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The Reaction between Diisopropylbenzene Dihydroperoxide and Iron(II) or Some of its Complexes in Aqueous Solutions of Vinyl Compounds[1]

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The rate constant for the reaction: $\mathrm{HOOC(CH_3)_2C_6H_4C(CH_3)_2OOH + Fe(II) \rightarrow HOOC(CH_3)_2C_6H_4C(CH_3)_2O^{\cdot} + Fe(III) + OH^-}$ is $k = 3 \times 10^{12}\, e^{-14,300/RT}$ l./mole/sec. at pH 4.2. The free radical reacts with iron(II) (at a rate k_{1o}), monomer (k_{1i}) and hydroperoxide (k_{1p}). $E_{1i} - E_{1o}$ and A_{1i}/A_{1o} were measured for the reaction in the presence of some water-soluble monomers with the following results: in acrylonitrile solution $E_{1i} - E_{1o} = -8.6$ kcal./mole, and $A_{1i}/A_{1o} = 3.1 \times 10^{-6}$; in methyl acrylate solution $E_{1i} - E_{1o} = -20$ kcal./mole and $A_{1i}/A_{1o} = 9.1 \times 10^{-15}$; and in methyl methacrylate solution $E_{1i} - E_{1o} = -15$ kcal./mole and $A_{1i}/A_{1o} = 1.1 \times 10^{-11}$. k_{1p}/k_{1o} is 10 at 40° and 4 at 25°, where k_{1p} is rate of reaction of radical with hydroperoxide. The free radical, after reacting with the monomer, yields a polymeric hydroperoxide which will react with iron(II), as long as the polymer molecule remains in aqueous solution. When the iron(II) is complexed with triethylenetetramine, a reaction occurs similar to that observed with monohydroperoxides.[2] The rate constant has been measured at different pH; $k = 10^{10}\, e^{-10,900/RT}$ l./mole/sec. at pH 10.7 and $k = 4 \times 10^{-9}\, e^{-10,700/RT}$ l./mole/sec. at pH 11.6. This reaction seems less sensitive to change of pH than was the case with monohydroperoxides. There was no necessity in interpreting the data to consider the reaction between iron(II) complex and polymeric hydroperoxide.

Introduction

This study is one of a series designed to give some idea of the role of hydroperoxide initiators in emulsion polymerization. The study has previously been confined to monohydroperoxides in the cumene and cyclohexane series in which the reactions with iron(II)[3-6] and with the iron(II)-polyethylenepolyamine complexes[2,7] were reported. Later work reported the tendency of the cumyloxy radicals to react with monomer.[8] When a sample of p-diisopropylbenzene dihydroperoxide became available, the present study seemed pertinent.

Experimental Methods

The dihydroperoxide (DHP) was obtained from Hercules Powder Co. either in 20% acetone solution or as a white powder of 80% hydroperoxide content. By evaporating the acetone and extracting the solids with benzene, the purity was raised to about 90%. This treatment should remove monohydroperoxides. Most of the remaining impurity was probably the alcohol resulting from thermal decomposition of the dihydroperoxide.

Purification of the other compounds used, as well as the analysis for iron(II), has been described previously.[4,6,7] In these same sources may be found descriptions of the methods used in performing an experiment, either using iron(II), or its polyethylenepolyamine complex as the reductant. To make a stock solution of the DHP, methanol was used to promote solubilizing so that the reaction occurred in an aqueous medium containing 0.5 to 2% methanol.

Two methods of removing samples for analysis were used, depending on the time interval between samples permitted by the reaction velocity. For the slower reactions, samples were removed by pipet, permitting a standard volume to be used. For the more rapid reactions, the sample was blown into a graduated centrifuge tube containing α,α'-bipyridine which complexed the iron(II) to an unreactive form, giving a color suitable for iron analysis.[9] The sample volume was measured after addition to the α,α'-bipyridine solution. It was possible to obtain samples at frequent intervals in this manner.

DHP is susceptible to polarographic analysis as demonstrated by the polarogram in Fig. 1. Since only relative concentrations were required, no absolute calibration was made between [DHP] and I_d. I_d was measured at −1.0 volt *vs.* a saturated calomel electrode.

Theoretical

(a). Primary Rate Constants in the Presence of Excess Monomer.—By analogy with previous mechanisms postulated for iron(II) and hydroperoxide reactions, the following mechanism should be written when monomer was present in such amount as to reduce $[\mathrm{RO^{\cdot}}]_{ss}$ to zero.

$$\mathrm{HOOC(CH_3)_3C_6H_4C(CH_3)_2OOH + Fe(II) \xrightarrow{k_1} Fe(III) + HO^- + HOOC(CH_3)_2C_6H_4C(CH_3)_2O\cdot}$$

$$\mathrm{HOOC(CH_3)_2C_6H_4C(CH_3)_2O^{\cdot} + \mathit{n}M \xrightarrow{k_{1i}} HOOC(CH_3)_2C_6H_4C(CH_3)_2OM_{\mathit{n}}^{\cdot}}$$

$$\mathrm{{}^{\cdot}M_{\mathit{n}}OC(CH_3)_2C_6H_4C(CH_3)_2OOH + Fe(II) \xrightarrow{k_2} Fe(III) + HO^- + {}^{\cdot}M_{\mathit{n}}OC(CH_3)_2C_6H_4C(CH_3)_2O^{\cdot}}$$

$$\mathrm{{}^{\cdot}M_{\mathit{n}}OC(CH_3)_2C_6H_4C(CH_3)_2O^{\cdot} + \mathit{n}M \xrightarrow{k_{2i}} {}^{\cdot}M_{\mathit{n}}OC(CH_3)_2C_6H_5C(CH_3)_2OM_{\mathit{n}}^{\cdot}}$$

The type of reaction outlined can be treated kinetically if $[\mathrm{Fe(II)}]_0 = 2[\mathrm{HP}]_0$, by the method outlined in the work of Frost and Schwemer.[10]

(b). Primary Rate Constants in the Absence of Monomer.—In the absence of monomer, conditions may be achieved where the oxidation of iron(II) constitutes the only radical consuming reaction. The initial decomposition is identical to that shown above which is characterized by k_1. The radical consumption step is

$$\mathrm{HOOC(CH_3)_2C_6H_4C(CH_3)_2O^{\cdot} + Fe(II) \xrightarrow{k_{1o}} HOOC(CH_3)_2C_6H_4C(CH_3)_2O^- + Fe(III)}$$

In the second step a novel species of hydroperoxide will be formed, which will lead to a novel type of radical

$$\mathrm{HOOC(CH_3)_2C_6H_4C(CH_3)O_2^- + Fe(II) \xrightarrow{k_3} {}^{\cdot}OC(CH_3)_2C_6H_4C(CH_3)_2O^- + Fe(III)}$$

This radical will be consumed by the reaction

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[1] Presented in part before the Division of Physical and Inorganic Chemistry, American Chemical Society, Minneapolis, Minnesota, September, 1955.

[2] R. J. Orr and H. L. Williams, *Disc. Faraday Soc.*, **14**, 170 (1953).

[3] J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **73**, 1634 (1951).

[4] J. W. L. Fordham and H. L. Williams, *ibid.*, **72**, 4465 (1950).

[5] R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952).

[6] R. J. Orr and H. L. Williams, *J. Phys. Chem.*, **57**, 925 (1953).

[7] R. J. Orr and H. L. Williams, *Disc. Faraday Soc.*, **14**, 170 (1953).

[8] R. J. Orr and H. L. Williams, THIS JOURNAL, **77**, 3715 (1955).

[9] L. H. Jackson, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 302 (1938).

[10] A. A. Frost and W. C. Schwemer, THIS JOURNAL, **74**, 1268 (1952).

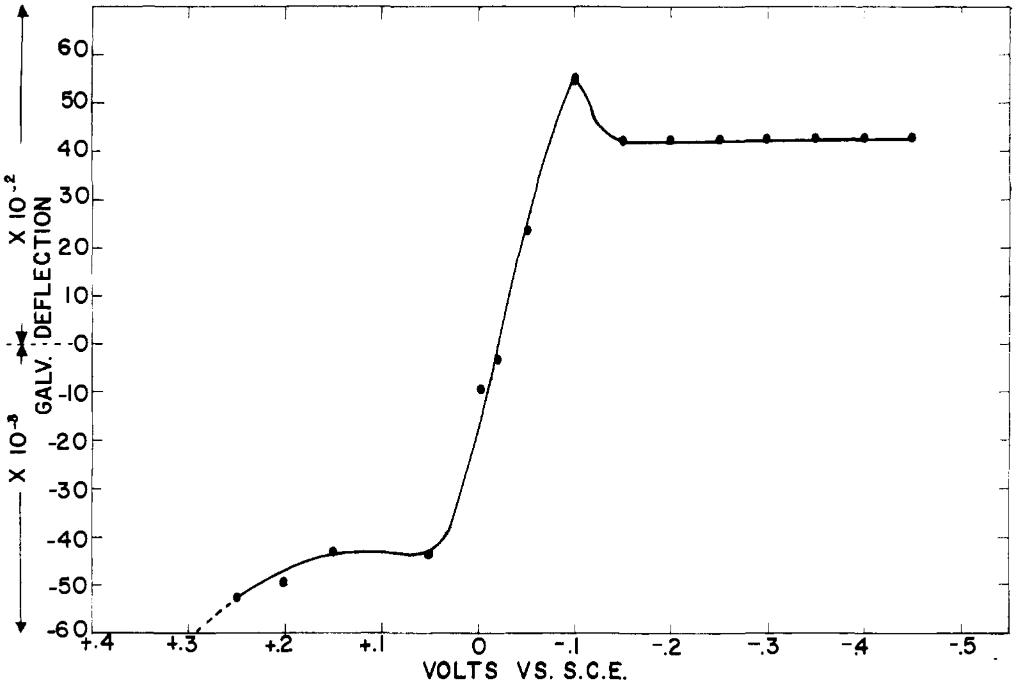

Fig. 1.—Polarogram of dihydroperoxide of diisopropylbenzene; T 40°; pH 8.8; [DHP] 10^{-3} M.

$$\cdot OC(CH_3)_2C_6H_4C(CH_3)_2O^- + Fe(II) \xrightarrow{k_{3o}} {}^-OC(CH_3)_2C_6H_4C(CH_3)_2O^- + Fe(III)$$

The mechanism will apply only when $[Fe(II)]_0 >> [DHP]_0$ so that no significant radical consumption through reaction of hydroperoxide may occur. Evaluation of k_5 and k_3 may be made if $k_2 \ll k_{1o}$ and $k_3 \ll k_{3o}$. The reaction may be treated kinetically when $[Fe(II)]_0 = 4[HP]_0$ by the methods described previously.

(c). **Mechanism and Rate Constants with Moderate Amounts of Monomer.**—By adjustment of initial concentrations, all possible reactions occur to a significant and measurable degree.[8] Analysis of the data from such reactions has provided information on what reactions occur and the relative rates of such reactions. There will be a total of three types of hydroperoxides resulting in the three corresponding radicals

	Hydroperoxides	Radicals
(1)	$HOOC(CH_3)_2C_6H_4C(CH_3)_2OOH$	$HOOC(CH_3)_2C_6H_4C(CHO_3)_2O\cdot$
(2)	$HOOC(CH_3)_2C_6H_4C(CH_3)_2COM_n\cdot$	$\cdot OC(CH_3)_2C_6H_5C(CH_3)_2OM_n\cdot$
(3)	$HOOC(CH_3)_2C_6H_4C(CH_3)_2O^-$	$\cdot OC(CH_3)_2C_6H_4C(CH_3)_2O^-$

The diradical resulting from the hydroperoxide is neglected since for the ratios of $[Fe(II)]_0$ and $[DHP]_0$ necessary to eliminate radical induced hydroperoxide decomposition, this will have little or no chance of formation. There are nine combinations of radicals reacting with monomer and iron(II) and of iron(II) reacting with hydroperoxide. It will be necessary also to consider the reaction of radicals with hydroperoxide which may give rise to nine further reactions.

Methods were developed[8] for analysis of the reaction data resulting from reduction of monohydroperoxides. It was necessary to consider only four simultaneous reactions of this nature. The methods used for the following analysis are basically similar with modifications for the additional reactions. The ratio (k_{1i}/k_{1o}) is determined by a method of successive approximations. The initial approximation neglects the contribution of radical induced hydroperoxide decomposition to the reaction. It is possible to show that over any time interval of reaction

$$\frac{\text{Iron(II) consumption due to oxidn. by radicals}}{\text{Monomer consumption due to initiation of polymn.}} =$$

$$\frac{\overline{[Fe(II)]}}{[\overline{M}]}\left\{\frac{k_{1o}[HOORO\cdot] + k_{2o}[\cdot OROM_n\cdot] + k_{3o}[\cdot ORO^-]}{k_{1i}[HOORO\cdot] + k_{2i}[\cdot OROM_n\cdot] + k_{3i}[\cdot ORO^-]}\right\} \quad (1)$$

A superscript bar refers to an average concentration over the time interval. The subscripts o and i after a rate constant refer to the iron(II) oxidation and monomer initiation reactions, respectively. The radical is identified by the initial numerical subscript which corresponds to the numbering sequence defined previously for the structure of radicals. The radical concentrations are steady-state concentrations; R refers to $(-C(CH_3)_2\text{-}C_6H_4C(CH_3)_{2-})$.

The left-hand side of equation 1 may be obtained experimentally. It is equal to

$$\frac{\Delta Fe(II)_{tot} - \Delta Fe(II)^*}{2\Delta Fe(II)^* - \Delta Fe(II)_{tot}} \text{ or } \frac{1}{\left\{\frac{\Delta Fe(II)_{tot}}{\Delta Fe(II)_{tot} - \Delta Fe(II)^*}\right\} - 2}$$

Both the total iron(II) consumption (Δ Fe(II)$_{tot}$) and the iron(II) consumption due to reaction with hydroperoxide (Δ Fe(II)*) must be known. $\overline{[Fe(II)]}$ is calculated from experimental data and $[\overline{M}]$ is taken as the initial monomer concentration. Errors (discussed previously[8]) will result from these numerical approximations only at finite time intervals.

The relations involved in the right-hand side of equation 1 indicate that it lies between k_{1o}/k_{1i} and $(k_{1o} + k_{2o} + k_{3o})/(k_{1i} + k_{2i} + k_{3i})$ and approaches k_{1o}/k_{1i} if experimental conditions be such that (ORO^-) is small (as must occur at all but very small monomer concentrations) and if $k_1 > k_2$. It is possible to calculate a first approximation of k_{1i}/k_{1o} (designated $(k_{1i}/k_{1o})''$) for any time interval of reaction. By determining the dependence of $(k_{1i}/k_{1o})''$ on the time interval, it is possible to compensate for the errors introduced by estimating $\overline{[\mathrm{Fe(II)}]}$, $[\dot{\mathrm{M}}]$ and ΔFe(II)*, by extrapolating to zero time interval. The extrapolated value represents a second approximation $(k_{1i}/k_{1o})'$. This approximation will also eliminate any contributions from terms dependent on $[\mathrm{OROM}_n\cdot]$ since this will approximate zero at short reaction times. However $(k_{1i}/k_{1o})'$ does contain errors arising from neglect of the radical induced hydroperoxide decomposition and results in $(k_{1i}/k_{1o})'$ being a function of $[\mathrm{M}]_0$. When radical induced decomposition of hydroperoxide is important the relation between $[\mathrm{M}]_0$ and $(k_{1i}/k_{1o})'$ is

$$\left\{\frac{k_{1i}}{k_{1o}}\right\}' = \left\{\frac{k_{1i}}{k_{1o}}\right\} + \left\{\frac{k_{1p}}{k_{1o}}\frac{[\mathrm{ROOH}]_o}{[\mathrm{M}]_o}\right\} \qquad (2)$$

where k_{1p} is the reaction rate of reaction

$$\mathrm{HOO{-}C(CH_3)_2C_6H_4C(CH_3)_2OOH} + \mathrm{HOO{-}C(CH_3)_2C_6H_4C(CH_3)_2{-}O\cdot} \longrightarrow \text{products}$$

(k_{1p}/k_{1o}) and $(k_{1i}/_{1o})$ may be determined by curve fitting.

Experimental Results

I. **Stoichiometry.**—The stoichiometric ratios for the reaction of iron(II) with DHP were investigated in acidic media and are in Table I. Experiments in the presence of monomer concentrations (acrylonitrile, methyl acrylate and methyl methacrylate) as low as 10^{-3} *M* gave ΔFe(II)/ΔHP = 2.0. The stoichiometric ratios indicate that the hydroperoxy radical is reluctant to react with iron(II).

II. **Primary Rate Constant Determination.** (a) In **the Presence of Monomer.**—These were determined, by methods previously described, where $[\mathrm{DHP}]_0 = 2[\mathrm{Fe(II)}]_0$. Initially, samples for analysis were taken every five minutes. The reaction was so rapid that a high weight had to be assigned to the results obtained with the initial samples. No significant change in the rate constant was noted after taking samples every minute, although the standard deviations tended to become smaller as the sampling frequency increased. Also determined was k_2 although due to the limited solubility of the polymeric hydroperoxide, it will not be an absolute measure of the hydroperoxide reactivity. The data are in Table II. The monomer solution used was 1.2 *M* acrylonitrile. The Arrhenius equations were calculated as

$$k_1 = 3 \times 10^{12}\, e^{-14,300/RT}\ \mathrm{l./mole^{-1}/sec.^{-1}}$$

and

$$k_2 = 3 \times 10^{15}\, e^{-19,500/RT}\ \mathrm{l./mole^{-1}/sec.^{-1}}$$

(b) In **the Absence of Monomer.**—Attempts to determine these at $[\mathrm{Fe(II)}]_0 = 4[\mathrm{HP}]_0$ were unsuccessful. Over the course of any single experiment k_3/k_1 (see mechanism outlined previously) was not constant and was so small as to indicate no significant deviation from a bimolecular reaction. The k_1 thus determined did not agree with the k_1 value determined in the presence of monomer. These data, and the stoichiometric ratios observed, indicate that the assumption of k_1 and k_3 being much smaller than the rate of reaction of the radical on iron(II) was unjustified.

TABLE I

STOICHIOMETRY OF Fe(II) + DHP REACTION IN ABSENCE OF MONOMER

$[\mathrm{DHP}]_0 \times 10^5$, *M*	$[\mathrm{Fe(II)}]_0 \times 10^5$, *M*	Fe(II)/HP
	25°	
2.75	8.10	2.1
2.75	10.32	1.9
2.75	17.20	4.0
5.50	17.90	3.1
5.50	18.10	3.3
	40°	
1.65	5.30	1.6
2.20	8.15	1.8
2.75	9.85	1.9
2.75	15.40	2.1
5.50	16.12	3.1
5.50	15.00	3.0

III. **The Reactivity of the *p*-Hydroperoxy Isopropyl Cumyloxy Radical. (a). Calculation of ΔFe(II)$_{\mathrm{tot}}$/(ΔFe(II)$_{\mathrm{tot}}$ − ΔFe(II)*).**—The calculation of the amount of iron(II) consumed by the primary reactions by consideration of the primary rate constants proved to be rather complex. For this reason all reactions used a standard hydroperoxide concentration (5.50×10^{-5}) and ΔFe(II)* was measured for various $[\mathrm{Fe(II)}]_0$ and time interval values in 1.2 *M* acrylonitrile solution. An example of such a calibration curve is Fig. 2. By graphical evaluation of ΔFe(II)*, ΔFe(II)$_{\mathrm{tot}}$/(ΔFe(II)$_{\mathrm{tot}}$−ΔFe(II)*) could be calculated for any time interval.

(b). **Dependence of $(k_{1i}/k_{1o})''$ on Time Interval.** The dependence of $(k_{1i}/k_{1o})''$ on time interval was not constant. It could increase, decrease or remain independent of time interval, depending on

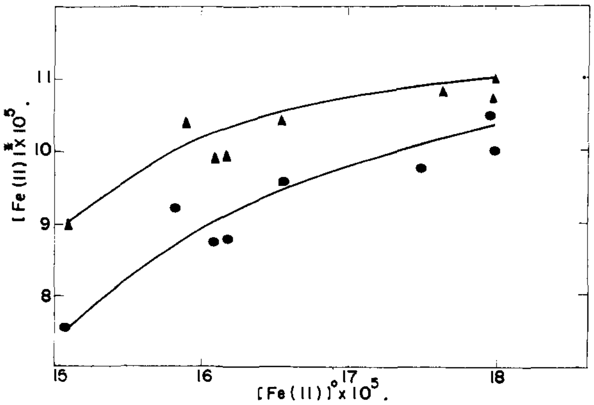

Fig. 2.—Calibration curve for ΔFe* at $[\mathrm{DHP}]_0$, 5.5×10^{-5} *M*; ●, ΔFe* at time interval 5 min.; ▲, ΔFe* at time interval 20 min.

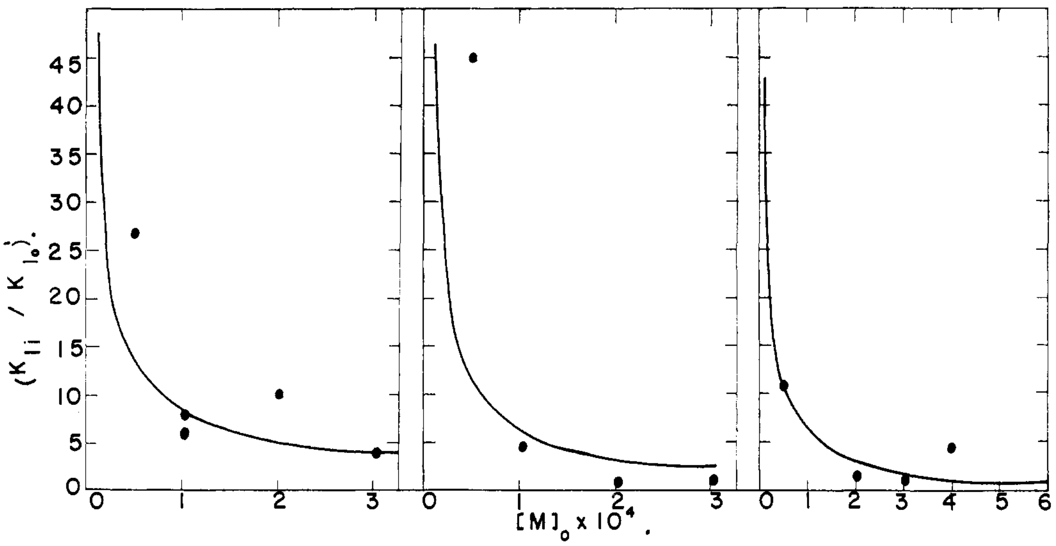

Fig. 3.—Fit of calculated $(k_{1i}/k_{1o})'$ *versus* $[M]_0$ curves with experiment: left, methyl acrylate, $k_{1i}/k_{1o} = 3$; middle, acrylonitrile, $k_{1i}/k_{1o} = 0.8$; right methyl methacrylate, $k_{1i}/k_{1o} = 0.3$.

TABLE II

PRIMARY RATE CONSTANT DETERMINATION FOR HYDROPEROXIDE DECOMPOSITION

T (°C.)	$[HP]_0 \times 10^5$, M	k_1, l./mole/sec.	k_2, l./mole/sec.	k_1, av.	s.d.	k_2, av.	s.d.
		Sampling frequency 5 min.					
40	2.20	382	95	333	36	82	7.6
	3.30	294	75				
	3.30	324	78				
25	2.20	163	31				
	2.75	114	29	130	23	30	0.7
	5.50	112	29				
		Sampling frequency 2 min.					
40	1.65	387	73	350	22	89	28
	2.20	329	130				
	2.75	336	70				
	3.30	348	83				
25	2.75	93	11	104	8	17	4
	2.20	112	19				
	1.65	107	20				

the initial experimental conditions. In all instances, a linear correlation was valid, within the precision of the data. $(k_{1i}/k_{1o})'$ was determined by extrapolation of $(k_{1i}/k_{1o})''$ to zero time interval.

(c). **Dependence of $(k_{1i}/k_{1o})'$ on Initial Monomer Concentration ($[M]_0$).**—In all instances $(k_{1i}/k_{1o})'$ was found dependent on values of $[M]_0$. This had been expected from the derivation of this quantity and indicated reaction of hydroperoxy radicals with the hydroperoxide. The values of $(k_{1i}/k_{1o})'$ for the various temperatures and monomer solutions are in Table III. $(k_{1i}/k_{1o})'$ was independent of the values of $[Fe(II)]_0$ used. This confirmed that no contributions from reactants other than the original hydroperoxide and the radical formed in the first decomposition step had to be considered.

(d). **Evaluation of (k_{1i}/k_{1o}) and (k_{1p}/k_{1o}).**—These were determined by curve fitting using the relation between $(k_{1i}/k_{1o})'$ and the monomer concentration discussed previously. The closeness of the fit of calculated and experimental curves is illustrated in Fig. 3. The values are in Table IV. k_{1p}/k_{1o} is a function of temperature only, but k_{1i}/k_{1o} varies with the monomer. The data for k_{1i}/k_{1o} were recalculated and are expressed in the standard Arrhenius form in Table V.

TABLE III

VALUES OF $(k_{1i}/k_{1o})'$ FOR REACTIONS OF p-HYDROPEROXY ISOPROPYL CUMYLOXY RADICAL

$[M]_0$	MA[a]	$(k_{1i}/k_{1o})'$ ACN[a]	MMA[a]
40°			
5×10^{-5}	27	45	12
1×10^{-4}	8	4.5	..
1×10^{-4}	6	..	..
2×10^{-4}	10	0.8	1.1
3×10^{-4}	4.5	0.8	0.6
4×10^{-4}	..	..	4.5
5×10^{-4}	..	..	0.3
6×10^{-4}	..	..	0.3
25°			
5×10^{-5}	3.5	3.5	6
1×10^{-4}	2.5	6	4
2×10^{-4}	5	2	6.5
3×10^{-4}	7.4	..	9
4×10^{-4}	..	..	0.5
5×10^{-4}	..	..	1.8
6×10^{-4}	..	..	0.5

[a] MA, methyl acrylate; MMA, methyl methacrylate; ACN, acrylonitrile.

TABLE IV

VALUES OF (k_{1i}/k_{1o}) AND (k_{1p}/k_{1o}) FOR p-HYDROPEROXY ISOPROPYL CUMYLOXY RADICAL

Monomer	k_1/k_{1o}	k_{1p}/k_{1o}
40°		
MA	3	10
ACN	0.8	
MMA	0.3	
25°		
MA	6	4
ACN	4	
MMA	1	

TABLE V

RELATIVE ARRHENIUS CONSTANTS FOR INITIATION AND OXIDATION

Monomer	$(E_{11} - E_{10})$ (kcal. mole)	A_{11}/A_{10}
MA	− 8.6	3.1×10^{-6}
ACN	−20	9.1×10^{-15}
MMA	−15	1.1×10^{-11}

IV. Reactions of the Triethylenetetramine Complex of Iron(II). (a). Effect of Monomer on Reaction Rates.—With hydroperoxide and triethylenetetramine (TET) concentrations of 10^{-3} and 10^{-2} *M*, respectively, it was found that methyl methacrylate up to a concentration of 10^{-2} *M* retarded the decomposition of hydroperoxide. Increasing the monomer concentration beyond 10^{-2} *M* caused no further change.

(b). Effect of Iron(II) on Rates.—In Fig. 4 may be seen the effect of adding various concentrations of iron(II) to the hydroperoxide–(TET) reaction. It was found that ascribing a pseudo first order in hydroperoxide to the reaction fit the data well indicating that the equation previously reported[2,7] between the complexes and monohydroperoxides held for this species, *i.e.*

$$\text{ROOH} + \text{RNH}_2\text{:Fe(II)} \longrightarrow \text{RO}\cdot + \text{H}_2\text{O} + \text{RNH}\cdot + \text{Fe(II)}$$

This would be pseudo first order when the polyethylenepolyamine was present in large excess over the iron(II), as was the case. This would imply that the reaction observed in IV(a), when no iron was added, was due to the presence of trace amounts of this metal as impurities. Such behavior was demonstrated with cumene hydroperoxide.[7] The rate data over the range of conditions studied indicate no need to consider a consecutive reaction with the polymeric hydroperoxide. This may be because the molecular weight of the polymethylmethacrylate did not permit sufficient solubility for interference with the initial reaction.

By determination of the pseudo first-order rate constants for a series of $[\text{Fe(II)}]_0$ values, and subtraction of the contribution of the residual iron(II) in the system, it was possible to evaluate the bimolecular rate constant for the reaction at a series of $[\text{Fe(II)}]_0$ concentrations. This was done for a range of *p*H and temperatures. The data are in Table VI. The data were recalculated in the conventional Arrhenius manner as apparent activation energy and frequency factor. The relative nature of the data is a result of possible temperature effects on the composition of the iron(II) complexes.[2,7]

*p*H	$E_{\text{app.}}$, (kcal./mole)	$A_{\text{app.}}$
10.7	10.9	10^{10}
11.6	10.7	4×10^{9}

V. Dihydroperoxide as Catalyst in Oxidation–Reduction Emulsion Polymerization of Butadiene and Styrene.—The dihydroperoxide was tested in emulsion polymerization recipes[11] containing sodium or potassium fatty acid soap emulsifiers, 5.0 parts per 100 parts monomer. Unless otherwise specified the activator was iron(II)-sulfate-potassium pyrophosphate complex containing 0.08 part iron(II) sulfate heptahydrate per 100 parts monomer.

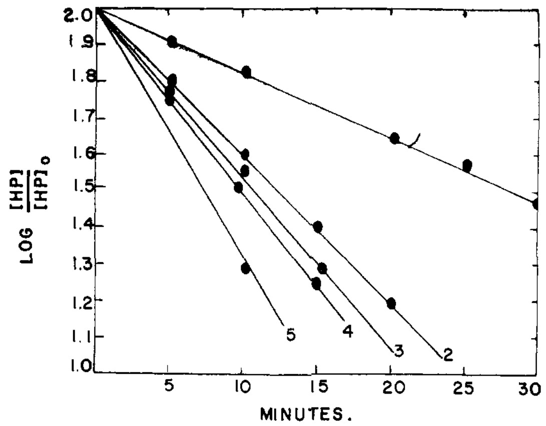

Fig. 4.—Effect of iron(II) addition on dihydroperoxide-triethylenetetramine reaction; *T* 40°; *p*H 10.9; TET 10^{-2} *M;* DHP 10^{-3} *M;* Iron(II): curve 1, 0; curve 2, 3×10^{-6} *M;* curve 3, 4×10^{-6} *M;* curve 4, 5×10^{-6} *M;* curve 5, 10×10^{-6} *M.*

Experiments were done to determine the minimal concentrations of the dihydroperoxide for satisfactory reaction, compared with diisopropylbenzene monohydroperoxide (DIP). The data are in Table VII. There was shown a lower limit of effective concentration for the dihydroperoxide than for the monohydroperoxide. The differences between the two hydroperoxides became more pronounced when a sodium rather than potassium soap was used.

TABLE VI

BIMOLECULAR RATE CONSTANTS FOR Fe(II)–TET–DIHYDROPEROXIDE REACTION

*p*H	$[\text{Fe(II)}]_0$	*k*, l./mole/sec.	*k*, av.	s.d.
40°				
11.6	1×10^{-6}	152	130	19
	2	143		
	5	118		
	10	106		
10.6	1×10^{-6}	223	253	39
	2	289		
	3	299		
	4	193		
	5	260		
10.8	3×10^{-6}	271	251	27
	4	272		
	5	254		
	10	206		
0°				
12.5	1×10^{-5}	10.5	10.9	0.8
	2	10.8		
	3	11.7		
	5	9.7		
11.2	1×10^{-5}	12.9	11.8	1.3
	2	9.8		
	4	12.8		
	5	11.4		
10.7	2×10^{-5}	23.9	20.7	3
	3	19.3		
	4	16.2		
	5	23.2		

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[11] R. Spolsky and H. L. Williams, *Ind. Eng. Chem.*, **41**, 1592 (1949).

The increasing difference with poorer emulsifying power was confirmed by studies of electrolyte addition to the recipes. The electrolyte (potassium sulfate) was increased for both hydroperoxides to a concentration (1.0 part per 100 monomers) where it began to interfere with emulsification. Yields from the recipe containing potassium fatty acid soap were measured and are in Table VIII.

Discussion

(I). **Reaction with Iron(II).**—It is of interest to compare this hydroperoxide with monohydroperoxides in reactions with reducers, and in the properties of the resultant free radical. Comparison of the frequency factors and activation energies for the bimolecular reaction of the hydroperoxide with iron(II) indicates that each is significantly higher than that obtained with monohydroperoxides. A relation had been found between the activation energy of this reaction and the Hammett σ-value of the *p*-substituent on the hydroperoxide.[6] This should allow calculation of the Hammett σ-value of the *p*-hydroperoxy isopropyl group from the activation energy. By plotting ($\log \sigma + 0.22$) against the activation energy of the monohydroperoxide series and extending this relation to $E = 14.3$, a value of σ of $+ 4.6$ is obtained. This is indicative of an extremely electronegative group. Its magnitude is more readily appreciated when it is considered that σ for p-NO_2 is $+ 0.778$.

The frequency factor for the reaction will not only be determined by the normal factors affecting this constant but should be increased by the symmetry of the molecule. The relation between frequency factor and activation energy valid for monohydroperoxides[6] indicates that the frequency factor for a reaction of this nature having $E = 14.3$ kcal./mole should be about 4×10^{11}. Comparing this with the actual value, there is an increase in the frequency factor of about 7.5 which may be due to the imposition of symmetry.

Symmetry may affect the frequency factor in more than one fashion. There should be a geometric factor, due to the larger portion of the molecule covered by hydroperoxide groups. There is also an electrostatic factor resulting from the presence of two dipoles which may attract iron(II). The relative amount of this latter may be calculated only on knowing the angle of approach of the ion to the line of the dipole.[12]

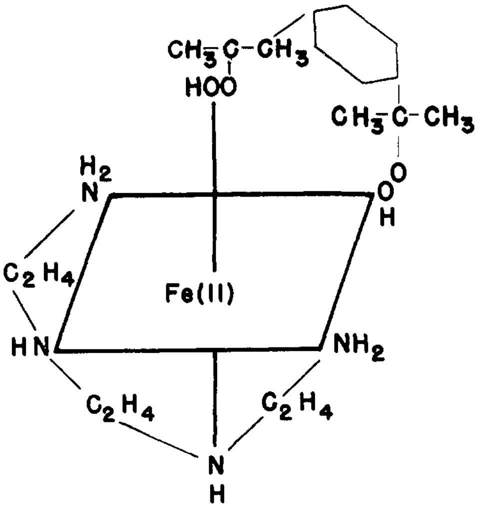

Fig. 5.—Activated complex for reaction of iron(II)-triethylenetetramine complex with diisopropylbenzene dihydroperoxide.

TABLE VII

EVALUATION OF HYDROPEROXIDES AS POLYMERIZATION INITIATORS

Hydroperoxide content (parts)	(% Conv. (17 hr.)) DHP	DIP	Hydroperoxide content (parts)	(% Conv. (17 hr.)) DHP	DIP
Sodium fatty acid soap[a]			Potassium fatty acid soap[a]		
0.02	21	4	0.01	23	..
.04	83	5	.02	90	29
.06	84	23	.04	97	..
.08	80	27			

[a] No added electrolyte.

TABLE VIII

INFLUENCE OF ELECTROLYTE[a] ON CATALYST ACTIVITY AT 12.8°

Hydroperoxide content (parts)	(% Conv. in 17 hr.) DHP	DIP
0.10	78	24
.20	100	70

[a] 1.0 part K_2SO_4/100 parts monomer.

(II). **Reaction with Iron(II)-Polyethylenepolyamine Complexes.**—When the iron(II) was complexed with triethylenetetramine, the reaction proceeded in the conventional manner insofar as reaction order was concerned. However, the lack of dependence of $E_{\text{app.}}$ on *p*H was contrary to that observed with this polyethylenepolyamine complex and monohydroperoxides.[2,7] In these a definite decrease of rate occurred as *p*H increased, indicating a change in the reactive form of the iron(II) complex. It was believed that this came about by a change in the number of solvated coördination spaces on the iron(II). A maximum in reactivity occurred when only one solvated coördination space was available. For the dihydroperoxide no alteration in the structure of the reaction species seemed to occur on changing the *p*H. The apparent frequency factor decreased, indicating removal of the reacting species from solution. These observations agree with those made on hydroperoxides if the unhydroxylated iron(II) complex be the reactive species.

Reaction could only occur if at least two coördination spaces were solvated. Since these two are used presumably to coördinate with the hydroperoxy groups in formation of the activated complex, a reasonable analogy with monohydroperoxides is apparent. The activated complex is shown diagrammatically in Fig. 5. The complex of hydroperoxide with the unisolvated complex must still be possible. However, the strong electronegativity of one *p*-hydroperoxy isopropyl group must stabilize it against further decomposition.

(III). **Reactivity of the *p*-Hydroxy Isopropyl Cumyloxy Radical.**—By far the outstanding characteristic of this radical is its tendency to react with

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(12) Moelwyn-Hughes, "Kinetics of Reaction in Solution," 1947, p. 121.

monomer rather than iron(II). Thus of all monomers investigated at both 25 and 40°, there was only one instance in which there was a significant tendency for the radical to react with iron(II) rather than with monomer (MMA at 40°). This is in marked contrast to the monohydroperoxy radicals investigated which normally react 500 to 1000 times as rapidly with iron(II) as with monomer. The reason for this lies in the variation of $E_{1i} - E_{1o}$ and A_{1i}/A_{1o} with the electronegativity of the *p*-substituent. Below is a comparison of the differences in activation energy for initiation and iron(II) oxidation as a function of Hammett σ-value, using some data previously reported[8] for solutions of acrylonitrile, in conjunction with the data above

σ	-0.191	0	0.778	4.5
$E_{1i} - E_{1o}$	8.0	0	-2.5	-20

There is a marked increase in the activation energy of iron(II) oxidation relative to that of reaction with monomer. Change in A_{1i}/A_{1o} values with σ tends to compensate for this effect. The compensation is by no means complete, with a resultant increase in activity toward monomer.

It is possible that a portion of this reactivity change is caused by resonance of the unpaired electron between the adjacent OOH and ·O group on the molecule which appear to be sufficiently close together to make hydrogen bonding possible. Under these conditions an electron only need shift to yield a resonance system which appears to represent a shift of hydrogen: ┌OOH ·O┐ ⇆ ┌OO····H····O┐ ⇆ ┌OO· HO┐.

(IV). **Utility as a Catalyst in Emulsion Polymerization.**—It is believed[8] that variations in the yield of polymer obtained from emulsion polymerizations when initiated by hydroperoxides of differing structure could be explained by the tendency of the hydroperoxy radical to indulge in non-polymerization side reactions. These side reactions comprise attack on iron(II) or hydroperoxide. With this catalyst, both of these have been suppressed with the result that it should be a superior initiator, if the above hypothesis is correct. Such was actually found to be the case, especially in recipes where conditions were so stringent that even the reasonably effective DIP failed.

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Paramagnetic Resonance of Liquid Sulfur: Determination of Molecular Properties[1]

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Paramagnetic resonance spectra have been obtained from liquid sulfur at temperatures from 189 to 414°. The paramagnetism, which increases reversibly with temperature, provides direct confirmation for the existence of long-chain sulfur polymers, and the results obtained are in quantitative agreement with the predictions of the theory due to Gee that postulates an equilibrium between long chains and S_8 rings. The heat of scission of sulfur–sulfur bonds in a long chain was found to be 33.4 ± 4.8 kcal./mole. The concentration of radicals at 300° was found to be $(1.1 \pm 0.6) \times 10^{-3}$ mole/l. and the average chain length is estimated to reach a maximum value of $(1.5 \pm 0.7) \times 10^6$ at 171°. Good agreement exists between these values and the estimates obtained from interpretation of the heat capacity data. The line width of the resonance increases markedly with temperature, but the spectroscopic splitting factor (*g*-value) is independent of temperature. The behavior of the line width is interpreted as evidence for a rapid radical displacement reaction giving for the rate constant $k = 2.8 \times 10^8 \exp(-3100/RT)$ l. (g.-atom)$^{-1}$ sec.$^{-1}$. Paramagnetic resonance spectra have also been observed from the black specks obtained by heating sulfur of ordinary purity. A description is given of the techniques of high temperature paramagnetic resonance spectroscopy and of the methods of obtaining absolute and relative paramagnetic intensities.

I. Introduction

For many years interest has been evoked by the occurrence of a transition in the physical properties of liquid sulfur at temperatures in the neighborhood of 160°; perhaps the most striking anomaly is the 10,000-fold *increase* in viscosity that takes place when the temperature is raised from 159 to 187°.[3] Studies have been made of the heat capacity,[4,5] the molecular aggregations,[6] the vapor pressure,[7] the composition of the vapor,[8,9] and the density.[10] Some of these measurements have been reviewed recently by Gee.[11] A number of investigators have also examined the properties of sulfur which has been quenched from a temperature above 160°: only a portion of the quenched sulfur dissolves rapidly in CS_2[12]; the material is elastic; repeated stretching increases the tensile strength by a factor of ten[13]; and after stretching a fiber X-ray diagram

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[1] Supported in part by Squier Signal Laboratory, U.S. Army Signal Corps.

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