TABLE VII

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

Ether (ml.)	Styrene (ml.)	T, °C.	(I)/(M)	$R_{P,obsd} \times 10^6$, 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).

The Reactions of Sulfur Atoms. IV. Further Investigations of the Insertion Reaction[1]

BY A. R. KNIGHT, O. P. STRAUSZ, 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 $P_{(COS)}$ *ca.* 200 mm., where $R_{(CO)}$ 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(^{1}D) atoms, or sulfur atoms in the (^{1}S) state. From a temperature study it was concluded that E_{act}(insertion) $\approx E_{act}$(deactivation), and that this value is 1.0 ± 0.2 kcal. more than E_{act}(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(^{1}D) 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 (^{1}D) state and interact with paraffinic C–H bonds either by insertion to yield the corresponding mercaptan, or by suffering deactivation to the (^{3}P) 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(^{3}P) 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 recoil S^{35} atoms from the nuclear reaction Cl^{35}(n,p)S^{35}

react with CO–C$_2$F$_4$Cl$_2$ and CO$_2$–C$_2$F$_4$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 investigations[6] 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).

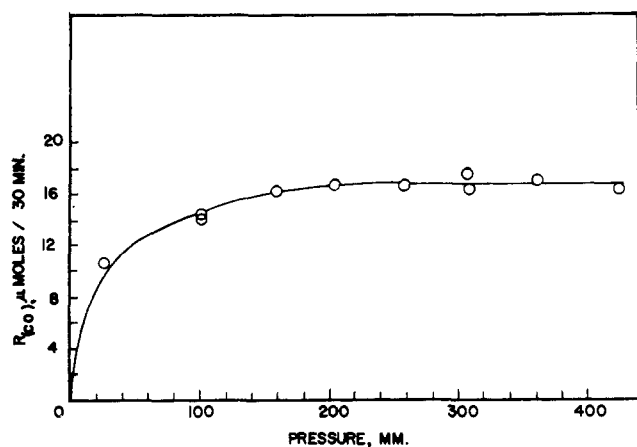(6) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963).

Fig. 1.—The rate of carbon monoxide formation as a function of pressure for the photolysis of carbonyl sulfide at 2288 Å.

to include two additional cyclic hydrocarbons and several deuterated propanes. The details of the investigation follow.

Experimental

The grease-free high vacuum apparatus used throughout the experiments has been described previously,[3] as well as the mercury-arc reaction cell assembly.[7] In experiments with the cadmium lamp, the cylindrical quartz cell, 200-mm. length, 50-mm. o.d., was independently mounted in a quartz-windowed aluminum block furnace with temperature controlled to ±0.5°. The light source was an Osram spectral Cd/1 cadmium resonance lamp. Both the furnace and lamp were mounted on an optical bench, to assure realignment following removal and flaming of the reaction cell after each experiment. The lamp intensity at 2288 Å. was monitored by a Photovolt Model 501M photometer, with the phototube positioned behind suitable interference filters at the rear of the reaction cell.

Carbonyl sulfide (Matheson) was purified by repeated trap-to-trap distillation at −130°, and by gas chromatography (g.c.), followed by thorough degassing. The principal impurities were CS_2, removed without difficulty by low temperature distillation, and CO_2, which could be effectively separated off only by preparative g.c. purification of the substrate.

Ethane (Phillips research grade), propane (Matheson instrument grade), deuterated propanes (Merck of Canada), cyclobutane, cyclopentane (A.P.I.), and cyclopropane (Ohio Chemicals U.S.P.) were further purified by low-temperature distillation and thoroughly degassed. The cyclopropane contained small amounts of propylene which were removed by pre-irradiation in the presence of COS.

The techniques used in preparation and introduction of reaction mixtures, as well as the analytical details, have been given previously.[3]

The only change in the present investigation was that, except for cyclobutane and cyclopentane, a 16-ft., 18% silicone 550 (with 2% stearic acid) column was used for all g.c. analyses. These data for the two cyclic substrates are as follows.

Cyclobutane.—The reaction mixtures were distilled into the cell at −64° (chloroform slush). At the end of the reaction, carbon monoxide was removed at −196° and determined in the gas buret, and the product condensable at −98° was analyzed by g.c. using an 8-ft. 20% tricresyl phosphate column at 40° with 80 cc./min. H_2 carrier.

Cyclopentane.—Reaction mixtures were admitted to the cell through a trap maintained at −45.3° (chlorobenzene slush), the CO was analyzed as above, and the product condensable at −84° (ethyl acetate slush) was analyzed using the silicone 550 column at 84°.

Cyclobutyl mercaptan was identified by its mass and gas-phase infrared spectrum. The latter spectrum was quite similar to that previously obtained for cyclopropyl mercaptan.[3]
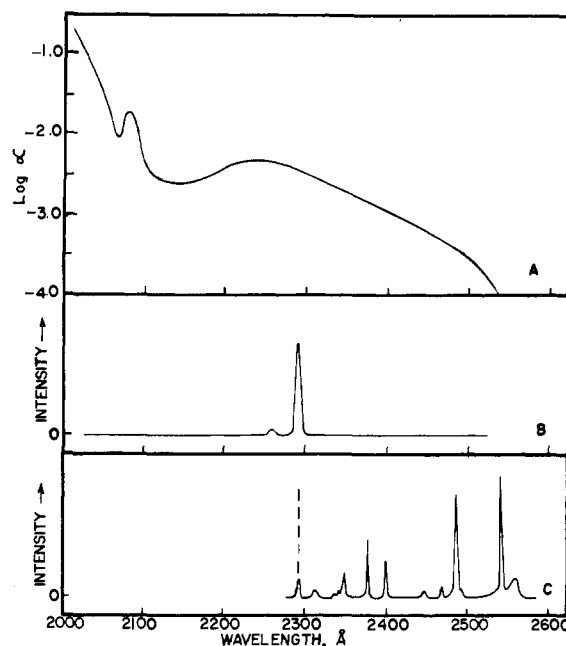
(7) O. P. Strausz and H. E. Gunning, J. Am. Chem. Soc., 84, 4080 (1962).

Fig. 2.—The ultraviolet absorption spectrum of carbonyl sulfide,[8] A, where $\alpha p d = \log I_0/I$, and p is in mm., d in cm.; the emission spectrum of a cadmium resonance lamp, B, and that of a medium pressure mercury arc with Vycor No. 7910 filter, C, plotted on an arbitrary intensity scale. The spectra were determined[9] using a Jarrell–Ash 0.5-m. grating spectrometer.

Results and Discussion

Pure Carbonyl Sulfide.—The photolysis of COS by 2288-Å. radiation was examined as a function of pressure, and the measured rates of CO formation are plotted in Fig. 1. The attainment of a constant value for $R_{(CO)}$ at COS pressures above 200 mm. is entirely consistent with the strong optical absorption of COS at λ 2288, Å., illustrated in Fig. 2.[8,9]

Table I gives the results of a series of runs where $R_{(CO)}$, from the decomposition of 200 mm. of COS at 2288 Å., was determined as a function of reaction temperature. The small rate increase from 30 to 100°

TABLE I

RATE OF CO PRODUCTION FROM THE 2288-Å. PHOTOLYSIS OF 200 MM. OF CARBONYL SULFIDE AS A FUNCTION OF REACTION TEMPERATURE

Temp., °C.	Exposure time, min.	CO formed, μmoles	$R_{(CO)}^0$, μmoles/min. × 10^2
30[a]	30/60[a]	. .	14.4[a]
104	30	4.46	14.9[b]
123	30	4.53	15.0[b]
164	30	4.53	15.0[b]
180	60	9.13	15.2[b]
223	30	4.40	14.7[b]
223	30	4.47	14.9[b]

[a] Average of six experiments.   [b] Mean $R_{(CO)}^0 = 14.9 \pm 0.3$ (104–223°).

is likely due to the sublimation of the sulfur product, normally deposited on the cell face, into the cell side arm which remained at room temperature. Sulfur removal is apparently complete at 100°, above which temperature $R_{(CO)}$ is constant within experimental error.

(8) G. S. Forbes and J. E. Cline, ibid., 61, 151 (1939).

(9) We are indebted to Dr. A. J. Yarwood of this laboratory for the spectra in Fig. 2.

TABLE II

RATES OF CO AND MERCAPTAN FORMATION FROM THE 2288-Å. PHOTOLYSIS OF CARBONYL SULFIDE AS A FUNCTION OF PRESSURE OF ADDED ETHANE[a]

	Ethane pressure, mm.	Rate, μmoles/min. × 10²		$2R_{(EtSH)}/R_{(CO)}^{0\,b}$	F^c × 10^{-2}
		CO	EtSH		
$P_{(COS)}$ = 50 mm.	0	12.6[d]	...	...	...
	44	9.00	1.70	0.27	1.62
	123	8.15	2.88	0.46	2.68
	215	7.20	2.95	0.47	4.58
	271	7.30	3.48	0.55	4.89
	340	7.19	3.48	0.55	6.14
	364	7.88	4.00	0.64	5.71
	411	7.13	3.98	0.63	6.47
	513	7.55	4.17	0.66	7.72
	662	7.30	4.13	0.66	10.0
	718	7.42	3.93	0.63	11.4
$P_{(COS)}$ = 200 mm.	0	14.4[d]	...	...	...
	108	10.7	1.80	0.25	4.32
	217	10.0	2.70	0.37	5.79
	217	9.85	2.63	0.37	5.94
	340	9.78	3.48	0.48	7.03
	473	9.86	3.95	0.55	8.62
	473	9.20	3.85	0.53	8.84
	762	9.74	4.29	0.60	12.8
	1009	9.30	4.40	0.61	16.5
	1400	8.95	4.80	0.67	20.9
	1400	9.18	5.02	0.70	20.0
	1600	8.55	4.91	0.68	23.5
	1600	8.31	4.77	0.66	24.1
	1800	8.23	4.83	0.67	26.8

[a] Exposure time, 60 min. [b] Fraction of S atoms inserting. [c] Calculated kinetic expression: $(R_{(CO)}^{0}/2)(P_{(EtH)}/R_{(EtSH)})$. [d] Average of three experiments.

The extent of thermal decomposition of COS at relatively low temperatures was also briefly examined. Partington and Neville[10] have reported two modes of thermolysis: (a) to CO_2 and CS_2, and (b) to CO and S. In our system, b was negligibly slow below ca. 250°, while detectable quantities of CS_2 (mode a) were produced only above 350°. The CS_2 rate could be increased sharply by packing the reaction vessel with Pyrex beads.

Carbonyl Sulfide–Paraffin Systems at Room Temperature.—To compare the present results with those of the previous study at $P_{(COS)}$ 50 mm. and λ 2290–2550 Å., the COS–ethane system was examined at λ 2288 Å. and $P_{(COS)}$ 50 and 200 mm. The data are presented in Table II. The fall-off in $R_{(CO)}$ and increase in $R_{(M)}$, the rate of mercaptan formation, to different constant values with increasing ethane pressure, parallels the behavior previously found in COS–paraffin systems.[3] The proposed sequence of reactions is shown in eq. 1–6. The steady-state treatment of this
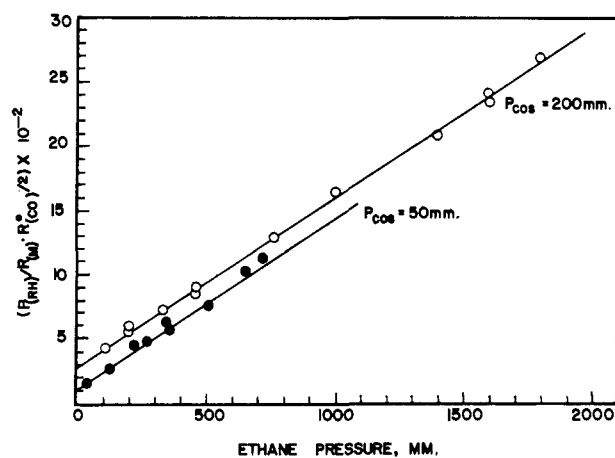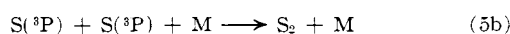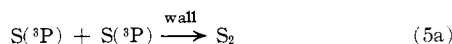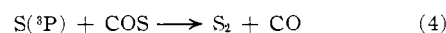
$$COS + h\nu \longrightarrow CO + S(^1D) \quad (1)$$

$$S(^1D) + RH \left\{ \begin{array}{l} \longrightarrow RSH \quad (2a) \\ \longrightarrow S(^3P) + RH \quad (2b) \end{array} \right.$$

$$S(^1D) + COS \longrightarrow S_2 + CO \quad (3)$$

$$S(^3P) + COS \longrightarrow S_2 + CO \quad (4)$$

$$S(^3P) + S(^3P) \overset{\text{wall}}{\longrightarrow} S_2 \quad (5a)$$

$$S(^3P) + S(^3P) + M \longrightarrow S_2 + M \quad (5b)$$

$$nS_2 \longrightarrow S_{2n} \quad (6)$$
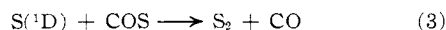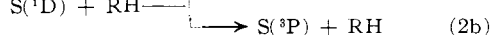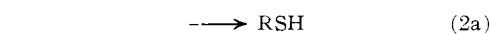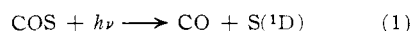
(10) J. R. Partington and H. H. Neville, J. Chem. Soc., 1230 (1951).

Fig. 3.—Plot of the expression $(P_{(RH)}/R_{(M)})(R_{(CO)}^{0}/2)$ vs. ethane pressure for the photolysis of 50 mm. (●) and 200 mm. (O) of carbonyl sulfide at 2288 Å.

mechanism yields expression I for the rate of mercaptan formation, where $R_{(CO)}^{0} = R_{(CO)}$ in the absence of

$$(R_{(CO)}^{0}/2)(P_{(RH)}/R_{(M)}) = \frac{k_3}{k_{2a}} P_{(COS)} + \frac{k_2}{k_{2a}} P_{(RH)} \quad (I)$$

ethane and $k_2 = k_{2a} + k_{2b}$. Equation I has been plotted for the COS–C_2H_6 system in Fig. 3. A straight-line relation is obtained for both sets of data, and, via the method of least squares, the intercepts gave values of 2.2 and 1.4 for k_3/k_{2a}, while the slopes gave 0.32 and 0.30 for k_{2b}/k_{2a} at COS pressures of 50 and 200 mm., respectively.

The rate of mercaptan formation from COS–propane mixtures was also determined at $P_{(COS)}$ 200 mm. The data are given in Table III, and eq. I, as calculated

TABLE III

RATES OF CO AND MERCAPTAN FORMATION FROM THE 2288-Å. PHOTOLYSIS OF 200 MM. OF CARBONYL SULFIDE AS A FUNCTION OF PRESSURE OF ADDED PROPANE[a]

Propane pressure, mm.	Rate, μmoles/min. × 10²		n-PrSH/	$2R_{(PrSH)}/$	F^c
	CO	PrSH	i-PrSH	$R_{(CO)}^{0\,b}$	× 10^{-2}
0	14.4[d]	..	...	..	...
200	9.35	2.52	3.4	0.35	5.68
309	9.01	3.21	3.5	0.45	6.88
516	9.37	3.54	3.4	0.50	10.4
749	8.67	4.36	3.2	0.61	12.2
1002	8.87	4.64	2.8	0.65	15.4
1202	8.78	4.83	3.1	0.68	17.7
1202	8.57	4.63	3.6	0.65	18.5
1402	9.50	5.19	2.9	0.73	19.3
1502	8.78	5.13	3.6	0.72	20.9
1502	8.33	5.26	2.6	0.74	20.4
1800	9.13	5.26	2.5	0.74	24.5

[a] Exposure time, 60 min. [b] Fraction of S atoms inserting. [c] Calculated kinetic expression: $(R_{(CO)}^{0}/2)(P_{(PrH)}/R_{(PrSH)})$. [d] Average of six experiments with pure COS.

from these data, is plotted in Fig. 4. The present data show that the n-PrSH/i-PrSH ratio remains constant, within experimental error, at 3 over the entire pressure range examined, as observed in the longer wave-length photolysis; that the behavior of the system follows rather closely that for COS–C_2H_6 mixtures; and that eq. I again yields a linear plot, giving values of 0.16 for k_{2b}/k_{2a} and 1.9 for k_3/k_{2a}.

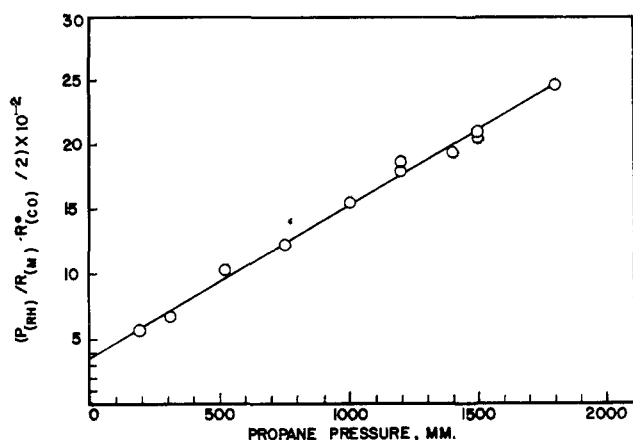A further series of experiments was carried out with 1500 mm. of ethane and COS pressures above 200 mm.

Fig. 4.—Plot of the expression $(P_{(RH)}/R_{(PrSH)})(R_{(CO)}^0/2)$ vs. propane pressure for the photolysis of 200 mm. of carbonyl sulfide at 2288 Å.

Fig. 5.—Plot of the expression $(P_{(RH)}/R_{(M)})(R_{(CO)}^0/2)$ vs. COS pressure for the photolysis of carbonyl sulfide at 2288 Å. in the presence of 1500 mm. of ethane.

where $R_{(S\ atoms)}$ is constant (cf. Fig. 1). The results are given in Table IV. As predicted by the mechanism, $R_{(CO)}$ rises and $R_{(M)}$ falls as the COS pressure is increased. Again, eq. I may be utilized and $(R_{(CO)}^0/2)(P_{(RH)}/R_{(M)})$ plotted against $P_{(COS)}$. The data yield the required straight line shown in Fig. 5, and the intercept gives a value of 0.30 for k_{2b}/k_{2a}—in good agreement with the values obtained for the ethane system at $P_{(COS)}$ 50 and 200 mm. The measured slope indicates a value of 1.1 for the ratio k_3/k_{2a}.

TABLE IV

RATES OF CO AND MERCAPTAN FORMATION FOR THE 2288-Å. PHOTOLYSIS OF CARBONYL SULFIDE WITH 1500 MM. OF ADDED ETHANE AS A FUNCTION OF COS PRESSURE[a]

$P_{(COS)}$, mm.	Rate, μmoles/min × 10² CO	Rate, μmoles/min × 10² EtSH	$2R_{(EtSH)}/R_{(CO)}^{0b}$	F^c × 10⁻⁴
200	8.95[d]	4.90[d]	0.68	2.19
320	9.07	4.92	0.68	2.19
452	8.67	4.41	0.61	2.44
586	9.28	4.13	0.57	2.60
804	9.98	3.78	0.52	2.85
994	10.5	3.69	0.51	2.92

[a] Exposure time, 60 min. [b] Fraction of S atoms inserting. [c] Kinetic expression: $(R_{(CO)}^0/2)(P_{(EtH)}/R_{(EtSH)})$. [d] Average of seven experiments at $P_{(C_2H_6)} > 1400$ mm.

Decomposition of the initially formed mercaptan in the ethane and propane systems at λ 2288 Å. was demonstrated by qualitative experiments carried out with 65 mm. of paraffin and 200 mm. of carbonyl sulfide. The condensable products were taken directly from the reaction cell into a break-seal for mass spectrometric analysis. The latter demonstrated that with both substrates there is a small but detectable fraction of mercaptan which suffers decomposition into disulfide at an exposure time of 60 min.

It is important to point out the limitations imposed by the nature of the present kinetic treatment. The ratio $(k_{2b} + k_{2a})/k_{2a}$, derived from the slope of the plot of eq. I, is rather insensitive, since with decreasing k_{2b} values this ratio approaches unity, and the value of k_{2b}/k_{2a} becomes subject to increasingly large uncertainties. Furthermore, the intercept values from eq. I are very sensitive to small changes in $R_{(M)}$, which, in turn, is affected at λ 2288 Å. by secondary photolysis and/or by cracking of hot RSH molecules. With these considerations in mind, the kinetic behavior of the systems may be discussed.
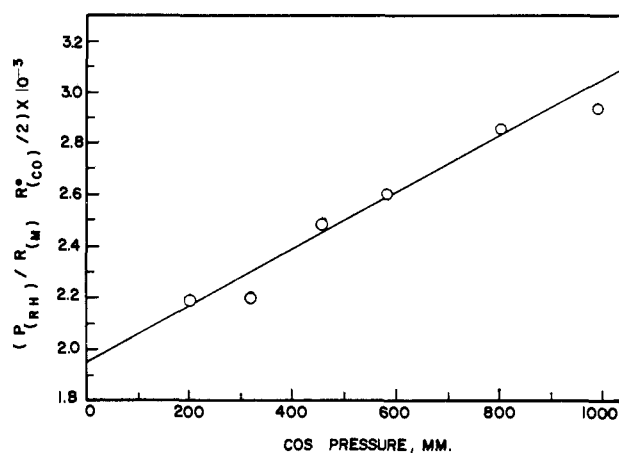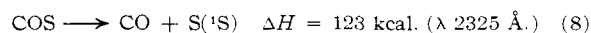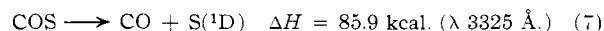
When 50 mm. of COS is photolyzed by 2290–2550 Å. light, the values obtained for the k_{2b}/k_{2a} and k_3/k_{2a} ratios were 0.71 and 2.0, respectively, with ethane as substrate,[3] as compared with values of 0.32 and 2.2 at λ 2288 Å. Thus while the ratio of rate constants for abstraction from COS and insertion remain essentially unchanged, there is an alteration in the k(deactivation)/k(insertion) ratio which is considerably larger than the uncertainty in the slope of the plot of eq. I. Comparing the systems at 2290–2550 and 2288 Å., the mercaptan yields are the same within experimental error at paraffin pressures up to 60% of that required for complete S-atom scavenging by the addend, while at higher pressures there is a ca. 20% increase in $R_{(M)}$ at the shorter wave length. The magnitude of the rate constant ratio, k_3/k_{2a}, for COS–C_2H_6 at 2288 Å. also suggests a pressure effect, having values of 2.2, 1.4, and 1.1 at $P_{(COS)}$ 50, 200, and >200. For propane at 200 mm. of COS, the value is 1.9. Although these values are subject to uncertainties, there is a definite trend to decreasing values of the ratio at higher COS and total pressures. A further wave-length effect is that whereas at 2290–2550 Å. ethane and propane give the same $R_{(M)}$ values, at 2288 Å. there is 6–8% more propyl than ethyl mercaptan formed.

The alteration brought about by wave-length change and the related effects of pressure are almost certainly linked to differences in reactivity of the atomic sulfur species involved. Taking D(OC–S) as 59.6 kcal.,[11] and E(S(^{1}D)) as 26.4 kcal. and E(S(^{1}S)) as 63.4 kcal.,[12] the following heats of reaction can be calculated.

$$COS \longrightarrow CO + S(^1D) \quad \Delta H = 85.9 \text{ kcal. } (\lambda\ 3325\ \text{Å.}) \quad (7)$$
$$COS \longrightarrow CO + S(^1S) \quad \Delta H = 123 \text{ kcal. } (\lambda\ 2325\ \text{Å.}) \quad (8)$$

The broad COS absorption band (Fig. 2) centered around 2300 Å. likely arises from only one transition, which gives rise to reaction 7. Approximate integration of the Hg-arc emission spectrum showed that ca. 3% of the output is at λ < 2325 Å., and thus the fraction of incident radiation capable of causing reaction 8 is negligible. This is consistent with our previous

(11) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(12) "Atomic Energy Levels," National Bureau of Standards Circular 467, ref. 11.

TABLE V

RATES OF CO AND MERCAPTAN FORMATION IN THE 2288-Å.
PHOTOLYSIS OF 200 MM. OF CARBONYL SULFIDE WITH ADDED
ETHANE AND PROPANE AS A FUNCTION OF REACTION
TEMPERATURE[a]

Temp., °C.	Rate, μmoles/min. $\times 10^2$ CO	RSH	n-PrSH/ i-PrSH	$R_{(M)}/$ $R_{(CO)}$
	1500 mm. of ethane added			
27	8.95[b]	4.90[b]	...	0.55
51	9.00	5.03	...	0.56
73	8.95	5.00	...	0.56
106	8.77	5.01	...	0.57
139	9.00	4.93	...	0.55
176	9.30	5.08	...	0.55
	1500 mm. of propane added			
27	9.08	5.00	2.9	0.55
77	8.92	4.50	3.0	0.50
99	9.16	4.72	3.0	0.52
139	9.44	5.31	2.6	0.55
179	9.42	4.96	2.7	0.53
	633 mm. of propane added			
25	8.94	3.93	3.0	0.44
49	8.89	4.26	2.9	0.48
77	9.24	4.18	3.2	0.45
132	9.69	4.54	2.6	0.47
199	9.80	4.65	(2.2)	0.47
224	9.90	4.98	2.7	0.50
	150 mm. of propane added			
25	11.1	2.19	2.8	0.20
75	11.7	2.56	3.0	0.22
113	11.2	2.69	3.0	0.24
178	11.6	2.85	2.8	0.25
212	12.6	3.03	2.9	0.24
220	12.2	3.32	2.7	0.27

[a] Exposure time, 60 min. [b] Average of seven experiments at $P_{(C_2H_6)} > 1400$ mm.

postulate that S(^{1}D) atoms are the inserting species at 2290–2550 Å.

The shorter wave-length COS absorption with λ_{max} 208 mμ may extend as far as 2288 Å., but absorption due to this transition is likely small at the latter wave length. There is, however, sufficient energy at 2288 Å. for reaction 8, and thus (^{1}S) sulfur atoms may be present.

Two hypotheses are consistent with the observed wave length and pressure effects. First, the insertion may involve exclusively (^{1}D) sulfur atoms, this species possessing increased translational energy at the shorter wave length. Second, both (^{1}D) and (^{1}S) atoms may be involved, the increased yields at 2288 Å. being due to the participation of the latter species. The increased rate of (2a) via either mechanism is offset at low pressures by decomposition of hot RSH molecules, and the effect is observable only at high pressures where collisional deactivation is extensive.

The exclusive production of (^{1}S) sulfur atoms in the system can likely be ruled out. The exothermicity of S(^{1}D) insertion into ethane C–H bonds is 85 kcal., a value close to the bond strengths in the mercaptan, and thus there is no significant decomposition. On the other hand, the same reaction with S(^{1}S) atoms is 122 kcal. exothermic, and thus cracking of highly excited RSH molecules, even at the pressures involved in the present study, should occur to such an extent as to decrease the mercaptan yield compared to the reaction at 2290–2550 Å.

COS–Paraffin Systems at Elevated Temperatures.— Four series of experiments, at $P_{(COS)}$ 200 mm., were made with 1500 mm. of C$_2$H$_6$, 1500 mm., 633 mm., and 150 mm. of C$_3$H$_8$, and CO and mercaptan yields determined as a function of temperature. Pressures were measured at room temperature. The data are summarized in Table V and show that the rate of mercaptan formation (as well as the n-PrSH/i-PrSH ratio for the propane reaction) is invariant over the temperature range studied at paraffin pressures of 1500 mm.

In this pressure region, steps 2a and 2b are the only fates of S(^{1}D) atoms, the rate of reaction 3 being negligible for $P_{(RH)} > 1400$ mm. If the activation energy of (3) is higher than that of (2a) or (2b), or if $E_{(2a)} \neq E_{(2b)}$, the mercaptan yield should be altered by increasing temperature. Since no change is found, it follows that, within experimental error, $E_{(2a)} = E_{(2b)} \geq E_{(3)}$.

There may be a small increase in $R_{(CO)}$ with temperature which could arise from an increase in the rate of S(^{3}P) abstraction relative to the recombination of this species, but the over-all change is less than ca. 6%.

In the series of runs at $P_{(C_3H_8)}$ 633 mm. and 150 mm., the data in Table V show that with increasing temperature $R_{(PrSH)}$ increases more rapidly than $R_{(CO)}$, suggesting that $E_2 > E_3$. The series at 150 mm. of propane pressure can be treated quantitatively, and an Arrhenius plot of the ratio of rates for (S(^{1}D) + RH)/(S(^{1}D) + COS) yields a value of 1.0 ± 0.2 kcal. for $E_2 - E_3$.

At the temperature involved here, there should be no thermal decomposition of the mercaptan. For C$_2$H$_5$SH, Sehon and Darwent[13] found activation energies of 54 and 64 kcal. for the molecular and free-radical modes of thermolysis.

COS–Cyclic Hydrocarbons.—In part III of this series it was shown that cyclopropyl mercaptan was the sole product of the S + cyclo-C$_3$H$_6$ reaction and that this substrate had a relative reactivity quite similar to that of other paraffinic hydrocarbons.

In the present investigation, we have found that cyclobutane and cyclopentane also yield the corresponding cyclic mercaptan. As far as can be determined, this is the first reported synthesis of cyclobutyl mercaptan. COS (41 mm.) was photolyzed at 2290–2550 Å. in the presence of varying pressures of each of the three cyclic hydrocarbons. The results are given in Table VI. A plot of eq. I showed that, within experimental error, all three substrates have the same relative reactivity toward (^{1}D) sulfur atoms. From the slope and intercept values we obtain $k_3/k_{2a} = 2.0$ and $k_{2b}/k_{2a} = 0.50$. The latter is to be compared to values of 0.71 for ethane and 0.64 for isobutane.

COS–Deuterated Propanes.—In several experiments with C$_3$H$_8$–C$_3$D$_8$ mixtures reported earlier,[3] the over-all rate of S-atom attack on these substrates was shown to be essentially the same, but attempts to demonstrate the absence of isotopic mixing failed. The data from an expansion of this work are summarized in Table VII and demonstrate that, within experimental error, the relative reactivities are the same and that the attack of singlet sulfur atoms on carbon–hydrogen bonds is indiscriminate not only with respect to bond

(13) A. H. Sehon and B. deB. Darwent, $J. Am. Chem. Soc.$, **76**, 4806 (1954).

TABLE VI

RATES OF CO AND MERCAPTAN FORMATION FROM THE 2290–2550 Å. PHOTOLYSIS OF CARBONYL SULFIDE AS A FUNCTION OF PRESSURE OF ADDED CYCLIC HYDROCARBON[a]

Pressure of cyclo-C_nH_{2n}, mm.	Rate, μmoles/min. $\times 10^2$		F^b $\times 10^{-2}$
	CO	Mercaptan	
0	7.20	...	...
	Cyclopropane		
43.2	5.88	1.05	1.47
84.8	5.51	1.23	2.48
167	5.23	1.86	3.22
167	5.68	1.88	3.19
252	5.05	2.09	4.34
331	5.01	2.02	5.89
380	4.96	1.97	6.86
	Cyclobutane		
56.2	..c	1.12	1.79
90.7	..	1.42	2.29
138	..	1.83	2.70
208	..	2.06	3.63
314	..	2.06	5.45
	Cyclopentane		
65.2	4.79	0.86	2.74
112	4.79	1.49	2.69
243	4.68	2.02	4.32
314	4.49	2.00	5.64
380	4.46	1.78	7.65

[a] Exposure time 120 min., COS pressure 41 mm. [b] Kinetic expression: $(R_{(CO)}{}^0/2)(P_{(RH)}/R_{(RSH)})$. [c] No CO analysis made in this series.

order but also to C–H and C–D bonds. Despite intensified efforts to prevent isotopic exchange reactions by trapping peaks from the chromatographic effluent in a specially designed grease-free system, and preheating of the mass spectrometer inlet, the product mercaptans from C_3D_8 (whose isotopic purity had been verified) again appeared as *ca.* 95% S–H mercaptan.

Summary

In the present investigation, we have attempted to extend our knowledge of the photolysis of pure carbonyl sulfide as a source of sulfur atoms in the gas phase, and

TABLE VII

RELATIVE RATES OF CO AND MERCAPTAN FORMATION FOR LIGHT AND HEAVY PROPANES[a]

Substrate	$R_{(PrSH)}/R_{(CO)}$	n-C_3H_7SH/i-C_3H_7SH
C_3H_8	0.30	3.0
	0.29	3.1
C_3H_8–C_3D_8	0.26	2.7
	0.28	3.3
C_3D_8	0.29	3.1
	0.25	2.7
$C_3H_2D_6{}^b$	0.28	2.8
	0.27	2.9
$C_3H_6D_2{}^c$	0.34	2.7
	0.26	3.2

[a] $P_{(COS)}$ 18.5 mm., $P_{(propane)}$ 155 mm., λ 2290–2550 Å. [b] Propane-1,1,1,3,3,3-d_6. [c] Propane-2,2-d_2.

have demonstrated that complete absorption of the incident radiation at 2288 Å. can be attained under experimentally convenient conditions and that the rate of S-atom production is temperature independent. In connection with this aspect of the study of S-atom reactions, a detailed examination of the quantum yield of the COS photolysis is currently being carried out in this laboratory.

We have shown here that there is only a small difference in the activation energies of insertion and abstraction by sulfur atoms. Excess energy in the inserting species markedly affects the kinetic behavior of the system, owing to either the participation of translationally hot $S(^1D)$ atoms or $S(^1S)$ atoms or both. Detailed studies on the reaction at various wave lengths should provide further insight into the type of excess energy present in the inserting S atom. The relative rates of insertion into C–H bonds and addition to olefinic double bonds are being examined in the system, COS–paraffin–olefin.

The cyclic hydrocarbon and deuterated propane studies have further demonstrated the general chemical characteristics of S-atom insertion, and we are presently extending this type of information in studies of the nature of products and kinetic behavior of a number of other substrates.