The Reactions of Sulfur Atoms. V. Further Studies on the Reactions with Olefins

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The reaction of S atoms, from the in situ photolysis of carbonyl sulfide, with ethylene and propylene has been re-examined using g.c. for product analyses. In addition to episulfides reported earlier, the novel, isomeric vinyl mercaptan (~45%) from ethylene, propenethiol (10–15%), and allyl mercaptan (10–15%) from propylene were also found as products. The reaction with 1,1-difluoroethylene yielded 1,1-difluoroethylene sulfide and 2,2-difluorovinyl mercaptan (~30%). Mercaptans are formed exclusively from the singlet S atom precursor, as was demonstrated by the suppressing effect of added carbon dioxide, while episulfides may be formed by either singlet or triplet S atoms. Possible mechanisms for product formation are discussed, including the roles of the $S(^1D)$ and $S(^3P)$ species in the reactions.

Introduction

In the first paper[1] of this series on atomic sulfur reactions, it was shown that the *in situ* photolysis of carbonyl sulfide is a convenient source of this species and that the sulfur atoms, produced by this means, readily undergo reactions with ethylene and propylene at room temperature. The three following communications[2] in the series were devoted to studies of S atom reactions with paraffinic hydrocarbons. While these latter investigations advanced smoothly, the further, yet-unpublished studies on olefin systems led to unexpected results which were finally found to be due to the presence of the hitherto-unknown, simple vinylthiols among the products and to the related product-handling and analytical problems. Recent developments[3,4] in vinylthiol chemistry, as well as in sulfur atom–paraffin reactions,[2] dictate a more detailed re-examination of the ethylene and propylene systems, using g.c. for product analysis.

The results of these investigations, along with those obtained for CF_2CH_2, follow.

Experimental

The apparatus, reaction system, and optical arrangement were essentially identical with those described previously.[1,2] The effective wave length region of the photolysis was 2290–2550 Å.

Carbonyl sulfide (Matheson) was purified by passage through a train of washing bottles containing dilute solutions of lead acetate and concentrated sodium hydroxide, kept at 0°, which effected the complete removal of the CO_2 and H_2S impurities. This was followed by degassing and trap-to-trap distillation at −130° (*n*-pentane slush). G.c. analysis of the purified material (on a 26-ft., 18% silicone 550 with 2% stearic acid on Celite column, at −23°, with H_2 carrier at 20 ml./min.) failed to reveal any impurity.

The ethylene, ethane (Phillips research grade), and CF_2CH_2 (Matheson) were purified by trap-to-trap distillation at −161° (isopentane slush), and propylene, at −130°. The carbon dioxide used was Airco assayed reagent.

In the runs with ethylene, carbon monoxide was removed at −210° (solid nitrogen); for the other olefins, it was removed at −196° and measured in a gas buret. Sulfur-containing products were analyzed on either of the following columns: 8-ft., 18% silicone 550 and 2% stearic acid on Celite (column I) and 8-ft. or 16-ft., 25% *o*-tricresyl phosphate on firebrick (column II).

For particular systems the following analytical procedures were applied.

Ethylene and Ethylene–Carbon Dioxide–Ethane Mixtures. After removing the CO product, the excess reactants were distilled at −130° and restored to the cell. The retained products (condensables) were measured in the gas buret and subsequently analyzed on column I at room temperature, with He carrier at 50 cc./min.

1,1-Difluoroethylene and Propylene. These compounds were handled as above, except that the condensable fractions were analyzed, respectively, on column II at 35° and column I at room temperature with He carrier flow of 50 cc./min. The products were kept at liquid nitrogen temperatures at all times, except during manipulations, to inhibit decomposition. Product characterizations were performed on the separated components of the g.c. effluents by mass spectrometric analysis, together with at least one of the following methods: g.c. retention time comparison, infrared, or n.m.r. spectroscopy. All experiments reported were carried out at 24 ± 4°.

Results

Ethylene. Careful re-examination of the reaction of S atoms—from the *in situ* photolysis of COS—with ethylene, showed the condensable fraction of the reaction mixture to be composed of two distinct products, separable by g.c. On column I, the retention time ratio of component B to component A was 2.4 under the operating conditions. Mass spectrometric analyses on the g.c. effluent indicated that both compounds A and B have a molecular weight of 60 with each containing one sulfur and four hydrogen atoms. Both the g.c. retention time and the mass spectral cracking pattern of component A agreed with those for vinyl mercaptan (VM), which had been synthesized by the

(1) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962).
(2) A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **85**, 1207 (1963); **85**, 2349 (1963); A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *ibid.*, **86**, 4243 (1964).
(3) F. A. Stacey and J. F. Harris, *ibid.*, **85**, 963 (1963).
(4) O. P. Strausz, T. Hikida, and H. E. Gunning, *Can. J. Chem.*, in press.

Table I. The Mass Spectra of Products from the Reaction of Sulfur Atoms with C_2H_4, CF_2CH_2, and C_3H_6[a]

m/e	VM[b] Product	VM Standard	ES[c] Product	ES Standard	m/e	DFVM[d]	DFES[e]
62	10.7	8.8	4.3	4.6	98	3.2	4.9
61	8.0	9.9	6.3	6.4	97	2.8	3.6
60	100	100	100	100	96	46.9	98.7
59	92.3	95.5	74.7	79.5	95	5.6	2.1
58	41.8	47.0	25.5	25.3	94	5.8	2.3
57	25.0	32.7	11.3	11.5	65	3.8	20.5
56	6.7	9.3	2.7	2.5	64	3.3	23.4
47	6.1	7.7	4.2	4.3	63	8.2	13.3
46	3.1	3.4	5.0	5.4	60	1.0	2.0
45	73.2	76.4	88.2	89.1	59	0.7	3.3
44	6.3	7.2	4.7	3.8	58	1.2	6.6
34	20.7	26.4	9.8	9.9	57	5.6	19.0
33	8.7	12.2	3.2	3.2	56	1.8	2.3
32	8.8	14.1	6.6	5.1	51	4.6	12.3
29	9.5	6.2	2.3	2.9	50	2.8	3.9
28	8.4	4.1	6.2	4.5	48	3.7	5.9
27	42.7	50.8	24.2	22.1	47	8.4	13.6
26	14.0	19.8	9.7	8.9	46	27.3	87.7
25	3.8	7.3	2.1	2.0	45	100	100
					44	10.1	58.4
					34	1.2	3.8
					33	9.8	34.4
					32	6.7	6.5
					31	10.6	19.5

m/e	MVM[f] Product	MVM Standard	PS[g] Product	PS Standard	AM[h] Product	AM Standard
76	8.7	9.9	6.2	5.6	8.3	7.0
75	4.2	4.0	4.5	3.9	5.0	4.1
74	83.3	81.1	99.9	100	100	97.2
73	16.3	15.7	10.8	11.1	8.7	8.8
72	2.8	1.9	...	...	1.2	1.3
71	8.7	9.0	3.9	3.9	4.8	4.2
70	1.4	1.4	...	...	...	...
69	8.7	8.4	3.0	3.3	5.1	4.4
68	2.2	2.6	...	...	1.5	1.3
61	1.2	1.8	1.6	...	...	...
59	13.2	12.7	33.4	32.4	8.2	10.0
58	8.5	8.0	9.8	11.0	3.6	3.8
57	4.7	4.8	4.2	4.2	3.3	3.3
48	3.0	2.4	3.6	3.6	2.9	2.1
47	17.4	22.2	14.0	16.1	24.6	20.2
46	18.1	18.3	50.0	49.2	17.4	19.1
45	70.8	70.5	56.2	55.5	40.6	40.4
44	1.2	4.0	2.9	2.6	...	...
43	6.6	5.3	...	1.3	6.2	11.9
42	8.7	7.8	8.5	5.8	6.9	11.5
41	100	100	100	97.0	97.8	100
40	7.2	6.4	6.2	5.8	8.5	8.7
39	56.2	55.5	41.7	42.4	72.5	71.3
38	8.8	8.5	6.4	6.4	11.1	10.5
37	6.3	7.0	4.0	3.9	6.8	6.2
36	1.6	1.9	1.0	1.9	1.2	1.2
35	4.0	4.2	1.7	1.5	2.1	1.8
34	2.1	2.5	2.0	1.4	3.3	3.0
33	3.4	3.4	1.8	1.1	4.2	3.3
32	...	3.4	...	3.4	...	...
29	3.3	2.7	2.3	2.7	3.9	3.7
28	...	2.9	...	3.0	...	...
27	11.6	11.8	12.4	12.6	10.9	11.1
26	4.6	4.9	5.5	5.7	4.0	3.9
15	2.8	3.0	2.6	3.8	2.7	2.9

[a] The spectra were obtained on a Metropolitan–Vickers Model MS-2 spectrometer at 70 e.v. [b] Vinyl mercaptan. [c] Ethylene episulfide. [d] 2,2-Difluorovinyl mercaptan. [e] 1,1-Difluoroethylene episulfide. [f] Methyl vinyl mercaptan. [g] Propylene episulfide. [h] Allyl mercaptan.

ultraviolet light-induced addition of H_2S to acetylene.[4] Further confirmation of this assignment came from the infrared spectrum, which showed strong absorption at 1580 cm.$^{-1}$ (C=C stretching) as reported for vinyl[4] and vinylic[3] mercaptans. The g.c. retention time and the mass spectral cracking pattern of component B were identical with those of ethylene episulfide (ES). The mass spectra of A and B, compared to those obtained with synthetic samples, are given in Table I. Thus, the reaction of S atoms with ethylene, in the present system, leads to the formation not only of ethylene sulfide as previously reported[1] but also of vinyl mercaptan. Failure to detect VM in our previous study[1] was largely due to the fact that product analyses were performed by mass spectrometry, and the mass spectra of ES and VM are quite similar. Furthermore, in runs of long exposure duration, performed to accumulate sufficient material for infrared analyses, considerable depletion of VM could occur since it readily polymerizes at room temperature. In addition, at that time, vinyl mercaptan and its simple derivatives were unknown and generally, by analogy with vinyl alcohol, were presumed not to exist as stable monomers.

To study the yield of products under various conditions and to deduce a possible mechanism for VM and ES formation, five series of quantitative experiments were performed.

Table II. Variation in Product Rates with Reaction Time in the COS–C_2H_4 System[a]

Time, min.	Rates, μmoles/min. × 10² CO	VM	ES	R(VM)/R(ES)	[R(VM) + R(ES)]/R(CO)
10	25.2	7.77	9.13	0.85	0.67
15	23.1	7.86	8.80	0.89	0.72
20	23.9	7.80	8.60	0.91	0.69
30	24.9	8.13	8.33	0.97	0.66
40	23.9	6.87	8.50	0.81	0.64
50	24.8	5.70	8.08	0.70	0.56
60	23.6	5.43	7.27	0.75	0.54

[a] $P(COS) = 127$ torr; $P(C_2H_4) = 280$ torr.

I. COS (127 torr) admixed with 280 torr of C_2H_4 was photolyzed in a 200-mm. long cell for an exposure duration of 10 to 60 min. From the results given in Table II it appears that both the $R(VM)/R(ES)$ ratio and the total condensable yield decline in the runs at longer exposures. The time dependence, however, is not significant at short exposures, and consequently both compounds are primary products of the reaction.

II. COS (100 torr) was photolyzed in the presence of various amounts of C_2H_4 in a 100-mm. cell for 30 min. From the data presented in Table III it is seen that, with increasing pressure of added ethylene, $R(CO)$ gradually decreases and, at $P(C_2H_4) = 800$ torr,

Table III. Variation in Product Rates with C_2H_4 Pressure in the $COS-C_2H_4$ Systems[a]

| $P(C_2H_4)$, torr | Rates, μmoles/min. $\times$ 10 | | | ΣR (VM, ES) | CO^0 $-$ CO | $R(VM)/$ $R(ES)$ | % re-covery[b] |
	CO	VM	ES				
0	3.01	...	...	...	...	...	..
25	2.27	0.21	0.30	0.51	0.74	0.70	69
50	2.08	0.28	0.413	0.693	0.93	0.68	75
100	1.99	0.417	0.533	0.950	1.02	0.78	93
200	1.80	0.480	0.560	1.040	1.21	0.86	86
300	1.73	0.503	0.567	1.070	1.28	0.89	84
400	1.67	0.537	0.573	1.110	1.34	0.94	82
600	1.64	0.560	0.590	1.150	1.37	0.95	84
800	1.57	0.573	0.603	1.176	1.44	0.95	82

[a] $P(COS) = 100$ torr; exposure time $= 30$ min. [b] % recovery of condensables in terms of $R^0(CO) - R(CO)$.

Table IV. Rates of Product Formation As a Function of Added CO_2 Pressure in the $COS-C_2H_4$ System[a]

| $P(CO_2)$, torr | Rates, μmoles/min. $\times$ 10 | | | $R(VM)/$ $R(ES)$ | % re-cov-ery[b] |
	CO	VM	ES		
0[c]	1.38	0.51	0.63	0.82	82.6
138	1.36	0.43	0.72	0.60	84.6
256	1.37	0.42	0.86	0.49	93.4
385	n.d.	0.26	0.91	0.29	...
500	1.35	0.18	1.03	0.17	89.6
760	1.35	0.09	0.87	0.10	71.1
1000	1.35	0.09	1.00	0.09	80.7

[a] $P(COS) = 50$ torr; $P(C_2H_4) = 200$ torr; exposure time $= 30$ min. [b] % recovery in terms of $R^0(CO) - R(CO)$. [c] Average of three runs.

does markedly decrease the ratio of $R(VM)/R(ES)$; that is, ES formation is enhanced at the expense of VM. These data would suggest that VM formation is associated exclusively with $S(^1D)$ atom reactions while ES formation is not. In order to substantiate further this conclusion, two series of runs were made with added C_2H_6 as a monitor for $S(^1D)$ atoms.[2] In series IV, the $COS-C_2H_4-C_2H_6$ system was first examined.

IV. To this end, a mixture of 127 torr of COS and 280 torr of C_2H_4 was photolyzed in the presence of various amounts of added C_2H_6. The data are tabulated in Table V. With increasing pressure of added C_2H_6 the rate of formation of ethyl mercaptan (EM) rises from zero to a maximum at $P(C_2H_6)$ exceeding

Table V. Product Rates in the $COS-C_2H_4-C_2H_6$ System As a Function of C_2H_6 Pressure[a]

| $P(C_2H_6)$, torr | $P(C_2H_6)/$ $P(C_2H_4 + C_2H_6)$ | Rates, μmoles/min. $\times$ 10 | | | | $R(EM)/$ $[R(VM)$ $+$ $R(ES)]$ | $R(EM)/$ $R(VM)$ | % re-cov-ery[c] |
		CO	VM	EM[b]	ES			
0	0.00	2.31	0.787	0.000	0.880	0.0	0.0	..
11	0.04	2.40	0.767	0.000	0.893	0.0	0.0	..
117	0.29	2.37	0.600	0.280	0.613	0.23	0.47	..
200	0.42	2.33	0.520	0.453	0.693	0.37	0.87	..
300	0.52	2.41	0.527	0.713	0.720	0.55	1.24	..
400	0.59	2.62	0.420	0.833	0.693	0.75	1.98	74
500	0.64	2.50	0.407	0.927	0.633	0.89	2.28	79
650	0.70	2.40	0.360	1.13	0.580	1.20	3.12	83
900	0.76	2.34	0.267	1.11	0.580	1.32	4.17	84

[a] $P(COS) = 127$ torr; $P(C_2H_4) = 280$ torr; exposure time $= 15$ min. [b] Ethyl mercaptan. [c] % recovery of condensables in terms of CO formed.

$R(CO)$ is within *ca.* 5% of $R^0(CO)/2$, where $R^0(CO)$ is the rate for pure COS. Simultaneously, $R(VM)$ and $R(ES)$ rise as the primary S atoms are increasingly scavenged by C_2H_4. The percentage yields for the condensable products maximize at 93% in terms of the $R(CO)$ decrease at $P(C_2H_4) = 100$ torr.

III. To test the possible role of any excited species, such as $S(^1D)$ atoms or energy-rich adduct molecules, present in the system, upon the distribution of products, a mixture of 50 torr of COS and 200 torr of C_2H_4 was photolyzed in the 200-mm. cell for an exposure duration of 30 min. in the presence of various amounts of added CO_2. Carbon dioxide has been shown to undergo no reactions with S atoms and serves only as an efficient deactivator of $S(^1D)$ atoms.[2] The results of these experiments are listed in Table IV, where it is seen that the addition of CO_2 to the system has no effect on $R(CO)$ or the combined VM $+$ ES rates but

650 torr while $R(VM)$ and $R(ES)$ decrease. The decrease, however, is more rapid for VM than ES. Now ethane[2] has been shown to react with $S(^1D)$ atoms *via* two routes: (a) insertion to form EM and (b) collisional deactivation to the ground triplet-P state, with the ratio of $b/a = 0.71$. Thus, ethylenic products resulting from $S(^1D) + C_2H_4$ reactions, because of competition with ethane, should gradually fall off while products resulting from $S(^3P) + C_2H_4$ reactions should reach a limiting value of 0.71 EM. It can be seen from the data in Table V that at 900 torr, the highest C_2H_6 pressure employed, VM formation is not yet completely suppressed. We can, however, estimate $R(ES)$ by the relation $R(ES) = 1.14 R(VM) + 0.71 R(EM)$, where 1.14 is the interpolated value for the ratio $R(ES)/R(VM)$ at $P(C_2H_4) = 280$ torr, from Table III. The experimental values, as is evident from the data, are lower. If, however, it is assumed that the

Table VI. Rates of Product Formation As a Function of Added CO_2 Pressure in the $COS-C_2H_4-C_2H_6$ System[a]

| $P(CO_2)$, torr | Rates, μmoles/min. × 10 | | | | ΣR (VM, EM, ES) | $R(VM)/$ $R(EM)$ | $[R(VM)$ $+$ $R(EM)]/$ $R(ES)$ | % recovery[b] |
	CO	VM	EM	ES				
0	1.21	0.15	0.29	0.34	0.78	0.52	1.29	64.5
133	1.17	0.11	0.23	0.39	0.73	0.48	0.87	64.6
252	1.19	0.10	0.21	0.45	0.76	0.48	0.69	63.9
504	1.22	0.08	0.17	0.50	0.75	0.47	0.50	61.5
800	1.17	0.05	0.10	0.59	0.74	0.50	0.25	63.2

[a] $P(COS) = 50$ torr; $P(C_2H_4) = P(C_2H_6) = 200$ torr; exposure time = 60 min. [b] % recovery of condensables in terms of CO formed.

Table VII. Variation in Product Rates with CF_2CH_2 Pressure in the $COS-CF_2CH_2$ System[a]

| CF_2CH_2, torr | Rates, μmoles/min. × 10 | | | ΣR (DFVM, DFES) | CO^0 $- CO$ | $R(FVM)/$ $R(DFES)$ | % recovery[b] |
	CO	DFVM	DFES				
0	4.43	..	..	..	..	..	..
50	2.95	0.07	0.53	0.60	1.48	0.13	41
100	2.71	0.20	0.77	0.97	1.71	0.26	54
200	2.53	0.30	0.81	1.11	1.89	0.37	59
300	2.43	0.33	0.86	1.19	2.00	0.38	60
400	2.33	0.38	0.90	1.28	2.09	0.42	61
600	2.25	0.38	0.93	1.31	2.17	0.41	60
800	2.21	0.39	0.87	1.26	2.21	0.45	58

[a] $P(COS) = 100$ torr; exposure time = 15 min. [b] % recovery of condensables in terms of $R^0(CO) - R(CO)$.

loss in the condensable yield $[R^0(CO) - R(CO) - R(VM + EM + ES)]$ is mainly due to loss in ES, at least in the higher pressure runs, the agreement is acceptable.

V. Finally, the data obtained from the photolysis of a mixture of 50 torr of COS, 200 torr of C_2H_4, and 200 torr of C_2H_6 in the presence of varying amounts of added CO_2 are given in Table VI. The parallel decrease in VM and EM and the equivalent increase in ES observed here prove unambiguously that VM formation is associated exclusively with $S(^1D)$ atom reactions.

Two preliminary runs were also performed on perdeuterioethylene to test the effect of deuterium substitution on the ratio VM/ES. The values obtained under similar conditions (100 torr of COS and 400 torr of ethylene) were $[R(VM)/R(ES)]_D = 0.89$ and $[R(VM)/R(ES)]_H = 0.94$.

1,1-Difluoroethylene. The condensable fraction of the reaction products with this substrate was also found to be composed of two compounds, which could be separated by g.c. analysis. The relative retention time of components A and B was 1.5 on column II. The infrared spectrum of component A showed strong absorption at 1710 cm.$^{-1}$ which is consistent with the $CF_2=CHSH$ structure since the stretching frequencies of the $C=C$ vibration in the parent molecules C_2H_4 to CF_2CH_2 are at 1626 and 1730 cm.$^{-1}$, respectively.[5] The mass spectra of the two components given in Table I indicate a molecular weight of 96 for both compounds. The parent mass is relatively more intense in the spectrum of B and so is the thioformaldehyde positive ion peak intensity. These facts, taken in conjunction with the infrared spectrum, make possible a tentative identification of component B as 1,1-difluoroethylene episulfide (DFES), and component A as 2,2-difluorovinyl mercaptan (DFVM).

(5) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, 41, 263 (1945).

Three series of quantitative experiments were carried out on the $COS-CF_2CH_2$ system.

I. A mixture of 100 torr of COS and 400 torr of CF_2CH_2 was photolyzed in the 100-mm. cell for various exposure durations. It can be seen from the results shown graphically in Figure 1 that both DFVM and DFES are primary products of the reaction of S atoms with CF_2CH_2 and that the relative yield of these products is exposure time dependent. The ratio of DFVM/DFES declines with increasing exposure duration, and a linear extrapolation yields a limiting value of 0.44 at zero exposure time.

II. The results of experiments in which 100 torr of COS was photolyzed in the presence of varying amounts of CF_2CH_2 are tabulated in Table VII. Here it should be noted that $R^0(CO)$ is reduced to $R^0(CO)/2$ upon addition of 800 torr of CF_2CH_2. The optimum yield of condensable products, 61% in terms of CO decrease, obtains at a CF_2CH_2 pressure of 400 torr. The ratio of mercaptan to episulfide is lower here than in the $COS-C_2H_4$ system and follows a similar, although more accentuated, pressure trend.

III. The effect of CO_2 on the reaction was tested by photolyzing a 50 torr of COS–50 torr of CF_2CH_2 mixture with various amounts of added CO_2. The results shown in Figure 2 indicate the expected suppression of mercaptan formation. The yield of DFVM monotonously decreases with pressure while that of DFES starts to fall off slowly only after an initial rise.

In Figure 2 a plot indicating the effect of added CO_2 on the $R(CO)$ values from 50 torr of COS is also given. A similar slight decrease is apparent as with the $COS-CF_2CH_2$ mixture.

It should perhaps be noted here that, in the corresponding experiment with C_2H_4, where the $(C_2H_4)/(COS)$ ratio was 4 (*cf.* Table IV), no change in $R(CO)$ was found.

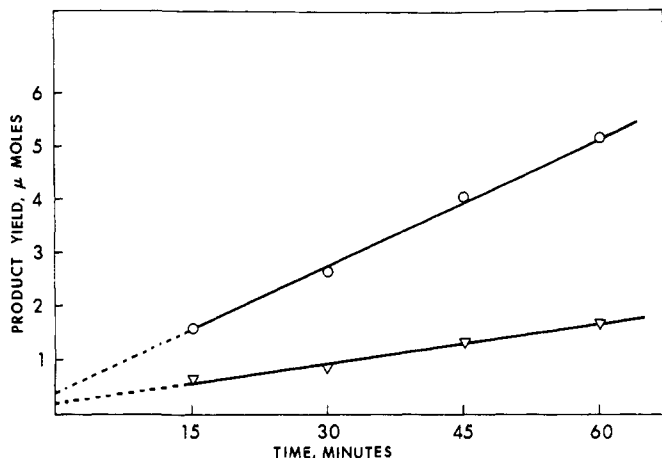*Propylene.* The reaction of S atoms with C_3H_6

Figure 1. Yields of 1,1-difluoroethylene episulfide (DFES) and 2,2-difluorovinyl mercaptan (DFVM) formation as a function of exposure time for the $COS-CF_2CH_2$ system. $P(COS)$ = 50 torr; $P(CF_2CH_2)$ = 50 torr. DFES, O; DFVM, ∇.

Figure 2. Lower diagram: rates of CO, DFES, and DFVM formation as a function of added CO_2 pressure for the $COS-CF_2CH_2$ system. $P(COS)$ = 50 torr; $P(CF_2CH_2)$ = 50 torr; exposure time = 30 min. CO, ●; DFES, O; DFVM, ∇. Upper diagram: rate of CO formation from pure COS as a function of added CO_2 pressure. $P(COS)$ = 50 torr; exposure time = 30 min.

resulted in three condensable products separable by g.c. From a comparison of their g.c. retention time values, mass spectra, infrared, and n.m.r. spectra with those of standard samples,[4] they were identified as propylene episulfide (PS), propenethiol(s), methylvinyl mercaptan (MVM), and allyl mercaptan (AM). Using g.c. column I the relative retention times AM:MVM:PS were 1.00:1.24:1.61. The mass spectra are given in Table I. In high pressure runs three additional minor products appeared on the chromatogram, but their combined yields were always less than 5 area % of the total. One of these was shown to be CS_2.

Two series of quantitative experiments were made with the $COS-C_3H_6$ system.

I. A mixture of 100 torr of COS and 200 torr of C_3H_6 was photolyzed for various lengths of irradiation time. The results presented in Figure 3 are similar to those obtained in the two previous cases in that all the products appear to arise from the primary interaction of S atoms with the substrate molecule.

II. In this series 100 torr of COS was photolyzed with various amounts of C_3H_6. The results are summarized in Table VIII. The kinetic behavior is obviously similar to that found for the previous two substrates. The following features of the reaction should be noted: the decline in $R(CO)$ with pressure is about the same here as with C_2H_4 or CF_2CH_2; at 800 torr, the highest propylene pressure employed, the S atom cleanup is very nearly complete; the yields of both mercaptans increase slightly with pressure while the total condensable yield appears to be somewhat higher at low pressures.

A brief study was also made of the effect of added CO_2 on product rates in this system. The results clearly indicated a significant rise in the episulfide rate at the expense of the total mercaptan rate, similar to the behavior found for C_2H_4 and CF_2CH_2.

Discussion

It is evident from the data of the foregoing section that the reactions of the three olefinic substrates examined here exhibit similar features which are probably characteristic of the reactions of $S(^1D)$ atoms with olefinic hydrocarbons in general. The following steps
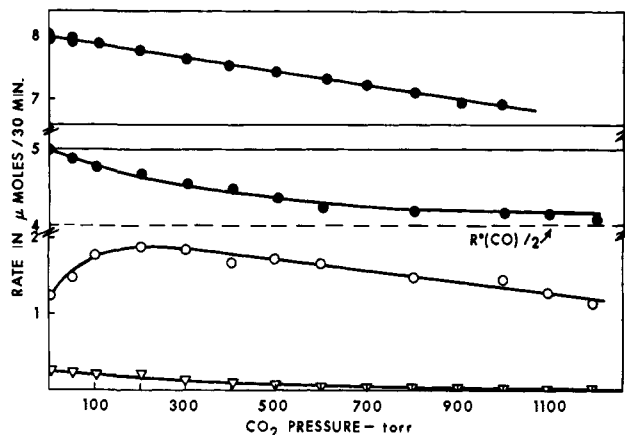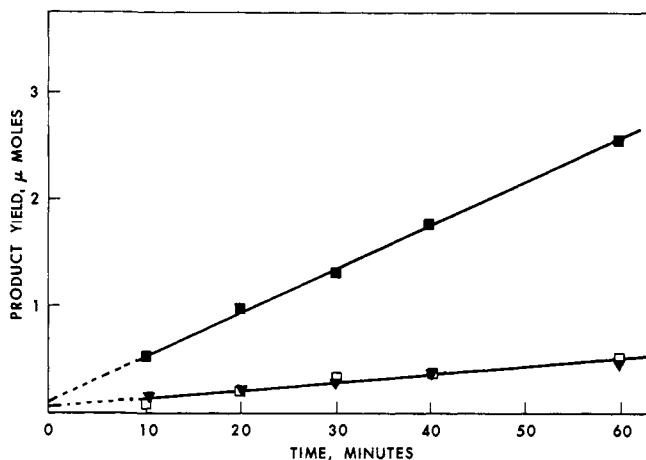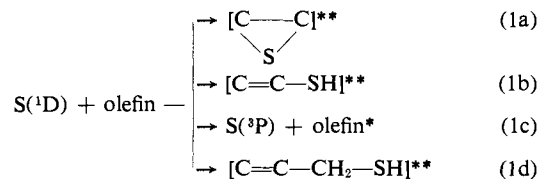

Figure 3. Yields of propylene episulfide (PS), methyl vinyl mercaptan (MVM), and allyl mercaptan (AM) formation as a function of exposure time from the $COS-C_3H_6$ system. $P(COS)$ = 50 torr; $P(C_3H_6)$ = 50 torr. PS, ■; MVM, □; AM, ▲.

must be considered for the primary reaction

$$S(^1D) + olefin \begin{cases} \rightarrow [C \overset{\diagdown \diagup}{S} C]^{**} & (1a) \\ \rightarrow [C{=}C{-}SH]^{**} & (1b) \\ \rightarrow S(^3P) + olefin^* & (1c) \\ \rightarrow [C{=}C{-}CH_2{-}SH]^{**} & (1d) \end{cases}$$

Episulfide formation in step 1a results from the interaction of singlet sulfur atoms with the π-bond of the olefin in a single step, insertion-type process; that is, the reaction proceeds without going through a biradical state. This step is exothermic by ca. 73 kcal./mole, which is ample to bring about the isomerization of the episulfide molecule to the vinyl mercaptan structure

$$\left[\begin{array}{c} C{-}C \\ \diagdown S \diagup \\ I \end{array} \right]^{**} \rightleftarrows [C{=}C{-}SH]^{**} \qquad (2)$$
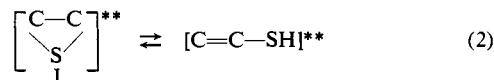
If these processes are operative, they should be nearly pressure independent in the range encountered in these

Table VIII. Variation in Product Rates with C_3H_6 Pressure in the COS–C_3H_6 System[a]

| $P(C_3H_6)$, torr | Rates, μmoles/min. $\times$ 10 | | | | | | | | ΣR (MVM, AM)/ R(PS) | % re-cov-ery[b] |
	CO	MVM	AM	PS	ΣR (MVM, AM, PS)	CO^0 – CO	R(MVM)/ R(PS)	R(AM)/ R(PS)		
0	2.12					0				
25	1.57	0.049	0.047	0.343	0.439	0.546	0.14	0.14	0.28	81
51	1.48	0.060	0.046	0.366	0.472	0.640	0.16	0.13	0.29	74
103	1.36	0.083	0.076	0.377	0.536	0.754	0.22	0.20	0.42	71
205	1.28	0.092	0.099	0.410	0.601	0.836	0.22	0.24	0.47	72
305	1.25	0.084	0.103	0.450	0.637	0.870	0.19	0.23	0.42	73
406	1.20	0.075	0.094	0.450	0.619	0.920	0.17	0.21	0.38	67
505	1.11	0.113	0.121	0.470	0.704	1.00	0.24	0.26	0.50	70
604	1.11	0.097	0.127	0.480	0.704	1.00	0.20	0.27	0.47	70
802	1.09	0.106	0.123	0.490	0.719	1.03	0.22	0.25	0.47	70

[a] P(COS) = 101 torr; exposure time = 30 min. [b] % recovery of condensables in terms of R^0(CO) – R(CO).

experiments (*ca.* 100–900 torr) since the olefin pressure does not seem to influence appreciably the mercaptan/ episulfide ratios in the C_2H_4 and C_3H_6 systems. This would indicate that the lifetime of the excited episulfide molecules is short, shorter than the average collision interval. The lifetime, on the other hand, should greatly depend on the number of internal degrees of freedom in the molecule, and consequently the mercaptan/episulfide rate ratio would be expected to be higher for C_2H_4 than for C_3H_6. The experimental values of 0.70–1.0 for C_2H_4 (Table III) and 0.14–0.24 for C_3H_6 (Table VIII) are consistent with these considerations. Here, however, it should be noted that the two values are not directly comparable for two reasons. First, the number of vinylic H atoms is different in the two molecules; second, in the propylene reaction the interaction between S(^{1}D) atoms and the methyl group of the molecule may lead not only to allyl mercaptan formation but also, as with paraffins in general,[2] to electronic relaxation of the excited sulfur atoms to the ^{3}P state. The triplet sulfur atoms formed thereby will react with the π-bond of the olefin and increase the yield of episulfide. Taking proper corrections for these effects, we obtain for the propylene reaction MVM/PS = 0.22–0.41, which is still less than half of the mercaptan/episulfide ratio found for the ethylene system.

On the other hand the DFVM/DFES ratio appears to show a significant increase with pressure in the CF_2CH_2 system. It is, however, difficult to establish whether this trend is genuine because the combined yield of mercaptan and episulfide is generally low and, in addition, changes with pressure.

Step 1b can be envisaged as a process analogous to the insertion reaction which has been shown to occur with paraffinic C–H bonds. As was convincingly shown by the CO_2 studies (Tables IV and VI and Figure 2), this reaction can occur only with singlet sulfur atoms. Now, if VM formation results exclusively from (1b), it would follow that the rate of insertion per C–H bond is faster in C_2H_4 than in C_2H_6 ($k_{(C_2H_4)}/k_{(C_2H_6)}$ = 1.12 per C–H bond) in spite of the presence of the reactive π-orbitals. Also, if the value for the rate constant ratio for deactivation to insertion is taken to be 0.71, as for the paraffins,[2] the rate ratio for the primary interactions of S(^{1}D) atoms with the C–H bonds to that with the π-bond in the C_2H_4 molecule would be *ca.* 3.

Neither of these conclusions appears to be particularly appealing.

The possibility of the isomerization of highly excited VM molecules to episulfide should also be taken into consideration, as signified by the use of double arrows in step 2.

It is not possible to determine the importance of (1c) at present. However, if only (1a) and (1b) were operative, as was pointed out in the earlier study, the relation

$$[R(CO) - R^0(CO)/2]^{-1} = R_3^{-1} = \frac{P_{\text{olefin}}}{kR^0(CO/2)} + \frac{2}{R^0(CO)} \quad (I)$$

should obtain, where $k = k_3 P_{\text{COS}}/(k_{1a} + k_{1b})$ and k_3 and R_3 are the rate constant and the rate, respectively, for the competing abstraction reaction

$$S(^1D) + COS \longrightarrow CO + S_2 \quad (3)$$
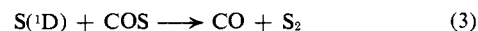
Plots of the left-hand side of eq. 1 against olefin pressure do not give the expected straight-line relation. Furthermore the relation[1]

$$\frac{R^0(CO)}{2} \times \frac{P(\text{olefin})}{R^0(CO) - R(CO)} = P(\text{olefin}) + k \quad (II)$$

is also invalid. The rate constant ratio $(k_{1a} + k_{1b})/k_3$ appears to be pressure dependent for all three substrates examined. With increasing olefin pressures, the ratio first declines, as was pointed out in the previous study.[1] It then passes through a minimum and starts to increase again, as can be seen from the data presented in Table IX. This feature of the reaction is an indication of some complexity in the mechanism. It is probably partly related to the formation of triplet atoms *via* (1c) and their subsequent competing reactions
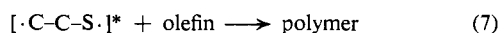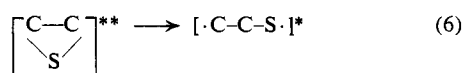
$$S(^3P) + \text{olefin} \longrightarrow \underset{S}{\overset{C——C}{\diagdown\diagup}} \quad (4)$$

$$S(^3P) + COS \longrightarrow CO + S_2 \quad (5)$$
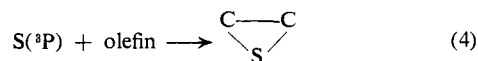
This view is also supported by the observed decrease of R(CO) in the COS–CF_2CH_2–CO_2 system (*cf.* Figure 2) which requires that $(k_{1a} + k_{1b})/k_3 < k_4/k_5$.

In this connection, the small but regular trend apparent in the condensable product yield with olefin pressure should also be noted. With C_2H_4 and CF_2CH_2 and possibly with C_3H_6 as well, the rates for the con-
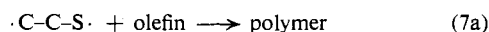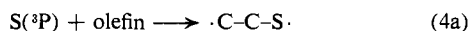
Table IX. Variation in the Rate Constant Ratios $(k_{1a} + k_{1b})/k_3$ with Olefin Pressure for the C_2H_4, CF_2CH_2, and C_3H_6 Systems

Olefin pressure, torr	$(k_{1a} + k_{1b})/k_3$		
	C_2H_4	CF_2CH_2	C_3H_6
25	3.8	...	4.3
50	3.1	4.0	3.0
100	2.0	3.5	2.4
200	1.7	2.9	1.9
300	1.8	3.1	1.5
400	1.9	4.4	1.6
600	1.5	8.3	3.0
800	2.1	...	3.8

densables increase with olefin pressure to a maximum and then start to decline. This could possibly be explained by a deactivating effect on the highly excited adduct molecule I, which would, through ring opening, otherwise undergo polymerization reactions with the substrate

$$\left[\begin{matrix} C\!\!-\!\!C \\ \diagdown S \diagup \end{matrix} \right]^{**} \longrightarrow [\cdot C\!-\!C\!-\!S\cdot]^* \qquad (6)$$

$$[\cdot C\!-\!C\!-\!S\cdot]^* + \text{olefin} \longrightarrow \text{polymer} \qquad (7)$$
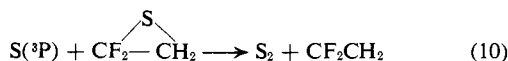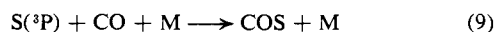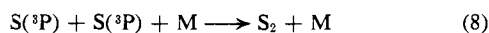
At still higher pressures, where the deactivation is nearly complete, the reaction of ground-state biradicals, formed from the addition reaction of $S(^3P)$ atoms, gain in importance with rising pressure

$$S(^3P) + \text{olefin} \longrightarrow \cdot C\!-\!C\!-\!S\cdot \qquad (4a)$$

$$\cdot C\!-\!C\!-\!S\cdot + \text{olefin} \longrightarrow \text{polymer} \qquad (7a)$$

This latter process could also explain the slight increase in the VM/ES ratios with pressure at the higher pressure levels since it would decrease the apparent rate of ES formation without affecting that of VM.

On the other hand, the effect of CO_2 on the CF_2CH_2 reaction seems to point up the possibility of some other competing reaction for the triplet atoms formed through the deactivating effect of CO_2. The initial rise in R(DFES) with CO_2 (cf. Figure 2) may be explained in terms of the increase in concentration of triplet sulfur atoms and in the resulting decrease in R(DFVM) if it is assumed that the initial rate ratio of DFVM to DFES formation is the same at low as at the high olefin pressures (cf. Table VII) and if the observed discrepancy results from the insufficient cooling of the hot DFVM molecules at low pressures.

The descending part of the R(DFES) plot and the decline in R(CO) with CO_2 pressure make it necessary to consider the following competing reactions

$$S(^3P) + S(^3P) + M \longrightarrow S_2 + M \qquad (8)$$

$$S(^3P) + CO + M \longrightarrow COS + M \qquad (9)$$

$$S(^3P) + CF_2\!\!-\!\!CH_2 \xrightarrow{\quad S \quad} S_2 + CF_2CH_2 \qquad (10)$$

Reaction 8 would be too slow to account for the effect; (9) and (10), however, could be sufficiently rapid to have significance.[6] Reaction 10 has been shown to be

(6) The addition reaction of a ground-state oxygen atom to CO is about as fast as to C_2H_4: K. J. Laidler, "The Chemical Kinetics

much faster than the $S(^3P) +$ butene-1 $\rightarrow$ butene-1 episulfide reaction.[7]

Reaction 1d, insertion in the paraffinic C–H bond of the alkyl substituent, explains the formation of AM from propylene and is consistent with the mechanism established for the paraffin reactions.[2]

From the data, relative rate constant values can be estimated

$$k(S(^1D) + C_2H_4)/k(S(^1D) + C_2H_6) = 0.75\text{–}1.60$$

The lower value was obtained assuming that only VM arises from singlet atom reactions and all the ES arises from triplet addition, while the higher value was computed on the assumption that both VM and ES arise purely from singlet insertion.

For the propylene reaction, assuming all products to be formed from $S(^1D)$ reaction, we obtain $k(S(^1D) +$ vinyl$)/k(S(^1D) + CH_3) \sim$ 5–6; i.e., the rate of reaction with the vinyl group is 5 to 6 times more efficient than insertion in the CH_3 group of the propylene molecule. On the assumption that $k(S(^1D) + CH_3)$ is about half of that of ethane, which is probably correct within a factor of 2 or 3, we obtain $k(S(^1D) +$ vinyl$)/k(S(^1D) +$ ethane$) \sim$ 2–3, or, in other words, the rate constant for the reaction with the vinyl group in propylene is 2 to 3 times larger than that for ethane; hence, $k(S(^1D) +$ vinyl in $C_3H_6)/k(S(^1D) +$ ethylene$) \sim 2$.

Finally, the existence of a possible, large H/D isotope effect could have been taken as support in favor of mechanism 1a against 1b for VM formation, since paraffinic C–H insertions show no isotope effect.[2] The observed lack of any isotope effect in the reaction, however, gives no information in distinguishing between (1a) and (1b) since it may be consistent with either mechanism.

Conclusion

While it has been clearly demonstrated in the present study on the reaction of $S(^1D)$ atoms with olefins that both alkyl and vinylic-type mercaptans originate from singlet S atom precursors, the precise mechanism for the formation of vinylic mercaptans, as well as that for episulfides, remains open. The alkyl mercaptans are produced by $S(^1D)$ atom insertion as with paraffins. Vinylic mercaptans, on the other hand, could be formed either by C–H insertion and/or by isomerization of hot episulfide molecules. The most likely route for episulfide formation is the stereospecific addition of $S(^1D)$ atoms to the π-bond of the olefin. It has also been demonstrated that the $S(^3P) +$ olefin reaction leads exclusively to episulfide formation. For the COS–olefin systems, however, this route for episulfide synthesis is probably of minor importance.

of Excited States," Clarendon Press, Oxford, England, 1955, p. 79, R. J. Cvetanović, *Advan. Photochem.*, 1, 142 (1963).
(7) K. S. Sidhu, O. P. Strausz, and H. E. Gunning, to be published.