[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LIMITED]

The Efficiency of Initiation by Cumyloxy and Sulfoxy Radicals in Free Radical Polymerization[1]

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The efficiencies of peroxy compounds in initiating polymerization can be explained by comparing the iron(II) induced decomposition reactions in aqueous media in the presence of monomer (M). The resultant free radical (RO·) may enter into the reactions: $RO\cdot + Fe(II) \rightarrow RO^- + Fe(III)$ (k_2); $RO\cdot + M \rightarrow ROM\cdot$ (k_3); $RO\cdot + ROOH \rightarrow RO_2\cdot + ROH$ (k_4). The ratios k_3/k_2 and k_4/k_2 were evaluated for different monomers and *p*-*t*-butylcumyloxy, cumyloxy, *p*-nitrocumyloxy, and sulfoxy ion free radicals. $E_3 - E_2$ and A_3/A_2 decreased in the cumyloxy series as the substituent group became more electronegative. The ratio k_4/k_2 increased as the substituent group became more electronegative. The ratios k_3/k_2 and k_4/k_2 for the sulfoxy ion radical depended on the ionic strength of the medium. At zero ionic strength the values were small due to the electronegative character of the free radical. The rates of the reactions of *p*-*t*-butylcumyloxy, *p*-nitrocumyloxy and sulfoxy ion radicals with methanol increased with the electronegativity of the *para* substituent. This can account for the inhibiting effect of methanol in polymerization reactions. The radical $CH_2OH\cdot$ was postulated as a product of this reaction and its rate of formation relative to the rate of reaction 2 was estimated.

Introduction

Since the advent of oxidation–reduction systems to initiate polymerization reactions at low temperatures[2,3] much interest has centered about the induced decomposition of cumene hydroperoxide, substituted cumene hydroperoxides and potassium persulfate and the ability of the products of the decomposition reaction to initiate polymerization in emulsion. Studies of substituted cumene hydroperoxides have been made[4–7] in which it was shown that substitution of an alkyl group in the *p*-position improved the performance in low temperature emulsion polymerization. The superiority could be due to a more rapid induced decomposition[4,8] by iron(II), a lower water solubility[5,9] or the formation of a more reactive free radical.[6] Data on the induced decomposition by iron(II) were available for *p*-nitrocumene, *p*-*t*-butylcumene and cumene hydroperoxide.[4,8,10] Data were available for the reaction between iron(II) and potassium persulfate[11,12] although it was necessary to extend these over a wider temperature range. This paper is concerned with the rates of the reactions of the free radicals produced in the above decomposition reactions with some monomers and methanol relative to the rates of the reactions of the radicals with iron(II).

Experimental Methods

The cumene hydroperoxide and derivatives were obtained from Hercules Powder Co. The nitrocumene (NCHP) and *p*-*t*-butylcumene hydroperoxides (TBCHP) were concentrated by cooling and separating crystals. These were recrystallized from benzene or petroleum ether and analyzed 95–100% pure iodimetrically. The cumene hydroperoxide (CHP) was precipitated as the sodium salt, washed with benzene, dried and regenerated by dissolving in water and adjusting to *p*H 8. The hydroperoxide was liberated into a petroleum ether layer which was separated. Evaporation yielded a product between 95 and 100% pure. The potassium persulfate was reagent grade analyzing >99% pure and was used without further purification. Methyl methacrylate (MMA), acrylonitrile (AcN), methyl acrylate (MA) and vinyl acetate were the center fractions from the distillation of technical material. Iron(II) sulfate, α,α'-bipyridine, glacial acetic acid and sodium acetate were C.P. grade. Nitrogen, fine grade, obtained from Canadian Liquid Air Co., was purified by passing through three alkaline pyrogallol scrubbers and over hot copper filings at 400°. These filings were cleaned with dilute nitric acid before each experiment so that the surface was free of oxides. The methanol was the center fraction of once distilled technical grade. Water was purified by redistilling once-distilled water from an alkaline solution of permanganate.

The rate constant for the primary decomposition reaction was obtained at the specified temperatures and ionic strengths by methods which have been described elsewhere.[4,8,10,12] The reaction cell was identical with the exception of minor additions to bring about good agitation of the contents.

Hydroperoxides, iron(II) sulfate and monomers were dissolved in water and added to the cell volumetrically. The solution was buffered at a *p*H of 4.2 using a sodium acetate–acetic acid buffer. Oxygen was removed by bubbling purified nitrogen through the solution of all reagents (except hydroperoxide) for 15 minutes. The iron(II) sulfate was dissolved in oxygen-free water. The oxygen was removed from the hydroperoxide solution separately and its addition to the reaction cell was considered as the start of the reaction. Unless otherwise stated, during the first four minutes of reaction the solution was kept under violent agitation to minimize errors due to incomplete mixing. This was provided by a stirrer rotating at 1500 r.p.m. The "blade" was an open tube tilted to the axis of the stirrer and so designed as to cause liquid to flow through the blade as the stirrer rotated thereby scooping the liquid at one end of the tube at one level in the flask and ejecting it from the other end of the tube at another level in the flask. At zero time and at intervals samples of the solution were removed and analyzed for iron(II) by a colorimetric procedure.[13] The same procedure was used in the experiments with methanol in the medium. It was necessary in the case of the *p*-*t*-butylcumene hydroperoxide to use 1% methanol to solubilize the hydroperoxide in the stock solution.

Theoretical

The investigation uses the ideas developed by Baxendale, *et al.*,[14] in a comparable study. By adjusting the concentration of reactants it is

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[1] Presented in part before the Division of Physical and Inorganic Chemistry, American Chemical Society, Kansas City, March, 1954, and the Symposium on Initiation Processes of the Division of Polymer Chemistry, American Chemical Society, New York, September, 1954.

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[3] J. M. Mitchell, R. Spolsky and H. L. Williams, *ibid.*, **41**, 1592 (1949).

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

[5] C. F. Fryling and A. E. Follett, *J. Polymer Sci.*, **6**, 59 (1951).

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

[9] S. J. Putnam, Hercules Powder Co., private communication.

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

[11] R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

[12] J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **73**, 4855 (1951).

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

[14] J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

possible to cause the decomposition of hydroperoxide in the presence of monomer to approach the mechanism

$$\begin{array}{lll}
\mathrm{ROOH} + \mathrm{Fe(II)} \longrightarrow \mathrm{RO}\cdot + \mathrm{Fe(III)} & k_1 & (1)\\
\mathrm{RO}\cdot + \mathrm{Fe(II)} \longrightarrow \mathrm{Fe(III)} + \mathrm{RO}^- & k_2 & (2)\\
\mathrm{RO}\cdot + \mathrm{M} \longrightarrow \mathrm{ROM}\cdot & k_3 & (3)\\
\mathrm{ROM}\cdot + \mathrm{M} \longrightarrow \mathrm{ROM}_2\cdot \ldots \longrightarrow \mathrm{ROM}_n\cdot & k_p & (4)\\
\mathrm{ROM}_n\cdot + \mathrm{A}\cdot \longrightarrow & & \\
\quad \mathrm{ROM}_n\mathrm{A}\ (\mathrm{A}\cdot \text{ may be any free radical}) & k_t & (5)
\end{array}$$

These conditions would be favored when the concentration of iron(II) is much greater than the concentration of hydroperoxide and with moderate amounts of monomer present. A stoichiometric ratio of 2 moles Fe(II)/1 mole hydroperoxide would be observed in the absence of monomer and unity in the presence of excess monomer. Rates of reaction 1 are known[4] but constants of reactions 2 and 3 are unknown. A kinetic analysis expressing the ratio of the total rate of iron(II) oxidation to the rate of iron(II) oxidation from reaction 2 is possible. Substitution for the steady rate concentration of the RO· radical, and expressing the consumption of iron(II) due to reaction 2 in terms of the total iron(II) consumption and that due to reaction 1, makes it possible to show that over a time interval

$$\frac{\Delta[\mathrm{Fe(II)}]_{\mathrm{Total}}}{\Delta[\mathrm{Fe(II)}]_{\mathrm{Total}} - \Delta[\mathrm{Fe(II)}]_{\mathrm{I}}} = \frac{k_3[\overline{\mathrm{M}}]}{k_2[\overline{\mathrm{Fe(II)}}]} + 2$$

$[\overline{\mathrm{M}}]$ and $\overline{[\mathrm{Fe(II)}]}$ are the average concentrations of monomers and iron(II), respectively, over the time interval. $\Delta\mathrm{Fe(II)}_\mathrm{I}$ is the consumption of Fe(II) by reaction 1. The total change in iron(II) concentration is the only observed value. It is necessary to estimate $[\overline{\mathrm{M}}]$, $\overline{[\mathrm{Fe(II)}]}$ and $\Delta[\mathrm{Fe(II)}]_\mathrm{I}$. $\overline{[\mathrm{M}]}$ was taken equal to the initial monomer concentration since this quantity is much larger than either hydroperoxide or Fe(II) concentration. The polymer will precipitate removing the contribution of the propagation step to the change in monomer concentration. An error will be introduced into the determination of k_3/k_2 through this choice of $\overline{[\mathrm{M}]}$ and will give values of k_3/k_2 which are low. The average iron(II) concentration is higher than the actual, giving rise to high values of k_3/k_2. The errors become smaller as the time interval which starts at zero time decreases and vanish when the time interval approaches zero.

The change in iron(II) concentration due to reaction 1 was calculated from the rate equation for the reaction. This implies that it is the only reaction contributing to the removal of iron(II). There is simultaneous removal of iron(II) due to reaction (2), hence the expression will lead to a high value of (k_3/k_2). The error introduced will decrease with both the time interval and the amount of reaction. An attempt to determine (k_3/k_2) over finite intervals would result in a first approximation of (k_3/k_2), as the quantity defined by $(k_3/k_2)''$. By determining the dependence of $(k_3/k_2)''$ on the time interval it becomes possible to estimate $(k_3/k_2)''$ at zero time interval, and so obtain a second approximation $(k_3/k_2)'$.

Two reactions have been described which are not considered in the above development and which may interfere with the validity of the treatment. The first is the reaction of RO· radical and hydroperoxide, RO· + ROOH → Products .... (k_4). This lowers the stoichiometric ratio $\Delta[\mathrm{Fe(II)}]/\Delta[\mathrm{ROOH}]$ to less than two. If the rate constant of this reaction is k_4, then $(k_3/k_2)'$ is equal to $[(k_3/k_2) + k_4\,[\mathrm{ROOH}]_0]/k_2[\mathrm{M}]_0$. The value of (k_4/k_2) may be determined experimentally from the dependence of $(k_3/k_2)'$ on monomer concentration. If there is a dependence, it is necessary to use a method of curve fitting. As the monomer concentration is increased, the contribution of $(k_4/k_2)[\mathrm{ROOH}]_0/[\mathrm{M}]_0$ becomes less and $(k_3/k_2)'$ approached (k_3/k_2). The method chosen to determine (k_4/k_2) was to assign arbitrary values to (k_4/k_2) and choose one which made (k_3/k_2) either independent of or linear with monomer concentration.

A second reaction[15] of interest is the oxidation of iron(II) by soluble, growing polymer chains

$$\mathrm{M}_n\cdot\ (\text{soluble}) + \mathrm{Fe(II)} + \mathrm{H_2O} \longrightarrow \mathrm{M}_n\mathrm{H} + \mathrm{Fe(III)} + \mathrm{HO}^-$$

This would increase the iron(II) consumption and make $(k_3/k_2)' < (k_3/k_2)$. If there is a significant contribution the plot of $(k_3/k_2)' - (k_4/k_2)([\mathrm{ROOH}]_0/[\mathrm{M}]_0)$ will not be independent of monomer concentration but will show an approximately linear dependence. The value of (k_3/k_2) was estimated by extrapolating this relation to zero monomer concentration. The same reasoning applies to reactions with other substrates such as methanol.

Results

Measurement of Rate Constants for Decomposition of Persulfate.—The rate constants of the reaction $\mathrm{Fe}^{++} + \mathrm{S_2O_8}^{=} \rightarrow \mathrm{Fe}^{+++} + \mathrm{SO_4}^{=} + \mathrm{SO_4}\cdot^{-}$ were measured at 25 and 40° (Table I). The ionic strength was 0.15, the same value which was used later in the studies on the reactions of the radical.

TABLE I

RATE CONSTANTS OF IRON(II) INDUCED DECOMPOSITION OF PERSULFATE ION

T, °C.	Initial [iron(II)], $M \times 10^5$	Initial [persulfate], $M \times 10^6$	Initial [acrylonitrile], M	k, l./mole/sec.	$k$av.
40	17.4	6.3	0	66.5	67.6
40	18.0	6.3	0	68.0	
40	18.3	6.3	0	68.1	
25	16.5	6.3	0.53	23.9	24.0
25	16.5	6.3	.53	23.8	
25	15.2	6.3	.53	24.3	

The tendency of the free radical to react other than by oxidation of iron(II) at lower temperatures prevented derivation of the rate constant by methods applicable at the higher temperature.[16] Determination in the presence of excess acrylonitrile[8,10] was required.

Study of Reactivity of Peroxy Free Radicals with Monomer, Iron (II) and Hydroperoxide.—The study was by determining $(k_3/k_2)''$ and $(k_3/k_2)'$ under varying conditions. Agitation which is im-

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(15) D. James, "Ferrous Iron Sensitized Acrylonitrile Polymerization," Can. High Polymer Forum, London, Ontario, Canada, Nov. 29, 1953.

(16) J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **72**, 4465 (1950).

portant, was mechanical and by a nitrogen stream. The value of $(k_3/k_2)''$ decreased on mechanical agitation of the mixture. This may be because samples taken at short time intervals were from a non-homogeneous solution and did not give a true value for the iron(II) concentration.

Since it was not convenient to carry out determination of hydroperoxide, and since monomer concentrations were known only at zero time, values of $(k_3/k_2)''$ were obtained over time intervals beginning at zero. Instances were observed where $(k_3/k_2)''$ increased with, decreased with, and was independent of the time interval indicating differing contributions from the various approximations to the total error. By extrapolating to zero time interval these errors were eliminated. The best fit of the data appeared to be obtained by a linear $(k_3/k_2)''$ *versus* time interval plot. Some data are in Fig. 1. At low rates of radical production $(k_3/k_2)''$ was negative due to a mixing effect significant only at short time intervals. This difficulty was avoided by measuring at high rates of radical production. $(k_3/k_2)'$ was normally dependent on monomer concentration, ($[M]_0$), as illustrated by Fig. 2 but could vary from quite marked dependence to near independence. This initial dependence is a result of the reaction of peroxy radical with hydroperoxide and the degree of dependence is determined by the magnitude of (k_4/k_2).

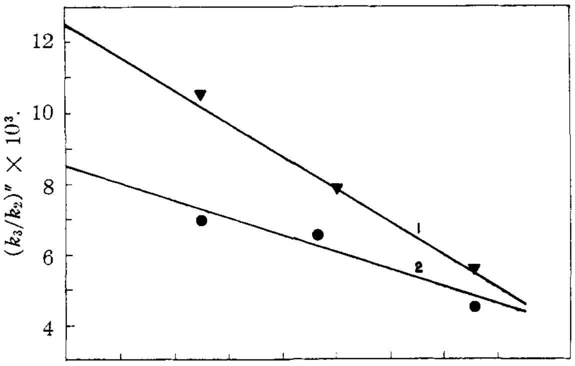


Fig. 1.—The ratio $(k_3/k_2)''$ *versus* time interval for which it was calculated for the reaction system containing *t*-butylcumene hydroperoxide and acrylonitrile at 20° (upper line) and 14° (lower line).

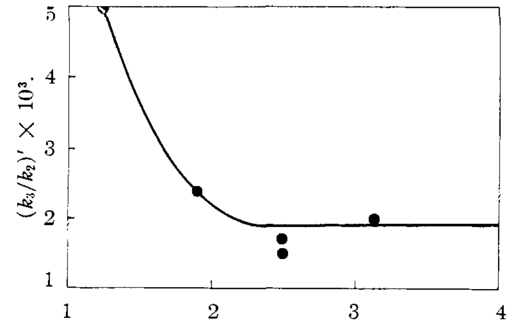


Fig. 2.—Dependence of ratio $(k_3/k_2)'$ on initial monomer concentration for system containing cumene hydroperoxide and methyl methacrylate at 14°.

Calculating $(k_3/k_2)' - (k_4/k_2)([ROOH]_0/[M]_0)$ for the reactions at higher temperatures did not give results independent of monomer concentration for any value of (k_4/k_2). There was a linear decrease in $(k_3/k_2)' - (k_4/k_2)([ROOH]_0/[M]_0)$ with increasing monomer concentration. This may be due to the oxidation of iron(II) by the soluble portion of the growing polymer. The relation was extrapolated to zero monomer concentration to obtain the value of $(k_3/k_2)' - (k_4/k_2)$

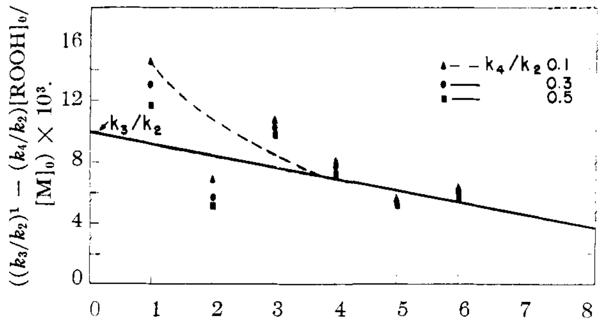


Fig. 3.—Determination of ratio (k_4/k_2) and (k_3/k_2) for system nitrocumene hydroperoxide and acrylonitrile at 48°.

TABLE II

VALUES OF (k_3/k_2) AND (k_4/k_2) FOR SOME PEROXY RADICALS AND MONOMERS

T, °C.	Peroxy compd.	Monomer	$(k_3/k_2) \times 10^3$	(k_4/k_2)
40	NCHP	MMA	8	1.0
		AcN	10	
		MA	8.0	
48		MMA	8	0.3
		AcN	10	
		MA	9.0	
59		MMA	6	<0.2
		AcN	8	
		MA	6.3	
14	CHP	MMA	0.76	0.2
25		MMA	2.0	<0.2
		AcN	1.3	
		MA	0.7	
48		MMA	1.5	0
		AcN	3.0	
		MA	2.0	
59	CHP	MMA	3.5	0
		AcN	2.0	
		MA	3.0	
0	TBCHP	MMA	0.8	0.4
		AcN	4.5	
14		MMA	3.0	<0.2
		AcN	8.1	
		MMA	6.7	<0.2
20		AcN	12	
25	$K_2S_2O_8$	MMA	4	2.5 ($\mu = 0.15$)
		AcN	2	
		MA	3	
40		MMA	0.6	0.5
		AcN	0.6	
		MA	2	

($[ROOH]_0/[M]_0$) which did not contain contributions from this reaction and hence could be equated to the actual (k_3/k_2). In Fig. 3 is a series of plots for the nitrocumyloxy radical showing the residual slope of the (k_3/k_2) − (k_4/k_2)($[ROOH]_0/[M]_0$) *vs.* monomer concentration when (k_4/k_2) was given a value which made the relationship linear. The values of (k_4/k_2) and (k_3/k_2) determined for the various monomer hydroperoxide combinations are in Table II.

The data for potassium persulfate are only true at the ionic strength (μ) shown. The Brønsted-Bjerrum equation[17] gives the relation between rate constant and μ for a reaction between two ions. It is possible from the above relation to determine the rate constant ratios at zero ionic strength. Some data are in Table III.

TABLE III

(k_3/k_2) FOR PERSULFATE SYSTEM

Monomer	(k_3/k_2) × 10^4 (25°)	(k_3/k_2) × 10^4 (40°)
AcN	3	0.8
MMA	6	0.8
MA	4.5	2.8

(k_4/k_2) was not corrected to zero ionic strength. It was large for the sulfoxy ion radical, partially because the ionic strength had a large effect, and would decrease with decreasing ionic strength. The ratio (k_4/k_2) increased with decreasing temperature and became less important on substitution of electropositive groups on the cumene nucleus.

The values of (k_3/k_2) at the different temperatures were expressed as the ratio of frequency factors (A_3/A_2) and the difference in activation energies ($E_3 - E_2$). For the sulfoxy ion radical these were calculated at zero ionic strength. The value of the Hammett constants for the groups on the cumene series are included.[18] The values are in Table IV.

TABLE IV

(A_3/A_2) AND ($E_3 - E_2$) VALUES FOR THE VARIOUS MONOMER–PEROXIDE PAIRS

Radical	Monomer	(A_3/A_2)	($E_3 - E_2$), kcal./mole	σ
p-t-Butylcumyl-oxy	AcN	2×10^{10}	8	−0.197
	MMA	1×10^{4}		
Cumyloxy	AcN	2×10^{-3}	0	0
	MMA	0.9×10^{-3}	3	
	MA	1×10^{3}	8.6	
Nitrocumyloxy	AcN	2×10^{-4}	− 2.5	+0.778
	MMA	4×10^{-4}	− 1.9	
	MA	4×10^{-5}	− 3.4	
Sulfoxy ion	AcN	1×10^{-16}	−17	
	MMA	6×10^{-22}	−26	
	MA	7×10^{-9}	− 7	

A least-squares plot of the data for CHP and MMA showed a 95% confidence interval of ±4 kcal./mole. In view of the small temperature interval available for study, and the inherent difficulties involved in precise curve fitting, these errors do not seem unreasonable.

Reaction of Peroxy Radicals with Methanol.—Reaction of iron(II) and nitrocumene or cumene hydroperoxide in the presence of vinyl acetate ($1^{-8} \times 10^{-2}$ *M*) and methanol (0.4–3.0 *M*) indicated a stoichiometric ratio of unity. The reaction between iron(II) and *p-t*-butylcumene hydroperoxide in the absence of monomer indicated that methanol in concentrations up to 0.13 *M* had no effect on the stoichiometric ratio of the reaction. With cumene hydroperoxide, addition of methanol (up to 2.6 *M*) in the absence of monomer brought about a decrease in the stoichiometric ratio, Δ[Fe(II)]/Δ[ROOH], below two. Similar behavior was observed with potassium persulfate. Data are in Table V.

TABLE V

STOICHIOMETRIC CONCENTRATION IN PRESENCE OF METHANOL AT 40°

Methanol, *M*	Peroxy compd.	Stoichiometric ratio Δ[Fe(II)]/ Δ[ROOH]
1.32	Cumene hydroperoxide	1.10
2.64	Cumene hydroperoxide	1.10
0.132	Potassium persulfate	1.17
0.264	Potassium persulfate	1.05
0.428	Potassium persulfate	1.00

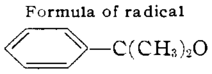
These reactions have a stoichiometric ratio of 2.0 in the absence of methanol. The free radical formed by the primary reaction must react with the methanol to give a free radical unreactive toward iron(II). Experience with other hydroperoxides and potassium persulfate[4,11,12] indicated that where the unshared electron is on an oxygen atom, the free radical is reactive toward iron(II). The hydrogen must have been abstracted from a carbon–hydrogen bond, according to the reaction

$$RO\cdot + CH_3OH \longrightarrow ROH + \cdot CH_2OH$$

It was possible to obtain the ratio of rate constants for the two reactions: $RO\cdot + CH_3OH \rightarrow ROH + \cdot CH_2OH$ . . . (k_5) and $RO\cdot + Fe(II) \rightarrow RO^- + FE(III)$ . . . (k_2). The ratios (k_5/k_2) are in Table VI. The sulfoxy radical is much more reactive toward methanol than is the cumyloxy type. This, with the information that the *p-t*-butylcumyloxy radical was not reacting at all with methanol, indicates that the greater the negative charge density about the unshared electron, the more reactive is the radical toward methanol. The efficiency of utilization of free radicals is decreased by reaction with iron(II) or methanol.

TABLE VI

VALUES FOR (k_5/k_2) IN REACTION OF FREE RADICALS WITH METHANOL AND IRON(II) AT 40°

Methanol, *M*	Formula of radical	(k_5/k_2)
1.3		2×10^{-4}
2.6		5×10^{-4}
0.13	$SO_4.^-$	5×10^{-3}
0.26		8×10^{-3}

Discussion

A correlation exists between ($E_3 - E_2$), (A_3/A_2) and the Hammett constants for the group in the

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(17) J. N. Brønsted, *Z. physik. Chem.*, **115**, 337 (1925); N. Bjerrum, *ibid.*, **118**, 251 (1925).

(18) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

p-position on the benzene nucleus in the cumene series. As the substituent group becomes more electronegative both $(E_3 - E_2)$ and (A_3/A_2) decrease. The influence of electronegative groups on the availability of the unpaired electron is more pronounced for reaction with monomer than with iron(II). The only difference in relative reactivity of free radicals toward monomer was evident for the *p*-*t*-butylcumyloxy radical.

The differences between the $(E_3 - E_2)$ and (A_3/A_2) for the reaction of the three cumyloxy radicals are considerable. There are two reasons for this. The activation energy for the primary step showed such a dependence on the Hammett σ value and a plot of E *vs.* log $(\sigma + 0.22)$ was linear.[4] The relation between $(E_3 - E_2)$ and σ is the same. This relation may be useful in predicting values of (k_3/k_2) for substituted cumenehydroperoxy radicals such as *p*-chlorocumyloxy, which have not been studied.

The variation of $(E_3 - E_2)$ and (A_3/A_2) indicate that changes in structure may have opposite effects on the activation energy and frequency factors of the two reactions. A group with a negative value would cause E_3 and A_3 to increase and E_2 and A_2 to decrease. The reaction involving transfer of an electron from iron(II) to hydroperoxide[4,8] was characterized by a decrease of E with decreasing σ. This was evidence for the formation of an intermediate coördination complex between the electron donor and the electron acceptor.

The reaction with monomer does not involve an electron transfer but the tendency of the unpaired electron to pair with one of the electrons from the carbon–carbon double bond. The effect of a low value is to attract the electron toward the benzene nucleus and render it less easily paired with the electrons of the double bond.

The reactions of the negatively charged sulfoxy ion radical revealed small $(E_3 - E_2)$ and (A_3/A_2) values. The reason for the magnitude of these is that the iron(II) free radical reaction has abnormally high activation energy and frequency factor. A high value of the frequency factor is expected due to the strong electrical attraction set up between the oppositely charged reactants. A for the reaction $Cr(H_2O)_6^{3+} + CNS^-$ was found[19] to be 3.3×10^{19}.

For ions of unlike charge[20,21] the collision number is greater than that for uncharged reactants by a factor $(e^{\Delta S^{\ddagger}/R})$ where $\Delta S^{\ddagger}$ is entropy of activation. The high activation energy of the reactions is due to an electrostatic contribution.

The data agree with the numerical values and trends reported at 60° in pure monomer. Practically all the radicals produced from any of the hydroperoxides initiate chains. The value of $(k_3/k_2) = 2 \times 10^{-1}$ for acrylonitrile and hydroxyl radical reported by Baxendale, *et al.*,[13] seems high. They made no attempt to correct for the approximations and meant the value to represent an order of magnitude.

The reactions of free radicals with alcohols in the absence of monomer have been described[22] although no evidence was found for a reaction between methanol and peroxide, possibly due to the lower temperatures. Since the stoichiometric ratio never decreased below unity, there did not seem to be any reaction between the $\cdot CH_2OH$ radical and peroxide. The fate of the $\cdot CH_2OH$ is probably mutual termination or disproportionation to form ethylene glycol or formaldehyde.

In the presence of vinyl acetate, the $\cdot CH_2OH$ shows a strong preference for the monomer[23] and is reported to form relatively short chain alcohols.

Extension of Results to Emulsion Polymerization.—The major factor affecting the utility of an hydroperoxide for polymerization purposes is the tendency of the corresponding free radical to engage in wastage reactions. There are three types: reaction with iron(II), reaction with hydroperoxide and reaction with impurities such as methanol.

In the recipe for alkaline emulsion polymerization the iron(II) is present as a chelate complex. The free iron(II) is governed by the dissociation constant of this complex. The concentration in the aqueous phase is about 10^{-9} M if the total iron(II) concentration is 1.8×10^{-3} M and if the dissociation constant is approximately 10^{-13}. If no complexing agent is present there is a rapid initial burst of polymerization followed by the cessation of the reaction at low conversions. One reason for this is that the radicals react with the iron(II) rather than with monomer. By decreasing the iron(II) content with a complexing agent to yield a complex unreactive toward hydroperoxy radicals or hydroperoxide, the rate of initiating radical production and the rate of radical wastage is slowed with an increase in the proportion reacting with monomer. It is possible to calculate some efficiencies using the present knowledge of emulsion polymerization mechanisms.

If all reaction between iron(II) and hydroperoxide occurs in the aqueous phase, then the hydroperoxide concentration in the aqueous phase is important. The concentration is determined by the partition coefficient of the hydroperoxide between the monomer and the aqueous phase. If the initiation of the polymer chain occurs in the aqueous phase, the effective monomer concentration at the site of initiation is determined by its solubility in the soap–water solution. For purposes of comparison the solubilities for TBCHP, CHP and potassium persulfate were taken such that the molar partition coefficients between oil and water were 99/1, 999/1 and 0/100. These are arbitrary estimates which reflect the trend shown in the water solubilities of these peroxides.[9] This renders the data subsequently obtained suitable only for visualizing trends. For styrene the presence of soap doubles, essentially, the concentration of monomer which would have been dissolved in pure water, assuming that a micelle is equivalent to a dissolved monomer molecule. The presence of emulsifier will make little difference in the recipe containing

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acrylonitrile. The ratios (k_3/k_2) for styrene and acrylonitrile are considered to be equal for any given hydroperoxide radical. Conversion rates of these two monomers in emulsion polymerization are sufficiently close that this seems a fairly reasonable approximation.

To obtain the k_3/k_2 values at 5°, the data from higher temperatures were extrapolated using the Arrhenius plot.

Data are presented in Table VII on the ratio of free radicals reacting with hydroperoxide and iron (II) to those reacting with monomer. K is the dissociation constant of the iron(II) complex, R_1 and R_2 are the ratios of radicals reacting with monomer to those reacting with iron(II) and peroxy compound, respectively.

TABLE VII

CALCULATED EFFICIENCIES IN EMULSION POLYMERIZATION AT 5°

Peroxy compd.	Monomer	K	R_1	R_2
CHP	Styrene	10^{-13}	80	7×10^{-2}
	Acrylonitrile	10^{-13}	100,000	0
	Styrene	10^{-10}	2	
	Acrylonitrile	10^{-10}	10,000	
	Styrene	[a]	4×10^{-4}	
	Acrylonitrile	[a]	0.4	
TBCHP	Styrene	[b]	. . .	6
	Acrylonitrile	[b]	. . .	0
$K_2S_2O_8$ ($\mu = 0.15$)	Styrene	[b]	. . .	0
	Acrylonitrile	[b]	. . .	4

[a] No complexing agent. [b] Data not calculated or not relevant.

In the presence of complexing agent, the important radical wastage reaction is with hydroperoxide. At higher values of the dissociation constant and in the absence of complexing agent, reaction with iron(II) becomes more important. As the solubility of the monomer increases, side reactions become less important.

The increase in hydroperoxide solubility in the aqueous phase caused by the presence of alcohol must be considered in addition to the reaction of radicals with methanol. TBCHP radicals did not react with methanol while CHP radicals did. It is not surprising that TBCHP is a much preferred hydroperoxide for polymerization reactions in the presence of methanol. As the temperature increases the monomer solubility increases and (k_4/k_2) decreases. At 50° (k_4/k_2) is zero or nearly so for almost all hydroperoxides, though not for potassium persulfate. At this temperature the efficiency of utilization of free radicals is 100%. Some over-all initial efficiencies are in Table VIII (for a complexing agent with $K = 10^{-13}$). These were calculated from the R_1 and R_2 values in Table VII by obvious methods.

TABLE VIII

PROPORTION OF RADICALS INITIATING POLYMERIZATION (EFFICIENCY)

Temp., °C.	Peroxy compd.	Monomer	Efficiency, %
5	TBCHP	Styrene	86
	CHP	Styrene	7
	CHP	AcN	100
25	$K_2S_2O_8$	Styrene	0
	$K_2S_2O_8$	AcN	41

CHP shows a low value which may indicate a lower partition coefficient than was assigned. The calculations are valid for acid-side emulsion polymerization. In alkaline media the reaction rate of radicals with hydroperoxide will remain the same but their reaction rate with iron(II) ought to be greater due to the formation of the more reactive $Fe(OH)^+$. These data (Table VIII) relate to the efficiency of free radical utilization at the beginning of the reaction. As the reaction proceeds the hydroperoxide will be consumed and the concentration of hydroperoxide in the aqueous phase will decrease. The monomer concentration will remain approximately at saturation. The efficiency will increase as the reaction proceeds and as the hydroperoxide concentration decreases. When half of the cumene hydroperoxide has been decomposed in the 5° recipe the efficiency should increase from 7 to 14%. The number of chains initiated is the product of the rate of hydroperoxide decomposition and the efficiency. The rate of hydroperoxide decomposition is proportional to the hydroperoxide concentration in the aqueous phase. The efficiency is proportional to the reciprocal of the hydroperoxide concentration. The number of chains initiated may be constant throughout the course of the reaction.

When mixed hydroperoxides are used the probability of the radical of one hydroperoxide reacting with the other must be included. This may cause wastage of hydroperoxide which will reduce the ultimate conversion attained without adversely affecting the initial polymerization rate.

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