

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Chain Transfer in the Hydroperoxide Initiated Polymerization of Styrene

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The reaction between styrene and *t*-butyl and cumene hydroperoxides in benzene at 70° has been studied by following monomer and peroxide disappearance and the molecular weight of the polymer formed. Results are consistent with the idea that almost all of the peroxide disappearance is accounted for by chain initiation and chain transfer reactions, although some (presumably polar) reaction to form styrene oxide may take place as well. Infrared spectra and chemical properties of the polymer indicate that the transfer reaction involves O-H bond scission, and a kinetic scheme is developed to account for the over-all kinetics. The transfer constants for *t*-butyl and cumene hydroperoxides obtained are 0.060 and 0.10 at 70°.

Organic hydroperoxides are substances of growing interest to the organic chemist because of their role as intermediates in autoxidation processes and because of their increasing availability as materials for study. Their chemistry presents a particularly absorbing problem since they readily take part in both polar and free radical type reactions.

Typical of their free radical reactions is thermal decomposition. Although hydroperoxides are among the most stable organic peroxides toward heat, they decompose at elevated temperatures in rather a complex manner. The rate of the process varies with the solvent¹⁻³ and is accelerated by added free radical sources.^{2,4} It thus has all of the characteristics of a composite reaction involving both primary scission into free radicals and induced decomposition involving free radical chains.⁵

An interesting example of such an induced decomposition occurs in the presence of suitable olefins. This reaction was first described by Farkas and Passaglia,⁶ who noted that, while cyclohexyl hydroperoxide shows no measurable decomposition in benzene in 270 hours at 70°, a 0.0288 molar solution in 1:1 benzene-styrene has a half-life of only 150 hours at the same temperature. Simultaneously the styrene is converted to a low molecular weight polymer ($\bar{P} = 1100$), approximately 328 molecules of styrene being polymerized per molecule of hydroperoxide consumed. These authors suggested that the accelerated decomposition is the result of either a failure of peroxide fragments to recombine in the presence of a reactive monomer, or else an "electron transfer" process involving peroxide and monomer. A more plausible explanation appears to be an induced decomposition via a chain transfer process similar to that demonstrated in the case of benzoyl peroxide-styrene,⁷ but occurring with much greater ease. Advancing this interpretation, Tobolsky has determined the apparent transfer constants⁸ for cumene hydroperoxide (CHP) and *t*-butyl hydroperoxide (TBHP) with styrene from molecular weight measurements on polymer formed at various initiator-monomer

ratios,⁹ and has also obtained a transfer constant for the CHP-methyl methacrylate system.¹⁰

Results on the over-all kinetics of hydroperoxide-olefin systems are complex and to some extent contradictory. Several workers have reported first-order rate constants for hydroperoxide decomposition,^{1,6,11} but not always with sufficient variation of concentration to make identification of the kinetic order certain. On the other hand Stannett and Mesrobian² reported a rate law as $-d[\text{CHP}]/dt = k[\text{CHP}]^{3/2}[\text{Styrene}]^{1/2}$ for the cumene hydroperoxide-styrene system, while Bateman and Hughes have reported kinetic orders varying from 3/2 to 2 for the decomposition of cyclohexene hydroperoxide in several olefins.¹² Because of these inconsistencies we have undertaken a more detailed study of the decomposition of CHP and TBHP in the presence of styrene, determining the rates of disappearance of both hydroperoxide and monomer, and also the molecular weight of the polymer being formed, since all of these must be accounted for by any satisfactory kinetic scheme. In addition we have obtained evidence that the transfer process involves O-H rather than O-O scission in the hydroperoxide molecule.

Experimental

Purification of Materials. Cumene Hydroperoxide.—Commercial cumene hydroperoxide obtained from Hercules powder company containing about 75% cumene hydroperoxide was first transformed into its sodium salt by adding 200 ml. of commercial hydroperoxide slowly to 600 ml. of a previously cooled 25% aqueous solution of sodium hydroxide with stirring and subsequent filtering by suction and washing with low boiling petroleum ether several times. The sodium salt was then suspended in low boiling petroleum ether and the hydroperoxide was liberated by treatment with Dry Ice. After most solvent was removed by concentrating the solution under reduced pressure the residue was distilled under low pressure to give about 100 ml. of the purified product (b.p. 62-64° (0.01 mm.), $n_D^{20} 1.5232$, 97% cumene hydroperoxide by titration).

t-Butyl hydroperoxide was obtained from the Lucidol Division of Novadel-Agene Corp. containing about 60% of *t*-butyl hydroperoxide and was also purified *via* its sodium salt. The regeneration of this hydroperoxide was done in saturated aqueous solution of its sodium salt by treatment of Dry Ice. The separated layer was first dried over anhydrous potassium carbonate and then fractionated through a 15-plate column under reduced pressure to give about 50% yield of the product (b.p. 38° (18 mm.), $n_D^{20} 1.3961$, 95-96% *t*-butyl hydroperoxide by titration).

Styrene.—Dow styrene N-99 was fractionated through a 15-plate column under reduced pressure to give the product

- (1) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).
- (2) V. Stannett and R. B. Mesrobian, *THIS JOURNAL*, **72**, 4125 (1950).
- (3) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *Disc. Faraday Soc.*, **10**, 242 (1951).
- (4) F. H. Seubold, Jr., F. F. Rust and W. E. Vaughan, *THIS JOURNAL*, **73**, 18 (1951).
- (5) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).
- (6) A. Farkas and E. Passaglia, *ibid.*, **72**, 3333 (1950).
- (7) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951).
- (8) F. R. Mayo, *ibid.*, **65**, 2324 (1943).

- (9) D. H. Johnson and A. F. Tobolsky, *ibid.*, **74**, 938 (1952).
- (10) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).
- (11) T. I. Yozhenko, D. K. Toloko and V. N. Puchin, *Doklady Akad. Nauk. S.S.S.R.*, **74**, 85 (1950).
- (12) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

boiling at 45.5° (16 mm.) with n_D^{20} of 1.5424. The freshly distilled material was used in each series of runs.

C.P. benzene, thiophene free, from Fisher Scientific Company was used without further purification.

Procedures. Kinetic Runs.—Weighed amounts of styrene and hydroperoxide were mixed in a 250-ml. measuring flask with C.P. benzene to the mark. Two samples of 10 ml. of the solution were drawn from the flask for the initial hydroperoxide titer determinations. The rest of the solution was then divided into six Pyrex tubes equipped with standard taper joints and previously cleaned with nitric acid and flamed. The tubes were attached to the vacuum line and the samples were frozen in Dry Ice- CCl_4 - CHCl_3 mixture. The tubes were then evacuated and samples were degassed twice by thawing and refreezing. The tubes were then sealed at the pressure of 1–2 μ . The polymerization reactions were carried out in a thermostat of $70 \pm 0.1^\circ$, and samples were taken out periodically for the determination of hydroperoxide and the isolation of polymer.

Isolation of Polymer. (1) *High Molecular Weight Polymer.*—A portion of 10 to 30 ml. of the reaction mixture was pipetted out and weighed and then quantitatively transferred into a conical flask containing about 200 ml. of C.P. methanol. Through continuous scrubbing the gummy polymer was disintegrated into small particles which were filtered through a Cenco sintered glass funnel and repeatedly washed with methanol. The nearly drained precipitate after applying gentle suction was then heated in a 80–90° oven for about six hours until constant weight is obtained. (2) *Low Molecular Weight Polymer.*—The reaction mixture was pipetted into a small egg-shaped flask and weighed as described above and then concentrated under reduced pressure below 40°. The residue was redissolved into a small amount of benzene and transferred into a weighing tube and then treated according to the frozen method given by Lewis and Mayo.¹³

Determination of Hydroperoxide.—A portion of 10 to 30 ml. of the reaction mixture was used for the determination of the titration titer according to the method given by Wagner, Smith and Peters.¹⁴

Determination of the Polymer Molecular Weight. (1) *Polymer of High Molecular Weight.*—Solution viscosities were determined in benzene at $26.70 \pm 0.01^\circ$ using a standard Ostwald viscosimeter. Fairly dilute solutions were used, yielding linear plots and the molecular weights of the polymers were estimated according to the relation

$$\log \bar{M}_n = 1.370 \log [\eta] + 5.223$$

employed by Mayo, Gregg and Matheson.⁷ Molecular weights determined in this way on successive samples from a given run showed some scatter but no significant trend, so averages of these values were taken as the best values for molecular weights at low conversion.

Properties of the Polymer.—For examination of the nature of the end-groups a sample of polymer of low molecular weight was prepared by heating a 1:1 styrene TBHP mixture (approximately 0.4 molar in each) in benzene for 36 hours at 70° in a sealed tube. The polymer, isolated as described above, appeared as a slightly yellow viscous material with a viscosity molecular weight of 1059. Its benzene solution gave no precipitate when diluted with methanol. Its infrared spectrum shows little absorption at 2.90 μ but medium absorption at 7.25 and 11.50 μ in addition to bands common with a standard polystyrene sample. The significance of these bands is discussed below.

Chemical examination of the sample showed no hydroperoxide by the standard titration.¹⁴ However, HI titration by the procedure for di-*t*-butyl peroxide¹⁵ gave an equivalent weight per dialkylperoxide unit of 480. Analysis¹⁶ of the polymer showed C, 80.09; H, 7.69; O (direct), 12.15.

Isolation and Identification of Styrene Oxide.—A number of 1:1 styrene-TBHP runs were made by refluxing 0.4 molar reactants in benzene for 48 hours. During this time 7–9% of the TBHP decomposed. Such a reaction mixture

was concentrated rapidly under reduced pressure and the distillate refractionated to yield a fraction, b.p. 81–82° (15 mm.), n_D^{20} 1.5350. The infrared spectrum and analysis of this product were identical with those of styrene oxide.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{O}$: C, 79.93; H, 6.71; mol. wt., 120.1. Found: C, 80.01; H, 6.57; mol. wt., 115, 120 (cryoscopically in benzene).

As a further identification 2.0 g. was hydrogenated in 95% ethanol using Pd on BaSO_4 . The sample took up 0.97 equivalent of hydrogen and gave after distillation 1.4 g. of a mixture of products boiling at 71–75° (2.5 mm.) with n_D^{20} of 1.5325. This mixture was heated with 3,5-dinitrobenzoyl chloride according to the procedure given by Shriner and Fuson.¹⁷ The separated solid was then crystallized from methanol several times to give long needles melting at 107–107.5°. The mother liquor was then diluted with water and allowed to stand in the refrigerator overnight. The separated solid was recrystallized several times from aqueous methanol to give needle-like crystals melting at 88–91°. The reported values of the melting points of 3,5-dinitrobenzoates of β - and α -phenylethanol are 108 and 95°, respectively.¹⁷

The actual yield of styrene oxide in several similar experiments was determined as 10–20% of the peroxide decomposed by HCl titration,¹⁸ a method with which other components in the reaction mixture were shown not to interfere.

Results and Discussion

Rate Data.—Kinetic runs, carried out as described in the Experimental part, give reproducible results providing highly purified samples of hydroperoxide are employed, and individual points yield smooth curves with no sign of induction periods or other abnormalities. When monomer disappearance is plotted as a 3/2-order reaction the data of individual runs give good straight lines (Figs. 1 and 2), while first- and second-order plots are appreciably curved. However, 3/2-order rate constants calculated from individual runs decrease with decreasing monomer concentration indicating that we are actually dealing with a kinetically more complex reaction. Accordingly we have employed an alternative treatment of the data, using the 3/2-

TABLE I
CUMENE HYDROPEROXIDE-STYRENE

Run no.	[M] ₀	[P] ₀	$-\frac{d[M]}{dt}$ (mole/l./sec. $\times 10^3$)	$-\frac{d[P]}{dt}$ (mole/l./sec. $\times 10^3$)	\bar{P}
2	4.99	0.198	7.256	5.50	193.8
3	4.08	.198	4.503	4.27	157.7
4	2.91	.204	1.999	3.55	107.6
5	1.97	.199	0.836	2.53	72.1
7	2.91	.101	1.739	1.40	226.2
9	2.91	.0505	1.375	0.57	446.7
10	2.91	.0240	0.972	0.27	781.1

TABLE II
t-BUTYL HYDROPEROXIDE-STYRENE

Run no.	[M] ₀	[P] ₀	$-\frac{d[M]}{dt}$ (mole/l./sec. $\times 10^3$)	$-\frac{d[P]}{dt}$ (mole/l./sec. $\times 10^3$)	\bar{P}
11	5.07	0.227	2.629	9.20	342.2
12	4.00	.227	1.510	8.08	270.3
13	2.99	.227	0.720	5.70	203.2
15	4.00	.113	1.358	4.90	531.9
16	4.00	.0567	1.142	1.23	968.7
17	4.00	.0284	0.970	0.72	1872

(13) F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

(14) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 979 (1947).

(15) Shell Chemical Corp., "Analytical Methods for Product Specification Tests," 1950, analytical method N-50-49.

(16) All analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(17) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(18) G. King, *J. Chem. Soc.*, 1980 (1951).

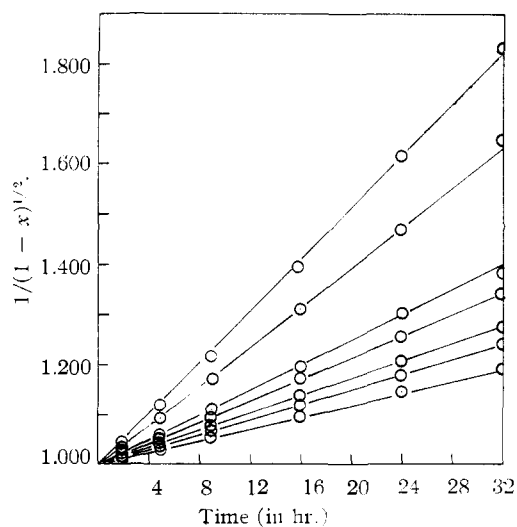


Fig. 1.—Styrene polymerization in the presence of CHP: x = fraction polymerized: top curve, [Styrene] = 4.99 mole/l., [CHP] = 0.198 mole/l., 2nd curve, 4.08: 0.198; 3rd curve, 2.91:0.204; 4th curve, 2.91:0.101; 5th curve, 2.91:0.204; 6th curve, 1.97:0.199; 7th curve, 2.91:0.0240.

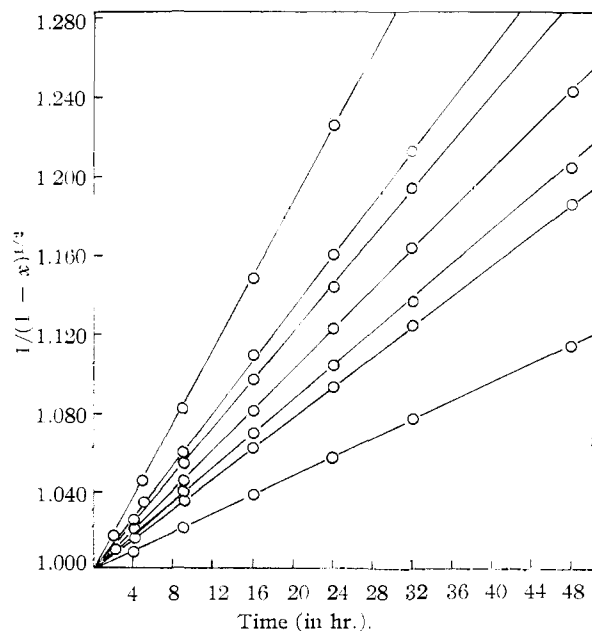


Fig. 2.—Styrene polymerization in the presence of TBHP: x = fraction polymerized; top curve, [Styrene] = 5.07 mole/l., [TBHP] = 0.227 mole/l.; 2nd curve, 4.00:0.227; 3rd curve, 4.00:0.113; 4th curve, 4.00:0.057; 5th curve, 2.99:0.227; 6th curve, 4.00:0.028; 7th curve, 2.03:0.227.

order plots to determine initial rates (Tables I and II) and then investigating the relation between these rates and peroxide and monomer concentrations (with other variables held constant).

Figure 3 shows the results of log log plots of polymerization rate *vs.* monomer and peroxide concentrations, the other component being held constant in each series. Each series of points lies on a good line the slopes of which indicate polymerization rate laws

$$\text{(CHP)} \quad -d[M]/dt = k[M]^{2.28}[P]^{0.86} \quad (1a)$$

$$\text{(TBHP)} \quad -d[M]/dt = k[M]^{2.88}[P]^{0.21} \quad (1b)$$

where $[M]$ and $[P]$ are monomer and peroxide concentrations.

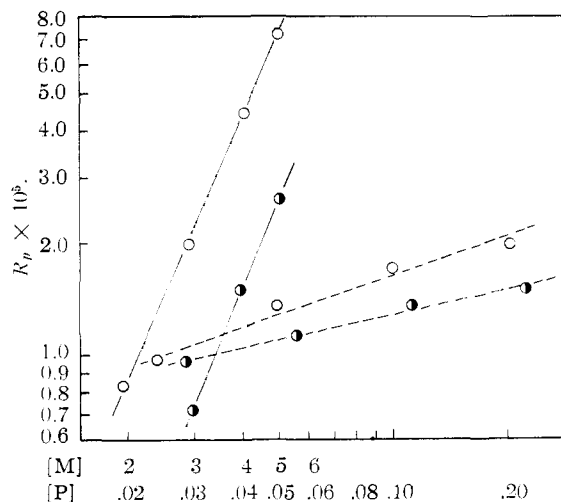


Fig. 3.—Variation of polymerization rate of styrene with $[M]$ and $[P]$: O, CHP; ●, TBHP; —, R_p vs. $[M]$; ----, R_p vs. $[P]$.

A similar treatment may be applied to peroxide disappearance. Here, again individual runs give good 3/2-order plots against which may be used to determine initial rates of peroxide decomposition, and log log plots similar to Fig. 3 give rate laws

$$\text{(CHP)} \quad -d[P]/dt = k[M]^{0.81}[P]^{1.18} \quad (2a)$$

$$\text{(TBHP)} \quad -d[P]/dt = k[M]^{0.87}[P]^{1.07} \quad (2b)$$

The apparent kinetic orders for our peroxide disappearance thus lies between the $[M]^{0.5}[P]^{1.5}$ relation reported by Mesrobian and the first-order law noted by others, but there is actually considerable experimental uncertainty, particularly in the case of TBHP. In complex chain processes of this sort over-all kinetics are frequently the most difficult property of the system to account for satisfactorily. Accordingly, before attempting any detailed treatment, we prefer to examine first the basic assumption that chain transfer is actually the major path for peroxide disappearance, and treat equations 1 and 2 above for the time being as purely empirical relationships.

Determination of Transfer Constants.—The "classic" method of investigating chain transfer reactions involves molecular weight measurements and is based upon the relation

$$\bar{P} = \frac{\text{rate of chain propagation}}{\sum \text{rates of formation of polymer ends}} \quad (3)$$

where \bar{P} is the average degree of polymerization.⁸ In systems such as these involving solvent, monomer and initiator four possibilities of polymer end formation exist: chain termination, chain transfer with initiator, chain transfer with monomer, and chain transfer with solvent. The transfer constants of polymerizing styrene with monomer (8.5×10^{-5})¹⁹ and with benzene (3.2×10^{-6} , interpolated from the data of Gregg and Mayo²⁰) are

(19) W. Cooper, *J. Chem. Soc.*, 2408 (1932).

(20) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

small enough so that these reactions may be neglected, but polymer end formation by the termination of kinetic chains remains an important correction. If chain termination by coupling of growing polymer chains is assumed the degree of polymerization is given by the relationship

$$\frac{1}{\bar{P}} + \frac{k_t d[M]/dt}{k_p^2 [M]^2} = C \frac{[P]}{[M]} \quad (4)$$

where C is the transfer constant (k_{tr}/k_p) for peroxide. Taking k_t/k_p^2 as 676 at 70° from extrapolation of Matheson's²¹ values of $2k_t/k_p^2$ between 25 and 60°, experimental values of the left-hand side of equation 4 are plotted against $[P]/[M]$ in Fig. 4. The slopes of the resulting lines give $C_{CHP} = 0.10$ and $C_{TBHP} = 0.060$, in reasonable agreement with Johnson and Tobolsky's⁹ values of 0.063 and 0.035, respectively, at 60°. Although the linear nature of the plots in Fig. 4 is evident, extrapolation to zero initiator concentration gives slightly negative values for $1/\bar{P}$. However, it should be noted that the correction for termination of kinetic chains is very large (as indicated by the dashed lines in Fig. 4 where $[P]/[M]$ has been plotted against $1/\bar{P}$, alone) and the amount of the correction depends upon the value of k_t/k_p^2 chosen, a quantity which is somewhat uncertain.²² Such an error could well change the intercepts of Fig. 4, and have a small effect upon the transfer constants determined.

This correction for chain termination yields further significant information, since one half its reciprocal in this interpretation is directly the kinetic chain length. In the CHP experiments these chain lengths vary from 250 to about 6000. During their course an average of 1-3 transfer reactions take place. TBHP experiments involve chains of about 500-1000, again with 4 or less transfers apiece.

An alternative method of determining transfer constants is by the relative rates of disappearance of monomer and transfer agent. If we assume that peroxide is consumed solely by chain transfer and a thermal decomposition which initiates chains we may obtain

$$\frac{d[P]}{d[M]} = C \frac{[P]}{[M]} - \frac{k_t d[M]/dt}{k_p^2 [M]^2} \quad (5)$$

identical in form to equation 4 above, but with $d[P]/d[M]$ replacing $1/\bar{P}$. The value of the transfer constant might be obtained from equation 5 by a plot similar to Fig. 4 or, better here, by comparing the observed value for the rate of total peroxide decomposition with that calculated from equation 5 using the transfer constants evaluated above. Such a material balance appears in Table III. The average ratio of calculated to observed rates of peroxide disappearance are 0.61 for CHP and 0.88 for TBHP. Several complications may account for the discrepancy. First, there may be some wastage of peroxide in the initiation process, radical sources in general being only 50-100% efficient in starting chains.²³ Second, as indicated

(21) M. S. Matheson, E. E. Auer, F. B. Bevilacqua and E. J. Hart, *THIS JOURNAL*, **73**, 1700 (1951).

(22) For a summary of different values of this ratio see A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

(23) Cf. for example, L. M. Arnett and J. H. Peterson, *THIS JOURNAL*, **74**, 2031 (1952).

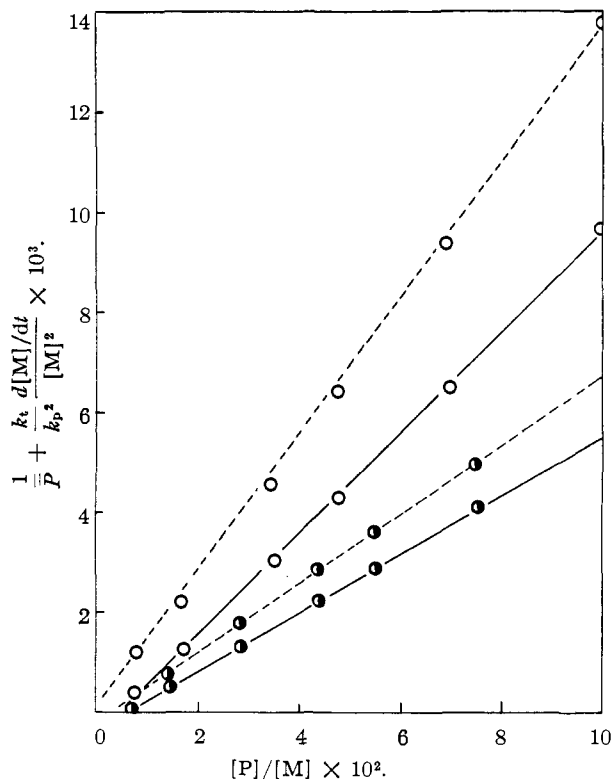


Fig. 4.—Determination of transfer constants from degree of polymerization, \bar{P} : O, CHP; ●, TBHP. Dashed lines and corresponding points represent data uncorrected for termination of kinetic chains (second term in ordinate neglected).

below there is evidence for a competing polar reaction between styrene and peroxide. Nevertheless, it is evident that initiation and transfer account for the major part of the peroxide consumed, in contrast to the cyclohexyl hydroperoxide-styrene system where some 2/3 of the peroxide disappears by some other path.⁶

TABLE III
COMPARISONS OF RATES OF DISAPPEARANCE OF HYDROPEROXIDES

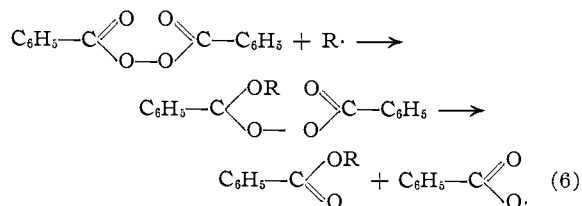
	CHP			TBHP	
	($\times 10^7$ moles/l./sec.) Calcd.	Obsd.		($\times 10^8$ moles/l./sec.) Calcd.	Obsd.
R-2	4.34	5.50	R-11	8.88	9.20
R-3	3.01	4.27	R-12	6.11	8.08
R-4	1.72	3.55	R-13	3.67	5.70
R-5	0.97	2.53	R-15	3.10	4.90
R-7	.85	1.40	R-16	1.48	1.23
R-9	.39	0.57	R-17	0.80	0.72
R-10	.16	0.27			

The Nature of the Transfer Reaction.—In general, radical displacement reactions such as occur in chain transfer involve the weakest bond in molecules. In peroxides this is the O-O linkage, and the products obtained from the induced chain decomposition of benzoyl peroxide in a number of solvents such as ethers and alcohols may be accounted for satisfactorily on this basis,^{24,25}

(24) W. E. Cass, *ibid.*, **69**, 500 (1947).

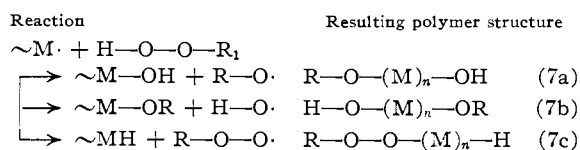
(25) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

although a more complex process involving double bond addition, *i.e.*



may be involved. A similar O-O cleavage of hydrogen peroxide has been suggested for oxidations involving Fenton's reagent,²⁶ and for hydroperoxides in their reactions with various radicals.²⁷ On the other hand, Vaughan and his group have obtained very definite evidence for O-H cleavage of hydroperoxides, particularly by reaction with alkoxy radicals.⁴ Such a result may at first seem surprising in view of the known low tendency of the hydroxyl hydrogen of alcohols to take part in radical displacement reactions, but, as has been pointed out by Uri,²⁸ the O-H bond of hydroperoxides is apparently significantly weaker than that of alcohols and water.

In order to make a decision between the three possible chain transfer processes



we have examined the low molecular weight polymer obtained on heating together equimolecular quantities of styrene and TBHP (approximately 0.4 molar) in benzene as described in the experimental part. The infrared spectrum of the polymer, in addition to the characteristic bands of polystyrene, shows absorption at 7.25μ indicative of methyl groups (C-CH₃) and a band at 11.50μ . This band is a characteristic of the infrared spectra of a number of peroxides and has been identified by Shreve, *et al.*,²⁹ as indicative of the -O-O- linkage. On the other hand, the spectrum shows no appreciable peak in the hydroxyl region around 3μ . Such a result appears to rule out reactions 7a and 7b but is in accord with a chain transfer process *via* O-H cleavage, reaction 7c, rather than by scission of the -O-O- bond.

Further evidence, while less satisfactory, also supports the same conclusion. The polymer, while inert toward the usual peroxide titration¹⁴ as expected of a dialkyl peroxide, liberates iodine from HI under the conditions used for the determination of di-*t*-butyl peroxide.¹⁵ The amount liberated, however, corresponds to a molecular weight of 480 (assuming one peroxide group/molecule) compared with a viscosity molecular weight for the sample of 1059. Several factors could account for this dis-

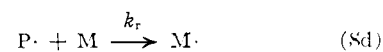
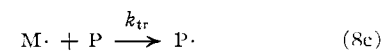
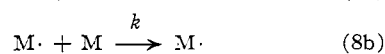
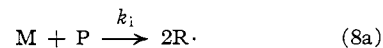
crepancy, *e.g.*, a broad molecular weight distribution in the polymer, or the HI reduction of small quantities of contaminants in the polymer, so its significance is hard to assess.

The oxygen content of the polymer (12.15%) is also compatible with peroxide linkages in the polymer, but the actual result is high indicating the apparent presence of oxygen containing contaminants, presumably of low molecular weight. Some idea of the nature of such low molecular weight products was obtained by the actual isolation of styrene oxide from a larger reaction mixture obtained by heating together equimolecular quantities of styrene and TBHP, 0.4 molar in benzene. Titration indicated that styrene oxide formation actually accounts for 10-20% of the peroxide consumed under these conditions. While such a product might conceivably arise by a radical reaction, it seems more likely that it is the result of a parallel polar reaction between styrene and TBHP analogous to the conversion of olefins to oxides by peracids. A similar reaction may well account for the formation of cyclohexene oxide in the autoxidation of cyclohexene,²⁹ by reaction of cyclohexene hydroperoxide with unreacted olefin. The polymer itself contains no epoxide linkages by titration, but might contain reaction products of styrene oxide with other species in the reaction mixture.

If such a reaction were important in our kinetic experiments, it could well account for the high peroxide consumption shown in some of the experiments listed in Table III. However, attempts to determine the presence of styrene oxide in several experiments by titration gave such erratic results that no definite conclusion was possible.

Interpretation of Over-all Kinetics.—In the previous sections we have seen that our results are consistent with the idea that we are actually dealing with a chain transfer reaction (presumably involving O-H bond scission) and that, in addition, there is a relatively rapid primary decomposition of both hydroperoxides in the presence of styrene. We may now try to combine these conclusions into a kinetic scheme compatible with the observed, and admittedly rather complex, over-all kinetics.

As a start, we may consider the reactions



Here 8a represents initiation by reaction of styrene and peroxide to yield free radicals of unspecified structure. While the details of such a process are unknown, the fact that the decompositions are rapid compared with those in inert solvents^{2,3} points to direct participation of olefin in the reaction. Further, since such rapid decompositions in the presence of an olefin have only been observed with *hydroperoxides*, and the

(26) J. H. Merz and W. A. Waters, *Discs. Faraday Soc.*, **2**, 179 (1947).

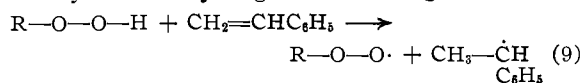
(27) M. S. Kharasch, A. Fono, W. Nudenberg and B. Bishof, *J. Org. Chem.*, **17**, 207 (1952).

(28) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

(29) O. D. Shreve, M. R. Heather, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

(30) Farmer and Sundralingham, *J. Chem. Soc.*, 121 (1942).

absence of -OH groups in the polymer suggest that it may involve hydrogen transfer, *e.g.*,

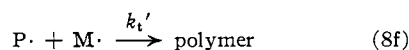


such a scheme yields, as an over-all rate expression

$$\frac{-d[\text{M}]}{dt} = k_p[\text{M}]^{3/2} \left(\frac{k_i[\text{P}]}{k_t} \right)^{1/2} \quad (10)$$

The 3/2-order reaction in respect to monomer agrees with the data on individual runs (Figs. 2 and 3) but not with the plots of Fig. 3. Contributions from an initiation process of higher order in monomer would improve the agreement, *i.e.*, from a termolecular initiation reaction.³¹

Another alternative would be through the introduction of a second termination process



This leads as a limiting value, to a rate expression

$$\frac{-d[\text{M}]}{dt} = k_p[\text{M}]^2 \left(\frac{k_i k_r}{k_t' k_{tr}} \right)^{1/2} \quad (11)$$

although the calculations in our discussion of the transfer reaction based upon \bar{P} and the known relation between polymerization rate and the rate of reaction 8e show that normal termination by polymer chain coupling must necessarily account for at least 25-50% of all the termination reactions in our kinetic runs. Reaction 8f merits further discussion. At first it may appear unlikely that, in a system where chain transfer occurs only once in every several hundred chain propagation steps, the concentration of P· radicals will be high enough to figure in the termination process. However, studies of the polymerization of styrene in the presence of oxygen, which leads to the formation of a linear polyperoxide by the sequence

(31) Recent evidence indicates that the thermal initiation of styrene polymerization is itself a termolecular process, *cf.* F. R. Mayo, *THIS JOURNAL*, **75**, 6133 (1953).



shows a pronounced drop in over-all rate of styrene disappearance as the amount of oxygen in the polymer increases.³² This, in turn, suggests that reactions of the type of 8d above are slow compared with ordinary chain propagation, *i.e.*,

$$k_p > k_r$$

Further, termination reactions between unlike radicals often show enhanced rates; but, even taking both of these factors into consideration, it seems unlikely that reaction 8f can account for more than a portion of the chain terminations.

Intrusion of 8f into the kinetic scheme would also alter the picture of the peroxide transfer reaction, since now every transfer results in the termination of *two* chains. Accordingly transfer constants measured by either of the methods discussed would be too large by a factor of two if every transfer were to end a chain and, in practice, may be somewhat high.

Since peroxide decomposition occurs by two different processes related to monomer consumption, which is already complex, it is probably best treated as in the preceding section without attempting to derive time-dependent kinetic expressions, particularly since significant quantities apparently disappear by other processes—either polar or radical—which are not taken into account in our reaction scheme. In fact, it is doubtful if any of the empirical expressions for hydroperoxide disappearance in the presence of olefins are of much theoretical significance at this time.

Acknowledgment.—The authors wish to thank E. I. du Pont de Nemours and Co. for a grant to Columbia University, a portion of which was used to support this investigation.

(32) S. Medvedev and P. Zetlin, *Acta Physicochim. U.R.S.S.*, **20**, 3 (1945).

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Enzyme-catalyzed Exchange of Oxygen Atoms between Water and Carboxylate Ion¹

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The hydrolysis of acetylcholine and ethyl acetate catalyzed by acetylcholinesterase, and the alkaline hydrolysis of acetylcholine have been shown to involve splitting of the -CO-O- bond. Acetylcholinesterase has been found to catalyze the exchange reaction between the oxygen atoms of fatty acids and water: $\text{RCO}_2^{16}\text{H} + 2\text{H}_2\text{O}^{18} = \text{RCO}^{18}_2\text{H} + 2\text{H}_2\text{O}^{16}$. The extent of the exchange is greatest with acetic acid, diminishes with propionic and formic acid, and is least pronounced with butyric acid. Similarly, two lipase preparations have been shown to catalyze the same general reaction, but in this case the extent of exchange was greatest with butyric acid. The nature of the activation process involved in esterase action is discussed in relation to these results.

Although enzyme action is generally interpreted in terms of a reactive enzyme-substrate complex,

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little is known of the process leading to formation of the initial complex. In an investigation of the nature of this activation process, Sprinson and Rittenberg⁴ observed that chymotrypsin brought about the exchange of the carboxyl oxygen atoms of carbobenzyloxy-L-phenylalanine with the oxygen atoms of the solvent, water. The exchange did not take place in the absence of the enzyme. Similarly,

(4) D. B. Sprinson and D. Rittenberg, *Nature*, **167**, 484 (1951).