

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

BY WILLIAM A. PRYOR<sup>1</sup> AND GERALD L. KAPLAN<sup>2</sup>

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By techniques similar to those used in the previous paper,<sup>3</sup> 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  $3.3 \times 10^{-9}$  sec.<sup>-1</sup> using either dioxane or benzene as solvent. The transfer constant is  $7.6 \times 10^{-4}$  in dioxane-styrene mixtures and  $9.2 \times 10^{-4}$  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.<sup>3</sup> 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 Mosher<sup>4</sup> 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 Mosher<sup>5</sup> 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.<sup>6,7</sup>

The infrared spectrum of the peroxide is in agreement with that reported by Mosher.<sup>9</sup> 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  $\mu$ , respectively. The spectrum of the peroxide showed no absorption at 2.8 or 5.8  $\mu$ , and a small peak corresponding to about 0.2% sulfonate at 8.5  $\mu$ .

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  $\alpha$  hydrogens; a broad unresolved peak centered at 1.47 p.p.m. with relative intensity of 2.0 due to the four  $\beta$  and  $\gamma$  hydrogens; and a very

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

The very easily obtained n.m.r. and infrared spectra are entirely adequate analyses for purity.<sup>8</sup> 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 series<sup>3</sup> 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,<sup>9</sup> and the degree of polymerization calculated using the Mayo relation.<sup>10</sup> In addition, the degree of polymerization has been calculated by the procedure of Henrici-Olivé, Olivé, and Schulz,<sup>11</sup> 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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(2) Based on the thesis submitted by G. L. Kaplan in partial fulfillment of the requirements for the Master of Science degree at Purdue University, 1964.

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

TABLE I  
THE POLYMERIZATION OF STYRENE BY BUTYL PEROXIDE  
AT 60°<sup>a</sup>

(I)	$R_p \times 10^4$	$R_p \times 10^6$	$[\eta]^b$	$10^4/\bar{P}^b$	$10^4/\bar{P}^c$	$C \times 10^{4d}$
Dioxane as solvent						
0.47	6.1	6.0	1.39	4.11	4.10	
0.47	6.1	6.0	1.36	3.98	4.24	5.5
0.93	7.7	7.7	1.05	5.83	6.12	
0.93	7.9	7.8	1.06	5.74	6.01	7.3
1.42	10.1	10.1	0.856	7.73	8.16	
1.42	10.1	10.1	0.856	7.72	8.15	
1.42	10.1	10.1	0.879	7.44	7.84	7.0
1.89	9.1	9.1	0.755	9.17	9.93	
1.89	11.2	11.2	0.791	8.61	9.62	
1.89	11.3	11.3	0.749	9.28	9.89	7.8
2.36	12.8	12.8	0.669	10.81	11.59	
2.36	12.6	12.6	0.676	10.66	11.43	
2.36	12.4	12.4	0.682	10.55	11.30	7.6
2.84	13.2	13.2	0.640	11.50	12.37	
2.84	12.5	12.5	0.621	11.99	12.99	
2.84	13.6	13.6	0.607	12.36	13.33	
2.84	9.9	9.9	0.616	12.12	13.46	8.0
Benzene as solvent						
0.24	3.7	3.6	1.40	3.94		
0.24	4.1	4.0	1.40	3.94		28
0.47	6.1	6.0	1.19	4.90		
0.47	4.0	3.9	1.14	5.19		19
0.71	7.4	7.3	1.11	5.38		8.8
0.83	7.7	7.6	1.08	5.64		7.2
1.18	9.0	9.0	0.804	8.42		13.1
2.01	13.0	13.0	0.711	9.95		6.8
2.48	13.4	13.4	0.609	12.30		9.3
2.60	13.8	13.8	0.630	11.74		7.6

<sup>a</sup> Styrene concentration held at 4.3 M by addition of dioxane or benzene. <sup>b</sup> Calculated from the Gregg and Mayo equations. See ref. 9 and 10. <sup>c</sup> Calculated from the Olivé-Schulz equations. See ref. 11 and the discussion in text. <sup>d</sup> Calculated using Mayo molecular weights and eq. 1. Average values are given for duplicate runs.

### Discussion

In a method analogous to that used in the previous paper, the transfer constant was calculated for butyl peroxide using eq. 1. The transfer constants obtained by this method are in the last column of Table I. (These transfer constants were calculated using the degree of polymerization data calculated from the Mayo relation.<sup>10</sup>) If data below 1 M peroxide are discarded,<sup>3</sup> the average transfer constants are  $7.6 \times 10^{-4}$  in dioxane and  $9.2 \times 10^{-4}$  in benzene.

Figure 1 is a graph of the data in the form of the Mayo equation. In the case of *t*-butyl peroxide, where the availability of the peroxide allowed a large number of runs to be done, the barely observable curvature in this plot could be detected. In the present case, as was true for propyl peroxide,<sup>12</sup> the data do not reveal the curvature. (The solid circles and open circles in Fig. 1 are for data in dioxane and benzene, respectively, calculated using the Mayo molecular weight equation. The squares are for dioxane data calculated using the Olivé relations, and these data will be discussed below.)

Figure 2 is a graph of the data in the form of eq. 2. As was true in the case of *t*-butyl peroxide, the dioxane and benzene data agree closely. The slopes for the two sets of data are  $1.88 \times 10^{-6}$  and  $1.94 \times 10^{-6}$ ,

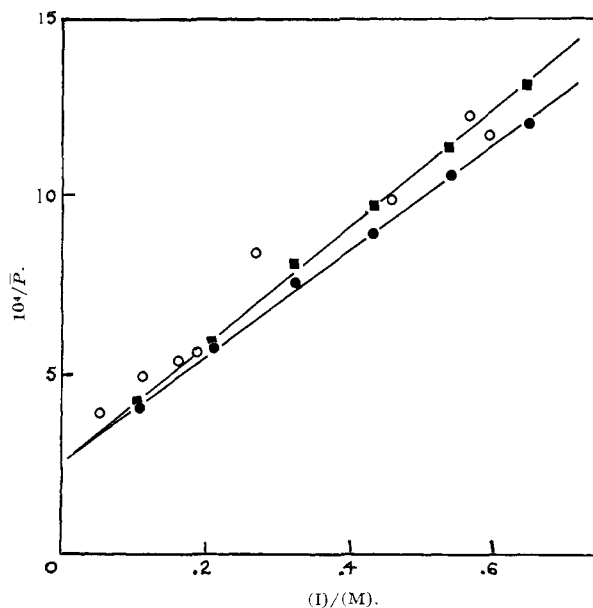


Fig. 1.—Graph of  $1/\bar{P}$  vs. (butyl peroxide)/(styrene) at 60°. Code: ●, dioxane as solvent, Mayo molecular weights; ○, benzene as solvent, Mayo molecular weights; ■, dioxane as solvent, Olivé-Schulz molecular weights.

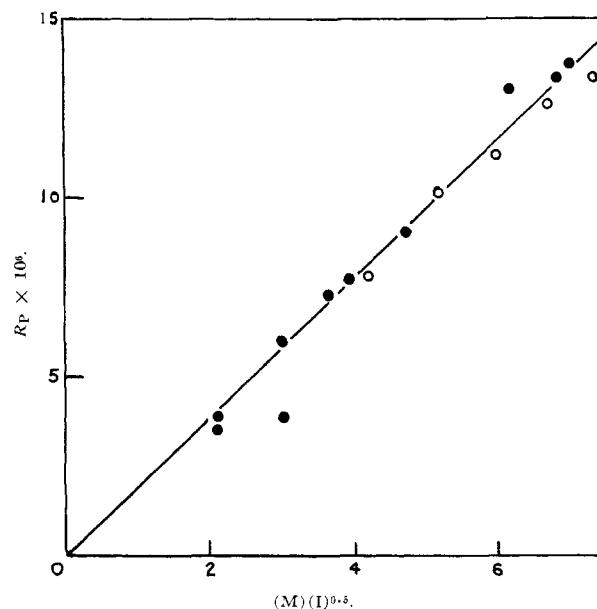


Fig. 2.—Graph of the rate of polymerization vs. (butyl peroxide)<sup>0.5</sup>(styrene) at 60°: ○, dioxane as solvent; ●, benzene as solvent.

respectively. If  $\delta^2 (= k_t/k_p^2)$  is taken as 900 as before,<sup>3</sup> the value of  $k_d f$  in either solvent is  $3.3 \times 10^{-9}$  sec.<sup>-1</sup> at 60°. This is very similar to the value obtained for *t*-butyl peroxide.

**Measurement of  $\delta^2$  in the Presence of Butyl Peroxide.**—Table II lists data on the polymerization of styrene by azoisobutyronitrile (AIBN) at 60° in solutions of 50:50 styrene:dioxane. Figure 3 of the preceding paper shows a plot of these data in the form of eq. 2. The slope of the line gives  $f^{0.5}/\delta$  as 0.0195, from which  $\delta^2$  can be calculated to be 1580 if  $f$  is assumed to have its usual value of 0.6 and to be constant.

The last run given in Table II gives data on the polymerization of styrene using both AIBN and butyl peroxide. This run was done with the purpose of measuring  $\delta^2$  in the presence of butyl peroxide as a

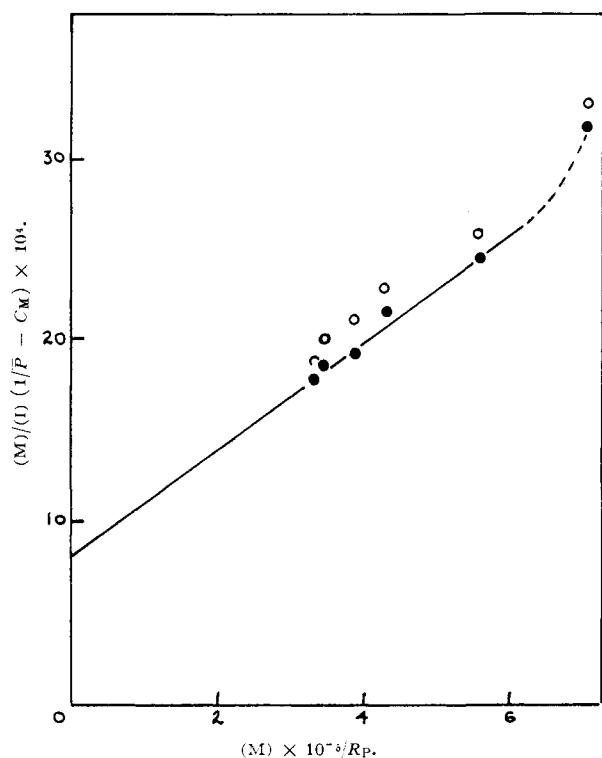


Fig. 3.—Graph of eq. 5 for data in dioxane-styrene at 60°C: ●, Mayo molecular weights; ○, Olivé-Schulz molecular weights.

solvent. If two initiators are present, AIBN and butyl peroxide, the rate of polymerization can be written as

$$R_{P,\text{total}}^2 = R_{P,\text{AIBN}}^2 + R_{P,\text{peroxide}}^2 + R_{P,\text{th}}^2 \quad (4)$$

Substitution of eq. 3 and neglecting the small term in the thermal rate, gives an equation which can be written as

$$\delta^2 = \frac{(M)^2}{R_{P,\text{total}}^2} [(6.7 \times 10^{-6})(\text{AIBN}) + (3.3 \times 10^{-9})(\text{peroxide})]$$

where  $3.3 \times 10^{-9}$  is the value of  $k_d f$  for butyl peroxide and  $6.7 \times 10^{-6}$  is that for AIBN. Substitution of the concentrations of styrene, AIBN, and butyl peroxide given in the last line in Table II leads to  $\delta^2 = 990$ .

TABLE II  
THE POLYMERIZATION OF STYRENE BY AZOISOBUTYRONITRILE AT 60°C<sup>a</sup>

(AIBN)	(Dioxane)	(Butyl peroxide)	$R_{P,\text{obsd}} \times 10^5$	$10^4/P$
0.00931	5.8	0	2.75	
0.00931	5.8	0	2.83	19.8 <sup>b</sup>
0.0124	5.8	0	3.29	
0.0124	5.8	0	3.17	22.3 <sup>b</sup>
0.0155	5.8	0	3.58	
0.0155	5.8	0	3.49	23.8 <sup>b</sup>
0.0186	5.8	0	3.83	
0.0186	5.8	0	3.78	27.2 <sup>b</sup>
0.00622	0.98	2.36	3.09	

<sup>a</sup> Styrene concentrations held constant at 4.3 M. <sup>b</sup> Average of duplicate determinations.

In this mixed solvent consisting of 50% styrene, 40% peroxide, and 10% dioxane,  $\delta^2$  has a value very near that of pure styrene. Thus, although it is not realistic to assume that  $f$  is a constant in solvents in which the ratio of dioxane to peroxide varies, the value of 900

for  $\delta^2$  appears to be a reasonable value for solutions which contain high concentrations of peroxide.

**Evaluation of  $\delta^2$  Using Eq. 1.**—The data given in Table IV of the previous paper in this series<sup>3</sup> show that  $f^{0.5}/\delta$  varies as the nature of the solvent is changed. This variation could be due to a dependence of either  $f$  or  $\delta^2$  on the solvent. Some of this variation is undoubtedly due to a variation in  $\delta^2$ ; it was pointed out in the previous paper that the values of  $f^{0.5}/\delta$  increase in roughly the same order as do the viscosities of the solvents. (Higher viscosity solvents should lead to smaller values of  $k_t$  and larger values of  $f^{0.5}/\delta$ , as is observed.<sup>3</sup>)

However, most of the variation in  $f^{0.5}/\delta$  is due to a dependence of  $f$  on the solvent system. The data in Table II can be used to derive a value of  $\delta^2$  using eq. 1. The transfer constant for AIBN is zero,<sup>13</sup> and  $C_M$  is a constant. Therefore, a graph of  $1/\bar{P}$  vs.  $R_{P,\text{obsd}}$  gives a line of slope  $\delta^2/(M)^2$ . When the data of Table II for the dioxane-styrene system are graphed in this way, the slope of the line gives  $\delta^2 = 935$ . The values of  $f^{0.5}/\delta$  given in Table IV of the preceding paper of this series<sup>3</sup> can now be used to calculate  $f$  for AIBN: in pure styrene,  $\delta^2 = 900$ ,  $f^{0.5}/\delta = 0.0258$ , and  $f = 0.60$ ; in one-to-one styrene-dioxane,  $\delta^2 = 935$ ,  $f^{0.5}/\delta = 0.0195$ , and  $f = 0.36$ . This marked dependence of the efficiency of an initiator on the concentrations of solvents used in styrene polymerizations is in agreement with the findings of Olivé, who has suggested that varying amounts of primary radical termination may be responsible.<sup>14a</sup> George and Onyon<sup>14b</sup> have postulated a specific solvent effect on the rate of geminate recombination reaction for AIBN in styrene solutions.

**Elimination of  $\delta^2$ .**—Combination eq. 1 through 3 gives an equation, derived by Mayo, Gregg, and Matheson,<sup>15</sup> from which  $\delta^2$  has been eliminated

$$\frac{(M)}{(I)} \left[ \frac{1}{\bar{P}} - C_M - \frac{\delta^2 R_{P,\text{th}}^2}{(M)^2 R_{P,\text{obsd}}} \right] = C + \frac{(M)k_d f}{R_{P,\text{obsd}}} \quad (5)$$

The term which includes  $R_{P,\text{th}}$  is negligible for all except those points involving the lowest peroxide concentrations.

Figure 3 is a graph of the peroxide-dioxane-styrene data from Table I in the form of eq. 5. The value of  $k_d f$  can be calculated from the slope of the line shown, and  $3.0 \times 10^{-9}$  is obtained, in good agreement with  $3.3 \times 10^{-9}$  sec.<sup>-1</sup> from Fig. 2. The intercept is equal to  $C$ , and a value of  $8 \times 10^{-4}$  is obtained, in good agreement with  $7.6 \times 10^{-4}$  which was found using eq. 1. The figure shows that the points for runs at low peroxide concentrations, on the far right of the figure, do not lie on the line defined by the points at high peroxide concentrations. The same phenomenon was observed for benzoyl peroxide by Mayo, Gregg, and Matheson (see their Fig. 3). For these points, the thermal rate of polymerization represents an appreciable part of the

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(b) M. H. George and P. F. Onyon, *Trans. Faraday Soc.*, **59**, 1390 (1963).

(15) F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951). Their equation does not include the term in  $R_{P,\text{th}}$  since at that time it was felt that thermal initiation was due to biradicals and, therefore, did not contribute any chain ends (e.g., see their eq. 12, 13, and 17). Further study of thermal initiation has led to a revision of this view. Mayo (*ibid.*, **75**, 6133 (1953)) has measured the contribution to  $1/\bar{P}$  from thermal initiation at 60°C as  $1.26 \times 10^{-3} (M)^{0.5}$ , or about  $0.26 \times 10^{-4}$  for the runs reported here.

total rate, and the most likely explanation<sup>15</sup> of this discrepancy is that some unknown complication occurs in the rate of thermal initiation at low rates of polymerization. Figure 3 also shows the same relationship using molecular weights calculated by the Olivé-Schulz equation, and these data are discussed below.

**Data at 80°.**—Table III gives data for the polymerization of styrene by butyl peroxide at 80°. Unfortunately, dioxane was used for these higher temperature runs before the peroxide-benzene-styrene system was chosen as the standard system. The transfer constant calculated on runs using greater than 0.9 M peroxide is  $29 \times 10^{-4}$ . A graph analogous to Fig. 4 gives  $C = 25 \times 10^{-4}$ . A graph of the data in the form of eq. 2 gives a line with slope  $1.53 \times 10^{-5}$ , and using  $\delta^2 = 260$  at 80°, a value of  $k_d f$  can be obtained as  $6.1 \times 10^{-8}$  sec.<sup>-1</sup>.

TABLE III  
THE POLYMERIZATION OF STYRENE BY BUTYL PEROXIDE  
AT 80°<sup>a</sup>

(I)	$R_p \times 10^6$ <sup>b</sup>	$[\eta]$	$10^4/\bar{P}^c$	$10^4/\bar{P}^d$	$C \times 10^4$ <sup>c</sup>
0.47	4.54	0.655	11.1	11.9	38.5
0.93	6.44	0.494	16.4	17.8	32.2
1.42	7.72	0.417	20.7	22.5	28.6
1.89	8.89	0.377	23.8	25.9	24.9
2.36	10.87	0.300	32.5	35.9	31.2
2.84	11.43	0.283	35.2	39.1	28.8

<sup>a</sup> Styrene molarity held constant at 4.3 using dioxane as solvent. <sup>b</sup> At 80°,  $R_{p,th}$  is negligible. <sup>c</sup> Gregg and Mayo relations used. See ref. 9 and 10. <sup>d</sup> Olivé-Schulz relations used. See ref. 11.

**Activation Energies.**—The values of  $k_d f$  at 60 and 80° of  $3.3 \times 10^{-9}$  and  $6.1 \times 10^{-8}$  give an activation energy for the dissociation reaction of 34.3 kcal./mole. A value between 35 and 37 kcal./mole would be expected from studies of other alkyl peroxides.<sup>16</sup>

Using the data in dioxane as solvent, the values of  $C$  at 60 and at 80° are  $7.6 \times 10^{-4}$  and  $29 \times 10^{-4}$ , giving an apparent activation energy for the transfer reaction of 16 kcal./mole. If  $E_p$  is taken as 7.3 kcal./mole, then  $E_{tr}$  is 23 kcal./mole.

(16) (a) P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 104 (1959); (b) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).

**Olivé-Schulz Molecular Weights.**—Henrici-Olivé, Olivé, and Schulz have developed a method for calculating molecular weights which attempts to take into account the change in molecular weight distribution which accompanies chain transfer.<sup>11</sup> Their method involves calculation of a viscosity-average degree of polymerization and correcting this to a number-average degree of polymerization using a function which depends on the rate of polymerization and on  $\delta^2$ . Tables I and III give the degree of polymerization calculated by both methods. At low peroxide concentration, where the amount of termination by transfer is small, the two methods agree very closely. However, as expected,<sup>11</sup> the agreement becomes poorer at higher peroxide concentrations. Figure 1 shows this graphically; the solid circles are the peroxide-dioxane-styrene data calculated using the Mayo equations, and the squares are for the Olivé-Schulz equations. As Olivé has pointed out, the Olivé-Schulz equations lead to slightly higher transfer constants. This is best seen in Fig. 3, where the open circles give the results of calculations using the Olivé-Schulz calculations, and the transfer constant is obtained as  $10 \times 10^{-4}$  instead of  $8 \times 10^{-4}$ .

At this stage, however, the results do not appear to be worth the effort. The Olivé-Schulz calculations require knowledge of  $\delta^2$  in order to calculate the degree of polymerization, and the correct value of  $\delta^2$  remains the largest imponderable of any method. For our purposes, it seems better to calculate the degree of polymerization in the same way for each peroxide and to regard the data as accurate only within the series of similar compounds. We hope to have a better idea of the absolute accuracy of the transfer constants when we complete our measurements of transfer constants for these peroxides using the radioactive tracer method.

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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. XI. Ethyl Peroxide, Isopropyl Peroxide, and *sec*-Butyl Peroxide

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The dissociation constants and chain transfer constants are given for ethyl peroxide, *sec*-butyl peroxide, and isopropyl peroxide at 60 and 80° in styrene solutions. These data are compared with comparable data previously reported for propyl peroxide, butyl peroxide, and *t*-butyl peroxide. All these dialkyl peroxides have values of  $k_d f$  at 60° of about  $10^{-9}$  sec.<sup>-1</sup>, activation energies for dissociation of 34–37 kcal./mole, and transfer constants in the range of  $3$  to  $9 \times 10^{-4}$  at 60°. It is proposed that the predominant mechanism for transfer in this system is hydrogen abstraction. Preparation of the dialkyl peroxides and hazards in handling them are discussed. The transfer constant of *t*-butyl ether is also reported.

This paper reports data on the three peroxides named in the title. No previous kinetic studies have been reported on either isopropyl peroxide or *sec*-butyl peroxide. Data on the unimolecular decomposition

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of ethyl peroxide have been reported in the gas phase by three groups of workers,<sup>2–4</sup> but no previous liquid phase results have been published.

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(3) R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, **20**, 574 (1952).

(4) K. Moriya, *Rev. Phys. Chem. Japan (Horiba Vol.)*, 143 (1946).