The Metal-catalyzed Autoxidation of Tetralin. V. The Effect of Fatty Acid Solvents

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(Received May 31, 1965)

Recently, the solvent effect on the autoxidation of hydrocarbons has attracted much attention. Hendry and Russell,¹⁾ and Howard and Ingold²,³⁾ have studied the several hydrocarbons and tried to correlate the rate constant value of $k_3/k_6{}^{1/2}$ with the dielectric function, $(D-1)/(2D+1)$. The present author, in a previous paper,⁴⁾ derived $k_3/k_6{}^{1/2}$ from the limiting rate of the metal-catalyzed oxidation of tetralin. Mostly, his values showed good agreement with those obtained by a quite different method, that is, azobisisobutyronitrile-catalyzed oxidation.

For this paper the effect of fatty acid solvents, from acetic to myristic acids, on the rate of the cobalt-catalyzed oxidation of tetralin, and also the effect of small amounts of stronger organic acids, were studied.

A possible kinetic scheme⁵⁾ describing the overall reaction is:

$$\mathrm{ROOH} + n\mathrm{Me} \xrightarrow{k_1'} \text{radical} \xrightarrow{\mathrm{RH}} \mathrm{R}\cdot \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2}\cdot \tag{2}$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{ROOH} + \mathrm{R}\cdot \tag{3}$$

$$\mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_6} \text{non-radical} + \mathrm{O_2} \tag{4}$$

Under stationary conditions:

$$-\mathrm{dO_2}/\mathrm{d}t = k_3(k_1'/2k_6)^{1/2}(\mathrm{ROOH})^{1/2}(\mathrm{Me})^{n/2}(\mathrm{RH}) - k_1'(\mathrm{ROOH})(\mathrm{Me})^n/2 \tag{5}$$

When the rate of the decomposition of hydroperoxide equals its rate of formation, the limiting rate of oxidation is given by:

$$-\mathrm{dO_2}/\mathrm{d}t = k_3{}^2(\mathrm{RH})^2/2k_6 \tag{6}$$

Experimental

The purification of tetralin and the oxygen absorption apparatus have been described previously.⁵,⁶⁾ All the experiments described in this work were performed at 50°C. The cell-cleaning procedure was that of Chalk and Smith.⁷⁾ Tetralin hydroperoxide was prepared and analyzed by the method of Woodward and Mesrobian.⁸⁾

Cobalt decanoate prepared by the method of Heaton and Uri⁹⁾ was used as a catalyst. The fatty acids used as solvents were acetic, propionic, butyric, pentanoic, octanoic, nonanoic, decanoic, lauric and myristic acids.

Results and Discussion

The Decomposition of Tetralin Hydroperoxide by Cobalt Salt in Fatty Acid Solvents.—The decomposition of tetralin hydroperoxide by cobalt decanoate was carried out in a fatty acid-benzene solution (1 : 1 by volume); its rate was found to be first order with respect to hydroperoxide and second order with respect to cobalt, regardless of fatty acids, from acetic to myristic, which were used, at cobalt concentrations from 5×10^{-4} to 5×10^{-3} mol./l.; i. e.:

$$-\mathrm{dROOH}/\mathrm{d}t = k_1'(\mathrm{Co})^2(\mathrm{ROOH}) \tag{7}$$

The values of k_1', as Table I shows, increased markedly with the increase in the carbon number of the fatty acid.

TABLE I. THE RATE CONSTANTS OF THE COBALT-CATALYZED DECOMPOSITION OF TETRALIN HYDROPEROXIDE IN A 1 : 1 BY VOLUME FATTY ACID-BENZENE SOLUTION

Fatty acid	k_1' mol^{-2} l^2 sec^{-1}	k'' sec^{-1}
Acetic	244	18600
Propionic	495	22000
Butyric	754	22100
Pentanoic	963	20500
Heptanoic	1440	18000
Nonanoic	2440	20000

However, further experiments confirmed that the decomposition rate is inversely proportional to the square of the concentration of acid, as has been shown in the case of acetic acid;⁵⁾ i. e.:

$$-\mathrm{dROOH}/\mathrm{d}t = k''(\mathrm{CO})^2(\mathrm{ROOH})/(\mathrm{Acid})^2 \tag{8}$$

The most interesting feature of this experiments

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1) D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2368 (1964).

2) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 (1964).

3) J. A. Howard and K. U. Ingold, ibid., **42**, 1250 (1964).

4) Y. Kamiya and K. U. Ingold, ibid., **42**, 2424 (1964).

5) Y. Kamiya, K. U. Ingold, S. Beaton and A. Lafortune, ibid., **41**, 2020 (1963).

6) Y. Kamiya, K. U. Ingold, S. Beaton and A. Lafortune, ibid., **41**, 2034 (1963).

7) A. J. Chalk and A. H. Smith, *Trans. Faraday Soc.*, **53**, 1214 (1957).

8) A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

9) F. W. Heaton and N. Uri, *J. Lipid. Res.*, **2**, 152 (1956).

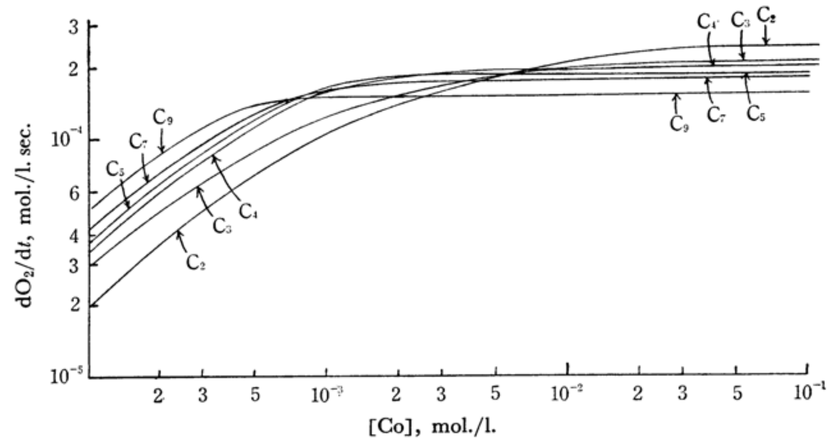
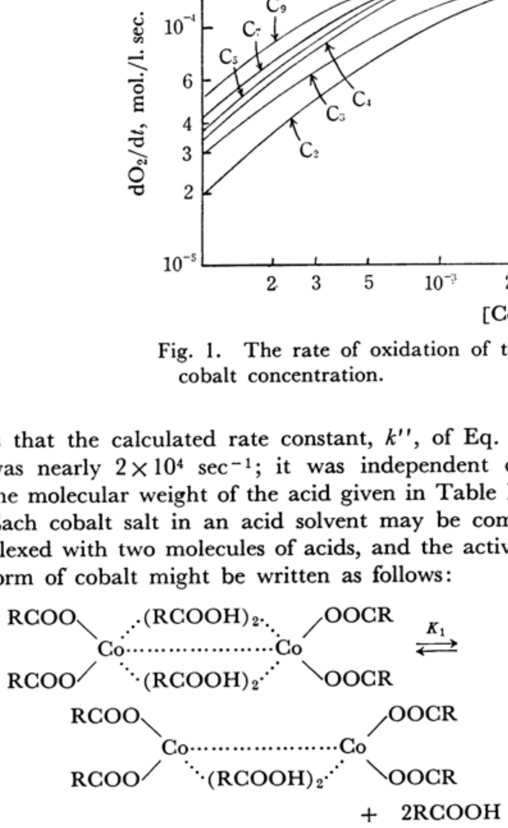


Fig. 1. The rate of oxidation of tetralin in the fatty acid as a function of cobalt concentration.

is that the calculated rate constant, k'', of Eq. 8 was nearly 2×10^4 sec^{-1}; it was independent of the molecular weight of the acid given in Table I. Each cobalt salt in an acid solvent may be complexed with two molecules of acids, and the active form of cobalt might be written as follows:



Thus,

$$\text{Active cobalt}=K_1(\text{Co})^2/(\text{acid})^2$$

Therefore, it can be concluded that the rate constant of the decomposition of tetralin hydroperoxide in an acid solvent may be attributed mainly to the kind of metal[2] and very little to the acid.

The Oxidation of Tatralin in the Fatty Acid Solvent.—Previously,[4,5] it was proved that the rate of the oxidation of tetralin reaches a limiting rate at high catalyst concentrations; this was explained by the mechanism suggested by Tobolsky;[10]

$$-\mathrm{d}O_2/\mathrm{d}t=k_3^2(\mathrm{RH})^2/2k_6$$

The rates of the oxidation of tetralin against the cobalt concentration in several fatty acids are shown in Fig. 1. At cobalt concentrations higher than 5×10^{-2} mol./l., the rate reaches a limiting value according to the solvent used. The lower the dielectric constant of the acid, the lower the limiting rate. In contrast, the order of the rate of oxidation was completely reversed at low catalyst concentrations; this is due to the effect of the higher initiation rate caused by the solvent. Recently, the rate of autoxidation has been correlated as a dielectric function by several workers.[1,2,11] Hendry showed that the oxidation rate could be roughly correlated with the dielectric constant (D) of the solvent by means of the function $(D-1)/(2D+1)$, which describes the bulk effect of solvents on dipole-forming reactions.

That is, the rate constant, k', for a reaction in a solution[13] is given by:

$$\ln k'=\ln k_0'-\frac{1}{\boldsymbol{k}T}\frac{D-1}{2D+1}\left(\frac{\mu^2{}_\mathrm{A}}{a^3{}_\mathrm{A}}+\frac{\mu^2{}_\mathrm{B}}{a^3{}_\mathrm{B}}-\frac{\mu^2{}_{\mathrm{M}\neq}}{a^3{}_{\mathrm{M}\neq}}\right)+\frac{\phi_\mathrm{A}+\phi_\mathrm{B}-\phi_{\mathrm{M}\neq}}{\boldsymbol{k}T}$$

k_0' is the specific rate constant in a solvent with a unit dielectric constant, while μ and a are the dipole moment and the radius of the reactants (A and B) and transition state (M). ϕ is a correction factor for non-electrostatic forces between the solvent and the reactants, and the solvent and transition state (e. g., dipole quadruple forces, van der Waals forces, and other specific solvation effects). Provided the non-electrostatic terms are small enough to be neglected, a plot of $\log k'$ against $(D-1)/(2D+1)$ should be linear.

Howard and Ingold[2] obtained a rather more linear correlation with styrene than was obtained by Hendry[1] with cyclohexene, but there was still the same sharp increase in the rate for the solvents with very high dielectric constants. The correlation between $\log(k_3/k_6{}^{1/2})$ and $(D-1)/(2D+1)$ is not significantly improved by multiplying the dielectric function by the ratio of the density

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[10] A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

[11] G. E. Zaikov and Z. K. Maizus, *Inst. Chem. Phys. Acad. Sci. USSR*, **1962**, 1102.

[12] Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **42**, 1027 (1964).

to the molecular weight of the solvent. Later, Howard and Ingold also studied the oxidation of α-methylstyrene, tetralin, 4-methyl cyclohexene and cumene, and plotted the $k_3/k_6^{1/2}$ values for the first three hydrocarbons against the $k_3/k_6^{1/2}$ value for styrene. They concluded that the increase in the oxidation rate with an increase in the solvent dielectric constant results mainly from the interaction of the solvent with the dipolar transition state of the propagation reaction.

The values of $k_3/k_6^{1/2}$ calculated in this work from the limiting rate of the oxidation of tetralin in the fatty acid solution, are plotted against $(D-1)/(2D+1)$ in Fig. 2; an excellent linear correlation is obtained. The very good result in the case of the fatty acid solvent can be attributed to the lack of any deactivation of the catalyst and also, presumably, to little difference in the correction factor, ϕ, upon a change in solvent.

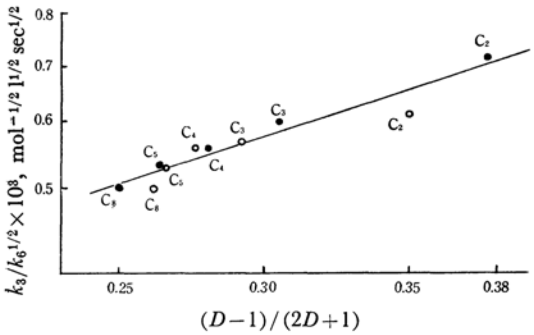

Fig. 2. Plot of $k_3/k_6^{1/2}$ for the oxidation of tetralin in the fatty acid against dielectric function, $(D-1)/(2D+1)$.
C_n: n represents the carbon number of fatty acid.
● Tetralin 1.22 mol./l.
○ Tetralin 3.67 mol./l.

As a result, the limiting rate of the oxidation of tetralin in an acid solvent can easily and accurately be estimated when its dielectric constant is known.

At low catalyst concentrations, the rate of oxidation can be written by Eq. 5. When the hydroperoxide concentration is high enough compared with cobalt, the term (Co)(ROOH)$^{1/2}$ nearly equals (Co), because, as has been suggested by many workers,⁵⁾ cobalt and hydroperoxide form an intermediate complex. Therefore, Eq. 5 can be simplified as follows:

$$-\mathrm{dO_2}/\mathrm{d}t=k_3(k_1'/k_6)^{1/2}(\mathrm{RH})(\mathrm{Me})-k_1'(\mathrm{Me})^2/2$$

k'_1 can be obtained by the direct determination of the decomposition rate of hydroperoxide, or from k'', which is nearly 2×10^4 sec^{-1}, while $k_3/k_6^{1/2}$ can be obtained from the dielectric constant or the limiting rate of oxidation. The rate of oxidation calculated by Eq. 5 and the observed values at cobalt concentrations of 3×10^{-4} and 1×10^{-4} mol./l. in the six fatty acids are shown in Table II.

TABLE II. THE CALCULATED AND OBSERVED VALUES OF THE RATE OF OXIDATION OF TETRALIN

Solvent	$-\mathrm{dO_2}/\mathrm{d}t\times 10^5$ (mol./l. sec.)			
	CoDe$_2$ 3×10^{-4} mol./l.		CoDe$_2$ 1×10^{-4} mol./l.	
	Calcd.	Obs.	Calcd.	Obs.
Acetic	6.1	5.2	2.3	2.0
Propionic	7.6	6.5	3.0	2.9
Butyric	8.0	8.5	3.4	3.2
Pentanoic	8.4	9.0	3.8	3.5
Heptanoic	8.8	10.1	4.7	4.1
Nonanoic	11.0	12.0	5.2	5.1

The calculated values showed an excellent agreement with the experimental results, thus justifying the limiting-rate theory.

It may be concluded that not only the limiting rate of tetralin oxidation, but also the rate of tetralin oxidation at low catalyst concentrations, can be estimated with very good accuracy.

The Effect of Stronger Organic Acids on the Rate of Oxidation.—When dichloro- or trichloro-acetic acids were used as solvents, the oxidation of tetralin did not proceed at all at cobalt concentrations lower than 5×10^{-2}. However, monochloroacetic acid gave a limiting rate of 2.62×10^{-4} mol./l. sec., as compared with that of 2.5×10^{-4} mol./l. sec. in acetic acid, which is a quite reasonable value in view of its dielectric constant. In the case of monochloroacetic acid, a slow but steady deactivation of the catalyst took place, probably due to the formation of an inactive complex between cobalt and monochloroacetic acid. Incidentally, no oxygen absorption was observed at 5×10^{-3} mol./l. (Co) in a monochloroacetic acid solution. Even a small amount of monochloroacetic acid reduced the rate of the cobalt-catalyzed oxidation of tetralin in acetic acid. The effect of a small amount of various organic acids on the oxidation rate of tetralin in acetic acid was studied in the limiting-rate region, i. e., 5×10^{-2} mol./l. (Co).

Benzene carboxylic acids produced in a slight decrease of the rate of oxidation, but oxalic acid, which showed the strongest effect of all acids tested, was found to deactivate an equimolar amount of cobalt. The solvent effect of chloroacetic acids was studied by Ohta¹⁴⁾ for p-xylene and by Levanevskii¹⁵⁾ for n-decane; they found a marked increase in the rate of oxidation compared with the rate in acetic acid. The difference between their results and those of experiment can be attributed to the strong temperature-dependency of the metal-deactivating effect of chloroacetic acids.

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13) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

14) N. Ohta, E. Takahashi and H. Horikiri, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 768 (1960).

15) O. E. Levanevskii and T. Zhumabylov, *Neftkhim*, **1963**, 264; *Chem. Abstr.*, **60**, 13111 (1963).

The True Limiting Rate of the Oxidation of Tetralin.—The limiting rate of the oxidation of tetralin was, in the previous paper, calculated from the limiting rate of the oxidation in acetic acid to be 1×10^{-3} mol./l. sec.; just the dilution effect due to the $(RH)^2$ term was considered. It was concluded that it showed an excellent agreement with the theoretical value of 1×10^{-3} mol./l. sec. However, as has been described above, the dielectric effect should be taken into consideration. After correcting for the dielectric effect, the measured limiting rate of the oxidation of tetralin is 7.8×10^{-4} mol./l. sec. The difference between the theoretical rate and observed rate after the correction may be attributed to the non-radical decomposition of hydroperoxide. The products of the decomposition of tetralin hydroperoxide by cobalt salt have been shown by gas chromatography to be composed of 50% α-tetralone and 50% a mixture of α-tetralol and dihydronaphthalene. Dyer et al.[16] obtained similar results by chemical analysis.

In the limiting-rate region, as has been described previously, the expected ratio of alcohol to ketone is 2 : 1. The non-radical decomposition of hydroperoxide may yield α-tetralone as follows:

$$\mathrm{ROOH} + n\mathrm{Me} \xrightarrow{k^*} \alpha\text{-tetralone} + \mathrm{H_2O} + n\mathrm{Me}$$

Therefore, the radical-producing decomposition may be calculated to be 75%; i. e.: $k_1'/k_1'+k^*=0.75$

Accordingly, the limiting rate of the oxidation of tetralin at 50°C becomes $0.75\times10^{-3}=7.5\times10^{-4}$, which agrees excellently with the theoretical value of 7.8×10^{-4}.

Summary

The rate of the cobalt-catalyzed decomposition of tetralin hydroperoxide in fatty acid solvents was first order with respect to hydroperoxide and second order with respect to the cobalt, and it was inversely proportional to the square of the acid concentration; i. e., $-\mathrm{dROOH}/\mathrm{d}t=k''(\mathrm{Co})^2\cdot(\mathrm{ROOH})/(\mathrm{Acid})^2$. The rate constant, k'', was found to be almost constant, regardless of the molecular weight of the acid. The values of $k_3/k_6{}^{1/2}$ obtained from the limiting rate of the oxidation showed an excellent linear correlation against the dielectric function of $(D-1)/(2D+1)$. The rate of the oxidation of tetralin calculated by $-\mathrm{dO_2}/\mathrm{d}t=k_3(k_1'/2k_6)^{1/2}(\mathrm{RH})(\mathrm{Co})-k_1'(\mathrm{Co})^2/2$ showed an excellent agreement with the value observed at cobalt concentrations lower than 3×10^{-4} mol./l. Strong organic acids such as chloroacetic acids deactivated the cobalt catalyst, and oxalic acid, which has shown the strongest deactivating effect of all the acids tested, deactivated equimolar cobalt salt.

The author wishes to express his thanks to Professor Shingo Ando and Dr. K. U. Ingold for their continued advice and encouragement in this work.

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[16] E. Dyer K. R. Carle and D. E. Weiman, *J. Org. Chem.*, **23**, 1464 (1958).