The Reactions of Sulfur Atoms. VIII. Further Investigation of the Reactions with Olefins. Relative Rates of Addition of Sulfur (^{3}P) and (^{1}D) Atoms

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Abstract: The reactions of S atoms with cyclic olefins, chlorinated and methyl-substituted ethylenes, and perfluorocyclobutene have been examined. The salient features of these reactions are similar to those already reported for other olefins. From rate measurements, it is concluded that episulfides arise from S(^{1}D) as well as S(^{3}P) atom addition to olefins and that the fraction of sulfur atoms, from the photolysis of COS, reacting in the triplet state is less than 0.3. Relative rate constants have been obtained for the addition of S(^{1}D) and S(^{3}P) atoms to a representative series of olefins. The electrophilic character of S(^{3}P) atoms clearly manifests itself in the trend of reactivity with olefin structure. Singlet atoms are probably also electrophilic, but they are generally less selective than triplet.

The reactions of sulfur atoms with ethylene, propylene, 1-butene, isobutylene, 1,3-butadiene, *cis*- and *trans*-2-butene, and 1,1-difluoroethylene have been reported.[1] Episulfides and vinylic and alkenyl-type mercaptans are the principal products of electronically excited S(^{1}D)-atom reactions, while ground-state triplet atoms afford only episulfides. The alkenyl-type mercaptans form in a random insertive reaction into the C–H bonds of the olefin, while the vinylic-type mercaptan formation may equally well be envisaged from double-bond addition, through isomerization of the energy-rich episulfide biradical intermediate.[1c,2]

With *cis*- and *trans*-2-butene, the episulfide-forming reaction is stereospecific not only with S(^{1}D), but also with S(^{3}P) atoms. Consequently the extent of triplet S-atom participation in COS–2-butene systems cannot be estimated from the product geometry.

The objectives of the present investigation were twofold: (a) to extend our studies on the effects of substituents and structural changes in the parent olefin molecule on the nature of the reaction and its products, and (b) to establish the order of reactivity of triplet- and singlet-state atoms as a function of structural parameters for a representative series of olefins.

Experimental Section

The photolysis assembly and product-handling procedures were essentially the same as in the previous studies on S-atom reactions.[1] Materials were the best available grade. Product analyses were carried out by gas chromatography on the low-temperature condensates.

Results

Cyclopentene. The condensable fraction of the reaction products was found to consist of three gas chromatographically separable components (I–III). According to their mass spectra, shown in Table I, all three are isomers of empirical formula C_5H_8S. I and II were formed in sufficient amounts to enable identification by nmr spectroscopy. The major product (II) is the episulfide. The nmr spectrum of I consisted of two sets of doublets centered at τ 8.39 and 8.57 and two singlets at τ 4.28 and 4.34. The doublet absorptions occur in the region to be expected for thiol protons, and the singlets are probably due to vinylic protons. Therefore I actually consists of two isomers and these are probably alkenyl mercaptans, cyclopentene-3-thiol and cyclopentene-4-thiol. Intensity considerations showed that the concentration ratio of the two isomers was *ca.* 2:1, but it could not be determined which was present in the larger yield. The only structure possible for product III is that corresponding to cyclopentene-1-thiol. Its retention time corresponded to that of an authentic sample.[3]

The COS–cyclopentene system was examined as a function of cyclopentene pressure, and added CO_2 pressure, exposure time, and wavelength of radiation. Figure 1 shows rates of product formation as a function of cyclopentene pressure. At pressures >200 torr the rate is constant and R(mercaptan)/R(episulfide), (R(M)/R(E)), has a limiting value of 0.80. At the highest pressure used (300 torr) R(CO) is nearly equal to R^0(CO)/2. With increasing exposure time, the onset of secondary reactions and the attenuation of incident light intensity due to polymer deposition result in a decrease in the rate, but R(M)/R(E) remains approximately constant.

The effect of added CO_2 on a reaction mixture consisting of 100 torr of COS and 51 torr of cyclopentene is shown in Figure 2. R(M)/R(E) decreases from an initial value of 0.44 to 0.03 in the presence of 1250 torr of CO_2. Product recoveries, in terms of R(CO)–R^0(CO)/2 were independent of CO_2 pressure, indicating efficient stabilization of the initially formed "hot" episulfide even at low pressures.

The effect of wavelength of the exciting radiation was examined using a mixture consisting of 100 torr of COS and 250 torr of cyclopentene. The effective radiation of a medium-pressure mercury arc in the photolysis of COS is 2490 A; under these conditions R(M)/R(E) = 0.8 Using the 2288-A resonance line from a cadmium lamp, the ratio becomes 0.9.

Cyclohexene. The sulfur-containing products were resolved by gc into two peaks (I and II). II was identified as the episulfide by comparison of the nmr and mass

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[1] (a) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962); (b) H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **87**, 1443 (1965); (c) K. S. Sidhu, E. M. Lown, O. P. Strausz, and H. E. Gunning, *ibid.*, **88**, 254 (1966).

[2] H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

[3] D. C. Sen, *J. Indian Chem. Soc.*, **13**, 268 (1936).

Table I. Mass Spectra of Products from the Reactions of Sulfur Atoms with Cyclopentene, Cyclohexene, Trimethylethylene, Tetramethylethylene, Vinyl Chloride, and *trans*-1,2-Dichloroethylene[a]

m/e	Cyclopentene-1-thiol	Cyclopentene-3-thiol + -4-thiol	Cyclopentene episulfide	Cyclohexene-3-thiol + -4-thiol	Cyclohexene episulfide	Trimethylethylene episulfide	Tetramethylethylene mercaptan	Tetramethylethylene episulfide	Vinyl chloride episulfide	*trans*-1,2-Dichloroethylene episulfide
26				10.6					11.4	8.9
27	6.9	8.3	8.6	47.8	36.6	33.2	21.6	15.5	16.1	
28	14.4				53.9					
29				18.2		19.0	41.2	11.6		
31				16.0			47.2			
33							19.2			
34							47.5			
39	18.8	30.8	28.8	70.3	64.5	45.0	65.5	35.4		
40	5.2	8.5	7.7	12.8			12.9			
41	18.8	31.2	30.4	73.5	60.5	100.0	37.6	88.5		
42				28.7		14.2	19.5			
43				27.6			54.1	21.8		
45	7.3	14.7	14.2	26.6	16.3	35.5	31.1		100.0	100.0
47	13.0	6.8		39.4		13.5	14.6		7.2	8.0
49										72.7
50	15.5			10.6						
51				20.2	13.5					
53				20.2	24.4	29.0	17.4			
54				77.5	84.7					
55		5.3		21.2	12.9	35.5	43.6	26.8		
56							12.8			
57							15.1	21.2	16.1	24.1
58						10.2			45.6	19.8
59						26.2	58.3	100.0	56.7	
60					12.9	25.0		13.7	7.5	
61						17.8		10.1	5.8	7.8
62									5.8	
65	15.3	29.7	18.4	11.7	10.8					
66	35.8	39.7	29.6							
67	100.0	100.0	100.0	100.0	100.0	11.6	31.8	12.9		
68	10.2	6.0	9.5							
69						45.0	100.0	27.6		
70						13.6				
73				13.8			11.3			
74						70.5	27.8	76.3		
77				21.2	12.5		18.5			
79				39.4	18.7					12.6
80				22.4	26.4					
81				37.2	43.1					
82				37.2	37.0					
83						16.5	12.7			
84							44.2	11.6		
85	6.9	5.4	15.9				12.0			
87						17.6				
92										7.1
93										31.5
94									62.9	
95										12.5
96									22.8	
97							13.4			
100	10.6	8.1	27.3							
102						77.5				
111							52.5			
114				17.0	21.8					
116							11.0	43.2		
128										36.5
130										25.5

[a] The spectra were obtained on a Metropolitan-Vickers Model MS-2 spectrometer at 70 ev.

spectra with those of an authentic sample. The nmr spectrum of I indicated that two isomeric alkenyl mercaptans were present in approximately equal proportions; they are probably cyclohexene-4-thiol and cyclohexene-3-thiol. At 2490 A, *R*(M)/*R*(E) = 0.8 for a mixture consisting of 100 torr of COS and 76 torr of cyclohexene. The extrapolated value in the complete pressure stabilization region is *ca.* 1.0. The addition of CO_2 also suppresses mercaptan formation and enhances the episulfide yields.

Perfluorocyclobutene. Photolysis of COS–perfluorocyclobutene mixtures at 2288 A yielded CO, and a solid deposited on the walls of the reaction vessel. Oxidation of the solid gave SO_2 and smaller amounts of CO_2 indicating a slow reaction between S atoms and perfluorocyclobutene. The perfluorocyclobutene episul-

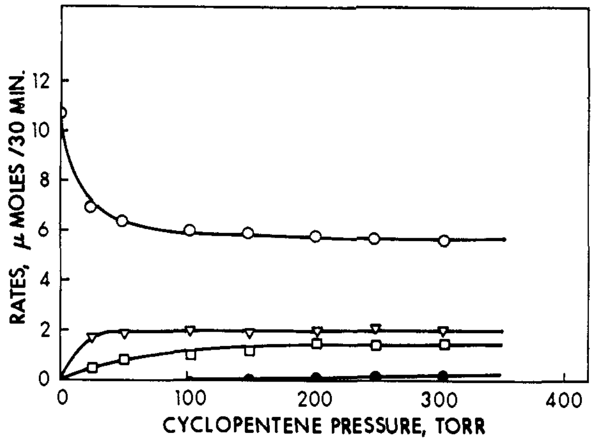

Figure 1. Addition of sulfur atoms to cyclopentene. Rates of product formation as a function of cyclopentene pressure: ○, CO; ▽, cyclopentene episulfide; □, cyclopentene-3-thiol + cyclopentene-4-thiol; ●, cyclopentene-1-thiol.

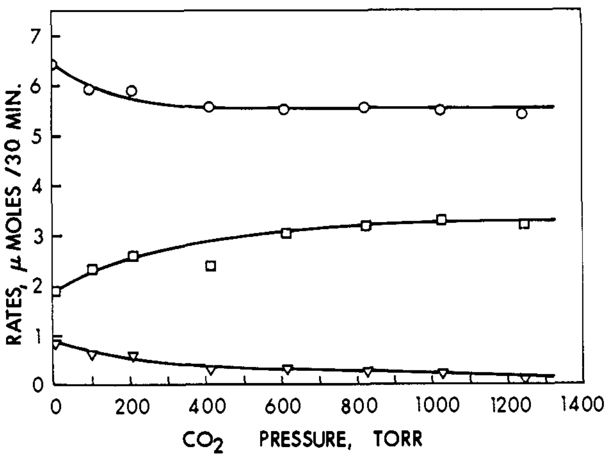

Figure 2. Addition of sulfur atoms to cyclopentene. Rates of product formation as a function of CO_2 pressure: ○, CO; ▽ cyclopentene-3-thiol + cyclopentene-4-thiol; □, cyclopentene episulfide.

fide product could indeed be detected in flash photolysis (400 μ of COS and 800 μ of cyclo-C_4F_6) by kinetic mass spectrometry.[4] It appears to be unstable at room temperature, undergoing decomposition with a half-life of the order of minutes.

The rate of CO formation in the static experiments decreases with increasing pressure of cyclo-C_4F_6 (Figure 3a) and approaches $R^0(\mathrm{CO})/2$ for a mixture consisting of 100 torr of COS and over 1000 torr of cyclo-C_4F_6.

When cyclo-C_4F_6 was added in increasing amounts to a mixture of 100 torr of COS and 75 torr of cyclopentene, no suppression of the cyclopentene reaction resulted up to 500 torr of cyclo-C_4F_6 (Figure 3b) although the ratio of mercaptan to episulfide was diminished considerably.

From comparison of the data in Figures 1–3 it is concluded that the reactivity of cyclo-C_4F_6 with S atoms is less than one-tenth of that of cyclopentene, but cyclo-C_4F_6 and CO_2 are about equally efficient in promoting the electronic relaxation of $S(^1D)$ atoms

$$S(^1D) + \text{cyclo-}C_4F_6 \longrightarrow S(^3P) + \text{cyclo-}C_4F_6 \qquad (1a)$$

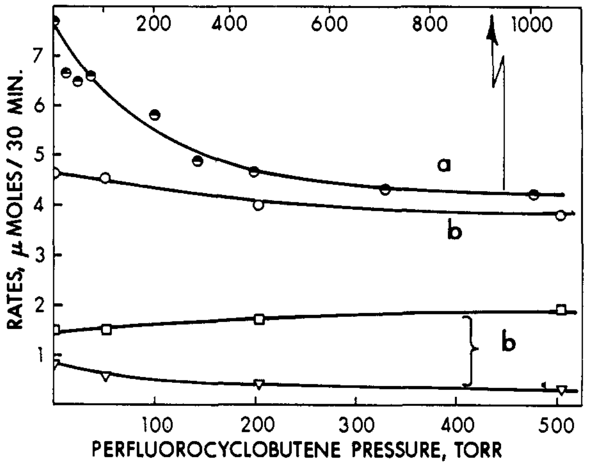

Figure 3. (a) Rates of product formation as a function of perfluorocyclobutene pressure (P(COS) = 100 torr): ◓, CO (upper scale). (b) Addition of sulfur atoms to cyclopentene. Rates of product formation as a function of perfluorocyclobutene pressure (lower scale) (P(COS) = 100 torr, P(cyclo-C_5H_{10}) = 75 torr): ○, CO; □, cyclopentene episulfide; ▽, cyclopentene-3-thiol + cyclopentene-4-thiol.

Trimethylethylene. In low-conversion runs, four gas chromatographically separable sulfur-containing products were formed. All of them were isomers with molecular weight 102 ($C_5H_{10}S$). Upon addition of CO_2 to the system, one was formed in increasing amounts, at the expense of the other three, and therefore it has been identified as the episulfide. The remaining ones are probably isomeric alkenyl mercaptans. In a mixture consisting of 100 torr of COS and 300 torr of trimethylethylene, $R(\mathrm{M})/R(\mathrm{E})$ was found to be 0.73 at 2490 A.

Tetramethylethylene. A gc analysis of the condensable fraction showed two reaction products; both had molecular weights of 116 ($C_6H_{12}S$). Identification of one of them as the episulfide was made in a manner similar to that used for trimethylethylene. Tetramethylethylene episulfide is an unstable compound and decomposes readily (on the gc column) to yield tetramethylethylene and sulfur. In a mixture of 100 torr of COS and 125 torr of tetramethylethylene, $R(\mathrm{M})/R(\mathrm{E})$ was 0.73 at 2490 A.

Vinyl Chloride. The COS–vinyl chloride system yielded two products. Both had molecular weights of 94 (C_2H_3ClS). One was identified by nmr spectroscopy as the episulfide. The nmr spectrum of the other was consistent with a chlorovinyl mercaptan structure, but insufficient amounts were formed to determine whether it is the *cis* or *trans* isomer, or a mixture of both. The effect of increasing pressure of vinyl chloride on the rates at a constant pressure of COS (100 torr) is shown in Figure 4; photolyses were performed at 2288 A. The general features of the reaction are consistent with those observed in other COS–olefin systems, except that at the highest pressure used (772 torr), $R(\mathrm{CO})$ is slightly less than $R^0(\mathrm{CO})/2$; this is probably due to competitive absorption by vinyl chloride. $R(\mathrm{M})/R(\mathrm{E})$ is also pressure dependent and reaches a limiting value of 0.19 at 600 torr of vinyl chloride.

***trans*-1,2-Dichloroethene.** Photolysis of COS-*trans*-1,2-dichloroethene mixtures using the 2490 A source at moderate total pressures resulted in the formation of

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[4] W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 4277 (1966); W. K. Duholke, R. Messmer, P. Kebarle, O. P. Strausz, and H. E. Gunning, to be published.

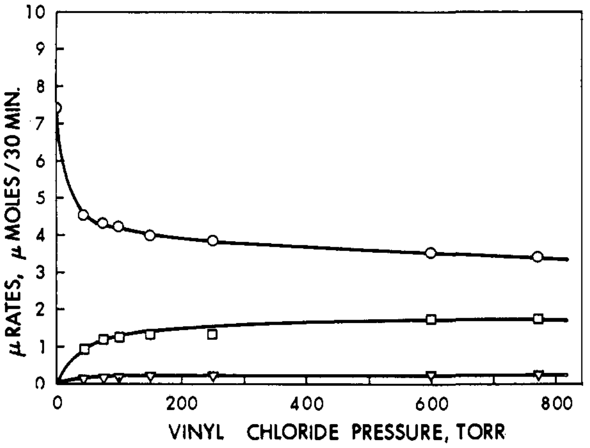

Figure 4. Addition of sulfur atoms to vinyl chloride. Rates of product formation as a function of vinyl chloride pressure: ○, CO; □, vinyl chloride episulfide; ▽, 1-chloroethene-2-thiol.

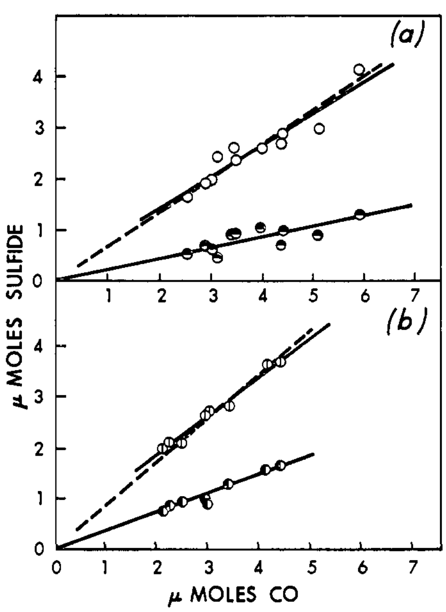

Figure 5. (a) Addition of S(^{3}P) atoms to propylene and *trans*-2-butene. Sulfide *vs.* CO yields for [C_3H_6]/[C_4H_8] = 1.42 (*P*(CO_2) = 1223, *P*(COS) = 31.5, *P*(C_3H_6) = 25.5, *P*(*trans*-2-C_4H_8) = 18.0 torr): ◒, propylene sulfide; ○, *cis*- + *trans*-2-butene sulfide × 1.42. (b) Addition of S(^{3}P) atoms to propylene and *trans*-2-butene. Sulfide *vs.* CO yields for [C_3H_6]/[C_4H_8] = 2.63 (*P*(CO_2) = 1244, *P*(COS) = 32.2, *P*(C_3H_6) = 44.7, *P*(*trans*-2-C_4H_8) = 17 torr): ◐, propylene sulfide; ◑, *cis*- + *trans*-2-butene sulfide × 2.63.

CO and a dark brown polymeric deposit. No volatile sulfur-containing products were found. In flash photolysis, however, the addition product with empirical formula of $C_2H_2Cl_2S$ could be detected by kinetic mass spectrometry, in relatively large yields. Therefore the static experiments were repeated with an excess of added CO_2, under which conditions a condensable product was isolated and resolved by gc into two components. Both compounds were shown by mass spectral analysis to correspond to the formula $C_2H_2Cl_2S$. Since episulfides are the only major products arising from the photolysis of COS–CO_2–olefin systems, they can only be geometrical isomers of the episulfide of 1,2-dichloroethene. By analogy with the results obtained in the COS–CO_2–*cis*-1,2-dichloroethene (*vide infra*) and the COS–CO_2–2-butene systems,[1c] the *trans*-episulfide represented *ca.* 90% of the total products (as compared to 98% in the COS–CO_2–*trans*-2-butene system[1c]). Product yields, calculated in terms of *R*(CO)–*R*^{0}(CO/2), increased with CO_2 pressure up to *ca.* 80%.

***cis*-1,2-Dichloroethene.** Condensable products were not observed unless a large excess of CO_2 was present. Experiments were performed using the Hg arc source. Two products were formed, which eluted on the gc column at the same time as those formed in the COS–CO_2–*trans*-1,2-dichloroethene system, and by similar reasoning the component, which represented 80% of the total, was taken to be the *cis* and the other the *trans* isomer. Product yields were *ca.* 10–20% at high pressures of CO_2.

Relative Rates of Addition of S(^{3}P) Atoms. Relative rates were determined in competitive systems where olefin pairs were chosen such that they could be recovered from the reaction mixture by low-temperature distillation. All experiments were done with the Hg arc source. Total olefin pressures did not exceed 60 torr; COS and CO_2 pressures were *ca.* 30 and 1250 torr, respectively. Under these conditions mercaptans were formed in trace quantities only. Rates for formation of episulfides were determined as a function of exposure time. Yields, calculated in terms of *R*^{0}(CO)–*R*(CO), were in the range of 80–90% except in the case of C_5 olefins where they were *ca.* 60%. At least six runs were performed for each olefin pair at various exposure times. The results obtained for ethylene, propylene, 1-butene, isobutylene, *trans*-2-butene, *cis*-2-butene, 1-pentene, 2-methyl-1-butene, cyclopentene, and vinyl chloride are given in Table II. Although the conversions were kept as short as possible, secondary decompositions could not be entirely prevented; this is evidenced by the small positive intercept shown by the representative plot in Figure 5. In the least-mean-squares calculation of the rate constants, the origin was weighted twice to give a zero intercept (broken line,

Table II. Relative Rate Data for the Addition of S(^{3}P) Atoms to Olefins

Olefin pair	Pressure, torr: Olefin	COS	CO_2	k_2/k_1[a]	% yield[b]
(1) Ethylene	32.5	32.5	1256	6.9	85
(2) Propylene	11.5				
(1) Propylene	26.0	30.0	1262		
(2) Isobutylene	19.0			7.2	86
(1) Propylene	(I) 25.5	31.5	1223		
	(II) 44.7	32.2	1244	(I) 3.4	75
(2) *trans*-2-Butene	(I) 18.0	31.5	1223	(II) 2.3	77
	(II) 17.0	32.2	1244		
(1) *trans*-2-Butene	23.5	33.0	1317		
				0.48	83
(2) 1-Butene	24.4				
(1) Propylene	44.7	32.5	1231		
(2) *cis*-2-Butene	23.0			2.3	87
(1) *cis*-2-Butene	67.0	32.0	1217		
(2) 2-Methyl-1-butene	8.20			3.5	83
(1) 1-Pentene	64.0	31.5	1250		
(2) 2-Methyl-1-butene	10.7			5.8	63
(1) 1-Pentene	23.0				
(2) Cyclopentene	24.0	31.5	1250	1.9	54
(1) Vinyl chloride	150	100	1190		
(2) Propylene	30			4.8	77

[a] k_2/k_1 = *k*(S + olefin (2))/*k*(S + olefin (1)). [b] Average yields, on the basis of *R*^{0}(CO) – *R*(CO).

Figure 5). The error in the analytical data is believed not to exceed ±10%.

The measured values of relative rate constants are tabulated in Table III in comparison with the corresponding literature data for oxygen and selenium atom reactions.

Table III. Relative Rates of Addition of $S(^3P)$, $O(^3P)$, and $Se(^3P)$ Atoms to Olefins

Olefin	$O(^3P)^a$	$Se(^3P)^b$	$S(^3P)$
Ethylene	1.00	1.00	1.00
Propylene	5.75	2.6	6.9
trans-Butene-2	28.3	56	20
cis-Butene-2	23.8	23.9	16
1-Butene	5.75	7.1	10
Isobutylene	25.0	44.7	50
Pentene-1	...	5.0	10
2-Methylbutene-1	...	...	56
Cyclopentene	29.8	...	18
Vinyl chloride	...	1.3	1.4

[a] Reference 6. [b] Reference 11.

Relative Rates of Addition of $S(^1D)$ Atoms. Relative rates of addition were determined for ethylene, propylene, and isobutylene. Product distributions and ratios, as measured by gc, are reported in Table IV. At least five experiments were performed at various conversions, and since secondary decompositions were negligible the table lists average values, reproducible to ±10%.

Table IV. Addition of $S(^1D)$ Atoms to Ethylene, Propylene, and Isobutylene. Product Distributions in Competitive Systems

Olefins	Rates µmole/µmole of CO		Episulfide ratio (2)/(1)	Total product ratio
	Mercaptan	Episulfide		
(1) $C_2H_4{}^a$	0.164^b	0.147^b	2.93	1.72
(2) $C_3H_6{}^a$	0.103^b	0.431^b		
(1) $C_3H_6{}^c$	0.094^d	0.161^d	2.55	2.02
(2) $i\text{-}C_4H_8{}^c$	0.105^d	0.411^d		

[a] $P(COS) = 91$, $P(C_2H_4) = P(C_3H_6) = 151$ torr. [b] Average of five experiments; CO = 3–4 µmoles. [c] $P(COS) = 77$, $P(C_3H_6) = P(i\text{-}C_4H_8) = 130$ torr. [d] Average of six experiments; CO = 3–6 µmoles.

The propylene–isobutylene rate constant ratio was also examined for a 1:1 mixture at a total olefin pressure of 3.06 torr; two mass spectrometric determinations gave $k(S + i\text{-}C_4H_8)/k(S + C_3H_6) = 2.01 \pm 0.08$, and therefore the rate constant ratio seems to be independent of total olefin pressure.

Discussion

The general kinetic features of the olefins examined here are very similar to those found earlier for the lower molecular weight compounds. The three principal products are episulfide and alkenyl- and vinylic-type mercaptans. The relative mercaptan yield is pressure dependent and exhibits a rising trend with increasing olefin pressures up to several hundred torr and a decreasing trend with added CO_2 pressure.

With cyclopentene (Figure 1) the alkenyl mercaptans, cyclopentene-3-thiol and cyclopentene-4-thiol, account for about 44% of the total product yield. The proportion of these mercaptans was 2:1, and they probably arise from statistical insertion at the 3 and 4 positions, respectively. Small yields of the vinylic mercaptan, cyclopentene-1-thiol, up to *ca.* 5% of the total, were also found, which is the first instance that a nonterminal vinylic mercaptan from the reaction of $S(^1D)$ atoms with an olefin could be detected. The tautomeric equilibrium between the 1-thiol and thioketone proceeds spontaneously at room temperature, but it is strongly shifted (*ca.* 80%) to the thiol side.[3]

Product recoveries varied with experimental conditions, and the optimum values were 77% for the Hg arc and 60% for the Cd lamp experiments. The loss was probably due to some polymerization process or cracking reactions. It has been shown elsewhere[5] that the photolysis of COS at 2288 A produces translationally "hot" $S(^1D)$ atoms; under these conditions, the rate of insertion, relative to abstraction, increases, and collisional stabilization of the vibrationally excited products is less efficient. This explains the higher $R(M)/R(E)$ values and lower product yields in the shorter wavelength photolysis. In the reaction of $O(^3P)$ atoms with cyclopentene, one of the major products is ethylene (27%) formed in a pressure-independent fragmentation.[6] The exothermicity resulting from the addition of $S(^1D)$ and $O(^3P)$ atoms is nearly equal, but we found no direct evidence for a similar cracking with sulfur.

The effect of CO_2 on the reaction (Figure 2) is explained in terms of electronic relaxation of the excited $S(^1D)$ atoms to the ground state

$$S(^1D) + CO_2 \longrightarrow S(^3P) + CO_2 \qquad (1b)$$

It has been shown[1b,7] that mercaptans arise solely from $S(^1D)$ atom percursors, whereas episulfides are formed from $S(^3P)$ and/or $S(^1D)$ atoms. If we take the relative yield of mercaptan as a measure of the $S(^1D)$ atom concentration in the system, at 1250 torr of added CO_2 more than 90% of the $S(^1D)$ atoms are quenched.

The CO yield is also slightly retarded by CO_2. It is known from previous studies[8,9] that the rate constant ratio $k(S + \text{olefin})/k(S + COS)$ is at least 30 times larger for triplet than singlet S atoms. Consequently, conversion of $S(^1D)$ to $S(^3P)$ will diminish the significance of the abstraction step

$$S + COS \longrightarrow CO + S_2 \qquad (2)$$

with a concomitant decrease in $R(CO)$ to the limiting value, $R^0(CO)/2$. This should be accompanied by an increase in episulfide yields such that $R(\text{episulfide})/R(CO) = 1$, which, however, never obtains. This deficiency, in agreement with earlier observations,[1b] suggests that the hot episulfides even from triplet atom addition undergo polymerization reactions with olefins very readily, and that the abstraction of sulfur by S atoms to form S_2 and olefin is fairly rapid.

From the few experiments carried out with cyclohexene, it appears that this olefin behaves similarly to cyclopentene with the exception that, owing to the larger

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(5) A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *J. Am. Chem. Soc.*, **86**, 4243 (1964).

(6) R. J. Cvetanović, *J. Chem. Phys.*, 30, 19 (1959).

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(8) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *ibid.*, **88**, 2412 (1966).

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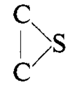
number of CH_2 groups in the molecule, the relative mercaptan yield is somewhat higher than in cyclopentene.

The behavior of cyclo-C_4F_6 is interesting in that it reveals a drastic decrease in π-bond reactivity caused by the strong electron-withdrawing power of fluorine atoms and thereby provides additional evidence for the electrophilic nature of sulfur atom attacks (*vide infra*) on olefinic π bonds. Furthermore, the stability of cyclo-C_4F_6 episulfide is low, and its probable mode of decay is the bimolecular reaction

$$2\text{cyclo-}C_4F_6S \longrightarrow 2\text{cyclo-}C_4F_6 + S_2 \tag{3}$$

The reactions of sulfur atoms with mono- and dimethylsubstituted ethylenes have been reported earlier.[1b,c] In order to complete the series we have examined the reaction with tri- and tetramethylethylene. The mercaptan yields in these reactions were 42 and 50% (in the pressure stabilization region), respectively. Thus with progressive methyl substitution in ethylene the yield of the methyl insertion product rises gradually from 20 to 50% of the total. Since the rate of $S(^1D)$ insertion per C–H bond should not be greatly dependent on the number of methyl groups in the molecule, the relative reactivity of the π bonds in the series can be estimated. This turns out to be approximately constant. On the other hand, the relative rate measurements for ethylene, propylene, and isobutylene (Table IV) indicates a moderate increase in π-bond reactivity with increasing methyl substitution in the molecule. The apparent contradiction can be resolved by invoking a steric effect exerted by the methyl groups on the incipient  bond. The problem will be discussed further below.

The reaction with vinyl chloride leads to the formation of episulfide and smaller amounts of 1-chloroethene-2-thiol. It is seen from the pressure study (Figure 4) that the kinetics of this system again follows the established trend. Product recoveries were somewhat lower, up to 46%, than with other olefins.

The major reactions of $S(^1D)$ atoms with 1,2-dichloroethenes leads to polymerization. Thermalized $S(^3P)$ atoms add stereospecifically to the double bond to yield predominantly *cis* or *trans* episulfides from *cis*- or *trans*-1,2-dichloroethene, respectively, proving the generality of the stereospecific nature of triplet S-atom additions.

The products obtained from the tetramethyl- and chloroethylene reactions have not been described previously in the literature; this is probably their first reported synthesis.

In the relative rate studies (Table III), triplet sulfur atoms were obtained by the collisional relaxation of excited singlet atoms. In a concurrent study[9] triplet atoms were produced directly by the $Hg(^3P_1)$ photosensitization of COS, and rate constants were measured for ethylene, propylene, and isobutylene addition. The values obtained, 1:6.8:56, respectively, are in good agreement with the present determination.

A comparison of relative rates of sulfur atom addition to those reported by Cvetanovic, *et al.*, for oxygen,[10] and Callear and Tyerman for selenium,[11] reveals an impressive correlation between the chemical reactivity of the oxygen group elements. All three species exhibit a clear electrophilic tendency, first shown by Cvetanovic for oxygen, in that the reactivity of the ground-state atoms increases with increasing electron-donating power of the olefin molecule.

In spite of the broad agreement some dissimilarity is also apparent in the fine details. The entropy factor of the oxygen addition is invariant with olefin structure, and the variation in rates is due entirely to activation energy effects. For selenium, the entropy factor changes, but with no obvious trend, and for sulfur a definite trend appears. This is evident from the 2-butene data. Substitution of a methyl group in ethylene causes a sevenfold rate increase. A second methyl on the same carbon causes a further sevenfold rise, but on the neighboring carbon only a *ca.* threefold increase. This is in spite of the fact that the ionization potentials, localization, and excitation energies, which largely determine the magnitude of the activation energy of the process, are nearly identical for the three isomeric butenes. Similar trends have been observed for monovalent electrophilic radical additions and attributed to the steric hindrance of the methyl groups. A compilation of the relevant data is given in Table V; in all cases isobutylene is the most reactive and *trans*-2-butene is only slightly more reactive than the *cis* isomer.

Table V. Relative Rates of Addition of H Atoms, Br Atoms, and CH_3 and CF_3 Radicals to Olefins

Olefin	H[a]	Br[b]	CH_3[c]	CF_3[d]
C_2H_4	1.0	1.0	1.0	1.0
C_3H_6	1.5	18	1.3	1.2
1-C_4H_8	. . .	23	1.6	. . .
i-C_4H_8	4.5	384	2.1	3.7
cis-C_4H_8	0.9	95	0.08	0.86
trans-C_4H_8	1.1	99	0.15	1.0

[a] K. Yang, *J. Am. Chem. Soc.*, **84**, 3795 (1962). [b] I. Abell, *Trans. Faraday Soc.*, **60**, 2214 (1964). [c] G. E. Owens, Jr., J. M. Pearson, and M. Szwarc, *ibid.*, **61**, 1722 (1965). [d] A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).

The data on the relative rates of $S(^1D)$-atom additions (Table IV) are valuable in spite of their limited range because of the scarcity of information on the relative reactivity of atoms in their different electronic levels. In the competitive systems involving $S(^1D)$ atoms, the evaluation of rate constants is complicated by the possibility of singlet → triplet deactivation. The following reaction scheme is considered

$$S(^1D) + Ol_1(Ol_2) \longrightarrow M_1(M_2) \tag{4}$$

$$\longrightarrow EP_1(EP_2) \tag{5}$$

$$\longrightarrow S(^3P) + Ol_1(Ol_2) \tag{6}$$

$$S(^3P) + Ol_1(Ol_2) \longrightarrow EP_1(EP_2) \tag{7}$$

where Ol_1 and Ol_2 are the two olefins and M_1, M_2 and EP_1, EP_2 are the respective mercaptans and episulfides.

If episulfides are formed only from the addition of triplet atoms, then the observed episulfide ratio should correspond to that obtained for $S(^3P)$-atom addition.

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(10) R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963).

(11) A. B. Callear and W. J. R. Tyerman, *Proc. Chem. Soc.*, 296 (1964); private communications.

The data in Tables III and IV show that this is not the case, and therefore the episulfide-forming step must involve the participation of $S(^1D)$ atoms.

It is also clear that $S(^1D)$ atoms are less selective than (^3P) atoms. Upper limits for the relative rate constants are 1, 2.9, and 7.5 for ethylene, propylene, and isobutylene, respectively. The relative importance of $S(^1D)$ addition cannot be evaluated from the present study. It is estimated that 70% or more of the episulfides are formed from singlet atoms. The data can best be rationalized by assuming that the same factors influence the rates of addition of both species; that is, the rate increases with increasing alkyl substitution in the olefin. A lowering in the activation energy and the consequent decrease in selectivity for the excited-atom reaction is not surprising, since the intersection of the corresponding potential energy surfaces in this case occurs at 26 kcal/mole higher energy and equivalently longer intermolecular separation. Assuming similar contours for the repulsive potentials, this results in lowering the energy separation of the point of intersection from that of the separated olefin + S-atom surface, which determines the magnitude of the activation energy barrier.

In intermolecular competing reactions, the π-bond reactivity increases in the order ethylene < propylene < isobutylene, whereas the intramolecular competition between mercaptan and episulfide formation suggests that the π-bond reactivity in the series propylene, 2-butene, trimethylethylene, and tetramethylethylene (*vide supra*) is the same. The discrepancy can be resolved if it is assumed that in the α,β-methylated ethylenes the methyl groups exert a steric hindrance, compensating for the increased reactivity of the π bond. Thus the interpretation of both $S(^3P)$ and $S(^1D)$ atom reactivity makes it necessary to invoke steric hindrances in methylated ethylenes.

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Equilibria between Metallic Sodium and Aromatic Hydrocarbons[1]

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Contribution from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California. Received October 29, 1966

Abstract: The visible and electron spin resonance spectra of a series of alkyl-substituted aromatic hydrocarbons which were allowed to react with sodium in tetrahydrofuran solutions were investigated as a function of temperature. A marked increase in the optical density at the wavelengths of the charge-transfer peaks at low temperatures was found to be accompanied by an increase in free spin concentrations, both phenomena being reversible. The occurrence of sodium precipitation on raising the temperature and dissolution at low temperatures was also found to be reversible. These observations were interpreted as being the result of the shifts in the equilibrium of the reaction between sodium and the aromatic hydrocarbons. The electron affinity of the aromatic hydrocarbons as calculated by means of the Hückel MO theory was correlated with the experimentally determined ΔH values.

Although the reaction between numerous aromatic hydrocarbons and alkali metals to yield intensely colored solutions in appropriate solvents has been known for a long time,[2] the effects of temperature on the optical absorption spectra of the resulting radical ions have not been investigated until recently.[3–5] Only in some materials has a very pronounced change in the absorption intensity as a function of temperature been observed, and this has been attributed to a shift in the equilibrium[3,4a] of the reaction

$$\mathrm{Me} + \mathrm{Ar} \rightleftarrows [\mathrm{Me}^+\mathrm{Ar}\cdot^-] \qquad (1)$$

where Me is the alkali metal, Ar is the aromatic unit, Me^+ is the metal cation, $\mathrm{Ar}\cdot^-$ is the aromatic free radical anion, and $[\mathrm{Me}^+\mathrm{Ar}\cdot^-]$ represents either a tightly or loosely bound ion pair. It has also been shown[4a] that since the enthalpy for (1) is negative, precipitation of sodium dust occurs as the temperature is raised.[6]

Reactions of this type are usually carried out in aprotic organic solvents of relatively low dielectric constant and are known to be subject to various complications such as changes in solvation of the individual ions with temperature,[3] dissociation or formation of ion pairs or even higher aggregates,[7] and disproportionation according to

$$2\mathrm{Ar}\cdot^- \rightleftarrows \mathrm{Ar} + \mathrm{Ar}^{2-} \qquad (2)$$

The disproportionation equilibrium 2, which was reviewed by McClelland,[5b] however, is generally of im-

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(1) (a) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

(2) H. D. Scott, J. F. Walker, and V. J. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(3) A. A. Shatenshtein, E. S. Petrov, and M. J. Belousova, *Org. Reactivity*, **1**, 191 (1964) (in Russian).

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(7) R. M. Fuoss and C. A. Krauss, *J. Am. Chem. Soc.*, **55**, 2387 (1933); N. Hirota and S. I. Weissman, *ibid.*, **86**, 2538 (1964); I. M. Brown, S. I. Weissman, and L. C. Snyder, *J. Chem. Phys.*, **42**, 1105 (1965).