

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Reactions of Radicals.¹ II. The Rates of the Spontaneous and Induced Decomposition of Propyl Peroxide¹⁻⁴

BY WILLIAM A. PRYOR AND EDMUND P. PULTINAS, JR.

RECEIVED JULY 6, 1962

The rate of decomposition in solution has been reported for only one aliphatic peroxide, namely *t*-butyl peroxide. Even in that case, only the spontaneous decomposition has been studied; the rate of the induced decomposition has been assumed to be too small for measurement. This paper is the first of a series in which the rates of the spontaneous and the induced decomposition of aliphatic peroxides will be reported. In the present paper, the methods are summarized and the data presented for propyl peroxide. The method involves a study of the polymerization of styrene catalyzed by the peroxide. Rates of polymerization and molecular weights are measured. The data yield the following: the spontaneous decomposition of propyl peroxide at 60° has a rate constant $2 k_{af}$ equal to 5.4×10^{-9} sec.⁻¹. This agrees with the value extrapolated from the gas phase measurements of Harris, done at 146 to 175°. The rates of decomposition in the liquid and the gas phase are therefore similar, and the efficiency of production of initiating radicals from the peroxide is high. The chain transfer constant for propyl peroxide is found to be 8.4×10^{-4} . If the propagation constant for the polymerization of styrene is taken as 145 l. mole⁻¹ sec.⁻¹ at 60°, then the rate of the decomposition of propyl peroxide induced by the polystyryl radical has the rate constant 0.12 l. mole⁻¹ sec.⁻¹. Both the first- and the second-order rate constants for propyl peroxide are similar to those found for *t*-butyl peroxide, yet the former is a potential explosive and the latter a reasonably stable peroxide. A possible explanation for this is suggested.

Introduction

In the first paper³ in this series, the transfer constants were reported for the series of aliphatic disulfides from methyl disulfide through *t*-butyl disulfide. These transfer constants, which give the rates of attack by the polystyryl radical on these disulfides, were discussed with reference to a model for bimolecular homolytic displacements (SH₂ reactions).⁵ An important extension of that work is to obtain the transfer constants for the analogous series of peroxides. Moreover, the transfer constants of peroxides and their rates of spontaneous decomposition are of considerable theoretical and practical interest in themselves. Although a number of studies⁶ have been made of the SH₁ reaction of *t*-butyl peroxide, detailed data have not been reported on the simultaneous SH₁ and SH₂ reactions of any aliphatic peroxide.⁷ In this paper, methods will be developed for obtaining such data from polymerization studies, and the data given for propyl peroxide. Subsequent papers will present the data for other aliphatic peroxides.

(1) This work was supported in part by grant RG-9020 from the National Institutes of Health. Grateful acknowledgment is made to the donors of that fund.

(2) Based in part on the thesis submitted by E. P. Pultinas, Jr., in partial fulfillment of the requirements for Master of Science.

(3) Part I, W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).

(4) In papers in this series, peroxides will be named analogously to ethers, sulfides and disulfides. Thus di-*n*-propyl peroxide is propyl peroxide. This is "Chemical Abstracts" usage (*C. A.*, **39**, 5939 (1945)) but it has not usually been followed.

(5) Transfer reactions are bimolecular, homolytic reactions and are here termed SH₂ reactions. An example is the so-called induced decomposition of a peroxide. Unimolecular bond scission reactions are here termed SH₁ reactions. An example is the spontaneous decomposition of a peroxide.

(6) (a) L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 3558 (1960); (b) J. K. Allen and J. C. Bevington, *Proc. Roy. Soc. (London)*, **262A**, 271 (1961); (c) J. A. Offenbach and A. V. Tobolsky, *J. Am. Chem. Soc.*, **79**, 278 (1957); (d) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953); **13**, 122 (1954); (e) J. H. Raley, F. R. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948); (f) **70**, 1336 (1948); (g) E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950); (h) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962); (i) R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951).

(7) Such data have been reported for aryoyl peroxides and the field is reviewed in refs. 8 and 9a. Also see: (a) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); (b) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947); (c) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951); (d) W. Cooper, *J. Chem. Soc.*, 3106 (1951); (e) 2408 (1952); (f) D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, **74**, 938 (1952).

(8) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 48-57.

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (a) pp. 159-161, (b) p. 67, (c) p. 84.

Experimental

Propyl peroxide was synthesized by the method of Mosher¹⁰ modified as follows: 220 g. of a 50% aqueous potassium hydroxide solution was added dropwise to a mixture of 443 g. of propyl methanesulfonate^{10b} (n_D^{25} 1.4224), 214 g. of 30% hydrogen peroxide and 250 ml. of methanol. The mixture was stirred at 5 to 15° for 2 hr., then at 25° for 9 hr. Upon addition of 100 ml. of water, an upper layer separates. This layer is removed and distilled twice giving propyl peroxide, in about 30% yield, b.p. 43° (51 mm.), n_D^{25} 1.3897. The infrared spectrum is identically that summarized by Mosher. The peroxide shows no absorption at 2.9 μ (where propanol and propyl hydroperoxide absorb) or at 5.92 μ (propanal). Mass spectral analysis (kindly performed by Dr. S. Meyerson) showed a parent peak at 118m/e. Analysis by infrared can easily detect 1% propanol or propanal in ether, and on this basis the peroxide is better than 99% pure. Less than 1% alcohol or aldehyde would not be critical since they have transfer constants less than that of the peroxide.^{11a}

Experimental procedures and the method used for measuring the degree of polymerization were described previously.³ The method used in Part 1 for obtaining rates of polymerization is not sufficiently accurate for present purposes, and the procedure of Lewis and Mayo was employed.^{11b}

TABLE I
DATA FOR PROPYL PEROXIDE

Total vol. rx. soln., ml.	Hours at 60.0°	Yd. of polymer, g.	(I) ^a	(M) ^b	10 ^c / \bar{P}	$R_{P,obs}$ ^d × 10 ⁶	R_P × 10 ⁶ , ^e l. moles ⁻¹ sec. ⁻¹
7	17.3	0.6317	1.43	6.70	5.50	1.39	1.38
10	17.3	1.0350	1.43	6.70	5.60	1.60	1.59
7	17.3	0.5300	1.28	6.91	4.94	1.16	1.14
8	13.5	.5762	1.26	7.10	4.58	1.42	1.41
7	13.5	.4718	1.23	7.13	4.68	1.33	1.31
7	13.5	.4944	1.03	7.42	4.04	1.40	1.38
8	13.5	.4646	0.900	7.57	3.71	1.15	1.13
7	13.5	.4154	.824	7.65	3.64	1.17	1.16
9	15.0	.5732	.641	7.92	2.97	1.14	1.11
8	15.0	.4042	.480	8.27	2.16	0.90	0.88
7	15.0	.3640	.412	8.20	2.07	.93	.90
7	15.0	.2725	.206	8.45	1.57	.69	.67
8	15.0	.2899	.180	8.50	1.53	.645	.61
9	15.0	.3216	.160	8.51	1.49	.637	.60

^a Initial concentration of propyl peroxide in moles/liter. ^b Initial concentration of styrene. ^c Calculated from viscosity data as in ref. 3. ^d Calculated from $R_{P,obs} = -\Delta M/\Delta t = (g. polymer)/(104) (l. rx. soln.) (sec.)$. ^e Calculated from eq. 8 using $R_{P,th} = 2.1 \times 10^{-8}$ moles l.⁻¹ sec.⁻¹ (ref. 6c). Other values up to 2.5×10^{-8} have been reported (see E. P. Bonsall, L. Valentine and H. W. Melville, *J. Polymer Sci.*, **7**, 39 (1951) and ref 7c). However, the value of this constant is not critical.

(10) (a) F. Welch, H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **77**, 551 (1955); (b) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2987 (1954).

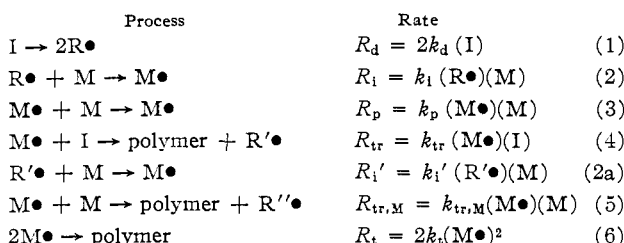
(11) (a) R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953); (b) F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem.*, **17**, 134 (1945).

Data.—The experimental data are presented in Table I. The table lists the total volume of the reaction solution, the reaction time at 60.00° the total yield of polymer, the initial concentration of the propyl peroxide in moles per liter (I), the initial concentration of styrene (M), the inverse of the degree of polymerization $1/\bar{P}$, the observed rate of polymerization $R_{P,obs}$, and the rate corrected for the thermal rate R_P . (The method of correcting the observed total rate for the portion due to thermal initiation is given in eq. 8.)

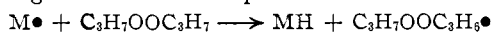
Discussion

Several alternative methods of calculating the transfer constant of a peroxide, C , will be developed. They all result from algebraic manipulation of the same basic equation, and if the experimental data fit this equation perfectly all the methods would lead to the same value of C . However, since the methods weigh the experimental variables differently, they give slightly different values of C . As a control, the transfer constant for benzoyl peroxide has been calculated by each of the methods using the data of Mayo, Gregg and Matheson.^{7c} This is helpful in evaluating the calculational methods since the data on benzoyl peroxide are more precise than are the data for propyl peroxide. Benzoyl peroxide is a solid and is easier to purify and is less susceptible to light-induced decomposition once pure; it is also a more effective initiator and transfer agent, and larger transfer constants can be determined with more absolute accuracy.¹²

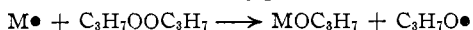
The Chemical System.—The chemical equations for the polymerization of styrene by a peroxide are



The symbols are those usually used,¹³ and the usual assumptions are made: The rate constant for any step is independent of the chain length of the polymer undergoing reaction,¹⁴ and no primary radical termination occurs.¹⁵ Notice that the mechanism of the transfer reaction, eq. 4, is not specified. The total rate of transfer observed will be the sum of the rates of all hydrogen abstraction steps



and of the SH₂ reaction on oxygen



Note also that the rate constants for eq. 1 and 6 are written on a per radical basis.¹⁶

(12) Benzoyl peroxide is sufficiently reactive so that the most concentrated solution which must be examined is 0.16 M, and the concentration of styrene is unchanged in this solution. With propyl peroxide, up to 1.5 M solutions must be studied, and in these concentrated solutions of peroxide the styrene monomer has been appreciably diluted. The effect of this on the theory of chain transfer is not entirely known. See W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **56**, 407 (1960); **57**, 1928 (1961); C. H. Bamford, A. D. Jenkins and R. Johnston, *Trans. Faraday Soc.*, **55**, 1451 (1959); A. D. Jenkins, *ibid.*, **54**, 1885 (1958). Also, with benzoyl peroxide, molecular weight lowerings can be easily obtained that are 6-fold those obtainable with propyl peroxide, and these larger $1/\bar{P}$ values can be determined with greater absolute accuracy. Also see J. P. Van Hook and A. V. Tobolsky, *J. Phys. Chem.*, **62**, 257 (1958).

(13) Reference 9, pp. 64–67.

(14) This assumption, although necessary for studies such as that reported here, is becoming increasingly suspect. See footnote 12 and Table 3-11, p. 84, of ref. 8. The assumption probably is adequate for this study where P changes only by a factor of 6.

(15) *I.e.*, all $R\bullet$ and $R'\bullet$ rapidly reinitiate polymerization and do not enter into, and thus change the rate and mechanism of, the termination step.

(16) This conforms with the American convention, but is contrary to the English; see *e.g.*, ref. 9, p. 67, and ref. 17, p. 2.

(17) J. C. Bevington, "Radical Polymerization," Academic Press, Inc., New York, N. Y., 1961; (a) p. 29; (b) pp. 103, 136.

Basic Equations for Chain Transfer.—The following equations can be derived from the usual steady state approximations^{6d,6i,9b}

$$(M\bullet) = (R_i/2k_t)^{1/2} \quad (7)$$

$$R_P = [R_{P,obs} - R_{P,th}]^{1/2} \quad (8)$$

$$R_i = 2k_d f(I) = 2k_t R_P^2/k_p^2(M)^2 \quad (9)$$

where R_i is the rate of initiation due to propyl peroxide after subtraction of the rate of thermal initiation,⁶ⁱ f is the efficiency of radical production from the peroxide^{17a}, $R_{P,obs}$ is the observed rate of polymerization, and R_P is the rate of polymerization due to the peroxide alone after correction for the thermal rate.

For styrene, where termination is by combination^{17b}

$$\bar{P} = R_P/[1/2R_i + \Sigma(\text{all transfer})]$$

Substitution of eq. 3, 4 and 5 into this relation and inversion gives^{17b}

$$\frac{1}{\bar{P}} = \frac{R_i}{2R_P} + C_M + C \frac{(I)}{(M)} \quad (10)$$

where $C_M = k_{tr,M}/k_p$, and $C = k_{tr}/k_p$. Substitution for R_i from eq. 9 gives

$$\frac{1}{\bar{P}} = \frac{k_t}{k_p^2(M)^2} R_P + C_M + C \frac{(I)}{(M)} \quad (11)$$

The transfer constant for styrene, C_M , has been evaluated^{7c,7f} as 0.60×10^{-4} with an accuracy of about 25%. The value of k_t/k_p^2 has been measured by several groups of workers. Walling^{9c} has compiled five sets of values, and the agreement is quite good. The most extensive and precise data are those of Tobolsky and Offenbach,¹⁸ who find $k_t/k_p^2 = 5.68 \times 10^{-6} e^{12.460/RT}$, which gives 910 at 60°. The data of Mayo, Gregg and Matheson^{7c} yield 908 for k_t/k_p^2 at 60°. The value of k_t/k_p^2 of 900 will be used here; it is probably accurate to $\pm 20\%$.

By substituting values of C_M and k_t/k_p^2 in eq. 11, a value of C can be calculated on each point in Table I. This gives an average $C = 8.6 \times 10^{-4}$ with a standard deviation¹⁹ $s = 2.2 \times 10^{-4}$. For benzoyl peroxide, this procedure gives $C = 0.035$ with $s = 0.033$ (calculated using the 10 runs of highest peroxide concentration).

The transfer constant can also be calculated from a modification of eq. 10, first derived by Tobolsky and Baysal,^{6d} which does not involve the peroxide concentration. Substitution of the expression for (I) from eq. 9 into eq. 11 gives

$$\frac{1}{\bar{P}} = C_M + \frac{k_t}{k_p^2(M)^2} R_P + \frac{CR_P^2}{K^2(M)^3} \quad (12)$$

where Tobolsky and Baysal have defined K as in eq. 13.

$$R_P = K(M)(I)^{1/2} \quad (13)$$

From eq. 13 and eq. 3 and 7

$$K^2 = k_d f k_p^2/k_t \quad (13a)$$

Figure 1 is a graph of eq. 13 and a straight line through the origin fits the data excellently. Least squares analysis give the values: slope = $K = 1.74 \times 10^{-6}$, intercept = 0.02×10^{-6} . From this value of K , and using eq. 13a, $k_d f$ for propyl peroxide is found to be $2.7 \times 10^{-9} \text{ sec}^{-1}$. A similar procedure for benzoyl peroxide gives $K^2 = 2.2 \times 10^{-9}$, $k_d f = 2.0 \times 10^{-6} \text{ sec}^{-1}$.

Using these values of K^2 and eq. 12, a value of C can be calculated from each point in Table I. This gives $C = 8.8 \times 10^{-4}$ with a standard deviation of $2.2 \times$

(18) A. V. Tobolsky and J. Offenbach, *J. Polymer Sci.*, **16**, 311 (1955). Tobolsky defines $A' = (2k_{td} + k_{tc})/k_p^2$. For styrene, where termination is by combination, $A' = k_t/k_p^2$.

(19) $s = [\Sigma(C_i - C_{avg})^2/(n - 1)]^{1/2}$.

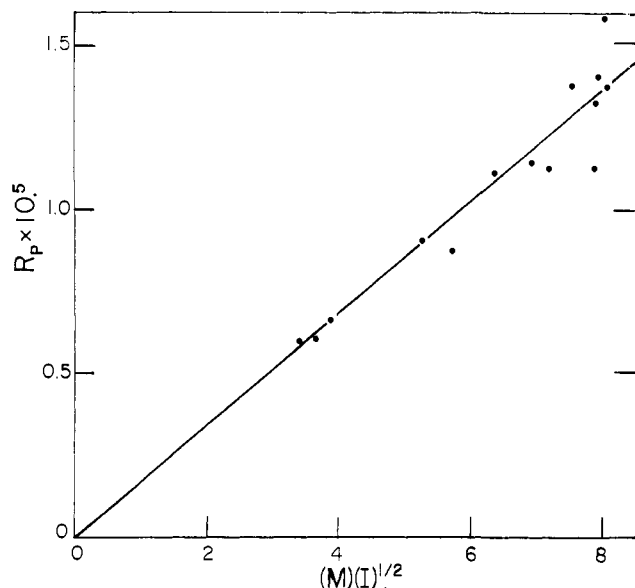


Fig. 1.—Graph of eq. 13; least square analysis: intercept 0.02×10^{-5} , slope = $K = 1.74 \times 10^{-6}$. Therefore, $k_{df} = 2.7 \times 10^{-9}$ sec. $^{-1}$.

10^{-4} for propyl peroxide, and $C = 0.034$ with $s = 0.033$ for benzoyl peroxide.

The transfer constant can also be calculated from an equation which is similar to that used by Mayo, Gregg and Matheson^{7c} in their study of benzoyl peroxide. Substitution of eq. 9 into 10 and rearrangement gives

$$\frac{(M)}{(I)} \left[\frac{1}{\bar{P}} - C_M \right] = C + \frac{(M)k_{df}}{R_p} \quad (14)$$

Figure 2 shows the data graphed as in eq. 14. The value of k_{df} obtained from the slope is 2.6×10^{-9} sec. $^{-1}$ and the value of C from the intercept is 8.0×10^{-4} . For benzoyl peroxide this treatment^{7c} gives $C = 0.055$ and $k_{df} = 1.9 \times 10^{-6}$ sec. $^{-1}$.

In summary, the data of Table I lead to the following values for propyl peroxide

$$k_{df} = 2.7 \times 10^{-9} \text{ sec.}^{-1}$$

$$C = 8.4 \times 10^{-4}$$

If the propagation constant for styrene is taken as 145 l. mole $^{-1}$ sec. $^{-1}$, then $k_{tr} = 0.12$ l. mole $^{-1}$ sec. $^{-1}$ for propyl peroxide.

Limiting Case: Initiation Ignored.—If propyl peroxide were not an initiator, the rate of polymerization would not be a function of (I) . Table I shows this is incorrect; it is interesting, however, to examine the value of C obtained using this limiting assumption. If R_p in eq. 11 is constant, then a graph of $1/\bar{P}$ versus $(I)/(M)$ should be a straight line with slope C . Figure 3 gives this graph and the data define an excellent straight line. The intercept of this line should be the value of $1/\bar{P}$ obtained for pure styrene, 1.16×10^{-4} . A least squares analysis gives the slope 20.7×10^{-4} and the intercept 1.12×10^{-4} . It is apparent that this graph is not a sensitive test for initiation, and a graph such as Fig. 1 must be used. This graph for benzoyl peroxide, which is a more effective initiator, is not as straight line but is a smooth curve. A value for C can be calculated from the limiting slope of Fig. 3 as 0.108 and this limiting slope extrapolates to an intercept of 9×10^{-4} . Thus, an initiator as active as benzoyl peroxide can be detected from a graph of $1/\bar{P}$ versus $(I)/(M)$.

Limiting Case: Transfer Ignored.—Tobolsky and Offenbach¹⁶ use eq. 12 as a test for determining whether

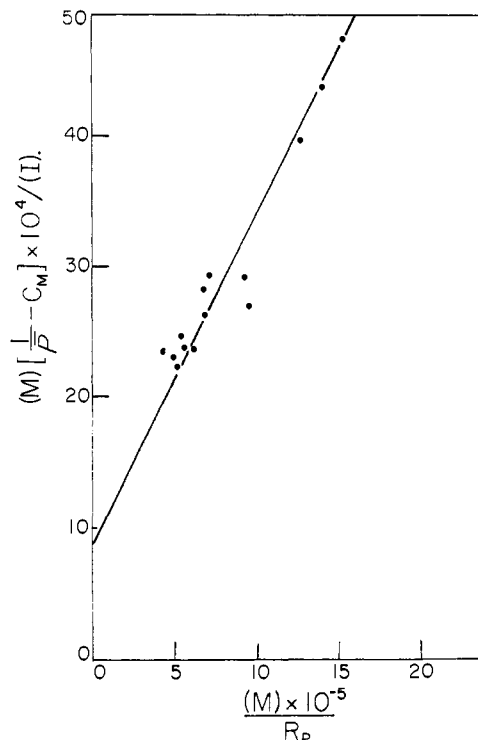


Fig. 2.—Graph of eq. 14; slope = $k_{df} = 2.6 \times 10^{-9}$ sec. $^{-1}$, intercept = $C = 8.0 \times 10^{-4}$.

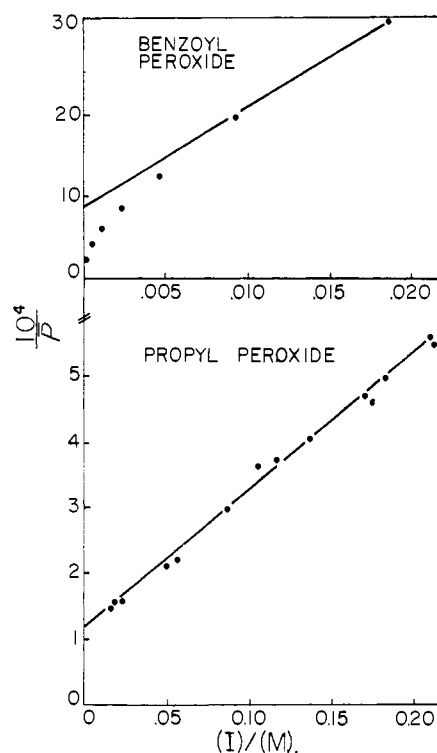


Fig. 3.—Graph of eq. 11 assuming that R_p is a constant. For propyl peroxide slope = $C = 20.9 \times 10^{-4}$, intercept = 1.12×10^{-4} . For benzoyl peroxide, limiting slope = 0.108, extrapolated intercept = 9×10^{-4} .

transfer occurs. They state that if a graph of $1/\bar{P}$ versus $R_p/(M)^2$ is a straight line, C must be zero. Although algebraically this is correct, in practice this test for transfer, like the test for initiation discussed above, is extremely insensitive. A graph of eq. 12 using data for *t*-butyl peroxide (TBP) at 90° is a straight line¹⁸; from this it has frequently been concluded that TBP does not undergo transfer. Actually, TBP does

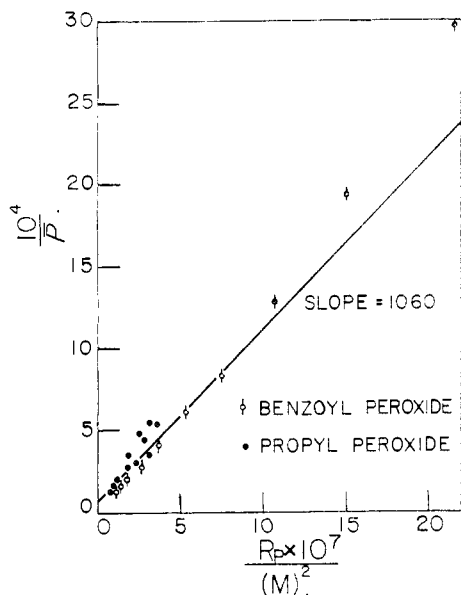


Fig. 4.—Graph of eq. 12 assuming C is zero. Slope should be k_t/k_p^2 and intercept should be C_M .

undergo transfer at 60° but with a small transfer constant.^{20,21}

A graph of $1/\bar{P}$ versus $R_p/(M)^2$ for propyl peroxide and benzoyl peroxide is given in Fig. 4. Figure 4 should be a line of slope k_t/k_p^2 and intercept C_M if C in eq. 12 were zero; if C/K^2 has some small finite value, then Fig. 4 will not be a straight line, but will show curvature at large values of R_p . The figure shows that this region of curvature is accessible only with benzoyl peroxide. Note, however, that for neither compound is the slope of Fig. 4 equal to 900, the best value for k_t/k_p^2 .

The Spontaneous Decomposition of Propyl Peroxide.

—The rates of decomposition of propyl peroxide in the gas phase at 145 – 175° have been reported by Harris.²² Using his rate constants and activation energy, 36.5 kcal., the extrapolated rate constant at 60° is 3.0×10^{-9} sec.⁻¹. The value of $2k_d f$ found here is 5.4×10^{-9} sec.⁻¹. The similarity of these values implies that f , the efficiency of production of initiating radicals from propyl peroxide, is high, as is true for TBP^{6c,f} and for other initiators.^{6d}

The Explosive Decomposition of Aliphatic Peroxides.

—TBP is a relatively stable compound and propyl per-

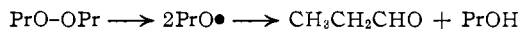
(20) The transfer constant of TBP at 60° is 8.6×10^{-4} ; W. A. Pryor, *J. Phys. Chem.*, in press.

(21) Since the SH_2 reaction of a peroxide has higher activation energy than the SH_1 reaction, the first order process will consume a larger fraction of the peroxide at higher temperature. Thus, it might be thought that at 90° TBP does not undergo transfer. However, Batt and Benson (ref. 6h) have found evidence for transfer even in the gas phase decomposition of TBP at 130 – 160° . It is apparent that TBP does transfer. Ethers, ketones, alcohols, and even hydrocarbons such as heptane have measurable transfer constants (see ref. 11a). It would be highly unexpected to find that TBP had a transfer constant which was identically zero.

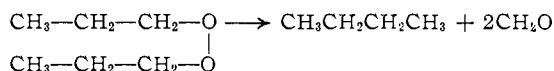
(22) E. J. Harris, *Proc. Roy. Soc. (London)*, **173A**, 126 (1939).

oxide is regarded as a potential explosive. Yet the rate constant for the spontaneous decomposition of both these peroxides is approximately 2×10^{-9} sec.⁻¹ at 60° , corresponding to a half-life of over 10 years. Furthermore, the transfer constants of these two peroxides are very similar. These surprising and seemingly contradictory facts require comment.

Harris and Egerton²³ have studied the gas phase decomposition of ethyl peroxide in detail, and Harris has reported²² a somewhat less detailed study of propyl peroxide. The two peroxides behave similarly. Both decompose by two different reactions: One a homogeneous, unimolecular decomposition which is not explosive, and the other an explosive decomposition which is accompanied by light emission and a knocking-like sound. The two reactions give different products. The "slow" decomposition is²³



The explosion is²²



The "slow" decomposition is dominant at 146 – 175° in the gas phase²² and is undoubtedly the unimolecular reaction which occurs in solution at 60° . Therefore, the energy of activation calculation in the preceding section was on rates of the same reaction.

A critical pressure exists, above which explosion occurs and below which the "slow" decomposition is dominant. This limit is about 10 mm. at 200° for both ethyl and propyl peroxide. At lower temperatures, the critical pressure increases rapidly. Thus, for ethyl peroxide, the critical pressure is 40 mm. at 180° , the lowest temperature at which Harris could study the explosion.

Both ethyl and propyl peroxide are sensitive to light and air, whereas TBP can be distilled in the light and in the presence of air.

In view of these facts, it is very doubtful that the high temperature, gas-phase explosive reaction of propyl peroxide could be responsible for any of the hazard in handling this compound at 25 – 60° . Pure, liquid aliphatic peroxides of any structure seem completely stable at room temperature.²⁴ A hypothesis which explains the more dangerous nature of propyl peroxide despite the similarity of its first-order and induced rates of decomposition to the relatively stable TBP is: The peroxides themselves are not explosives at 25 – 60° , but their peroxidation products are. Thus, just as propyl or isopropyl ether peroxidize to form dangerous, shock-sensitive explosives so propyl and isopropyl peroxides may. TBP therefore may be more stable to storage because it lacks reactive α -hydrogens.

(23) E. J. Harris and A. C. Egerton, *ibid.*, **168A**, 1 (1938).

(24) G. R. McMillan, *J. Am. Chem. Soc.*, **83**, 3018 (1961), reports his inability to detonate isopropyl peroxide by shock. We have observed non-explosive decompositions of these liquid peroxides at temperatures up to 100° .