

total rate, and the most likely explanation¹⁵ 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 29×10^{-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 1.53×10^{-5} , and using $\delta^2 = 260$ at 80°, a value of k_{df} can be obtained as $6.1 \times 10^{-8} \text{ sec.}^{-1}$.

TABLE III
THE POLYMERIZATION OF STYRENE BY BUTYL PEROXIDE
AT 80°^a

| (1) | $R_p \times 10^5$ ^b | $[\eta]$ | $10^4/\bar{P}^c$ | $10^4/\bar{P}^d$ | $C \times 10^4$ ^c |
|------|--------------------------------|----------|------------------|------------------|------------------------------|
| 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 |

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

Activation Energies.—The values of k_{df} at 60 and 80° of 3.3×10^{-9} and 6.1×10^{-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.¹⁶

Using the data in dioxane as solvent, the values of C at 60 and at 80° are 7.6×10^{-4} and 29×10^{-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.¹¹ 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 δ^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,¹¹ 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 10×10^{-4} instead of 8×10^{-4} .

At this stage, however, the results do not appear to be worth the effort. The Olivé-Schulz calculations require knowledge of δ^2 in order to calculate the degree of polymerization, and the correct value of δ^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.

Acknowledgment.—This work was supported in part by Contract AT (11-1)-1169 (at Purdue) and by AT (40-1)-3180 (at LSU) from the Atomic Energy Commission and by Public Health Service Research grants from the National Institutes of Health at both Purdue and L.S.U. Grateful acknowledgment is made to the donors of these funds.

[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

BY WILLIAM A. PRYOR,^{1a} D. M. HUSTON, T. R. FISKE, T. L. PICKERING,^{1b} AND E. CIUFFARIN^{1c}

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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_{df} at 60° of about $10^{-9} \text{ sec.}^{-1}$, activation energies for dissociation of 34–37 kcal./mole, and transfer constants in the range of 3 to 9×10^{-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

(1) (a) Department of Chemistry, Louisiana State University, Baton Rouge, La.; (b) National Science Foundation Undergraduate Research Participant during 1962–1963 at Purdue University; (c) Post doctoral Fellow 1962–1964.

of ethyl peroxide have been reported in the gas phase by three groups of workers,^{2–4} but no previous liquid phase results have been published.

(2) E. J. Harris and A. C. Egerton, *Proc. Roy. Soc. (London)*, **A 168**, 1 (1938).

(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).

Secondary alkyl peroxides are difficult to obtain in good yield. Primary alkyl peroxides, including ethyl peroxide, can be obtained in about 50% yield using the appropriate alkyl methanesulfonate and the synthesis developed by Mosher, *et al.*⁵ Tertiary peroxides can be obtained in 80 to 100% yields directly from the alcohol using the Milas method.⁶ In the case of secondary peroxides, however, the Milas method fails and the Mosher method gives very poor yields.

In their original report,^{5a} the Mosher group obtained a 17% yield for *sec*-butyl peroxide. However, in our laboratory, this procedure has not given yields of purified peroxide of greater than 11%. Similarly, isopropyl peroxide has not been prepared in our laboratory in yields of better than 10% using this method. The cause of the poor yields is known: both the alkyl methanesulfonate and the peroxide product are unstable in the strong basic solutions used in the Mosher method, and decomposition of both the starting material and the product competes with the accumulation of peroxide. Improved syntheses are described in the Experimental section in which the peroxides are removed from the reaction mixture as they are formed.

Experimental

Preparation of *sec*-Butyl Methanesulfonate.—A slightly improved yield of the sulfonate can be obtained by the following procedure: 296 g. of *sec*-butyl alcohol and 458 g. of methanesulfonyl chloride are held between 5 and 8° while 632 g. of pyridine is added over 4 to 6 hr. Stirring is continued for 1 hr. Then 1.4 l. of 6 N HCl is added, keeping the temperature below 30°. Distillation [b.p. 58° (0.5 mm.)] gives yields of 78 to 81%.

Preparation of *sec*-Butyl Peroxide.—In a 1.5-l. flask are placed 228 g. of *sec*-butyl methanesulfonate, 75 g. of 30% hydrogen peroxide, and 200 ml. of methanol. The temperature is kept below 10° while 83 g. of KOH in an equal weight of water is added over 30 min. A pressure of 500 to 550 mm. is applied and the flask is heated to 60° and methanol allowed to distil into a series of traps. Additional methanol is added as the reaction proceeds to keep the mixture homogeneous. After heating for 2 hr. 50 ml. more of hydrogen peroxide is added, and the reaction is allowed to run for another 4 to 6 hr. The trap contents are then extracted with Tetralin, washed with 5% KOH and water, and dried over sodium sulfate. The resulting solution is bright orange, but the color disappears when distillation begins. The peroxide is distilled through a short Vigreux column at 61–63° (50 mm.). The yield is 19.1 g. (17%).

Purity of *sec*-Butyl Peroxide.—The n.m.r. (neat) consists of a triplet centered at 0.90 p.p.m. (relative intensity 3.0) due to the γ -methyl group, a doublet at 1.13 p.p.m. (intensity 3.0) due to the β -methyl group, a complex quintet at 1.45 p.p.m. (intensity 2.0) due to the methylene group, and a sextet at 3.92 p.p.m. (intensity 1.0) due to the α -hydrogen atom. The infrared spectrum is an excellent diagnostic of purity. The peroxide has peaks at 3.4, 6.9, 7.4, 7.6, 7.7 (weak), 8.0 (weak), 8.9 (broad), 9.0, 9.8, 10.1, 10.2, 10.4, 11.2, 12.1, and 12.8 μ .

Preparation of Isopropyl Peroxide.—This peroxide has not been well characterized previously.⁷ Isopropyl methanesulfonate⁸ is conveniently prepared on a 3.5-mole scale in 80% yield. The peroxide is then best prepared as follows. Isopropyl methanesulfonate (139.4 g.) is placed in a 1-l. three-necked flask equipped with stirrer, reflux condenser, and dropping funnel. The flask is heated to 51–52° and held there throughout the

following preparation and distillation. A 20-ml. aliquot of a solution of 52.6 g. of KOH diluted to 120 ml. with water is combined in the dropping funnel with a 12-ml. portion of 30% hydrogen peroxide (both solutions cooled to 0°). This mixture is added to the flask over 5 min. After 5 more min., 2 ml. more of hydrogen peroxide is added. After 5 more min., the entire procedure is repeated. This addition cycle is repeated a total of six times. After the sixth cycle, the external stirrer is replaced with a magnetic stirrer, and the dropping funnel is replaced with a simple distillation head with condenser and receiving flask (both held at 0°) and a trap held at –78°. The reaction mixture is allowed to rapidly distil by reducing the pressure until 71 mm. is reached (flask still at 51°), at which point the distillation is stopped. The distillate is extracted twice with hexane, and the combined organic phases are washed with three 15-ml. portions of 5% aqueous KOH followed by three 15-ml. portions of water. The organic phase is then dried over sodium sulfate and distilled through a 4-in. column packed with Heli-Pack. The fraction boiling at 55–58° at 233 mm. is collected. In six preparations, yields varied from 16 to 26% and averaged 20%.

Purity of Isopropyl Peroxide.—Several elemental analyses gave average values of C, 60.32; H, 11.90, compared with calculated values of 60.97 and 11.94. However, *elemental analysis is hazardous and we no longer use it.* Although neither we nor McMillan⁷ have been able to purposely detonate isopropyl peroxide at room temperature by shock, we have experienced a violent explosion during an elemental analysis. The compound exploded while flowing through a quartz tube at 200° in an oxygen stream, conditions which are known to detonate peroxides.² Infrared and n.m.r. spectra are safe and entirely satisfactory diagnostics of purity. The n.m.r. shows isopropyl groups with a doublet at 1.06 and 1.13 p.p.m. and a heptet centered at 4.1 p.p.m., with an intensity ratio of 6:1. Isopropyl hydroperoxide has a peak at 8.6 p.p.m. (the peak is shifted to 8.9 p.p.m. at 0°). The infrared spectrum shows peaks at 3.4, 6.85, 7.3, 7.4, 7.6, 8.7 to 9.0 (broad), 10.85, and 12.2 μ . Acetone may be easily identified by its 5.8 μ peak and less than 0.2% is present. The sulfonate has peaks at 8.4 and 9.4 μ and less than 0.2% is present. Isopropyl ether has a spectrum almost identical with that of the peroxide, but has a strong peak at 9.9 μ which is absent in the peroxide. Isopropyl hydroperoxide has a peak at 2.9 μ . The hydroperoxide is easily removed by washing with 5% potassium hydroxide and distillation.

Data

Ethyl Peroxide.—The necessary equations are repeated below.^{9,10}

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

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

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

Table I gives the data for ethyl peroxide obtained at 60 and 80°, and the last column gives the value of the transfer constant calculated using eq. 1. Using the standard conditions^{9,10} of 50 vol. % styrene, peroxide concentrations greater than 1 M, and benzene as a solvent, the average value of the transfer constant is 6.6×10^{-4} at 60° and 24×10^{-4} at 80°.

The data at 60° suggest that the standard conditions used for measuring transfer constants give a reproducible constant which is not sensitive to minor changes in concentrations. In the studies reported here, the most concentrated peroxide solutions consist of 50 vol. % peroxide and 50 vol. % styrene. In the case of *t*-butyl peroxide, this 50% solution contains 2.7 M peroxide. However, because of the lower molecular weight of ethyl peroxide, the 50% solution is 4.4 M in peroxide. It is encouraging to note in Table I that C

(5) (a) F. Welch, H. R. Williams, and H. S. Mosher, *J. Am. Chem. Soc.*, **77**, 551 (1955); (b) W. A. Pryor and D. M. Huston, *J. Org. Chem.*, **29**, 512 (1964).

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

(7) G. R. McMillan has reported the synthesis and photolysis of isopropyl peroxide [*ibid.*, **83**, 3018 (1961), and private communications]. The only physical constant which McMillan was able to obtain is the boiling point at atmospheric pressure (ca. 94°). He has summarized the literature on this peroxide (see his note 5). Although the peroxide has been listed in secondary sources, these are either incorrect citations of the original literature or were unsupported by data. McMillan's is the first *bona fide* preparation.

(8) H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2987 (1954).

(9) W. A. Pryor, A. Lee, and C. E. Witt, *ibid.*, **86**, 4229 (1964).

(10) W. A. Pryor and G. L. Kaplan, *ibid.*, **86**, 4234 (1964).

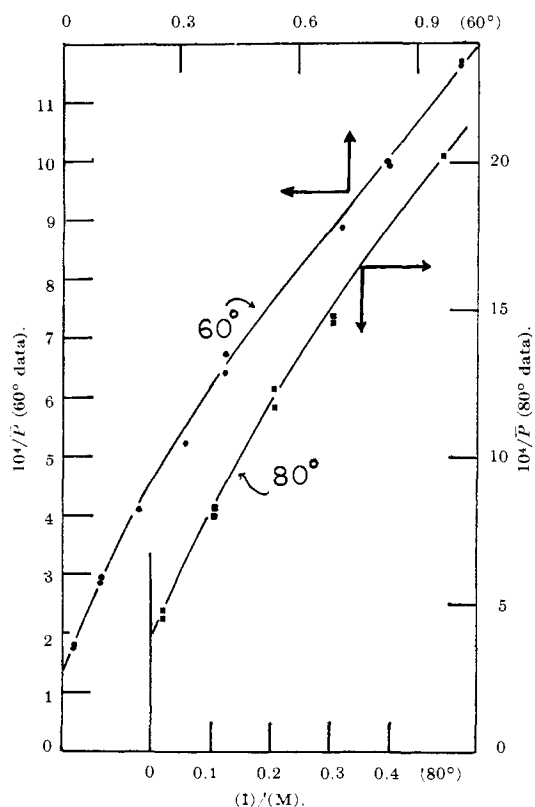


Fig. 1.—Graph of $1/\bar{P}$ vs. (ethyl peroxide)/(styrene) at 60 and at 80°. For 60° data use upper and left-hand scales; for 80° data use lower and right-hand scales.

has a constant value, within the experimental precision, for peroxide solutions from about 0.8 to 4.4 M .

Figure 1 is a graph of the degree of polymerization in the form of the Mayo equation. As was true for *t*-butyl peroxide,⁹ the slight curvature in this plot can be seen, particularly in the data at 60° where the concentration range is greater.

Figure 2 is a graph of the rate data in the form of eq. 2. As was true for *t*-butyl peroxide, the data at 60° do not lie on a straight line. Line A, which passes through the point at 2.7 M peroxide, correlates a range of concentrations similar to those used for the other peroxides in this series of papers. The slope of this line, 1.18×10^{-6} , gives a value of k_{df} of 1.2×10^{-9} if the normal value of 900 is taken for δ^2 at 60°. Line B, which passes through the point at the higher peroxide concentration, has a slope of 1.04×10^{-6} , giving a value of k_{df} of 1.0×10^{-9} sec.⁻¹.

Line C, which correlates the data obtained at 80°, has a slope of 9.4×10^{-6} and leads to a value of k_{df} equal to 2.4×10^{-8} sec.⁻¹ if 260 is taken for δ^2 at 80°.

The values of 1.2×10^{-9} and 2.4×10^{-8} sec.⁻¹ for k_{df} at 60 and 80° give an Arrhenius activation energy for the dissociation step of 35.2 kcal./mole. This is in reasonable agreement with the value of 34.1 kcal./mole which was obtained by Hanst and Calvert¹¹ from a compilation of the data from kinetic studies of ethyl peroxide in the gas phase. However, the situation is less satisfactory than this would indicate. Table II compares data from previous gas phase studies with the data obtained here. As the table shows, there is a 100-fold range in the values predicted for k_d from an extrapolation of the higher

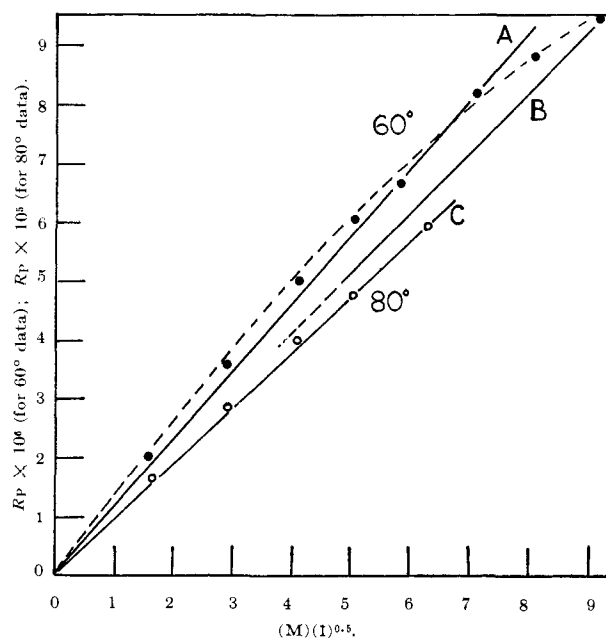


Fig. 2.—Graph of the rate of polymerization vs. (styrene)(ethyl peroxide)^{0.5}.

temperature, gas phase studies. Furthermore, the rate obtained here is some 10-fold slower than that predicted from the best values of A and E_d chosen by Hanst and Calvert. The present study measures k_{df} rather than k_d , and it is conceivable that the efficiency of

TABLE I
THE POLYMERIZATION OF STYRENE BY ETHYL PEROXIDE^a

| (I) | $R_{P, \text{obsd}} \times 10^6$ | $R_P \times 10^6$ | $[\eta]$ | $10/\bar{P}$ | $C \times 10^4$ |
|-------------|----------------------------------|-------------------|----------|--------------|-----------------|
| Runs at 60° | | | | | |
| 0.13 | 2.24 | 2.00 | 2.48 | 1.80 | 7.4 |
| 0.13 | 2.24 | 2.00 | 2.50 | 1.72 | 4.8 |
| 0.44 | 3.72 | 3.58 | 1.72 | 2.98 | 6.9 |
| 0.44 | 3.74 | 3.61 | 1.76 | 2.88 | 5.7 |
| 0.88 | 5.1 | 5.0 | 1.36 | 4.08 | 5.6 |
| 1.33 | 6.1 | 6.0 | 1.14 | 5.23 | 6.0 |
| 1.77 | 7.0 | 6.9 | 0.95 | 6.75 | 7.2 |
| 1.77 | 6.6 | 6.5 | 0.98 | 6.44 | 6.9 |
| 2.66 | 8.2 | 8.1 | 0.82 | 8.25 | 6.3 |
| 2.66 | 8.3 | 8.3 | 0.77 | 8.90 | 7.3 |
| 3.54 | 9.0 | 9.0 | 0.71 | 10.0 | 6.3 |
| 3.54 | 8.7 | 8.7 | 0.71 | 9.98 | 6.5 |
| 4.43 | 9.5 | 9.5 | 0.63 | 11.7 | 6.6 |
| 4.43 | 9.5 | 9.5 | 0.63 | 11.7 | 6.5 |
| Runs at 80° | | | | | |
| 0.13 | 16.6 | 16.6 | 1.28 | 4.44 | 51 |
| 0.13 | 16.1 | 16.1 | 1.28 | 4.45 | 49 |
| 0.44 | 29.0 | 29.0 | 0.81 | 8.29 | 35 |
| 0.44 | 28.3 | 28.3 | 0.83 | 8.00 | 33 |
| 0.88 | 40.7 | 40.7 | 0.61 | 12.2 | 29 |
| 0.88 | 38.7 | 38.7 | 0.63 | 11.6 | 28 |
| 1.33 | 47.3 | 47.3 | 0.53 | 14.8 | 24 |
| 1.33 | 47.0 | 47.0 | 0.54 | 14.6 | 24 |
| 2.11 | 59.1 | 59.1 | 0.43 | 20.1 | 23 |

^a Concentration of styrene maintained at 50% by volume by use of benzene as solvent.

initiation of polymerization by ethyl peroxide is 0.1. However, this is contrary to the behavior of *t*-butyl peroxide, where efficiencies are closer to 1.0. The pre-exponential term obtained here agrees with that preferred by Hanst and Calvert; the difference in rate is mainly due to a somewhat larger activation energy.

This difference, 1.1 kcal./mole, may not be significant in view of the experimental uncertainty in the activation energies obtained here. However, the value of 34 kcal./mole was accepted by Hanst and Calvert as anomalously low, and it is possible that 35 kcal./mole is more correct. The direct measurement of k_d for ethyl peroxide and further liquid phase measurements on this peroxide are in progress in these laboratories.

TABLE II
COMPARISON OF TEMPERATURE DEPENDENCE DATA FOR THE UNIMOLECULAR DISSOCIATION OF ETHYL PEROXIDE

| Ref. | Phase | E_d , kcal./mole | A , sec. ⁻¹ | k_d , sec. ⁻¹ , 60° ^a |
|----------------------------------|--------|-----------------------|-----------------------------|--|
| Harris ² | Gas | 31.5 | 5.1×10^{14} | (1.5×10^{-6}) |
| Rebber-Laidler ³ | Gas | 31.7 | 2.1×10^{13} | (4.6×10^{-8}) |
| Moriya ⁴ | Gas | 29.9 | 1.1×10^{12} | (2.3×10^{-8}) |
| "Best compilation" ¹¹ | Gas | 34.1 | 1.6×10^{14} | (1.0×10^{-8}) |
| This work | Liquid | 35.2 | 1.0×10^{14} | 1.2×10^{-9} |

^a The values in parentheses are extrapolated from higher temperatures.

The two values for the transfer constant, 6.6×10^{-4} and 24×10^{-4} at 60 and 80°, give an apparent activation energy for transfer of 15.1 kcal./mole. If the activation energy for the propagation step in styrene polymerization is taken as 7.3 kcal./mole, then E_{tr} for ethyl peroxide is 22 kcal./mole.

sec-Butyl Peroxide.—Table III gives data obtained at 60 and 80° for *sec*-butyl peroxide under the standard conditions of 50 vol. % styrene and benzene as a solvent. The last column gives the values of C , the transfer constant, calculated using eq. 1. If only runs containing more than 1 M peroxide are used, the average C is 4×10^{-4} at 60° and 21×10^{-4} at 80°.

TABLE III
THE POLYMERIZATION OF STYRENE BY *sec*-BUTYL PEROXIDE^a

| (I) | $R_{p,obsd}$ $\times 10^6$ | $R_p \times 10^6$ | $[\eta]$ | $10^4/\bar{P}$ | $C \times 10^4$ |
|-------------|-------------------------------|-------------------|----------|----------------|-----------------|
| Data at 60° | | | | | |
| 0.140 | 2.79 | 2.61 | 2.108 | 2.25 | 12.8 |
| 0.140 | 2.71 | 2.51 | 2.206 | 2.11 | 9.6 |
| 0.280 | 3.74 | 3.60 | 1.842 | 2.70 | 6.1 |
| 0.280 | 3.74 | 3.60 | 1.850 | 2.68 | 5.9 |
| 0.467 | 4.65 | 4.55 | 1.516 | 3.53 | 7.4 |
| 0.467 | 4.80 | 4.09 | 1.473 | 3.67 | 8.0 |
| 1.12 | 6.88 | 6.82 | 1.189 | 4.92 | 4.4 |
| 1.12 | 6.85 | 6.78 | 1.196 | 4.88 | 4.2 |
| 2.24 | 9.13 | 9.07 | 0.940 | 6.79 | 3.6 |
| 2.24 | 9.09 | 9.03 | 0.963 | 6.57 | 3.2 |
| Data at 80° | | | | | |
| 0.140 | 21.3 | 21.3 | 1.485 | 3.63 | 0 |
| 0.280 | 28.7 | 28.7 | 0.875 | 7.49 | 43 |
| 1.12 | 53.2 | 53.2 | 0.541 | 14.5 | 24.7 |
| 2.24 | 70.9 | 70.9 | 0.438 | 19.3 | 16.8 |

^a Concentration of styrene is maintained at 50 vol. % by use of benzene as solvent.

When these data are plotted in a graph analogous to Fig. 1, curvature is apparent, indicating that the peroxide is both a transfer agent and an initiator. A graph analogous to Fig. 2 is concave downward. Lines drawn to fit the points at high peroxide concentration give slopes of 1.42×10^{-6} and 1.1×10^{-5} at 60 and 80°, respectively. These slopes give k_{df} as 1.8×10^{-9} and 3.2×10^{-8} at 60 and 80°.

The values of 1.8×10^{-9} and 3.2×10^{-8} for k_{df} at 60 and 80° give an activation energy for the dissociation step of 34 kcal./mole. Since only limited amounts of *sec*-butyl peroxide were available, the precision of the data on this peroxide is somewhat lower than for the other peroxides. However, it is clear that *sec*-butyl peroxide dissociates at very similar rates with the other aliphatic peroxides studied.

The transfer constants of 4×10^{-4} and 21×10^{-4} at the two temperatures give an apparent activation energy for C of 19 kcal./mole, leading to a value of 26 kcal./mole for E_{tr} .

Isopropyl Peroxide.—Table IV gives data for isopropyl peroxide. The values of k_{df} are 0.62×10^{-9} at 60° and 14.6×10^{-9} at 80°. The average transfer

TABLE IV
THE POLYMERIZATION OF STYRENE BY ISOPROPYL PEROXIDE

| (M) | (I) | $R_p \times 10^6$ | $10^4/\bar{P}$ | $C \times 10^4$ |
|------------------|------|-------------------|----------------|-----------------|
| 60° | | | | |
| 7.1 ^a | 1.21 | 6.9 | 2.32 | 3.4 |
| 6.1 ^a | 1.99 | 6.9 | 3.37 | 3.6 |
| 5.8 ^a | 2.33 | 7.4 | 4.20 | 4.3 |
| 4.3 ^a | 1.75 | 4.6 | 4.38 | 3.9 |
| 4.3 ^a | 2.62 | 5.4 | 4.68 | 2.5 |
| 4.3 ^a | 2.62 | 6.1 | ... | .. |
| 4.3 | 3.5 | 6.9 | 6.64 | 3.5 |
| 4.3 | 3.5 | 6.0 | 5.43 | 2.5 |
| 4.3 | 3.5 | 6.1 | 5.40 | 2.5 |
| 4.3 | 3.5 | 6.8 | ... | .. |
| 80° | | | | |
| 4.3 ^a | 1.75 | 46.8 | 14.9 | 18.7 |
| 4.3 ^a | 2.62 | 54.6 | 18.0 | 15.8 |
| 4.3 | 3.5 | 58.4 | 19.7 | 13.5 |
| 4.3 | 3.5 | 53.1 | 18.0 | 12.1 |

^a Styrene concentration held at 50 vol. % by use of benzene as solvent.

constants are 3×10^{-4} at 60° and 15×10^{-4} at 80°. Activation energies are 37.3 kcal./mole for k_{df} and 18.6 kcal./mole for C , giving E_{tr} of 26 kcal./mole.

Discussion

Table V gives comparative data for the aliphatic peroxides. The most striking feature of these data is the similarity of both the dissociation constants and the transfer constants of all of the peroxides. It might seem remarkable that peroxides such as ethyl or propyl, which detonate at high temperatures, decompose at 60° at the same rate as *t*-butyl peroxide which is an unusually stable peroxide.¹² The obvious explanation is that the high temperature explosion and the moderate temperature decomposition have different mechanisms.

Mechanisms of the Homolytic Decomposition Reactions of Alkyl Peroxides.—These peroxides have not been studied in the detail necessary to outline the mechanisms of their decomposition reactions with certainty, but some reactions are known to occur.¹³ *t*-Butyl peroxide and ethyl peroxide have been studied in most detail and the reactions of these compounds can be discussed with the most confidence.

(12) See, e.g., A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 364-372.

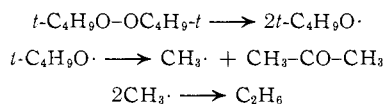
(13) References are summarized in: (a) A. G. Davies, "Organic Peroxides," Butterworth, London, 1961, pp. 165, 166; (b) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., Princeton, N. J., 1961, pp. 192-199; (c) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); (d) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (e) ref. 12.

TABLE V
COMPARISON OF DATA FOR ALIPHATIC PEROXIDES

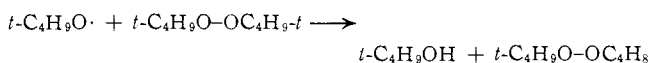
| R in R ₂ O ₂ | <i>k_d</i> ^f × 10 ⁹ present liquid phase data, sec. ⁻¹ at 60° | <i>k_d</i> × 10 ⁹ extrap- olated from gas phase, sec. ⁻¹ at 60° | <i>C</i> × 10 ⁴ 60° | — <i>E_d</i> , ^a kcal./mole— | | <i>E_{tr}</i> , ^b kcal./ mole | Ref. |
|------------------------------------|---|--|--------------------------------------|---|-------------------|--|--------------|
| | | | | This work | Lit. value | | |
| Ethyl | 1.2 | 10 ^c | 7 | 35 | 34.1 ^c | 22 | .. |
| Propyl | 2.7 | 3.0 ^d | 8 | .. | 36.5 ^d | .. | ^f |
| Isopropyl | 0.6 | .. | 3 | 37 | .. | 26 | .. |
| Butyl | 3.3 | .. | 9 | 34 | .. | 23 | ^g |
| sec-Butyl | 1.8 | .. | 4 | 34 | .. | 26 | .. |
| <i>t</i> -Butyl | 1.5 | 1.2 ^e | 6 | 35 | 37.4 ^e | 22 | ^h |

^a Arrhenius activation energy for unimolecular dissociation. When calculated from polymerization data, the assumption is made that *f* is a constant over the temperature range studied. ^b The Arrhenius activation energy for the bimolecular transfer reaction of the peroxide with the polystyryl radical. The value of *E_p* is taken as 7.3 kcal./mole. ^c Best fit of data of several workers. See ref. 11. ^d Reference 15. ^e Reference 14. ^f W. A. Pryor and E. P. Pultinas, *J. Am. Chem. Soc.*, **85**, 133 (1963). ^g Reference 10. ^h Reference 9.

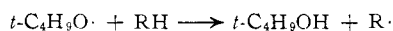
t-Butyl peroxide has been the subject of over 25 kinetic studies and its reactions are well understood. However, it is not a typical member of the series. In the gas phase, its main decomposition products are ethane and acetone.



The rate constant for its decomposition is very similar in the gas phase and solution. However, some induced decomposition does occur in both phases. In the gas phase, up to 1% yields of *t*-butyl alcohol are produced in a bimolecular reaction.¹⁴



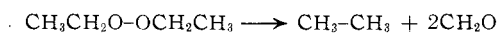
In the presence of hydrogen donors which are more active than the peroxide, more of this product is formed.



Ethyl peroxide has been found to undergo two different decompositions in the gas phase, the first being an explosion and the second a more controlled decomposition. Harris² has reported that at temperatures between 190 and 224°, and at pressures defined by the equation

$$\log P = 23,174/RT - 24.40$$

an explosion occurs, the main products of which are ethane and formaldehyde.



Apparently formaldehyde, which is the compound whose electronic transition is responsible for the blue flash sometimes observed¹⁵ in these detonations, is a key intermediate in the explosive decompositions.¹⁶

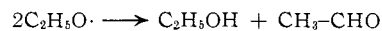
The second decomposition reaction of ethyl peroxide is nonexplosive and has been stated² to give ethanol and acetaldehyde as products. This reaction is known

(14) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).

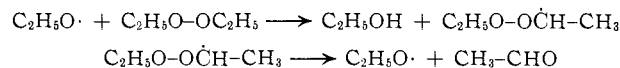
(15) E. J. Harris, *Proc. Roy. Soc. (London)*, **A173**, 126 (1939).

(16) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, pp. 479-489.

to involve alkoxy radicals since it has an activation energy equal to the dissociation energy of the O-O bond. Furthermore, its rate constant at 200° agrees with an extrapolation from the rate constant obtained in solution at 60°, where it is most probable that alkoxy radicals are involved. However, the mechanisms of product formation are not known. The alcohol and carbonyl products could arise in a disproportionation reaction of the ethoxy radicals.



However, an induced decomposition involving α -hydrogen abstraction could give the same products.



The extent to which the induced decomposition competes with the first-order path under varying conditions is not known.

Studies of the combustion of hydrocarbons can lead to information related to these problems. The reaction of hydrocarbon fuels in oxygen occurs as either a controlled reaction or as an explosion, depending on the pressure, temperature, and composition of the system, analogous with the behavior of these peroxides. Details of the chemical changes which occur in such flames are just beginning to be studied.¹⁷

The remarkable similarity and low values of both rate and transfer constants for all of these peroxides suggests that they all can be handled as liquids at 60° without danger. However, detonations of aliphatic peroxides have been reported to be initiated by shock at moderate temperatures. It is possible that these are unreproducible "hot-spot" phenomena. However, to date, neither we nor McMillan⁷ have been able to detonate the pure peroxides by shock. It also is possible that alkyl peroxides which have α -hydrogens react with atmospheric oxygen to form compounds which are shock-sensitive, and that the explosions which have been observed at room temperature are not detonated by the pure peroxide. Since ethyl and isopropyl ether peroxidize to form shock-sensitive compounds, it is not unreasonable to postulate that the analogous peroxides might also.

The insensitivity of the rate of decomposition of aliphatic peroxides to the nature of the alkyl substituent is in sharp contrast to the behavior of peresters¹⁸ or of azo compounds.¹⁹ In aliphatic peroxides, where the rate process is simple O-O bond scission and none of the odd electron density is delocalized onto the alkyl group, the nature of the substituent on the O-O bond is without effect on the rate.

The Importance of the Bimolecular Path in the Decomposition of Aliphatic Peroxides.—The transfer constants of the peroxides shown in Table V imply that

(17) A. A. Westernberg and R. M. Fristrom, *J. Phys. Chem.*, **65**, 591 (1961); "Eighth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1962, pp. 439-448; R. M. Fristrom, "Ninth Symposium (International) on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1963, pp. 560-575; J. O. Hirschfelder, *ibid.*, pp. 553-559; C. F. Cullis, A. Fish, and D. L. Trimm, *ibid.*, pp. 167-176; C. P. Fenimore and G. W. Jones, *ibid.*, pp. 597-606; G. Dixon-Lewis and A. Williams, *Quart. Rev. (London)*, **17**, 243 (1963).

(18) P. D. Bartlett has summarized this work in "Aspects of the Chemistry of Peresters," in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishing Co., New York, N. Y., 1962, pp. 1-10.

(19) C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 975 (1959); A. U. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, **84**, 2922 (1962).

an appreciable fraction of the peroxide decomposes by the second-order, induced path. For example, the data for benzoyl peroxide, which is known to undergo large amount of induced decomposition,²⁰ can be compared with data for *t*-butyl peroxide. At 60°, the value of k_{df} for *t*-butyl peroxide is some 10³ smaller, and its transfer constant is some 10² smaller than for benzoyl peroxide. The relationship between the magnitude of these constants and the fraction of an initiator which decomposes by a first- and by a second-order path can be seen from the equation^{20a, 21}

$$1/\bar{P} = C_M + C(I)/(M) + [\delta/(M)](k_{df})^{0.5}(I)^{0.5} \quad (3)$$

where the first term on the right-hand side is proportional to the number of chain ends formed by transfer to monomer, the second to those formed by transfer to the initiator, and the third to unimolecular dissociation of the initiator. Thus, at comparable concentrations of peroxide and monomer, the number of chain ends formed by transfer to *t*-butyl peroxide is 100-fold smaller than for benzoyl peroxide, and the number formed by initiation is (1000)^{0.5}, or 32-fold smaller. Therefore, the ratio of the amount of peroxide undergoing the second-order, induced decomposition relative to that undergoing unimolecular decomposition is about three times greater in the case of benzoyl peroxide than for *t*-butyl peroxide.

Since high concentrations of these peroxides are normally used, the fraction of chain ends due to transfer is a substantial part of the total. For example, using 1 *M* *t*-butyl peroxide, the values of the three terms on the right of eq. 3 are: 0.5, 1.5, and 3.0 (all times 10⁻⁴). Thus, 1.5/(3.0 + 1.5), or 33% of the peroxide, decomposes by the second-order path, and 1.5/5.0, or 30%, of the end groups in the polymer are due to transfer to the peroxide.

A Comparison of the Transfer Constants of Peroxides and Disulfides.—We have suggested that the mechanism of the transfer reaction of these peroxides is predominantly hydrogen abstraction.²² This is supported by the comparison of the transfer constants of peroxides and disulfides.

The predominant mode of transfer of disulfides is known²³ to be attack on sulfur to cleave the S-S bond, and the magnitude of the transfer constant is very sensitive to the nature of the alkyl substituent on sulfur. On the other hand, hydrogen abstraction, which also occurs in disulfides, is much less dependent on the nature of the alkyl substituent. For example, the relative rate constants for attack on sulfur or for hydrogen abstraction by phenyl radicals from a series of disulfides are shown in Table VI. The profile of transfer constants for peroxides given in Table V is relatively insensitive to the nature of the alkyl substituent, suggesting that the mechanism is hydrogen abstraction rather than attack on oxygen to cleave the O-O bond.

If peroxides undergo transfer predominantly by hydrogen transfer, then it should be possible to express the total transfer constant of a given peroxide as the sum of the reactivity of each type of hydrogen atom

TABLE VI
DATA FOR REACTION OF PHENYL RADICALS WITH
DISULFIDES^a

| R in RSSR | Relative rate for | |
|-----------------|-------------------|----------------------|
| | Attack on sulfur | Hydrogen abstraction |
| Ethyl | 76 | 5.2 |
| Propyl | 70 | 7.2 |
| Isopropyl | 14 | 7.6 |
| <i>t</i> -Butyl | 1.0 | 1.0 |

^a Reference 23b.

which is present in the compound. Such an additive relationship appeared to be valid for the hydrogen abstraction reaction of phenyl radicals with disulfides.^{23b} However, one feature of the transfer constants for peroxides reported here makes this treatment of doubtful value. The system chosen for measuring transfer constants (50 vol. % styrene, and benzene as solvent) gives a different profile of transfer constants than would have been obtained had a different solvent system been used. For example, for *t*-butyl peroxide, \bar{C} is 6 × 10⁻⁴ in benzene and 2 × 10⁻⁴ in dioxane; for butyl peroxide these values are 9.2 × 10⁻⁴ and 7.6 × 10⁻⁴. Thus, the relative order of the transfer constants of the two peroxides remains the same in both solvent systems, but the ratio changes drastically.

Transfer by *t*-Butyl Peroxide.—The α -hydrogen would be expected to be the most labile hydrogen in peroxides, and since *t*-butyl peroxide has no α -hydrogens it would be predicted to have a small transfer constant. This expectation is supported by data on aliphatic disulfides, where *t*-butyl disulfide undergoes hydrogen abstraction by either polystyryl^{23a} or phenyl^{23b} radicals at the slowest rate. In fact, it would seem reasonable to expect the transfer constants of *t*-butyl peroxide and *t*-butyl disulfide to be very similar.²⁴ They are not, and it is the peroxide transfer constant which is anomalously large.

Strain is present in *t*-butyl peroxide, and it seemed possible that its transfer constant might be enlarged because of a steric acceleration. The heat of formation of *t*-butyl peroxide is -84.6 kcal./mole, from the measured heat of combustion.²⁵ The heat of formation can be calculated to be -87.0 kcal./mole for a hypothetical strainless *t*-butyl peroxide from the heat of formation of the *t*-butoxy radical,²⁶ and the known bond energy. Therefore, *t*-butyl peroxide has some 2.4 kcal./mole of strain, and an enhanced transfer constant could arise from a steric acceleration. However, in order for this to be true, the strain in *t*-butyl peroxide must be relieved in the transfer step, and it is not clear how this could occur.

To test the possible effect of strain on transfer constants, we have measured the transfer constant of *t*-butyl ether. This compound has 7.6 kcal./mole of thermochemical strain.^{27a} The ether was synthesized

(24) Unpublished data of J. Carter in these laboratories show that the rates of hydrogen abstraction by phenyl radicals from *t*-butyl peroxide and *t*-butyl disulfide are very similar. However, the former is attacked on oxygen very slowly, if at all, whereas the latter is attacked on sulfur and hydrogen at equal rates (see ref. 23b).

(25) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948).

(26) Gray and Williams, ref. 13c. The heat of formation of the *t*-butoxy radical is based on combustion data on *t*-butyl alcohol which were obtained by the same workers (ref. 25) that measured the heat of combustion of *t*-butyl peroxide.

(27) (a) E. J. Smutny and A. Bondi, *J. Phys. Chem.*, **65**, 546 (1961); (b) J. L. E. Erickson and W. H. Ashton, *J. Am. Chem. Soc.*, **63**, 1769 (1941).

(20) (a) F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951); (b) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

(21) D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

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

(23) (a) W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962); (b) W. A. Pryor and H. Guard, *ibid.*, **86**, 1150 (1964).

TABLE VII
DATA OBTAINED FROM THE POLYMERIZATION OF STYRENE
IN THE PRESENCE OF *t*-BUTYL ETHER

| Ether (ml.) | Styrene (ml.) | <i>T</i> , °C. | (I)/(M) | $R_{p, \text{obsd}} \times 10^6$, l. mole ⁻¹ sec. ⁻¹ | $10^4 \bar{P}$ |
|----------------|------------------|----------------|---------|---|----------------|
| 3 | 3 | 60 | 0.67 | 3.3 | 3.92 |
| 2 | 4 | 60 | 0.33 | 3.8 | 3.05 |
| 4 | 2 | 60 | 1.33 | 1.7 | 5.86 |
| 2 | 2 | 60 | 0.67 | 3.3 | 3.79 |
| 1 | 2 | 80 | 0.34 | 6.7 | 1.98 |
| 1 | 3 | 80 | 0.22 | 7.1 | 1.86 |

using the method of Erickson,^{27b} and data on its transfer reactions with styrene at 60 and 80° are given in Table VII. Mayo graphs of these data give a transfer constant of 2.6×10^{-4} at 60° and about 1×10^{-4} at

80°. Rates of polymerization are slightly larger than predicted but this is not unusual in transfer systems.²⁸ Thus, *t*-butyl ether, which is considerably more strained than is *t*-butyl peroxide, has an entirely normal transfer constant. At present, therefore, the unexpectedly large transfer constant of *t*-butyl peroxide toward the polystyryl radical remains unexplained.

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(28) T. Huff and E. Perry, *J. Polymer Sci.*, **1A**, 1553 (1963).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA]

The Reactions of Sulfur Atoms. IV. Further Investigations of the Insertion Reaction¹

BY A. R. KNIGHT, O. P. STRAUZ, S. M. MALM,² AND H. E. GUNNING

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The photolysis of gaseous COS as an *in situ* source of S atoms has been re-examined using the cadmium resonance line at 2288 Å. where COS absorption is intense. In a 200-mm. path length cell, at 25°, the rate of CO formation reaches its limiting high value at $P_{(\text{COS})}$ ca. 200 mm., where $R_{(\text{CO})}$ shows no temperature dependence up to 233°. COS, at pressures of 50 and 200 mm., was photolyzed at 2288 Å. in the presence of ethane and propane; and, from the measured rates of mercaptan and CO formation, the ratios of rate constants for insertion, abstraction from COS, and deactivation to the triplet level of singlet S atoms were determined. These values were compared with those obtained previously at longer wave lengths. There is increased insertion at 2288 Å. which is ascribed to involvement of "hot" S(¹D) atoms, or sulfur atoms in the (¹S) state. From a temperature study it was concluded that $E_{\text{act}}(\text{insertion}) \approx E_{\text{act}}(\text{deactivation})$, and that this value is 1.0 ± 0.2 kcal. more than $E_{\text{act}}(\text{abstraction from COS})$ by singlet S atoms. Cyclobutane and cyclopentane were found to produce the corresponding mercaptan exclusively on reaction with S atoms, and the relative reactivities of these two substrates, and cyclopropane, toward S(¹D) atoms were found to be the same within experimental error. Rate determinations with various deuterated propanes demonstrated that the rate of attack on these substrates is the same and that there is no detectable isotope effect in either the insertion or deactivation process.

Introduction

In parts II and III of this series,³ it was demonstrated that S atoms, produced in the gas-phase photolysis of COS in the region λ 2290–2550 Å., are in the (¹D) state and interact with paraffinic C–H bonds either by insertion to yield the corresponding mercaptan, or by suffering deactivation to the (³P) ground state. In the presence of large pressures of inert gas, deactivation of the initially produced S atoms is complete and mercaptan formation is eliminated, indicating that S(³P) atoms do not react with paraffins. For all substrates examined, methane excepted, the mercaptan is the only heavy product formed. In addition, the substrates ethane, propane, isobutane, and cyclopropane were found to have very similar rates of reaction with singlet sulfur atoms. The isomeric distribution of mercaptans from propane and isobutane was the same, within experimental error, as the statistical distribution of like bonds in the molecule.

Recently, Lee, *et al.*,⁴ have demonstrated that reoiled S³⁵ atoms from the nuclear reaction $\text{Cl}^{35}(\text{n,p})\text{S}^{35}$

react with $\text{CO}-\text{C}_2\text{F}_4\text{Cl}_2$ and $\text{CO}_2-\text{C}_2\text{F}_4\text{Cl}_2$ gaseous mixtures to produce OCS^{35} presumably by an insertion reaction, although the exact nature of the inserting species has not yet been demonstrated.

Analogies which have been drawn previously between the reaction of sulfur and oxygen atoms have been further substantiated by some recent investigations on the reactions of singlet O atoms.⁵ The occurrence of singlet-triplet conversion of oxygen atoms on collision with inert gas molecules, in a manner analogous to the sulfur atom process, has been convincingly demonstrated.

The role of singlet and triplet states in the methylene reaction has also been delineated more closely in investigations⁶ wherein by addition of a scavenger, the radical component is eliminated and thus, for example, statistical product ratios attributable to exclusive insertion reactions obtain with increasing oxygen concentration for reactions with paraffins.

The purpose of the present investigation has been to carry out a more detailed examination of the photolysis of pure COS and to examine the effects of wave length, pressure, and temperature on the kinetics of the system. In addition, we have extended our previous examination of various hydrocarbon substrates

(1) Presented in part to the Western Regional Conference, Chemical Institute of Canada, Trail, B. C., Sept., 1963. This work was supported, in part, by a grant from Imperial Oil Limited, which support is gratefully acknowledged.

(2) Summer Research Assistant, 1963.

(3) A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **85**, 1207, 2349 (1963).

(4) E. K. C. Lee, Y. N. Tang, and F. S. Rowland, 146th National Meeting of American Chemical Society, Denver, Colo., Jan., 1964.

(5) H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.*, **39**, 1902 (1963); **40**, 582 (1964); O. F. Raper and W. B. DeMore, *ibid.*, **40**, 1053 (1964).

(6) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963).