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Reactions of Radicals. IX. *t*-Butyl Peroxide

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The dissociation rate constant, k_{df} , and the chain transfer constant, C , have been measured in styrene solution for *t*-butyl peroxide using the molecular weight technique. Data have been obtained for solutions which contain only peroxide and styrene, and also in mixtures of peroxide and styrene in which benzene, dioxane, or heptane were used as a solvent. The use of a solvent permits the concentration of styrene to be held constant as the peroxide concentration is varied. The values of k_{df} and C which are obtained are found to depend on the solvent system. Possible reasons for this are discussed, and it is concluded that it is most realistic at present simply to adopt a system which is insensitive to minor variations in conditions and to obtain data for all of the aliphatic peroxides under these conditions. The data so obtained can be expected to have a high degree of relative accuracy, but to be of unknown absolute accuracy. The system chosen involves the use of benzene as solvent, concentrations of peroxide greater than 1 *M*, and a constant styrene concentration of 50 vol. %. Under these conditions, k_{df} is 1.5×10^{-9} and 2.9×10^{-8} sec.⁻¹ at 60 and 80°, respectively, and C is 6×10^{-4} and 22×10^{-4} at the two temperatures. The values of k_{df} agree well with previous measurements and with extrapolations from gas-phase data. The values of C at the two temperatures lead to an apparent Arrhenius activation energy for C of 15.1 kcal./mole, giving a value of 22 kcal./mole for the activation energy for transfer, E_{tr} , if the activation energy for the propagation step for the polymerization of styrene is taken as 7.3 kcal./mole. This value is quite reasonable; for example, the activation energy for the transfer reaction of *t*-butylbenzene with styrene is 21 kcal./mole. Values of f/δ^2 have been measured for these same solvent mixtures using azobutyronitrile (AIBN) where $\delta^2 = k_t/k_p^2$. A marked dependence of f/δ^2 on the nature of the solvent system is found. If the standard value of 0.6 is taken for f for AIBN, then the values of δ^2 obtained here are in agreement with data of other workers.

Introduction

In this series of papers,² the rates of the spontaneous decomposition and the chain transfer constant (which is proportional to the rate of induced decomposition) are reported for a series of aliphatic peroxides at 60 and 80° in styrene solutions. This paper gives data for *t*-butyl peroxide,³ and the following papers give similar data for butyl peroxide, ethyl peroxide, *sec*-butyl peroxide, and isopropyl peroxide. Comparable data for propyl peroxide were reported in an earlier publication.⁴ Although, as is discussed below, the method has ambiguities, all of the data reported here were obtained in an identical way for this series of six alkyl peroxides. Therefore, the relative precision of the data is undoubtedly high, despite some uncertainty in absolute accuracy. Furthermore, although the rate constants for most of these peroxides have not been reported before, some have, and where comparisons with earlier values can be made the agreement is quite good.

t-Butyl peroxide is available commercially and is a

(1) Department of Chemistry, Louisiana State University, Baton Rouge, La.

(2) Part VIII: W. A. Pryor and H. Guard, *J. Am. Chem. Soc.*, **86**, 1150 (1964).

(3) In all the papers in this series, peroxides are named according to *Chemical Abstracts* [39, 5939 (1945)] usage. Thus, di-*t*-butyl peroxide is *t*-butyl peroxide, and di-*n*-butyl peroxide is butyl peroxide.

(4) W. A. Pryor and E. P. Pultinas, *J. Am. Chem. Soc.*, **85**, 133 (1963);

very useful initiator, and many studies have been reported of the kinetics of its decomposition and of the products formed. These references were summarized in an earlier publication.⁵

Experimental

Experimental procedures have been described.^{4,5} The only modification made here is that dilute benzene solutions were made up from the entire yield of polymer, and these solutions were filtered through Whatman 41 filter paper before viscosities were determined. This technique did not change the average viscosity but greatly increased precision. The $1/\bar{P}$ value for styrene polymerized thermally at 60° was obtained as 1.1×10^{-4} in agreement with literature values.⁶ The reproducibility of the data is indicated by the values for duplicate runs given in Table I.

The dioxane was purified by the procedure of Wiberg⁷; heptane was DuPont 99 mole % material, and the benzene was reagent grade.

Data and Discussion

The equations which relate the rate of polymerization, R_p , and the degree of polymerization, \bar{P} , for

(5) W. A. Pryor, *J. Phys. Chem.*, **67**, 519 (1963). In this paper, eq. 9 should have read: $R_{th} + R_d = R_i$, and eq. 13 should have been: $R^* = k_{df}(TBP) + C(TBP)R_p/(M)$. The value of k_{df} should have been given as 2.0×10^{-9} , rather than 1.0×10^{-9} .

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

(7) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1960, p. 245.

TABLE I
THE POLYMERIZATION OF STYRENE BY *t*-BUTYL PEROXIDE.
DATA FOR DUPLICATE RUNS^a

T, °C.	Inert solvent	(M)	(I)	$R_P \times 10^5$	$10^4/\bar{P}$	$C \times 10^4$
60	Dioxane	4.3	1.16	7.07	4.41	1.97
60	Dioxane	4.3	1.16	7.15	4.53	2.30
60	Dioxane	4.3	1.16	7.27	4.69	2.66
60	Dioxane	4.3	1.16	7.16	4.58	2.44
			Av.	7.16	4.55	2.34
80	Benzene	4.3	0.387	3.03	7.93	31.0
80	Benzene	4.3	0.387	3.01	8.38	36.3
80	Benzene	4.3	0.387	3.01	8.42	36.6
80	Benzene	4.3	0.387	3.16	8.37	33.8
80	Benzene	4.3	0.387	3.17	8.74	37.8
			Av.	3.08	8.35	35.1

^a For explanatory notes, see Table II.

styrene polymerized by a peroxide initiator were given previously.^{4,6,8a} They are

$$1/\bar{P} = [\delta^2/(M)^2]R_{P,obsd} + C_M + C(I)/(M) \quad (1)$$

$$R_{P,obsd}^2 = R_P^2 + R_{P,th}^2$$

$$R_P = [(k_d f)^{0.5}/\delta](M)(I)^{0.5} \quad (2)$$

where $\delta^2 = k_t/k_p^2$, (M) and (I) are the molarities of the monomer and initiator, respectively, $R_{P,obsd}$ is the observed rate of polymerization in l. mole⁻¹ sec.⁻¹, $R_{P,th}$ is the thermal rate of polymerization, and R_P is the rate of polymerization due to the initiator. Literature values of δ^2 have been reviewed,⁴ and the best value in pure styrene was concluded to be 900 at 60° and 260 at 80° from the work of Tobolsky and Offenbach.^{8,9}

Table II gives the data obtained from polymerizations of styrene at 60° initiated by *t*-butyl peroxide. In the top section of the table, data are given in which styrene and *t*-butyl peroxide were mixed without any third solvent; in these runs the molarity of the styrene monomer varies from pure styrene down to a solution that is half peroxide and half styrene. The last column of Table II gives the transfer constant, C , calculated for each point using eq. 1. The transfer constant has a large value at very low concentrations of *t*-butyl peroxide, and as the peroxide concentration is raised C levels off at about 3×10^{-4} . Mayo, Gregg, and Matheson⁶ have discussed the accuracy of transfer constants obtained by this technique. For benzoyl peroxide, they obtain values for C ranging from 0.053 to 0.187 depending on which value they adopt for the monomer transfer constant,¹⁰ the dissociation constant of the peroxide, and the parameters in the Mark-Houwink equation. They also found that constant values of C could only be obtained at relatively high concentrations of the peroxide.

Values of the transfer constant obtained at low concentrations of peroxide are inherently inaccurate. Equation 1 consists of a sum of terms, and at low values of (I)/(M) the term involving the transfer constant is the smallest of these terms. For example, at 0.54 *M* peroxide in benzene-styrene (the first run in Table II in the benzene-styrene-peroxide system), the three

(8) (a) D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, **74**, 938 (1952); (b) A. V. Tobolsky and J. Offenbach, *J. Polymer Sci.*, **16**, 311 (1955).

(9) Also see: G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **37**, 71 (1960).

(10) The value of C_M has been taken as 0.5×10^{-4} at 60° and 0.7×10^{-4} at 80° throughout the present work; see ref. 8b.

TABLE II
THE POLYMERIZATION OF STYRENE BY *t*-BUTYL PEROXIDE
AT 60°^a

Third solvent	(M) ^b	(I) ^c	$R_{P,obsd} \times 10^5$	$R_P \times 10^{5d}$	$10^4/\bar{P}^e$	n^f	$C \times 10^{4g}$
None	8.6	0	2.1			4	
None	8.6	0.054	4.2	3.7	1.37	3	57
None	8.5	0.108	5.3	4.9	1.49	3	28
None	8.4	0.163	6.3	5.9	1.64	1	18
None	8.2	0.271	7.5	7.2	1.85	1	9.4
None	8.1	0.300	8.0	7.7	2.00	2	11
None	7.8	0.543	9.4	9.1	2.07	1	2.9
None	7.0	1.08	10.5	10.5	3.10	4	3.8
None	6.5	1.35	11.1	11.1	3.53	2	3.2
None	6.3	1.45	11.0	11.0	3.90	2	3.9
None	5.8	1.80	11.0	10.9	4.42	2	3.2
None	4.3	2.71	9.2	9.2	7.35	16	3.9
Dioxane	4.3	0.39	4.6	4.5	2.80	3	1.6
Dioxane	4.3	1.16	7.2	7.2	4.55	4	2.3
Dioxane	4.3	1.93	8.6	8.6	5.70	2	2.4
Benzene	4.3	0	1.1			4	
Benzene	4.3	0.54	5.0	4.9	3.20	6	2.3
Benzene	4.3	1.10	6.7	6.6	4.75	6	4.4
Benzene	4.3	1.37	7.2	7.1	5.20	6	4.0
Benzene	4.3	1.64	7.7	7.6	5.42	5	6.3
Benzene	4.3	1.90	8.0	8.0	6.02	6	6.1
Benzene	4.3	2.19	8.5	8.5	6.70	6	6.0
Heptane	4.3	0.39	2.6	2.4	2.60	4	9.3
Heptane	4.3	0.45	3.3	3.1	3.02	2	8.9
Heptane	4.3	0.77	4.1	4.0	4.07	4	9.4
Heptane	4.3	0.90	4.5	4.4	4.15	2	7.9
Heptane	4.3	1.16	5.3	5.3	5.02	4	7.5
Heptane	4.3	1.35	6.0	6.0	4.85	2	6.5
Heptane	4.3	1.55	6.5	6.4	5.70	2	6.8
Heptane	4.3	1.81	7.1	7.1	5.30	2	5.3
Heptane	4.3	1.93	7.7	7.6	6.16	5	6.2
Heptane	4.3	2.26	8.1	8.1	6.07	2	5.1
Heptane	4.3	2.32	8.6	8.6	6.80	4	5.8

^a Solutions consist of styrene and *t*-butyl peroxide plus the third component listed. ^b Styrene in moles/l. ^c *t*-Butyl peroxide in moles/l. ^d $R_P = (R_{P,obsd}^2 - R_{P,th}^2)^{0.5}$. $R_{P,th} = 2.1 \times 10^{-6}$ for (M) = 8.6; 1.0×10^{-6} for (M) = 4.3. ^e See ref. 4 for details. ^f Number of duplicates. ^g Calculated using eq. 1.

terms on the right side of eq. 1 are: 2.35×10^{-4} (initiation by peroxide); 0.50×10^{-4} (transfer to monomer); and 0.35×10^{-4} (transfer to peroxide). In this concentration range, only 0.35/(0.35 + 2.35), or 13%, of the peroxide decomposes by the induced path. Thus, there is justification for discarding the values of C obtained at low peroxide concentrations. If this is done, the value of 3×10^{-4} may be taken as a reproducible value for the transfer constant of *t*-butyl peroxide in these styrene-peroxide solutions.

However, in all the runs in the top section of Table II, the concentrations of both styrene and peroxide are varied simultaneously. It is known that the usual analysis of polymerization kinetics does not entirely adequately represent the mechanism when rates vary widely and the monomer concentration is varied.¹¹

(11) (a) J. P. Van Hook and A. V. Tobolsky, *J. Phys. Chem.*, **62**, 257 (1958); (b) J. H. Bradbury and H. W. Melville, *Proc. Roy. Soc. (London)*, **A222**, 456 (1954); (c) H. W. Melville, J. C. Robb, and R. C. Tutton, *Discussions Faraday Soc.*, **14**, 150 (1953); (d) W. J. Kirkham and J. C. Robb, *Trans. Faraday Soc.*, **57**, 1757 (1961); (e) J. C. Bevington, J. Toole, and L. Trossarelli, *ibid.*, **54**, 863 (1958); (f) M. R. Gopalan and M. Santappa, *Makromol. Chem.*, **50**, 83 (1961); (g) M. R. Gopalan and M. Santappa, *J. Polymer Sci.*, **25**, 333 (1957); (h) S. W. Benson and A. M. North, *J. Am. Chem. Soc.*, **84**, 935 (1962); (i) W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **56**, 407 (1960); **57**, 1928 (1961); (j) C. H. Bamford, A. D. Jenkins, and R. Johnston, *ibid.*, **55**, 1451 (1959); (k) A. D. Jenkins, *ibid.*, **54**, 1885 (1958); (l) ref. 9; (m) ref. 12; (n) Table 3-11, p. 84, of ref. 13 gives unpublished data of C. Sivertz; (o) M. H. George and P. F. Onyon, *Trans. Faraday Soc.*, **59**, 1390 (1963);

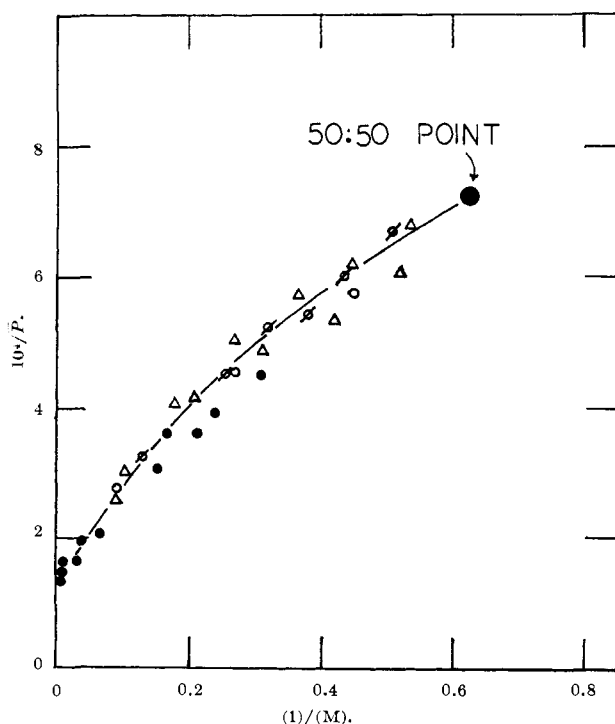


Fig. 1.—Graph of $1/\bar{P}$ vs. (*t*-butyl peroxide)/(styrene) at 60°. Code: ●, no third solvent; ○, dioxane is solvent; △, heptane is solvent; ∅, benzene is solvent.

Therefore, experiments were done in which a third solvent was present to permit the concentration of styrene to be held constant while the peroxide concentration was varied. Nandi and Palit¹⁴ have shown that two transfer agents act independently of one another, and Chadha and Misra¹⁵ have shown that transfer constants are not affected by the presence of an initiator. Thus, in theory, solvents should have no influence on the transfer constant of the peroxide. Three solvents were chosen of widely differing chemical properties: dioxane, benzene, and heptane. Dioxane is of interest since Henrici-Olivé and Olivé find that δ^2 is constant in various styrene-dioxane mixtures.⁹ Benzene and heptane were used since they represent different types of hydrocarbons and both have very small transfer constants.¹²

The lower sections of Table II give data obtained in the presence of these three solvents. In dioxane, C is fairly constant at about 2×10^{-4} . In benzene, C has low values at very low concentrations of peroxide and levels off at a value of about 6×10^{-4} at higher concentrations. In heptane, C starts high and levels off at about 6×10^{-4} .

Figure 1 is a graph of these data as the inverse of the degree of polymerization vs. $(I)/(M)$. Plotting the data in this way, *i.e.*, in the form of the Mayo equation, should yield a straight line if the first term of eq. 1 were a constant.⁴ As was true for propyl peroxide, *t*-butyl peroxide is so ineffectual an initiator at 60°

(12) G. Henrici-Olivé and S. Olivé, *Fortschr. Hochpolym.-Forsch.*, **2**, 496 (1961).

(13) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., New York, N. Y., 1962.

(14) U. S. Nandi and S. R. Palit, *Nature*, **185**, 235 (1960). In the presence of a third solvent, the extra term $C_g(S)/(M)$ should be added to eq. 1, where C_g is the transfer constant of the solvent and (S) is its molarity. However, the transfer constants of all of the solvents used here are so small that this correction is negligible. For values of the transfer constants, see ref. 12.

(15) R. N. Chadha and G. S. Misra, *Makromol. Chem.*, **14**, 97 (1954).

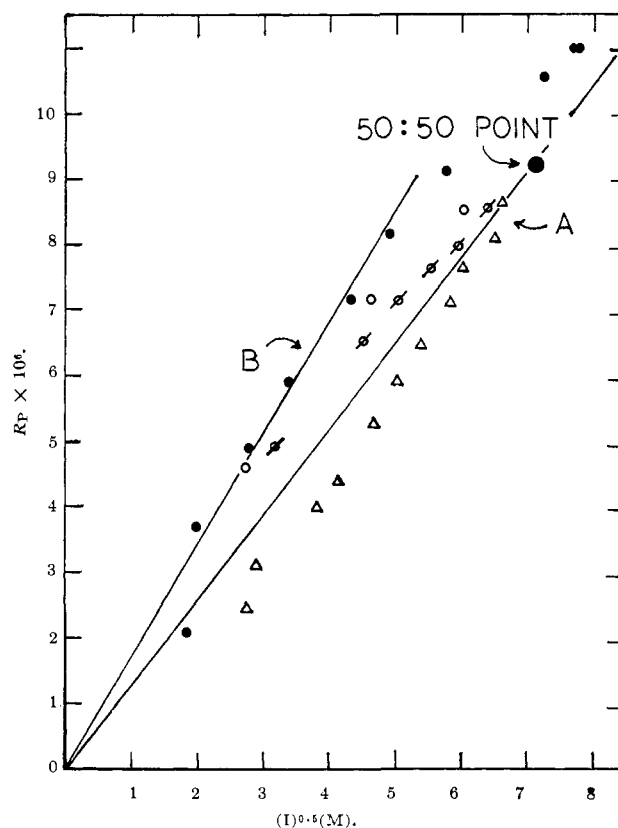


Fig. 2.—Graph of the rate of polymerization vs. (*t*-butyl peroxide)^{0.5}(styrene). Points coded as in Fig. 1.

that the curvature in Fig. 1 is very slight. However, the curvature is real. The intercept on the $1/\bar{P}$ axis for pure styrene should be 1.1×10^{-4} ; therefore, the curve can be seen to be concave downward with the greatest amount of curvature at low values of $(I)/(M)$. This phenomenon is well known. Mayo, Gregg, and Matheson⁶ have discussed a graph of $1/\bar{P}$ for the data on benzoyl peroxide (Fig. 7 in their publication), and their graph is strongly concave downward. (Since (M) is a constant in all of the runs discussed here, their figure is analogous to Fig. 1.) The curvature in these figures results from the fact that the first term on the right of eq. 1 is not a constant but varies with $(I)^{0.5}$. Thus, although *t*-butyl peroxide is a relatively poor transfer agent and initiator at 60°, there is no question but that it is acting in both capacities. The tendency to regard *t*-butyl peroxide as an initiator in which induced decomposition does not occur is incorrect.

Although Fig. 1 shows some scatter, the trends are probably real. That is, molecular weights are lowest (*i.e.*, $1/\bar{P}$ values are highest) in solutions containing heptane, intermediate in benzene, and highest in dioxane.

Figure 2 is a graph of the data of Table II in the form of eq. 2; the slopes of the lines should equal $(k_{df})^{0.5}/\delta$. In this graph, discrepancies between the different solvent systems are much more pronounced than in Fig. 1. Line A, drawn through the point at 50:50 styrene:peroxide, has a slope of 1.28×10^{-6} , giving k_{df} as 1.5×10^{-9} sec.⁻¹ if the value of 900 is taken for δ^2 . This is in fair agreement with the value of 2.0×10^{-9} sec.⁻¹ obtained using a tracer method.⁵ It is also in agreement with an extrapolation of the collected^{5,16} gas-

(16) (a) J. A. Offenbach and A. V. Tobolsky, *J. Am. Chem. Soc.*, **79**, 278 (1957); (b) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).

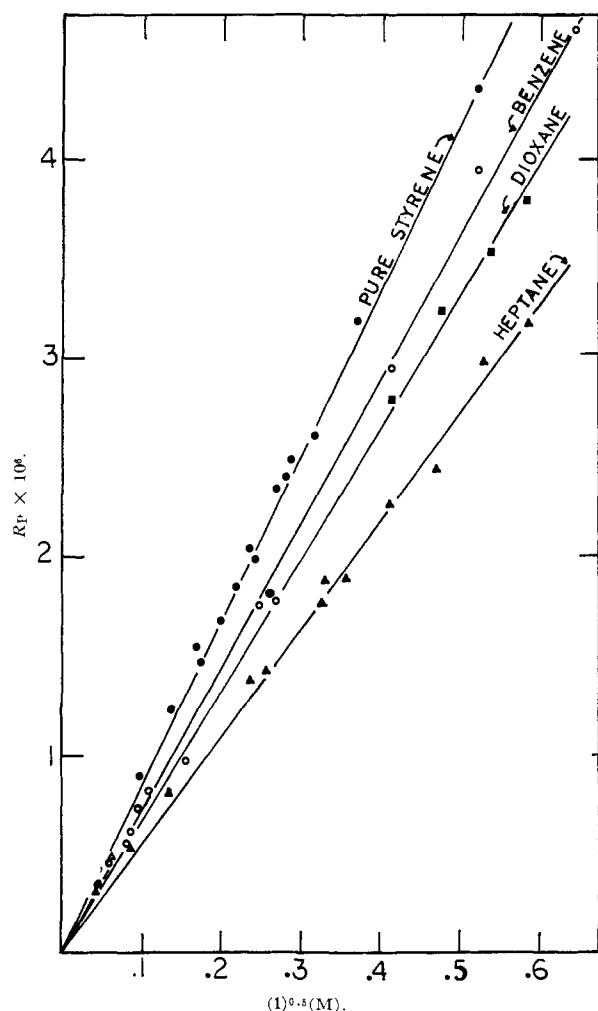


Fig. 3.—Graph of the rate of polymerization *vs.* (styrene)·(AIBN)^{0.5}: ●, pure styrene; ○, benzene-styrene; ■, dioxane-styrene; ▲, heptane-styrene. (All solvent-styrene mixtures are 50 vol. % styrene.)

phase and solution-phase determinations which gives $k_d f$ as 1.2×10^{-9} sec.⁻¹ at 60°, using 37.4 kcal. as the Arrhenius activation energy. These data indicate, as has been pointed out before,^{5,16a} that *t*-butyl peroxide decomposes at about the same rate in solution and in the gas phase.

Line B in Fig. 2 is drawn through the points in pure styrene at low peroxide concentration which were ignored in drawing line A. The slope of this line is 1.7×10^{-6} , in fair agreement with the value of 1.9×10^{-6} determined by Offenbach and Tobolsky using the same technique.^{16a} A slope of 1.7×10^{-6} gives a value of $k_d f$ of 2.5×10^{-9} sec.⁻¹.

It is striking that the variations between different solvent systems are much greater in Fig. 2 than in Fig. 1. From eq. 2, the slope of the lines in Fig. 2 is $(k_d f)^{0.5}/\delta$. The value of k_d for *t*-butyl peroxide is remarkably independent of the nature of the solvent, and it is likely that k_d has a constant value for all of the points shown in Fig. 2. The range of slopes observed for the different solvent systems, therefore, is due to a variation in $f^{0.5}/\delta$ with the nature of the third component. The value of $f^{0.5}/\delta$ can be seen to decrease in the order: pure styrene > benzene > dioxane > heptane.

Experiments Using AIBN.—Values of $f^{0.5}/\delta$ can be obtained¹⁷ by studying the rate of polymerization of

styrene by an initiator of known rate of initiation and applying eq. 2. This has been done using azoisobutyronitrile (AIBN) as the initiator.¹⁸ Table III gives the data, and Fig. 3 is a graph in the form of eq. 2. Table IV lists the values of $f^{0.5}/\delta$ obtained from Fig. 2. The order is the same as is found for *t*-butyl peroxide, namely: pure styrene > benzene > dioxane > heptane. Thus, whatever the factors which are responsible for the variation in $f^{0.5}/\delta$, the variations are qualitatively the same whether the initiator is AIBN or *t*-butyl peroxide.²¹

TABLE III
THE POLYMERIZATION OF STYRENE BY AZOISOBUTYRONITRILE AT 60°^a

(AIBN) × 10 ⁴	(M)(I) ^{0.5}	R _p × 10 ⁶	<i>n</i>	(AIBN) × 10 ⁴	(M)(I) ^{0.5}	R _p × 10 ⁶	<i>n</i>
Pure styrene				50:50 styrene:benzene			
1.31	0.0980	8.75	1	0.94	0.0417	3.39	1
2.63	0.139	12.3	1	1.87	0.0588	4.48	1
3.71	0.166	15.4	1	2.81	0.0717	5.54	1
3.95	0.172	14.7	1	3.75	0.0835	5.98	1
5.25	0.197	16.7	1	4.70	0.0932	7.19	1
6.57	0.220	18.4	1	6.57	0.110	8.07	1
7.42	0.231	20.3	1	13.3	0.157	9.52	1
7.89	0.242	19.9	1	33.5	0.249	17.5	2
9.27	0.262	23.3	1	36.0	0.261	18.0	1
10.5	0.279	23.0	1	39.8	0.271	17.7	1
11.1	0.286	24.9	1	93.0	0.415	29.5	1
13.2	0.312	26.0	1	147	0.524	39.5	1
18.5	0.370	31.9	1	220	0.640	46.4	1
37.1	0.523	43.5	1	50:50 styrene:heptane			
55.7	0.642	51.5	1	1.10	0.042	3.10	1
				1.90	0.059	4.80	1
				3.80	0.084	6.20	1
				9.50	0.132	8.00	1
				30.0	0.237	13.8	4
				33.5	0.256	14.1	3
				57.0	0.328	17.6	1
				59.6	0.335	18.8	5
				67.0	0.356	18.9	3
				89.0	0.412	22.5	4
				119	0.474	24.3	4
				149	0.530	29.8	2
				179	0.581	31.8	4

^a See Table II for explanatory notes.

If f is assumed to be a constant, values of $f^{0.5}/\delta$ can be used to calculate δ^2 . The next to last column in Table IV gives values of δ^2 if f for AIBN is taken²² as 0.6. The values of δ^2 obtained in this way agree well with previous determinations. For example, Van Hook and Tobolsky^{11a} have shown that at both 30 and 60° the value of δ^2 increases by a factor of 1.4 in going from pure styrene to a 50:50 styrene:benzene mixture. This predicts a value of δ^2 of 1270 for the diluted system, compared with 1360 found here.

(17) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

(18) The value of k_d for AIBN is 1.13×10^{-4} at 60° (ref. 19) and 1.80×10^{-4} sec.⁻¹ at 80° (ref. 20).

(19) J. C. Bevington and H. G. Troth, *Trans. Faraday Soc.*, **58**, 186 (1962).

(20) J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).

(21) A quantitative comparison of values of f/δ^2 for AIBN and *t*-butyl peroxide is of questionable value. The lines in Fig. 2 are curved, whereas the data for AIBN give straight lines as predicted by simple theory. It was this difference which first led us to use solvents in the experiments with *t*-butyl peroxide so that the monomer concentration could be held constant. (AIBN is a solid and its concentration can be varied without varying the concentration of the styrene solvent.)

(22) J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955).

TABLE IV

VALUES OF $f^{0.5}/\delta$ AND OF δ^2 CALCULATED FROM THE AIBN DATA OF TABLE III

Solvent ^a	T, °C.	$f^{0.5}/\delta$	δ^2 from eq. 2 ^c	δ^2 from eq. 1 ^d
None	60	0.0258	900	900
Benzene	60	0.0210	1360	
Dioxane	60	0.0195	1580 ^b	935 ^b
Heptane	60	0.0163	2250	
None	80	0.0480	260	260

^a Solvent is 50% by volume. ^b See W. A. Pryor and G. L. Kaplan, *J. Am. Chem. Soc.*, **86**, 4234 (1964). ^c Calculated from the AIBN data using eq. 2 assuming that f is 0.6 independent of the solvent and the monomer concentration. ^d Calculated by fitting the AIBN data to eq. 1. See the following paper for discussion.

Bevington^{11e} has found this factor to be 1.38 at 60° and 1.20 at 80°. Gopalan and Santappa^{11g} report that δ^2 increases from 900 in pure styrene to 1000 in 50:50 styrene:toluene at 60°.

Despite this agreement with literature values, it is probable that *neither* f nor δ are independent of the solvent system. Values of δ would be expected to depend on the inverse of the viscosity of the solvent,²³ and the variations in $f^{0.5}/\delta$ shown in Table IV are qualitatively in accord with this prediction.²⁴ Therefore, it is probable that variations in δ contribute to the scatter of slopes found in Fig. 2 and 3. However, data will be presented in the following paper which indicate that variations in f also occur and are a more important cause of the variations observed in $f^{0.5}/\delta$. Since f is not independent of the solvent system, the values of δ^2 given in the next to last column of Table IV can be in error. The values of δ^2 given in the last column of Table IV were calculated by a method which does not require a knowledge of f , and these values will be discussed in the following paper.

The situation is complex and not entirely satisfying. Values of $f^{0.5}/\delta$ for both AIBN and *t*-butyl peroxide depend markedly on the nature of the inert solvent, and the calculation of a transfer constant therefore is subject to uncertainty. As an initial approach, we decided to choose a system that gives reproducible values of C which are not sensitive to minor changes in conditions and to use this system to obtain comparable data for all of the aliphatic peroxides. For this purpose, we choose benzene as the standard solvent, concentrations of peroxide greater than 1 *M*, and a constant styrene concentration of 50 vol. %. The transfer constant for *t*-butyl peroxide at 60° is then 6×10^{-4} under these standard conditions.

Data at 80°.—Polymerizations were carried out in benzene-peroxide-styrene mixtures as given in Table V. The runs above 1 *M* in peroxide give C equal to 22×10^{-4} . A graph analogous to Fig. 1 is a straight line with slope equal to 24×10^{-4} . A graph analogous to Fig. 2 gives a slope of 1.05×10^{-5} . If the value of 260 is used for δ^2 , then k_{df} can be calculated to be $2.9 \times$

TABLE V

THE POLYMERIZATION OF STYRENE BY *t*-BUTYL PEROXIDE AT 80°^a

Solvent	(M)	(I)	$R_p \times 10^{10}$ ^b	$10^4/P$	η^c	$C \times 10^4$
None	8.6	0	1.1			2
Benzene	4.3	0	0.25			4
Benzene	4.3	0.387	3.08	8.35	5	38
Benzene	4.3	1.16	4.99	14.9	4	27
Benzene	4.3	1.93	6.06	17.8	4	20
Benzene	4.3	2.71	6.95	22.3	4	15

^a See Table II for explanatory notes. ^b At 80°, $R_{p,th}$ is negligible. ^c Number of duplicate runs.

10^{-8} sec.⁻¹. This is in good agreement with an extrapolation of gas and solution phase work, which gives k_d as 2.8×10^{-8} using an activation energy of 37.4 kcal./mole.

Activation Energies.—The values of 1.5×10^{-9} and 2.9×10^{-8} sec.⁻¹ for k_{df} at 60 and 80°, lead to an Arrhenius activation energy for the unimolecular dissociation step of 35 kcal./mole. This agrees, within the accuracy of the method, with the value of 37 kcal./mole obtained from a compilation of literature data.^{5,16b}

The transfer constants of 6×10^{-4} and 22×10^{-4} at the two temperatures in benzene as solvent lead to an apparent activation energy for C of 15.1 kcal./mole. The transfer constant C is equal to k_{tr}/k_p , and the apparent activation energy for C , therefore, is equal to $E_{tr} - E_p$. The activation energy for the propagation step in styrene polymerization is 7.3 kcal./mole,²⁵ and the activation energy for transfer to *t*-butyl peroxide, E_{tr} , therefore, is 22 kcal./mole. This value is in agreement with the hypothesis²⁶ that the transfer step is due to abstraction of a hydrogen atom. For example, the activation energy for transfer by *t*-butylbenzene is 21 kcal.²⁵

Comparison with the Transfer Constant Measured by the Tracer Technique.—We have previously reported^{5,27} the transfer constant for *t*-butyl peroxide as 8.6×10^{-4} and k_{df} as 2.0×10^{-9} sec.⁻¹ at 60°. These values were determined by using radioactive *t*-butyl peroxide and measuring the rate at which radioactivity becomes incorporated into the polymer. The values determined by the radioactive method should agree with those measured here. At first we believed that the radioactive method was quite precise; however, subsequent work on isopropyl peroxide has shown that the values determined are somewhat subject to the isolation procedure used. Clearly, the absolute accuracy of the transfer constant determined by the present method is in considerable doubt. Therefore, it is possible that the agreement between the values of 6×10^{-4} and 8.6×10^{-4} for the transfer constant, and 1.5×10^{-9} and 2.0×10^{-9} for k_{df} , are the best which can be expected. We are reinvestigating the tracer method for obtaining these constants and, in particular, are attempting to isolate all of the low molecular weight polymer produced. The comparison of

(23) (a) Reference 11h; (b) A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57**, 859 (1961); (c) J. N. Atherton and A. M. North, *ibid.*, **58**, 2049 (1962); (d) S. W. Benson and A. M. North, *J. Am. Chem. Soc.*, **80**, 5625 (1958); (e) S. W. Benson and A. M. North, *ibid.*, **81**, 1339 (1959).

(24) The viscosities (at 25° in cp.) are: 1.216, 0.605, and 0.396 for dioxane, benzene, and heptane, respectively. See R. H. Stokes, P. J. Dunlop, and J. R. Hall, *Trans. Faraday Soc.*, **49**, 886 (1953).

(25) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc. New York, N. Y., 1957, pp. 95, 152.

(26) W. A. Pryor, *Tetrahedron Letters*, 1201 (1963).

(27) The value of 13×10^{-4} which was reported even earlier (ref. 13, p. 53) was from measurements of E. P. Pultinas in pure styrene using low concentrations of peroxide. Table II shows that this system leads to systematically higher results than the system adopted here.

the tracer method and the molecular weight methods for obtaining transfer constants must await the completion of those studies.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA, AND PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Reactions of Radicals. X. Butyl Peroxide

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By techniques similar to those used in the previous paper,³ the rate constant for dissociation and the chain transfer constant are obtained for butyl peroxide at 60 and 80° in styrene. At 60°, the dissociation rate constant is 3.3×10^{-9} sec.⁻¹ using either dioxane or benzene as solvent. The transfer constant is 7.6×10^{-4} in dioxane-styrene mixtures and 9.2×10^{-4} in benzene-styrene at 60°. The activation energy is 34.3 kcal./mole for the unimolecular dissociation step. The activation energy for transfer, E_{tr} , is 23 kcal./mole if the value of 7.3 kcal./mole is taken for E_p . The Olivé-Schulz method of calculating molecular weights of polymers, which takes into account changes in molecular weight distribution with differing amounts of transfer, is discussed briefly.

Introduction

Butyl peroxide, a representative straight-chain dialkyl peroxide, can be synthesized in good yield. We wished to study this peroxide to extend and confirm our data on propyl peroxide and to allow comparison of butyl peroxide with the previously studied *t*-butyl peroxide.³ No previous rate studies have been reported for butyl peroxide.

Experimental

Preparation of Butyl Peroxide.—Butyl methanesulfonate was prepared by the method of Williams and Mosher⁴ on a 6.0-mole scale. The sulfonate ester was distilled through a 6-in. Vigreux column (b.p. 66° at 0.2 mm.). The yield of distilled ester was 70%. The peroxide was prepared by the Mosher⁵ method using 367 g. of sulfonate, 120 g. of 30% hydrogen peroxide, and 264 g. of 50% aqueous KOH. The peroxide was distilled through a 6-in. Vigreux column at 61° and 20 mm., and yields of 30 to 40% of distilled material were obtained.

Peroxide Purity.—An elemental analysis was obtained on one sample and gave 66.79% C and 12.86% H, in agreement with the calculated 65.71 and 12.41%. However, elemental analysis on these aliphatic peroxides is quite hazardous, and we have abandoned using it.^{6,7}

The infrared spectrum of the peroxide is in agreement with that reported by Mosher.⁹ In addition, 1% solutions of butanol, butyraldehyde, and butyl methanesulfonate were prepared in carbon tetrachloride and infrared spectra determined in a fixed thickness cell. These solutions gave strong peaks at 2.8, 5.8, and 8.5 μ , respectively. The spectrum of the peroxide showed no absorption at 2.8 or 5.8 μ , and a small peak corresponding to about 0.2% sulfonate at 8.5 μ .

The n.m.r. spectrum (determined neat with TMS as internal standard) consists of three groups of peaks: a triplet at 3.94 p.p.m. with relative intensity of 1.0 due to the two α hydrogens; a broad unresolved peak centered at 1.47 p.p.m. with relative intensity of 2.0 due to the four β and γ hydrogens; and a very

unsymmetrical triplet at 0.90 p.p.m. with relative intensity of 1.50 due to the three δ hydrogens.

The very easily obtained n.m.r. and infrared spectra are entirely adequate analyses for purity.⁸ They are safely and rapidly obtained, and control solutions containing 1% of the expected impurities show large, easily detectable peaks. It is recommended that these analyses be used in place of elemental analysis, which is hazardous, or refractive index, which is insensitive to impurities.

Data

The previous paper in this series³ gives the equations for polymerization of a monomer M by a peroxide initiator I.

$$\frac{1}{\bar{P}} = [\delta^2/(M)^2]R_{P,obsd} + C_M + C(I)/(M) \quad (1)$$

$$R_{P,obsd}^2 = R_P^2 + R_{P,th}^2$$

$$R_P = [(k_{df})^{0.5}/\delta](M)(I)^{0.5} \quad (2)$$

In the discussion to follow, it will be convenient to use eq. 2 in the form

$$R_P^2 = [k_{df}/\delta^2](I)(M)^2 \quad (3)$$

Table I gives data for styrene polymerizations at 60° in which either dioxane or benzene was used as a solvent. In all runs, the styrene concentration was held constant at 50 vol. %. The data which are tabulated are similar to those given in the previous paper: the observed rate of polymerization, the rate of polymerization after correction for the thermal rate, the intrinsic viscosity calculated using the Gregg and Mayo equation,⁹ and the degree of polymerization calculated using the Mayo relation.¹⁰ In addition, the degree of polymerization has been calculated by the procedure of Henrici-Olivé, Olivé, and Schulz,¹¹ the details of which will be discussed below.

(8) W. A. Pryor and D. M. Huston, *J. Org. Chem.*, **29**, 512 (1964).

(9) R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2372 (1948).

(10) F. R. Mayo, *ibid.*, **75**, 6133 (1953).

(11) G. Henrici-Olivé, S. Olivé, and G. V. Schulz, *J. Polymer Sci.*, **56**, 233 (1962); also see G. Henrici-Olivé and S. Olivé, *Fortschr. Hochpolym.-Forsch.*, **2**, 496 (1961).

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(3) W. A. Pryor, A. Lee, and C. E. Wilt, *J. Am. Chem. Soc.*, **86**, 4229 (1964).

(4) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2987 (1954).

(5) F. Welch, H. R. Williams, and H. S. Mosher, *ibid.*, **77**, 551 (1955).

(6) W. A. Pryor, *Tetrahedron Letters*, 1201 (1963).

(7) (a) E. J. Harris, *Proc. Roy. Soc. (London)*, **A173**, 126 (1939); (b) E. J. Harris and A. C. Egerton, *ibid.*, **A168**, 1 (1938).