

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1963, by the American Chemical Society

VOLUME 85, NUMBER 16

AUGUST 20, 1963

## PHYSICAL AND INORGANIC CHEMISTRY

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

### The Reactions of Sulfur Atoms. III. The Insertion in Carbon-Hydrogen Bonds of Paraffinic Hydrocarbons

By A. R. KNIGHT, O. P. STRAUZ AND H. E. GUNNING

RECEIVED APRIL 5, 1963

$S(^1D)$  atoms, produced in the *in situ* photolysis, at 25° in a static system, of gaseous carbonyl sulfide in the wave length region 2290–2550 Å., were found to react with paraffinic hydrocarbons. The following substrates were examined: methane, ethane, propane, cyclopropane, and isobutane, and in each case the sole primary product was the corresponding mercaptan. In the methane system, secondary decomposition of the mercaptan occurred giving rise to a number of additional products. With propane and isobutane, the isomeric distribution of mercaptans,  $n\text{-PrSH}/i\text{-PrSH} = 2.85 \pm 0.05$  and  $i\text{-BuSH}/t\text{-BuSH} = 8.8 \pm 0.1$ , demonstrates the indiscriminate nature of the attack on C-H bonds. With increasing paraffin pressures,  $K_{(\text{RSH})}$  reaches a limiting value of 55% and the attack of sulfur atoms on COS cannot be further suppressed. On the basis of the observed product distributions, energetic considerations, and the kinetic behavior of the systems, the primary interaction between  $S(^1D)$  atoms and paraffin molecules may be represented by equations 2a and 2b. The addition of high pressures of inert gas completely eliminates mercaptan formation through collisional deactivation of singlet sulfur to the ground, triplet state. Thus triplet sulfur does not react with paraffinic C-H bonds. Relative rate constant values have been obtained for some of the elementary steps.

#### Introduction

In a previous publication<sup>1</sup> from this Laboratory, it has been shown that sulfur atoms, produced in the gas phase photolysis of carbonyl sulfide at room temperature, are chemically reactive species which, in the triplet state, readily add to olefinic double bonds in a process analogous to the  $O(^3P)$ -atom reaction. In a subsequent preliminary communication,<sup>2</sup> the insertion of  $S(^1D)$  atoms into paraffinic C-H bonds was reported.

Since the possibility of the occurrence of the corresponding oxygen atom reaction has not been appreciated, and since, in general, only a few gas phase atomic insertion reactions are known at the present time, the S-atom insertion is of special interest; particularly since carbonyl sulfide is an excellent source of  $S(^1D)$  atoms and because of the absence of complicating side reactions and the general stability of the initial products formed.

The most widely studied insertion reaction is that of singlet methylene.<sup>3</sup> In the liquid phase, this species inserts into C-H bonds and the product distribution is statistical. In the gas phase, however, the reaction is not completely random in that some deviation from the theoretical distribution has been observed. The lifetime of singlet methylene is short, and at pressures as

high as 1200 mm. decay to the triplet state occurs at a rate comparable to that of the insertion reaction. Triplet methylene abstracts and, through the recombination of the resulting radicals, the products are the same as those of the insertion process. However, the abstraction reaction is selective and thus the over-all product distribution will not correspond to completely indiscriminate attack. Inert gases promote the singlet  $\rightarrow$  triplet transition and thus increase the discriminate character of the reaction. The relative rates of insertion into C-H bonds and addition to olefinic double bonds are of the same order of magnitude. A three-centered complex has been proposed as the transition state in the insertion reaction.

The insertion into C-H bonds of  $C^{11}$  atoms, in recoil from nuclear reactions,<sup>4</sup> and by the species, CCO, produced in the photolysis of carbon suboxide,<sup>5</sup> has been reported. The  $C^{11}$ -atom reaction is of interest in the present investigation in that it has been suggested<sup>4</sup> that the inserting species is in the triplet state. In the case of sulfur atoms, in the absence of low-lying triplet mercaptan states, spin is conserved on insertion only by  $S(^1D)$  atoms, whereas triplet state  $C^{11}$  gives rise to a biradical in the insertion reaction, and thus spin may be conserved.

In the case of singlet oxygen,<sup>6</sup> any insertion reaction is exothermic by well over 100 kcal./mole and thus the decomposition of primary products is extremely rapid, rendering detection of insertion processes difficult under these conditions. However, another important factor influencing the occurrence of insertion reactions may be the electronegativity of the inserting species. Thus, since sulfur and carbon have the same value, 2.5, for this

(1) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962).

(2) A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **85**, 1207 (1963).

(3) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956); H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957); H. M. Frey, *ibid.*, **80**, 5005 (1958); R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959); W. von E. Doering and H. Prinzback, *Tetrahedron*, **6**, 24 (1959); G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959); H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960); F. A. L. Anet, R. F. W. Bader, and A. Van der Auwera, *ibid.*, **82**, 3217 (1960); W. von E. Doering and L. H. Knox, *ibid.*, **83**, 1989 (1961); J. N. Butler and G. B. Kistiakowsky, *ibid.*, **82**, 759 (1960); **83**, 1324 (1961); D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **83**, 1934 (1961); H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 79 (1962); K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 1015 (1962); J. A. Bell and G. B. Kistiakowsky, *ibid.*, **84**, 3417 (1962).

(4) C. MacKay and R. Wolfgang, *ibid.*, **83**, 2399 (1961); P. Polak, H. E. Rosenberg, and R. Wolfgang, *ibid.*, **84**, 308 (1962).

(5) K. D. Bayes, *ibid.*, **83**, 3712 (1961); **84**, 4077 (1962).

(6) A recent survey of oxygen atom reactions has been made by L. Kaufman in "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, New York, N. Y., 1962.

property, the greater electronegativity of the oxygen atom, 3.5, may favor abstraction over insertion.

In this investigation the insertion of sulfur atoms into the C-H bonds of methane, ethane, propane, cyclopropane, and isobutane has been examined under a variety of conditions with the aim of gaining insight into the general nature of elementary insertion reactions.

### Experimental

Standard high vacuum techniques and apparatus were employed throughout the investigation. Grease-free mercury float and Hoke, Model TY440, valves were used throughout the reaction and analytical systems. The description of the mercury arc and reaction cell assembly has been given previously.<sup>1</sup> Most of the experiments were performed using identical light intensities, the principal exception being the main series of methane runs where the intensity was increased by a factor of approximately 6.

Carbonyl sulfide (Matheson) was purified by trap-to-trap distillation at  $-130^{\circ}$  (*n*-pentane slush), followed by thorough degassing. Although each series of experiments was begun with one run considered to be a pre-irradiation and not reported here, the results in most cases were in agreement, within experimental error, with subsequent runs. Thus the problem encountered with SO<sub>2</sub> formation, and attendant scatter in CO data, in the work with olefins as substrates<sup>1</sup> did not appear to be as serious when paraffinic hydrocarbons were examined. In the main series of methane experiments, each run was carried out using a fresh reaction mixture and it was found that reasonably good reproducibility could be achieved, providing care was taken to ensure complete degassing.

Methane, ethane, and isobutane (Phillips research grade), propane (Matheson instrument grade), perdeuteriopropane (Merck), and cyclopropane (Ohio Chemicals, U.S.P.) were used, after thorough degassing, without further purification. Krypton and carbon dioxide were Airco Assayed Reagent and were introduced into the reaction cell directly. In several runs, carbon dioxide was obtained by distillation of Dry Ice into the system, followed by thorough degassing and distillation at  $-130^{\circ}$ . Reaction mixtures were degassed prior to each experiment and distilled into the cell through a trap maintained at  $-98^{\circ}$  (methanol slush) to exclude mercury vapor.

Sulfur-containing products were analyzed by g.l.c. with hydrogen carrier using one of the following two columns: 8 ft., 20% tricresyl phosphate on Kromat (CI); or 8 ft., 15% silicone 550 (with 2% stearic acid) on Celite (CII). Where the fraction non-condensable at liquid or solid nitrogen temperatures contained products or substrate in addition to carbon monoxide, the mixture was analyzed on a third column—10 ft., 30/60 mesh molecular sieves (CIII). At the conclusion of the experiments, the following analytical procedures were carried out:

**Ethane Reaction.**—Carbon monoxide was removed at  $-196^{\circ}$  and measured in gas buret, C<sub>2</sub>H<sub>6</sub> was partially removed at  $-161^{\circ}$  (isopentane slush), and the remaining C<sub>2</sub>H<sub>6</sub>-COS mixture restored to the cell by distillation at  $-130^{\circ}$ . The retained products were analyzed on CI (flow 80 ml./min., temp. 76°).

**Propane.**—CO was analyzed as above. With added krypton present, the CO was removed at  $-210^{\circ}$ . The C<sub>3</sub>H<sub>8</sub>-COS mixture was replaced in reaction cell by distillation at  $-112^{\circ}$  (ethanol slush) and the condensables at this temperature were analyzed on CI (flow 80 ml./min., temp. 42°).

**Isobutane.**—The CO analysis was as given above. The COS and a small amount of isobutane were distilled off at  $-130^{\circ}$  and frozen out in reaction cell with the remaining substrate separated from the products at  $-98^{\circ}$ . Products condensable at  $-98^{\circ}$  were analyzed on CI (flow 80 ml./min., temp. 54°).

**Cyclopropane.**—Carbon monoxide was removed and analyzed as above. The cyclopropane and carbonyl sulfide were distilled from the products at  $-112^{\circ}$  and condensables analyzed on CII (flow 65 ml./min., temp. 27°).

**Methane.**—In the main series (Table VI) CO and CH<sub>4</sub> were pumped off at  $-196^{\circ}$ , COS at  $-130^{\circ}$ , and the remaining fraction analyzed on CI (flow 60 ml./min., temp. 76°). In the two comparison runs (Table VII), the analysis was the same except that CO was initially removed, along with a small amount of methane, at  $-210^{\circ}$  (solid N<sub>2</sub>), measured in the gas buret, and analyzed for CO on CIII (flow 80 ml./min., temp. 27°).

Identification of the reaction products was made, in preliminary experiments, by mass spectrometric analysis of the condensable fractions, and later confirmed by retention time comparisons and mass spectra of products trapped from the chromatographic effluent. Authentic samples of all reaction products were readily available except for cyclopropyl mercaptan which, previous to this investigation, had been unknown.

The characterization of the cyclopropyl mercaptan was made on the basis of mass spectrometric, infrared, and n.m.r. analysis. The mass spectrum showed a molecular weight of 74, with the most intense peak at mass 41 (cyclo-C<sub>3</sub>H<sub>5</sub>). A gas-phase, infrared spectrum displayed peaks centered at 3100, 3030 (C-H

cyclopropane), 2580 (S-H), 1530, 1290, 1030, and 890 cm.<sup>-1</sup>. The last two bands are typical of compounds containing the cyclopropyl ring. The spectrum is consistent with that expected for cyclopropyl mercaptan. The n.m.r. spectrum of the reaction product was determined in CCl<sub>4</sub> solution, using ca. 8 mg. of solute, and consisted of four complex multiplets centered on  $\tau$ -values of A, 8.05; B, 8.23; C, 9.26; D, 9.53; with the integrated areas being, respectively, in the ratio 1:1:2:2, within the limit of accuracy dictated by the very small sample size. Spin-decoupling experiments demonstrated that peaks B, C, and D are coupled to A. Simultaneous irradiation of peaks C and D collapsed peak A to a broadened doublet of spacing ca. 1.2 c.p.s. Peaks A and B may be assigned to the methylene protons on the cyclopropyl ring, the occurrence of such signals at high field having been previously observed for cyclopropylamine and methyl cyclopropanecarboxylate.<sup>7</sup> Peaks A and B are evidently ascribable to single protons, and since peak B resembles that observed for the methine proton in methyl cyclopropanecarboxylate<sup>7</sup>; a similar assignment here would leave peak A associated with the mercaptoproton. The various isomers of cyclopropyl mercaptan were also considered as possible reaction products. As far as was possible, the spectra and other properties of these compounds were determined directly or obtained from published reports and compared with those of the observed reaction product. No evidence was obtained from these comparisons to suggest that the identity of the product was other than cyclopropyl mercaptan. In view of the close similarity of the g.l.c. retention times of cyclopropyl and allyl mercaptan, it was clearly important to establish that, despite the fact that the former compound was the major reaction product, small quantities of the allyl compound were not also present. A synthetic mixture of ca. 2% allyl mercaptan in the reaction product was therefore analyzed by g.l.c. via CII. The chromatogram showed two distinct peaks, demonstrating that it would be possible to detect even small (ca. 1-2%) yields of allyl mercaptan if it were formed in the reaction.

### Results and Discussion

On addition of 50 mm. of carbonyl sulfide to 200 to 500 mm. of paraffinic hydrocarbon and irradiation of the mixture at room temperature in the wave length region 2290 to 2550 Å., the products of the reaction were found to consist of carbon monoxide and sulfur (formed as a non-volatile deposit on the walls of the reaction vessel), along with the corresponding mercaptan as the only condensable product of importance, and, in minor yields, other products as noted below. Carbon disulfide formed in many of the runs, but its yield (except from methane, *vide infra*) was invariably quite small. It is important to point out that sulfur formation could be discerned even in the pressure region where the rates of formation of CO and mercaptan were constant and independent of pressure. With ethane, propane, isobutane, and cyclopropane as substrate, there was no evidence for the presence of alkyl radicals. In addition, there was no detectable yield of hydrogen or H<sub>2</sub>S<sub>2</sub> from these substrates, nor could any alkyl radical combination or disproportionation products be found. Thus a specific search for ethylene in the ethane system, for C<sub>6</sub> compounds in propane, neooctane in isobutane, and diallyl in cyclopropane, showed that these products were not formed in the reaction.

On the basis of this evidence, an abstractive attack by the reactive species in the system must be excluded and S-atom insertion into C-H bonds, as will be substantiated by a more detailed interpretation of the results to follow, appears to be the unique mode of mercaptan formation.

With ethane as substrate, ethyl mercaptan was the only sulfur-containing product observed at exposure times of 120 min. or less. After 10 hr. of irradiation, however, the condensable products were found to contain ca. 4% diethyl disulfide. The absence of this compound at the shorter exposure times likely indicates its formation in the secondary photolysis of the mercaptan. The results of a series of experiments, for exposure times of 120 min. and carbonyl sulfide pressure of 50 mm., with ethane pressures up to 870 mm., are given in Table I. A similar series of runs was performed with

(7) Varian Associates, "N.M.R. Spectra Catalog," Palo Alto, Calif., 1962.

TABLE I

ETHANE REACTION: RATES OF CARBON MONOXIDE AND ETHYL MERCAPTAN FORMATION AS A FUNCTION OF ETHANE PRESSURE<sup>a</sup>

$P_{(C_2H_6)}$ , mm.	Rate, $\mu\text{moles}/120$ min.		$R_{(CO)} - \frac{R_{(CO)}^0}{2}$ ( $R_{(abst)}$ )	$R^0_{(CO)} - R_{(CO)}$ $\frac{R_{(EtSH)}}{R_{(comb)}}$	$\frac{R_{(comb)}}{R_{(abst)}}$	$\frac{R_{(comb)}}{(R_{(abst)})^2}$	$\frac{2R_{(EtSH)}}{R^0_{(CO)}}$
	CO	EtSH <sup>b</sup>					
0	18.6 <sup>c</sup>	..	9.3	..	..	..	..
30	12.4	1.87	3.1	4.3	1.4	0.45	0.29
70	12.2	3.10	2.9	3.3	1.1	.39	.33
139	11.7	4.11	2.4	2.8	1.2	.35	.44
234	11.2 <sup>d</sup>	4.41	2.1	2.7	1.3	.61	.47
329	11.2 <sup>d</sup>	4.78	2.1	2.4	1.1	.54	.51
372	11.7 <sup>d</sup>	4.73	2.1	2.4	1.1	.54	.51
557	11.5 <sup>d</sup>	4.96	2.1	2.2	1.0	.50	.53
870	11.6 <sup>d</sup>	5.10	2.1	2.1	1.0	.48	.55

<sup>a</sup> Carbonyl sulfide pressure, 50 mm.; exposure time, 120 min. <sup>b</sup> Corrected for secondary decomposition (*cf.* propane data). <sup>c</sup> Corrected for increased sulfur formation (*cf.* text). <sup>d</sup> In subsequent calculations for these runs, a mean value of  $R_{(CO)} = 11.4 \mu\text{moles}/120$  min. has been used.

TABLE II

ISOBUTANE REACTION: RATES OF CARBON MONOXIDE AND BUTYL MERCAPTAN FORMATION AS A FUNCTION OF ISOBUTANE PRESSURE<sup>a</sup>

$P_{(i-C_4H_{10})}$ , mm.	Rate, $\mu\text{moles}/120$ min.			$i\text{-BuSH}$ $i\text{-BuSH}$	$\frac{R_{(CO)} - R_{(CO)}^0}{2}$ ( $R_{(abst)}$ )	$\frac{R^0_{(CO)} - R_{(CO)}}{R_{(BuSH)}}$ ( $R_{(comb)}$ )	$\frac{R_{(comb)}}{R_{(abst)}}$	$\frac{R_{(comb)}}{(R_{(abst)})^2}$	$\frac{2R_{(BuSH)}}{R^0_{(CO)}}$
	CO	$i\text{-BuSH}$ <sup>b</sup>	$\Sigma\text{BuSH}$ <sup>b</sup>						
0	18.6 <sup>c</sup>	..	..	..	9.3	..	..	..	..
40	11.8	0.25	2.24	2.49	8.8	2.5	4.5	1.8	0.72
70	11.7	.30	2.66	2.96	8.9	2.4	4.2	1.8	.72
160	11.4 <sup>d</sup>	.52	4.57	5.09	8.7	2.1	2.6	1.2	.59
323	11.5 <sup>d</sup>	.49	4.25	4.74	8.7	2.1	2.5	1.2	.56
554	11.3 <sup>d</sup>	.50	4.39	4.89	8.8	2.1	2.3	1.1	.73

<sup>a, b, c, d</sup> See footnotes to Table I.

isobutane pressures in the range 40 to 554 mm. (Table II). Here, the condensable products consisted of a mixture of iso- and *tert*-butyl mercaptan.

In these tables two corrections have been applied to the observed data. Since the deposition of sulfur reduces the effective intensity of the lamp with increasing reaction duration, the observed CO yield at  $P_{(RH)} = 0$  ( $R^0_{(CO)}$ ) has been corrected, using the data in Fig. 2, to the rate observed when the sulfur deposition is at the same level as that in the experiments with added hydrocarbon. The formation of diethyl disulfide at long exposure times and the change in rate of mercaptan formation with time, observed in detail in the propane reaction (see Table III), indicates that the mercaptan formed is undergoing some secondary decomposition, and thus the values given in Tables I and II have been corrected for this loss, from the data presented for the propane reaction in Fig. 2.

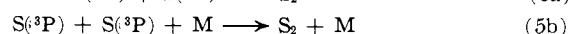
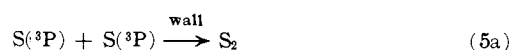
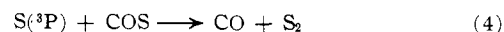
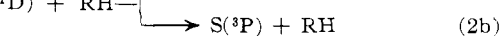
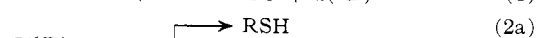
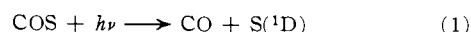
TABLE III

PROPANE REACTION: RATES OF CARBON MONOXIDE AND PROPYL MERCAPTAN FORMATION AS A FUNCTION OF REACTION TIME<sup>a</sup>

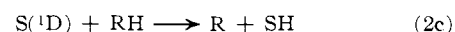
Reaction time, min.	Rate, $\mu\text{moles}/\text{min.} \times 10^2$				$\frac{n\text{-PrSH}}{i\text{-PrSH}}$	$\frac{R_{(PrSH)}}{R_{(CO)}}$
	CO	$i\text{-PrSH}$	$n\text{-PrSH}$	$\Sigma\text{PrSH}$		
40	9.62	1.05	3.07	4.12	2.9	0.43
80	9.36	1.00	2.77	3.77	2.8	.40
115	9.65	0.956	2.76	3.72	2.9	.39
183	10.3	1.00	2.89	3.89	2.9	.38

<sup>a</sup> Carbonyl sulfide pressure, 50 mm.; propane pressure, 559 mm.

On the basis of the results presented thus far, the following mechanism is proposed for the reaction of S atoms, produced in the photolysis of COS, with paraffinic hydrocarbons.



Evidence for the formation of  $\text{S}^{\text{(1D)}}$  atoms in reaction 1 has been adduced in part I of this series.<sup>1</sup> Reaction 2a is proposed as the mode of mercaptan formation, since the alternative route, through the sequence



would be accompanied by disproportionation and combination reactions of R and SH radicals, giving rise to a variety of products, none of which was, in fact, observed. In the isobutane reaction, the pressure-independent ratio  $R(i\text{-BuSH})/R(\text{tert-BuSH})$  has a value of  $8.8 \pm 0.1$ —identical, within experimental error, with the ratio of primary to tertiary bonds in the molecule. By analogy with the behavior of the methylene systems discussed previously, this indiscriminate attack on C-H bonds is further qualitative evidence for the proposed insertion reaction.

If reaction 2b were excluded from the proposed mechanism, it is apparent that with increasing hydrocarbon pressure, the rate of carbon monoxide formation,  $R_{(CO)}$ , should decrease to one-half of its initial value, ( $R^0_{(CO)}$ ), while there should be a concomitant rise in the rate of mercaptan formation,  $R_{(RSH)}$ , to the same value. However, the results demonstrate that neither of these conditions obtains in the present systems. Furthermore, sulfur formation occurs even after  $R_{(CO)}$  and  $R_{(RSH)}$  have attained constant values. Now in the reaction of sulfur atoms with olefins, recent studies in this Laboratory<sup>8</sup> on *cis*- and *trans*-butene-2 have confirmed the earlier suggestion<sup>1</sup> that, although  $\text{S}^{\text{(1D)}}$  atoms are formed in the initial photodecomposition of COS, collisional deactivation by the olefins to the triplet state

(8) J. A. Poole, E. M. Beatty, O. P. Strausz, and H. E. Gunning, to be published.

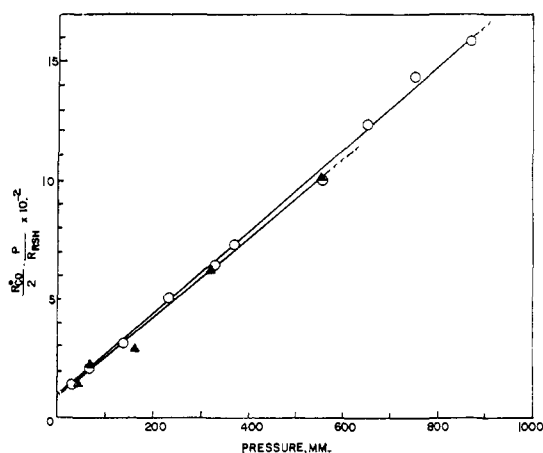
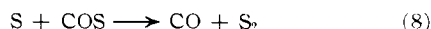


Fig. 1.—Plot of the expression  $(R^0_{(CO)}/2)(P/R_{(RSH)})$  as a function of substrate pressure, for ethane, O, and isobutane,  $\Delta$ ; for experiments with carbonyl sulfide pressure = 50 mm. and exposure time = 120 min. The data used in the calculation are given in Tables I and II.

occurs and thus the cyclic sulfide product is formed by the addition of  $S(^3P)$  atoms to the olefin *via* an intermediate biradical. In these systems, however, at sufficiently high olefin pressure it was found that  $R_{(CO)}$  was, in fact, equal to  $R_{(sulfide)}$ . Therefore, the results with paraffinic hydrocarbons demonstrate that  $S(^3P)$  atoms are present in the system, but that they are incapable of participating in the insertion reaction. Thus reaction 2b must be the alternative result of the encounter of an  $S(^1D)$  atom with an alkane molecule. Triplet sulfur formed in this reaction will then disappear *via* reactions 4 or 5. Kondratjev<sup>9</sup> reported a value of 6 kcal./mole for the over-all reaction



However, the relative contributions of singlet and triplet sulfur atoms were not determined. Thus, while the rate of reaction 4 will evidently be considerably less than that of 3, it should make a significant contribution since the only alternative fate for  $S(^3P)$  atoms are the third body-restricted recombination processes, 5a and 5b. Abstraction from the hydrocarbon, which was not, in fact, observed, is furthermore energetically unfavorable. Thus, for example, the abstraction of an H atom from even the tertiary position in isobutane is endothermic to the extent of 14.5 kcal./mole, taking 89.5 kcal./mole for  $D(C-H)^{10}$  and assuming a value of about 75 kcal./mole for  $D(S-H)^{10,11}$

A steady-state treatment of the reaction mechanism yields the following expression for the rate of mercaptan formation

$$\frac{R^0_{(CO)}}{2} \frac{P}{R_{(RSH)}} = \frac{k_{(2)}}{k_{(2a)}} [COS] + \frac{k_{(2)}}{k_{(2a)}} P \quad (1)$$

where  $P$  is the paraffin pressure in mm. and  $k_{(2)} = k_{(2a)} + k_{(2b)}$ . If the proposed sequence of reactions adequately describes the system, this expression should be a linear function. Equation 1 has been plotted for the ethane and isobutane reactions in Fig. 1, and both sets of data yield a straight line. The intercepts are identical and give a value of 2.04 for the ratio  $k_{(3)}/k_{(2a)}$ —the ratio of rate constants for abstraction and insertion by  $S(^1D)$  atoms. From the slopes, the ratio  $k_{(2b)}/k_{(2a)}$ , the ratio of rate constants for deactivation to triplet and insertion of  $S(^1D)$  atoms, has calculated values of 0.71 (ethane) and 0.64 (isobutane).

(9) V. Kondratjev, *Acta Physicochim. U.R.S.S.*, **16**, 272 (1942).

(10) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962.

(11) T. F. Palmer and F. P. Lossing, 45th Conference, Chemical Institute of Canada, Edmonton, May, 1962.

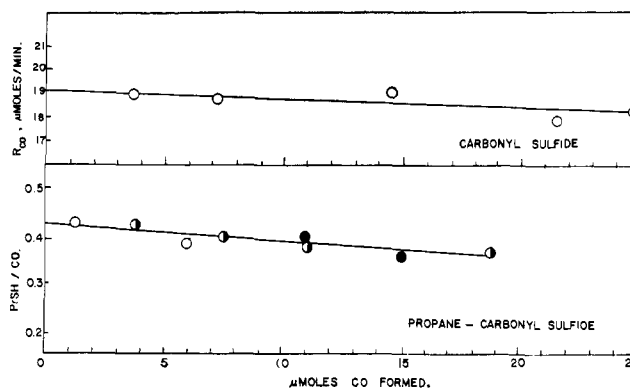


Fig. 2.—The rate of carbon monoxide formation as a function of  $\mu$ moles of CO formed for the photolysis of 50 mm. of pure COS. The ratio of rates of formation of propyl mercaptan to carbon monoxide as a function of  $\mu$ moles of CO formed for COS pressure of 50 mm. and propane pressures of 559 mm.,  $\bullet$  (data from Table III); 299 mm.,  $\circ$ ; and 332 mm.,  $\bullet$  (runs carried out in preliminary experiments at higher light intensity).

Returning now to the data presented in Tables I and II, it follows from the mechanism that the over-all rate of S atom abstraction is given by

$$R_{(abst)} = R_3 + R_4 = R_{(CO)} - R^0_{(CO)}/2 \quad (II)$$

The data show that  $R_{(abst)}$  decreases to a constant value of 2.1  $\mu$ moles/120 min., which is evidently the extent of abstraction by  $S(^3P)$  atoms in reaction 4. Similarly, the combination rate may be obtained from

$$R_{(comb)} = R_{3a} + R_{3b} = R^0_{(CO)} - R_{(CO)} - R_{(RSH)} \quad (III)$$

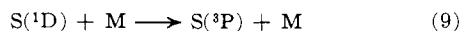
The value of this expression, however, shows a continuing decline with increasing alkane pressure. To determine the relative importance of reactions 5a and 5b, the two ratios,  $R_{(comb)}/R_{(abst)}$  and  $R_{(comb)}/(R_{(abst)})^2$ , have been calculated. The gas phase reaction 5b requires that the latter ratio increase linearly with increasing pressure, whereas the observed values are constant within experimental error. On the other hand, combination on the wall may result in  $R_{(comb)}/R_{(abst)}$  being inversely proportional to the pressure. Thus the results indicate that the dominant reaction is on the wall, but the gas phase combination step is likely occurring as well. It should be pointed out that the experimental error in the measured yields have been considerably magnified in these ratios and the suggested relative importance of reactions 5a and 5b must remain tentative.

The ratio  $2R_{(RSH)}/R^0_{(CO)}$  represents the fraction of initially produced  $S(^1D)$  atoms which result in mercaptan formation and, as indicated in the discussion of the mechanism above, its value is less than unity due to the formation of triplet sulfur in reaction 2b.

With propane as substrate, sulfur-containing reaction products consisted of *n*- and isopropyl mercaptan and the ratio  $R_{(n-PrSH)}/R_{(i-PrSH)}$  was independent of pressure and exposure time at the value of  $2.84 \pm 0.05$ —again demonstrating the lack of any preference for the weaker C-H bond. The propane reaction was examined as a function of exposure time and the results are summarized in Table III. With increasing exposure time, there is a slight but definite decrease, to the extent of ca. 10% in the ratio  $R_{(PrSH)}/R_{(CO)}$ . This decrease is most likely due to the secondary photolysis of the mercaptans which absorb in the wave length region used. Since neither diiso- nor di-*n*-propyl disulfide were detected in analysis, secondary destruction of the mercaptan by some additional or alternative process, accompanied perhaps by a small increase in CO formation, cannot be excluded. The detailed interpretation of the alteration of the  $R_{(RSH)}/R_{(CO)}$  ratio with in-

creasing exposure time must therefore await a specific examination of these systems at greater extents of decomposition. The propane results are also plotted in Fig. 2 as a function of  $\mu$ moles of CO formed, along with several other experiments wherein only the total yield of mercaptan was determined. This figure also gives the results of a series of runs with pure carbonyl sulfide in which the rate of CO formation was determined as a function of  $\mu$ moles formed. In this case,  $R_{(\text{CO})}$  decreases with increasing exposure time owing to the deposition of increasing amounts of sulfur on the incident window of the cell and consequent attenuation of the effective intensity. The two curves in Fig. 2 have been used, as pointed out above, to correct the amount of CO formed in the absence of hydrocarbon since in the alkane-free system more sulfur is deposited than when the reaction is carried out with added alkane and also to correct the measured mercaptan yield for the observed decline in rate of formation with time. The latter correction was applied on the assumption that this decline will be the same, within experimental error, for all the mercaptans involved in the present investigation.

The propane reaction was also used as a model to study the effect of added inert gas. The results are summarized in Table IV. With inert gas present, the additional reaction



must be included in the mechanism. In the first two runs, with a carbonyl sulfide pressure of 50 mm., the addition of 420 mm. of krypton had no detectable effect. When, however, the COS pressure was reduced to 10 mm. and  $\text{CO}_2$  added at a pressure of 1892 mm. there was a marked change in the observed yields. In the absence of propane, the added  $\text{CO}_2$  has the effect of increasing the triplet sulfur population, and thus the rate of abstraction from COS is diminished and there is an increased contribution from reaction 5. While the rate of mercaptan formation from a mixture of 10 mm. each of propane and carbonyl sulfide is  $0.568 \times 10^{-2}$   $\mu$ mole/min., the addition of 1892 mm. of  $\text{CO}_2$  completely eliminates mercaptan formation. Thus reactions 9 and 3 are the only fates of singlet sulfur atoms under these conditions. This behavior again demonstrates both the unique participation of singlet sulfur in the insertion reaction 2a and the conversion of sulfur from the singlet to triplet state *via* reaction 2b.

TABLE IV

PROPANE REACTION: EFFECT OF INERT GAS ON THE RATES OF CARBON MONOXIDE AND PROPYL MERCAPTAN FORMATION

$P_{(\text{C}_3\text{H}_8)}$ , mm.	$P_{(\text{COS})}$ , mm.	Inert gas		Reac- tion time, min.	Rate, $\mu$ moles./min. $\times 10^2$	
		Added gas	Press., mm.		CO	$\Sigma$ PrSH
70	49	..	..	120	1.02	2.27
71	50	Kr	420	120	0.992	2.26 <sup>a</sup>
0	50	..	..	120	1.53	...
0	10	..	..	502	3.56	...
0	10	$\text{CO}_2$	1892	600	3.01	...
10	10	..	..	600	2.91	0.568 <sup>a</sup>
10	10	$\text{CO}_2$	1892	600	2.88	0.000

<sup>a</sup>  $(n\text{-PrSH})/(i\text{-PrSH}) = 2.88$ ; no other products observed.

The data given previously in Tables I and II show that with increasing pressure in the system, the ratio  $R_{(\text{comb})}/R_{(\text{abst})}$  decreases, having values of 1.1 and 1.0 for 554 mm. isobutane and 870 mm. ethane, respectively. The data given in Table IV for pure COS at a pressure of 10 mm. with 1892 mm. added  $\text{CO}_2$  yields a value of 0.44 for the combination-abstraction ratio, again demonstrating the fact that the gas phase combination of sulfur atoms is very inefficient, and thus at high pressures abstraction is favored over wall recombination.

In an attempt to gather further evidence for the absence of abstraction reactions, equimolar mixtures of  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{D}_8$  were examined and the isotopic distribution in the mercaptans produced determined in the mass spectrometer. The results are summarized in Table V, along with a comparison run with pure  $\text{C}_3\text{H}_8$  under the same conditions. The data are valuable in demonstrating that the over-all rate of attack on C-H and C-D bonds is essentially the same, but the validity of the  $\text{C}_3\text{D}_7^-/\text{C}_3\text{H}_7^-$  ratios is uncertain owing to adsorption of the mercaptans in the mass spectrometer. The principal aim of these experiments, to demonstrate the insertion reaction by illustrating the absence of isotopic mixing with  $\text{C}_3\text{H}_8$  and  $\text{C}_3\text{D}_8$  as co-substrates, could not be achieved, however, owing to the occurrence of the exchange reaction



A blank run with pure  $\text{C}_3\text{D}_8$  showed that reaction 10 is indeed important in the mass spectrometer, since the mercaptan formed in this run was found to be entirely  $\text{C}_3\text{D}_7\text{SH}$ .

TABLE V

PROPANE REACTION: RATES OF CARBON MONOXIDE AND PROPYL MERCAPTAN FORMATION AND ISOTOPIC DISTRIBUTION OF MERCAPTAN FORMED FROM A MIXTURE OF  $\text{C}_3\text{H}_8$  AND  $\text{C}_3\text{D}_8$

Run <sup>a</sup>	Pressure, mm.			Reac- tion time, min.	$\mu$ moles formed CO	$\Sigma$ PrSH	Parent mass ratio 83/76	$R_{(\text{PrSH})}/R_{(\text{CO})}$
	$\text{C}_3\text{H}_8$	$\text{C}_3\text{D}_8$	COS					
A	322	0	50.0	313	10.9	4.42	..	4.1
B	200.3	199.4	50.7	332	11.0	4.59	0.36	4.2
C	200.3	199.4	50.7	425	12.5	5.37	.52	4.3
D	200.3	199.4	50.7	506	13.4	5.71	.90	4.3

<sup>a</sup> Run designations indicate the sequence in which experiments and attendant analyses were carried out.

Cyclopropane, on reaction with S atoms, yields cyclopropyl mercaptan as the sole sulfur-containing product. The absence of allyl mercaptan as a product is surprising since the energetics of reaction 2a would suggest that some isomerization of cyclo- $\text{C}_3\text{H}_5\text{SH}$  should occur. Assuming that the heat of reaction for the insertion process is about the same as for methane (see Table VIII) the excess energy of the mercaptan formed should be sufficient to bring about isomerization if the activation energy for this step is the same as that for the cyclopropane-propylene isomerization, 65 kcal./mole.<sup>12</sup>

The reaction appears to follow quite closely the behavior of the propane system. The data from quantitative comparison runs will be given in a summary, to be presented later, of relative rates for all substrates studied in this investigation.

Preliminary experiments demonstrated that the methane reaction is considerably more complex than that of the other substrates examined. The reaction products, in addition to sulfur and carbon monoxide (with percentage of the total products in a typical run given in parentheses for each), were: methyl mercaptan (63%), dimethyl disulfide (12%), dimethyl sulfide (6%), ethane (6%), hydrogen (7%), and carbon disulfide (6%)—considerably larger than the yield generally found; *cf.* above). A further minor product could be detected, but its yield varied erratically and insufficient material could be accumulated to allow a definite identification to be made. In any event, it accounted for a maximum of *ca.* 2% of the products. In view of the possibility of  $\text{H}_2\text{S}$  formation in this system, it should be pointed out that this product would not have been detected here since its separation from excess carbonyl sulfide is virtually impossible. Since dimethyl di-

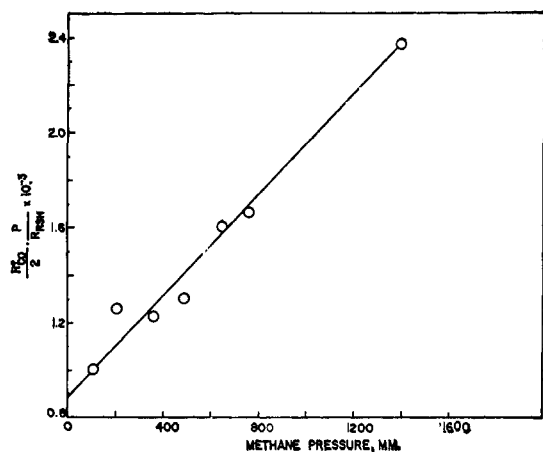


Fig. 3.—Plot of the expression  $(R^0_{(CO)}/2)(P/R_{(RSH)})$  as a function of methane pressure for experiments with carbonyl sulfide pressure = 50 mm. and exposure time = 120 min. at a light intensity *ca.*  $6\times$  that used for other substrates. The data used in the calculations are given in Table VI.

sulfide would be expected to arise from the combination of  $\text{CH}_3\text{S}$  radicals, some contribution from the disproportionation of this species is likely and thus  $\text{CH}_2\text{S}$  may also be formed in the reaction. Such a product would lead, however, to the thioformaldehyde trimer which would not have been detected by the analytical technique employed here.

Using a light intensity approximately 6 times greater than that employed in runs previously reported, a series of runs was performed with methane pressures in the range 102 to 1400 mm. at constant  $\text{COS}$  pressure of 50 mm. and exposure time of 120 min. The results, for the four products analyzed throughout the series, are given in Table VI. It was not possible to separate the carbon disulfide and dimethyl sulfide on the g.c. column used, but mass spectrometric analysis of this peak showed it represented an approximate 50–50 mixture of the two components. The total yield of  $\text{CH}_3\text{S}$  radicals has been calculated and the last two columns give the fraction of thioalkoxy radicals which result in mercaptan formation,  $(\text{CH}_3\text{SH})/\Sigma\text{CH}_3\text{S}$ , and in disulfide formation,  $(\text{CH}_3\text{S}_2\text{CH}_3)/(\Sigma\text{CH}_3\text{S})$ . These ratios are invariant with substrate pressure increasing, and the mean values are  $0.67 \pm 0.03$  for  $(\text{CH}_3\text{SH})/(\Sigma\text{CH}_3\text{S})$  and  $0.26 \pm 0.03$  for  $(\text{CH}_3\text{S}_2\text{CH}_3)/(\Sigma\text{CH}_3\text{S})$ .

TABLE VI

METHANE REACTION: RATES OF FORMATION OF SULFUR CONTAINING PRODUCTS AS A FUNCTION OF METHANE PRESSURE<sup>a</sup>

$P_{\text{CH}_4}$ , mm.	Rate, $\mu\text{moles}/120 \text{ min.}$					$\text{CH}_3\text{-SH}$	
	$\text{CH}_3\text{SH}$	$(\text{CH}_3\text{S})_2$	$\text{CS}_2^b$	$\Sigma\text{Sulfur products}^b$	$\Sigma\text{CH}_3\text{S}$	$\Sigma\text{CH}_3\text{S}$	$\Sigma\text{CH}_3\text{S}_2$
102	3.62	0.643	1.00	5.26	5.41	0.67	0.24
201	5.59	1.21	1.58	8.38	8.80	.64	.28
355	10.4	1.85	2.01	14.3	16.1	.65	.23
494	14.8	2.66	2.12	19.6	21.2	.70	.25
654	15.2	3.16	2.29	20.7	22.7	.67	.28
766	18.1	3.19	2.48	23.8	25.7	.70	.25
1400	24.6	5.56	2.75	32.9	37.1	.66	.30

<sup>a</sup> Carbonyl sulfide pressure, 50 mm.; exposure time, 120 min.; light intensity *ca.* 5.5 times that used in other runs. <sup>b</sup> The total yield of sulfur products was measured in the gas buret and the yield of  $(\text{CH}_3\text{SCH}_3 + \text{CS}_2)$  calculated from the difference between this value and the g.c. determined yield of  $\text{CH}_3\text{SH}$  and  $(\text{CH}_3\text{S})_2$ .

If the secondary decomposition of the mercaptan is momentarily neglected, the mechanism proposed above, and expression I derived therefrom, should apply with the modification that the total  $\text{CH}_3\text{S}$  yield  $\Sigma\text{CH}_3\text{S}$  is equivalent to the previously measured mercaptan yield

$R_{(RSH)}$ . Thus in Fig. 3,  $P_{(\text{CH}_4)}/(\Sigma\text{CH}_3\text{S})$  has been plotted as a function of  $P_{(\text{CH}_4)}$  and the resulting straight line indicates the applicability of eq. I. From the slope and intercept values rate constant ratios of  $k_{(2b)}/k_{(2a)} = 0.05$  and  $k_{(3)}/k_{(2a)} = 17.8$  were obtained, and from these values,  $k_{(3)}/k_{(2b)} = 357$  may be calculated. The large value of  $k_{(3)}/k_{(2b)}$  indicates that methane is very much less efficient in the deactivation of singlet sulfur than ethane where this ratio has a value of 2.87. Even at  $P_{(\text{CH}_4)} = 1400$  mm. the  $\Sigma\text{CH}_3\text{S}$  yield has not reached a constant value, whereas in the propane reaction, 1900 mm. of  $\text{CO}_2$  is sufficient to eliminate completely mercaptan formation (see Table IV); thus methane would appear to be even less efficient than carbon dioxide.

In view of the remarkable similarity of rate constants and their ratios for ethane, propane, and isobutane and the indiscriminate nature of the attack on primary, secondary, and tertiary C–H bonds, the reason for the large value of  $k_{(3)}/k_{(2a)}$ , 17.8, as compared with the value of 2.04 for the same ratio in the ethane system, from which ratios a value of 0.115 for  $k_{(2a)}$  (methane)/ $k_{(2a)}$  (ethane) may be calculated, is not immediately apparent. However, the formation of a transient complex may be required for the conversion of the electronic energy, released by the  $\text{S}(^1\text{D}) \rightarrow \text{S}(^3\text{P})$  deactivation, to vibrational excitation of the acceptor molecule. Methane may be less efficient than ethane or propane because of its small size (relative to the sulfur atom), while  $\text{CO}_2$  may be more efficient than methane because of its electronic configuration.

Returning now to the discussion of the observed product distribution, it is clear that on the basis of the methane results alone, the occurrence of abstraction and/or insertion reactions are consistent with the experimental results. However, in view of the observed insertion in the other substrates examined, the methane results can be logically interpreted in terms of the formation of a  $\text{CH}_3\text{SH}$  species, in reaction 2a, which subsequently suffers secondary decomposition.

The exothermicities of reaction 2a have been calculated and the data are given in Table VII. These data show that the reaction is strongly exothermic in all cases, but the observed lack of decomposition, even at low substrate pressures, in the case of ethane or isobutane indicates that the mercaptan has a sufficient number of internal degrees of freedom to permit stabilization of the product. Methyl mercaptan, on the other hand, evidently lacks the ability of self-stabilization, and thus the excited  $\text{CH}_3\text{SH}$  formed in reaction 2b suffers unimolecular decomposition.

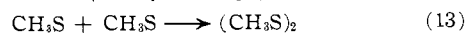
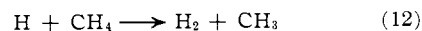
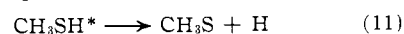
TABLE VII

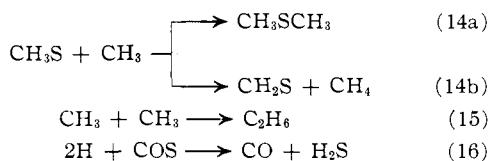
CALCULATION OF THE EXOTHERMICITY OF REACTION 2a<sup>a</sup>

Substrate	$\Delta H_f$ (substr.) <sup>b</sup>	$\Delta H_f$ (mercap.) <sup>c</sup>	$\Delta H$ (2a)
Methane	-17.9	-20.9	-82.7
Ethane	-20.2	-26.4	-85.8
Propane	-24.8	-31.6 <sup>d</sup>	-86.4

<sup>a</sup> All values in the table are in kcal./mole;  $\Delta H_f(\text{S})$  taken as 53.3 kcal./mole (National Bureau of Standards, Circular 500, 1952);  $E[\text{S}(^1\text{D})] - E[\text{S}(^3\text{P})] = 26.4$  kcal./mole. <sup>b</sup> American Petroleum Institute, Research Project 44. <sup>c</sup> United States Bureau of Mines, Bulletin 595, 1961. <sup>d</sup> Value given for *n*-propyl mercaptan.

The following mechanism is proposed to account for the product distribution from the secondary decomposition of methyl mercaptan.





Reaction 11 is suggested as the mode of  $\text{CH}_3\text{SH}^*$  decomposition in preference to the alternative C-S bond cleavage since the latter would result in the formation of SH radicals and thus  $\text{H}_2\text{S}_2$  as a reaction product, whereas this compound was not observed. The S-H bond split is also favored by the observed yield of molecular hydrogen. A small contribution from the reaction producing  $\text{CH}_3$  and SH radicals cannot be excluded, but the evidence points to reaction 11 as the predominant route of the unimolecular decomposition. If this is so, the calculated  $\Delta H$  for reaction 2a sets an upper limit of *ca.* 83 kcal./mole for  $D(\text{CH}_3\text{S}-\text{H})$ . Since the ratios  $\text{CH}_3\text{SH}/\Sigma\text{CH}_3\text{S}$  and  $(\text{CH}_3\text{S})_2/\Sigma\text{CH}_3\text{S}$  are independent of total pressure, even up to 1450 mm. total pressure, collisional deactivation evidently does not occur within the investigated range. Since the removal of one or two vibrational quanta would be sufficient to lower the excess energy of  $\text{CH}_3\text{SH}^*$  below that required for S-H bond rupture, it would appear that the lifetime of this species is extremely short and it may, in fact, decompose within the time required for one vibration.

Comparing this behavior to that of the ethane system, where reaction 2a is 3 kcal./mole more exothermic than in methane, the observed lack of decomposition of ethyl mercaptan demonstrates the marked effect on lifetime of the availability of additional normal modes of vibration in the molecule and the capacity of the mercaptan for stabilization by equipartition of its excess energy.

To allow an over-all comparison of the relative rates for each of the five substrates examined, Table VIII gives a summary of these data, along with product

TABLE VIII

RELATIVE RATES OF CARBON MONOXIDE AND MERCAPTAN FORMATION FOR MIXTURES OF CARBONYL SULFIDE AND METHANE, ETHANE, PROPANE, ISOBUTANE, AND CYCLOPROPANE<sup>a</sup>

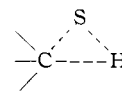
Substrate	— $P_{(\text{RH})} = 70$ mm.—			— $P_{(\text{RH})} = 560$ mm.—		
	Rate, $\mu\text{moles}/120$ min.		$R_{(\text{RSH})}/R_{(\text{CO})}$	Rate, $\mu\text{moles}/120$ min.		$R_{(\text{RSH})}/R_{(\text{CO})}$
Methane	12.7	0.84 <sup>b</sup>	0.066	(8.4) <sup>c</sup>	3.95 <sup>b</sup>	(0.470)
Ethane	12.2	3.10	.254	11.5	4.96	.431
Propane	12.3	3.02 <sup>d</sup>	.246	11.6	4.94 <sup>d</sup>	.426
Isobutane	11.7	2.96 <sup>e</sup>	.395	11.3	4.89 <sup>e</sup>	.433
Cyclopropane	12.5	2.95	.236	11.5	5.13	.446

<sup>a</sup> Carbonyl sulfide pressure, 50 mm.; exposure time, 120 min. All mercaptan yields have been corrected for secondary decomposition. <sup>b</sup> Calculated yield of  $\text{CH}_3\text{S}$ . <sup>c</sup> CO recovery from excess methane likely incomplete. <sup>d</sup>  $n\text{-PrSH}/i\text{-PrSH} = 2.85 \pm 0.05$ . <sup>e</sup>  $i\text{-BuSH}/t\text{-BuSH} = 8.8 \pm 0.1$ .

ratios where applicable. The results for ethane and isobutane are taken from Tables I and II, and the propane data, from Table III. All other results are from comparison runs, not previously reported, carried out with each substrate under identical experimental conditions. Except for methane, where the yields are markedly lower due to the unusually low values of the rate constants for this substrate mentioned previously, the over-all mercaptan yields and the  $R_{(\text{CO})}/R_{(\text{RSH})}$  ratios are very nearly the same for all substrates examined.

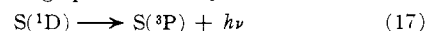
To determine the validity of the small differences in rates observed, an examination of the mercaptan and CO yields from a reaction mixture, comprised of equimolar quantities of all five substrates over a wide pressure range, would be extremely valuable. Current further investigations in this Laboratory on the S-atom insertion reaction will include an examination of relative rates using this competitive technique.

The transition complex for the insertion reaction of  $\text{S}(^1\text{D})$  atoms is likely similar to that proposed<sup>3</sup> for the methylene reaction and may be represented as



Despite the fact that the insertive attack is completely indiscriminate, the rate of the reaction is comparatively slow since  $k_{(3)}/k_{(2a)}$ , the ratio of abstraction from COS to insertion in C-H bonds, has a value of about 2 for ethane, and isobutane (*cf.* Table VIII), and the abstraction reaction 3 has an activation energy of about 6 kcal./mole.<sup>9</sup> The activation energy for the insertion process is currently under investigation in this Laboratory.

Several interesting differences between the sulfur and methylene systems may be noted. Whereas singlet methylene has a very short lifetime, the transition to the triplet level occurring spontaneously, the transition



is strongly forbidden, and thus triplet sulfur arises only by collisional deactivation of singlet atoms. The sulfur system is distinctive also in that deactivation can be effected by the substrate itself, in reaction 2b. The third difference is that sulfur, unlike  $\text{CH}_2$ , does not insert into C-H bonds of olefins. This arises undoubtedly from the slow rate of the insertion reaction and the high efficiency of olefins in singlet  $\rightarrow$  triplet deactivation.<sup>1,8</sup>

Although it is probable that  $\text{S}(^1\text{D})$  atoms formed in reaction 1 have translational energies in a wide spectrum corresponding to the wave length range employed, it is apparent from the results that "hot" sulfur atoms do not detectably influence the course of the reaction. Thus, in the COS-propane system, for example, values of the ratio  $n\text{-PrSH}/i\text{-PrSH}$ , obtained at:  $P_{(\text{COS})} = 50$  mm. and  $P_{(\text{C}_3\text{H}_8)} = 70$  and 560 mm. (Table VIII);  $P_{(\text{COS})} = P_{(\text{C}_3\text{H}_8)} = 10$  mm. (Table IV); and  $P_{(\text{COS})} = 50$  mm.,  $P_{(\text{C}_3\text{H}_8)} = 71$  mm., and  $P_{(\text{Kr})} = 420$  mm. (Table IV); are all  $2.85 \pm 0.05$ ; whereas deactivation of translationally-hot sulfur atoms would presumably manifest itself in alterations in the isomeric distribution of the mercaptan product with change in the total pressure. It is thus apparent that if  $\text{S}(^1\text{D})$  atoms initially possess excess translational energy, they are thermalized before any reaction occurs.

The results obtained for the isomeric distribution of mercaptans from propane and isobutane enable singlet sulfur atoms to challenge the present position of methylene as the most indiscriminate reagent in organic chemistry.

**Acknowledgments.**—The authors take pleasure in expressing their thanks to Mr. Gene Fried for valuable assistance in the experimental work and to Drs. R. J. Crawford and W. G. Paterson for assistance in the infrared and n.m.r. analyses of cyclopropyl mercaptan. This work was supported, in part, by a grant from Imperial Oil Limited which support is gratefully acknowledged.