

Radical Formation in the Reactions of *t*-Butyl Hydroperoxide with Styrene¹

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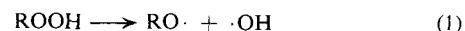
Rates of polymerization and hydroperoxide disappearance have been studied in several styrene-solvent systems at 70°. Hydroperoxide disappears by three paths: homolytic scission to induce polymerization, induced decomposition (chain transfer), and an apparent polar reaction yielding largely styrene oxide and *t*-butyl alcohol. The three processes for 0.2 M hydroperoxide in pure styrene account for 1.6, 7.9, and 90.5% of the decomposition, respectively. The rate of polymerization initiation, R_i , varies in a complex manner with solvent and peroxide concentration and, with deuterio-peroxide, $ROOD$, shows a highly variable kinetic isotope effect. Some of this variation is attributed to changes in the state of the hydroperoxide which exists as monomer, dimer, and complexes with aromatic solvents. When these are corrected for, radical formation appears to involve a unimolecular homolysis, a bimolecular reaction of hydroperoxide and styrene, and in benzene a termolecular process involving benzene as well. At high peroxide concentrations polymerization is slower than anticipated, and the result is consistent kinetically with chain transfer with hydroperoxide dimer to yield an unreactive radical.

A. Introduction

The important role of organic hydroperoxides in autoxidation reactions has led to an extensive study of their decompositions. These, in turn, have proved to be extraordinarily complex, varying with structure and reaction conditions and including simple homolytic scission of the O-O bond, oxidation-reduction, induced radical chains, and a number of polar reaction paths.³

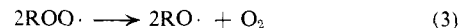
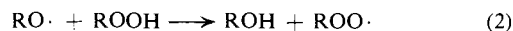
The thermal decomposition of *t*-butyl hydroperoxide (TBHP), which might well be expected to be a simple process and typical of *t*-hydroperoxides in general, well illustrates these complexities and poses a number of unresolved questions as to mechanism. In a number of solvents, e.g., benzene, cyclohexane, and CCl_4 , TBHP is quite stable showing no measurable decomposition in 5 hr. at 73.5°. Slow decomposition occurs at higher temperatures in aliphatic solvents⁵ or in the gas phase.^{5,6} Under these conditions first-order rate constants are concentration dependent, suggesting an initial homolytic scission of the O-O bond, accompanied

by some induced chain decomposition. The extrapolated rate constant for the homolytic scission (eq. 1) in

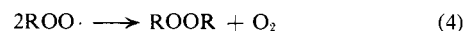


octane at 150–180° was originally estimated as $10^{15} \exp(-39,000/RT) \text{ sec.}^{-1}$, but it has been pointed out that this activation energy is unexpectedly low.⁷ Recently Benson, who has given a more complete kinetic analysis of the chain decomposition, questioned the determination of activation energy, and estimated $D(RO-OH)$ as 42.1 kcal., which should be the minimum possible value for E_a .⁸

In contrast to these relatively slow decompositions, pure TBHP decomposes completely in 24 hr. at 95–100° giving an almost quantitative yield of O_2 and *t*-butyl alcohol.⁹ A similar fast decomposition occurs at 140° in "inert" solvents such as chlorobenzene,⁵ and Bell, *et al.*,⁵ have proposed that it involves the chain sequence ($R = t-C_4H_9$)

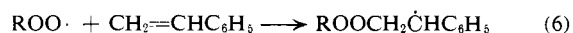
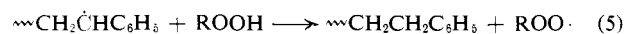


This formulation has been generally accepted,¹⁰ and step 3 and the extent to which it competes with a termination step such as



has become an important question in the interpretation of other reactions involving *t*-peroxy radicals.^{11,12}

In olefinic solvents such as styrene, the decomposition becomes very complex. The chain sequence 2 and 3 is suppressed by the trapping of peroxy radicals, but another induced decomposition *via* chain transfer takes its place and may be detected by its effect on polymer molecular weight.^{13–15}



Significant formation of styrene oxide has led to the suggestion that considerable TBHP is also consumed *via* a polar epoxidation reaction with olefin.^{15,16} However, the most interesting feature of the decomposition is the finding that the polymerization rate ob-

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 504.

(8) S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1964). Some other conclusions of this paper are discussed further below.

(9) N. A. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).

(10) D. B. Denney and J. D. Rosen, *Tetrahedron*, **20**, 271 (1964).

(11) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

(12) T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, **24**, 30 (1960); P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).

(13) R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951).

(14) D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, **74**, 938 (1952).

(15) C. Walling and Y. W. Chang, *ibid.*, **76**, 4878 (1954).

(16) W. F. Brill, *ibid.*, **85**, 141 (1963).

(1) Taken from the Ph.D. Thesis of L. Heaton, Columbia University, 1963. Support of this work by grants from the National Science Foundation is gratefully acknowledged.

(2) American Cyanamid Fellow, 1961–1962.

(3) General discussions and references are available in several recent texts: e.g., A. G. Davies, "Organic Peroxides," Butterworth and Co., London, 1961; E. G. E. Hawkins, "Organic Peroxides," E. and F. F. Spon, Ltd., London, 1961; J. O. Edwards, Ed., "Peroxide Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962.

(4) V. Stannett and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 4125 (1950).

(5) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

(6) A. D. Kirk and J. H. Knox, *Trans. Faraday Soc.*, **56**, 1296 (1960).

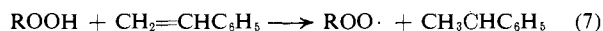
Table I^a

Solvent	[M] ₀ , mole/l.	[P] ₀ , mole/l.	[P] _c ^c mole/l.		R _p × 10 ⁸ , moles/l. sec.		R _i × 10 ⁸ , moles/l. sec.		R _i ' × 10 ⁸ , moles/l. sec.		
			TBHP	TBDP	TBHP	TBDP	TBHP	TBDP	TBHP	TBDP	
Benzene	3.81	0.431	0.1626	0.0896	1.68	2.42	2.27	4.91	3.66	5.33	
	3.80	0.216	0.0869	0.0467	1.49	1.97	1.80	3.14	2.17	3.23	
	3.80	0.108	0.0451	0.0248	1.33	1.43	1.43	1.65	1.51	1.67	
	3.80	0.0539	0.0230	0.0124	1.11	1.06	1.00	0.91	1.02	0.91	
	3.80	0.0269	0.0115	...	0.89	...	0.64	...	0.64	...	
	3.80	0.0215	0.0094	0.0050	0.79	0.70	0.51	0.40	0.51	0.40	
	3.80	0.0135	0.0059	...	0.68	...	0.37	...	0.37	...	
	4.76	0.216	0.0860	0.0458	2.63 ^b	2.54	3.57	3.33	4.06	3.40	
	2.85	0.216	0.0877	0.0490	0.72 ^b	1.38	0.75	2.74	0.99	2.84	
	7.15	0.016	0.0091	...	1.26	...	0.36	...	0.36	...	
	6.67	0.0216	...	0.0045	...	1.13	...	0.34	...	0.34	
	6.19	0.0216	0.0092	...	1.21	...	0.45	...	0.45	...	
	4.75	0.0216	0.0094	0.0048	1.01	0.81	0.53	0.34	0.53	0.34	
	4.27	0.0216	0.0094	0.0049	0.91	0.74	0.53	0.35	0.53	0.35	
CCl ₄	3.80	0.432	0.2254	0.1292	1.94	3.40	3.04	9.35	4.87	9.96	
	3.80	0.216	0.1204	0.0688	1.60	2.48	2.07	4.97	2.50	5.09	
	3.80	0.172	...	0.0562	...	2.22	...	3.99	...	4.05	
	3.80	0.108	0.0629	0.0358	1.32	1.63	1.41	2.15	1.51	2.16	
	3.80	0.0539	0.0321	0.0183	1.03	1.03	0.86	0.86	0.88	0.86	
	3.80	0.0269	0.0162	...	0.74	...	0.44	...	0.44	...	
	3.79	0.0215	0.0130	0.0074	0.67	0.71	0.38	0.41	0.38	0.41	
	3.79	0.0135	0.0082	0.0047	0.55	0.60	0.25	0.29	0.25	0.29	
	4.75	0.216	0.1114	0.0593	2.12	3.29	2.33	5.60	2.67	5.64	
	2.84	0.215	0.1317	0.0812	1.10	1.67	1.75	4.04	2.19	4.12	
	6.67	0.0216	0.0101	0.0050	1.10	1.12	0.32	0.33	0.32	0.33	
	4.75	0.0216	0.0119	0.0064	0.82	0.87	0.35	0.39	0.35	0.39	
	None	8.08	0.217	0.0830	0.0412	3.90	4.34	2.72	3.38	2.97	3.78
		8.16	0.108	0.0429	0.0210	2.79	3.20	1.37	1.80	1.42	1.80
8.21		0.0541	0.0221	0.0105	2.08	1.98	0.75	0.68	0.77	0.68	
8.23		0.0271	0.0113	0.0053	1.46	1.48	0.37	0.38	0.37	0.38	
8.24		0.0217	0.0090	0.0042	1.31	1.34	0.30	0.31	0.30	0.31	
8.24		0.0173	...	0.0034	...	1.19	...	0.24	...	0.24	
8.24		0.0136	0.0057	...	1.04	...	0.19	...	0.19	...	
Chloro- benzene		3.83	0.434	0.1704	...	1.82	...	2.64	...	4.00	...
		3.82	0.217	0.0918	...	1.59	...	2.02	...	2.47	...
		3.82	0.108	0.0477	...	1.48	...	1.75	...	1.84	...
		3.82	0.0542	0.0245	...	1.31	...	1.37	...	1.40	...
		3.82	0.0271	0.0126	...	0.96	...	0.74	...	0.74	...
		3.82	0.0217	0.0101	...	0.91	...	0.66	...	0.66	...
		3.82	0.0136	0.0063	...	0.78	...	0.49	...	0.49	...
	<i>o</i> -Dichloro- benzene	3.84	0.218	0.0883	...	1.75	...	2.43	...	2.79	...
3.83		0.109	0.0463	...	1.72	...	2.12	...	2.21	...	
3.83		0.0543	0.0236	...	1.45	...	1.62	...	1.64	...	
3.83		0.0272	0.0120	...	1.21	...	1.05	...	1.05	...	
3.83		0.0218	0.0097	...	1.17	...	0.98	...	0.98	...	

^a All concentrations are in moles/l. at 70°. ^b Taken from ref. 15. ^c Concentrations of "free" peroxide have been calculated using equilibrium constants given in Table X. Values listed for TBDP corresponding to high [P]₀ probably represent maximum [P] values since additional styrene complexes may be formed by TBDP in CCl₄ and bulk styrene.¹⁹

served implies a rate of radical formation many times higher than the total rate of peroxide decomposition in solvents such as benzene. This phenomenon was first noted by Farkas and Passaglia for the cyclohexyl hydroperoxide-styrene system.¹⁷ It appears to be quite general for hydroperoxide-olefin systems and has been discussed by several investigators.^{8, 15, 18}

Walling and Chang¹⁵ have suggested a bimolecular hydrogen transfer (the reverse of a radical disproportionation) as the radical-forming process.



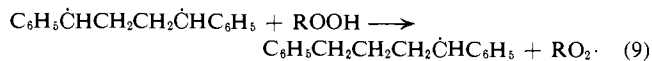
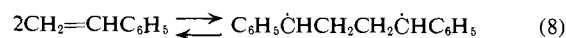
Tobolsky and Matlack,¹⁸ observing even more rapid radical formation in the presence of solvents such as pyridine and benzyl alcohol, have included bimolecular reactions (of unspecified mechanism) with these sol-

(17) A. Farkas and E. Passaglia, *J. Am. Chem. Soc.*, **72**, 3333 (1950).

(18) A. V. Tobolsky and L. R. Matlack, *J. Polymer Sci.*, **55**, 49 (1961).

(19) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 48 (1965).

vents as well, and Benson⁸ has added a polymolecular route



The objective of the work reported here has been to reinvestigate in detail the reactions occurring between styrene and TBHP at 70° in the hope of better sorting out these various reaction paths and establishing their possible mechanisms. For this purpose the following experimental methods appeared appropriate:

(1) Rates of styrene polymerization would provide a measure of the rates of effective radical production from TBHP.

(2) Polymer molecular weight would yield transfer constants and, accordingly, the importance of induced chain decomposition.

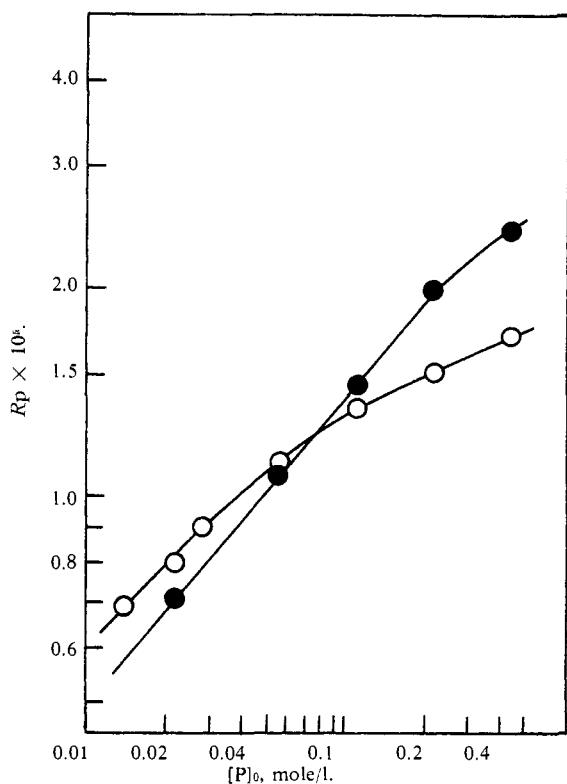


Figure 1. Polymerization initiated by TBHP (○) and TBDP (●) in benzene containing 3.8 M styrene at 70°.

(3) Comparison of TBHP and deuterioperoxide, ROOD (TBDP), would indicate the importance of O-H bond breaking in hydroperoxide decomposition.

(4) Measurement of over-all TBHP decomposition would indicate whether additional paths for hydroperoxide consumption would have to be considered, while identification of any low molecular weight products might suggest the nature of any such reactions.

As the work progressed, it became evident that polymerization rates showed a very complex dependence upon concentration of hydroperoxide, styrene, and solvent and that this was perhaps due to various association interactions of the hydroperoxide with itself, styrene, and solvent. Accordingly, these were investigated as well and are described in the accompanying paper.¹⁹

B. Polymerization Rates and Chain Initiation

The usual kinetic expression for the rate of radical polymerization R_p

$$R_p = k_p[M](R_i/2k_t)^{1/2} \quad (10)$$

is well established for styrene in not too dilute solution.²⁰ Equation 10 may be rewritten as

$$R_i = 2k_t(R_p/k_p[M])^2 \quad (11)$$

and, since $2k_t/k_p^2$ has a value of 1184 at 70° from the extensive correlation of available data by Tobolsky and Offenbach,²¹ rates of chain initiation, R_i , may be calculated from polymerization rates at known monomer concentrations. If chain initiation is through

(20) Reference 7, Chapter 3.

(21) A. V. Tobolsky and J. Offenbach, *J. Polymer Sci.*, **16**, 311 (1955).

attack by fragments arising from homolytic scission of a peroxide bond, occurring with a rate R_d

$$R_i = 2fR_d \quad (12)$$

where f represents the fraction of fragments actually starting chains and not wasted, *e.g.*, through cage recombination, and R_p provides a minimum value for the actual rate of radical production.

Polymerization rates in most of our work were measured dilatometrically in sealed, degassed systems, and the technique was checked in early experiments by gravimetric determination of polymer. Initial conversions were linear with time, and results (together with calculated R_i values) are listed in Table I.

The calculation of R_i assumes that hydroperoxide has no significant effect on polymerization rate other than its role as a chain initiator (*e.g.*, that chain transfer does not lead to significant retardation). This is a critical point and was checked by comparing rates of polymerization in azobisisobutyronitrile (AIBN) initiated systems in the presence and absence of hydroperoxide under conditions where AIBN accounted for about 95% of the initiation process (Table II). Cal-

Table II. Effect of Added AIBN on Polymerization Rates and Peroxide Disappearance in Benzene at 70°

Initiator	[M] ₀ , moles/l.	[AIBN] ₀ , mole/l.	[P] ₀ , mole/l.	$R_p \times 10^4$, moles/l. sec.		$-dP/dt \times 10^5$, moles/l. sec.
				Calcd.	Obsd.	
TBHP	3.8	...	0.22	...	0.15	2.0
TBHP	3.8	0.17	.22	2.99	2.91	9.5
TBDP	3.822	...	0.20	...
TBDP	3.8	0.17	.22	2.99	2.97	...

culated and observed rates agree well at the peroxide level investigated (0.22 M) although, as shown later, there is evidence for retardation at higher concentrations. Hydroperoxide decomposition *via* chain transfer is accelerated in the presence of AIBN, and the magnitude of the increase will be important later in identifying additional decomposition paths.

If initiation occurs through some sort of polymolecular reaction between hydroperoxide and styrene, over-all kinetics might be expected to take the form ($[P]_0$ = total hydroperoxide)

$$R_p = k[M]^\alpha[P]_0^\beta \quad (13)$$

with

$$R_i = 2fk_d[M]^{2\alpha-2}[P]_0^{2\beta} \quad (14)$$

where, for a simple bimolecular initiation, $\alpha = 3/2$ and $\beta = 1/2$. Our data indicate a much more complex situation in which α and β vary with solvent and peroxide concentration; and, more remarkably, when TBHP and TBDP are compared, the kinetic isotope effect changes drastically with experimental conditions. Figure 1 illustrates this situation in a log-log plot of R_p vs. $[P]_0$ for 3.8 M styrene in benzene, and other systems yield equally striking results. Later in this paper we will attempt to give an interpretation to these peculiarities in terms of changes in hydroperoxide activity and, for the time being, will simply use our observed polymerization rates as empirical measures of

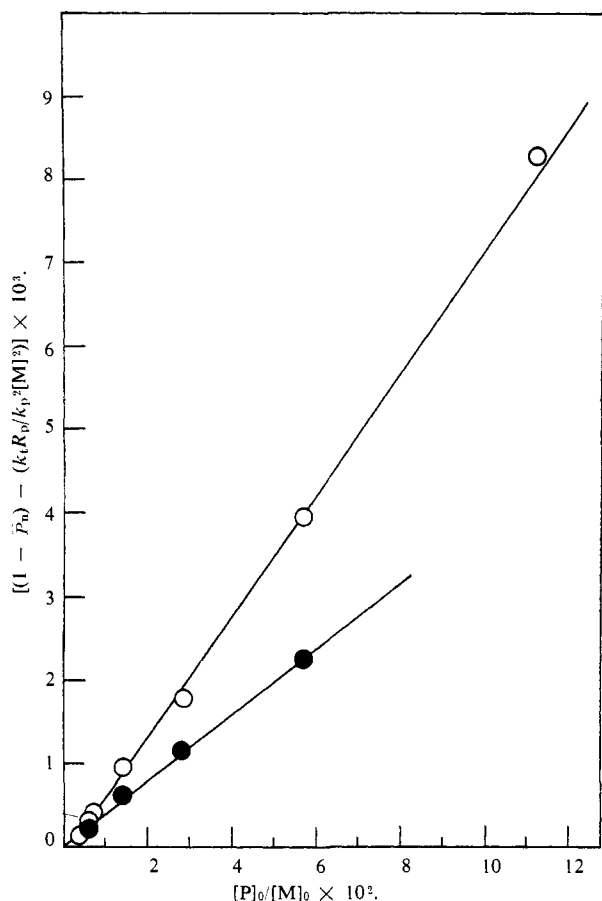


Figure 2. Determination of transfer constants: $[M]_0 = 3.8$ mole/l.; solvent, benzene; temp., 70° ; ○, TBHP; ●, TBDP.

the rate of hydroperoxide disappearance by homolytic scission, without regard for the detailed mechanism of the processes involved.

C. Chain Transfer and Induced Decomposition

In inert aromatic solvents (but not in CCl_4 which has a significant transfer constant of its own), the average degree of polymerization, \bar{P} , of styrene prepared in the presence of TBHP should be given by the usual chain-transfer equation

$$1/\bar{P} - k_t R_p / (k_p [M])^2 = C [P]_0 / [M] \quad (15)$$

and the transfer constant, $C = k_{tr}/k_p$, may be determined by plotting the left-hand side of (15) vs. $[P]_0/[M]$. Figure 2 illustrates the linear nature of such plots for 3.8 M styrene plus TBHP and TBDP in benzene, and Table III lists the transfer constants determined in

Table III. Transfer Constants for Initiator in Styrene Polymerization at 70°

Solvent	$[M]_0$, moles/l.	C	
		TBHP	TBDP
None	8.2	0.064	0.039
Benzene	3.8	0.066	0.039
Chlorobenzene	3.8	0.066	...
<i>o</i> -Dichlorobenzene	3.8	0.063	...

several solvents. Agreement with previous values of 0.060 at 70° ¹⁵ and 0.035 at 60° ¹⁴ is reasonable,

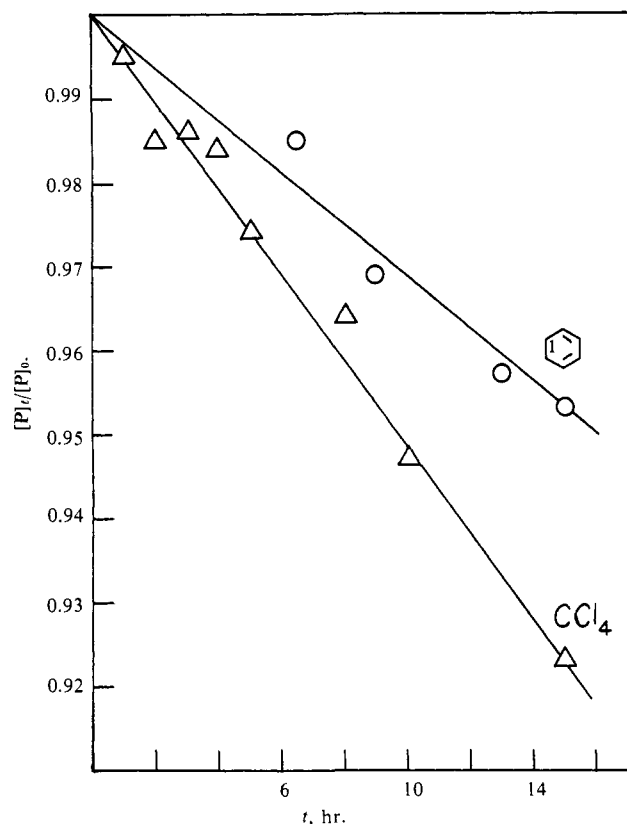


Figure 3. Decomposition of 0.22 M TBHP in solvents containing 3.8 M styrene at 70° .

and several conclusions may be drawn from the data. First, unlike R_i , C varies little with concentration of solvent, styrene, or peroxide, indicating that activity coefficients for hydroperoxide and the transition states for transfer must at least change in the same manner. Second, $k_H/k_D = 1.7$. This number is large enough to demonstrate conclusively that O-H bond breaking is involved in the transfer step as postulated in eq. 5. On the other hand, it is smaller enough than its maximum theoretical value to indicate a highly unsymmetric transition state. Since transfer should be quite endothermic,²² this transition state is probably one in which the new C-H bond is almost completely formed.

Finally, since the rate of the transfer process is given by CR_p , the data of Tables I and III make it possible to calculate the actual rates of consumption of hydroperoxide by transfer, quantities which will be useful in separating the different paths of hydroperoxide disappearance below.

D. Rates and Products of Hydroperoxide Decomposition

As we have seen, measurement of R_p and \bar{P} permit calculation of TBHP consumption *via* radical formation and induced decomposition. Comparison of the sum of these quantities with the over-all rate of peroxide disappearance should indicate whether TBHP is also being consumed by other reactions. In practice, accurate determination of peroxide disappearance proves somewhat difficult since measurements must be made at only a few per cent reaction before too

(22) $D(\text{ROO-H})$ is probably approximately 88 kcal. (*cf.* ref. 8, footnote 20), significantly larger than $D(\text{R-H})$ where R is a benzylic group.

extensive polymerization of styrene has occurred, and accordingly represent small differences between large titration values. The resulting scatter of points for decompositions of TBHP in 3.8 *M* styrene-benzene and styrene-CCl₄ are shown in Figure 3 and are typical of the precision achieved. Decomposition rates in all systems studied are listed in Table IV. Attempts

Table IV. Decomposition of 0.216 *M* Peroxide at 70°

Solvent	[M] ₀ , moles/l.	<i>k</i> ₁ × 10 ⁶ , sec. ⁻¹	
		TBHP	TBDP
Benzene	3.8	0.92	0.84
Chlorobenzene	3.8	1.25	...
<i>o</i> -Dichlorobenzene	3.8	1.57	...
CCl ₄	3.8	1.45	1.30
None	8.2	3.96	4.19

to assign an empirical kinetic order to the reaction again lead to rather variable and inconsistent results. Log-log plots of rate vs. [P]₀ have unit slope up to 0.1 *M* peroxide in CCl₄ and 0.2 *M* in benzene and then rise more sharply. At 0.22 *M* peroxide the order with respect to styrene varies from 1.2 to 2.26, depending on solvent.

Table V. Influence of Solvent Composition on the Fraction of 0.22 *M* Peroxide Consumed by Initiation of Polymerization, Chain Transfer, and Other Reactions at 70°

Solvent	[M] ₀ , moles/l.	Fraction consumed					
		By initiation		By chain transfer		By other reactions	
		TBHP	TBDP	TBHP	TBDP	TBHP	TBDP
None	8.08	0.016	0.019	0.079	0.050	0.905	0.932
Benzene	4.76	0.054	0.059	0.273	0.158	0.674	0.784
	3.80	0.045	0.087	0.324	0.242	0.631	0.673
Chlorobenzene	2.85	0.030	0.129	0.329	0.385	0.641	0.486
	3.82	0.038	...	0.229	...	0.735	...
<i>o</i> -Dichlorobenzene	3.83	0.036	...	0.185	...	0.780	...
CCl ₄	3.80	0.033	0.089

Table VI. Some Products of the Decomposition of 0.22 *M* TBHP in the Presence of 3.8 *M* Styrene at 70°

Solvent	Reaction time, days	Moles of product/mole of TBHP decomposed			
		<i>t</i> -BuOH	(CH ₃) ₂ CO	>C=	H ₂ O
Chlorobenzene	14.5	0.67	Absent	Absent	Present
	70	0.65 ± 0.04	0.07 ± 0.02	Absent	Present
CCl ₄	37	0.61 ± 0.02	Absent	Absent	Present
	76	0.44 ± 0.03	0.06	Present	Present
	17	0.16

The most significant feature of the rate measurements, however, is the apparent partition between reaction paths shown in Table V. *It is evident that radical formation and induced decomposition account for at most less than half of the peroxide decomposition, and 50-93% of the peroxide is actually being consumed by some other path.*

A priori, three possibilities must be considered for this "extra" decomposition, which, in order of increasing plausibility, are: a very low and variable efficiency (*f* value in eq. 12); an induced chain not involving styrene, and a nonradical reaction between TBHP and styrene.

A small *f* value certainly seems unlikely. Bartlett's studies of the *t*-butoxy radical derived from di-*t*-butyl peroxyate and similar peroxides indicate that it undergoes negligible cage recombination and can be completely scavenged.²³ Further, *f* values would have to decrease with increasing styrene concentration, and, in pure styrene, one would have to conclude that only 16/931 or 1.7% of the radicals initiate chains. While some wastage may occur, it is probably a very small fraction of this amount.

An induced chain not involving styrene is a possibility, but seems ruled out by the AIBN experiments in Table II. Here the rate of polymerization was increased 20-fold, while peroxide disappearance increased only fivefold, about the amount anticipated from the chain-transfer reaction. Again, addition of 5.6 × 10⁻⁴ *M* *p*-cresol to 0.216 *M* TBHP in 3.8 *M* styrene in CCl₄ (which enormously decreases peroxide decomposition in the absence of styrene) leads to only a 39% decrease in decomposition rate although polymerization was noticeably inhibited. The remaining alternative, a nonradical reaction between styrene and TBHP, is further supported by study of the low molecular weight products produced.

Identifiable products produced from decomposi-

tion of 0.2 *M* TBHP in the presence of styrene included styrene oxide, *t*-butyl alcohol, and water. No oxygen, acetone, or di-*t*-butyl peroxide were detected.

Since conditions could not be found for exact analysis of *t*-butyl alcohol in the presence of TBHP, alcohol was determined after complete decomposition of hydroperoxide. Still longer heating led to the appearance of acetone (presumably from the slow decomposition of polymeric peroxide produced by chain transfer) and, in CCl₄, partial conversion of *t*-butyl alcohol to isobutylene. Typical yields are shown in Table VI.

(23) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

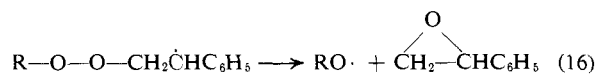
Styrene oxide could be determined at early stages in the reaction. The yield based upon TBHP consumed decreased on longer heating so it is evidently also consumed during reaction, and yields reported in Table VII are minimum values. Other products detected

Table VII. Yields of Styrene Oxide from Decomposition of 0.2 M TBHP in the Presence of Styrene at 70°

[M] ₀ , moles/l.	Solvent	Reaction time, hr.	TBHP decomposed, %	Moles of styrene oxide/mole of TBHP decomposed
3.80	Benzene	47	~14.5	0.42 ± 0.02
3.82	Chlorobenzene	17	~5.5	0.29 ± 0.04
8.08	None	13	~24.0	0.24 ± 0.03

by v.p.c. at low conversion were also apparently attacked, and only trace quantities remained on longer heating. These included a product, "x," about equal to styrene oxide, and another, "y," formed in quantities two to four times greater. The combined higher boiling fractions also contained a carbonyl component with an infrared peak at 5.90 μ in CCl₄, corresponding to the peak observed by Mayo in the products of styrene autoxidation and assigned by him to a C₆H₅-COCH₂-end group.²⁴

Mayo's studies of styrene autoxidation also yielded considerable styrene oxide, formed by the γ-scission process



The same sort of β-peroxy radical arises in our system as a consequence of chain transfer (reactions 5 and 6). Extrapolation of Mayo's data²⁴ on the ratio of styrene oxide formed to oxygen consumed to zero oxygen pressure indicates that 60% of his β-peroxy radicals undergo such decomposition at 50°. Assuming our radicals arising from chain transfer behave similarly at 70°, 60% of the hydroperoxide consumed by chain transfer should yield styrene oxide in pure styrene, and 76% should in 3.8 M styrene. However, in pure styrene this would only account for a 5% yield of styrene oxide, compared with 24% observed. Similarly, with 3.8 M styrene in benzene, chain transfer should yield 25% styrene oxide, and 42% is detected. Particularly when it is recognized that styrene oxide is being consumed during peroxide decomposition, it appears likely that a large portion of the "nonradical" decomposition is a simple epoxidation reaction between TBHP and styrene, yielding styrene oxide and *t*-butyl alcohol. On the other hand, other nonradical products are formed as well, but it appears plain that any attempts to interpret the over-all kinetics of hydroperoxide decomposition in olefinic systems, particularly in terms of radical chain processes,⁸ probably have little validity.

E. Rates and Products of TBHP Decomposition in the Absence of Styrene

Although the matter lies somewhat outside the main object of our research, we have carried out a few experiments on the rates and products of TBHP decom-

(24) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958).

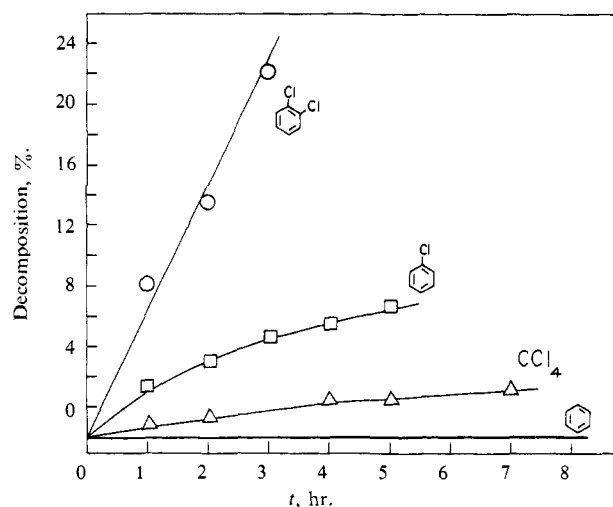


Figure 4. Decomposition of 0.2 M TBHP in solution at 70°.

positions in the same solvents used for the styrene work but in the absence of styrene. Some typical decomposition plots are shown in Figure 4, and rates, based upon the first hour of decomposition, are summarized in Table VIII. Striking differences are ob-

Table VIII. Approximate Rates of Decomposition of 0.2 M TBHP in Various Solvents Based on the First Hour of Reaction

Solvent	Rate × 10 ⁷ , moles/l./sec.
Benzene	0.1
Benzene + 0.5 M pentene-2	0.4
CCl ₄ + 1.0 M pentene-2	1
CCl ₄ + 0.5 M pentene-2	2
CCl ₄	5
Styrene	8.6
Chlorobenzene	21
<i>o</i> -Dichlorobenzene	67

served, paralleling previous reports, the decomposition being slow in benzene, very rapid in chlorobenzene and *o*-dichlorobenzene, and intermediate in CCl₄. The fast reactions are presumably induced chains, since *p*-cresol decreases the rate in CCl₄ by a factor of 66.

The slower rates observed in the chlorobenzenes containing styrene (compare Table IV) presumably also involve interception of the induced chain, and we see that pentene-2 produces a similar retardation in CCl₄. On the other hand, styrene and pentene-2 produce an *increase* in rate in benzene presumably by the superposition of nonradical processes on the homolysis.

The products of decomposition of TBHP in all four solvents are *t*-butyl alcohol, water, oxygen, and di-*t*-butyl peroxide (DTBP). Typical yields of alcohol and peroxide for the CCl₄ system are given in Table IX. DTBP is probably a chain-termination product of *t*-butyl peroxy radicals,^{11,12} and, when decompositions are forced to completion by long heating at 70°, it in turn disappears, *t*-butyl alcohol decreases, and new low-boiling products including acetone and isobutylene appear.²⁵

(25) Interestingly, acetone was also an initial product (1-6% in CCl₄) from decompositions in which light was not carefully excluded. Here decompositions were also more rapid, and the process, apparently induced through Pyrex by ordinary fluorescent lighting, certainly deserves further study.

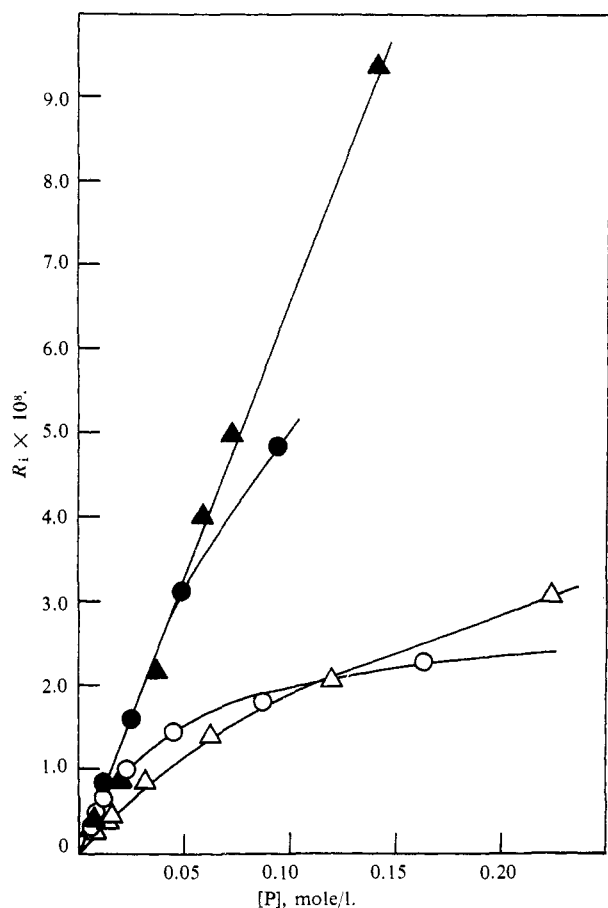


Figure 5. Dependence of R_i on the concentration of unassociated peroxide for 3.8 M styrene in benzene (\circ) and CCl_4 (Δ) at 70° ; white = TBHP; black = TBDP.

The foregoing results are consistent with the O_2 -forming chain (reactions 2 and 3), but its high rate in chlorobenzenes compared with benzene is puzzling. Conceivably the difference could arise in part from the formation of phenolic inhibitors by the attack of OH

Table IX. Some Products of the Decomposition of TBHP in CCl_4 at 70°

[P] ₀ , mole/l.	Re- action time, days	Mole per mole of TBHP decomposed		
		$(\text{CH}_3)_2\text{COH}$	$\text{COOC}(\text{CH}_3)_3$	$(\text{CH}_3)_2\text{CO}$
0.63	28	0.95	0.04	Absent
0.44	37	0.90	0.04	Absent
0.22	37	0.92	0.03	Absent
0.07	154	0.88	Trace	0.13

radicals on benzene. The corresponding chlorophenols might be expected to be less effective, but we may note that decomposition rates drop off with time in chlorobenzene and *o*-dichlorobenzene as well.

F. Kinetics and Nature of the Homolytic Reaction

Now that we have analyzed the various paths of hydroperoxide decomposition in the presence of styrene, we may return to a more detailed consideration of the homolytic process which results in the initiation of polymerization, and the complex dependence on medium and peroxide concentration described in

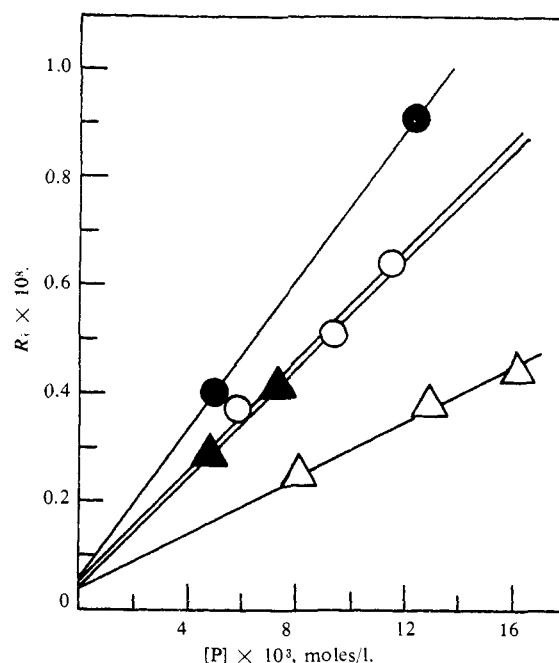


Figure 6. Dependence of R_i on $[P]$ for low concentrations of peroxide in benzene, \circ , and CCl_4 , Δ , containing 3.8 M styrene at 70° ; white = TBHP; black = TBDP.

section B. Since reaction rates, from transition-state theory, depend upon the difference in free energy of reactants and transition states, such changes in rate may depend upon variations in the energies of either or both. As we show in the accompanying paper,¹⁹ the state and energy of TBHP varies markedly with solvent and concentration, being determined by the equilibria summarized in Table X. These equi-

Table X. Equilibrium Constants for Formation of Hydrogen-Bonded Complexes at 70°

Substrate	Complex	K_H^a	K_D^a
P	P-P	0.60	0.64
Styrene	P-M	0.17	0.50
P, styrene	P-P-M	0.1	0.3
Benzene	P-S	0.11	0.25
Chlorobenzene	P-S	0.10	
<i>o</i> -Dichlorobenzene	P-S	0.13	
P, benzene	P-P-S	0.07	0.15
P, chlorobenzene	P-P-S	0.06	
P, <i>o</i> -dichlorobenzene	P-P-S	0.08	

^a Equilibrium constants are based on concentrations in moles/l.

libria in turn make it possible to determine "free" peroxide concentrations in our systems and thus, by correcting for variations in activity coefficients, remove contributions from changes in the energy of the reactant hydroperoxide.²⁶ Such "free" peroxide concentrations, designated as $[P]$, are included in Table I. In Figure 5, R_i is plotted vs. $[P]$ for 3.8 M styrene systems in benzene and CCl_4 . The resulting curves are linear at low $[P]$, although of differing slope. At higher concentrations they curve downward, curva-

(26) The basis of the correction is that the partial free energy of a substance in solution is equal to the partial molar free energy of the uncomplexed monomeric solute: cf. J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 33. This book gives an excellent discussion of the whole problem.

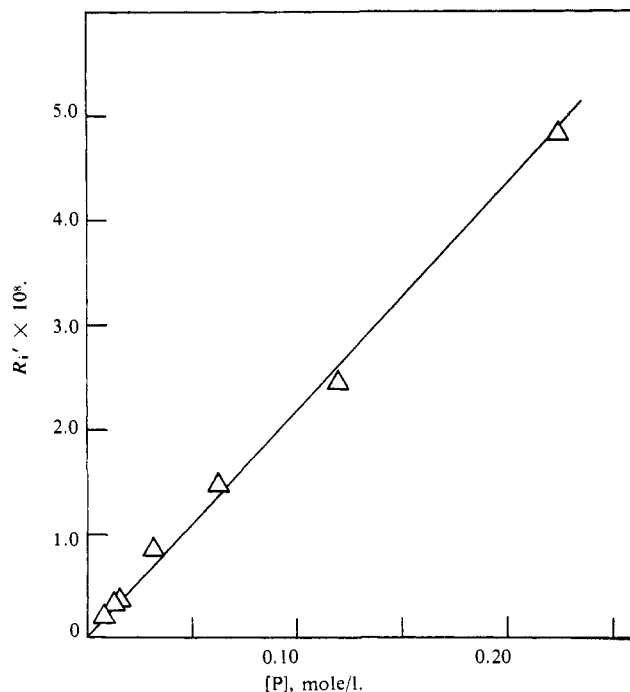


Figure 7. Dependence of R_i' on the concentration of unassociated TBHP in CCl_4 containing 3.8 M styrene at 70°.

ture being more pronounced for TBHP experiments than for those involving TBDP.

An enlargement of the lower left-hand corner of Figure 5 is shown in Figure 6. While it might appear most logical to examine first the linear portion of the curves at low peroxide concentration, our best data are actually at the higher concentrations. Furthermore, only a small number of points fall within the linear region shown in Figure 6, making accurate determination of the slopes of the resulting curves difficult using low peroxide data alone. Accordingly we will first attempt to develop a "straightening function" based upon a reasonable explanation of the curvature which will enable us to use all the data to obtain a best value for the R_i -[P] relation in the low [P] range.

The downward curvature suggests that some sort of retardation occurs at high peroxide concentration, and examination of the data shows that the curves depart from linearity at about the point where hydroperoxide dimerization becomes appreciable. Accordingly, we advance the hypothesis that peroxy radicals arising from chain transfer also complex with hydroperoxide to form relatively unreactive dimeric species. The proposal has precedent in other examples of peroxy radical stabilization by hydrogen bonding with -OH functions²⁷ and our own work on alkoxy radical solvation.²⁸ To put our hypothesis in form for kinetic analysis we shall assume that such hydrogen-bonded dimer radicals arise by chain transfer with peroxide dimer and disappear by bimolecular reaction without restarting chains. Table X indicates two such peroxide dimers, P-P and, in benzene, P-P-S.

(27) F. F. Rust and E. A. Youngman, *J. Org. Chem.*, **27**, 3778 (1962); E. A. Youngman, F. F. Rust, G. M. Coppinger, and H. E. De La Mare, *ibid.*, **28**, 144 (1963); I. V. Berezin and A. M. Ragimova, *Zh. Fiz. Khim.*, **36**, 581 (1962); E. T. Denisov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 53 (1960).

(28) C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963); **86**, 3368 (1964).

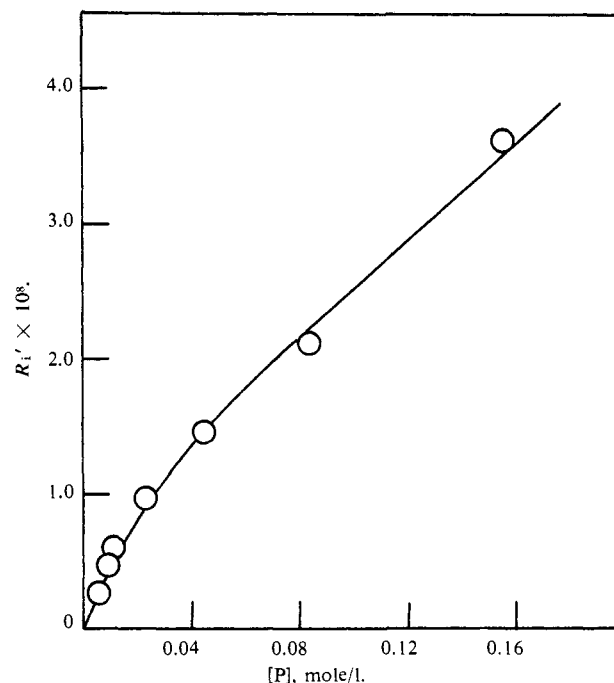


Figure 8. Dependence of R_i' on the concentration of unassociated TBHP in benzene containing 3.8 M styrene at 70°.

Under such circumstances, R_i must now be calculated from the steady-state relation

$$R_i' = 2k_t[M\cdot]^2 + k_{tr}'[M\cdot][P-P] + k_{tr}''[M\cdot][P-P-S] \quad (17)$$

Since, as we have seen in section C, transfer constants using total peroxide concentrations are independent of the state of the peroxide, we are justified in setting $k_{tr}' = k_{tr}'' = 2k_{tr}$ (as defined in eq. 15), and obtaining the relation

$$R_i' = \frac{2k_t R_p^2}{k_p^2 [M]^2} + \frac{2CR_p}{[M]}([P-P] + [P-P-S]) \quad (18)$$

Calculated values of R_i' are included in Table I, and eq. 18 obviously reduces to (11) at low peroxide concentration. Styrene- CCl_4 systems represent the simplest case, since P-P-S is absent; in Figure 7, R_i' is plotted vs. [P]. The result is essentially a linear relation, supporting the qualitative validity of the scheme,²⁹ and its success also provides a good explanation for the much more linear plots of TBDP data in Figure 5. Deuterioperoxide forms less dimer and more P-M complex, and what dimer is present undergoes less chain transfer to yield inactive radicals.

Plots of R_i' vs. [P] for styrene-benzene systems appear in Figure 8, and it is evident that some further additional retardation occurs at the highest peroxide concentrations. At this point our arguments have grown too tenuous to attempt a quantitative explanation, but perhaps we are observing the same sort of interaction between peroxy radicals and phenolic derivatives formed from benzene suggested to account for the low rate of hydroperoxide decomposition in that solvent.

(29) In any case, the treatment provides a good straightening function for the TBHP data, and the slope of the line in Figure 7 was that actually employed in subsequent calculations.

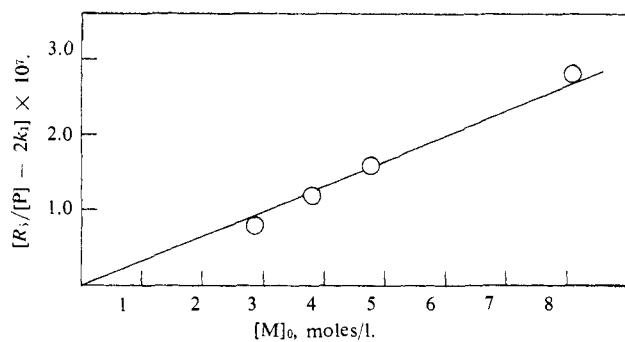


Figure 9. Dependence of the rate of initiation of styrene polymerization by TBHP on $[M]_0$ in CCl_4 at 70°

The observed dependence of R_i' on styrene concentration in CCl_4 may be used to examine a hypothesis similar to that proposed by Tobolsky and Matlack¹⁸ that radical formation is the sum of unimolecular and bimolecular processes, *i.e.*

$$R_i' = 2k_1[P] + 2k_2[P][M] \quad (19)$$

Slopes of the R_i' vs. $[P]$ plots shown in Figure 7 yield the following average values of k_1 and k_2 for TBHP over the concentration range studied: $k_1 = 3.9 \times 10^{-8} \text{ sec.}^{-1}$, $k_2 = 1.7 \times 10^{-8} \text{ l. mole}^{-1} \text{ sec.}^{-1}$. In Figure 9, inclusion of the limited rate data in CCl_4 at intermediate styrene concentrations is seen to give a reasonably good straight line when $(R_i'/[P] - 2k_1)$ is plotted vs. $[M]$.

Evaluation of rate constants for initiation by TBDP at high peroxide concentrations in CCl_4 is complicated by the presence of additional complexes involving peroxide dimer.¹⁹ The lack of sufficient data to determine accurately the equilibrium constants at 70° for these complexes makes the concentration of "free" peroxide somewhat uncertain for TBDP at high $[P]_0$ in CCl_4 . Rate data at low $[P]_0$ is free of this complication, however. Using only this low concentration data and neglecting any secondary isotope effect on k_1 , a value of $4.8 \times 10^{-8} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ is obtained for k_2 . Thus $k_2(H)/k_2(D) = 0.28$, almost precisely the same as the ratio of the equilibrium constants for peroxide-styrene complexes in Table X, suggesting either that it is the complex itself which decomposes or that the transition states and complexes have very similar structures. In either case, the result seems to rule out both our earlier proposal¹⁵ (reaction 7) of a hydrogen transfer which should certainly yield $k_2(H)/k_2(D) > 1$ or a termolecular process (reactions 8 and 9) as suggested by Benson.⁸

A similar examination of the dependence of initiation rates on styrene concentration can be made for the benzene system by using only the data at low peroxide concentration where R_i' vs. $[P]$ plots are linear. Unlike the CCl_4 system, reactions in benzene solvent fail to give a linear plot of eq. 19. They can be rationalized, however, by including a third termolecular initiation term

$$R_i = 2k_1[P] + 2k_2[P][M] + 2k_3[P][M][S] \quad (20)$$

Rearranging 20 gives

$$[(R_i/[P]) - 2k_1]/[M] = 2k_2 + 2k_3[S] \quad (21)$$

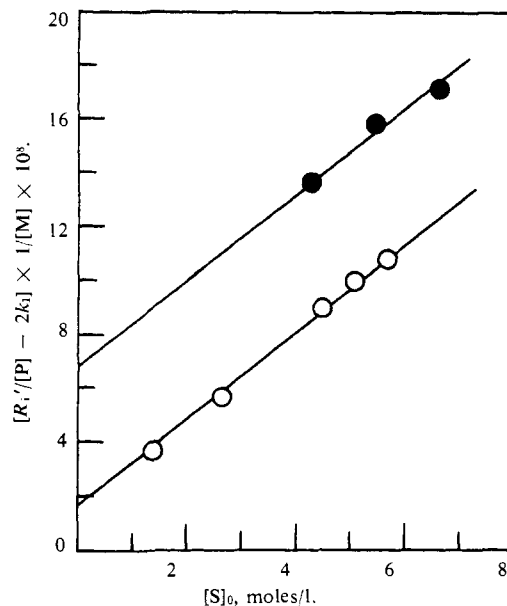


Figure 10. Dependence of the rate of initiation of styrene polymerization by TBHP (○) and TBDP (●) on $[S]_0$ in benzene at 70° .

Assuming k_1 (which makes only a small contribution) is the same as in CCl_4 -styrene systems, eq. 21 is plotted in Figure 10, yielding the following k values.

	$k_2 \times 10^8$, l./mole/sec.	$k_3 \times 10^8$, l. ² /mole ² /sec.
TBHP	0.9	0.8
TBDP	4.0	0.8

k_2 values are somewhat smaller than those obtained in CCl_4 solvent but show the same sort of isotope effect. However, k_3 values (which account for 80% of the reaction in 3.8 M styrene-benzene) show no isotope effect at all.

Although the nature of the termolecular process is unknown, a possibility would be the reaction of a (known) peroxide-benzene complex with styrene. Since K_H/K_D for the complex is 1/2.3, this would imply a k_H/k_D ratio for its reaction of 2.3, suggesting here the possibility of a hydrogen transfer as the initiation step, although admittedly on little direct evidence.

In the foregoing discussion a number of assumptions have been introduced, of which perhaps the most drastic are those of the nature of retardation processes at high peroxide concentration. However, in considering the solvent dependence of initiation, these assumptions are used only as an empirically successful method for straightening the data and obtaining the best value for the dependence of initiation on free peroxide concentration. For the CCl_4 -TBHP system the correction is important since our best data are at $[P]_0 = 0.2 M$ where some retardation occurs. In benzene-TBHP, only data at low $[P]_0$ have been used to obtain values of k_2 and k_3 , while with TBDP so little inhibition occurs that $R_i = R_i'$, and no correction is required for most of the concentrations studied.

A final observation indicates that there are actually additional mysteries concealed in our results. Values of R_i (or R_i') all contain a contribution from the thermal initiation of styrene polymerization. Intercepts at zero peroxide concentration (Figure 6) are in

good agreement with the literature values³⁰ for the thermal-initiation process. However, in pure styrene a zero intercept is observed, a result for which we have no explanation.

Experimental

Materials. *Solvents* were commercial materials, dried and distilled before use. *Styrene* was fractionated under reduced pressure, b.p. 40–40.5° (15 mm.), stored at –20°, and used within 24 hr. *t-Butyl hydroperoxide* was distilled under reduced pressure through a 15-plate column. The middle cut, b.p. 39–40° (20 mm.), was collected and stored at –20°. Titration indicated 97–98% purity. Deuterated *t*-butyl hydroperoxide was prepared by equilibration with five successive portions of 99.5% D₂O (equal volumes of D₂O and TBHP) using a countercurrent technique so that initial equilibrations were with partially spent D₂O. The final product was stored overnight at 0°, any D₂O separated, and fractionated under reduced pressure, b.p. 39–40° (20 mm.), titration 97–98%. The first equilibration was found to give at least 60% deuteration, and the final product showed no detectable –OH by n.m.r. spectroscopy, and only a small diffuse –OH band by infrared spectroscopy.

Polymerization rates were, for the most part, determined dilatometrically, using sealed degassed dilatometers of conventional design essentially as described previously.³¹ Since experiments were run to low conversion, volume contraction was linear with time and was converted to per cent reaction using literature values for relative densities of solutions of styrene and polystyrene.³² In a few cases, particularly in preliminary experiments, polymer was determined gravimetrically by precipitating with methanol and drying to constant weight. Here experiments were run to higher conversion and initial rates were calculated from three-halves-order plots which empirically gave the best straight lines. Agreement between the two methods averaged 2–3%. The AIBN experiments (Table II) were also followed gravimetrically and here gave good first-order plots as expected. A few experiments in *o*-dichlorobenzene were followed by change in index of refraction.

Degree of polymerization was determined by measurement of intrinsic viscosity of polymer isolated by methanol precipitation at the termination of kinetic runs. Most determinations were made at 25° in benzene using the equation of Mayo, Gregg, and Mathe-

son,³³ although a few were run in toluene, using the equation of Toohey and Weale.³⁴

Peroxide decomposition rates were determined in sealed degassed tubes. Rates were found to depend upon pretreatment of the tubes and a procedure was standardized which involved cleaning with concentrated nitric acid, thorough rinsing, and drying in an oven, since this yielded the slowest, most reproducible rates. Even then, rates at high conversion were variable, so quantitative work was limited to early stages in the decomposition, taking initial concentrations as those found in tubes after 12 min. of heating. Peroxide was determined by iodimetric titration³⁵ and Figure 3 indicates typical reproducibility.

Product Analysis. Oxygen. The tip of a reaction tube was scratched to facilitate later breakage, a piece of polyethylene tube softened by heating, slipped over the tip, and wired in place. The other end of the tube was connected to a three-way stopcock with a rubber serum cap over one arm, the system evacuated through the other, and, while the reaction tube was frozen in Dry Ice, the tip was broken inside the polyethylene. A sample of gas was then drawn into a syringe through the serum cap and analyzed by absorption in alkaline pyrogallol.³⁶ In reaction systems containing styrene no gas was evolved, so analysis was negative. Evolved gases were also analyzed by infrared spectroscopy, and no products other than solvent and *t*-butyl alcohol detected. *Water* was determined with commercial Karl Fischer reagent corrected by blank determinations on starting materials. *Other products* were determined by gas chromatography (g.l.c.) using previously calibrated internal standards to give quantitative results. In experiments containing styrene, standards were included in the initial reaction mixture, all volatile products separated from polymer by vacuum distillation, and the distillate was immediately analyzed. Styrene oxide, a known product,¹⁵ was identified by retention time on three substrates. It was accompanied by two other unknown materials, "x" and "y" of slightly shorter retention time on a Carbowax 20M column and a smaller amount of "z" of much longer retention time. *t*-Butyl alcohol could only be determined quantitatively on samples which had been reacted to complete consumption of TBHP. It was identified by collection and infrared spectrum. Other products were, in general, identified by retention time.

(30) R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2373 (1948); G. V. Schulz, A. Dinglinger, and E. Husemann, *Z. physik. Chem.*, **B43**, 385 (1939).

(31) C. Walling and N. Indictor, *J. Am. Chem. Soc.*, **80**, 5814 (1958).

(32) For aromatic solvents, see the data of W. Patnode and W. Scheiber, *ibid.*, **61**, 3449 (1939); in CCl₄, those of T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

(33) F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

(34) A. C. Toohey and K. E. Weale, *Trans. Faraday Soc.*, **58**, 2439 (1962).

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

(36) D. A. Davenport and A. N. Saba, *J. Chem. Educ.*, **39**, 617 (1962).