

# Metal-Catalyzed Autoxidation. The Unrecognized Consequences of Metal-Hydroperoxide Complex Formation

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**Abstract:** Although transition metal ions are normally catalysts for autoxidation, they can change very suddenly to potent inhibitors as their concentration rises above a certain sharply defined "critical" level. The reaction  $\text{RO}_2\cdot + \text{M}^{n+} \rightarrow \text{RO}_2^- + \text{M}^{(n+1)+}$  was initially proposed as the explanation of this phenomenon. Although this reaction explains why metals can act as inhibitors at high concentrations, it does not explain some of the most important data associated with the catalyst-inhibitor transition; namely, why it is extremely abrupt, why it is observed only in media of low polarity, and at what metal concentration should it occur. The present paper shows that these observations can all be explained by a mechanism involving initiation through formation of a metal-hydroperoxide catalyst complex. A computer program which demonstrates this is described. The mechanism described here also explains why the assumption of steady-state hydroperoxide concentration at the limiting rate cannot be applied to metal-catalyzed oxidations in media of low polarity. This explanation accounts for experimental observations which previously appeared confusing due to a lack of realization that the Tobolsky-Mesrobian mechanism for the limiting rate is valid only in media of high solvating power such as acetic acid. The new mechanism also explains the pulsation which is sometimes observed in the rate for the early stages of metal-catalyzed oxidations in nonpolar media.

Although a considerable literature dealing with the homogeneous autoxidation of organic compounds catalyzed by transition metal ions has been developed, a number of puzzling phenomena still exist. One example is the ability of transition metals such as Cu, Co, Mn, etc., to change extremely abruptly from catalysts to inhibitors as their concentration in solution is increased.<sup>1-4</sup> This ability has been attributed to the reaction



But, although this reaction explains why the metals can become inhibitors at higher concentrations, it provides a very limited and inadequate explanation of the experimental data associated with reports of this phenomenon. The above reaction does not explain the abruptness of the transition, the concentration at which it occurs, or the fact that the observation of this phenomenon is limited to media of low polarity.

The abruptness of the effect is illustrated by Figure 1, which presents data from Kamiya and Ingold<sup>1</sup> on the oxidation of tetralin at 65 °C, catalyzed by either cobalt or manganese decanoate. Regarding these experiments, Ingold<sup>5</sup> has stated that the transition from rapid reaction to inhibition occurred over such a small concentration range that it was difficult to establish exactly where it took place. A similar observation was made by Knorre et al.<sup>2</sup> for the copper stearate catalyzed oxidation of *n*-decane at 125 °C. He states that as the catalyst concentration increases up to 0.060 mol %, the induction period of the reaction increases gradually and is measured in minutes. With a further increase in the copper stearate concentration of only 0.005 mol %, the reaction practically stops, the induction period becoming longer than 15 h.

Also incompletely explained are observations with respect to the "limiting rate" of metal-catalyzed oxidations. Tobolsky<sup>6</sup> attributed the limiting rate to the fact that hydroperoxides, which initiate and are products of autoxidation, are decomposing as fast as they are being formed. This mechanism was confirmed by Woodward and Mesrobian,<sup>7</sup> who showed that hydroperoxide concentration stops increasing once the limiting rate is reached. The Tobolsky-Mesrobian mechanism is called upon frequently since it is useful in providing an additional, steady-state relationship for the algebraic analysis of reaction mechanisms. But Woodward and Mesrobian used acetic acid as a solvent and other investigators have shown that their results are not reproduced when working in solvents of low polarity.<sup>4,2</sup> Kamiya and Ingold<sup>8</sup> report that in the cobalt-cata-

lyzed oxidation of undiluted tetralin "The hydroperoxide concentration increases fairly steadily throughout the region of the steady maximum rate of oxidation". In a later publication<sup>9</sup> they present plots showing the same type of behavior for tetralin oxidation catalyzed by manganese, nickel, or iron.

A third unexplained phenomenon is the pulsation which is sometimes observed in the early stages of metal-catalyzed oxidations. Figure 2 presents an example of this effect reported by Kamiya and Ingold<sup>9</sup> for the autoxidation of tetralin at 50 °C catalyzed by manganese decanoate and the same effect was noted for cobalt decanoate. At present there is no explanation for pulsating reaction rates in nonpolar environments.

This paper presents theoretical arguments to show that these apparently unrelated and poorly understood phenomena can be explained as direct consequences of the complex formation which takes place between multivalent metal ions and hydroperoxides in media of low polarity. In most cases where these phenomena have been observed, hydroperoxides are demonstrably present. In others, their presence can be suspected since, even though precautions are taken to purify the reactants, it is frequently difficult to completely remove hydroperoxides. By considering the consequences which should result from metal-hydroperoxide complex formation, it is possible to explain why the catalyst-inhibitor transition occurs in such an abrupt manner as the critical metal concentration level is exceeded as well as to predict the expected value for the critical concentration level. Since highly polar molecules such as acetic acid are more effective than hydroperoxides in complexing with metal ions, it can be predicted that abrupt catalyst-inhibitor transitions should not be expected in highly polar solvents. This prediction is consistent with existing data.<sup>1-4</sup> Metal-hydroperoxide complex formation also explains why the Tobolsky-Mesrobian mechanism predicting a constant hydroperoxide concentration after the limiting rate has been reached does not and, in fact, should not be expected to apply to transition metal catalyzed oxidations in media of low polarity. Finally, through a mathematical model based upon initiation via hydroperoxide complex formation it is possible to explain why a pulsation in the reaction rate can be observed in the metal-catalyzed oxidation of pure hydrocarbons.

## I. The Oxidation Mechanism Including Metal-Hydroperoxide Complex Formation

The idea that chain initiation in metal-catalyzed autoxidation is due to the unimolecular decomposition of a complex

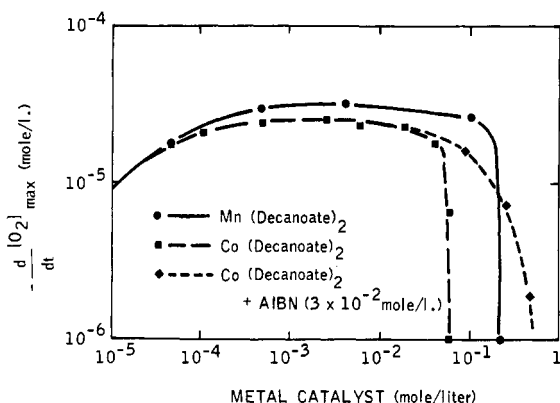
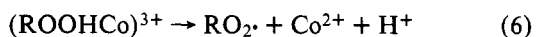
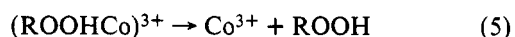
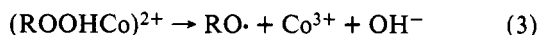
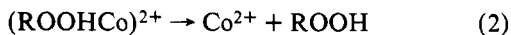


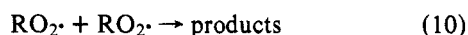
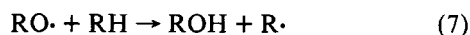
Figure 1. Metal-catalyzed autoxidation of tetralin at 65 °C by Kamiya and Ingold.<sup>1</sup>

between the metal ion and hydroperoxides was proposed in early work by Banks et al.<sup>10</sup> for iron and generalized to other transition metals by Chalk and Smith.<sup>11,12</sup> Additional experimental evidence for this initiation path has since been reported by a number of investigators.<sup>8,9,13,14</sup> Ultraviolet as well as ESR evidence<sup>3</sup> for transition metal-hydroperoxide complexes has been obtained. But although complex formation as the first step in metal ion catalyzed oxidation has often been proposed, its influence on the subsequent course of the reaction, on product distribution, and on the catalyst-inhibitor transition has been largely overlooked.

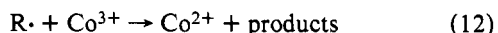
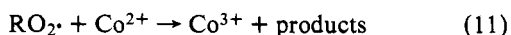
The initiation of autoxidation through catalysis by metal-hydroperoxide complexes is illustrated by the following reactions<sup>15</sup> using cobalt as an example of the multivalent metal.



The course of the reaction subsequent to initiation has received a great deal of attention.<sup>16-19</sup> Chain propagation is usually assumed to proceed by reactions 7-9 and reaction 10 is an accepted termination step.



Two reactions have been proposed to explain the inhibition which is observed in the presence of multivalent ions.<sup>41</sup>



Reaction 11 was proposed in early work by George et al.<sup>22</sup> and this reaction was cited by Kamiya and Ingold<sup>1</sup> to account for the inhibition they observed with cobalt and manganese. Although reaction 12 is probably not important for cobalt or manganese, there is evidence that it predominates over reaction 11 for copper<sup>24-26</sup> and for iron.<sup>27</sup>

The inclusion of the reaction  $\text{RO}\cdot + \text{M}^{n+} \rightarrow \text{RO}^- + \text{M}^{(n+1)+}$  as a termination step parallel to reaction 11 was considered during the course of our studies. It was left out on the basis that it would introduce a needless point of controversy.

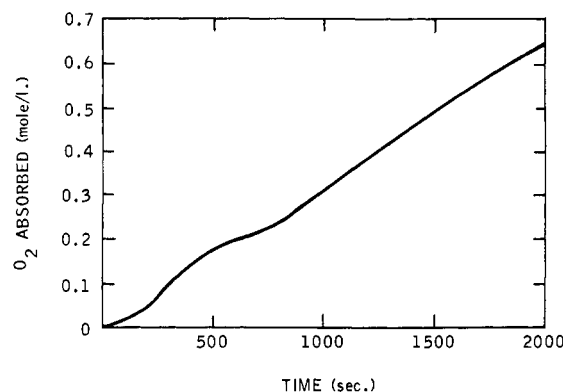


Figure 2. Pulsation in the autoxidation of tetralin at 50 °C, manganese decanoate = 0.3 mol/L,  $[\text{ROOH}]_0 = 0.4$  mol/L. By Kamiya and Ingold.<sup>9</sup>

Its inclusion does not provide an alternative explanation for any of the phenomena being considered here and has little effect upon any of the discussions. In low polarity systems there are also justifiable grounds for questioning its importance in relation to other alkoxy radical reactions.<sup>13</sup>

Another reaction which could be included is  $\text{RO}_2\cdot + \text{M}^{3+} \rightarrow \text{R}^+ + \text{O}_2 + \text{M}^{2+}$  as proposed by Kharasch et al.<sup>20,21</sup> This was omitted for reasons similar to those cited above.

## II. Explanation for the Catalyst-Inhibitor Conversion Phenomenon

As pointed out above, the involvement of metal-hydroperoxide complex formation in the initiation of transition metal catalyzed oxidation has been known for some time and has appreciable experimental support. The influence of complex formation on the subsequent course of the reaction, however, has been largely overlooked. This oversight has apparently resulted from a lack of appreciation of how the formation of the metal-hydroperoxide complex can restrict the concentration of the initiating and inhibiting species.

For example, from reactions 1-6, the initiation rate can be written as

$$R_i = \frac{k_1 k_3}{k_2 + k_3} [\text{Co}^{2+}][\text{ROOH}] + \frac{k_4 k_6}{k_5 + k_6} [\text{Co}^{3+}][\text{ROOH}]$$

This expression has the same outward form as would be obtained from simple bimolecular initiation steps. But there is an important difference in that  $[\text{Co}^{2+}]$ ,  $[\text{Co}^{3+}]$ , and  $[\text{ROOH}]$  are not the initial concentrations at which these species were added, but are the concentrations in equilibrium with the complexes which have formed. This means that under some conditions the availability of  $\text{Co}^{2+}$ , which can act as an inhibitor through reaction 11, can be severely limited.

The manner in which this can occur is illustrated in Figure 3, in which are plotted the equilibrium concentrations of  $[\text{Co}^{2+}]$ ,  $[\text{ROOH}]$ , and  $[\text{ROOHC}]\text{Co}^{2+}$  which would be produced using a total  $[\text{ROOH}]$  of  $5 \times 10^{-2}$  mol/L and a total  $[\text{Co}^{2+}]$  ranging from  $10^{-4}$  to  $10^{-1}$  mol/L. Results are presented for equilibrium constants of  $10^3$ ,  $10^5$ , and  $10^7$ . For the sake of simplicity, redox equilibrium between  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  can be ignored.

Taking the curve for  $K = 10^5$ , if the total cobalt concentration is  $1.0 \times 10^{-4}$  mol/L, most of the Co originally introduced as  $\text{Co}^{2+}$  is complexed with the peroxide and the concentration of uncomplexed  $\text{Co}^{2+}$  is only about  $2 \times 10^{-8}$  mol/L. If the total cobalt concentration were to be increased, the equilibrium concentration of uncomplexed  $\text{Co}^{2+}$  would remain low as long as the total metal concentration is less than that of the peroxide. However, when the initial total cobalt is increased by a factor of 4 between  $2 \times 10^{-2}$  and  $8 \times 10^{-2}$  mol/L, the

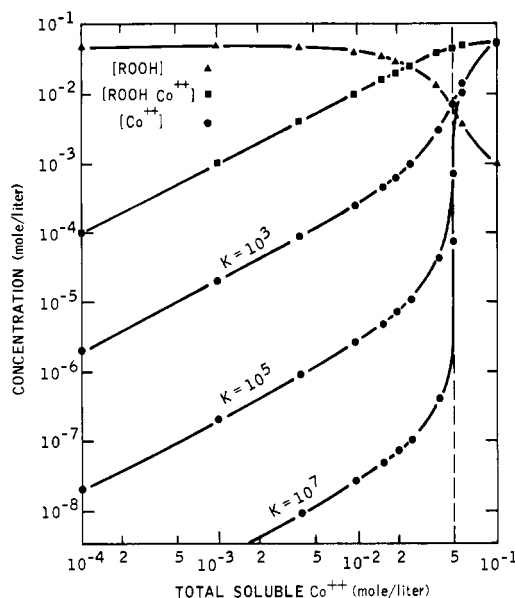


Figure 3. Effect of complex formation on  $[Co^{2+}]$  concentration,  $[ROOH]_0 = 5 \times 10^{-2}$  mol/L,  $K = [ROOHC^{2+}]/[Co^{2+}][ROOH]$ .

equilibrium concentration of uncomplexed  $Co^{2+}$  increases by a factor of 4500, going from  $6.7 \times 10^{-6}$  up to  $3.0 \times 10^{-2}$  mol/L. This means that in a series of experiments in which the total cobalt concentration is continually increased, as the total metal concentration exceeds that of the total peroxide, the equilibrium concentration of a powerful inhibitor (uncomplexed  $Co^{2+}$ ) increases suddenly to the point at which the oxidation can no longer proceed. The change in the equilibrium concentration of uncomplexed  $Co^{2+}$  which can be brought about by a fourfold change in total cobalt is given in Table I for equilibrium constants varying from  $10^3$  to  $10^8$ .

The preceding analyses show that if the consequences of hydroperoxide complex formation are taken to their logical conclusion, it can be seen why the transition from catalysis to inhibition should be abrupt and that this transition should occur near where the concentration of the transition metal exceeds that of the hydroperoxide. This theory is consistent with the shape of Kamiya and Ingold's<sup>1</sup> curves in Figure 1. It is also consistent with the concentration at which they observe the transition to inhibitor to take place.

The catalyst concentrations at which induction periods are observed with transition metal catalyzed reactions in nonpolar media are also explained by this theory. In studying the oxidation of various pure paraffins and olefins in the presence of  $5 \times 10^{-5}$  to  $2 \times 10^{-4}$  mol/L of cobalt as a catalyst, Betts and Uri<sup>4</sup> state that "the minimum cobalt concentration at which an induction period occurs is lower, the greater the purity of the substrate". Kamiya and Ingold<sup>9</sup> observe that the induction period for the manganese-catalyzed oxidation of tetralin is effectively eliminated when the Mn to ROOH ratio is less than one.

A transition from catalysis to inhibition requires that the chain length,  $L$ , becomes less than unity. From the assumption that reaction 11 as well as 10 are the important chain termination steps,

$$L = \frac{k_9[RH]}{k_{10}[RO_2^*] + k_{11}[Co^{2+}]}$$

According to Howard,<sup>28</sup> an acceptable value of  $k_9$  is  $5.6 \times 10^6 e^{-8300/RT} M^{-1} s^{-1}$ , which would make  $k_9 = 24.2 M^{-1} s^{-1}$  at 65 °C. Howard also reports (Table 40, p 134) that Tochina et al.,<sup>35</sup> using chemiluminescence techniques, found  $k_{11}$  to be  $3.8 \times 10^5 M^{-1} s^{-1}$  for the reaction of  $Co^{2+}$  with ethylbenzylperoxy radicals at 60 °C. On the same page, Howard cites

Table I. Rapid Change in Equilibrium  $Co^{2+}$  at Critical Concentration Level<sup>a</sup>

$([ROOH]_0 = 5 \times 10^{-2}; K = [ROOHC^{2+}]/[Co^{2+}][ROOH])$			
$K$	Free $Co^{2+}$ when total Co is		Free $Co^{2+}$ increases by
	$2 \times 10^{-2}$	$8 \times 10^{-2}$	
$10^3$	$6.32 \times 10^{-4}$	$3.15 \times 10^{-2}$	50
$10^4$	$6.63 \times 10^{-5}$	$3.02 \times 10^{-2}$	455
$10^5$	$6.66 \times 10^{-6}$	$3.00 \times 10^{-2}$	$4.5 \times 10^3$
$10^6$	$6.67 \times 10^{-7}$	$3.00 \times 10^{-2}$	$4.5 \times 10^4$
$10^7$	$6.67 \times 10^{-8}$	$3.00 \times 10^{-2}$	$4.5 \times 10^5$

<sup>a</sup> Units are mol/L.

evidence obtained by Gol'dberg and Obukhova<sup>45</sup> that the quenching of chemiluminescence by  $Co^{2+}$  salts can produce values of  $k_{11}$  which are an order of magnitude high. Taking these factors into consideration it would seem that an acceptable value of  $k_{11}$  for the reaction of  $Co^{2+}$  with tetralinperoxy radicals at 65 °C would be about  $1 \times 10^5 M^{-1} s^{-1}$ . It would therefore be expected that at 1.22 mol/L tetralin, the chain length,  $L$ , should become less than unity and inhibition should result when the concentration of uncomplexed  $Co^{2+}$  becomes greater than  $3 \times 10^{-4}$  mol/L. The fact that this value is two orders of magnitude less than the cobalt concentration at which the onset of inhibition was observed by Ingold in Figure 1 is further evidence that the  $Co^{2+}$  available for inhibition through reaction 11 is actually only a small fraction of the total dissolved cobalt.

Although  $Co^{2+}$  and  $Co^{3+}$  have been written as the bare ions in eq 1-12 and the complex has been written in simplified form, it is recognized that transition metal ions such as cobalt must actually be present in a more highly coordinated state. In solvents of moderate or high polarity, carboxylate salts of these transition metals have been established usually to be dimers, sometimes of mixed valence.<sup>29,30</sup> These are prevented from agglomerating into micelles by coordination with solvent molecules.

Micelle formation is adopted by Kagami<sup>31</sup> to explain the data presented in Figure 4. He attributes his results to a loss of catalysis due to the formation of soap micelles which are catalytically inactive. This explanation does not go far enough since Kamiya and Ingold<sup>1</sup> present evidence that the metals act as true inhibitors at concentrations above the critical level. Their dotted line in Figure 1 shows that in the presence of  $3 \times 10^{-2}$  mol/L of azobisisobutyronitrile (AIBN), high cobalt concentrations reduce the oxidation rate below the value found for AIBN alone.

In solvents of low polarity, the micelle formation observed by Kagami should be expected when the critical concentration is exceeded. As pointed out above, the transition metal dimers are protected against agglomeration into micelles by compounds of moderate or high polarity which can preferentially occupy the coordination positions through which agglomeration takes place. Below the critical metal concentration the hydroperoxides fulfill this protective role. Micelle formation should be expected above the critical concentration, however, since that is the first point at which soap dimers not complexed with hydroperoxide can appear at concentrations high enough for agglomeration into micelles to occur. The molecular weight effect observed by Kagami is not, therefore, a cause of the catalyst-inhibitor transition but is a parallel effect of metal-hydroperoxide complex formation.

The inhibition mechanism proposed in this paper, involving the formation of stable metal-hydroperoxide complexes, is not expected to apply to oxidations in polar solvents. Although hydroperoxides can replace solvent molecules of low or moderate polarity<sup>29,30</sup> in complexing with transition metals, they compete poorly with highly polar molecules such as acetic acid.

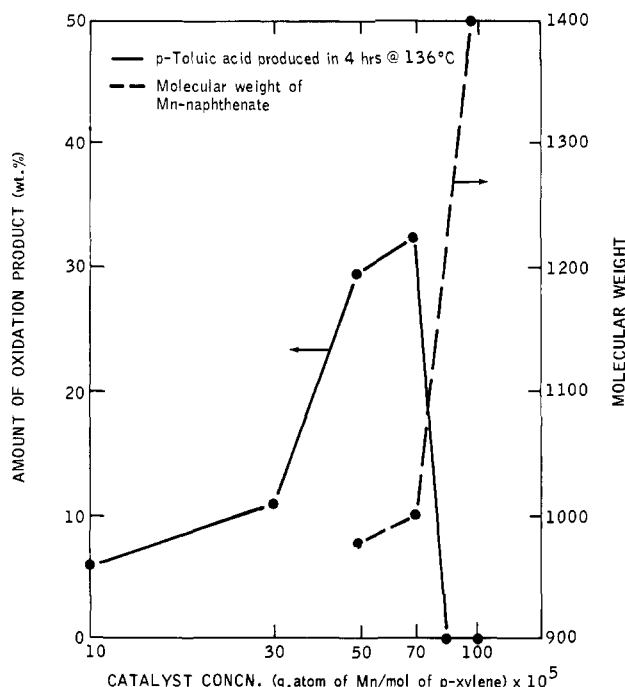


Figure 4. Relation between the concentration of manganese naphthenate, its activity for catalyzing xylene autoxidation, and its molecular weight by Kagami.<sup>31</sup>

Table II. Existence of Extended Induction Periods in Tetralin Oxidation<sup>a</sup>

Solvent	No oxidn obsd in 3000-5000 s	Immediate or slightly delayed oxidn
<i>n</i> -Decane	X	
Carbon tetrachloride	X	
<i>tert</i> -Butylbenzene	X	
Benzene	X	
Acetic acid		X
Chlorobenzene	X	
<i>tert</i> -Butyl alcohol	X	
<i>o</i> -Dichlorobenzene	X	
Nitrobenzene		X
Dimethyl phthalate		X
Nitromethane		X
Acetonitrile		X

<sup>a</sup> 0.35 mol tetralin/L;  $5 \times 10^{-2}$  mol tetralin hydroperoxide/L;  $5 \times 10^{-2}$  mol cobalt decanoate/L.

Consequently, the phenomenon of an extremely abrupt transition from catalysis to inhibition should be observed only in media of low polarity.

That this is the case is demonstrated in Table II, taken from Kamiya and Ingold,<sup>1</sup> which shows the inhibition periods observed for the oxidation of 0.35 mol/L of tetralin in a variety of solvents in the presence of  $5 \times 10^{-2}$  mol/L of both tetralin hydroperoxide and cobalt decanoate. The solvents are arranged in order of increasing oxidation rate when the reaction is initiated by azobisisobutyronitrile. It can be seen that long induction periods were observed only in solvents of relatively low solvating capability. The inhibition mechanism based upon metal hydroperoxide formation explains why the data line up in this manner.

### III. A Computer Program for Transition Metal Catalyzed Liquid Phase Autoxidation

Algebraic analyses based upon steady-state approximations were employed to a limited extent in the previous discussions.

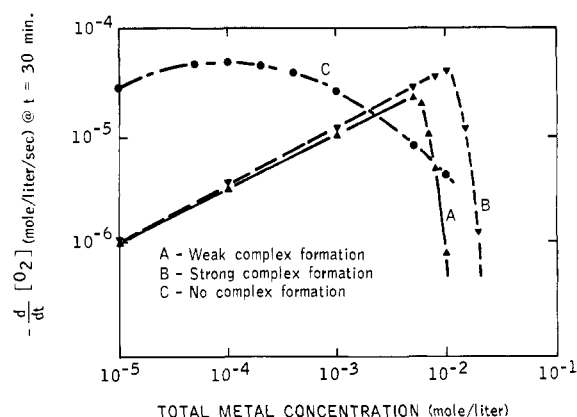
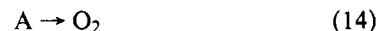


Figure 5. Computer program output for metal-catalyzed tetralin autoxidation at 65 °C and 1 atm O<sub>2</sub> [ROOH]<sub>0</sub> =  $10^{-2}$  mol/L.

However, a complete algebraic analysis of the results which would be predicted by reactions 1-12 produces equations which are too complicated to be of much value. One reason for this is that bimolecular chain termination through reaction 10 leading to quadratic expressions for [RO<sub>2</sub>•] must be included in the kinetics over the concentration range where the transition from metal catalysis to metal inhibition takes place. Also, the assumption of steady-state peroxide concentration at constant limiting rate cannot be used to simplify the analysis in view of theoretical and experimental considerations which will be discussed in a later section.

The chemical effects which should result from the mechanism have been analyzed successfully, however, through a computer model for liquid-phase oxidation which is yielding very useful and credible results. The model is based upon a computer program developed by Laurendeau and Sawyer<sup>32</sup> for modeling gas-phase combustion processes. A description is provided in Appendix A.

In applying this program to determine the results which should be predicted by the mechanism outlined in reactions 1-12, three additional reactions were included.



Equation 13 takes recognition of radical-induced hydroperoxide decomposition. The last two equations are used to establish a steady-state concentration of dissolved oxygen.

This program has been applied to test the extent to which the mechanism outlined in reactions 1-15 is capable of reproducing the extremely abrupt catalyst to inhibitor conversion reported by Kamiya and Ingold<sup>1</sup> for the cobalt-catalyzed oxidation of tetralin in chlorobenzene solution at 65 °C (Figure 1). The rate constants used for reactions 1-15 and the source for each are presented in Table III. The initial hydroperoxide concentration was put at the maximum level permitted by stability considerations as discussed in Appendix A, namely,  $1.0 \times 10^{-2}$  mol/L. The results are presented in Figure 5.

Curve A, which is the result of assuming weak complex formation ( $K = 2 \times 10^3$ ) characteristic of cobalt, shows an abrupt change from catalysis to inhibition followed by a catastrophic decline in reaction rate at a total metal concentration slightly below that of the hydroperoxide in the system. This behavior is similar to that observed experimentally for cobalt (Figure 1) and is consistent with the inhibition reported in Table II for equal concentrations of cobalt decanoate and of tetralin hydroperoxide in nonpolar solvents.

The effect of hydroperoxide complex formation in causing this phenomenon is illustrated in Figure 6. Here curve A from

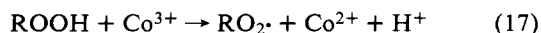
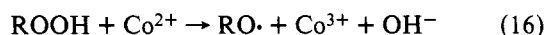
**Table III.** Rate Constants ( $\text{mol L}^{-1} \text{s}^{-1}$ ) Used for the Metal-Catalyzed Oxidation of Tetralin in Nonpolar Media at 65 °C

Eq	Reaction	$k$ (65 °C)	Source
(1)	$\text{Co}^{2+} + \text{ROOH} \rightarrow (\text{ROOHC}\text{Co})^{2+}$	40	Selected to give an equilibrium $K$ of $2 \times 10^3 \text{ mol}^{-1} \text{ L}$ which is consistent with the data from ref 8, p 2036, Figure 3, while $k_2$ gives a dissociation rate ten times decomposition.
(2)	$(\text{ROOHC}\text{Co})^{2+} \rightarrow \text{Co}^{2+} + \text{ROOH}$	$2 \times 10^{-2}$	
(3)	$(\text{ROOHC}\text{Co})^{2+} \rightarrow \text{RO}\cdot + \text{Co}^{3+} + \text{OH}^-$	$2 \times 10^{-3}$	Selected to give oxidation rates consistent with ref 1.
(4)	$\text{Co}^{3+} + \text{ROOH} \rightarrow (\text{ROOHC}\text{Co})^{3+}$	40	Same as for 1–3 for $\text{Co}^{2+}$ . In the absence of data on the relative reactivity of $\text{Co}^{2+}$ and $\text{Co}^{3+}$ this assumption has been made for the sake of simplicity.
(5)	$(\text{ROOHC}\text{Co})^{3+} \rightarrow \text{Co}^{3+} + \text{ROOH}$	$2 \times 10^{-2}$	
(6)	$(\text{ROOHC}\text{Co})^{3+} \rightarrow \text{RO}_2\cdot + \text{Co}^{2+} + \text{H}^+$	$2 \times 10^{-3}$	
(7)	$\text{RO}\cdot + \text{RH} \rightarrow \text{ROH} + \text{R}\cdot$	$1 \times 10^6$	$6.5 \times 10^5$ at 40 °C <sup>33,34</sup> gives $1 \times 10^6$ at 60 °C (corresponds to $\Delta E = 3.6 \text{ kcal}$ )
(8)	$\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$	$3 \times 10^8$	Reference 18
(9)	$\text{RO}_2\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$	24	$k_{(9)} = 5.6 \times 10^6 e^{-8300/RT}$ , ref 28, p 101.
(10)	$\text{RO}_2\cdot + \text{RO}_2\cdot \rightarrow \text{products}$	$6.6 \times 10^6$	$k_{(10)} = 4.0 \times 10^9 e^{-4300/RT}$ , ref 28, p 101.
(11)	$\text{RO}_2\cdot + \text{Co}^{2+} \rightarrow \text{Co}^{3+} + \text{products}$	$1 \times 10^5$	From Table 40 and discussion on p 134, ref 28; also ref 35.
(12)	$\text{R}\cdot + \text{Co}^{3+} \rightarrow \text{Co}^{2+} + \text{products}$	$5 \times 10^4$	Since $\text{Co}^{2+}$ has been established as the inhibiting valence state <sup>13,46</sup> this is assigned a rate slower than reaction 11.
(13)	$\text{RO}\cdot + \text{ROOH} \rightarrow \text{ROH} + \text{RO}_2\cdot$	$1 \times 10^7$	Reported to be about $4 \times 10^6$ at 30 °C <sup>36</sup> (corresponds to $\Delta E = 5.3 \text{ kcal}$ )
(14)	$\text{A} \rightarrow \text{O}_2$	$1 \times 10^{-4}$	Selected to give an equilibrium concentration of $\text{O}_2$ of $6.7 \times 10^{-3} \text{ mol/L}$ . This is the $\text{O}_2$ solubility calculated using the method of solubility parameters <sup>37</sup> for 1.22 mol/L tetralin in chlorobenzene at 65 °C in contact with pure oxygen at 1 atm.
(15)	$\text{O}_2 \rightarrow \text{A}$	$1.6 \times 10^2$	

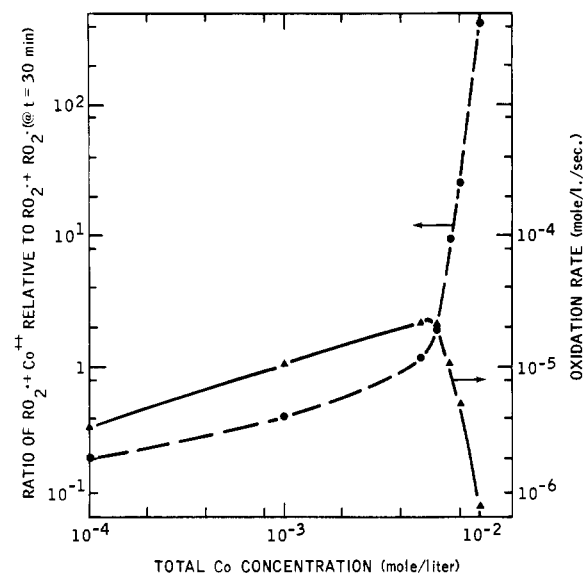
Figure 5 is compared with the ratio of the calculated rates of chain termination by  $\text{Co}^{2+}$  vs. bimolecular termination (reaction 11 vs. 10). This comparison demonstrates how the abrupt change from catalysis to inhibition is associated with a sudden increase in the importance of  $\text{Co}^{2+}$  termination as would have been predicted from Figure 3.

Curve B in Figure 5 presents the behavior calculated for strong complex formation. This output is produced by reducing the rate constants for reactions 2 and 5 down to  $1.0 \times 10^{-7} \text{ s}^{-1}$ , which requires that once a complex is formed, it will almost always decompose to radicals rather than dissociate into the hydroperoxide and the ion. The other constants remain the same. The transition from catalysis to inhibition now takes place at a higher metal concentration. Behavior similar to this is exhibited by manganese in Figure 1. This observation is consistent with the fact that in experiments parallel to those described for Co in Table II, Kamiya and Ingold<sup>1</sup> found that Mn very seldom produced inhibition. Strong complex formation is also consistent with the reaction rate pulsation experienced with Mn<sup>9</sup> as will be discussed in a later section.

Curve C in Figure 5 presents the behavior calculated by ignoring complex formation and adopting the assumption of previous investigators,<sup>1,2</sup> namely, that the catalyst-inhibitor conversion phenomenon can be explained entirely by inhibition through reaction 11 at high metal concentrations. These results were produced by replacing reactions 1–6 with an initiation scheme similar to that suggested by Haber and Weiss<sup>38</sup> for aqueous phase hydroperoxide decomposition.



The rate constant for each of these reactions was taken to be  $40 \text{ mol L}^{-1} \text{s}^{-1}$ , a value which produced calculated maximum oxidation rates equivalent to those observed by Kamiya and Ingold.<sup>1</sup> The rate constants for reactions 7–15 were unchanged. It can be seen that in the absence of metal-hydroperoxide complex formation the catalyst-inhibitor conversion would not be abrupt and the oxidation rate is predicted to decline at

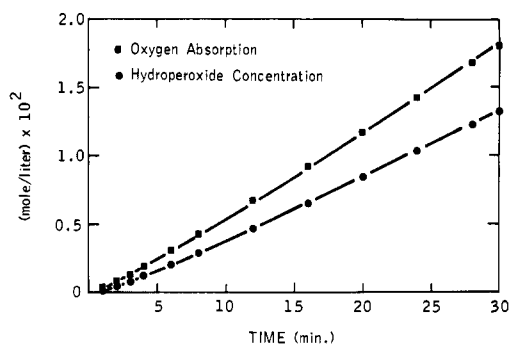


**Figure 6.** Computed autoxidation rate for cobalt-catalyzed tetralin autoxidation at 65 °C and 1 atm  $\text{O}_2$  (curve A from Figure 5) vs. chain termination by  $\text{Co}^{2+}$ ,  $[\text{ROOH}]_0 = 10^{-2} \text{ mol/L}$ .

a total metal concentration much lower than that which is observed.

#### IV. The Limiting Oxidation Rate

Autoxidations are characterized by reaction velocities which finally level off at a "limiting" rate. This behavior was initially attributed by Tobolsky<sup>6</sup> to the fact that hydroperoxides have reached a steady state. This mechanism was confirmed by Woodward and Mesrobian<sup>7</sup> in experiments on the cobaltous acetate catalyzed oxidation of tetralin in acetic acid. The mechanism has proved useful in providing an additional steady-state relationship to simplify the algebraic treatment of autoxidation kinetics. Its application leads to the expres-



**Figure 7.** Computed oxygen absorption vs. hydroperoxide formation for Co-catalyzed tetralin autoxidation at 65 °C and 1 atm O<sub>2</sub> with weak complex formation (curve A in Figure 5), [ROOH]<sub>0</sub> = 10<sup>-2</sup> mol/L; total Co = 5 × 10<sup>-3</sup> mol/L.

sion

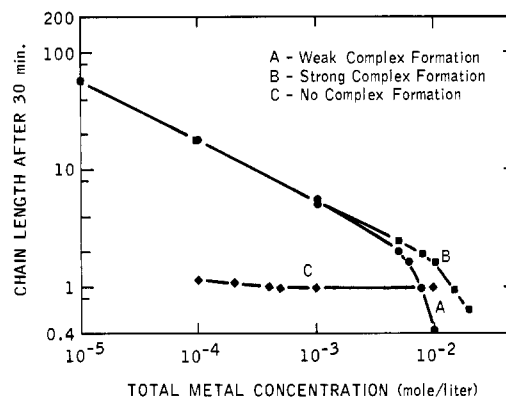
$$\lim_{t \rightarrow \infty} \frac{-d[RH]}{dt} [RH] = \frac{n k_p^2}{f 2k_t} [RH]^2$$

where  $n$ , the average number of initiating radicals per ROOH decomposed, and  $f$ , the fraction of RH consumed by reaction with peroxy radicals, are generalizations suggested by Walling.<sup>39</sup> The rate constants  $k_p$  and  $k_t$  are for propagation and termination, respectively.

This rate expression is presented by most authors as the accepted explanation for the limiting rate in metal ion catalyzed oxidations without mentioning that it has been confirmed only in media of high solvating capability. On the contrary, when deviations from the Tobolsky–Mesrobian mechanism have been encountered in the oxidation of nonpolar materials such as pure hydrocarbons, these deviations have been explained away as due to experimental artifacts. For example, in their thorough confirmation of the existence of steady-state hydroperoxide concentration under limiting rate conditions for cobalt-catalyzed oxidations carried out in acetic acid solution, Woodward and Mesrobian<sup>7</sup> attribute reported observations of continued hydroperoxide buildup after the limiting rate has been established in the cobalt-catalyzed oxidation of pure tetralin to “experimental difficulties”. Kamiya, Ingold, et al. carried out a detailed study of the validity of the Tobolsky–Mesrobian mechanism in media of differing polarity.<sup>1,8,9,42</sup> They confirm Mesrobian’s results in acetic acid solution.<sup>42</sup> But with respect to the metal ion catalyzed oxidation of pure tetralin, they report that with Co, Ni, Mn, and Fe the hydroperoxide concentration is observed to increase steadily even after the oxidation rate (as evidenced by O<sub>2</sub> absorption) has leveled off at a limiting value.<sup>9</sup> Various mechanisms, such as catalyst deactivation, were tried to account for these observations but none of them could provide very satisfactory agreement between the data and the Tobolsky–Mesrobian mechanism.

The mechanism proposed in this paper to provide a more complete understanding of catalyst-inhibitor conversion phenomena can also be applied to dispel the confusion just discussed. This mechanism discloses why a steadily increasing hydroperoxide concentration should be expected under limiting rate conditions in pure hydrocarbons or in solvents of low polarity, and accounts for the fact that this relationship differs from that predicted and confirmed by Tobolsky and Mesrobian in polar solvents.

When an oxidation has reached its limiting rate it is obviously not inhibited but is proceeding rapidly. For this to occur in media of low polarity the metal ion concentration must be below the critical level so that the hydroperoxide concentration is in excess. Under these conditions, the rate of reaction will level off after a time owing to the fact that a steady rate of



**Figure 8.** Computed chain length at 1800 s vs. total metal concentration for curves A, B, and C in Figure 5.

initiation has been established by redox equilibrium between the hydroperoxide complexes of the higher and lower valence ions. If the concentration of hydroperoxide is already in excess, the concentrations of each of these catalyst complexes will be limited by the total concentration of the respective ion. Hydroperoxide concentration, therefore, can and should continue to increase without changing the rate of oxidation since the concentration of the initiators (i.e., the metal ion hydroperoxide complexes) will not be affected.

This expected behavior is exhibited in the output from our computer program presented in Figure 7. The conditions are the same as those taken for weak complex formation (curve A in Figure 5). The output in Figure 7 shows that the oxygen rate levels off after 15 min but the hydroperoxide concentration continues to rise. As mentioned previously, the constant rate of reaction results from the establishment of a constant rate of initiation due to the steady-state concentration of each metal-hydroperoxide complex. Since the termination rate equals the initiation rate, the concentration of [RO<sub>2</sub>·] radicals is also in steady state. The chain length is constant but is not unity, as can be seen from Figure 8, which presents the chain length observed at 30 min reaction time for the conditions leading to each of the three curves in Figure 5. The reaction relationships which produce a constant chain length greater than unity after a constant maximum oxidation rate has been reached are illustrated in Table IV, which presents results from our computer program for a metal-catalyzed oxidation with strong complex formation.

The limiting rate behavior which results from the assumption that no hydroperoxide complex formation is involved in the initiation (the same conditions as curve C in Figure 5) is shown in Figure 9. After 30 min, the oxygen is being absorbed at a constant rate and the hydroperoxide concentration has also become constant. As suggested by Tobolsky,<sup>6</sup> this occurs because hydroperoxide is decomposing as fast as it is being formed. Such a balance requires that the chain length be unity under the control of either reaction 10 (RO<sub>2</sub>· termination) and/or reaction 11 (Co<sup>2+</sup> + RO<sub>2</sub>· termination), depending upon the total Co concentration. That this is the case is shown by curve C in Figure 8. Under the reaction conditions represented by the lower concentration end of curve C, the limiting rate has not quite been reached after 30 min of reaction.

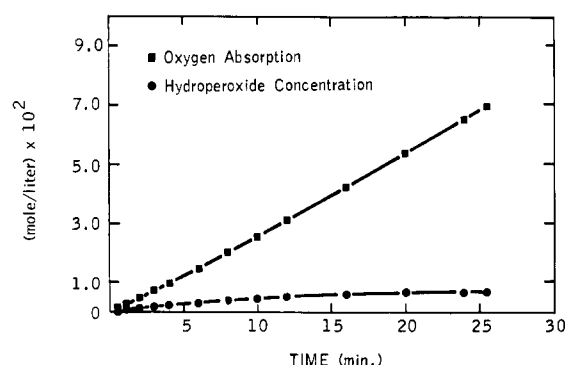
## V. Reaction Rate Pulsation

Figure 2 presented an example of the pulsation observed by Kamiya and Ingold<sup>9</sup> for the autoxidation of tetralin at 50 °C with manganese decanoate as the catalyst. For media of low polarity, this type of behavior is readily explainable through the assumption of metal complex formation.

Under appropriate conditions, a pulsation in the reaction rate is produced by our computer program. This effect is fa-

**Table IV.** Course of Reaction<sup>a</sup> with Total Metal =  $1 \times 10^{-3}$ ;  $[\text{ROOH}]_0 = 1 \times 10^{-2}$  (Strong Complex Formation—Curve B in Figure 5)

Reaction time, min	1	2	4	12	24	30
Chain length	5.704	5.669	5.647	5.615	5.592	5.587
Rate of						
$(\text{R} \cdot + \text{O}_2) \times 10^5$	1.316	1.303	1.265	1.214	1.199	1.195
$(\text{RO}_2 \cdot + \text{RH}) \times 10^5$	1.139	1.136	1.128	1.119	1.116	1.114
$(\text{RO}_2 \cdot + \text{RO}_2 \cdot) \times 2 \times 10^6$	1.979	1.971	1.947	1.935	1.952	1.958
$(\text{RO}_2 \cdot + \text{M}^{2+}) \times 10^8$	1.811	3.294	5.000	5.681	4.293	3.820
Concn of						
$[\text{ROOH}] \times 10^2$	0.923	0.979	1.089	1.526	2.177	2.501
$[\text{M}^{2+}] \times 10^3$		0.001	0.001	0.001	0.001	0.001
$[\text{M ROOH}^{2+}] \times 10^3$	0.895	0.808	0.685	0.513	0.489	0.488
$[\text{M}^{3+}] \times 10^3$	0.005	0.004	0.003	0.002	0.001	0.001
$[\text{M ROOH}^{3+}] \times 10^3$	0.100	0.187	0.310	0.483	0.509	0.510

<sup>a</sup> Data in  $\text{mol L}^{-1} \text{s}^{-1}$ .**Figure 9.** Same conditions as Figure 7 except that no complex formation is assumed (curve C in Figure 5) and total Co =  $5 \times 10^{-5}$  mol/L.

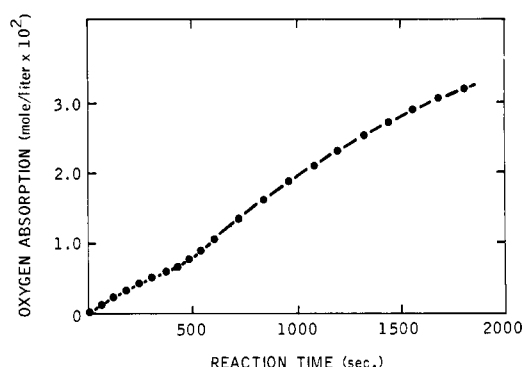
vored by metal concentrations which are close to the initial hydroperoxide concentration level. A pulsation similar to the Kamiya and Ingold curve is presented in Figure 10, which presents results using the rate constants which produced curve B in Figure 5.

Detailed results from our computer program show why a pulsation in the reaction can be observed. The changing oxidation rate which is responsible for this pulsation is presented as the lower curve of Figure 11. The kinetic relationships which produce the inflections in the reaction rate curve can be understood by considering the other curves in Figures 11 and 12.

During the first 7.5 min, the computed reaction rate is declining since hydroperoxide is being decomposed in the initiation step faster than it is being regenerated (chain length is less than unity). The  $\text{Mn}^{2+}$  concentration is also declining, however, owing to conversion to  $\text{Mn}^{3+}$ . During this early period,  $\text{Mn}^{3+}$  cannot act as an initiator since the available ROOH is already tied into the very stable  $[\text{ROOHMn}]^{2+}$  complex.

The reaction rates responsible for the chain length are shown in Figure 12, where it can be seen that, initially, the chain length is increasing. After about 7.5 min reaction time, the concentration of uncomplexed  $\text{Mn}^{2+}$  declines past the level at which the rate of termination by uncomplexed  $\text{Mn}^{2+}$  becomes less than the propagation rate and the chain length becomes greater than unity. New hydroperoxide is now being produced which permits  $\text{Mn}^{3+}$  to enter into complex formation and act as an initiator. An abrupt, discontinuous increase in the computed reaction rate results at this point.

The growth in the chain length is soon limited, however, as the importance of bimolecular  $\text{RO}_2 \cdot$  termination (reaction 10) grows to a level at which it accounts for about 40% of the  $\text{RO}_2 \cdot$  removal. The chain length levels off and begins to drop slowly due to the  $\text{Mn}^{2+}$  concentration starting to increase as the rate of initiation by  $[\text{ROOHMn}]^{3+}$  decomposition (reaction 6) surpasses the sum of the  $[\text{ROOHMn}]^{2+}$  decomposition (re-

**Figure 10.** Computed rate for metal-catalyzed tetralin autoxidation at 65 °C and 1 atm  $\text{O}_2$  with strong metal-hydroperoxide complex formation,  $[\text{ROOH}]_0 = 10^{-2}$  mol/L,  $[\text{Mn}^{2+}] = 1.5 \times 10^{-2}$  mol/L.

action 3) and the  $\text{Mn}^{2+}$  termination (reaction 11). The important factor in establishing the time constant for pulsation is the rate of dissociation of the metal-hydroperoxide complex.

## VI. Inhibition by the Higher Valence Ion

In the autoxidation reactions just discussed involving Co or Mn as the catalyst/inhibitor, there is considerable evidence that inhibition is due to  $\text{RO}_2 \cdot$  oxidation of the metal in its lower valence state through reaction 11. However, this behavior is not characteristic of all transition metals.

In a thorough study of the copper-catalyzed decomposition of hydroperoxides, Kochi<sup>13,24-26</sup> established that  $\text{Cu}^+$ , the lower valence ion, acts as the catalyst while  $\text{Cu}^{2+}$  acts as a chain terminating agent by scavenging hydrocarbon radicals. When a cuprous salt was used as the catalyst, the decomposition started immediately. The use of the cupric salt always produced an induction period. Walling<sup>27</sup> shows a similar situation holding for iron with  $\text{Fe}^{3+}$  ion being the hydrocarbon radical scavenger.

The mechanism described by reactions 1-13 can also be applied when the higher valence ion is the inhibitor by adopting a large rate for reaction 12 and an appropriately smaller rate for reaction 11. Similar principles apply in establishing the presence of a critical concentration level and our computer model has been used to show that an abrupt, catastrophic decline in reaction rate can be predicted. There are, however, important differences between this case and that for which the lower valence ion is the inhibitor.

With a metal such as Co, for example, the requirement for inhibition is that  $\text{Co}^{2+}$  ions are reacting more rapidly than RH with  $\text{RO}_2 \cdot$  radicals. This means that termination by reaction 11 is more rapid than chain propagation by reaction 9 and that  $[\text{Co}^{2+}] > k_9[\text{RH}]/k_{11}$ . For undiluted tetralin at 65 °C, using the rate constants from Table III, the minimum  $[\text{Co}^{2+}]$  which

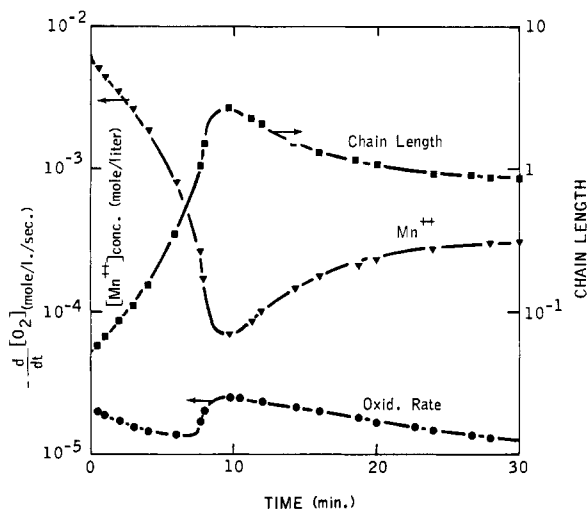


Figure 11. Reaction characteristics responsible for the rate pulsation in Figure 10.

can satisfy this equation turns out to be  $1.76 \times 10^{-3}$  mol/L and inhibition cannot be produced by  $\text{Co}^{2+}$  ions below this concentration.

With metals for which the higher valence ion is the inhibitor (e.g., Cu), inhibition requires that the  $\text{Cu}^{2+}$  ion be capable of competing with  $\text{O}_2$  for R· radicals. It is therefore necessary that  $[\text{Cu}^{2+}] > k_8[\text{O}_2]/k_{12}$ . This is a different and more severe requirement than for metals such as Co. The rate of reaction 8 is considered close to diffusion limited<sup>18</sup> and with Cu the rate of reaction 12 is somewhat less.<sup>40</sup> Since the solubility of pure  $\text{O}_2$  in hydrocarbons is of the order of  $7 \times 10^{-3}$  mol/L,<sup>37</sup> the minimum concentration for inhibition by  $\text{Cu}^{2+}$  would probably lie within an order of magnitude of  $10^{-1}$  mol/L. At high temperatures where the reverse of reaction 8 becomes significant or under conditions of reduced oxygen availability,  $\text{Cu}^{2+}$  can act as an inhibitor at concentrations appreciably below  $10^{-1}$  mol/L.

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#### Appendix A. Computer Program for Modeling Liquid-Phase Autoxidation

The development of a computer program for predicting the course of liquid-phase autoxidation was not a primary aim of the present research. But as noted in the text, some method was needed for evaluating the significant consequences of the mechanism described by reactions 1–13. It is fortunate that a well-proven program for predicting the course of gas reactions was available<sup>32</sup> and could be adopted to liquid phase.

The program is capable of operating in an isothermal, constant volume mode with concentrations expressed in moles/unit volume. Liquid-phase reaction conditions were simulated by employing a pressure sufficient to produce liquid-phase molal concentrations. This procedure should provide a satisfactory treatment for liquid systems in which the reaction rate constants can be considered to be pressure independent.

The rate equations are of the form  $d[y_i]/dt = f_i([y_i], t)$  where  $[y_i]$  is the concentration of the  $i$ th reactant. The terms of  $f_i([y_i], t)$  which are not unimolecular may contain the concentration of reactants other than  $y_i$ . The stability of the integration is defined by the values of  $S_i = h\partial f_i/\partial y_i$  where  $h$  is the current time step size. For stability it is necessary that  $-1.4 < S_i < 0$  for all values of  $S_i$  and the program controls the value of  $h$  so that this relationship is satisfied. Minor species

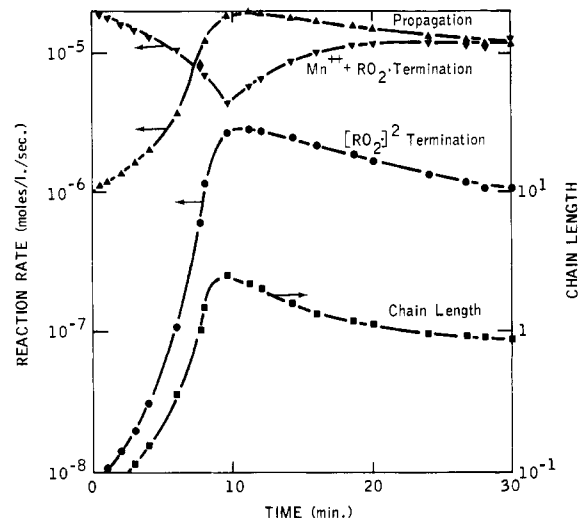


Figure 12. Reactions contributing to chain length in Figure 11.

which have a large negative value for  $\partial f_i/\partial y_i$  can be handled by a steady-state analysis procedure so that they do not excessively limit the size of the time steps. This approach is satisfactory for species such as free radicals for which the steady-state assumption might be expected to apply. It cannot be applied, however, to major constituents, which has prevented application of the program to metal or peroxide concentrations much above  $10^{-2}$  mol/L without incurring excessive computer time.

Major inputs to the program are the pressure, temperature, the rate equations, the rate constants (which can be in temperature-dependent form), the molecular weights of all species involved, the number of reactants which will be permitted to go into steady state, the concentrations of the initial reactants in mol/mL, and the total number of mol/mL at the start. Other mathematical inputs include the required iteration accuracy, the frequency at which steady-state concentrations will be recalculated, the running time, the printout schedule, etc.

The output provided at specified reaction times and/or after specified numbers of iterations includes the reaction time, the concentration of each product or reactant species, the rate at which each of these concentrations is changing, and a table of how each of the reactions included in the program is contributing to the rate of change in the concentration of each chemical species.

The program starts out taking very small ( $\sim 10^{-8}$  s) reaction time steps. After the free-radical species have in turn been put into steady state the time step will depend upon the stability requirements previously discussed.

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which implies that only the addition of a proton is needed to result in the generation of a complex which can produce initiation through reaction 6. Evidence against the validity of this implication is the fact that the lower valence ions of  $\text{Co}^{1,3,22}$  and  $\text{Mn}^{11,23}$  are experimentally observed to produce true inhibition. To do so they must react to remove one of the radicals responsible for chain propagation by a reaction which cannot result in the initiation of another chain. Emanuel et al.<sup>14</sup> postulate the production of a ketone as a noninitiator product from reaction 18. Tkáč et al.<sup>43</sup> postulate the production of a very stable, long-lived radical complex which does not convert to a hydroperoxide. Ingold<sup>44</sup> cites evidence against this conclusion. In any case, as mentioned before, the experimental evidence for inhibition indicates that the radical scavenging action of  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  ions does not regenerate a chain initiator.

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## Radical Ions in Photochemistry. 5. Photosensitized (Electron Transfer) Cyanation of Olefins<sup>1</sup>

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**Abstract:** The ultraviolet irradiation of phenyl olefins (1,1-diphenylethylene (Ia), 2-phenylnorbornene (Ib), and 1-phenylcyclohexene (Ic)) and potassium cyanide in acetonitrile-2,2,2-trifluoroethanol solution, in the presence of 1-cyanonaphthalene (II) or methyl *p*-cyanobenzoate (III) photosensitizer (electron transfer), gives good yields of nitriles having the anti-Markownikoff orientation. The reaction is believed to involve electron transfer from the olefin (Ia-c) to the singlet excited state of the sensitizer (II or III) and subsequent reaction of the radical cation of the olefin. Fluorescence quenching studies (the olefins (Ia-c) quench the fluorescence emission of II) and thermodynamic considerations ( $E_{1/2}^{\text{ox}}$  of Ia-c,  $E_{1/2}^{\text{red}}$  of II and III, and singlet energies) are consistent with the proposed mechanism.

### Introduction

We have shown, in previous parts of this series, that the photosensitized (electron transfer) addition of oxygen-centered nucleophiles to olefins can be a synthetically useful reaction for the preparation of alcohols, ethers, and esters having the anti-Markownikoff orientation.<sup>3</sup> The utility of this type of reaction has now been extended to include carbon-carbon bond formation; we have found conditions where cyanide ion can serve as the nucleophile.

There are many photochemically induced nucleophilic aromatic substitution reactions.<sup>4</sup> Several of these examples involve substitution with cyanide ion. However, the examples of photoaddition of nucleophiles to aromatic hydrocarbons<sup>5</sup> are rare and this report describes the first examples of the addition of cyanide ion to olefins.

We found that when 1,1-diphenylethylene (Ia), 2-phenylnorbornene (Ib), or 1-phenylcyclohexene (Ic), in acetonitrile-2,2,2-trifluoroethanol solution, was irradiated in the presence of 1-cyanonaphthalene (II) or methyl *p*-cyanoben-

zoate (III), (electron acceptor sensitizer), and potassium cyanide (reactions 1, 2, and 4), good yields (between 40 and 50%) of the nitriles having the anti-Markownikoff orientation (IV, VI, VIII, XII, and XIV) were obtained. Products having the Markownikoff orientation were not detected.

Ethers resulting from the anti-Markownikoff addition of the 2,2,2-trifluoroethanol, present as a nonnucleophilic proton source in the reaction mixture, were sometimes formed in small yield (<7%).

The mechanism we propose for the photosensitized (electron transfer) cyanation of olefins is similar to that invoked for the addition of oxygen-centered nucleophiles<sup>3</sup> and is summarized in Scheme I.

In this paper we report the characterization of the products from the photosensitized (electron transfer) addition of cyanide ion to olefins (Ia-c) in acetonitrile and 2,2,2-trifluoroethanol (or methanol-*O-d*) mixtures and the results of photophysical studies which support the proposed mechanism (Scheme I). We also report the oxidation potential of the olefins Ib and Ic