# Photochemistry of Low-Temperature Matrices Containing Carbonyl Sulfide: Reactions of Sulfur Atoms with the Phosphorus Trihalides PF<sub>3</sub> and PCl<sub>3</sub> and the Hydrocarbons $CH_4$ , $C_2H_4$ , and $C_2H_2$

## Michael Hawkins,<sup>†</sup> Matthew J. Almond, and Anthony J. Downs<sup>\*</sup>

Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England (Received: February 19, 1985)

Exposure of a solid argon matrix containing the molecules OCS and PX<sub>3</sub> (X = F or Cl) at ca. 20 K to broad-band ultraviolet radiation leads to the formation of CO and the corresponding thiophosphorus(V) halides SPX<sub>3</sub>, as witnessed by the infrared spectrum of the matrix. Photolysis of a solid methane matrix containing OCS at 13-20 K on exposure to radiation with wavelengths near 230 nm gives rise to CO, methanethiol, CH<sub>3</sub>SH, thioformaldehyde, H<sub>2</sub>C=S, and carbon disulfide, CS<sub>2</sub>, as the only products to be detected by their infrared spectra. Yet there is no sign of either  $CH_3SH$  or  $H_2C=S$  on photolysis of OCS in a CH<sub>4</sub>-doped argon matrix with the composition Ar:CH<sub>4</sub>:OCS = 100:20:1. Evidently the photolysis of OCS generates <sup>1</sup>D sulfur atoms which add to an adjacent  $CH_4$  molecule with the formation of a vibrationally activated intermediate [ $CH_4S$ ]\*; this relaxes to give CH<sub>3</sub>SH or decomposes to give H<sub>2</sub>C=S. Similar experiments have been carried out with solid argon matrices including OCS and either  $C_2H_4$  or  $C_2H_2$ . In the presence of  $C_2H_4$  there is no hint of C-H insertion; instead the

 $C_2H_4$  undergoes sulfur atom addition at the double bond to give thiirane,  $CH_2CH_2S$ , as the sole product to be identified by its infrared spectrum. By contrast, C<sub>2</sub>H<sub>2</sub> yields thioketene, H<sub>2</sub>C==C==S, ethynethiol, HC==CSH, and carbon disulfide,

CS<sub>2</sub>, as the main products, as well as thiirene, CH=CHS, as a minor product. The response of the hydrocarbon molecules in argon matrices can be interpreted in terms of the diffusion and reaction of ground-state <sup>3</sup>P sulfur atoms but not of <sup>1</sup>D sulfur atoms which are too short-lived to undergo significant migration. It appears that <sup>3</sup>P sulfur atoms react with both  $C_2H_4$  and  $C_2H_2$  to yield a triplet diradical: that derived from  $C_2H_4$  favors cyclization, whereas that derived from  $C_2H_2$  rearranges preferentially to  $H_2C=C=S$  and this in turn enters into secondary reactions to give HC=CSH and  $CS_2$ .

#### I. Introduction

Matrix isolation can be exploited to engineer bimolecular changes of the type

$$AX + B \rightarrow A + BX$$

in which an atom X is transferred from one reaction center to another. Such a process, normally induced by photolysis, may involve the intermediacy of the free X atom or it may proceed via the photolysis of a complex formed by the parent molecules, as in the reactions between ozone and  $PF_{3}$ ,<sup>1</sup> AsF<sub>3</sub>,<sup>1</sup> or ICl.<sup>2</sup> The method admits the possibility of reactions involving atoms in electronically excited as well as ground states, e.g.

> $N_2 + O(^1D) \rightarrow N_2O$  ref 3  $E + S(^{1}S) \rightarrow ES$  (E = Ar, Kr, or Xe) ref 4

In contrast to the many examples of oxygen atom transfer known to take place in low-temperature matrices, 1.2.5 there are still relatively few reports of analogous reactions involving sulfur atoms.<sup>5</sup> The reactions of sulfur atoms with organic substrates in the gas phase may be well documented,<sup>6</sup> but the only matrix reactions to be investigated to data are those with sulfur and oxygen atoms<sup>7</sup> or with the molecules  $O_2^{7-9}$  and NO.<sup>8</sup> As part of a study to explore the scope for controlled synthesis and the mechanisms of matrix reactions involving sulfur atoms,<sup>8,10</sup> we report here some matrix reactions of sulfur atoms with the molecules  $PX_3$  (X = F or Cl) and with the hydrocarbons  $CH_4$ ,  $C_2H_4$ , and  $C_2H_2$ . The course of the reactions has been charted by measuring the infrared spectra of the matrices, and the products thus identified are discussed in relation to the light they shed on the mechanisms of the primary and any secondary reactions.

We have chosen as the source of sulfur atoms in our matrices carbonyl sulfide, OCS. This compound has the advantage that its photolytic behavior in a matrix environment is better documented than that of any other potential precursor.<sup>7-10</sup> Of the sulfur atoms generated by photolysis of gaseous carbonyl sulfide at wavelengths in the region 214-254 nm, about 70% are estimated to be in the electronically excited <sup>1</sup>D state and the rest in the

ground (<sup>3</sup>P) state, the overall quantum yield being 1.81;<sup>11</sup> no <sup>1</sup>S

- (2) Hawkins, M.; Andrews, L.; Downs, A. J.; Drury, D. J. J. Am. Chem. Soc. 1984, 106, 3076.
- (3) Walker, N.; Tevault, D. E.; Smardzewski, R. R. J. Chem. Phys. 1978, 69, 564.

09, 564.
(4) Taylor, R. V.; Walker, W. C. Appl. Phys. Lett. 1979, 35, 359.
(5) Perutz, R. N. Chem. Rev. 1985, 85, 77.
(6) See for example: (a) Gunning, H. E.; Strausz, O. P. Adv. Photochem.
1966, 4, 143. (b) Gunning, H. E. In "The Chemistry of Sulfides"; Tobolsky, A. V., Ed.; Interscience: New York, 1968; p 23. (c) Green, M.; Lown, E. M.; Strausz, O. P. J. Am. Chem. Soc. 1984, 106, 6938.
(7) Cook, G.; Krogh, O. D. J. Chem. Phys. 1981, 74, 841 and references cited therein

cited therein.

(8) Hawkins, M.; Downs, A. J. J. Phys. Chem. 1984, 88, 1527, 3042.
(9) Tso, T.-L.; Lee, E. K. C. J. Phys. Chem. 1984, 88, 2781.
(10) Hawkins, M. D.Phil. Thesis, University of Oxford, 1981.
(11) Sidhu, K. S.; Csizmadia, I. G.; Strausz, O. P.; Gunning, H. E. J. Am.

- Chem. Soc. 1966, 88, 2412.
  - (12) Strausz, O. P. Pure Appl. Chem., Suppl. 1971, 4, 165.
  - (13) Gollnick, K.; Leppin, E. J. Am. Chem. Soc. 1970, 92, 2217.

(14) Brom, J. M., Jr.; Lepak, E. J. Chem. Soc. 1970, 92, 2217.
 (14) Brom, J. M., Jr.; Lepak, E. J. Chem. Phys. Lett. 1976, 41, 185.
 Fournier, J.; Lalo, C.; Deson, J.; Vermeil, C. J. Chem. Phys. 1977, 66, 2656.
 Taylor, R. V.; Walker, W. C.; Monahan, K. M.; Rehn, V. J. Chem. Phys. 1980, 72, 6743.

sulfur atoms are generated in these conditions. <sup>1</sup>D<sub>2</sub> sulfur atoms, which may be distinguished chemically from <sup>3</sup>P sulfur atoms, are metastable and have the relatively long radiative lifetime of 28.0 s in the gas phase where they can survive many collisions before decaying. By contrast, photolysis of OCS in the condensed phase at wavelengths near 254 nm results in an increase in the proportion of  ${}^{3}P$  sulfur atoms.<sup>6,12</sup> This has been cited<sup>11</sup> as evidence for intersystem crossing to an excited triplet state which correlates with <sup>3</sup>P sulfur atoms, but the depletion of <sup>1</sup>D sulfur atoms may reflect no more than the increased efficiency of collisional deactivation in the condensed phase.<sup>13</sup> The electronic states of the sulfur atoms produced on photolysis of matrix-isolated OCS have been identified positively in only one case; vacuum-ultraviolet radiation ( $\lambda$  = ca. 147 nm) has been shown to give <sup>1</sup>S sulfur atoms which have been characterized by a luminescence near 780 nm resulting from their decay to the <sup>1</sup>D state.<sup>14</sup> Photolysis at wavelengths greater than 200 nm has been assumed to give rise to <sup>3</sup>P sulfur atoms as the only reactive species present in the matrix, any <sup>1</sup>D atoms being quenched by interaction with the matrix.

<sup>(1)</sup> Downs, A. J.; Gaskill, G. P.; Saville, S. B. Inorg. Chem. 1982, 21, 3385. Gaskill, G. P. D.Phil. Thesis, University of Oxford, 1978.

<sup>&</sup>lt;sup>†</sup> Present address: Sevenoaks School, Sevenoaks, Kent TN13 1HU, U.K.

There is evidence to support this view: photolysis and annealing of matrix-isolated OCS results in thermoluminescence in three regions of the visible spectrum. Two of these systems have been attributed<sup>15,16</sup> to emission from the S<sub>2</sub> molecule in an excited  $c^{1}\Sigma_{u}$ state formed in the diffusion-controlled reaction of two sulfur atoms. This state correlates directly with two sulfur atoms each in the <sup>3</sup>P ground state. The third and strongest emission, observed in thermoluminescence and laser- or mercury arc-excited fluorescence, is considered to originate in S<sub>2</sub> molecules in the  $B^3\Sigma_{\mu}$ excited state which correlates not with  $({}^{3}P)S + ({}^{3}P)S$  but with  $({}^{3}P)S + ({}^{1}D)S$ . It is possible that emission from the  $B''{}^{3}\Pi_{u}$  state, which correlates with  $({}^{3}P)S + ({}^{3}P)S$ , also contributes to the luminescence and that it is associated with the  $B^{3}\Sigma_{u}^{-}$  state via a mechanism involving intersystem crossing.<sup>15,16</sup> Thus the full range of luminescence has been rationalized on the basis that the predominant active species are sulfur atoms in their <sup>3</sup>P ground state, although <sup>1</sup>D sulfur atoms may also be implicated to some extent. One of the ambitions of the present studies was to determine whether <sup>1</sup>D sulfur atoms play any role in the matrix photochemistry of OCS.

## **II. Experimental Section**

Apparatus. The cryogenic equipment used in our laboratory has been described elsewhere.<sup>8,10</sup> Matrices were deposited on a CsI window cooled to 13–20 K by means of a Displex refrigerator (Air Products, Model CS 202) inside a shroud maintained at a pressure less than  $10^{-7}$  torr. The temperature of the window was measured with a chromel vs. iron-doped gold thermocouple or with a hydrogen vapor bulb, and was varied by adjusting the voltage applied to a 20-W heater wound around the second stage of the refrigerator.

The infrared spectra of the matrices were recorded in the range 4000–200 cm<sup>-1</sup> with either a Perkin-Elmer Model 225 or a Perkin-Elmer Model 580A spectrophotometer. The wavenumbers of sharp bands were reproducible within 0.4 cm<sup>-1</sup>, those of the broader bands which were typical of the hydrocarbon-containing matrices, within 1-2 cm<sup>-1</sup>. The spectral resolution varied from ca. 0.5 to 1 cm<sup>-1</sup>.

Sample photolysis was carried out with the radiation derived from one of three sources: (i) a Philips HPK 125-W mediumpressure mercury arc, (ii) a Hanovia "Uvitron" 100-W highpressure mercury arc, or (iii) a Philips 070 T 25-W cadmium arc. A 2- or 4-cm water filter served to reduce the amount of infrared radiation reaching the matrix when one of the mercury arcs was in use. Whereas the primary UV emission of a mercury arc is in the region of 254 nm, that of a cadmium arc is at 228 nm.<sup>17</sup>

Chemicals. Argon, methane, and ethene gas (grade "X") were used as received from the British Oxygen Co. Carbonyl sulfide, as supplied by Matheson, and ethyne, as supplied by British Oxygen, were each purified by fractionation in vacuo. Methane- $d_4$ (99 atom % deuterium) was used as supplied by Merck, Sharp and Dohme. Ethene- $d_4$  was prepared by the dehydration of ethanol- $d_6$  (B.D.H., 99 atom % deuterium) under the action of sulfuric acid- $d_2$  (B.D.H., 99 atom % deuterium); after purification by fractionation in vacuo, the product was shown by its infrared spectrum to contain at least 92% of the isotopomer C<sub>2</sub>D<sub>4</sub>.

**Procedure.** Standard manometric techniques were used to prepare gaseous mixtures with matrix gas:OCS proportions in the order of 100:1. Most of the experiments involved pulsed deposition of the matrix sample<sup>18</sup> with a window temperature of ca. 20 K. With the OCS/C<sub>2</sub>H<sub>2</sub> system, however, it was more advantageous to deposit slowly an argon matrix including these molecules at 20 K and to photolyze the sample *during*, as well as after, de-



Figure 1. Regions 2600–1900 and 1000–250 cm<sup>-1</sup> in the infrared spectrum of an Ar matrix deposited at 20 K and containing 1% OCS and 1% PF<sub>3</sub>: (A) after deposition; (B) after irradiation with the unfiltered emission of an Hg arc for 55 min; (C) after annealing the matrix to 38 K for 10 min.

position; this increased the yield of photoproducts.

### **III. Results and Discussion**

(a) Photochemistry of the Systems  $OCS/PF_3$  and  $OCS/PCl_3$ . The infrared spectrum of an argon matrix containing OCS and  $PF_3$  in the proportions Ar:OCS:PF\_3 = 100:1:1, as illustrated in Figure 1, consisted simply of a superposition of the bands associated with each of the molecules OCS and PF<sub>3</sub>. Whereas mixtures of O<sub>3</sub> and PF<sub>3</sub> show additional infrared bands which originate in a loosely bound complex O<sub>3</sub>·PF<sub>3</sub>,<sup>1</sup> there was no sign that the vibrational properties of PF3 or OCS are perturbed by their coexistence in the same matrix. We note that the intense doublet near 850 cm<sup>-1</sup> due to the antisymmetric P-F stretching mode  $\nu_3$ of PF<sub>3</sub> displayed on its low-frequency flank a broad shoulder attributable to aggregates  $[PF_3]_n^{18}$  Photolysis of the matrix using full Hg-arc emission produced a simultaneous decay of the bands associated with OCS and PF<sub>3</sub>. As shown in Figure 1 and detailed in Table I, this was accompanied by the appearance and growth of a new absorption near 2140 cm<sup>-1</sup> characteristic of CO<sup>8,19</sup> and of five prominent absorptions near 976, 942, 692, 438, and 405 cm<sup>-1</sup> which, on the evidence of their growth pattern, had a common origin. That this origin is the molecule SPF<sub>3</sub> we conclude on the strength of the close match in frequencies and relative intensities between the features which grew on photolysis and those characterizing the infrared spectrum of the gaseous molecule.<sup>20</sup> The yield of SPF<sub>3</sub> was quite high. Thus, changes in the intensities of the bands due to OCS and PF3 after 55-min photolysis indicated that the matrix had been depleted by about 24% in PF, and 60% in OCS. Hence it appears that some 40% of the sulfur atoms generated by photolysis of the OCS had reacted to form SPF<sub>3</sub> in accordance with the overall process

$$OCS + PF_3 \xrightarrow{n\nu} OC + SPF_3 \tag{1}$$

In addition to the bands attributable to the formation of CO and monomeric  $SPF_3$ , photolysis resulted in the development of weak bands at ca. 1530, 1400, 908, 676, and 471 cm<sup>-1</sup>. The feature

<sup>(15)</sup> Lee, Y.-P.; Pimentel, G. C. J. Chem. Phys. 1979, 70, 692.

<sup>(16)</sup> Lee, Y.-P.; Pimentel, G. C. J. Chem. Phys. 1978, 69, 3063. Pimentel,
G. C. Ber. Bussenges. Phys. Chem. 1978, 82, 2. Tevault, D. E.; Smardzewski,
R. R. J. Chem. Phys. 1978, 69, 3182. Bondybey, V. E.; English, J. H. J.
Chem. Phys. 1980, 72, 3113.

<sup>(17)</sup> Meggers, W. F.; Corliss, C. H.; Scribner, B. F. "Tables of Spectral-Line Intensities, Part I", 2nd ed.; National Bureau of Standards: Washington, D.C., 1975; Monograph 145.

<sup>(18)</sup> Perutz, R. N.; Turner, J. J. J. Chem. Soc., Faraday Trans. 2, 1973, 69, 452.

<sup>(19)</sup> Dubost, H. Chem. Phys. 1976, 12, 139.

<sup>(20)</sup> Müller, A.; Krebs, B.; Niecke, E.; Ruoff, A. Ber. Bunsenges. Phys. Chem. 1967, 71, 571.

TABLE I: Wavenumbers ( $\tilde{\nu}$ ) and Assignments of Infrared Absorptions between 2500 and 200 cm<sup>-1</sup> Exhibited before and after Photolysis by Ar Matrices Containing OCS and PF<sub>3</sub> at ca. 20 K

initial deposit		bands appearing a	after photolysis <sup>a</sup>	assignment		gaseous molecule
$\widetilde{\nu}$ , b cm <sup>-1</sup>	intens <sup>c</sup>	$\widetilde{\nu}, b \text{ cm}^{-1}$	intens <sup>c</sup>	molecule	vibrat mode	$\widetilde{\nu}$ , cm <sup>-1</sup>
		2141.6 <sup>d</sup>	S	[CO], <sup>e</sup>	ν(C≡O)	·····
		2137.5 <sup>d</sup>	S	CO <sup>e</sup>	ν(C≡O)	2143.3 <sup>e</sup>
2106.2 <sup>d</sup>	W			OCS	$4\nu_2$	2104.8 <sup>f</sup>
$2059.0^{d}$	m			)	-	
$2054.1^{d}$	m			$\left[ OCS \right]_n^g$	v(C=O)	
2052.3 <sup>d</sup>	m			)		_
2049.3 <sup>d</sup>	vs			OCS	$\nu_3(\Sigma^+)$	$2062.2^{f}$
$2044.8^{d}$	m			)	-	
$2041.7^{d}$	w			$\left[ OCS \right]_{n}^{g}$	$\nu$ (C=O)	
2039.8 <sup>d</sup>	ms			)		
2033.1 <i>d</i>	m			$[OCS]_n$ ?	$\nu$ (C=O)	
2013.5 <sup>d</sup>	w			18OCS	$\nu_3(\Sigma^+)$	$2026.2^{f}$
1996.8 <sup>d</sup>	mw			O <sup>13</sup> CS	$\nu_3(\Sigma^+)$	2009.3 <sup>f</sup>
1885	w, br			OCS	$\nu_1 + 2\nu_2$	$1892.2^{f}$
1710 <b>.9<sup>d</sup></b>	w			OCS	$2\nu_1$	$1711.0^{f}$
		1526.0	w	CS <sub>2</sub>	$\nu_{3}(\Sigma_{u}^{+})$	1532,5 <sup>h</sup>
		1410	vw, br	OPF <sub>3</sub>	$v_1(a_1)$	1417 <sup>i</sup>
1048.3 <sup>d</sup>	mw			OCS	$2\nu_2$	$1047.0^{f}$
		975.6	VS	SPF <sub>3</sub>	$v_1(a_1)$	981 <sup>j</sup>
		944.3	sh	COF	1. (a)	04 <i>5</i> j
		942.3	S	§ 5113	$\nu_4(e)$	<b>945</b>
		908.4	vw	$S[PF_3]_n$ ?	$\nu(P-F)$	
885.1 <sup>d</sup>	VS			PF	n (a)	897 <sup>i</sup>
877.9 <sup>d</sup>	sh			<b>1</b> 1 3	$\nu_1(a_1)$	0,52
850.9 <sup>a</sup>	VS			PF + OCS	$\nu_3(e)$	860'
849.3 <sup>a</sup>	sh			, 11 3 + 000	$\nu_1(\Sigma^+)$	859.0 <sup>7</sup>
840-830	s, br	,		$[PF_3]_n^l$	ν( <b>P-</b> F)	,
		692.0 <sup>a</sup>	wm	SPF <sub>3</sub>	$\nu_2(a_1)$	695 <sup>j</sup>
		675.1 <sup>a</sup>	W	coordinated $S_2$ ?	$\nu$ (S-S)?	
520.0	m			OCS	$\nu_2(\Pi)$	520.4
485.4	8			PF <sub>3</sub>	$v_{2}(a_{1})$	487'
		471	VW	OPF <sub>3</sub>	$\nu_{5}(e)$	472
		438.1	m	SPF <sub>3</sub>	$\nu_{3}(a_{1})$	440
and od		404.8	m	SPF3	$v_{s}(e)$	402
347.04	m			PF <sub>3</sub>	$\nu_4(e)$	344'

<sup>a</sup> Photolysis with the unfiltered radiation of a Hg arc. <sup>b</sup> Error limits  $\pm 1.0$  cm<sup>-1</sup> unless indicated otherwise. <sup>c</sup> s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad. d Error limits ±0.4 cm<sup>-1</sup>. e See, for example, ref 19. f See, for example: Davis, K. A.; Overend, J. Spectrochim. Acta, Part A 1976, 32A, 233. See also: Fayt, A.; Vandenhaute, R. Mol. Phys. 1976, 31, 1861. <sup>g</sup> See, for example: Verderame, F. D.; Nixon, E. R. J. Chem. Phys. 1966, 44, 43. <sup>h</sup> See, for example, ref 21. <sup>i</sup> Reference 1. <sup>j</sup> References 20 and 24.

at 908 cm<sup>-1</sup> increased in intensity when the matrix was annealed at temperatures up to 38 K for 10 min, whereas the others remained unchanged. Under these conditions aggregation of PF<sub>3</sub> occurs and a plausible explanation of the band at 908 cm<sup>-1</sup> is that it arises from the product of sulfur atom addition to  $[PF_3]_n$ . The weak band near 1530 cm<sup>-1</sup> indicates the formation of a small amount of  $CS_2^{8,21,22}$  while the weak bands near 1400 and 471 cm<sup>-1</sup> indicate that OPF<sub>3</sub> is also formed in low yield.<sup>1</sup> The location of the remaining band (near 676 cm<sup>-1</sup>) suggests that it may represent the vibration of an  $\hat{S}_2$  molecule<sup>23</sup> perturbed and rendered active in infrared absorption by interaction with a second molecule, possibly PF<sub>3</sub>.

Photolysis of an argon matrix containing OCS and PCl<sub>3</sub> in the proportions Ar:OCS:PCl<sub>3</sub> = 100:1:1 with the full emission of an Hg arc followed a similar course (see Figure 2 and Table II). New bands attributable to CO and  $SPCl_3^{24}$  appeared and grew at the expense of those due to OCS and PCl<sub>3</sub>. By contrast, although CO was formed, there was no spectroscopic sign of any other product when  $PX_3$  (X = F or Cl) gave place to NF<sub>3</sub>, PH<sub>3</sub>, AsF<sub>3</sub>, or HCl, or when nitrogen or xenon replaced argon as the matrix gas.<sup>10</sup> Hence the range of molecular substrates which have been shown to react with sulfur atoms in low-temperature matrices has been extended from  $O_2^{7-9}$  and NO<sup>8</sup> to PX<sub>3</sub>, but the scope of

sulfur atom transfer depends evidently on the efficiency with which the initial "hot" adduct is quenched and on the photolability of the product more than, say, the donor properties of the substrate. However, little can be deduced from the results of these experiments about the electronic state of the reacting sulfur atoms.

(b) Photochemistry of the System  $OCS/CH_4$ . Ultraviolet photolysis of gaseous carbonyl sulfide in the presence of alkanes other than methane gives rise to a thiol as the only product.<sup>6,12</sup> This reaction involving insertion into the C-H bond of the alkane is characteristic of sulfur atoms in the <sup>1</sup>D state, for ground-state (<sup>3</sup>P) sulfur atoms do not react with alkanes.<sup>25</sup> In the case of methane, however, the molecules (CH<sub>3</sub>)<sub>2</sub>S, CH<sub>3</sub>SSCH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>,  $H_2$ , and  $CS_2$  have been detected in addition to  $CH_3SH$ . This diversity of products has been rationalized on the basis of dissociation of the vibrationally activated adduct [CH<sub>4</sub>S]\* formed between the <sup>1</sup>D sulfur atom and methane (eq 2). Other alkane

$$CH_{4} + (^{1}D)S \longrightarrow [CH_{4}S]^{*} \qquad CH_{3}S + H (2a)$$

$$CH_{3} + SH (2b)$$

$$CH_{2} + H_{2}S (2c)$$

$$H_{2}C = S + H_{2} (2d)$$

molecules do not behave in this manner on reaction with <sup>1</sup>D sulfur atoms because, it is argued,<sup>6</sup> the vibrationally activated adduct [alkane-S]\* has sufficient vibrational degrees of freedom to dissipate the excess energy.

<sup>(21)</sup> Loewenschuss, A.; Givan, A. Spectrosc. Lett. 1977, 10, 551.
(22) Jacox, M. E.; Milligan, D. E. J. Mol. Spectrosc. 1975, 58, 142.
(23) Meyer, B. J. Chem. Phys. 1962, 37, 1577. Brewer, L.; Brabson, G. D.; Meyer, B. Ibid. 1965, 42, 1385. Barletta, R. E.; Claassen, H. H.; McBeth, R. L. Ibid. 1971, 55, 5409. Hopkins, A. G.; Brown, C. W. Ibid. 1975, 62, 1508. 1598.

<sup>(24)</sup> Durig, J. R.; Clark, J. W. J. Chem. Phys. 1967, 46, 3057.

<sup>(25)</sup> Knight, A. R.; Strausz, O. P.; Gunning, H. E. J. Am. Chem. Soc. 1963, 85, 2349

TABLE II: Wavenumbers ( $\tilde{\nu}$ ) and Assignments of Infrared Absorptions between 2500 and 200 cm<sup>-1</sup> Exhibited before and after Photolysis by Ar Matrices Containing OCS and PCl<sub>3</sub> at ca. 20 K

initial de	initial deposit		bands appearing after photolysis <sup>a</sup>		assignment	
$\widetilde{\nu}, b \text{ cm}^{-1}$	intens <sup>c</sup>	$\widetilde{\nu}, b \text{ cm}^{-1}$	intens <sup>c</sup>	molecule	vibrat mode	$\widetilde{\nu}$ , cm <sup>-1</sup>
		2141.6	S	[CO],	ν(C≡O)	
		2137.5	S	CO T	$\nu(C\equiv O)$	2143.3 <sup>d</sup>
2110-1700	various			$OCS, [OCS]_{n}^{e}$	various	
		1526.0	w, br	CS,	$\nu_{2}(\Sigma_{1})^{+}$	1532.5 <sup>f</sup>
1048.3	mw		,	ocs	$2\nu_{2}$	1047.0 <sup>e</sup>
859.0	m			OCS	$\nu_1(\Sigma^+)$	859.0 <sup>e</sup>
		764.1	S	SPC1,	$\nu$ , (a, )	770 <sup>g</sup>
588.9	wm			OPCl, impurity	1 . 1,	
		544.0	S	SPC1,	$\nu_{A}(e)$	547 <sup>g</sup>
519.2	m			OCS	$\nu_2(\Pi)$	520.4 <sup>e</sup>
510.4	m			) DCI	(-)	c 1 ch
508.8	sh			FCI <sub>3</sub>	$\nu_1(a_1)$	515.
498.9	vs				(-)	50 AB
494.9	S			FPCI <sub>3</sub>	$\nu_3(e)$	504"
		430.4	w	SPC1.	$v_{a}(a_{1})$	431 <sup>g</sup>
259	vw. br			PCl.	$\nu_{a}(a_{1})$	$258^h$
-	,	256.3	vw	SPC1 <sub>3</sub>	$\nu_3(a_1) + \nu_5(e)$	250 <sup>g</sup>

<sup>a</sup> Photolysis with the unfiltered radiation of a Hg arc. <sup>b</sup> Error limits  $\pm 0.4$  cm<sup>-1</sup> for all but the broad bands. <sup>c</sup> s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad. <sup>d</sup> See, for example, ref 19. <sup>e</sup> Pattern and wavenumbers of features very similar to those for an Ar matrix containing OCS and PF<sub>3</sub>. See Table I. <sup>f</sup> See, for example, ref 21. <sup>g</sup> Reference 24. <sup>h</sup> Clark, R. J. H.; Rippon, D. M. J. Mol. Spectrosc. 1974, 52, 58.



Figure 2. Regions 2600-1900 and 1000-200 cm<sup>-1</sup> in the infrared spectrum of an Ar matrix deposited at 20 K and containing 1% OCS and 1% PCl<sub>3</sub>: (A) after deposition; (B) after irradiation with the unfiltered emission of an Hg arc for 60 min.

The photolysis of carbonyl sulfide isolated in a solid methane matrix might be expected to yield information about two important questions. First, do any <sup>1</sup>D sulfur atoms survive to react in the matrix? If so, how does the matrix environment influence the reaction channels open to the activated complex [CH<sub>4</sub>S]\*? It is possible for example that the complex is efficiently quenched by the matrix to form CH<sub>3</sub>SH as the unique product.

Figure 3 shows selected regions of the infrared spectrum of a methane matrix containing OCS ( $CH_4$ :OCS = 100:1) deposited at 20 K after 90-min photolysis with full Hg-arc emission. Several new bands were observed to develop with photolysis. These in-



Figure 3. Regions 3000-2800, 1600-1400, and  $1100-900 \text{ cm}^{-1}$  in the infrared spectrum of a CH<sub>4</sub> matrix containing 1% OCS deposited at 20 K: (A) after deposition; (B) after irradiation with the unfiltered emission of a medium-pressure Hg arc for 2 h; (C) after annealing the matrix to 40 K for 30 min; (D) after irradiation with the unfiltered emission of a medium-pressure Hg arc for a total of 4 h. The photoproducts are as follows: I, CH<sub>3</sub>SH; II, H<sub>2</sub>C=S; III, CS<sub>2</sub> (see text).

cluded the band near 2140 cm<sup>-1</sup> characteristic of CO and eight other features the growth patterns of which indicated that they arose from *three* distinct products, namely I (2938, 1444, 1434, 1070, and 961 cm<sup>-1</sup>), II (1057 and 994/991 cm<sup>-1</sup>), and III (1518 cm<sup>-1</sup>). Photolysis of a methane- $d_4$  matrix containing OCS (CD<sub>4</sub>:OCS = 100:1) showed a marked shift of all the product bands with the exception of those due to CO and III (1520 cm<sup>-1</sup>). Several of the bands due to the CD<sub>4</sub> products were obscured by strong absorptions associated with OCS, CO, or the CD<sub>4</sub> matrix itself (see Table III), but the bands ascribed to I at 1070 and 961 cm<sup>-1</sup> were observed to move to 823 and ca. 737 cm<sup>-1</sup>, respectively, and the doublet at 994/991 cm<sup>-1</sup> ascribed to II appeared to give place to an unresolved but rather broad feature centered near 790 cm<sup>-1</sup>. Continued photolysis caused the product bands to broaden

TABLE III: Wavenumbers ( $\tilde{\nu}$ ) and Assignments of Infrared Absorptions Appearing between 4000 and 200 cm<sup>-1</sup> on Photolysis<sup>a</sup> of CH<sub>4</sub> or CD<sub>4</sub> Matrices Containing OCS at ca. 20 K

$CH_4$ matrix		$CD_4$ matrix			molecule isolated	
$\widetilde{\nu}, b \text{ cm}^{-1}$	intens <sup>c</sup>	$\widetilde{\nu}, b \text{ cm}^{-1}$	intens <sup>c</sup>	molecule	vibrat mode	in an Ar matrix, $\tilde{\nu}$ , cm <sup>-1</sup>
2946 2938	sh m	d		} CH <sub>3</sub> SH	ν(C-H)	2950°
2137	s	2137	s	CO	ν(C≡O)	2137.5 <sup>f</sup>
$1528 \\ 1518$	sh s	} 1520	s, br	CS <sub>2</sub>	$\nu_{\mathfrak{z}}(\Sigma_{\mathfrak{u}}^{+})$	1526 <sup>f</sup>
1444 1434	m m	g g		$CH_3SH + H_2C=S$	antisym CH <sub>3</sub> deformation CH <sub>2</sub> wag	1448, 1438 <sup>e</sup> 1437 <sup>e</sup>
$1070 \\ 1057$	sm w	_823 g	w	$\begin{array}{c} CH_{3}SH(CD_{3}SD) \\ H_{2}C=S \end{array}$	$CH_3(CD_3)$ rocking $\nu(C=S)$	1069 <sup>e</sup> 1063 <sup>e</sup>
994 991	m sh	$-790^{h}$	m, br	$H_2C=S(D_2C=S)$	out-of-plane $CH_2(CD_2)$ deformation	993 (783) <sup>e</sup> 988 (779) <sup>e</sup>
961	m	~737 <sup>h</sup>	w	$CH_3SH(CD_3SD)$	$CH_{3}(CD_{3})$ rocking	956 <sup>e</sup>

<sup>a</sup> Photolysis with the unfiltered radiation of a Hg arc. <sup>b</sup> Error limits  $\pm 1 \text{ cm}^{-1}$ . <sup>c</sup> s, strong; m, medium; w, weak; sh, shoulder; br, broad. <sup>d</sup> Obscured presumably by the absorptions near 2100 cm<sup>-1</sup> due to CD<sub>4</sub>, CO, and unchanged OCS. <sup>e</sup> Values refer to the molecules CH<sub>3</sub>SH and H<sub>2</sub>C=S; values in parentheses refer to D<sub>2</sub>C=S. Reference 22. <sup>f</sup> See Tables I and II. <sup>g</sup> Obscured presumably by the absorption near 1000 cm<sup>-1</sup> due to the CD<sub>4</sub> matrix. <sup>h</sup> Partially obscured by absorptions due to the matrix.

(Figure 3D) making it difficult to assess changes in the concentrations of I, II, and III. With due allowance for changes of band shape, however, it appeared that gradual depletion in I and II occurred and that only III continued to accumulate.

By contrast, dilution of the methane with argon to produce matrices containing 1–20% CH<sub>4</sub> gave bands attributable only to the following photoproducts: CO, III (in much reduced yield), and CO<sub>2</sub>. There was no sign of the photoproducts I and II, even after prolonged photolysis (16 h with full Hg-arc emission). Such a result is not wholly surprising since neither I nor II gave bands of more than moderate intensity even with solid methane as the host (see Figure 3). Had the matrix concentration been reduced from this level by more than 1 order of magnitude, the product would probably have escaped detection.

Milligan and Jacox have studied the effects of mercury-arc photolysis on methanethiol,  $CH_3SH$ , isolated in a solid argon matrix with Ar: $CH_3SH = 400:1.^{22}$  Hence they established that photodecomposition afforded mainly CS<sub>2</sub> and CH<sub>4</sub> together with thioformaldehyde, H<sub>2</sub>C=S, and carbon monosulfide, CS, as secondary products. On the basis (i) of the infrared spectra which they report and (ii) of the response to deuteration established in the present experiments, we conclude that the product I is methanethiol, CH<sub>3</sub>SH, that II is thioformaldehyde, H<sub>2</sub>C=S, and that III is CS<sub>2</sub>. The relevant spectroscopic details are summarized in Table III. Three features merit further comment.

(i) That CH<sub>3</sub>SH is indeed produced on broad-band ultraviolet photolysis of a methane matrix containing OCS confirms that <sup>1</sup>D sulfur atoms survive long enough to react with an adjacent matrix molecule. Hence <sup>1</sup>D sulfur atoms generated simply by photolyzing OCS share with energetically more extravagant reagents like iron<sup>26a</sup> and copper<sup>26b</sup> atoms and with certain unsaturated organometallic species like ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)M(CO)<sub>2</sub> (R = H or CH<sub>3</sub>; M = Rh or Ir)<sup>26c</sup> the capacity to activate methane at low temperatures. Annealing the matrix at temperatures up to 40 K brought about changes in the concentrations of H<sub>2</sub>C=S and CS<sub>2</sub> but had no detectable effect on the concentration of CH<sub>3</sub>SH (see for example traces B and C of Figure 3).

(ii) On the other hand, the formation of  $H_2C=S$  may be explained in one of two ways. First, the earlier experiments of Milligan and Jacox<sup>22</sup> show that it is formed on broad-band ultraviolet photolysis of matrix-isolated CH<sub>3</sub>SH. Second, it is possible that the vibrationally excited complex [CH<sub>4</sub>S]\* is not deactivated completely by transfer of energy to the matrix lattice and decomposes via mode d in eq 2. There are three aspects of our results which favor the second of these routes. (a) CH<sub>3</sub>SH was formed only in relatively low concentrations, and previous

studies<sup>22</sup> have indicated that it is slow to undergo photodissociation. (b) We saw no hint of an absorption near  $1276 \text{ cm}^{-1}$  attributable to CS, whereas this is reported<sup>22</sup> to be a prominent feature of photolyzed argon matrices containing CH<sub>3</sub>SH. (c) H<sub>2</sub>C=S was still produced when the matrix was photolyzed with the unfiltered output of a cadmium arc (having wavelengths confined mainly to the region near 228 nm). In view of these observations, it seems unlikely that the photolysis of CH<sub>3</sub>SH is a major source of the  $H_2C=S$  we observe. The way the product concentrations varied with time during broad-band ultraviolet photolysis of a methane matrix containing OCS (q.v.) may well reflect the influence of photodissociation of CH<sub>3</sub>SH and its competition with sulfur atom addition to limit the buildup of the molecule in the matrix. On the other hand, the *relative* yields of  $CH_3SH$  and  $H_2C=S$  did not change appreciably even after prolonged photolysis (see Figure 3).

(iii) Less clear is the mechanism by which  $CS_2$  is formed on photolysis of a methane matrix containing OCS. We have noted elsewhere<sup>8</sup> that the reaction

$$[OCS]_2 \xrightarrow{h_{\nu}} CO_2 + CS_2 \tag{3}$$

occurs to a small extent in  $A_r/OCS$  matrices but, to judge by the absence of significant absorption due to  $CO_2$ , this would account for only a small fraction of the  $CS_2$  formed in  $CH_4/OCS$  matrices. Milligan and Jacox<sup>22</sup> associated the photoproduction of  $CS_2$  from  $CH_3SH$  with the synthesis of methane via cage recombination of photofragmented  $CH_3SH$  (eq 4). However, they do not specify

$$CH_3SH \xrightarrow{h\nu} [CH_3 + SH]_{cage} \rightarrow CH_4 + S$$
 (4)

the species with which the sulfur atom reacts to afford  $CS_2$ . The CS molecule is an obvious candidate in their experiments, but its absence in detectable amounts from the matrices we have studied casts doubt on its involvement. More likely is the reaction given in eq 5. Evidence that this is the pathway by which  $CS_2$  evolves

$$H_2C = S + ({}^{3}P)S \longrightarrow \left[H_2C \underbrace{s}_{s}\right] \longrightarrow H_2 + CS_2 (5)$$

in a methane matrix is advanced by the changes in the infrared spectrum which occurred when the photolyzed matrix was annealed. Whereas the concentration of CH<sub>3</sub>SH remained unchanged, that of H<sub>2</sub>C=S *decreased* and that of CS<sub>2</sub> *increased*. No new absorptions were observed to develop. That the reaction involves <sup>3</sup>P sulfur atoms we propose since there is no accretion of CH<sub>3</sub>SH. If <sup>1</sup>D sulfur atoms were involved, then the diffusion of the atoms induced by annealing the matrix would be expected to enhance the yield of CH<sub>3</sub>SH. Hence it appears that, although the CH<sub>3</sub>SH must result from addition of <sup>1</sup>D sulfur atoms to a neighboring CH<sub>4</sub> molecule in the matrix cage, the electronically

<sup>(26) (</sup>a) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. J. Am. Chem. Soc. 1980, 102, 7393. (b) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. J. Am. Chem. Soc. 1981, 103, 1574. (c) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. J. Chem. Soc., Chem. Commun. 1984, 624.

TABLE IV: Wavenumbers (7) and Assignments of Infrared Absorptions Appearing between 4000 and 200 cm<sup>-1</sup> on Photolysis<sup>a</sup> of Ar Matrices Containing OCS and either C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>D<sub>4</sub> at ca. 20 K

C <sub>2</sub> H <sub>4</sub>		$C_2D_4$				assignment <sup>d</sup>	
$\overline{\nu},^{b}$ cm <sup>-1</sup>	intens <sup>c</sup>	intens <sup>c</sup> $\overline{\nu}$ , b cm <sup>-1</sup> intens <sup>c</sup>		$v_{\rm H}/v_{\rm D}$	molecule	vibrat mode	$\tilde{\nu}, d \text{ cm}^{-1}$
3005	wm	2167	wm	1.387	thiirane	$\nu_1$ and/or $\nu_9$ ; $\nu$ (C-H)/ $\nu$ (C-D)	3012
2933	s	2142	s	1.000	$[CO]_2$	$\nu(C=R)$ $\nu(C\equiv O)$	
2138 f	S	2138 979	s w	1.000	CO thiirane	$\nu(C = 0)$ $\nu_{0}$ and/or $\nu_{10}$ ; CH <sub>0</sub> (CD <sub>0</sub> ) scissoring	1434 1454
1054	m	825	mw	1.278	thiirane	$\nu_{11}$ ; CH <sub>2</sub> (CD <sub>2</sub> ) wag	1050
1028 f	w	910 757	mw, br wm	1.130	thiirane thiirane	$\nu_4$ ; ring breathing $\nu_{14}$ ; CH <sub>2</sub> (CD <sub>2</sub> ) rocking	1024 945
823 <sup>8</sup>	wm	589	wm	1.397	thiirane	$\nu_{15}$ ; CH <sub>2</sub> (CD <sub>2</sub> ) twisting	824
622	m	038 i	wm, or		thiirane	$\nu_{12}$ ; ring deformation $\nu_5$ ; ring deformation	624

<sup>a</sup> Photolysis with the unfiltered radiation of a Cd arc. <sup>b</sup> Error limits  $\pm 2 \text{ cm}^{-1}$  (4000-2000 cm<sup>-1</sup>) or  $\pm 1 \text{ cm}^{-1}$  (2000-200 cm<sup>-1</sup>). <sup>c</sup>s, strong; m, medium; w, weak. "See ref 28a." Believed to be obscured by the intense absorption centered near 2050 cm<sup>-1</sup> due to unchanged OCS. Believed to be obscured by the intense absorption near 1440 or 950 cm<sup>-1</sup> due to unchanged C<sub>2</sub>H<sub>4</sub>. See, for example: Fredin, L.; Nelander, B. J. Mol. Struct. 1973, 16, 205. This band was obscured partially by a feature due to unchanged C<sub>2</sub>H<sub>4</sub>, but its presence was deduced from the finding that the intensity did not change appreciably on photolysis. "Band not observed, presumably for want of intensity. Believed to be obscured by the absorption near 520 cm<sup>-1</sup> due to unchanged OCS.

excited atoms do not survive long enough to migrate through the matrix to a significant extent.

On the evidence of these and earlier<sup>22</sup> experiments, we conclude that the sequence of reactions induced by ultraviolet photolysis of OCS trapped in a methane matrix is probably as set out in Scheme I.

(c) Photochemistry of the System  $OCS/C_2H_4$ . With the demonstration that ultraviolet photolysis of OCS isolated in a methane matrix yields a certain proportion of <sup>1</sup>D sulfur atoms, it was of interest to seek a more definitive test of the activity of both <sup>1</sup>D and <sup>3</sup>P sulfur atoms with respect to diffusion-controlled reactions occurring in a solid matrix at low temperatures. Such a test involved the doping of an argon matrix containing OCS with ethene,  $C_2H_4$ , a species known to be capable of reacting with both <sup>1</sup>D and <sup>3</sup>P sulfur atoms, but in a distinguishable manner.

The reaction between a sulfur atom and ethene can follow one of three pathways (eq 6-8) depending, in the first instance, on



the electronic state of the atom.<sup>6</sup> Although both thiirane and ethenethiol can be formed by the interaction of either <sup>1</sup>D or <sup>3</sup>P sulfur atoms with ethene, photolysis of gaseous mixtures of OCS and  $C_2H_4$  under conditions leading to the generation of only (<sup>3</sup>P)S SCHEME I



atoms yields thiirane as the sole product.<sup>6</sup> This suggests that the rearrangement of the biradical IV to form ethenethiol and thioacetaldehyde is either thermodynamically unfavorable or slow compared with organization to triplet thiirane (V). The formation of ethenethiol is a reaction characteristic of <sup>1</sup>D sulfur atoms in the gas phase,<sup>6</sup> and both direct insertion (eq 8) and isomerization of vibrationally excited thiirane (VI, eq 7) have been observed to extents dependent on the total pressure in the reaction system.<sup>27</sup> In a solid matrix where quenching of VI is expected to be faster, little ethenethiol is likely to emerge via the second of these channels.

An argon matrix containing OCS and C<sub>2</sub>H<sub>4</sub> in the proportions Ar:OCS: $C_2H_4 = 100:1:1$  was photolyzed with the unfiltered emission derived from either a mercury or a cadmium arc. The infrared spectra displayed by such a matrix, first on deposition (A) and then after 320-min irradiation at wavelengths near 228 nm (B), are illustrated in Figure 4 and the numerical details are summarized in Table IV. In addition to the band near 2140 cm<sup>-1</sup> due to CO, six new bands appeared (at 3005, 2933, 1054, 1028, 823, and 622 cm<sup>-1</sup>) on photolysis and grew at the expense of the bands due to  $C_2H_4$  which were observed to decrease by 13-20% of their initial intensity. Of the six new bands all but one (that at 2933 cm<sup>-1</sup>) can be assigned to the cyclic molecule thiirane,

 $CH_2CH_2S$ . The identity of this molecule is underpinned (i) by comparison with earlier accounts of the infrared spectrum of thiirane in the gas phase<sup>28a</sup> or when isolated in an argon matrix,<sup>28b</sup> and (ii) by experiments we have carried out to examine the response of the new bands to the replacement of  $C_2H_4$  by  $C_2D_4$  (see Table IV). In none of these experiments did the infrared spectra give any hint of features characteristic of ethenethiol, CH2=C-HSH, or its perdeuterated isotopomer, CD<sub>2</sub>=CDSD.<sup>29</sup> The

<sup>(27)</sup> Sherwood, A. G.; Safarik, I.; Verkoczy, B.; Almadi, G.; Wiebe, H. A.; Strausz, O. P. J. Am. Chem. Soc. 1979, 101, 3000.
(28) (a) Hirose, C.; Okiye, K.; Maeda, S. Bull. Chem. Soc. Jpn. 1976, 49, 916. (b) Le Brumant, J. C. R. Hebd. Seances Acad. Sci., Ser. B 1970, 270, 000.

<sup>801.</sup> 

<sup>(29)</sup> Almond, V.; Charles, S. W.; Macdonald, J. N.; Owen, N. L. J. Chem. Soc., Chem. Commun. 1977, 483. Lister, D. G.; Palmieri, P. J. Mol. Struct. 1978, 48, 133.



Figure 4. Regions 3150-2850, 2200-1950, and 1100-550 cm<sup>-1</sup> in the infrared spectrum of an Ar matrix deposited at 20 K and containing 1% OCS and  $1\% C_2H_4$ : (A) after deposition; (B) after irradiation with the unfiltered emission of a Cd arc for 320 min.

source of the weak band at 2933 cm<sup>-1</sup> we cannot identify, but it is neither CH<sub>2</sub>=CHSH nor CH<sub>3</sub>(H)C=S (cf. eq 6); it might be CH<sub>3</sub>SH although this seems a most unlikely photoproduct in the circumstances described; it is more plausibly identified with a product of the reaction between sulfur atoms and ethene aggregates  $[C_2H_4]_n$ .

The buildup of thiirane in the matrix was found to be relatively slow. This may be due in part to the secondary reaction

$$({}^{3}P)S + \overset{!}{C}H_{2}CH_{2}\overset{!}{S} \rightarrow CH_{2} = CH_{2} + S_{2}(\tilde{X}\Sigma_{g}) \quad \Delta H = -180 \text{ kJ mol}^{-1}$$

which is symmetry allowed in terms of both spin and orbital angular momentum and is reported to have  $E_{\rm a} \sim 0$  in the gas phase.<sup>6c,30</sup> There are grounds for believing that this reaction evolves through a thiosulfoxide VII which is both thermodynam-

ically and kinetically unstable with respect to decomposition to ethene and S<sub>2</sub>.<sup>6c</sup> Our experiments gave no hint of infrared absorptions which might originate in a species such as VII, but at no stage did the matrix ratio Ar:C<sub>2</sub>H<sub>4</sub>S drop significantly below ca.  $10^3$ :1. On the other hand, selective photolysis of a matrix including OCS and an organic sulfide like thiirane in comparable proportions, e.g., Ar:OCS: $C_2H_4S = 100:1:1$ , would plainly repay investigation.

The failure to detect ethenethiol among the matrix photoproducts we attribute to rapid deactivation of <sup>1</sup>D sulfur atoms by the matrix environment, thereby forestalling significant diffusion of these atoms through the matrix, and not to photolysis of any ethenethiol which may be formed under these conditions. Although ethenethiol exhibits an absorption band centered at 218 nm.<sup>27</sup> there is no definite evidence that the gaseous molecule is photolyzed when irradiated at wavelengths near 228 or 254 nm. The quenching of <sup>1</sup>D sulfur atoms is supported, moreover, by the results of earlier experiments<sup>6</sup> in which  $OCS/C_2H_4$  mixtures have been photolyzed in the gaseous, liquid, or solid states. The ratio of ethenethiol to thiirane formed during photolysis was 0.85:1 for the gaseous reagents but decreased to 0.45:1 and 0.2:1 for the liquid and solid reagents, respectively.

It is noteworthy too that experiments designed to investigate the reactions of ethene with the methylene radical, CH<sub>2</sub>,<sup>31</sup> or the imine radical, NH,<sup>32</sup> in low-temperature matrices have indicated exclusive cycloaddition to form cyclopropane in the first case or ethenimine in the second. The photolysis of the precursors to the methylene and imine radicals-diazomethane and hydrogen azide respectively-should yield at least a small proportion of the radicals in the singlet state, on the grounds of spin conservation. Thus, singlet methylene has been detected on photolysis of gaseous diazomethane<sup>33</sup> and, like singlet sulfur atoms, is characterized by insertion reactions. That no propene or vinylamine was detected in the matrix reactions with ethene has been attributed to the efficient quenching of the singlet states of CH<sub>2</sub> or NH in a matrix environment.32

Our experiments imply therefore that, while <sup>1</sup>D sulfur atoms are formed and can react with the matrix host, e.g., methane, their lifetime under these conditions is too short to allow them to enter into diffusion-controlled reactions with a matrix dopant. Such reactions are confined to sulfur atoms in their <sup>3</sup>P ground state.

(d) Photochemistry of the System  $OCS/C_2H_2$ . The reaction between sulfur atoms and ethyne in the gas phase does not proceed in the same way as that between sulfur atoms and an alkene.<sup>6</sup> The retrievable products from the reaction of ethyne with either <sup>3</sup>P or <sup>1</sup>D sulfur atoms are  $CS_2$ , benzene, and thiophene.<sup>34</sup> According to ab initio SCF-MO-CI calculations,<sup>35</sup> sulfur atoms may interact with ethyne in the following elementary reactions, all of which are exothermic and symmetry allowed in terms of both spin and orbital angular momentum.

$$(^{1}D_{2})S + HC \equiv CH \rightarrow S (S_{0}) \Delta H \sim -250 \text{ kJ mol}^{-1} (9)$$

$$(^{1}D_{2})S + HC \equiv CH \longrightarrow$$
  $HC = CH$   $(S_{1}) \Delta H \sim -190 \text{ kJ mol}^{-1} (10)$ 

$$(^{1}D_{2})S + HC \equiv CH \longrightarrow HC \equiv CSH \Delta H \sim -360 \text{ kJ mol}^{-1} (11)$$
  
HC == CH

$$({}^{3}P)S + HC = CH - (T_{0}) \Delta H \sim -25 \text{ kJ mol}^{-1} (12)$$

Three features merit further comment.

(a) Reaction 9 gives the cyclic molecule thiirene, notable for the pseudoantiaromatic character conferred by its  $4n-\pi$  electron shell. Together with its derivatives thicketene,  $H_2C==C=S$ , and ethynethiol, HC=CSH, this highly reactive molecule has been identified only recently by its infrared spectrum following photolysis of 1,2,3-thiadiazole (VIII)<sup>36,37</sup> or vinylene trithiocarbonate



<sup>(31)</sup> DeMore, W. B.; Pritchard, H. O.; Davidson, N. J. Am. Chem. Soc. 1959, 81, 5874.

<sup>(30)</sup> Klemm, R. B.; Davis, D. D. Int. J. Chem. Kinet. 1973, 5, 149. van Roodselaar, A.; Safarik, I.; Strausz, O. P. Ibid. 1984, 16, 899.

<sup>1959, 81, 5874.
(32)</sup> Jacox, M. E.; Milligan, D. E. J. Am. Chem. Soc. 1963, 85, 278.
(33) Woodworth, R. C.; Skell, P. S. J. Am. Chem. Soc. 1959, 81, 3383.
(34) van Roodselaar, A.; Safarik, I.; Strausz, O. P.; Gunning, H. E. J. Am. Chem. Soc. 1978, 100, 4068. Verkoczy, B.; Sherwood, A. G.; Safarik, I.; Strausz, O. P. Can. J. Chem. 1983, 61, 2268.
(35) Gosavi, R. K.; Strausz, O. P. Can. J. Chem. 1983, 61, 2596.
(36) Font, J.; Torres, M.; Gunning, H. E.; Strausz, O. P. J. Org. Chem.
1978, 43, 2487. Torres, M.; Clement, A.; Bertie, J. E.; Gunning, H. E.; Strausz, O. P. Ind 1978, 43, 2490. Strausz, O. P. Ibid. 1978, 43, 2490.



**Figure 5.** Regions 3400–3000, 1800–1500, and 1000–500 cm<sup>-1</sup> in the infrared spectrum of an Ar matrix containing 1% OCS and 1%  $C_2H_2$ . The matrix has been deposited at 20 K and irradiated with the unfiltered emission of a Cd arc *during*, and for 4 h *after*, deposition.

 $(IX)^{38}$  isolated in a solid inert matrix at low temperatures. The reactivity of thiirene is exemplified by its facile ring expansion in the reaction with a second molecule of ethyne to give thiophene.<sup>34</sup>

(b) Between ground-state (<sup>3</sup>P) sulfur atoms and ethyne there is but a single primary reaction to give the  $T_0$  state of thioketocarbene, as in eq 12. This is nearly isoenergetic with the  $S_1$  state derived, as in (10), from one of the three primary reactions involving <sup>1</sup>D sulfur atoms; both are double open-shell species best represented by the 1,3-diradical structures given above. To date neither the  $S_1$  nor the  $T_0$  state of the diradical has been characterized experimentally. There are probably two factors at work here: (i) the very small energy barrier opposing isomerization of the  $S_1$  state to thiirene or thioketene (eq 13) and (ii) relatively



efficient intersystem crossing promoted by the near-degeneracy of the  $T_0$  and  $S_1$  states. The second of these factors would explain why the electronic state of the sulfur atom does not have a major impact on the nature of the products, although it does affect somewhat their distribution.<sup>34</sup> The following reactions (eq 14)



of the thicketocarbene diradicals afford routes to identifiable products derived from the attack of sulfur atoms on ethyne in the gas phase.

(c) Insertion of a sulfur atom into a C-H bond of ethyne in accordance with eq 11 is unlikely to be a significant reaction channel and, although ethynethiol may be formed by isomerization of a thicketocarbene diradical, it plays little, if any, part in the gas-phase reaction of sulfur atoms with ethyne.<sup>34</sup>

It was of interest to us to investigate the course taken by the reaction between sulfur atoms and ethyne in a low-temperature matrix, particularly in the light of what happens in the gas phase,<sup>34</sup> and of the matrix experiments involving methane and ethene described in the preceding sections. The studies were motivated

TABLE V:	Wavenumbers $(\tilde{\nu})$ and Assignments of Infrared
Absorptions	Appearing between 4000 and 200 cm <sup>-1</sup> on Photolysis <sup>a</sup> of
Ar Matrices	Containing OCS and C <sub>2</sub> H <sub>2</sub> at ca. 20 K

observed features		assi		
$\tilde{\nu}, b \text{ cm}^{-1}$	intens	molecule	vibrat mode	₽, <sup>g</sup> cm <sup>-1</sup>
3317	m	HC=CSH	ν(C-H)	3315 <sup>d</sup>
2142	S	[CO] <sub>2</sub>	$\nu(C \equiv O)$	2142e
2138	S	CO T	$\nu(C=0)$	2138e
1751	m	$H_2C = C = S$	$\nu(C=C)$	17554
1526	s	$CS_2$	$\nu_3(\Sigma_u^+)$	1526
958	vw	HC=CSH	unassigned	959 <sup>d</sup>
913	vw	HC=CHS	in-plane C-H	912 <sup>d</sup>
702	vw, br	H <sub>2</sub> C=C=S	$\nu(C=S)$	692 <sup>d</sup>
654	vw, br	HC=CHS	symmetric ring deformation	657 <sup>f</sup>
636	wm	coordinated S <sub>2</sub> ?	$\nu(S-S)?$	
558	m, br	HC≡CSH +	H—C≡C bending	558d
		HC-CHS	out-of-plane C-H	563 <sup>d</sup>

<sup>a</sup> Photolysis with the unfiltered radiation of a Cd arc. <sup>b</sup> Error limits  $\pm 2 \text{ cm}^{-1}$  (4000-2000 cm<sup>-1</sup>) or  $\pm 1 \text{ cm}^{-1}$  (2000-200 cm<sup>-1</sup>). <sup>c</sup>s, strong; m, medium; w, weak; v, very. <sup>d</sup>Reference 37. <sup>c</sup>See Tables I and II. <sup>f</sup>See: Safarik, I.; Torres, M.; Strausz, O. P. Chem. Phys. Lett. **1980**, 72, 388 and ref 35. <sup>g</sup>Reported previously for molecule isolated in Ar matrix.

#### SCHEME II



also by the desire to find out what role, if any, is played by thiirene.

During deposition at 20 K, an argon matrix containing OCS and  $C_2H_2$  in the proportions Ar:OCS: $C_2H_2 = 100:1:1$  was irradiated with the unfiltered emission from a cadmium arc. After deposition was complete, the matrix was photolyzed for a further 240 min. Figure 5 depicts those regions of the infrared spectrum displayed by the matrix which revealed the growth of absorptions characteristic of neither OCS nor C<sub>2</sub>H<sub>2</sub>; details of the wavenumbers and intensities of the relevant features are listed in Table V. Setting aside the band due to CO, we are able to identify all but three of the absorptions which grew with photolysis as belonging to either ethynethiol, HC=CSH (3317, 958, and 558 cm<sup>-1</sup>), or thicketene, H<sub>2</sub>C=C=S (1751 and 702 cm<sup>-1</sup>), by comparison with the infrared spectra reported previously for these species as formed in an argon matrix.<sup>37</sup> Weak bands at 913 and 654 cm<sup>-1</sup> signal the presence of thiirene, CH=CHS,<sup>37</sup> in low concentrations, while the intense band at 1526  $\rm cm^{-1}$  must be associated with CS<sub>2</sub>.<sup>21,22</sup> There remains a feature at 636 cm<sup>-1</sup> of weak-to-medium intensity which we have been unable to identify positively; it does not correspond to any strong absorption of thiophene or benzene, although the coordinated S<sub>2</sub> unit is, once again, a possible source.

The products we have identified may be explained by the reaction network outlined in Scheme II. The only uncertainties concern the relative importance of the different routes B, C, and D leading from the initial adduct, the thioketocarbene diradical X, and C, E, and F giving access to ethynethiol. On the evidence of our experiments, X appears to decay in a matrix environment primarily by a 1,2-hydrogen shift to afford thioketene which is known to be photolabile.<sup>37</sup> This is consistent with the reactions of ethyne with <sup>3</sup>P oxygen atoms<sup>39</sup> or methylene radicals<sup>32</sup> in an

<sup>(37)</sup> Krantz, A.; Laureni, J. J. Am. Chem. Soc. 1974, 96, 6768; 1981, 103, 486.

<sup>(38)</sup> Torres, M.; Clement, A.; Gunning, H. E.; Strausz, O. P. Nouv. J. Chim. 1979, 3, 149.

SCHEME III



argon matrix which have been shown to yield as the only detectable products ketene,  $H_2C==C==O$ , or allene,  $H_2C==C==CH_2$ , respectively; in each of these systems a mechanism analogous to reactions A and D of Scheme II has been postulated.

The finding that thiirene was generated on photolysis of an argon matrix containing OCS and  $C_2H_2$  argues that some of the intermediate X decays by cyclization (reaction B in Scheme II). That the yield of thiirene is so low can be explained in one of two ways: (i) the distribution of products reflects simply the relative efficiencies of cyclization and hydrogen migration of the diradical X to yield thiirene and thioketene, respectively, or (ii) the thiirene undergoes photolysis to give ethynethiol, HC=CSH. The second process has been reported to occur on photolysis of thiirene isolated in an argon matrix with radiation having  $\lambda = 330-370$  nm.<sup>37</sup> However, the output of a cadmium arc is relatively meager at these wavelengths, and thiirene would be required to be extremely photosensitive for this to be a realistic mechanism. Accordingly we prefer the first explanation.

One of the most striking features of our matrix experiments is the emergence of ethynethiol as a major reaction product (cf. the conclusions drawn about the interaction of sulfur atoms with ethyne in the gas  $phase^{34}$ ). There are three possible sources of this product (reactions C, E, and F in Scheme II). As already indicated, we doubt whether thiirene is an important source (reaction E) under the conditions of our experiments. Ab initio MO calculations imply that rearrangement of X to ethynethiol (reaction C) features a substantial energy barrier and is unlikely to be promoted by the thermal energy available to X in an argon matrix at ca. 20 K.35 Hence thicketene is the most likely precursor to the ethynethiol (reaction F). Previous studies have established that thicketene is susceptible to secondary reactions. Thus, as formed in an argon matrix by Pyrex-filtered ( $\lambda > 300$  nm) photolysis of 1,2,3-thiadiazole (VIII),37 it rearranges to ethynethiol on irradiation at wavelengths between 220 and 250 nm. This is a region coinciding with the maximum output of the cadmium arc, and so the photoinduced isomerization of thioketene accounts satisfactorily for the appearance of ethynethiol in appreciable concentrations in our experiments. We believe that the matrix also suffers depletion in thicketene by its reaction with sulfur atoms to produce an unstable intermediate which undergoes C-C bond rupture to generate the fragments CH<sub>2</sub> and CS<sub>2</sub>. The intermediacy of sulfur atoms in the photodecomposition of thioketene has indeed been postulated previously.<sup>37</sup> The scavenging of sulfur atoms by thioketene would account for two features of our experiments: (i) the relatively high yield of  $CS_2$  which is invariably produced by the reaction of sulfur atoms with ethyne and (ii) the finding that thioketene and ethynethiol are formed in approximately equimolar proportions. But for the action of the sulfur atoms, we would have expected thicketene to be present in our matrices in appreciably

(39) Haller, I.; Pimentel, G. C. J. Am. Chem. Soc. 1962, 84, 2855.

greater abundance than ethynethiol if it is the main photochemical precursor to the thiol, in accordance with the precedents set by the distribution of products afforded by the matrix photolysis of VIII.<sup>37</sup>

Our experiments lead us to believe that <sup>3</sup>P sulfur atoms react with ethyne, as they do with ethene, in the first instance to produce a triplet diradical species. However, whereas the favored reaction of the diradical IV derived from ethene involves cyclization to generate thiirane (see section IIIc), cyclization to generate thiirene accounts for a relatively small fraction of the diradical X derived from ethyne. Instead X favors rearrangement to thioketene secondary reactions of which give rise in turn to HC=CSH and  $CS_2$ . In the circumstances it is unfortunate that OCS is not more photolabile so that ultraviolet radiation spanning a relatively narrow band of wavelengths could be used to produce more selective conditions of photolysis and so minimize the risks of secondary photochemical changes. Further investigations of the reaction between sulfur atoms and ethyne and, in particular, of the role of thiirene are likely to call either for a photolysis source more powerful than those available to us or for a source of sulfur atoms more photolabile than OCS.

#### **IV.** Conclusions

We set out to investigate by infrared spectroscopy the matrix reactions of inorganic and organic substrates with sulfur atoms generated by UV photolysis of carbonyl sulfide with the aim of establishing the scope and mechanisms of such reactions, with particular reference to the electronic state of the reacting atoms. On the strength of these and earlier<sup>7-9</sup> results, the sulfur atoms have been shown to react with a variety of substrates to give the products summarized in Scheme III. The results presented here imply, moreover, that both <sup>1</sup>D and <sup>3</sup>P sulfur atoms are formed by the photolysis of matrix-isolated OCS with radiation having wavelengths near 230-260 nm.

With PX<sub>3</sub> molecules (X = F or Cl) isolated in an argon matrix the sulfur atoms react to form the corresponding thiophosphoryl halides, SPX<sub>3</sub>. By contrast, no evidence of sulfur atom transfer has been found with the substrates NF<sub>3</sub>, PH<sub>3</sub>, AsF<sub>3</sub>, or HCl similarly isolated in an argon matrix or with N<sub>2</sub> or Xe even when used as the matrix material. Whether sulfur atoms add to a given substrate X depends, it seems, on the efficiency with which the initial "hot" adduct [XS]\* is quenched and on the photolability of the deactivated product XS.

In a solid methane matrix insertion of sulfur atoms occurs to give methanethiol, a reaction diagnostic of sulfur atoms in the <sup>1</sup>D excited state; a second pathway involves decomposition of the "hot" adduct [CH<sub>4</sub>S]\* to thioformaldehyde. However, neither methanethiol nor thioformaldehyde can be detected when sulfur atoms are formed in a methane-doped argon matrix (Ar:CH<sub>4</sub> = 5:1). The behavior of an ethene- or ethyne-doped argon matrix confirms that diffusion-controlled reactions involve only ground-state (<sup>3</sup>P) sulfur atoms, presumably because of efficient collisional quenching of the <sup>1</sup>D sulfur atoms. This contrasts with the corresponding reactions in the gas phase in which <sup>1</sup>D sulfur atoms have been shown to participate.<sup>6</sup> Thus, ethene adds sulfur atoms in an argon matrix to give thiirane, CH<sub>2</sub>CH<sub>2</sub>S, whereas ethyne produces thicketene,  $H_2C==C==S$ , and ethynethiol, HC=CSH, together with small amounts of thiirene, CH=CHS. For the matrix reactions of sulfur atoms with methane, ethene, or ethyne we have proposed mechanisms which are consistent with

the structures and relative proportions of the various products. Acknowledgment. We thank SERC for supporting this research

and for funding studentships for both M.H. and M.J.A.

**Registry No.** OCS, 463-58-1; PF<sub>3</sub>, 7783-55-3; PCl<sub>3</sub>, 7719-12-2; C<sub>2</sub>H<sub>4</sub>, 74-85-1; C<sub>2</sub>H<sub>2</sub>, 74-86-2; C<sub>2</sub>D<sub>4</sub>, 683-73-8; Ar, 7440-37-1; CH<sub>4</sub>, 74-82-8; CD<sub>4</sub>, 558-20-3; SPF<sub>3</sub>, 2404-52-6; OPF<sub>3</sub>, 13478-20-1; OPCl<sub>3</sub>, 10025-87-3; CO, 630-08-0; CS<sub>2</sub>, 75-15-0; CO<sub>2</sub>, 124-38-9; CH<sub>3</sub>SH, 74-93-1; H<sub>2</sub>CS, 865-36-1; CD<sub>3</sub>SD, 65871-23-0; D<sub>2</sub>CS, 58131-73-0; SPEt<sub>3</sub>, 597-51-3; thiirane, 420-12-2; ethynethiol, 53750-02-0; thioketene, 18282-77-4.