by the various inhibitors.

### iv. Products

A preliminary study was made of the products of the t-butyl hydroperoxide-1-octene-chromium (III) acetylacetonate reaction both in the presence and absence of oxygen (see Experimental Section, p. 146). The results obtained were inconclusive and the study is being pursued further.

# III. Experimental

## Chemicals

1-Octene was Phillips research grade (99.9 mole %) treated with ferrous ammonium sulphate to remove peroxide and distilled through a 2-foot Vigreux column prior to use (b.p. 120-121°). t-Butyl hydroperoxide was obtained from Wallace and Tiernan Inc. (Lucidol Division) as t-butyl hydroperoxide-90 and further purified by distilling off the lighter impurities under vacuum. Iodometric titration[162] indicated > 95% hydroperoxide. The metal acetylacetonates (McKenzie Chemical Corp.) were recrystallized from acetone and were shown to be pure by their infrared absorption spectra. Chromium (III) acetylacetonate was dissolved in benzene and precipitated with petroleum ether (b.p. 30-60°).[164] The melting point of the precipitated compound was 213.5-214° (lit. 214°).[165] Nitrogen and oxygen (Matheson) were used without further purification.

The chemicals used in the solvent study were pure grade or spectrograde where possible and in most cases used without further purification. Diphenyl ether was washed with NaOH solution to remove traces of phenol, dried, and vacuum distilled prior to use. p-Dioxane, tetralin, and cumene were treated with ferrous ammonium sulphate and distilled. The solvents used in all cases gave negative peroxide tests.

Pyridine, ethanol, methanol, and ethyl acetate were thoroughly dried[166] before using. Glacial acetic acid was treated with acetic anhydride. t-Butanol was recrystallized at 5-10° to remove moisture.

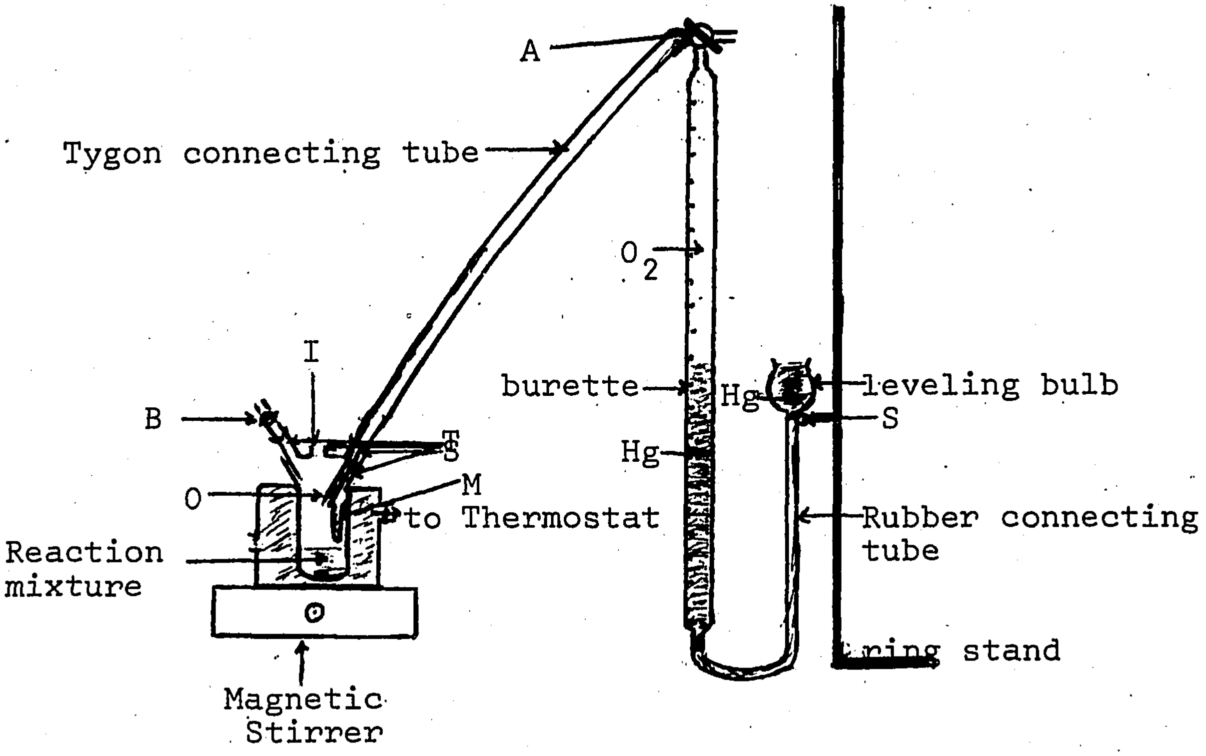
The chemicals used in the inhibitor study were taken from freshly opened bottles and, in general, used without further purification. Phenol was recrystallized from chloroform and aniline was distilled prior to use.

## Kinetics

A. Oxygen Absorption.--Oxygen absorption measurements were carried out in jacketed, 50 ml Pyrex cells. The temperature was maintained at ±0.1° by pumping thermostated water through the jacket using an Eastern Industries Model D-6 water pump. In those runs at very low temperatures, ice-cooled water was run through the jacket. At both temperature extremes (near 60° and near 0°) the temperature was measured by placing a thermometer in the reaction solution (see Figure 22). At a bath temperature of 50° the temperature in the reaction vessel was also 50°. By inserting a thermometer in various places in the reaction vessel and in the Tygon connecting tube (see Figure 22) it was observed that a temperature gradient of $< 0.5°$ existed in the vessel itself, while the oxygen in the burette and Tygon connecting tube were at the same temperature.

Stirring was accomplished by means of an A.H. Thomas Model 15 magnetic stirrer with a Teflon-coated stirring bar. The stirring rate was controlled by a Superior Electric Co.

Figure 22: Apparatus for Oxygen Absorption Study



A = 3-way stopcock

B = ordinary stopcock

I = inlet for thermometer (not shown)

M = molecular sieve

O = oxygen inlet

S = set screw

$\overset{T}{S}$ = standard joint

Type 3PN-116 "Powerstat." In several identical runs different stirrers and "Powerstat" settings were used with no effect on the reaction rate (see Table XI). A small test tube containing molecular sieve (Fisher Type 4A) was suspended in the cell to remove gaseous products which might interfere with the measurement of oxygen uptake.[46]

In a typical run, an appropriate amount of chromium (III) acetylacetonate stock solution (usually $4.0 \times 10^{-3}$ M in 1-chloroöctane solvent) was charged into either a 10 cc or 25 cc volumetric flask, using a volumetric pipette. The desired amounts of peroxide and olefin were added to the flask again using volumetric pipettes. The solutions were brought to volume with solvent (usually 1-chloroöctane). The flask was capped and the solution mixed by shaking. The solution was then poured into the reaction cell. The top of the cell which was previously fitted through ground glass joints with a stopper, a stopcock, and a gas inlet tube, which supports the tube of molecular sieve and was connected through Tygon tubing to the burette (see Figure 22), was then fitted to the bottom through a ground glass joint. All joints and stopcocks were lubricated with Dow Corning silicone stopcock grease. The standard joints are noted in Figure 22. The system was then flushed with oxygen by opening stopcock (B) and turning three-way stopcock (A) so as to bypass the burette and connect the oxygen tank directly to the reaction cell. After the cell has been flushed for about ten to twenty seconds, stopcock (A) is turned so as to connect the cell with the burette which has been previously filled with oxygen (see below). When the level of the mercury in the burette has reached that of the mercury in the leveling bulb, the stirrer is turned on and the system is allowed to equilibrate for about five to ten minutes and stopcock (B) is closed. In some cases the mercury level in the burette was observed to fluctuate. This condition could be corrected by opening and closing (B) until there is no further fluctuation.

The gas burette used had a total volume of 50 ml calibrated in tenths of a ml. Before filling it with oxygen, the leveling bulb was raised so that the entire burette was filled with mercury. With stopcock (A) turned so as to by-pass the burette, the Tygon connecting tube is flushed with oxygen. Without turning off the flow of oxygen, (A) is turned so as to connect the tank directly to the burette which is then filled completely with the gas, the leveling bulb is lowered to a point roughly opposite the 25 ml mark on the burette and (A) is turned so as to seal off the burette. When (A) is turned so as to connect the burette with the reaction cell, the mercury level rises to about the 25 ml mark. With stopcock (B) closed, the level of mercury in the burette is aligned with that in the bulb by adjusting a set screw (S) on the latter. It has been observed that upon opening stopcock (B) the volume at barometric pressure differs from the volume obtained by the technique indicated above by less than 0.5 ml, corresponding to a pressure difference of about 0.02 atmospheres. Therefore only a slight error (± 2%) is introduced by assuming the volume of oxygen is at one atmosphere. This error is in any case a systematic one which will affect each reading equally.

Readings are taken about every 400-500 seconds for normal runs, and 50-100 seconds for faster ones. In order to test the reproducibility of the readings, a reading was taken, the leveling bulb position was changed, and the reading taken again. It was found that the two readings did not differ by more than 0.02 ml, which reflects approximately the error in the scale reading. The above observation was done in the absence of a reaction system so that there could be no interference from chemical reaction.

The volume of oxygen was plotted versus time and the rates were taken from the initial linear portions of these graphs (see Figure 23). A graph of an inhibited run is included for comparison (see Figure 24). All reported rates are within the first hour of reaction. The rate was found to fall off with time. The rates were converted from ml/sec to moles/l-sec by multiplying by a factor which corrects for STP and the volume of the reaction mixture. The error in reading the slopes is ± 7-8% by a least square method.[167] The reproducibility of identical runs is approximately 3% (see Table XI).

No oxygen was picked up over a period of 5.5 hours, in the absence of metal acetylacetonates, by a solution of _t_-butyl hydroperoxide in 1-octene. All solvents were shown

Figure 23: Rate of Oxygen Uptake by 1-Octene in the Presence of t-Butyl Hydroperoxide and Chromium (III) Acetylacetonate (30°).

$[Cr(acac)_3]_0$ = 1.60 x 10-3 M

$[\underline{t}\text{-BuOOH}]_0$ = 0.76 M

$[\text{1-Octene}]_0$ = 2.56 M

Temp. = 30°

$\text{Press}_{O_2}$ = 1 atmosphere

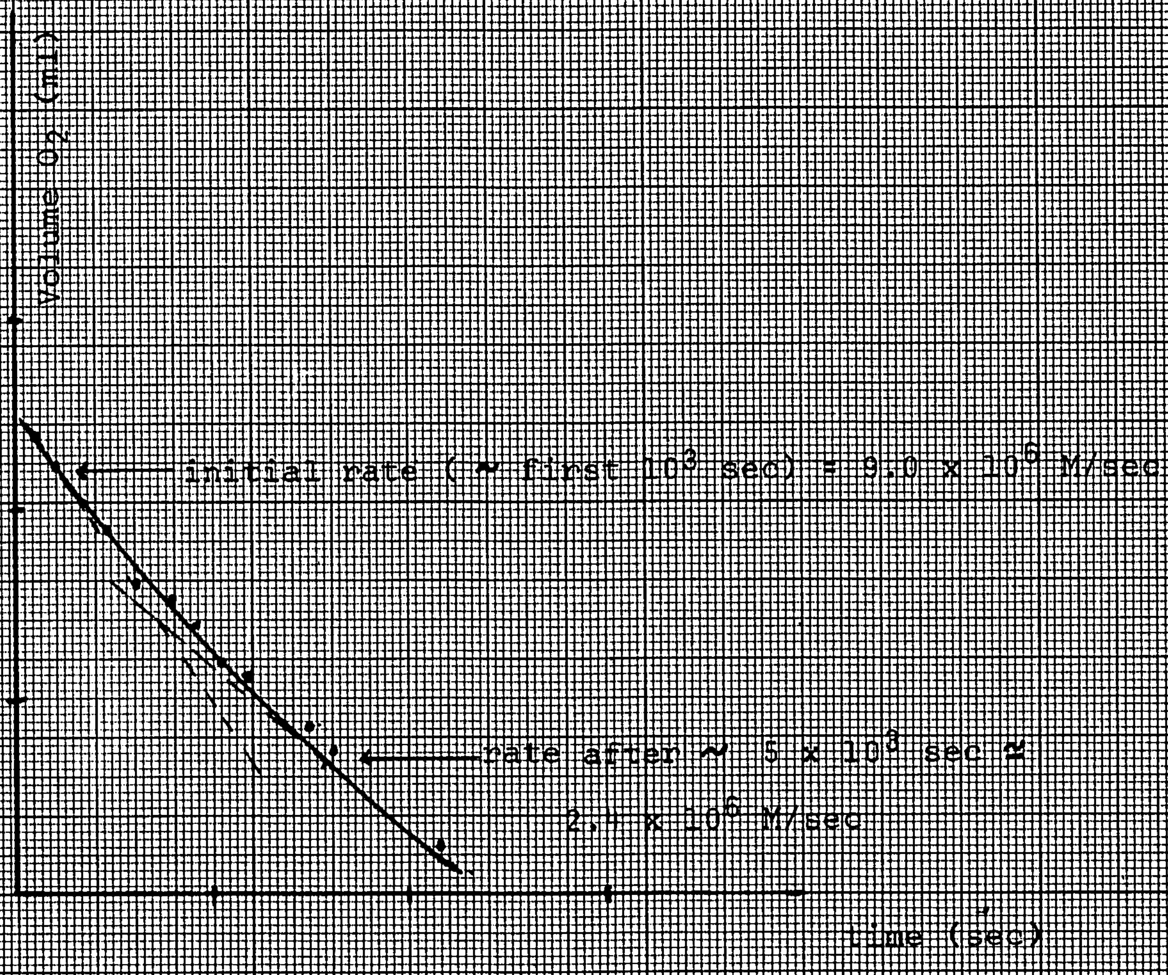


Figure 24: The Rate of Oxygen Uptake by 1-Octene, t-Butyl Hydroperoxide, and Chromium (III) Acetylacetonate in the Presence of Phenol

(30°)

$[Cr(acac)_3]_0 = 1.60 \times 10^{-3}$ M

$[\underline{t}\text{-BuOOH}]_0 = 0.76$ M

$[\text{1-Octene}]_0 = 2.56$ M

$[\text{Phenol}]_0 = 4.4 \times 10^{-5}$ M

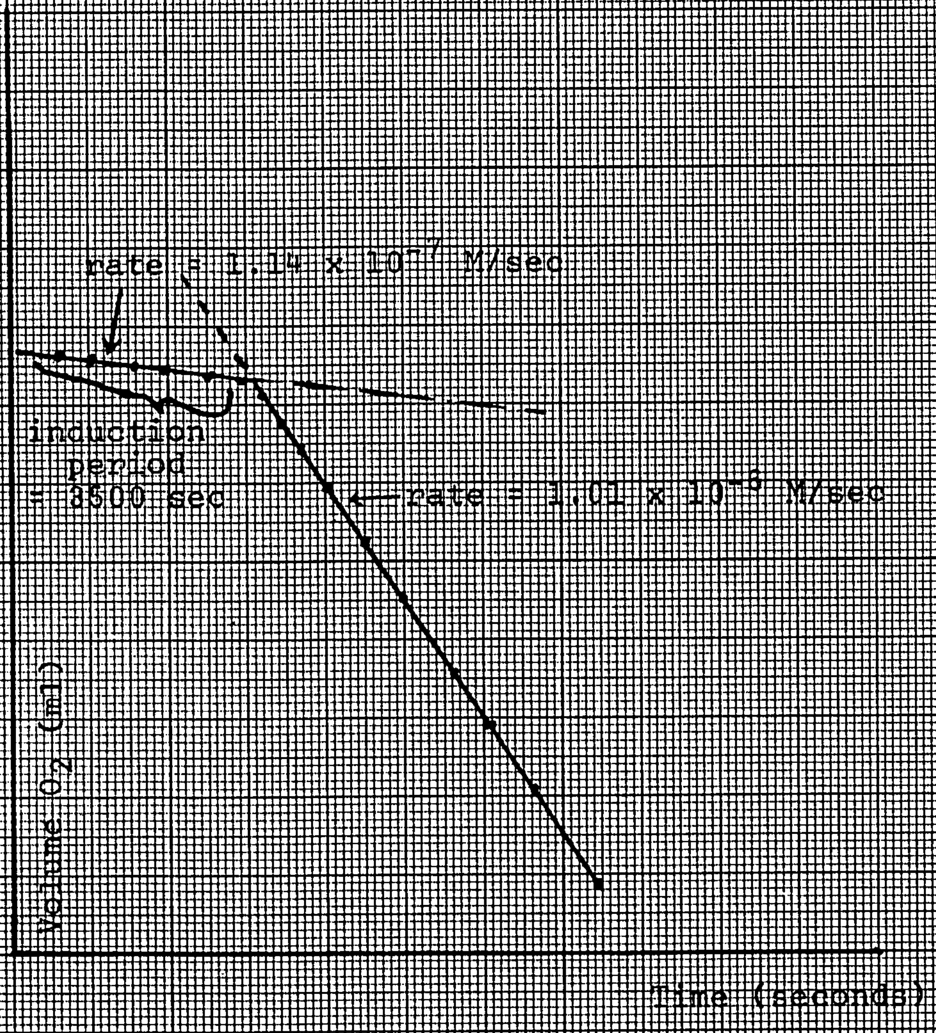


Table XI: Reproducibility of Rate Data[a]

A. Chromium (III) Acetylacetonate Disappearance[b]

| Run | $-(\Delta[Cr]/\Delta t)_0 \times 10^9$ M/sec | Deviation | % Deviation |
|---|---|---|---|
| 1 | 6.43 | 0.28 | 4.4 |
| 2 | 5.86 | 0.29 | 5.0 |
| Avg. | 6.15 | 0.29 | 4.7 |

B. Oxygen Uptake[c]

| Run | $-(\Delta[O_2]/\Delta t)_0 \times 10^6$ M/sec | Deviation | % Deviation |
|---|---|---|---|
| 1 | 2.25 | .02 | 0.9 |
| 2 | 2.33 | .06 | 2.6 |
| 3 | 2.22 | .05 | 2.3 |
| Avg. | 2.27 | .04 | 1.9 |

C. t-Butyl Hydroperoxide Decomposition[b]

| Run | $-(\Delta[\underline{t}\text{-BuOOH}]/\Delta t)_0 \times 10^4$ M/sec | Deviation | % Deviation |
|---|---|---|---|
| 1 | 0.761 | 0.038 | 5.0 |
| 2 | 0.684 | 0.039 | 5.7 |
| Avg. | 0.723 | 0.039 | 5.4 |

[a] $[Cr(acac)_3]_0 = 4.00 \times 10^{-4}$ M, $[\underline{t}\text{-BuOOH}]_0 = 0.76$ M, $[\text{1-octene}]_0 = 2.56$ M in 1-chlorooctane (30°)

[b] *in vacuo*

[c] oxygen pressure = 1 atmosphere

to be inert to oxidation under the stated conditions except where noted (see Solvent Effect Section, p. 93 ).

Since the decomposition of t-butyl hydroperoxide might produce oxygen[89] an experiment was done to see if oxygen was produced and at what rate. The reactants were charged into the reaction vessel as described above, however the burette was filled with nitrogen (Matheson) and the reaction cell was flushed with nitrogen. For a mixture containing 2 x $10^{-2}$ M chromium (III) acetylacetonate, 0.75 M t-butyl hydroperoxide, and 5.9 M 1-octene, evolution was observed at a rate of 1.7 x $10^{-7}$ M/sec. The evolved gas was absorbed in a solution of alkaline pyrogallol which yielded a qualitative test for oxygen,[168] i.e., the solution turned brown. Even if all of the evolved gas were oxygen, the rate of evolution represents less than 5% of the rate of absorption. Furthermore, the amount of chromium (III) acetylacetonate used in this experiment was fifty times greater than that used in a normal run. Using a mixture of 4 x $10^{-4}$ M chromium (III) acetylacetonate and 0.75 M t-butyl hydroperoxide in an inert solvent (1-chloroöctane), no evolution was observed over a period of seven hours.

All stock solutions were made up in 25 or 50 ml Kimax Model "A" Ray-Sorb volumetric flasks. The chromium (III) acetylacetonate solutions were allowed to remain at room temperature, but the peroxide and 1-octene were stored in a refrigerator to minimize decomposition. A Mettler Type H6T automatic balance was used in the weighing of all solids.

The general procedure for cleaning the autoxidation cells between runs was to wash with a solution of potassium dichromate in concentrated sulfuric acid followed successively by water, benzene, acetone, and methanol, and finally drying in a stream of air filtered through a column of molecular sieve. The other glassware used (pipettes, flasks, etc.) were in general cleaned in the same manner, except that they were dried on the house vacuum line. It was observed that in time the mercury coated the sides of the leveling bulb and the burette. These apparati were cleaned by soaking in concentrated nitric acid.

B. t-Butyl Hydroperoxide Decomposition.--t-Butyl hydroperoxide decomposition studies were carried out in the absence of oxygen. This was to prevent the formation of other hydroperoxides which would have given erroneous decomposition rates. In a typical experiment, appropriate amounts of metal acetylacetonate, hydroperoxide, and olefin were volumetrically pipetted into either a 10 ml or 25 ml volumetric flask. The solution was brought to volume with solvent. The flask was capped and the mixture well shaken. The solution was then divided into three to five approximately equal portions in new Carius tubes (Fisher Model 7-632 Size D). The tubes were degassed three to four times and sealed. The degassing process involved attaching the tube to a manifold, freezing the mixture in dry ice-isopropanol or liquid nitrogen and pumping out the tube (pressure ~ 1 torr) for about 30 seconds. The vacuum line was then closed off by means of a stopcock and the mixture was allowed to thaw. After one to two minutes the mixture had melted and the process was repeated. In those experiments involving small amounts of t-butyl hydroperoxide ( $<$ 0.1 M), the reaction mixture would not freeze even at -70° (the m.p. of 1-octene is -104°),[169] and liquid nitrogen was used to freeze the sample tubes.

After the tubes were sealed, they were thermostated at the desired temperature and removed at intervals. The tubes were wrapped in aluminum foil and placed in an immersion cage in a constant temperature water bath. The bath temperature was controlled by a YSI Model 72 "Proportional Controller" to ± 0.01°.

After a tube was removed, it was cut open using a triangle file or a glass cutter. An aliquot was removed (usually 1 ml) using a volumetric pipette and the tube was resealed with a serum cap (A.H. Thomas No. 8826 Sleeve Type rubber stopper). The tube was then placed in a dry ice-isopropanol bath to prevent further reaction. Aliquots were taken for chromium (III) acetylacetonate analysis or placed into a 250 ml iodine flask (Fisher No. 10-094). In the former case the aliquot was diluted to 10 ml with chlorobenzene. It was assumed that, once diluted, the reaction was essentially quenched, because it was found that the peroxide decomposition and the chromium disappearance rates fell off rapidly with dilution (see Table III) and that chlorobenzene retarded the rate of oxidation (see Table VI). If the above procedure was followed, i.e., dilution of the original aliquot, then 5 ml of this diluted mixture were transferred volumetrically to an iodine flask. The iodine flask had been previously filled with a small amount of dry ice and 5-10 ml of glacial acetic acid. After the aliquot (1 ml undiluted or 5 ml diluted) had been added to the dry ice-acetic acid mixture, 8-10 ml of saturated potassium iodide solution were added, the flask was stirred, and about 5 ml more of acetic acid were added. A polypropylene wash bottle (Nalge) was used for the addition of the acetic acid and was useful for rinsing down the sides of the flask. The mixture was capped and acetic acid was placed around the neck for a seal. The appearance of bubbles in the seal indicated that carbon dioxide was being evolved, thus maintaining a positive pressure in the flask. After about 15 minutes 25-50 ml of water was added and the red-yellow mixture was titrated to a colorless endpoint using either 0.025 N or 0.1 N sodium thiosulfate.[162] The burette used in these titrations was a 10 ml automatic filling burette with graduations .05 ml apart. The accuracy in reading the burette is ± 0.01 ml and the reproducibility of two identical titrations was better than 1%. The concentration of hydroperoxide in moles/l was calculated from Equation 190:

$$(190)\quad [\underline{t}\text{-butyl hydroperoxide}] = \frac{\text{ml titre} \times \text{normality of } S_2O_3^{=}}{2 \times \text{no. ml aliquot}}$$

This concentration was then plotted versus time and the rates were taken from the initial linear portions of the graph (see Figure 25). The rate was found to fall off with time after about ten hours. Most of the rates reported are within the first five hours of reaction. The error in reading the slopes is ± 2-3% by the least square method.[167]

For the rates reported using the series of metal acetylacetonates (cf. Table II of Appendix V)[19] the data are taken over a much longer period of time ( $\gg$ 20 hours) and the rates are average values over the whole reaction period. The reproducibility of identical runs is $\sim$ 5% (see Table XI). In the absence of metal acetylacetonates, t-butyl hydroperoxide was found to be stable for at least four days at 25° in 2,4,4-trimethyl-1-pentene,[91] and for about one week in 1-octene at 30°.[19] Even in the presence of small amounts of some metal acetylacetonates there was negligible decomposition after one week under the same conditions.[19]

C. Rate of Chromium (III) Acetylacetonate Disappearance.--The rate of chromium (III) acetylacetonate disappearance is measured by observing the disappearance of the ultraviolet absorption peak at 336 m$\mu$ ( $\epsilon$ = 15,500 l/mole-cm).[114] Samples for analyzing chromium (III) acetylacetonate were taken from the same tubes used for t-butyl hydroperoxide decomposition. As noted in Part B, these samples were diluted by a factor of 10 (in most cases) because of the large extinction coefficient. In order to keep the transmission at about 50%, the chromium (III) acetylacetonate concentration should be about $3.2 \times 10^{-5}$ M. Again as noted in Part B,

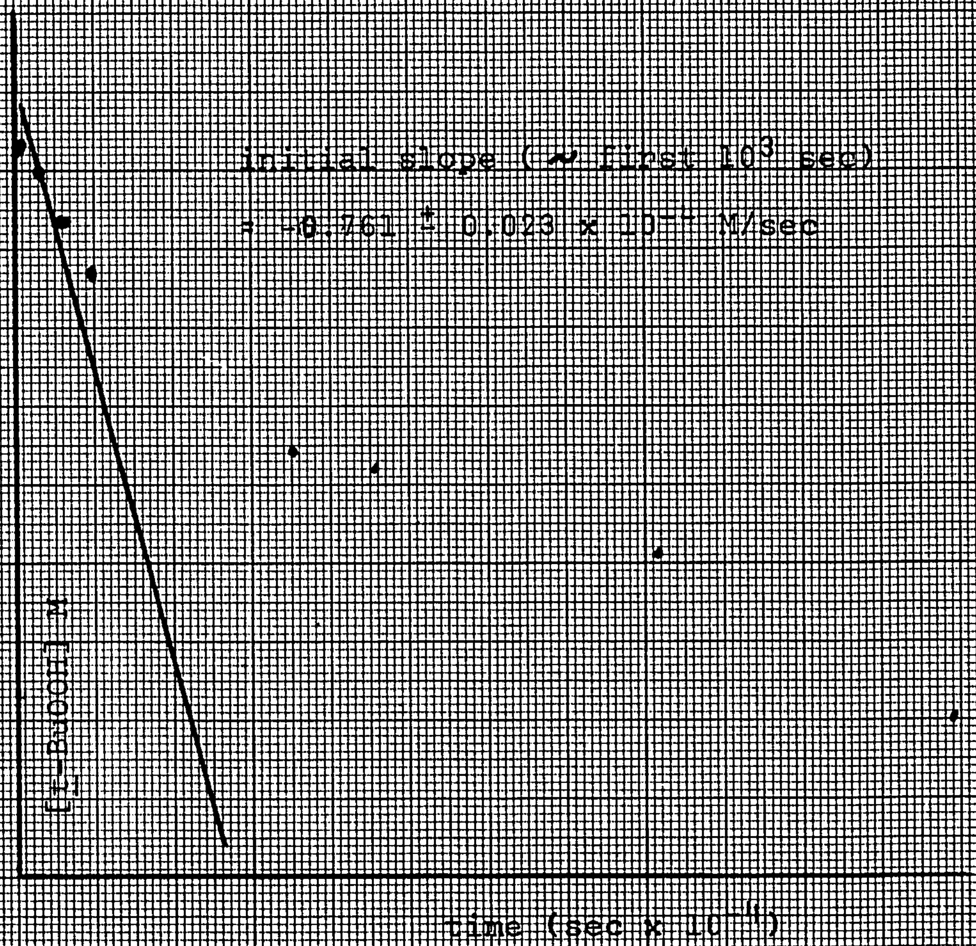
Figure 25: Determination of Rate of t-BuOOH Decomposition (30°)

$[Cr(acac)_3]_0 = 4.0 \times 10^{-4}$ M

$[\underline{t}\text{-BuOOH}]_0 = 0.76$ M

$[\text{1-Octene}]_0 = 2.56$ M

Temp. = 30° C *in vacuo*



initial slope ( ~ first $10^3$ sec)

$= -0.761 \pm 0.023 \times 10^{-4}$ M/sec it was assumed that dilution effectively quenched the reaction. The ultra-violet measurements were done on a Carey Model 14 or a Perkin-Elmer Model 202 spectrophotometer. The reference cell usually contained chlorobenzene which was used for diluting the original sample. It was observed that the presence of t-butyl hydroperoxide increased the absorption of the chromium (III) acetylacetonate. This was corrected for by making a calibration curve of absorption versus hydroperoxide concentration (see Figure 26). It was observed that this curve was linear at low concentrations of t-butyl hydroperoxide but rose sharply at concentrations $\geq$ 1.0 M. Another method for correcting this was to put an equal concentration of t-butyl hydroperoxide into the reference cell and thus cancel out this effect. The significance of this observation is discussed in another section (cf. Kinetics Section, p. 36). The chromium (III) acetylacetonate solutions were found to obey Beer's law over the range of concentration studied (see Figure 27). In the absence of t-butyl hydroperoxide, the rate of chromium (III) acetylacetonate disappearance is negligible for a period of several weeks (see Table III). Two consecutive measurements of the same sample agree to better than ± 0.2 %. The optical density was converted to concentration in moles/l using Equation 191:[163]

$$(191)\quad [\text{chromium (III) acetylacetonate}] = \frac{\text{optical density} \times 10}{\epsilon \times \text{path length}} = \frac{\text{optical density}}{1.55 \times 10^{3}}$$

The path length of the quartz cells used was 1 cm. The fac-

Figure 26: Effect of [t-BuOOH] on Ultra-violet Absorption by $4 \times 10^{-5}$ M Chromium (III) Acetylacetonate (@ 336 mμ).

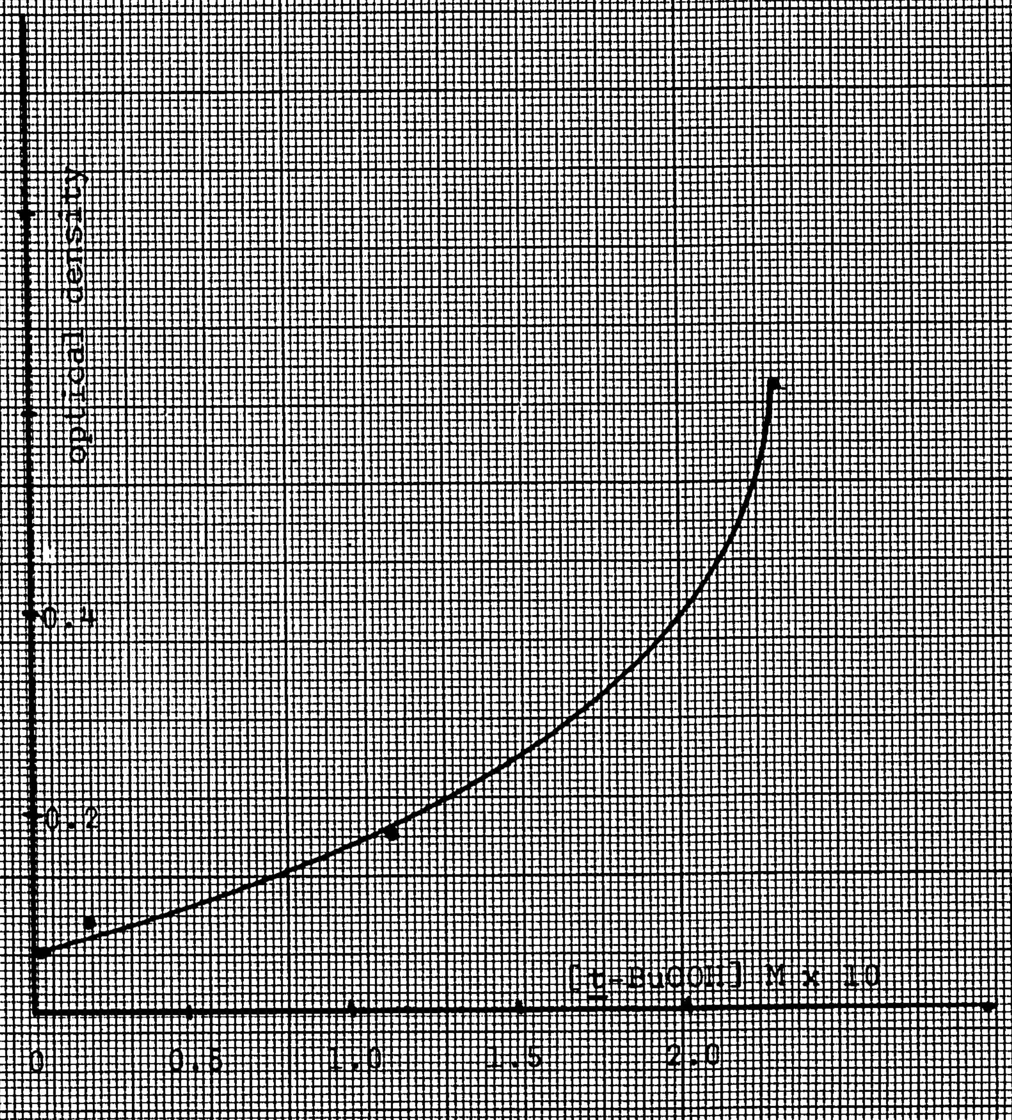
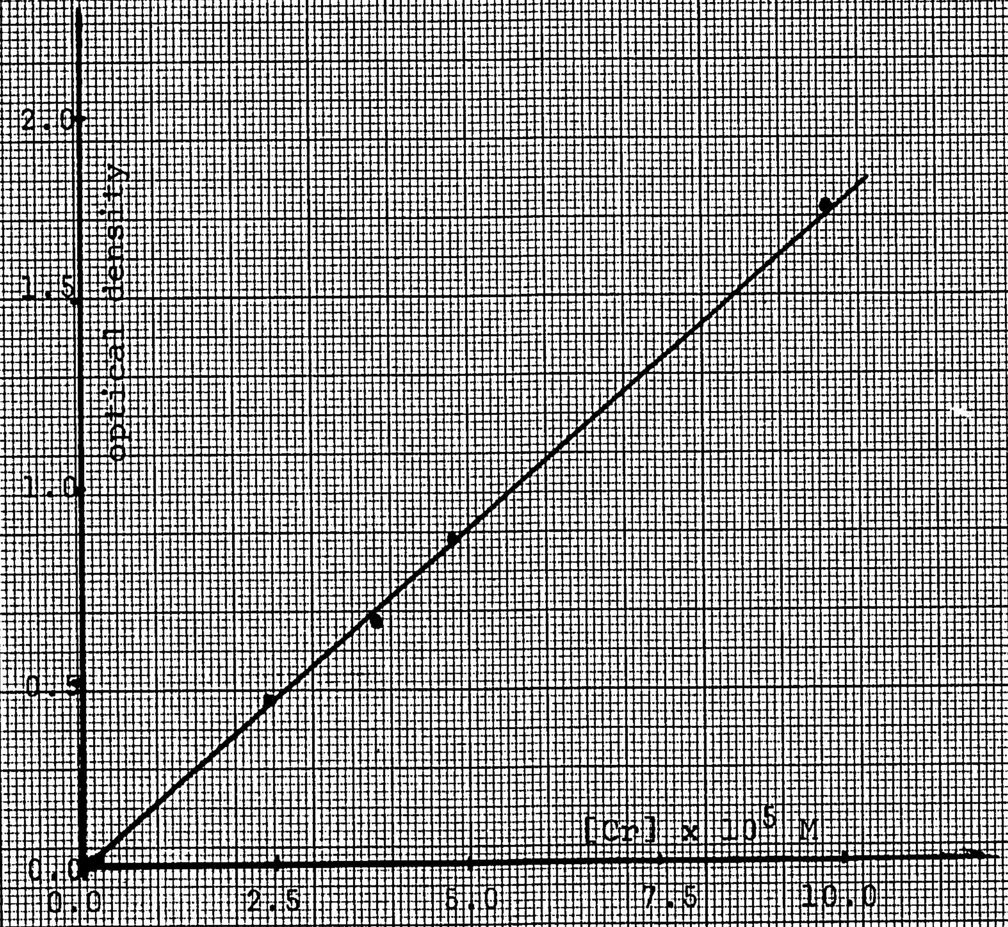
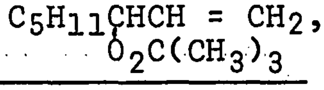


Figure 27: Beer's Law Plot for Absorbance by Chromium (III) Acetylacetonate @ 336 mμ



tor of 10 in the numerator is to account for the dilution effect. The concentrations were plotted versus time and the rates taken from the slopes of the curves (see Figure 28). The graphs were shown to be linear over a period of several days. Usually, the points were only taken over the first three to five hours. The error in reading the slopes is ± 2-3% by the least square method.[167] The agreement between two identical runs is ∼ 5% (see Table XI).

D. Product Analysis.--Product analysis was done by vapor phase chromatography on a Perkin-Elmer Model 154 gas chromatograph using a glass, 88-inch, carbowax 20 M column. Helium pressure was 10 psi. The column was wrapped with a Nichrome wire attached to a Superior Electric Co. Type 3PN-116 "Powerstat" so that the column could be heated independently of the injection block. The column temperature reached ∼ 150° when the Powerstat setting = 57 and the block temperature was 74°. The retention times of the reactants and the products under these conditions are given in Table XVI. The products were identified by retention time comparison with known compounds. These compounds were either purchased or prepared in the following manner.



1. Preparation of $C_5H_{11}\underset{O_2C(CH_3)_3}{CH}CH = CH_2$, $C_5H_{11}CH{=}CHCH_2O_2C(CH_3)_3$, 2-Octenal.-- Following the method of Kharasch and Fono[90] 0.033 g of cuprous chloride, 10 ml of 1-octene, and 2 ml of *t*-butyl hydroperoxide were mixed in a 100 ml three-necked round-bottom flask for about five hours at 60-70° under a stream of nitrogen. At the end of this

Figure 28: Determination of Rate of Chromium (III) Acetylacetonate Disappearance (30°).

$[Cr(acac)_3]_0 = 4.0 \times 10^{-4}$ M

$[\underline{t}\text{-BuOOH}]_0 = 0.76$ M

$[\text{1-Octene}]_0 = 2.56$ M

Temp. = 30° C. *in vacuo*

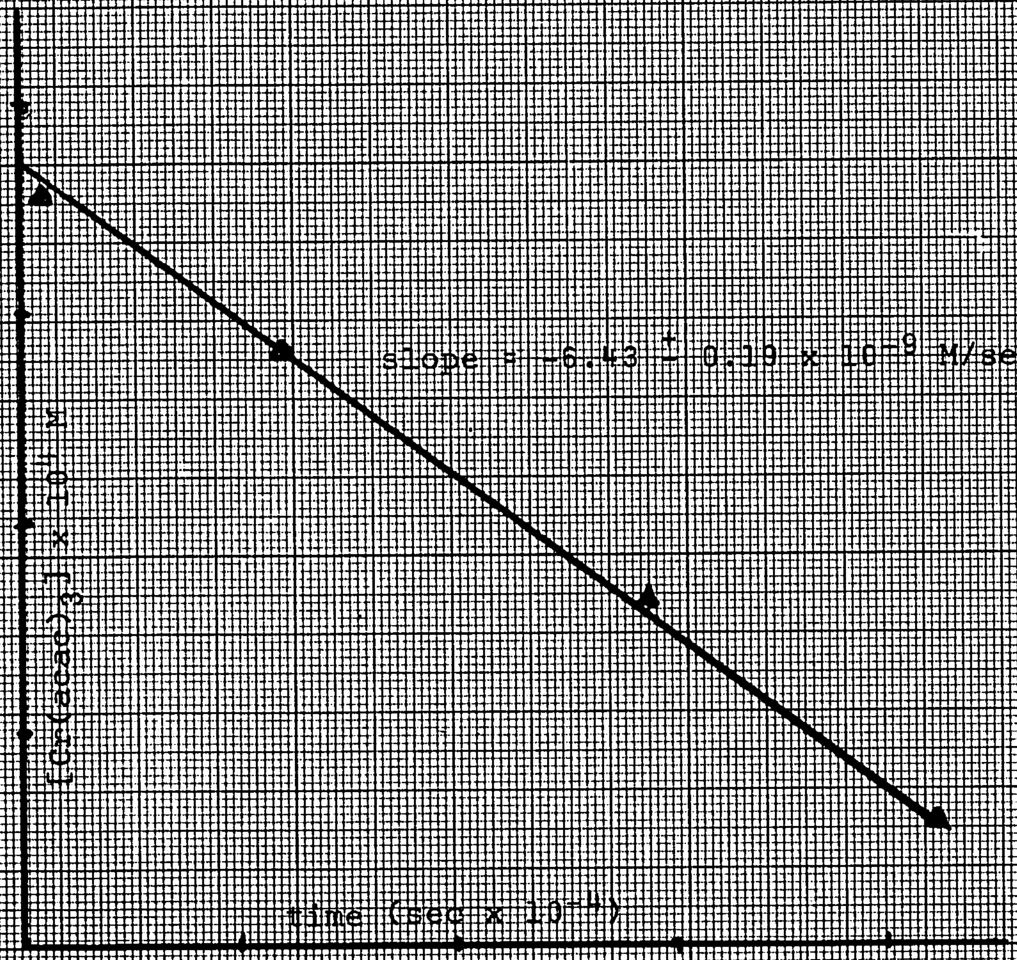


Table XII: Products of the Autoxidation of 1-Hexene[a] in the Presence of ABC[b] at 90° (753 min, oxygen pressure = 40 psi).

| Product | mmoles/mmole of oxygen consumed[c] |
|---|---|
| Hydroperoxide[d] | 0.258 |
| Alcohol[e] | 0.033 |
| 1-Hexen-3-one | 0.042 |
| 2-Hexenal | 0.040 |
| 1,2-Epoxyhexane | 0.048 |
| Pentanal | 0.017 |
| Residue | 0.324 |

[a] 384 mmoles

[b] $8.92 \times 10^{-3}$ M

[c] 18.1 mmoles of oxygen consumed

[d] mixture of isomers

[e] mixture of isomers

Table XIII: Products of the Autoxidation of 1-Octene[a] in the Presence of AIBN[b] at 70° (945 min, oxygen pressure = 15 psi)

| Product | mmoles/mmole of oxygen consumed[c] |
|---|---|
| Hydroperoxide[d] | 0.225 |
| Alcohol[e,f] | 0.147 |
| 1-Octen-3-one[f] | 0.138 |
| 2-Octenal[f] | 0.118 |
| 1,2-Epoxyoctane | 0.042 |
| Residue | not measured |

a 128 mmoles

b $9.75 \times 10^{-3}$ M

c 1.61 mmoles of oxygen absorbed

d may be a mixture of hydroperoxides

e may be a mixture of isomers

f Assignments made on basis of gas chromatographic comparison to work cited in Table XII. No rigorous structure proof done.

Table XIV: Products of the Reaction[a] of 1-Octene[b] and t-Butyl Hydroperoxide[c] in the Presence of Chromium (III) Acetylacetonate[d]

| Product | mmoles of Product | % Yield Based on t-BuOOH Reacted[e] |
|---|---|---|
| 1,2-Epoxyoctane | 0.007 | 0.09 |
| 2-Octenal[f,h] | 0.095 | 1.25 |
| 1-Octen-3-one[h] | 0.154 | 2.03 |
| Compound II[g] | 0.141 | 1.86 |

a in 1-chlorooctane (*in vacuo*) at 30° for 10 days

b 6.4 M

c $1.6 \times 10^{-3}$ M

d 0.76 M

e Based on complete decomposition of *t*-BuOOH (see Table III) and assuming 1 mole of product formed per mole of peroxide.

f mixture of cis/trans isomers

g see text

h See footnote f, Table XIII.

Table XV: Products of the Autoxidation[a] of 1-Octene[b] in the Presence of Chromium (III) Acetylacetonate[c] and t-Butyl Hydroperoxide (30°)

| | | | |
|---|---|---|---|
| Time (days) | 4.0 | 7.0 | 1.0 |
| [t-BuOOH]$_0$ (M) | $3.3 \times 10^{-4}$ M | 0.095 M | 0.76 M |
| Product | mmoles/mmole of oxygen consumed | | |
| Hydroperoxide[d] | 0.018 | --[g] | --[g] |
| 1-Octen-3-one[i] | 0.038 | 0.644 | 0.752 |
| Compound I[f] | 0.045 | 0.439 | 0.145 |
| 1,2-Epoxyoctane | 0.005 | 0.029 | 0.033 |
| 2-Octenal[e,i] | 0.068 | 0.040 | 0.171 |
| Residue | --[g] | --[g] | 0.232[f] |
| mmoles of $O_2$ consumed | 0.58 | 0.67 | 2.85 |
| % t-BuOOH decomposed (estimated) | --[h] | 100 | 100 |

a in 1-chloroöctane at 30°

b 6.4 M

c $1.6 \times 10^{-3}$ M

d may be a mixture of isomers

e may be a mixture of cis and trans isomers

f see text

g not measured

h Due to the extremely low rate of decomposition at this concentration of t-BuOOH (ca. 0.0, see Table III, footnote j) it is not possible to estimate the amount of peroxide decomposed.

i See footnote f of Table XIII.

Table XVI: Gas Chromatograph Retention Times[a] of Various Compounds

| Compound | Retention Time (minutes) |
|---|---|
| 1,2 epoxyoctane | 7.5 |
| 2-octenal[e] | 10.3 |
| 1-octen-3-one[e] | 13.5 |
| *t*-butyl-octenyl peroxide[b] | 19.5 |
| 1-octen-3-ol | 20.3 |
| Compound I[c] | 26.5 |
| Compound II[d] | 25.5 |

a for gas chromatograph conditions see Experimental Section

b mixture of isomers -- see text

c see text

d "unknown" compound from *in vacuo* reaction of *t*-butyl hydroperoxide, chromium (III) acetylacetonate, and 1-octene. See text.

e See footnote f , Table XIII.

time, 62% of the hydroperoxide had decomposed. When a 0.5 ml sample of the reaction mixture was injected into the gas chromatograph under the above conditions, four product peaks were observed. One of these was identified as t-butanol by comparison with a genuine sample. The retention times of the other three are given in Table XVI. Kharasch and Fono observed the three compounds mentioned above. Accordingly, the two peroxides were assigned to the two closely spaced peaks with the long retention times, while octenal was assigned to the remaining peak. The cuprous chloride used in the above reaction was prepared by mixing solutions of sodium bisulfite and cupric chloride and slowly adding sodium hydroxide solution (1-2 M) until a white precipitate (cuprous chloride) appeared (pH $\leqslant$ 4). The precipitate is filtered on a Buchner funnel, washed with methanol, and stored under nitrogen.

2. Oxidation of 1-Octene Initiated by Azobisisobutyronitrile (AIBN).--Following the procedure of Mayo and coworkers,[12] 0.032 grams of AIBN (recrystallized from ethyl ether) and 20 ml of 1-octene were placed in the oxidation apparatus described in Part A. In 16 hours at 65-70°, the above system consumed 36 ml of oxygen (p = 1 atmosphere). This volume of oxygen is corrected for the amount of nitrogen evolved by AIBN, calculated from its rate of decomposition at 65-70°[12] and the length of time of the reaction. Iodometric titration indicated that 0.36 millimoles of hydroperoxide had formed during the reaction. A 9 $\mu$l sample of

the reaction mixture was injected into the gas chromatograph. The peaks and their retention times are given in Tables XIII and XVI. The assignments are made on the basis of the products reported by Mayo's group for the autoxidation of 1-hexene under similar conditions.[170]

Product analysis was done on systems that had absorbed oxygen, as well as those that did not (see Tables XIV and XV). The oxygen absorption samples were taken from systems described in Part A. The oxygen-free samples were taken from systems described in Part B. In no case was a solvent used for product studies.

## Summary

In this dissertation we have attempted to solve some problems pertaining to metal-hydroperoxide reactions. Although several questions remain unanswered, we believe that we have shown the generality of the system in a variety of reactions and have indicated the feasibility of using this system as a possible investigative tool in free radical chemistry.

# Appendix I

## The Destructive Autoxidation of Metal Acetylacetonates

Mendelsohn et al.[46] have reported that some metal acetylacetonates will undergo destructive autoxidation at 100° in diphenyl ether. However chromium (III) acetylacetonate was shown to be inert under these conditions. It was shown in our work that aromatic solvents including diphenyl ether had a marked effect on the chromium (III) acetylacetonate-t-butyl hydroperoxide-initiated autoxidation of 1-octene. Furthermore Angelescu et al.[133] have shown that chromium (III) acetylacetonate is strongly complexed by aromatic solvents. Accordingly, it is felt that it might be constructive to reinvestigate the autoxidation of metal acetylacetonates and perhaps make a general study of solvent effects in this system.

Some preliminary work has been done using 1-chloro-octane for a solvent. It was observed that a solution of chromium (III) acetylacetonate in 1-chlorooctane picked up oxygen at a slow rate which was attributable only to the chelate. Work is being continued on this system, and it is possible that the order of reactivity or the reaction mechanism will be affected by a solvent change.

# Appendix II

## Free Radical Reactions Involving Hydrogen Abstraction from Metal Acetylacetonates

Gritter and Patmore[171] have shown that free radicals produced from di-t-butyl peroxide can abstract hydrogen atoms from the ligand portion of metal acetylacetonates. Indictor and Linder[45] have suggested that the metal acetylacetonate-t-butyl hydroperoxide-catalyzed polymerization of styrene is initiated by a radical derived from hydrogen abstraction from the chelate.

Although this is a possible mechanism for the chromium (III) acetylacetonate-t-butyl hydroperoxide-initiated autoxidation of 1-octene and the chromium (III) acetylacetonate-catalyzed decomposition of t-butyl hydroperoxide, it was felt that the initiating radical was produced via an oxidation-reduction mechanism because of the demonstrated existence of a Cr(VI) species, and other data which are discussed in this dissertation. Furthermore, the small concentrations of metal employed in these reactions would tend to make attack upon the chelate a negligible reaction, particularly in the systems where the chain lengths are long. It should be noted that the only metal acetylacetonates which react with t-butyl hydroperoxide to catalyze free radical reactions are those which are multivalent[19] and thus the involvement of oxidation-reduction reactions would appear to be important.

# Appendix III

## Possible Applications of the Chromium (III) Acetylacetonate-t-Butyl Hydroperoxide Initiating System

It was shown that chromium (III) acetylacetonate and t-butyl hydroperoxide would initiate the autoxidation of a variety of substrates (see Solvent Effect Section, p. 108 ). In the case of methanol, a product was formed which reacted with 2,4-dinitrophenyl hydrazine to yield the 2,4-dinitrophenyl hydrazone derivitive of formaldehyde.

Although no product study has been done on the autoxidation of compounds other than 1-octene, it would be of interest to obtain data on the yields and specificity of the products of the autoxidation of other substrates.

The free radical addition of small molecules to olefins and other substrates is well known.[172] The mildness of the conditions used in chromium (III) acetylacetonate-t-butyl hydroperoxide initiation might make this a useful tool for studying such reactions.

In addition to the above reactions, this system or other metal acetylacetonate-t-butyl hydroperoxide systems could be used to study a variety of free radical decompositions, isomerizations, and polymerizations.

# Appendix IV

## Recent Studies on Hydroperoxide Decompositions

Quite recently an extensive study of hydroperoxide decompositions initiated in various ways under different conditions was reported by Hiatt and coworkers.[173] This work was too recent to be included in the body of this dissertation, however it would be worthwhile summarizing it here and noting its implications in our work.

In addition to the thermal decomposition of hydroperoxides, various free radical initiators such as di-t-butyl peroxide, di-t-butyl peroxyoxalate, and azobisisobutyronitrile were used to induce hydroperoxide decomposition. A study was also made on metal-hydroperoxide reactions.

Among the hydroperoxides studied were α-tetralyl, α-cumyl, 3-cyclopentenyl, n-butyl, sec-butyl, and t-butyl hydroperoxide. In general, the products observed were those usually noted in hydroperoxide decomposition, i.e., dialkyl peroxides, alcohols, and carbonyl compounds. Although oxygen is often a product of these reactions,[89] its formation was found to be dependent on reaction conditions. In some cases carbon monoxide and carbon dioxide were observed among the products. It was noted that the relative rates of decomposition of tertiary, secondary, and primary hydroperoxides were a function of the reaction conditions. The kinetics were in most cases those which are expected for chain reactions. The rate laws, however, were dependent in many instances on reaction conditions. Chain lengths of 1-50 were observed depending on conditions (higher temperature and hydroperoxide concentration and low viscosity produced longer chain lengths). These authors have defined a chain length as the ratio of the rate of radical attack on hydroperoxide to the rate of termination. Thus the chain length in their case is the rate of formation of propagation products (alcohol and carbonyl compounds) to the rate of formation of termination products (dialkyl peroxide). Although no studies were done by Hiatt et al. on the rate of metal disappearance, this might have indicated a different expression for radical production. The view of this thesis assumes that each molecule of metal that disappears causes the formation of one radical. However, these authors have proposed a cyclic mechanism (Reactions 192, 193) for the initiation process in which the concentration of the original metal ions remains essentially unchanged.

(192) $ROOH + M^{n} \xrightarrow{k_1} RO\cdot + M^{n+1} + OH^-$

(193) $ROOH + M^{n+1} \xrightarrow{k_2} M^{n} + ROO\cdot + H^+$

Although it seems improbable that $k_{192}$ and $k_{193}$ are very much alike,[174] a similar mechanism has been proposed for the cobalt salt induced autoxidation of tetralin.[15] It should be noted, however, that several authors have shown that only certain oxidation states of some metals are effective as catalysts for hydroperoxide decompositions.[19,39,48]

The work of Hiatt et al., although different in many respects from out own, is consistent with several of our observations.

PLEASE NOTE:

Appendix V: Autoxidation of Octene-1 with t-Butyl Hydroperoxide and Metal Acetylacetonates, ©1966 by American Chemical Society, pages 161-163, not microfilmed at request of author. Available for consultation at The City University of New York Library.

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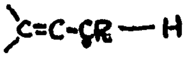
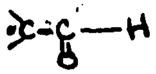
139. From Reference 13 the  bond is 24 kcal/mole stronger than the  bond.

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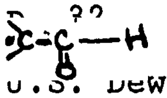
stronger than the 

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