

# The Reactions of Sulfur Atoms. IX. The Flash Photolysis of Carbonyl Sulfide and the Reactions of S(<sup>1</sup>D) Atoms with Hydrogen and Methane

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**Abstract:** From flash photolysis-kinetic absorption spectroscopic studies, indirect though compulsive kinetic evidence has been obtained that the S<sub>2</sub> molecule from the reaction, S(<sup>1</sup>D) + COS → S<sub>2</sub> + CO (4), is formed in one of its low-lying, metastable, excited singlet states (*x*<sup>1</sup>Δ<sub>g</sub> or *y*<sup>1</sup>Σ<sub>g</sub><sup>+</sup>). S(<sup>1</sup>D) atoms undergo insertion reactions with H<sub>2</sub> and CH<sub>4</sub> to yield vibrationally excited H<sub>2</sub>S and CH<sub>3</sub>SH, respectively. The cracking of the hot product molecules has been studied. In auxiliary experiments the flash photolysis of ethylene episulfide and H<sub>2</sub>S has also been examined. Absolute rate constants have been measured for ground-state S<sub>2</sub> recombination in the presence of various chaperons and have been estimated for S(<sup>3</sup>P) atom recombination and HS(<sup>2</sup>II) radical recombination and disproportionation. Lower limits for the rate constants of reaction 4 and of the insertion into H<sub>2</sub> and CH<sub>4</sub> have also been established.

Systematic studies on singlet- and triplet-state sulfur atom reactions have been described in a series of articles from this laboratory.<sup>1</sup> The source of S atoms used in these studies was the *in situ* photolysis of carbonyl sulfide. It has been shown that S atoms abstractively attack the substrate molecule COS to form S<sub>2</sub> and CO, but the detailed mechanism and the absolute rate constant of the reaction have not been established.

It has also been shown that the S(<sup>1</sup>D) atom in its reaction with paraffins, *via* an insertive attack on the C-H bond, yields only one type of product, alkyl mercaptan. Insertion reactions in general are characterized by one net bond formation and a resulting high exothermicity. With C<sub>2</sub> and higher paraffins there are sufficient internal degrees of freedom in the molecule to accommodate this excess energy and to assure a sufficiently long lifetime for its bimolecular removal. With methane, however, a large amount of cracking occurs.

In the present work, using flash photolysis with kinetic absorption spectroscopy, we have extended our studies on S-atom reactions to include the hydrogen molecule and have reexamined the S + COS and S + CH<sub>4</sub> systems.

Since extinction coefficient and rate data for sulfur-containing radicals are sparse, to check some of the results and the validity of the interpretation auxiliary experiments were also conducted on the flash photolyses of ethylene episulfide and hydrogen sulfide.

## Experimental Section

The essential details of the flash apparatus were as follows. The spectroflash tube was filled with 100 torr of Kr and discharged at 10 kv from a 3-μf capacitance; the photoflash tube used a filling of 60 torr of Kr and 10 torr of N<sub>2</sub>; the capacitance was 41 μf at 9 kv (1660 joules). The photoflash had a rise time of 13 μsec with subsequent decay with a half-life of 22 μsec. For the spectroflash these figures were 4.5 and 11 μsec, respectively. The flashes were monitored by a photocell-oscilloscope (Hewlett-Packard 130C) combination, the traces being recorded on Polaroid film Type

47. The delay time is measured from the onset of the photoflash to the point at which half the spectroflash energy has been dissipated.

The spectrograph was a Hilger medium quartz used with 20-μ slit width. Spectra were recorded on Kodak 103a-O plates, developed for 4 min in Kodak D 19 developer. Plate photometry was carried out on a Jarrell Ash recording microphotometer. Each plate was calibrated using a wedge of standard optical densities, placed immediately before the spectrograph slit. The intense diffuse absorption band at 2713 Å of the (13,0) B<sup>3</sup>Σ<sub>u</sub><sup>-</sup> ← X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> transition was used for the photometry of S<sub>2</sub>. The measured optical densities (OD's) of the maximum of this band were shown to obey Beer's law up to an OD of at least 0.6 by varying the irradiated length of the photolysis cell containing 14 torr of ethylene episulfide (*vide infra*) and taking calibrated spectra at a constant delay of 41 μsec. The OD's of S<sub>2</sub> were proportional to the irradiated length. A symmetrical dependence of OD on concentration and path length

$$\text{OD} = k(cl)^n \quad (\text{A})$$

was assumed,<sup>2</sup> where *n* = 1 for the Beer-Lambert relationship. The photometry of the HS radical used the (0,0) and (1,0) bands (3237 and 3050 Å), respectively, of the <sup>2</sup>Σ ← <sup>2</sup>II system. The value of *n* for this case is discussed in the text.

The photolysis cell constructed of Vycor 7910 glass (transmitted wavelength >2200 Å) was 500 mm in length and 47 mm in diameter and was connected to the vacuum line through a trap, kept at sufficiently low temperature to prevent the entrance of mercury vapor.

COS (Matheson) was purified as described earlier.<sup>3</sup> H<sub>2</sub>S (Matheson) was distilled at -139° (ethyl chloride slush) and degassed at -196°. Methane (Phillips research grade) was distilled at -183° and degassed at -210°. Hydrogen (Liquid Air) was passed through a heated Ag-Pd thimble (Milton Roy Co.) before use. CO<sub>2</sub> was Airco reagent and used without further purification. Ethylene episulfide (>99% pure) was prepared by distilling from a heated mixture of potassium thiocyanate and ethylene carbonate.<sup>4</sup>

CO and H<sub>2</sub> were measured volumetrically. The H<sub>2</sub>S and acetylene from the ethylene episulfide photolyses were estimated by mass spectrometry. Product H<sub>2</sub>S in the presence of excess COS was determined by gas chromatography using a 7-ft medium activity silica gel column. The H<sub>2</sub>S peak appeared on the tail of the COS peak, and for this reason measurements are only accurate to ±20%.

## Results and Discussion

**A. Pure Carbonyl Sulfide.** The only absorbing transient observed was S<sub>2</sub> in its ground electronic and

(2) A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, **62**, 371 (1966).

(3) H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 1443 (1965).

(4) S. Searles and E. F. Lutz, *ibid.*, **80**, 3168 (1958).

(1) For a review see H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

vibrational state, with the exception of a very feeble band system in the region of 3700–4300 Å which was apparent only in high-pressure (>400 torr) runs. OD's of S<sub>2</sub> vs. delay time at 7, 17, 65, and 410 torr COS pressures are displayed in Figure 1. All curves show well-defined maxima.

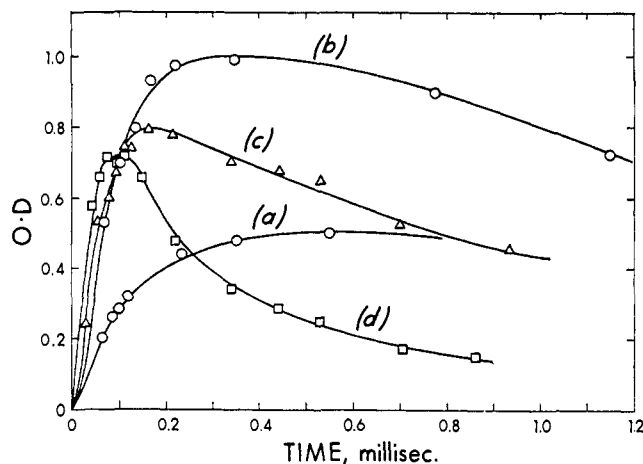
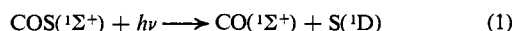
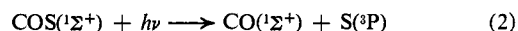


Figure 1. OD's of S<sub>2</sub> as a function of delay time in the flash photolysis of pure COS. Pressure of COS in torr: (a) 7, (b) 17, (c) 65, (d) 410.

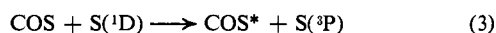
The primary step of the photodecomposition of carbonyl sulfide in the medium ultraviolet region is<sup>5</sup>



with the possible contribution of the spin-forbidden step



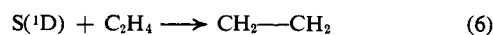
to the extent of a maximum of 26% of the total. Triplet-state atoms are also produced by collisional relaxation<sup>1</sup>



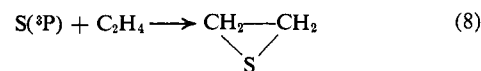
Even at the lowest pressure used, 7 torr, all the S atoms eventually react with COS in the reactions



since the addition of ~400 torr of ethylene causes a reduction in yield of CO per flash by exactly one-half, owing to the scavenging reactions



and



Recombination of S atoms can consequently be neglected.

From the plots of optical densities vs. delay times (Figure 1), it is seen that S<sub>2</sub> builds up relatively slowly and the position of the maximum on the time scale is an inverse function of pressure. The decay part of the curve is also pressure dependent and exhibits second-order kinetics as seen from the plots given in Figure 2.

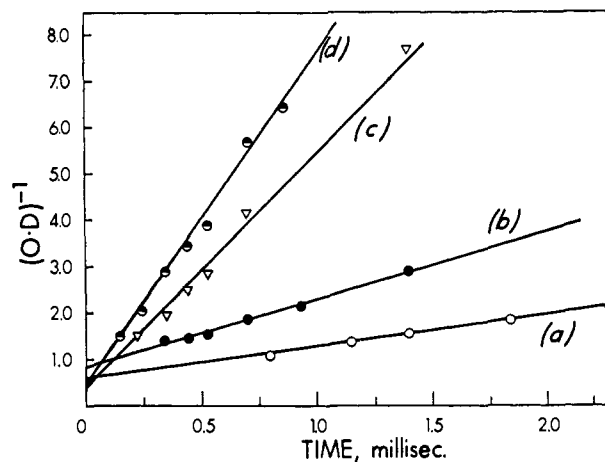


Figure 2. Second-order decay plots for S<sub>2</sub> from the flash photolysis of pure COS. COS pressure in torr: (a) 17, (b) 65, (c) 192, (d) 410.

In the ensuing discussion we shall assume that the participation of triplet, ground-state atoms is not significant. The abstraction by S(<sup>1</sup>D) (reaction 4) should be rapid since its rate constant is about twice that of the insertion reaction into paraffinic C–H bonds which is apparently entirely indiscriminate and hence of high efficiency. The rate of formation of ground-state S<sub>2</sub>, however, is slow. From gas kinetic collision frequencies<sup>6</sup>  $k_4 \sim 1.3 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$  and from the half-lives of S<sub>2</sub> buildup in Figure 1,  $\sim 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ . Peculiarly the S<sub>2</sub> absorption appears only from the zeroth vibrational level of the ground electronic state in all flash-photolysis experiments. Consequently, relaxation of the initially formed vibrationally excited S<sub>2</sub> must be very fast even at low pressures. (Vibrational energy transfer in the  ${}^3\Sigma_u^-$  excited state has been postulated to occur with near-unit-collision efficiency.<sup>7</sup>)

It seems reasonable to attribute the slow growth in the S<sub>2</sub> absorption to the initial formation of S<sub>2</sub> in a metastable excited state which is not detected by optical absorption in the spectral region studied and which decays by collisional relaxation to the ground state.

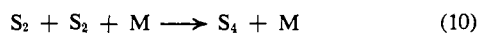


(5) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 2412 (1966).

(6) Collision diameters used in estimates of collision numbers are  $\sigma(\text{S}) = 1.9 \text{ \AA}$  and  $\sigma(\text{COS}) = 5.4 \text{ \AA}$ .

(7) E. Durand, *J. Chem. Phys.*, **8**, 46 (1940).

Ground-state  $S_2$  is then removed by the recombination reaction



The kinetics of the ground-state  $S_2$  transient should thus be given by

$$d[S_2^*]/dt = Af(t) - k_9[S_2^*] \quad (B)$$

$$d[S_2]/dt = k_9[S_2^*] - k_{10}[S_2]^2 \quad (C)$$

*i.e.*,

$$[S_2] = k_9 \int_0^t [S_2^*] dt - k_{10} \int_0^t [S_2]^2 dt \quad (D)$$

and

$$[S_2] = Ak_9 \int_0^t \int_0^t f(t) dt dt - k_9 \int_0^t [S_2] dt - k_9 k_{10} \int_0^t \int_0^t [S_2]^2 dt dt - k_{10} \int_0^t [S_2]^2 dt \quad (E)$$

*i.e.*, in terms of OD

$$(OD)_t = \epsilon l A k_9 I_1 - k_9 I_2 - \frac{k_9 k_{10}}{\epsilon l} I_3 - \frac{k_{10}}{\epsilon l} I_4 \quad (F)$$

where  $A$  is the limiting concentration of  $S_2$  produced per flash (*i.e.*, corresponding to  $t = \infty$  and no decay by reaction 10) and is equal to half the concentration of

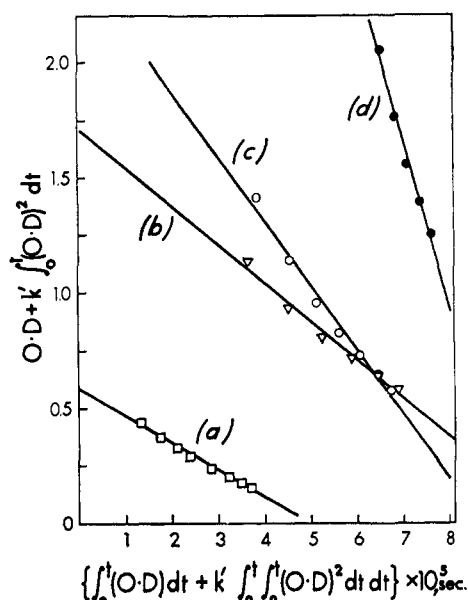


Figure 3. Normalized plots of eq F,  $k' = k_{10}/\epsilon l$ . Pressure of COS in torr: (a) 7, (b) 17, (c) 65, (d) 410.

CO produced per flash. The function  $f(t)$  is the relative intensity of the photoflash at time  $t$  such that  $\int_0^\infty f(t) dt = 1$ .  $\epsilon$  and  $l$  are respectively the molar extinction coefficient of  $S_2$  and the cell length.

The integrations were carried out graphically.  $I_1$

is obtained by plotting the fractional photoflash energy dissipation *vs.* time and measuring the area.  $I_2$  is obtained from area measurements of the plots in Figure 1, after making a smooth-line extrapolation from the shortest delay times used to  $t = 0$ .  $I_4$  is taken from a plot of  $(OD)_t^2$  *vs.*  $t$ . Finally  $I_3$  is evaluated from the area of a plot of  $I_4$  against time.

The values of  $k_{10}/\epsilon l$  are known from the pure decay kinetics. The resulting set of equations are normalized to  $I_1 = 10^{-4}$  sec and  $(OD)_t + k_{10}/\epsilon l I_4$  plotted against  $(I_2 + k_{10}/\epsilon l I_3)$ . The values of slope and intercept obtained were then used to reproduce more exactly the short delay portions of the OD *vs.*  $t$  curves (and derived plots), and the modified integrals were treated as before. Only one set of approximations was necessary. Figure 3 gives the resulting plots. The calculated values of  $\epsilon$ ,  $k_9$ , and  $k_{10}$  along with measured yields of the CO product are tabulated in Table I. The mean value of the extinction coefficient is  $1.10 \pm 0.16 \times 10^4 M^{-1} \text{ cm}^{-1}$  at the peak intensity of the 2713-A band which may be compared with the value of  $3.9 \times 10^3 M^{-1} \text{ cm}^{-1}$  reported earlier for this band at 3000°K by Gaydon, *et al.*<sup>8</sup>

Table I. Rate Constant and Extinction Data from the Flash Photolysis of Pure COS

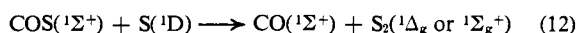
COS pressure, torr	CO yield/flash, $\mu\text{moles}$	$k_{10}^a \times 10^{-8}, M^{-1} \text{ sec}^{-1}$	$k_9^b \times 10^{-4}, \text{ sec}^{-1}$	$\epsilon^c \times 10^{-4}, M^{-1} \text{ cm}^{-1}$
7	1.52	1.8 <sup>c</sup>	$1.18 \pm 0.20$	$1.13 \pm 0.20$
17	3.26	$4.15 \pm 0.87$	$1.66 \pm 0.54$	$1.09 \pm 0.34$
65	2.40	$8.92 \pm 2.25$	$2.80 \pm 0.72$	$1.26 \pm 0.30$
192	2.94	$30.7 \pm 8.3$	...	...
410	3.46	$43.4 \pm 17.9$	$7.30 \pm 3.1$	$0.93 \pm 0.40$

<sup>a</sup> Errors are 95% confidence limits + error in  $\epsilon$ . <sup>b</sup> Confidence limits of  $2 \times 95\%$ . <sup>c</sup> Assumed value.

Returning now to the  $S_2$ -forming reaction, the following points should deserve consideration. The  $S_2$  molecule, like  $O_2$ , has two low-lying metastable singlet states,  $x^1\Delta_g \sim 13$  kcal and  $y^1\Sigma_g^+ \sim 24$  kcal above the ground state.<sup>9</sup> The spin-forbidden reaction



is exothermic by 54.8 kcal, so that the spin-allowed reactions



are energetically favorable. The spectroscopy and chemistry associated with the corresponding states of  $O_2$  molecules have in recent years attracted a great deal of attention. It has been shown that both electronic states, as expected, are strongly metastable with respect to optical transition to the ground state ( $\tau(\text{rad})(^1\Delta)$

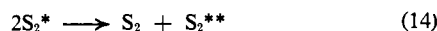
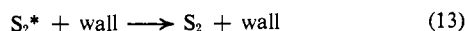
(8) A. G. Gaydon, G. H. Kimbell, and H. B. Palmer, *Proc. Roy. Soc. (London)*, **A279**, 313 (1964).

(9) R. F. Barrow and R. P. du Parc in "Elemental Sulfur," B. Meyer, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 251.

> 1 hr) and extremely resistant toward collisional relaxation (may survive many millions of collisions).<sup>10,11</sup> With S<sub>2</sub>, the optical selection rules would be expected to be less stringent because of the heavier S nuclei, and collisional relaxation may proceed more efficiently than with O<sub>2</sub>. Nevertheless, these states should still possess relatively long lifetimes. Pertinently, they have never been observed in optical absorption nor is there any chemical evidence for their presence in our (or any other) system.

While in the present study it was not possible to obtain direct evidence for the participation of metastable singlet S<sub>2</sub> in the reaction, there are indirect, though compulsive, kinetic indications for it. Inspection of the data in Table I reveals that  $k_9$ , expressed as a first-order rate constant, exhibits less than first-order dependence on COS pressure. A *ca.* 60-fold change in COS pressure caused a less than sevenfold variation in  $k_9$ . This is clearly incompatible with the abstraction reaction being the rate-controlling step for the appearance of S<sub>2</sub>. Additional points pertaining to this question will be brought up in the section dealing with the flash photolysis of COS-H<sub>2</sub> and COS-CH<sub>4</sub> mixtures.

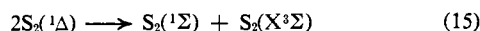
Now reaction 9 cannot be the sole mode of relaxation for excited S<sub>2</sub> molecules. Possible alternatives are



The radiative mode of decay is omitted on the grounds that in order to have significance it should have a lifetime of 10<sup>-6</sup>-10<sup>-8</sup>-fold of that estimated for the corresponding states of O<sub>2</sub>.

The importance of reactions 13 and 14 under certain experimental conditions has been demonstrated for the O<sub>2</sub> molecule.<sup>12,13</sup> Deactivation at the wall in the present case is negligible even at the lowest pressures used. The first-order rate constant for decay at the wall may be estimated as  $5.8D/r^2$ , where  $r$  is the radius of the cylindrical cell and  $D$  is the diffusion coefficient at the appropriate pressure.<sup>14</sup> Using a value of  $D = 6.5 \times 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$  at 1 atm, the first-order decay constant would be  $\sim 7.5 \text{ sec}^{-1}$  at 7 torr of COS, compared with  $\sim 10^4 \text{ sec}^{-1}$  actually obtained.

For energetic reasons step 14 would be possible only with S<sub>2</sub>(<sup>1</sup>Δ), that is



in which case the over-all process is approximately thermoneutral. This reaction could be competitive if the collision yield is  $>10^{-2}$ . The plots in Figure 3 allow some curvature in the direction of a competition between first-order and second-order decay of S<sub>2</sub><sup>\*</sup>, but the data and the treatment of it are not sufficiently precise to make a meaningful analysis. Finally, one

(10) L. W. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, **37**, 46 (1964).

(11) A. M. Winer and K. D. Bayes, *J. Phys. Chem.*, **70**, 302 (1966).

(12) R. A. Young and G. Black, *J. Chem. Phys.*, **42**, 3740 (1965).

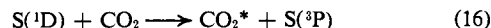
(13) S. J. Arnold, N. Finlayson, and E. A. Ogryzlo, *ibid.*, **44**, 2529 (1966).

(14) A. C. G. Mitchell and M. W. Zermansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London, 1934, p 247.

remaining possibility is that the larger deactivation yield per collision, at low pressures of COS, is caused by an increasing temperature rise during the flash. At the lowest pressure this is  $\sim 30$ - $40^\circ$ . No prediction can be made about the activation energy of reaction 9.

The value of the first-order decay constant at 410 torr pressure yields an upper limit of  $3.3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ , or less than one effective collision in  $5 \times 10^4$ , for  $k_{14}$ .

**B. Carbonyl Sulfide with Added Carbon Dioxide.** It has been shown that carbon dioxide is an efficient quencher of singlet excited sulfur atoms<sup>1</sup>



The rate constant of this reaction is comparable to that of the abstraction reaction and a 20-fold excess of CO<sub>2</sub> over COS brings about nearly complete deactivation.

We have carried out two series of flash experiments with the mixtures 17 torr of COS + 600 torr of CO<sub>2</sub> and 31 torr of COS + 850 torr of CO<sub>2</sub>. Optical densities of S<sub>2</sub> *vs.* delay times for the former system are plotted in Figure 4. Well-defined maxima in this case

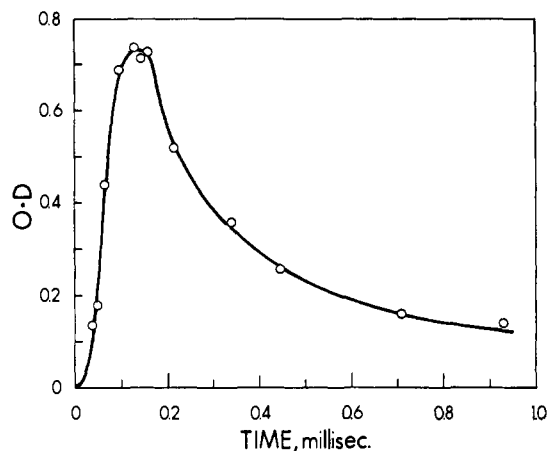
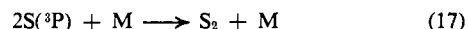


Figure 4. OD's of S<sub>2</sub> as a function of delay time in the flash photolysis of 17 torr of COS + 600 torr of CO<sub>2</sub>.

are also apparent. The yield of CO measured in the first mixture was 57% of that obtained in the absence of CO<sub>2</sub>, while in the case of the second mixture this figure was 51%. It seems clear that the S(<sup>1</sup>D) atoms are to a great extent (within experimental error, completely) deactivated and that the resulting ground-state atoms are largely removed by recombination

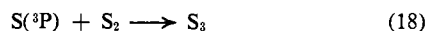


in contrast to the result at low light intensities<sup>3,15</sup> where most ground-state atoms disappear by the abstraction reaction 5.

The evaluation of the growth curve is more complicated in the present case because it is more difficult to take into consideration the finite length of the photo-

(15) H. A. Wiebe, O. P. Strausz, and H. E. Gunning, to be published.

flash duration for second-order kinetics than for first order. A further complication is the possibility of the reaction



A transient system of absorption bands in the range 3700–4300 Å has been observed in this and other systems where ground-state S atoms are generated in high concentration. This may be due to the  $S_3$  radical formed in reaction 18.

An estimate of the rate constant of reaction 17, correct to within a factor of 4, can be obtained from the half-life of the growth curve of  $S_2$  and the concentration of  $S(^3P)$  atoms produced in the flash. This corresponds

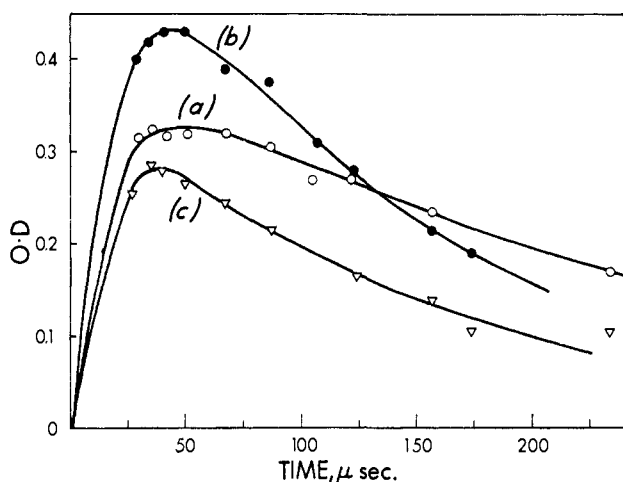
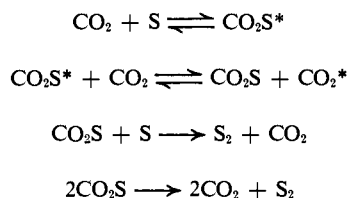


Figure 5. OD's of  $S_2$  as a function of delay time in the flash photolysis of pure  $C_2H_4S$ . Pressure of  $C_2H_4S$  in torr: (a) 10, (b) 13, (c) 19.

to a third-order rate constant of  $\sim 5 \times 10^{11} M^{-2} \text{sec}^{-1}$  or of the same order of magnitude as the rate constant of iodine atom recombination<sup>16</sup> in the presence of complex molecules, e.g., trimethylbenzene, and presumably involves a similar radical-molecule complex mechanism



where the  $CO_2S$  complex involves appreciable covalent bonding. (A similar complex may be responsible for the high efficiency of reaction 3 as well.)

The rate constant value for ground-state oxygen atom recombination is about two orders of magnitude smaller.<sup>17</sup>

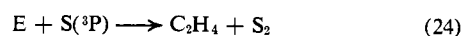
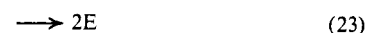
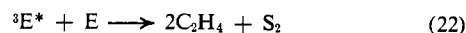
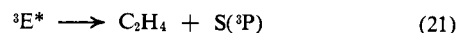
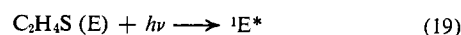
The decay of  $S_2$  is pseudo second order with a rate constant of  $5.3 \pm 1.4 \times 10^9 M^{-1} \text{sec}^{-1}$  at a pressure of

(16) G. Porter, *Discussions Faraday Soc.*, **33**, 198 (1962).

(17) F. Kaufman, *Progr. Reaction Kinetics*, **1**, 1 (1961).

600 torr of  $CO_2$ , so that  $CO_2$  and  $COS$  have very nearly the same efficiencies as chaperons.

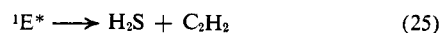
**C. Ethylene Episulfide.** To further substantiate some aspects of the  $COS$  study and to check on the presence of possible artifacts in the experimental technique, we have carried out a brief study on the flash photolysis of ethylene episulfide. A concurrent investigation of the low-intensity photolysis of this compound<sup>18</sup> has shown that the major product of the gas-phase reaction is ethylene with quantum yields of 1.67 at 7.3 torr and 1.57 at 16.0 torr. The mechanism suggested tentatively for the formation of this product is



where the superscript denotes the multiplicity of the electronic excited states. The S atoms are formed in their triplet ground state since mercaptans could not be found among the products on addition of paraffinic or olefinic hydrocarbons, although the episulfide of the added olefin was readily detectable.<sup>18</sup> Reaction 24 appears to be extremely rapid because it competes very favorably with the addition of  $S(^3P)$  to olefinic bonds.

In the flash photolysis the only important absorbing transient was  $S_2$  in its ground electronic and vibrational state. Very weak absorptions due to  $CS$  and  $HS$  were also observed. Plots of OD's of  $S_2$  vs. delay times at 10, 13, and 19 torr of  $C_2H_4S$  are shown in Figure 5. All three plots exhibit maxima at delay times of  $\sim 40 \mu\text{sec}$ . Since this is shorter than the duration of the photoflash ( $\sim 85\%$  dissipation of the latter), reaction 24 must indeed be rapid.

The product volatile at  $-139^\circ$  contained, in addition to ethylene, about 10% each of hydrogen sulfide and acetylene. These products likely arise from a molecular split of the excited singlet episulfide



The kinetics, assuming, as before, a second-order decay for  $S_2$ , is described by the differential equation

$$d[S_2]/dt = Af(t) - k_{10}[S_2]^2 \quad (G)$$

On integration

$$[S_2] = A \int_0^t f(t)dt - k_{10} \int_0^t [S_2]^2 dt \quad (H)$$

or in terms of OD

$$(OD)_t = AeI \int_0^t f(t)dt - \frac{k_{10}}{eI} \int_0^t (OD)_t^2 dt \quad (I)$$

(18) K. S. Sidhu, O. P. Strausz, and H. E. Gunning, to be published.

**Table II.** Rate Constant and Extinction Data from the Flash Photolysis of C<sub>2</sub>H<sub>4</sub>S

P(C <sub>2</sub> H <sub>4</sub> S), torr	C <sub>2</sub> H <sub>4</sub> yield, <sup>a</sup> μmoles	Aεl <sup>b</sup>	k <sub>10</sub> /εl <sup>c</sup> × 10 <sup>-4</sup> sec <sup>-1</sup>	k <sub>10</sub> <sup>c</sup> × 10 <sup>-10</sup> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>10</sub> × 10 <sup>-13</sup> /[C <sub>2</sub> H <sub>4</sub> S], M <sup>-2</sup> sec <sup>-1</sup>
10	1.18	0.424 ± 0.022	1.64 ± 0.22	1.01 ± 0.26	1.88 ± 0.48
13	1.60	0.615 ± 0.036	2.37 ± 0.28	1.46 ± 0.35	2.09 ± 0.50
19	1.30	0.407 ± 0.015	4.17 ± 0.29	2.56 ± 0.50	2.50 ± 0.50

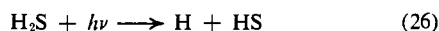
<sup>a</sup> ± 5%. <sup>b</sup> Errors are 95% confidence limits. <sup>c</sup> Errors are 2 × 95% confidence limits.

The integral was evaluated graphically for various values of  $t$  from a smoothed-out plot of  $(OD)_t^2$  against time.  $(OD)_t$  was taken from the smooth lines of Figure 5. The resulting linear equation system was then normalized (to  $\int_0^t f(t)dt = 1$ ).  $(OD)_t$  was plotted against  $\int_0^t (OD)_t^2 dt$  (Figure 6) and analyzed by least mean squares. The resulting values of  $A\epsilon l$  and  $k_{10}/\epsilon l$  together with measured yields of ethylene are summarized in Table II.

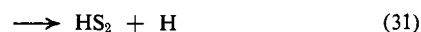
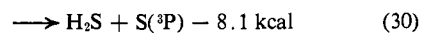
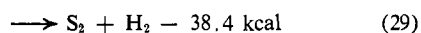
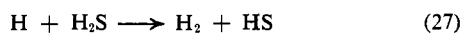
From the data, the extinction coefficient  $1.23 \pm 0.14 \times 10^4 M^{-1} \text{ cm}^{-1}$ , at the peak intensity of the 2713-Å band, can be calculated. This agrees well with the value from the COS study and is to be preferred to the latter since the evaluation of the data was more straightforward than in the COS study. The second-order rate constant,  $k_{10}$ , is again pressure dependent and  $k_{10}/[C_2H_4S]$  is nearly constant. Ethylene episulfide is about 50-fold more efficient as a third body for S<sub>2</sub> recombination than COS or CO<sub>2</sub>, and the gas kinetic collision yield at 19 torr of C<sub>2</sub>H<sub>4</sub>S is ~0.2. Further discussion of the recombination reaction will follow below in the light of additional experimental data.

From the ethylene episulfide study it may be concluded that the long delay time in ground-state S<sub>2</sub> appearance in the COS photolysis is real and not due to possible errors of our delay-time measuring device.

**D. Hydrogen Sulfide.** Since the HS radical is an important product of the reactions of S(<sup>1</sup>D) atoms with hydrogen and methane (*vide infra*), an investigation of the flash photolysis of H<sub>2</sub>S is described first. In this system the HS radical is formed in large concentration as the primary photolysis product which facilitates the study of its reactions. The primary photolytic step in the decomposition<sup>19</sup> is



The following sequence is considered for the mechanism.



The enthalpy of reaction 31 lies between -19 and +16 kcal since  $D(S-S)$  in HS<sub>2</sub> is probably intermediate between  $D(S-S)$  in S<sub>2</sub> and H<sub>2</sub>S<sub>2</sub>.

In the flash photolysis, both S<sub>2</sub> and HS appear

(19) G. Porter, *Discussions Faraday Soc.*, **9**, 60, (1950).

strongly in absorption. In addition, the diffuse band spectrum between 3200 and 3800 Å reported by Porter<sup>19</sup> was also observed. We have confirmed Porter's tentative assignment of this spectrum to the radical HS<sub>2</sub> in a separate study of the flash photolysis of H<sub>2</sub>S<sub>2</sub>. This species probably arises as a result of the abstractive attack of HS on the product H<sub>2</sub>S<sub>2</sub>



as suggested by Tiniakova, *et al.*<sup>20</sup>

Porter assigned a spectroscopic dissociation energy of 102 kcal to this radical. If this corresponds to dissociation of the S-S bond with formation of S in the excited singlet D state, then dissociation into ground-state products would require not more than 76 kcal, which would make reaction 31 energetically unfavorable.

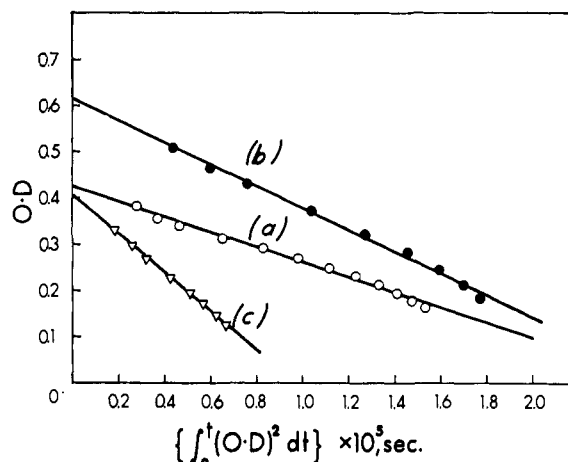


Figure 6. Normalized plots of eq I. Pressure of C<sub>2</sub>H<sub>4</sub>S in torr: (a) 10, (b) 13, (c) 19.

We have measured the intensity of the absorption of both transients S<sub>2</sub> and HS as a function of delay time for 30 torr of H<sub>2</sub>S with added inert gases (H<sub>2</sub> and CO<sub>2</sub>) at various pressures. The results are given in Figures 7-10. The growth portion of the S<sub>2</sub> and the whole of the HS absorption curves have only semi-quantitative significance since they are within the time duration of the photoflash.

The final products were H<sub>2</sub>, sulfur, and probably H<sub>2</sub>S<sub>2</sub>. The latter, however, could not be positively

(20) E. I. Tiniakova, E. K. Krennikova, and B. A. Dolgoplosk, *Zh. Obshch. Khim.*, **28**, 1689 (1958).

identified. A product involatile at  $-139^\circ$  was definitely formed, although it suffered surface decomposition into  $\text{H}_2\text{S}$  and sulfur before its mass spectrum could be taken, precisely the behavior which limited the investigation of the photochemistry of  $\text{H}_2\text{S}_2$ .

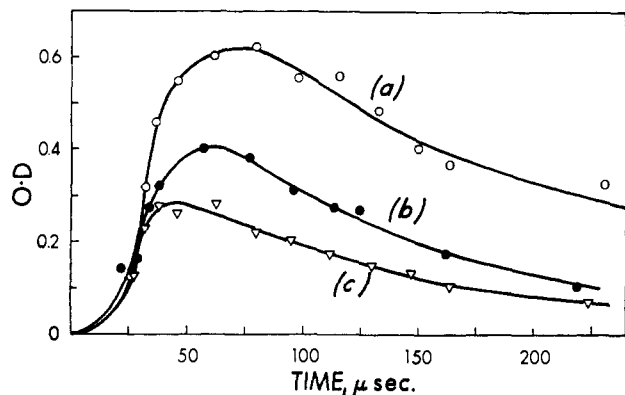


Figure 7. OD's of  $\text{S}_2$  as a function of delay time in the flash photolysis of 30 torr of  $\text{H}_2\text{S}$ : (a) no added gas, (b) +105 torr of  $\text{CO}_2$ , (c) +335 torr of  $\text{CO}_2$ .

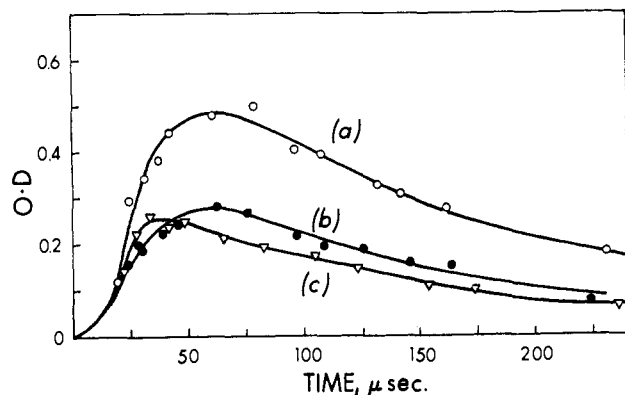


Figure 8. OD's of  $\text{S}_2$  as a function of delay time in the flash photolysis of 30 torr of  $\text{H}_2\text{S}$ : (a) +100 torr of  $\text{H}_2$ , (b) +323 torr of  $\text{H}_2$ , (c) +575 torr of  $\text{H}_2$ .

The effect of pressure increase on the reaction is fourfold: (a) decreases the yields of  $\text{S}_2$ , (b) shifts the position of the maxima to shorter delay times, (c) increases the (0,0) band intensities of the HS absorption while leaving the (1,0) band largely unaffected, and (d) depresses the hydrogen yield. Thus on addition of 335 torr of  $\text{CO}_2$ , the  $\text{H}_2$  yield fell from 3.75 to 3.12  $\mu\text{moles/flash}$  and the maximum  $\text{S}_2$  yield fell from  $\sim 0.9$  to  $\sim 0.4$   $\mu\text{mole}$ .

These observations strongly suggest a competition between reactions 28 and 29, the former passing through a vibrationally "hot"  $\text{H}_2\text{S}_2$  intermediate which requires collisional stabilization. The disproportionation reaction 29 probably cannot be completely suppressed by pressure increase; it occurs even in the low-temperature condensed-phase photolysis.<sup>21</sup> At 30 torr of  $\text{H}_2\text{S}$  without added inert gas the contribution of the dis-

(21) D. A. Stiles, W. J. R. Tyerman, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **44**, 2149 (1966).

proportionation step is about 30%, while with 335 torr of added  $\text{CO}_2$  it is about 15%.

The results of a low-intensity photolysis study<sup>22</sup> gave quantum yields in rough agreement with this picture ( $\phi(\text{H}_2) \sim 1.2$ ) but the pressure dependencies reported are not easy to explain.

The importance of reaction 30 cannot be established by the present study.

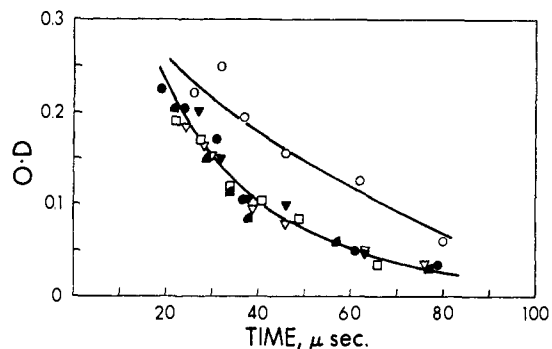


Figure 9. OD's of HS (1,0) band as a function of delay time in the flash photolysis of 30 torr of  $\text{H}_2\text{S}$ : O, no added gas; ●, +100 torr of  $\text{H}_2$ ; ▽, +323 torr of  $\text{H}_2$ ; □, +575 torr of  $\text{H}_2$ ; ■, +105 torr of  $\text{CO}_2$ ; ▼, +335 torr of  $\text{CO}_2$ .

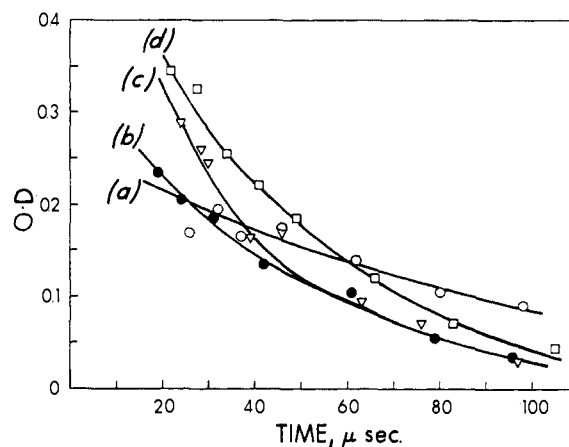


Figure 10. OD's of HS (0,0) band as a function of delay time in the flash photolysis of 30 torr of  $\text{H}_2\text{S}$ : (a) no added gas, (b) +100 torr of  $\text{H}_2$ , (c) +323 torr of  $\text{H}_2$ , (d) +575 torr of  $\text{H}_2$ .

The peculiar pressure dependence of the (0,0) HS absorption intensities (Figure 10) is probably related to the Lorentz broadening of the absorption contour. The (1,0) band is not similarly affected. In this respect it is noteworthy that the (1,0) absorption followed the Beer-Lambert relationship at both low and high pressures, as shown in Figure 11, while for the (0,0) band the value of  $n$  (eq A) changed from about 0.5 for 30 torr of  $\text{H}_2\text{S}$  without added gas to about 0.87 when 460 torr of  $\text{CO}_2$  was added, as seen from Figure 12.

The HS decay rate (Figure 9) is, as expected, faster in the presence of added inert gas. Increase of pressure

(22) B. de B. Darwent and R. Roberts, *Proc. Roy. Soc. (London)*, **A216**, 344 (1953).

above 100 torr, however, seems to have no further effect within experimental error.

The HS data were not treated by the method used for S<sub>2</sub> in section A since extrapolation to zero delay in this system is more difficult. A lower limit for the rate constant  $k_{28} + k_{29}$  is obtained from the half-life of the HS decay in Figure 9. Taking  $[\text{HS}]_{\text{lim}}$  (*i.e.*, in the hypothetical case of  $t = \infty$  and no decay) =  $7 \times 10^{-6} M$ , and  $t_{1/2} = 17 \mu\text{sec}$ , this rate constant becomes  $\sim 8 \times 10^9 M^{-1} \text{sec}^{-1}$ . The collision number is a factor of 10 higher.

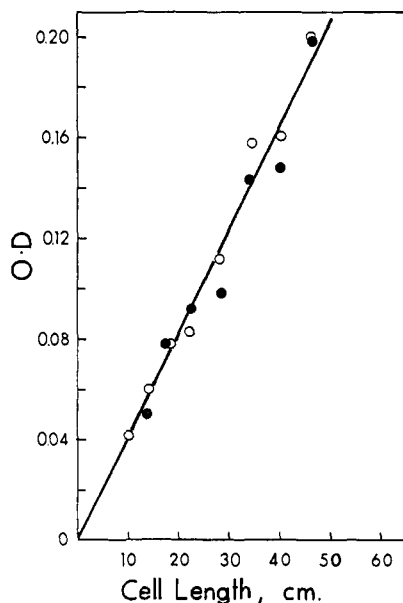


Figure 11. OD of HS (1,0) band as a function of irradiated cell length (delay = 24  $\mu\text{sec}$ ): O, 30 torr of H<sub>2</sub>S with no added gas; ●, 30 torr of H<sub>2</sub>S + 460 torr of CO<sub>2</sub>.

Second-order rate constant data from the H<sub>2</sub>S reaction are tabulated in Table VI. The values are close to those found for the limiting high-pressure cases (*vide infra*). The 30 torr of H<sub>2</sub>S probably accounts for the larger part of the pressure effect for the H<sub>2</sub>S + CO<sub>2</sub> mixtures.

**E. Carbonyl Sulfide with Added Hydrogen.** The same transients as observed in the flash photolysis of H<sub>2</sub>S are seen when mixtures of COS and H<sub>2</sub> are flashed, although the absorption due to HS<sub>2</sub> is very weak. The yield of S<sub>2</sub> (Figure 13) decreases as the H<sub>2</sub> pressure is increased, while the yield of HS either passes through a maximum or reaches a steady level (Table III). The ratio of the absorption intensity in the (0,0) band to that in the (1,0) band, in contrast to the observation in the flash photolysis of H<sub>2</sub>S, was independent of total pressure and equal to about 1.8. H<sub>2</sub>S is a permanent product, and its yield increases steadily with increasing H<sub>2</sub> pressure as seen from Table IV. These features are consistent with reaction scheme eq 33–37, where H<sub>2</sub>S\*

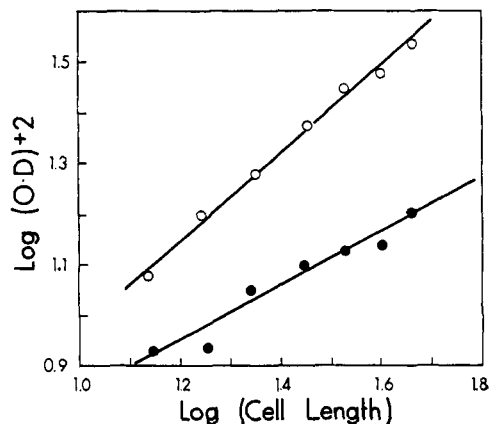
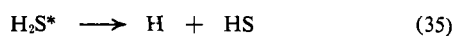
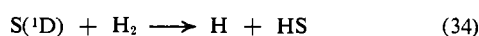
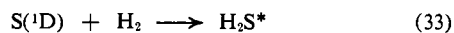


Figure 12. Log-log plot of eq A for (0,0) band of HS (delay = 24  $\mu\text{sec}$ ): O, 30 torr of H<sub>2</sub>S + 460 torr of CO<sub>2</sub>; ●, 30 torr of H<sub>2</sub>S with no added gas.

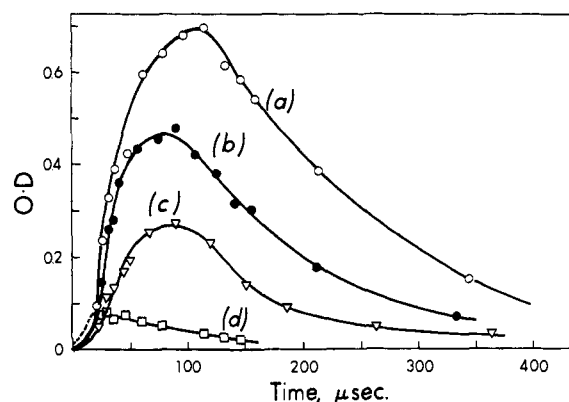
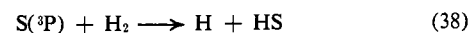


Figure 13. OD's of S<sub>2</sub> and HS as a function of delay time in the flash photolysis of COS–H<sub>2</sub> mixtures.  $p(\text{COS}) = 17$  torr: (a) +124 torr of H<sub>2</sub> (S<sub>2</sub>), (b) +252 torr of H<sub>2</sub> (S<sub>2</sub>), (c) +595 torr of H<sub>2</sub> (S<sub>2</sub>), (d) +124 torr of H<sub>2</sub> (HS, 0,0 band).



denotes a vibrationally excited molecule. The enthalpy change of reaction 33 is  $-97.2$  kcal/mole (for thermalized S(<sup>1</sup>D) atoms) while  $D(\text{HS}-\text{H})$  is only 91.5 kcal/mole;<sup>23</sup> consequently the hot H<sub>2</sub>S molecules undergo secondary cracking reactions. The yields of H<sub>2</sub>S are determined by competition between reactions 4 and 33 and between 35 and 36. Thus the reaction of S(<sup>1</sup>D) atoms with H<sub>2</sub> can best be envisaged as an insertion process in close analogy with the insertive attack of S(<sup>1</sup>D) atoms on paraffinic C–H bonds.

Triplet atoms, on the other hand, would not be expected to react with hydrogen because they do not insert into C–H bonds, and the abstraction reaction



being endothermic to the extent of 21 kcal/mole,<sup>23</sup> would be too slow at room temperature to have significance. This point was proven in auxiliary experi-

(23) (a) H. Mackle and P. A. G. O'Hare, *Tetrahedron*, **19**, 961 (1963); (b) H. Mackle, *ibid.*, **19**, 1159 (1963).



**Table III.** Yields of HS from the Flash Photolysis of COS as a Function of Added H<sub>2</sub> Pressure<sup>a</sup>

H <sub>2</sub> pressure, torr	HS, <sup>b</sup> OD
32.5	0.080
124	0.085
252	0.135
412	0.155
595	0.120

<sup>a</sup> COS pressure = 17 torr. <sup>b</sup> Maximum values observed at shortest delay times.

**Table IV.** Yields of H<sub>2</sub>S from the Flash Photolysis of COS as a Function of Added H<sub>2</sub> Pressure<sup>a</sup>

H <sub>2</sub> pressure, torr	(H <sub>2</sub> S)/(CO) <sub>0</sub> <sup>b</sup>
88	0.27
180	0.35
370	0.45
550	0.64

<sup>a</sup> COS pressure = 20 torr. <sup>b</sup> 2(CO)<sub>0</sub> is the yield of CO per flash in the absence of H<sub>2</sub>.

ments whereby the addition of a large excess of carbon dioxide to the system caused a severe reduction in the HS yields.

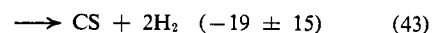
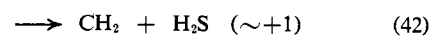
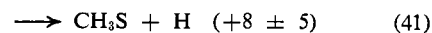
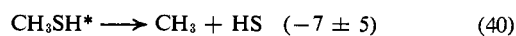
For the rate constant ratio of S(<sup>1</sup>D) atom abstraction from COS (eq 4) to insertion into H<sub>2</sub> (eq 33), an upper limit of <12 can be deduced from the data in Table IV. Furthermore, since in going from *ca.* 80 to 400–600 torr of H<sub>2</sub>, both the HS and H<sub>2</sub>S yields show a two-fold or larger increase, at the lower pressure the scavenging of the S(<sup>1</sup>D) atoms by H<sub>2</sub> cannot be more than 50%. This indicates a lower limit for the above ratio of *ca.* 4. The rate of formation of HS is rapid. The maximum in the OD *vs.* delay time curve, as seen in Figure 13, occurs at less than 30 μsec. Hence the rate constant of reaction 33 is not less than 10<sup>8</sup> M<sup>-1</sup> sec<sup>-1</sup>, and *k*<sub>4</sub> cannot, therefore, be less than 4 × 10<sup>8</sup> M<sup>-1</sup> sec<sup>-1</sup>. Assuming a steric factor of not greater than 0.5, the upper limit for the activation energy of reaction 4 becomes 3 kcal/mole.

It is important to note from Figure 13 that the maxima of the S<sub>2</sub> absorption curves occur at considerably longer delay times [(a) 110, (b) and (c) 90 μsec] than that of the HS absorption. The locations of the maxima are determined by the rates of formation and decay of the respective species. The decay rates can be estimated directly from the descending portions of curves a–d, and they are all equal within a factor of 2. This is in agreement with estimates of these rates from rate constants (*vide supra*) and concentration ratios ([S<sub>2</sub>]:[HS] > 3:1 at 124 torr of H<sub>2</sub>). Therefore, if the rate-controlling process for the appearance of both species involves the common precursor, the S(<sup>1</sup>D) atom, reacting at similar rates with both COS and H<sub>2</sub>, the maxima of S<sub>2</sub> and HS should closely coincide. The existence of this time lag between S(<sup>1</sup>D) atom disappearance and S<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) formation lends strong support to the postulate that, in reaction 4, the S<sub>2</sub> molecule is formed in one of its low-lying metastable singlet states.

**F. Carbonyl Sulfide with Added Methane.** The transients observed in this case are S<sub>2</sub>, HS, and CS, the latter appearing only very faintly. Optical densities *vs.* delay time plots for the first two species are given in Figures 14 and 15, respectively. In previous studies it has been shown that the initial primary product of the reaction of S(<sup>1</sup>D) atoms with methane is a vibrationally excited mercaptan, formed in an insertion-type process<sup>24</sup>



The accompanying enthalpy change is *ca.* 83 kcal/mole, and the hot methyl mercaptan undergoes secondary fragmentation [ $\Delta H^\circ$  values (kcal/mole) given in parentheses]



The reaction enthalpies<sup>23,25</sup> are maximum values for thermalized reactants. In fact, the sulfur atoms may possess excess translational energies up to 12 kcal/mole, and reactions 40–43 may all occur. The significance of reactions 40 and 41 and the presence of CH<sub>3</sub>S and CH<sub>3</sub> radicals in the system were indicated by the appearance of dimethyl sulfide, ethane, and dimethyl disulfide among the reaction products of the earlier low-intensity studies.<sup>24</sup> In the present study, in addition to the HS and CS transients, the final product H<sub>2</sub>S was also detected and measured. The variation of the concentration of HS radicals with methane pressure suggests that reaction 44 may occur in addition to 39.



Relative yields of H<sub>2</sub>S as a function of methane pressure are listed in Table V. In the low-pressure

**Table V.** Yields of H<sub>2</sub>S from the Flash Photolysis of COS as a Function of Added CH<sub>4</sub> Pressure<sup>a</sup>

CH <sub>4</sub> pressure, torr	(H <sub>2</sub> S)/(CO) <sub>0</sub> <sup>b</sup>
18	0.44
68	0.26
118	0.26
258	0.25
500	0.04

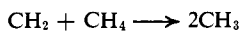
<sup>a</sup> COS pressure = 20 torr. <sup>b</sup> 2(CO)<sub>0</sub> = yield of CO per flash in absence of CH<sub>4</sub>.

region H<sub>2</sub>S seems to be the main reaction product, but its yield falls off with increasing pressure, indicating a hot precursor in agreement with the scheme proposed. For energetic reasons, the other product of the frag-

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

(25) W. B. de More and S. W. Benson, *Advan. Photochem.*, **2**, 226 (1964).

mentation, methylene, is probably formed in its ground triplet  $B_1$  state since the lowest estimate of the first excited  $^1A_1$  state is 9.8 kcal/mole above the ground triplet level.<sup>26</sup> The possible ensuing reactions are



From combination of the data in Table V with that from the previously reported low-intensity study, the rate constant ratio for abstraction (4) to insertion into methane (39) is unity, which places a lower limit of  $4 \times 10^8 M^{-1} \text{cm}^{-1}$  for the absolute rate constant of the

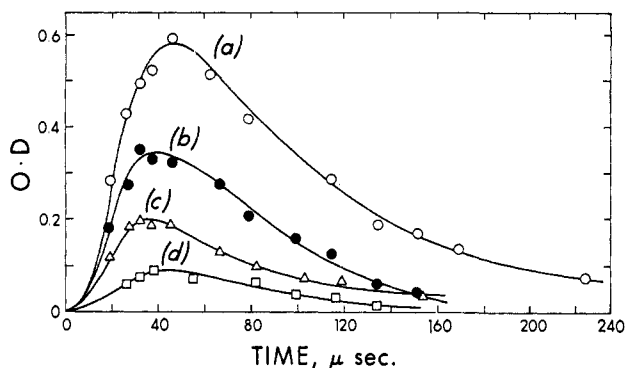
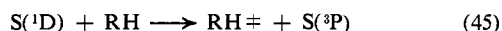


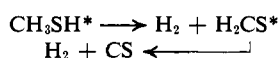
Figure 14. OD's of  $S_2$  as a function of delay time in the flash photolysis of COS- $\text{CH}_4$  mixtures.  $p(\text{COS}) = 31$  torr: (a) +30 torr of  $\text{CH}_4$ , (b) +70 torr of  $\text{CH}_4$ , (c) +290 torr of  $\text{CH}_4$ , (d) +590 torr of  $\text{CH}_4$ .

insertion step 39. The  $S_2$  yields in Figure 14 are also compatible with a reactivity ratio of unity. The earlier value<sup>24</sup> of 17.8 for  $k_4/k_{39}$  was derived from a product summation which did not include the  $\text{H}_2\text{S}$  yields. With the higher paraffins ( $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , etc.), fragmentation does not occur, and the rate ratios could be determined more accurately. These values were about 2. Thus methane appears to be slightly more reactive than its higher homologs, which fact may perhaps be related to the lower efficiency of this molecule in bringing about the collisional relaxation of  $S(^1D)$  atoms to the ground state



which has been shown to occur parallel to insertion with the higher paraffins and at a rate of about 0.6–0.7 of that of the insertion reaction. Both the previous low-intensity and the present flash-photolysis studies (Figure 14) have indicated an exceptionally low rate for reaction 45 with methane.

The reaction giving rise to CS formation (eq 43) is important only at low pressures which implies a hot molecule precursor with a relatively long lifetime. It may proceed in two steps



(26) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964.

As with hydrogen, the maxima in the HS absorption intensities always appears at shorter delay times than those of the  $S_2$  absorption intensities, further strengthening the argument in favor of initial formation of an excited metastable  $S_2$  molecule in reaction 4. The time delay between the two maxima, however, is short, indicating a greater efficiency as a quencher of the excited  $S_2^*$  molecules for methane than COS.

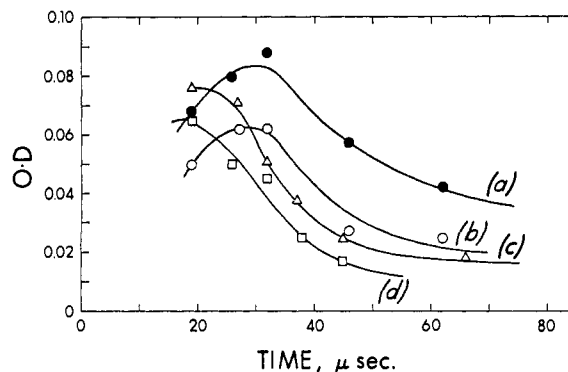


Figure 15. OD's of HS (0,0 band) as a function of delay time in the flash photolysis of COS- $\text{CH}_4$  mixtures.  $p(\text{COS}) = 31$  torr: (a) +30 torr of  $\text{CH}_4$ ; (b) +70 torr of  $\text{CH}_4$ ; (c) +290 torr of  $\text{CH}_4$ ; (d) +590 torr of  $\text{CH}_4$ .

The measured values of the second-order rate constants for  $S_2$  decay in the presence of various chaperons are summarized in Table VI. The highest value is  $8 \times 10^{10} M^{-1} \text{sec}^{-1}$ , and the convergence limit is prob-

Table VI. Summary of Second-Order Rate Constant Values for  $S_2$  Decay ( $k_{10}$ )

Pressure, torr	Added gas	Pressure, torr	$k_{10}^a \times 10^{-10} M^{-1} \text{sec}^{-1}$
COS			
17	None	...	$0.041 \pm 0.009$
65	None	...	$0.089 \pm 0.022$
192	None	...	$0.31 \pm 0.08$
410	None	...	$0.43 \pm 0.18$
17	$\text{CO}_2$	600	$0.53 \pm 0.14$
17	$\text{H}_2$	32	$0.7 \pm 0.3$
410	$\text{H}_2$	187	$1.8 \pm 0.4$
31	$\text{H}_2$	375	$4.0 \pm 1.2$
17	$\text{H}_2$	412	$3.3 \pm 0.8$
17	$\text{H}_2$	595	$6.6 \pm 2.0$
31	$\text{CH}_4$	30	$4.0 \pm 1.4$
31	$\text{CH}_4$	155	$5.9 \pm 3.7$
31	$\text{CH}_4$	290	$8.0 \pm 5.1$
$\text{C}_2\text{H}_4\text{S}$			
10	None	...	$1.01 \pm 0.26$
13	None	...	$1.46 \pm 0.35$
19	None	...	$2.56 \pm 0.50$
$\text{H}_2\text{S}$			
30	$\text{H}_2$	575	$4.5 \pm 1.4$
30	$\text{CO}_2$	105	$3.2 \pm 0.7$
30	$\text{CO}_2$	335	$4.9 \pm 1.7$

<sup>a</sup> 95% confidence limits + error in  $\epsilon(S_2)$ .

ably a little less than the gas kinetic collision number,  $12 \times 10^{10} M^{-1} \text{sec}^{-1}$ . This would be consistent with the energy-transfer mechanism for the chaperon effect,

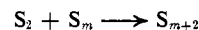
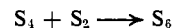
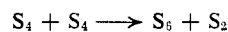
*i.e.*, in which the vibrationally hot  $S_4$  molecule formed in reaction 10 is collisionally stabilized in the presence of excess inert gas.<sup>27</sup>

A brief study of the kinetics of  $S_2$  recombination in the flash photolysis of  $CS_2$  has been reported by Callear.<sup>28</sup> Because the  $S_2$  buildup in the system was slow (about an order of magnitude slower than in our studies), it was permissible to neglect the finite length of flash duration and to arrive at an explicit formula for the time dependence of  $S_2$  concentration (assuming that  $S_2$  is formed by the recombination of S atoms). The formula correctly described the kinetics at a fixed pressure of inert gas ( $N_2$ ) but was inadequate in describing the effect of pressure variation. This was attributed to complicating processes such as the reaction of atomic S with  $S_2$  or higher sulfur polymers.

(27) M. Eusuf and K. J. Laidler, *Trans. Faraday Soc.*, **59**, 2750 (1963).

(28) A. B. Callear, *Proc. Roy. Soc. (London)*, **A276**, 401 (1963).

In a concurrent study of the flash photolysis of COS with kinetic mass spectrometry we verified the presence of large concentrations of  $S_6$ , along with some  $S_7$  species in flashed COS. These observations require additional polymerization steps in the mechanism, *e.g.*



The observed second-order kinetics of the  $S_2$  decay may be, therefore, to some extent fortuitous and the measured rate constant values should be regarded as upper limits for reaction 10.

**Acknowledgments.** The authors are thankful to Imperial Oil Limited and the National Research Council of Canada for financial support.

## Kinetic Study of the Reaction between Chlorine Dioxide and Potassium Iodide in Aqueous Solution

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*Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland. Received October 14, 1966*

**Abstract:** The rate of the reaction between chlorine dioxide and potassium iodide in aqueous solution was investigated spectrophotometrically by using a rapid-mixing syringe. Two distinctly different rates were observed in the pH range 5.5–8.5. The first reaction corresponds to the rapid formation of the intermediate  $[ClO_2I^-]$ . The second corresponds to the decomposition of the intermediate, which results in the formation of  $ClO_2^-$  and  $I_2$ . From the rate of the reaction as a function of temperature between 5 and 35°, activation enthalpies of 7.4 and 0.8 kcal/mole, respectively, were calculated for the two reactions.

The reactions and interactions of aqueous solutions of chlorine dioxide and sodium chlorite have recently been under investigation in this laboratory.<sup>1–6</sup> A common intermediate of the type  $[Cl_2O_2]$  which can act either as an oxidizing or reducing agent<sup>7</sup> has been suggested.<sup>8</sup> The oxidation of iodide by chlorine dioxide was reported by Bray<sup>9</sup> where it was used in the analytical determination of chlorine dioxide. The

purpose of this paper is to report on the intermediate formed in the reaction between chlorine dioxide and potassium iodide. This intermediate appears to have properties very similar to those reported for the  $[Cl_2O_2]$  intermediate.

### Experimental Section

All of the chemicals used were of analytical grade and were purified by techniques reported previously.<sup>1,4,6</sup> Chlorine dioxide was prepared from potassium chlorate and oxalic acid with the addition of small amounts of 4 M  $H_2SO_4$ .<sup>3</sup> The reaction was carried out in an all-Pyrex vessel which was shielded from light with aluminum foil. The liberated chlorine dioxide was passed through solutions of sodium carbonate to remove chlorine, hydrogen chloride, and carbon dioxide; the purified chlorine dioxide was collected in distilled water at ice temperature. Sodium perchlorate was prepared from sodium carbonate and perchloric acid and its concentration was determined as reported previously.<sup>4</sup> For some experiments sodium iodide was used in place of potassium iodide to minimize precipitation of potassium perchlorate.

**Procedure.** The aqueous solutions of  $I_2$  and  $I_3^-$  interfere with the spectrophotometric determination of chlorine dioxide. Therefore,

(1) F. Feldman and G. Gordon, *Inorg. Chem.*, **3**, 1728 (1964).

(2) G. Gordon and K. Kern, *ibid.*, **3**, 1055 (1964).

(3) D. M. H. Kern and G. Gordon, "Theory and Structure of Complex Compounds," Pergamon Press, New York, N. Y., 1964, pp 655–660.

(4) P. H. Tewari and G. Gordon, *J. Phys. Chem.*, **70**, 200 (1966).

(5) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).

(6) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966).

(7) For example, in aqueous solutions when sodium chlorite and sodium hypochlorite are mixed, the reaction mechanism is consistent with an intermediate of the type  $[Cl_2O_2]$  which can either disproportionate in concentrated solution to form chlorine dioxide and chlorine or in dilute solution to form chlorate and chloride. A similar intermediate is proposed in the disproportionation of chlorous acid and in the reaction between uranium(IV) and sodium chlorite.

(8) H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).

(9) W. C. Bray, *Z. Physik. Chem.*, **54**, 575 (1906).