The Reactions of Sulfur Atoms. VI. The Addition to C_4 Olefins. A Stereospecific Triplet-State Reaction

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Abstract: The reaction of $S(^1D)$ atoms with 1-butene, *cis*- and *trans*-2-butene, and isobutylene produces, as principal products, episulfide ($\sim 70\%$) and alkyl-type mercaptan ($\sim 30\%$) with yields up to $\sim 90\%$ of theoretical. Vinylic mercaptans may be formed in trace quantities. Mercaptans arise only from singlet sulfur precursors while episulfides form from triplet atoms and possibly from singlet atoms. With *cis*- and *trans*-2-butene the episulfide retains the geometrical configuration of the parent olefin (>87 and >98%, respectively) not only with singlet, as might be expected, but with triplet-state sulfur as well. Thus the criterion of stereospecificity for spin-state identification at least in the present systems appears invalid. The addition reaction with 1,3-butadiene has also been examined. The major products are vinylthiacyclopropane and thiophene. The addition is at least 91% in the 1,2-position.

The reaction of sulfur atoms with the lower alkenes, ethylene, propylene and 1,1-difluoroethylene, has been reported.[1] $S(^1D)$ atoms from the gas-phase photodissociation of COS yield episulfides with these olefins as well as vinylic and alkyl-type mercaptans. The mercaptan products arise exclusively from singlet sulfur atom reactions, and the episulfide presumably from singlet and certainly from triplet ground-state atoms. Thus, collisional relaxation of the excited sulfur atoms, induced by a large excess of the inert gas, CO_2, suppressed mercaptan formation with an equivalent rise in the episulfide production.

The mechanism and the nature of the intermediates of these reactions have not yet been established. Alkyl-type mercaptans are likely formed in an insertive attack of the singlet-state sulfur on the C–H bond of the saturated C atom(s) as with paraffins.[2] Vinylic mercaptans may form either by insertion into the vinylic C–H bond and/or by isomerization of hot episulfide molecules. For the episulfide-forming reaction the following possibilities should be considered: (a) insertion of $S(^1D)$ into the olefinic π bond, (b) formation of a short-lived singlet biradical with $S(^1D)$, or (c) if the mercaptans arise entirely *via* C–H insertion, some deactivating effect of the olefin resulting in the episulfide being formed exclusively from $S(^3P)$ addition. The occurrence of a singlet–triplet conversion appeared to be indicated by the kinetic behavior of these systems.

The objectives of the work to be described in the present article were to examine the above possibilities and more specifically (a) to ascertain whether the results obtained for the lower alkenes also apply for the higher olefins, (b) to examine the effect of molecular structure on the mercaptan- and episulfide-forming reactions, and (c) to study the nature of the short-lived intermediates in the episulfide-forming step *via* its geometrical isomerism.

Experimental Section

Direct Photolysis. The 2-butene reaction was studied in a mercury-free vacuum system, which in other respects was similar to those used in previous studies. The radiation source was a Hanovia low-pressure mercury resonance lamp equipped with a Vycor 7910 filter (λ_{eff} = 2537 Å.). The cylindrical quartz cell was 60 mm. in length and 50 mm. in diameter.

All other experiments were performed in a circulatory apparatus. The quartz reaction cell was 150 mm. in length and 50 mm. in diameter. Reactants were circulated by means of a magnetically operated glass stirrer having stainless steel blades. Other parts of the vacuum system and the lamp used (λ_{eff} = 2290–2550 Å.) were as above.

All the hydrocarbons were Phillips research grade and were further purified by low-temperature distillation and thoroughly degassed. Details of the carbonyl sulfide purification procedure have been given elsewhere.[1b] Carbon dioxide was Airco reagent grade and was used without further purification.

At the conclusion of irradiation, carbon monoxide was removed at −196 or −210° and determined in a gas buret. The condensable fraction was then analyzed as follows.

2-Butene. The excess reactant was distilled off at −112° (carbon disulfide slush) and the remaining fraction was transferred into a thin-wall vial, sealed, and placed in the crusher-flash vaporizer of a Gow-Mac gas chromatography unit. Analysis was made on a 12-ft. 30% tricresyl phosphate on firebrick column at a He flow rate of 80 cc./min. with temperature programming between 28 and 105° at a rate of 1.5°/min.

1-Butene. Excess reactants were distilled off at *ca.* −105° ("wet" methanol slush) and condensables analyzed by g.c. on a 12-ft. 10% tricresyl phosphate on Celite column, maintained at 62°. He carrier flow was 95 cc./min.

Isobutylene. Excess reactants were distilled off at −112°. The remaining fraction was analyzed on a 16-ft. tricresyl phosphate on firebrick column at 57° at a H_2 carrier flow of 80 cc./min.

1,3-Butadiene. Noncondensable gases were measured in a gas buret and analyzed on a 10-ft. molecular sieve column at 24°, using argon carrier at 38 cc./min. Hydrogen could be determined in this way, and the remaining CO found by difference. The excess substrate gases were distilled at −130 (COS, CO_2) and −98° (butadiene). The remaining condensable fraction was then analyzed on a 10-ft. tricresyl phosphate column at 57°, using H_2 carrier at 80 cc./min.

Mercury Sensitization. To avoid the direct photolysis of COS and ensure complete absorption of the 2537 Å. radiation by the mercury vapor exclusively, an electrodeless, water-cooled, low-pressure mercury discharge source, made of 10-mm. o.d. quartz tubing, was used in these experiments. It was mounted coaxially at the center of the helical cell. The entire assembly, including the tubular rotating sector employed, was similar to that used in monoisotopic photosensitization studies.[3] The reactants in all experiments were circulated by a magnetic stirrer, unless otherwise stated.

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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).

[2] A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **85**, 1207, 2349 (1963); A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *ibid.*, **86**, 4243 (1964).

[3] H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 220 (1963).

Table I. Mass Spectra of Products from the Reaction of Sulfur Atoms with Isobutylene, 1-Butene, *cis*- and *trans*-2-Butene, and 1,3-Butadiene[a]

m/e	Isobutylene sulfide	2-Methylpropene-3-thiol	2-Methylpropene-1-thiol	1-Butene sulfide	1-Butene-3-thiol	1-Butene-4-thiol	— 2-Butene sulfide —		2-Butene-1-thiol	1,3-Butadiene sulfide
							trans	*cis*		
26							11.8	16.1	13.2	12.2
27	35.6	38.8	54.0	47.5	34.8	36.3	42.6	43.5	47.1	38.6
28		18.4	32.1	15.1		19.0	12.0	16.6	25.6	15.0
29	35.6	55.8	68.4	35.7	43.1	27.1	35.1	20.0	64.9	
38			13.2			5.7		8.0		
39	72.5	78.7	88.5	46.4	32.1	38.8	37.6	38.1	55.0	51.1
40	11.0		16.7					6.4		
41	77.6	33.0	77.0	41.9	23.4	41.0	22.8	31.3	14.2	
42				13.3		15.4				
43	12.8		33.9					5.9		
44		65.5	27.6	17.5				6.8		12.0
45	62.3	40.4	59.8	69.4	18.2	32.2	68.3	75.2	45.0	66.9
46	30.2	11.3	18.4	96.2		29.8		5.3	8.4	
47	26.1	23.9	45.4	48.3	10.8	*100.0*	7.4	13.9	26.4	
48	14.8		17.2							
50			13.2				6.4	7.9	14.8	15.5
51			13.8				5.3	5.6	14.3	15.4
52									5.3	
53	19.3	29.9	41.9	13.2	15.3	12.4	18.3	15.9	33.6	32.2
54	34.8	48.2	63.2	25.5	22.0	30.6	22.4	18.6	61.5	21.8
55	*100.0*	*100.0*	*100.0*	87.7	*100.0*	41.0	72.5	53.7	*100.0*	
56	21.5	10.2	32.8	11.2	11.7	23.5	9.6	16.8	9.1	
57			14.4		11.8				5.5	
58				14.4			9.9	14.8	9.7	
59	25.3	11.2	17.8	28.5	11.4		*100.0*	*100.0*	15.9	
60	26.3	19.0	24.7	46.0		34.6	46.3	50.8	9.5	
61					12.7		10.7	11.7		
73	30.9	17.0	21.8	27.4			17.6	15.6	13.9	
84										10.1
85										*100.0*
86										66.5
88	96.7	73.6	63.2	*100.0*	19.0	35.6	74.8	61.8	60.7	

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

Synthetic samples of *cis*- and *trans*-2-butene sulfides were prepared from pure *cis*- and *trans*-2-butene, respectively. The corresponding 2,3-epoxides were obtained by the method of Wilson and Lucas,[4] and converted into episulfide using the technique suggested by Bordwell and Anderson.[5] The products were purified by preparative g.c. 2-Butene-1-thiol was prepared by the method employed by Lee, *et al.*,[6] distilled from a three-plate Vigreux column, and finally purified by preparative g.c.

Results

2-Butene. When carbonyl sulfide was photolyzed with 2-butene, in low-conversion runs, three gas chromatographically separable sulfur-containing products were found. They had relative retension times of 1.00 (I):1.17 (II):1.26 (III). According to their mass spectra, given in Table I, all three were isomeric addition products with molecular weights of 88. Identifications were made by comparing the g.c. retention times and the infrared, n.m.r., and mass spectra of the separated g.c. effluents with those of authentic samples of *trans*-2-butene sulfide (I), 2-butene-1-thiol (II), and *cis*-2-butene sulfide (III). This assignment of the geometrical isomers of the episulfides relies somewhat on the dependability of their stereospecific synthesis[4,5] which, however, appears to be satisfactorily demonstrated.[7] Furthermore, the *trans* isomer has been reported to have a higher vapor pressure than the *cis* structure.[8] In addition, for the g.c. column used here which separates according to boiling point, the product taken to be the *trans* episulfide eluted first. The n.m.r. spectrum of the *cis* isomer showed the ethylenic proton quartet to occur at τ 7.11, while the *trans* isomer gave the quartet at τ 7.49. These values may be compared to those reported for the *cis*- and *trans*-stilbene sulfides and oxides.[9] In stilbene oxide, the ethylenic proton quartets are located at τ values of 6.12 (*trans*) and 5.63 (*cis*); stilbene sulfide has quartets at τ 7.02 and 4.40, which were assigned to the *trans* and *cis* isomers, respectively. Furthermore the infrared spectrum of our *trans* episulfide isomer showed the characteristic C–H bending vibration at 1300 cm.$^{-1}$, which did not appear in the spectrum of the *cis* isomer.

Additional confirmation of the episulfide assignment comes from the fact that the episulfide-forming step is preponderantly stereoselective with singlet, as well as with triplet sulfur atoms (*vide infra*); that is, *trans*-2-butene gives mainly the *trans* episulfide and *cis*-2-butene mainly the *cis* episulfide.

The reaction was first examined as a function of exposure duration. The data are summarized in Tables II and III. With short exposures the three sulfur-containing products account nearly quantitatively for all of the sulfur atoms reacting with the

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[4] C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, **58**, 2396 (1936).

[5] F. J. Bordwell and H. M. Anderson, *ibid.*, **75**, 4959 (1953).

[6] D. F. Lee, B. Saville, and B. R. Trego, *Chem. Ind.* (London), 868 (1960).

[7] D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960); G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **25**, 1754 (1960); **27**, 2942 (1962).

[8] N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959).

[9] R. Ketcham and V. P. Shaw, *J. Org. Chem.*, **28**, 229 (1963).

Table II. Variation in Product Yields with Reaction Time in the COS-*trans*-2-Butene System[a]

Time, min.	Rates, µmoles/min. × 10^2					$R(trans)^b/(R(cis) + R(trans))$	Recovery,[c] %
	CO	2-Butene sulfide *trans*	2-Butene sulfide *cis*	2-Butene-1-thiol	Total C_4H_8S		
5.0	18.5	9.16	0.54	3.50	13.20	0.94	94
10.0	18.0	8.50	0.76	3.78	13.04	0.92	92
18.0	18.2	7.66	0.75	3.82	12.23	0.91	87
30.0	18.7	7.43	0.70	3.21	11.34	0.91	80
60.0	18.0	5.53	0.75	3.17	9.45	0.88	67
91.0	18.0	5.59	0.79	1.64	8.02	0.87	57

[a] P(COS) = 100 torr; P(*trans*-2-C_4H_8) = 100 torr; R^0(CO) = 0.323 µmole/min. [b] Episulfide. [c] In terms of R^0(CO) − R(CO).

Table III. Variation in Product Yields with Reaction Time in the COS-*cis*-2-Butene System[a]

Time, min.	Rates, µmoles/min. × 10^2					$R(cis)^b/(R(cis) + R(trans))$	Recovery,[c] %
	CO	2-Butene sulfide *cis*	2-Butene sulfide *trans*	2-Butene-1-thiol	Total C_4H_8S		
5.0	18.9	8.40	1.60	3.50	13.50	0.84	97
10.0	18.1	7.80	1.58	2.00	11.38	0.83	82
18.0	18.6	5.54	1.81	3.54	10.89	0.75	78
30.0	18.4	4.67	2.29	3.70	10.66	0.67	76
60.0	18.3	3.82	2.80	2.47	9.09	0.58	65
91.0	17.9	2.91	3.54	2.35	8.80	0.45	63

[a] P(COS) = 100 torr; P(*cis*-2-C_4H_8) = 100 torr; R^0(CO) = 0.323 µmole/min. [b] Episulfide. [c] In terms of R^0(CO) − R(CO).

Table IV. Variation in Product Yields with *trans*-2-Butene Pressure in the COS-*trans*-2-Butene System[a]

P(*trans*-2-C_4H_8), torr	Rates, µmoles/min. × 10						$R(trans)^b/(R(cis) + R(trans))$	Recovery,[c] %
	CO	CO^0 − CO	2-Butene sulfide *trans*	2-Butene sulfide *cis*	2-Butene-1-thiol	Total C_4H_8S		
0	3.23	...	...	...	...	...	...	...
10	2.14	1.09	0.75	0.015	0.067	0.832	0.98	76
20	2.01	1.22	0.76	0.022	0.18	0.962	0.97	79
50	1.92	1.31	0.75	0.033	0.32	1.103	0.96	84
100	1.81	1.42	0.76	0.072	0.38	1.212	0.91	85
200	1.66	1.57	0.75	0.038	0.41	1.198	0.95	76
400	1.62	1.61	0.76	0.014	0.41	1.184	0.98	74
600	1.65	1.58	0.77	0.015	0.39	1.175	0.98	74

[a] P(COS) = 100 torr; exposure time, 20 min. [b] Episulfide. [c] In terms of R^0(CO) − R(CO).

olefin. At longer exposures, owing to secondary reactions and attenuation of the incident light intensity by polymer deposition, the yields gradually decrease. With the *trans* substrate the episulfide product contains a minimum of 94% of the *trans* isomer, while in the *cis*-2-butene reaction, at least 87% of the episulfides is the *cis* isomer. Unfortunately, the data are not sufficiently accurate to permit a valid extrapolation to zero exposure time.

The 2-butene-1-thiol product from both the *cis*-2-butene and *trans*-2-butene reactions was a mixture of the two geometrical isomers. However, no g.c. column could be found which resolved the isomers. Hence the relative amounts of the two components could not be determined. That both isomers were present was inferred from the n.m.r. spectrum which displayed two triplet resonances for the SH protons centered at τ 8.81 and 8.84. The relative intensity of the two triplets was dependent on the sample origin. Thus the integrated signal ratios were 3.6 and 1.4 for the samples from the *trans*- and *cis*-2-butene reactions, respectively.

From the time studies, it is clear that in the reaction of atomic sulfur with the 2-butenes, the stereospecific episulfide and the 2-butene-1-thiol described above are primary reaction products.

It is also evident from Tables II and III that the rates of formation of the stereospecific addition products fall off with increasing exposure. The decrease is greater for the *cis* isomer, indicating higher reactivity. On the other hand, the increase in the rate of *trans* isomer formation in the case of *cis*-2-butene (Table III) is not due to *in situ* photoisomerization. This was demonstrated by irradiating *cis*-2-butene episulfide vapor (a) alone, (b) in the presence of CO_2, and (c) with added *cis*-2-butene under identical conditions. In none of these cases was the *trans* episulfide formed as a product. It is likely that the *trans* episulfide arises from the photolysis of the solid polymer which accumulates on the cell walls in prolonged exposures.

The product rates, as a function of 2-butene pressure, are presented in Tables IV and V. It is seen that the isomeric distribution of the episulfides is not affected seriously by pressure (in the 100–700-torr pressure range). At the highest 2-butene pressure used (600 torr), R(CO) is suppressed to nearly half the value found in the absence of olefins.

As with the other olefins studied,[1b] the rate of mercaptan formation increases with olefin pressure. Here it should be recalled that mercaptan is formed exclusively from singlet atoms. However, it is not possible to decide at present whether episulfide is formed ex-

Table V. Variation in Product Yields with *cis*-2-Butene Pressure in the COS-*cis*-2-Butene System[a]

P(*cis*-2-C$_4$H$_8$),	Rates, μmoles/min. × 10						R(*cis*)[b]/	Recovery,[c]
			2-Butene sulfide		2-Butene-	Total	(R(*cis*) +	
torr	CO	CO^0 − CO	*cis*	*trans*	1-thiol	C$_4$H$_8$S	R(*trans*))	%
0	3.23	...	...	...	...	...	...	...
10	2.15	1.08	0.49	0.14	0.077	0.71	0.78	66
50	1.94	1.29	0.47	0.20	0.23	0.90	0.70	70
100	1.87	1.36	0.53	0.17	0.28	0.98	0.76	72
200	1.81	1.42	0.61	0.17	0.32	1.10	0.78	77
400	1.69	1.54	0.66	0.14	0.37	1.17	0.83	76
600	1.71	1.52	0.62	0.090	0.41	1.12	0.87	74

[a] P(COS) = 100 torr; exposure time, 20 min. [b] Episulfide. [c] In terms of R^0(CO) − R(CO).

Table VI. Variation in Product Yields as a Function of Added CO$_2$ Pressure in the COS-*trans*-2-Butene System[a]

	Rates, μmoles/min. × 10					R(*trans*)[b]/	
P(CO$_2$),			2-Butene sulfide		2-Butene-	(R(*cis*) +	Recovery,[c]
torr	CO	CO^0 − CO	*cis*	*trans*	1-thiol	R(*trans*))	%
0	2.14	1.09	0.015	0.75	0.067	0.98	76
20	2.09	1.14	0.010	0.74	0.109	0.99	75
50	2.08	1.15	0.008	0.78	0.107	0.99	78
100	2.03	1.20	0.013	0.82	0.100	0.98	78
300	1.88	1.35	0.011	0.85	0.094	0.99	71
600	1.78	1.45	0.014	1.01	0.088	0.99	77

[a] P(COS) = 100 torr; P(*trans*-2-C$_4$H$_8$) = 10 torr; exposure time, 20 min. [b] Episulfide. [c] In terms of R^0(CO) − R(CO).

clusively from triplet or both triplet and singlet atoms. The limiting value of the ratio R(mercaptan)/R(episulfide) is 0.51, and therefore the value $^{0.51}/_{1.51}$ = 0.34 represents a minimum for the fraction of S atoms reacting in the ^{1}D state with 2-butene. The pressure trend exhibited by the ratio may be due to a change in the distribution of singlet- to triplet-state atoms in the system; alternatively the initially formed hot mercaptan molecules may require more collisional stabilization than does the episulfide.

To examine this question, two series of auxiliary experiments were carried out using COS–C$_2$H$_4$ mixtures, which exhibit a similar kinetic behavior to the present system with respect to mercaptan formation. Figure 1 indicates that at a constant ratio of COS to C$_2$H$_4$ a total increase in pressure from 60 to 1000 torr raises R(mercaptan)/R(episulfide) from 0.70 to 0.82. This indicates that a higher pressure of inert gas is required to stabilize the hot mercaptan than the episulfide. In turn the ratio declines with increasing COS pressure. Thus, as shown in Figure 1 with 100 torr of C$_2$H$_4$, an increase in COS pressure from 100 to 1000 torr causes a 50% drop in R(mercaptan)/R(episulfide). This indicates that COS is involved not only in the abstraction reaction

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

but also in a deactivation reaction with S(^{1}D) atoms

$$S(^1D) + COS \longrightarrow COS^* + S(^3P) \qquad (2)$$

with a relative rate constant ratio k_2/k_1 = 0.03.

The effect of the inert gas, CO$_2$, on the reaction of sulfur atoms with *trans*-2-butene was also studied and the resulting data are given in Table VI. The isomeric composition of the sulfides as well as the rate of mercaptan formation are again constant within experimental error. In the latter case we are probably dealing with a number of superimposed effects. On one hand, CO$_2$ functions as a stabilizer for the hot mercaptan molecules, thereby increasing their yields; on the other hand, CO$_2$ is also an efficient quencher of singlet sulfur atoms,[2] and since mercaptans are formed only by singlet atoms, their yield should decrease with CO$_2$ pressure. Thus while without CO$_2$, at 600 torr total pressure, R(mercaptan)/R(sulfide) = 0.5 (Table IV), at 710 torr total pressure, with 600 torr of CO$_2$ present, the above ratio has a value of 0.09 (Table VI). The total product yield, however, shows no significant change, being 1.11 μmoles with CO$_2$ and 1.18 μmoles without CO$_2$.

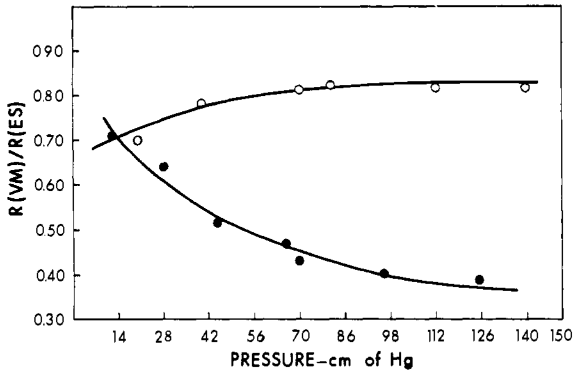

Figure 1. Variation in the rate ratio of vinyl mercaptan to ethylene episulfide, R(VM)/R(ES), in the reaction of S atoms from the 2537-Å. photolysis of COS with C$_2$H$_4$. For the open circles the abscissa shows the total pressure for [COS]/[C$_2$H$_4$] = 1. For the solid circles the abscissa gives the COS pressure at a constant C$_2$H$_4$ pressure of 100 torr.

1-Butene. In low-conversion runs the condensable fraction of the reaction mixture contained again three g.c.-separable components with relative retention times of 1.00 (I):1.67 (II):2.34 (III). The major product, compound III, was identified by its n.m.r. spectrum as the 1-butene episulfide. The other two minor products, according to their mass spectra, were isomers of the episulfide product, with molecular weights of 88.

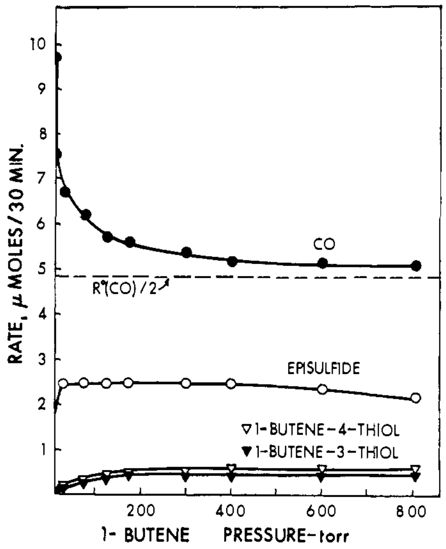

Figure 2. Rate of product formation in the reaction of S atoms, from the 2290–2550-Å. photolysis of COS, with 1-butene. *P*(COS) = 100 torr.

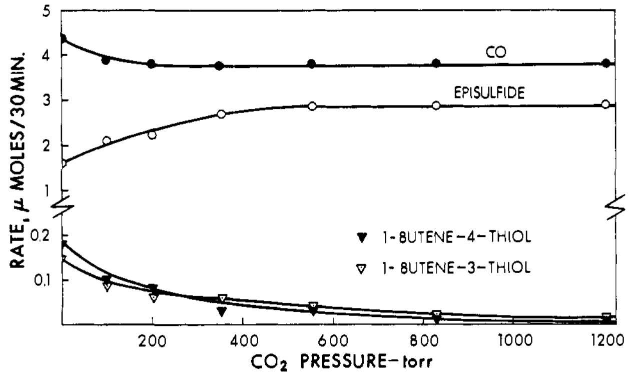

Figure 3. The effect of added CO$_2$ on the rate of product formation in the COS-1-C$_4$H$_8$ system. *P*(COS) = 30 torr; *P*(1-C$_4$H$_8$) = 30 torr.

Samples recovered for n.m.r. analysis were impure and the SH proton regions were too complex to allow a definite structural identification. However, the three vinylic proton resonance peaks were intact in both spectra, and therefore I and II are likely the alkyl-type mercaptans, 1-butene-3-thiol (I) and 1-butene-4-thiol (II).

The effect of olefin pressure on product yields is shown in Figure 2. Evidently, the kinetic features of this system are very similar to those exhibited by the *cis*- and *trans*-2-butene systems. Thus *R*(CO) gradually decreases with olefin pressure, approaching R^0(CO)/2 at pressures exceeding 800 torr. *R*(mercaptans) increases up to 200–300 torr, while *R*(episulfide) shows a slight decline above 400 torr. The total yield of sulfur-containing products monotonously increases between 30 and 400 torr.

In this system as well, carbon dioxide suppresses mercaptan formation with simultaneous increase in the yield of episulfide, as shown in Figure 3.

Isobutylene. Low-conversion experiments yielded two volatile products with relative retention times 1.00 (I) and 1.19 (II). These were isomeric with molecular weights 88. Product I was identified as isobutylene episulfide and II as 2-methyl-1-propene-3-thiol by infrared and n.m.r. spectroscopy. The mass spectrometric cracking patterns are given in Table I. In long exposure runs, a minute quantity of a third isomer was also detected, which was probably the vinylic 2-methyl-1-propene-1-thiol. Product yields, as a function of isobutylene pressure, are plotted in Figure 4.

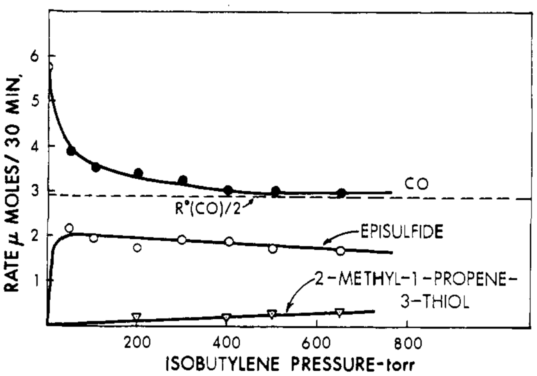

Figure 4. Rate of product formation in the reaction of S atoms, from the 2290–2550-Å. photolysis of COS, with isobutylene. *P*-(COS) = 112 torr.

1,3-Butadiene. By g.c. analysis three volatile products were detected with relative retention times of 1.00 (I):1.17 (II):2.22 (III). Product I was always present in trace quantities; therefore its structure could not be determined. Its mass spectrum showed a relatively large peak at mass 88 indicating a hydrogenated addition product which could be of secondary origin. Product II was found to be thiophene.

Product III proved to be very unstable, readily decomposing into 1,3-butadiene, thiophene, H$_2$, and a polymeric material. Its mass spectrum, given in Table I, indicates a molecular weight of 86. The infrared spectrum showed the characteristic cyclopropane C–H stretching vibrations at 2990 and 3005 cm.$^{-1}$ (in thiacyclopropane the corresponding frequencies occur at 3000 and 3080 cm.$^{-1}$). Evidence for a terminal vinyl group is seen in the characteristic vinyl absorptions at 3090 and 3020 cm.$^{-1}$; the out-of-plane deformations at 970, 950, 920, and 905 cm.$^{-1}$; and the characteristic band at 1820–1840 cm.$^{-1}$. The relatively intense C=C stretching band at 1660 cm.$^{-1}$ is compelling evidence against a five-membered symmetrical dihydrothiophene structure. The ring-deformation frequency at 1046 cm.$^{-1}$ coincides with that reported for thiacyclopropene at 1051 cm.$^{-1}$. The n.m.r. spectrum, in a CCl$_4$ solution, recorded on a Varian 100 Mc. spectrometer using tetramethylsilane as an internal standard, is consistent with the butadiene episulfide structure, but not with a dihydrothiophene structure. The spectrum consisted of four absorption regions: two quartets at τ 7.81–7.75 (I) and 7.48–7.41 (II), a complex band between τ 6.87 and 6.44 (III), and an olefinic absorption between τ 4.97 and 4.57 (IV). The integrated signal intensities were in the ratio 1:1:1:3, respectively. The quartets exhibited geminal coupling of the order of 5 c.p.s., as found in other model compounds (thiacyclopropane). Thus quartets I and II can be assigned to the methylenic ring protons, III to the ring proton on the substituted carbon, and IV to the three olefinic protons in the vinylthiacyclopropane molecule, CH$_2$=CH—CH—S—CH$_2$ (VTCP).

Table VII. Vapor Pressure of Vinylthiacyclopropane[a]

Temp., °C.	Pressure, torr
0.0	5.64
6.0	8.32
26.1	24.21
37.0	45.41
47.2	73.01
54.4	103.15
61.1	140.24

[a] Extrapolated b.p. 106° (760 torr); ΔH = 9.48 kcal./mole.

Table VIII. Variation in Product Yields with Butadiene Pressure in the COS-1,3-Butadiene System[a]

$P(C_4H_6)$, torr	Rates, μmoles/min. × 10^2					Distribution, %			Yield,[d] %
	CO	H_2	Thiophene	X[b]	VTCP[c]	X[b]	Thiophene	VTCP[c]	
0	34.6	...	...	...	...	...	...	...	...
31	25.7	0.066	1.167	0.100	5.533	1.4	17.2	81.4	76.4
54	23.0	0.010	1.429	0.100	4.700	1.5	25.8	72.7	53.7
103	20.2	0.010	1.133	0.233	3.333	5.0	24.1	70.9	32.6
147	18.4	0.010	0.933	0.367	1.967	11.2	28.6	60.2	20.2

[a] P(COS) = 105 torr; 24°; exposure time, 30 min. [b] Unidentified compounds, mol. wt. 88. [c] Vinylthiacyclopropane. [d] Based on R^0(CO) − R(CO).

Table IX. Yield of Products as a Function of Added CO_2 Pressure in the COS-1,3-Butadiene Systems[a]

$P(CO_2)$, torr	Rates, μmoles/min. × 10^2				Distribution, %			Yield,[d] %
	CO	X[b]	Thiophene	VTCP[c]	X[b]	Thiophene	VTCP[c]	
0	12.46	0.133	0.733	1.933	4.8	26.2	69.0	34.1
202	12.10	0.200	0.533	3.533	4.7	12.5	82.8	49.8
512	11.40	0.233	0.433	3.033	6.3	11.7	82.0	39.9
812	11.00	0.200	0.500	3.867	4.4	10.9	84.7	47.3
1267	10.87	0.233	0.400	3.433	5.8	9.8	84.4	41.2

[a] P(COS) = 58 torr; $P(C_4H_6)$ = 53 torr, exposure time, 30 min. [b] Unidentified compound, mol. wt. 88. [c] Vinylthiacyclopropane. [d] Based on R^0(CO) − R(CO).

Vapor pressure data for the VTCP product are given in Table VII.

Owing to the instability of this material, its g.c. detector response could not be determined accurately and was therefore assumed to be equal to that of thiophene.

The results of a brief study on product yields as a function of butadiene pressure are presented in Table VIII. The optimum yield of products was obtained at a C_4H_6 pressure of 31 torr, above which the yield of VTCP fell rapidly. The yield of the minor product, H_2, is an order of magnitude lower than that of thiophene, indicating that thiophene is probably formed in more than one process. The effect of added CO_2 on the reaction is seen from Table IX. Thiophene appears to be suppressed by increasing CO_2 pressure, indicating hot precursors in its formation, while VTCP yields were not affected by CO_2 except at low total pressures, where a stabilizing effect is apparent.

To determine whether thiophene is a primary product of the interaction of sulfur atoms with butadiene or whether it arises from some secondary decomposition of the primary VTCP, two comparison runs were performed in the circulatory system with a mixture of 300 torr of COS and 300 torr of butadiene. In one of the runs the reactant gases were circulated and the total sulfide product was removed from the gas phase by condensation in a cold trap, while in the other experiment the pump was shut off. Circulation of the gases resulted in a 54% increase in VTCP formation and in a 3.3-fold rise in the ratio of VTCP to thiophene. Taking the g.c. detector response equal for the two materials, thiophene comprised 9% of the combined sulfide yield.

Mercury Sensitization. The Hg $6(^3P_1)$ photosensitization of COS on the basis of spin conservation would be expected to yield only triplet, ground-state sulfur atoms. To test this assumption a set of experiments was performed with admixed propane-d_8. It has been shown in earlier work[2] that triplet sulfur atoms are inert with respect to paraffins, while $S(^1D)$ atoms readily undergo insertion reactions to form mercaptans. In a 2:1 mixture of COS and C_3D_8, at total pressures of 20, 50, and 100 torr, no mercaptan could be detected in low-conversion runs, indicating the complete absence of singlet atoms. We may therefore conclude that the COS-Hg $6(^3P_1)$ reaction provides a clean source for $S(^3P)$ atoms.

In the following experiments, COS admixed with *cis*-2-butene was mercury sensitized in the circulating system. In addition to CO, both isomers of 2-butene episulfide were formed. Table X indicates that, at low conversions, the episulfide was 85% *cis* isomer, when the total pressure in the system was *ca.* 30 torr. At higher conversions the episulfide yield rapidly declines and the *cis* isomer appears to be consumed more

Table X. Variation in Product Yields with Reaction Time in the $Hg(^3P_1)$-COS-*cis*-2-Butene System[a]

Exposure time	CO, μmoles	(R × 10)/R(CO) 2-Butene sulfide		*cis*-ES[b]/total ES
		trans	*cis*	
5	0.94	0.81	4.57	0.85
10	1.74	0.75	4.08	0.84
15	3.11	0.68	3.54	0.84
30	6.42	0.70	2.63	0.79
50	10.98	0.66	1.55	0.70

[a] Circulating system: P(COS) = 25.3 torr; $P(2\text{-}C_4H_8)$ = 4.7 torr. [b] Episulfide.

rapidly than the *trans*. It should be noted that no mercaptan is formed in this reaction, indicating again the absence of singlet-state sulfur atoms. Complications arising from the mercury sensitization of the 2-butene need not be considered since quenching by the olefin is only *ca.* 20% and the major reaction is the geometrical isomerization.[10]

Next the effect of pressure was examined. When the total pressure (at a COS to *cis*-2-butene ratio of 5.4) was increased from 5 to 115 torr, the concentration of *cis* episulfide gradually increased from 70.4 to 80.1% as can be seen from Table XI.

Table XI. Yield of Products as a Function of Pressure in the $Hg(^3P_1)$-COS-*cis*-2-Butene System[a]

Pressure, torr[b]	2-Butene sulfide *trans*	 *cis*	$R(cis)/(R(cis) + R(trans))$[c]
5	0.18	0.43	0.70
10	0.43	1.09	0.72
16	0.60	1.88	0.76
34	0.69	2.48	0.78
55	0.82	3.20	0.80
115	0.98	3.95	0.80

[a] Circulating system: exposure time, 30 min. [b] [COS]/(*cis*-2-butene] = 5.4. [c] Episulfide.

Finally the effect of added CO_2 on the reaction was also studied. The results are reported in Table XII. The *cis* component of the episulfide product showed a slight increasing trend with CO_2 pressure and reached a limiting high value of *ca.* 93%. The apparent drop of the total episulfide yield is due to the competitive quenching effect of CO_2. Similar results were also obtained with argon as inert gas.

Table XII. Variation in Product Yields as a Function of Added CO_2 Pressure in the $Hg(^3P_1)$-COS-*cis*-2-Butene System[a]

$P(CO_2)$, torr	Yields, μmoles 2-Butene sulfide *trans*-	 *cis*	$R(cis)/(R(cis) + R(trans))$[b]
0	0.45	1.69	0.79
57	0.32	1.73	0.84
150	0.23	1.81	0.89
324	0.13	1.35	0.91
410	0.10	1.26	0.93
490	0.09	0.93	0.91

[a] $P(COS)$ = 24 torr; $P(cis\text{-}2\text{-}C_4H_8)$ = 5 torr; exposure time, 30 min. [b] Episulfide.

Discussion

The results obtained in the present investigation are in general agreement with those obtained previously for the lower olefins, ethylene, propylene, and 1,1-difluoroethylene. Sulfur atoms, from the direct photolysis of COS, have been shown to give both episulfides and mercaptans with olefins, but when the photolysis is carried out in the presence of excess CO_2 the formation of mercaptans is suppressed with a concurrent rise in the yield of episulfide. The latter effect has been interpreted in terms of an efficient electronic relaxation of the $S(^1D)$ atoms, formed in the photolytic act

$$COS(^1\Sigma) + h\nu \longrightarrow CO(^1\Sigma) + S(^1D) \qquad (3)$$

$$S(^1D) + CO_2 \longrightarrow S(^3P) + CO_2^* \qquad (4)$$

with the implication that the mercaptan products arise only from the reactions of $S(^1D)$ atoms with olefins. The validity of this postulate has now been further substantiated by the fact that sulfur atoms, from the triplet mercury photosensitization of COS, do not produce mercaptans with either olefins or paraffins. In the $Hg(^3P_1) + COS(^1\Sigma)$ reaction, spin conservation would favor the formation of the triplet ground state ($^3P_{2,1,0}$) of the S atom. The $S(^3P)$ atoms react readily with COS[11] or an olefin *via*

$$COS + S(^3P) \longrightarrow CO + S_2 \qquad (5)$$

$$2C_4H_8 + S(^3P) \longrightarrow \text{episulfide} \qquad (6)$$

In direct photolysis experiments with propylene two types of mercaptans, alkyl (allyl mercaptan) and vinylic (propene-1-thiol), were produced. With the C_4 olefins, however, even when one pair of the terminal vinylic protons are intact in the molecule, as in isobutene or 1-butene, no vinylic mercaptan could be detected in the products, indicating that they could not be present in more than trace quantities.

If reaction 3 is assumed to be the only primary mode in the photolysis of COS, there is no system known which quantitatively reacts with $S(^1D)$ atoms by a C–H insertion mechanism. The trapping efficiency of paraffins, owing to a concurrent singlet → triplet deactivating effect, is *ca.* 59%, or at the most 74%. Kinetic complications observed earlier[1] and confirmed by more recent work[12] suggest the presence of triplet-state atoms in the olefinic systems, and therefore at least a part of the episulfide may arise from triplet addition (formed, for example, by collisional relaxation prior to singlet addition) to the double bond.

It was thought therefore that a study of the stereospecificity of the 2-butene reaction would provide some basis for the assessment of the relative importance of the singlet- and triplet-state reactions in the olefinic system and in addition shed light on the structures of the reaction intermediates. Photolysis of COS in the presence of *cis*- and *trans*-2-butene resulted in both cases in three products, *cis*- and *trans*-2-butene episulfide and the mercaptan, 2-butene-1-thiol. In short conversion runs, at a few hundred torr pressure, the episulfide fraction consisted of over 90% *cis* isomer from *cis*-2-butene (Tables III and V) and 98% *trans* isomer from *trans*-2-butene (Tables II and IV).

The high stereospecificity of the episulfide-producing reaction, by analogy with methylene chemistry, comes as no surprise if the reactive species are indeed singlet-state sulfur atoms. It was therefore expected that addition of CO_2 would decrease the stereospecificity of the process, since addition of CO_2 in COS–paraffin systems promotes the $S(^1D) \rightarrow S(^3P)$ transition, thereby eliminating the RSH insertion product.[2] According to the data given in Table VI, however, CO_2 has no effect on the isomeric distribution of episulfide, and it appears that triplet sulfur addition is just as stereospecific a

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[10] R. J. Cvetanovic, H. E. Gunning, and E. W. R. Steacie, *J. Chem. Phys.*, 31, 573 (1959); R. Cundall and T. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

[11] K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, to be published.

[12] E. M. Lown, O. P. Strausz, and H. E. Gunning, to be published.

process as that of singlet-state atoms. This unexpected behavior was further confirmed by the mercury-photosensitization studies in which a *cis* sulfide yield of 93% was obtained from the *cis*-2-butene reaction (Table X); or, if small corrections are introduced for secondary effect, the *cis*-sulfide yield exceeds 95%. Since the product yields in all these runs were reasonably high and the exposure time and pressure studies indicate the absence of significant secondary reactions, we must conclude that the addition of triplet-state sulfur atoms to the 2-butene is at least as stereospecific as the addition of singlet sulfur atoms. This is certainly a most surprising result.

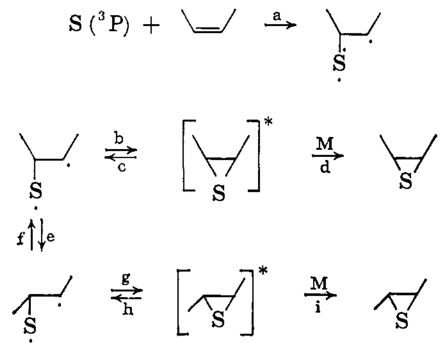
The widely held concept, evolved largely from methylene chemistry and originally put forward by Skell and Woodworth,[13] teaches that divalent singlet species add across olefinic double bonds *via* a three-center mechanism, with simultaneous bond formation to both of the olefinic carbon atoms. This is equivalent to an insertion-type mechanism into the π bond. This mode of reaction should lead to retention of geometrical configuration of the parent olefin in the resulting cyclic structure. In triplet addition, to preserve spin, the primary addition product is believed to be a triplet biradical in which rotation around the olefinic carbon atoms has a low-energy barrier. Since spin inversion has been regarded as slow compared to rate of rotation, triplet addition has been postulated to lead to nonstereospecific addition products. According to Gaspar and Hammond,[14] stereospecific addition in the gas phase demands that addition involves simultaneous formation of two bonds. Such a reaction could only be an adiabatic process if the attacking species is a singlet.

While most of the accumulated experimental evidence has been interpreted in terms of this hypothesis, DeMore and Benson[15] have recently suggested that both singlet and triplet additions proceed *via* a short-lived biradical intermediate and that the degree of stereospecificity will be determined largely by the relative rates of rotation *vs.* ring closure rather than by the spin state of the reagent. These authors have expressed some doubts concerning the acceptability of existing evidence as proof that the addition of triplet CH_2 to olefins is less stereospecific than that of singlet-state CH_2. Quite recently, however, some fairly unequivocal evidence has been obtained in methylene chemistry in support of the generally accepted view that stereospecificity is uniquely associated with singlet addition.[16]

The reaction of $S(^3P)$ atoms with olefins described here is probably the first reported stereospecific triplet-state addition reaction and as such provides experimental support for DeMore and Benson's proposal that a triplet-state addition can indeed be a stereospecific process. Clearly, therefore, at least in the reactions of sulfur atoms with olefins, stereospecificity as a criterion for spin state appears to be invalid.

The high stereospecificity observed in the triplet reaction demands that ring closure be a relatively efficient process compared to rotational isomerization. In addition, the excited episulfide initially formed in ring closure must possess a relatively long lifetime for efficient collisional stabilization to occur. From the data in Tables XII and V it is seen that to achieve maximum stereospecificity a total pressure of *ca.* 300–400 torr is required for the $S(^3P)$–*cis*-2-butene reaction and a pressure exceeding 700 torr for the $S(^1D)$–*cis*-2-butene system.

The detailed mechanism of the triplet-state addition appears to be consistent with the following sequence of elementary steps.



To obtain a high degree of stereospecificity obviously k_b and k_dM must be large compared to k_c and k_e. It is instructive to compare the kinetic parameters of this system to those for CH_2 addition. From the Rice–Rampsberger–Kassel relation

$$k_b = A([E - E_a]/E)^{s-1} \qquad (7)$$

For sulfur, s the number of internal degrees of freedom will be somewhat less than for CH_2. Also the ring strain in the episulfide molecule is less than in cyclopropane, which will tend to increase A and decrease E_a relative to the CH_2 reaction. The A factor may also be larger because the presence of the heavy sulfur atom may facilitate spin inversion. There should therefore be an increase in the value of k_b. The exothermicity of the reaction and the excess energy remaining in the radical should, however, be somewhat less in the sulfur case. If we accept the recently suggested high value of 66.0 kcal./mole for ΔH_f of S atoms,[17] the over-all exothermicity is *ca.* 60 kcal./mole and the total excess energy residing in the biradical may be of the order of *ca.* 10 kcal./mole, as compared to 32.7 kcal./mole for triplet methylene.[15] This will have a decreasing effect on k_b and may actually compensate for the other factors. The value of k_e, that is the rate of rotation, will be somewhat slower owing to the larger mass of the sulfur atom and the possibility of greater spin interaction. It seems reasonable to assume that this latter factor may be largely responsible for the high stereospecificity of the process. This assumption is supported by two observations indicating a long lifetime for thiadimethylene ($\cdot SCH_2CH_2\cdot$) diradicals. First, in all olefinic reactions the maximum yield of episulfide appears between *ca.* 30 and 100 torr of olefin pressure, when the COS pressure is *ca.* 100 torr. At lower olefin pressures the episulfide yield

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[13] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

[14] W. Kirmse, H. M. Frey, P. P. Gaspar, and G. S. Hammond, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1961.

[15] W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

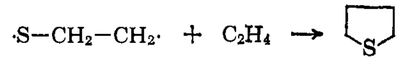
[16] R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965).

[17] T. F. Palmer, and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 4661 (1962); J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, **39**, 275 (1963); J. Mackle, Abstracts Sulfur Symposium, Calgary, Alberta, Canada, March 18–19, 1964.

falls off because of the competing reaction 1. At higher pressures, to explain the decrease in episulfide yield, a reaction between thiodimethylene biradicals and the olefin, leading to polymer formation, must be invoked.

$$\cdot S{-}C{-}C\cdot + {>}C{=}C{<} \longrightarrow \cdot S{-}C{-}C{-}C{-}C\cdot \xrightarrow{\text{olefin}} \text{polymer} \qquad (8)$$

The second observation comes from studies on the photolysis of ethylene episulfide vapor itself.[18] When this substrate is photolyzed in the presence of ethylene, small yields of tetrahydrothiophene are detected among the products. The most obvious reaction to account for tetrahydrothiophene formation would be the addition of thiodimethylene to the added ethylene.


(9)

When the episulfide photolysis is carried out in the presence of higher olefins, fairly good yields of a higher 1-olefin are found. Thus with propylene, 1-pentene is obtained.

$$\cdot S{-}CH_2{-}CH_2\cdot + CH_2{=}CH{-}CH_3 \longrightarrow \cdot S{-}CH_2CH_2CH_2\underset{\cdot}{C}HCH_3$$

$$\downarrow$$

$$CH_2{=}CH{-}CH_2{-}CH_2CH_3 + S(^3P) \qquad (10)$$

Again 1-olefin formation can be readily explained by the addition of thiodimethylene to the π bond, followed by an H-atom shift and loss of a sulfur atom. The above reactions strongly suggest that thiodimethylene diradicals have a long lifetime, and therefore the observed stereospecificity of the S(^{3}P) addition cannot be due to the facile nature of ring closure, but rather to the slow rate of rotation. Finally, k_c, which is given by

$$k_c = A'([E' - E_a']/E')^{s-1} \qquad (11)$$

will also be affected. Since the exothermicity of the reaction should not exceed by more than 10 kcal./mole the C–S bond dissociation energy in the episulfide, k_c should be somewhat smaller for the S-atom reaction than for CH_2, where the corresponding value is 27 kcal./mole.[15]

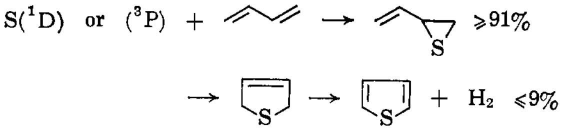
The greater stability and longer lifetime of the hot episulfide molecules are indicated by the difference in the pressure-stabilizing effect on the sulfur atom and methylene-addition reactions. From Tables XI and XII, the *cis* episulfide yield at 110 torr total pressure is 80–85%; or, if allowance is made for secondary photoreactions (Table X), the yield becomes 86–90%. At the same pressure, however, only 70% of the dimethylcyclopropane product is stabilized in the addition reaction of CH_2 to *cis*-2-butene.[19] A similar trend appears in the *trans*-2-butene reaction.

It also should be pointed out here that the addition of triplet oxygen atoms to *cis*- and *trans*-2-butene is a nonstereospecific process. In fact, both geometrical and extensive structural isomerization occur together with some fragmentation in the pressure range of a few hundred torr.[20]

Thus in the reaction of S atoms with the 2-butenes, it is seen that, while in the present study on stereospecific character valuable information was obtained on the general question of the addition of triplet-state species to olefins, it has not been possible to evaluate the relative importance of the singlet *vs.* triplet-state addition processes.

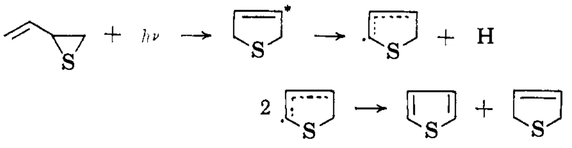
From Figures 2–4 it is seen that the other two C_4 olefins examined, 1-butene and isobutene, are very similar to the 2-butenes in their reaction with S(^{1}D) atoms.

With 1,3-butadiene the major reaction product is vinylthiacyclopropane (VTCP). Thiophene, at least in part, is a secondary product; and the upper limit for the thiophene fraction, which could have formed in a primary reaction, is 9%. Thus, the addition reaction with both triplet and singlet sulfur atoms is at least 91% in the 1,2-position.



(12)
(13)

The H_2 yield was always smaller than that of thiophene. It appears that the major portion of thiophene arises from the secondary photolysis of the VTCP product. That the photolysis of VTCP yields thiophene was demonstrated in separate experiments. A possible mechanism is



(14)
(15)

Small quantities of a third product with molecular weight of 88 were also detected.

From Table VIII it can be seen that the VTCP yield rapidly decreases with increasing pressure of butadiene, indicating that the biradical intermediate is more reactive toward conjugated dienes than monoolefins.

Addition of CO_2 to the system (Table IX) has a small stabilizing effect upon the VTCP product at low pressures but has no further effect at higher pressures. The formation of thiophene, however, seems to be suppressed by CO_2. Pertinently the rate of photodecomposition of ethylene episulfide is also retarded by inert gases.[18]

Thus the over-all mechanism of sulfur atom addition to butadiene is similar to that of CH_2[14] and O(^{3}P),[20] both of which species have been shown to add mainly or entirely by the 1,2-mode.

Returning now to the mechanism of mercaptan formation, the most curious feature of the reaction is the conspicuous absence of the vinylic-type mercaptans in the products. In Table XIII we have given a summary of the available relative rate data for the various types of product formation for sulfur atom reactions with olefins in comparison with the corresponding methylene reactions. It is seen that the relative importance of the mercaptan product is highest with ethylene. When the number of bonds in the molecule is increased by introducing various alkyl groups, the importance of the vinylic-type mercaptans rapidly decreases. With C_4

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[18] K. S. Sidhu, O. P. Strausz, and H. E. Gunning, to be published.
[19] H. M. Frey, *Progr. Reaction Kinetics*, 2, 165 (1962).
[20] R. J. Cvetanović, *Advan. Photochem.*, 1, 115 (1963).

Table XIII. Comparison of Relative Rates for Vinylic and Alkyl-Type Product Formation for the Reactions of Sulfur Atoms and Methylene with Olefins[a]

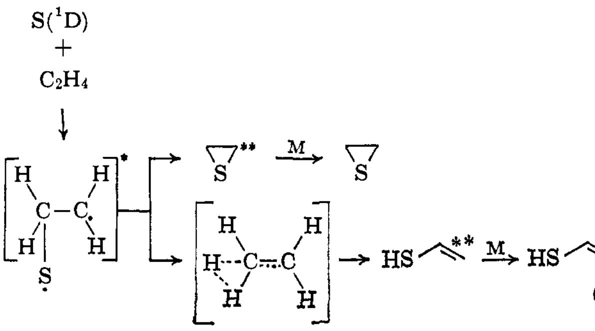
	S atoms[b]		Methylene	
Substrate	Vinylic	Alkyl type	Vinylic	Alkyl type
C_2H_4	0.95;	...	0.32 (from CH_2N_2)	...
	1.4 (2288 Å.)[c]	...	0.14 (from CH_2CO)	...
C_3H_6	0.22	0.26	0.27–0.09	0.33–0.18
	0.43 (2288 Å.)[c]	0.40 (2288 Å.)		
i-C_4H_8	~0	0.18	0.18–0.13	0.66–0.32
2-C_4H_8	~0	0.51	0.22	0.90
1,3-C_4H_6	~0	...	0.51–0.29	...
1-C_4H_8	~0	0.47	...	...
C_2H_3F	0.46[c]	...	...	...
CF_2CH_2	0.45	...	...	...
CFHCFH	0[c]	...	...	...
C_2F_3H	0[c]	...	...	...

[a] All values are relative to double bond addition as unity. [b] All S-atom data refer to the pressure-independent region, *i.e.*, $P > 300$ torr and Hg-arc photolysis unless otherwise indicated. [c] H. A. Wiebe, unpublished data from this laboratory.

olefins no vinylic mercaptan is formed, although the alkyl-type mercaptans are always present. This trend is particularly revealing when compared to the corresponding reactions of methylene. For alkyl-type mercaptans the correlation is quite good, indicating that these mercaptans are formed by an insertive attack of singlet sulfur on the alkyl-type C–H bond

$$S(^1D) + R{-}C{-}H \longrightarrow R{-}C{-}SH \qquad (16)$$

The drastic reduction in vinylic mercaptan products with increasing molecular complexity, however, could hardly be explained if the process giving rise to their formation is a direct C–H insertion. This structural effect could be better rationalized in terms of the rearrangement of energy-rich intermediates, *i.e.*

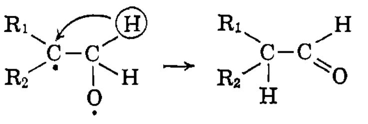


(17a)

(17b)

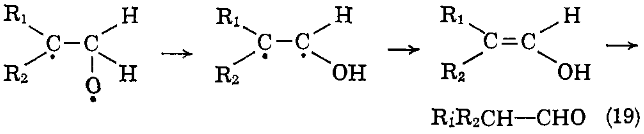
In the over-all reaction leading to either episulfide or mercaptan formation, the exothermicity is *ca.* 85 kcal./mole as noted above. Thus the intermediate biradicals have some 26 kcal./mole of excess energy which may be sufficient to bring about the required structural isomerization (with CH_2, the activation energy for isomerization is 9.5 kcal./mole).

The exothermicity of reaction 17 is about the same as that of the addition reactions of triplet oxygen atoms. Yet in the latter case, extensive isomerization, internal hydrogen, and alkyl group migration, as well as fragmentation, occur. Now it may be argued that the isomerization of the hot addition product should be capable of being quenched at higher pressure, whereas the experimental data show a general stabilizing effect of pressure up to several hundred torr. The argument, however, is not necessarily valid. Thus in the reaction with O(^{3}P) atoms, while the major portion of the fragmentation reactions can indeed be suppressed at high total pressure, the isomerization products, on the contrary, show a definite stabilizing effect with pressure up to several hundred torr, just as is the case of the S-atom system. With the oxygen atom adduct, hydrogen migration has been shown to be internal, that is



(18)

Methyl group migration, on the other hand, appears clearly to be a free-radical process. There seems to be no significant reason why hydrogen migration has to take place from one carbon atom to the other; migration to the oxygen atom would probably be just as favorable in terms of the energy and entropy changes involved. A hydrogen shift to the oxygen atom would yield a vinylic alcohol, which owing to its inherent instability would rapidly isomerize to the carbonyl structure, which is the isomerization product actually found.



(19)

The vinylic alcohol structure would obviously not be detected in normal kinetic experiments. However, in the sulfur atom case the sequence may well be arrested at the vinylic mercaptan stage. At lower pressures it is also possible that the vinylic mercaptan further isomerizes to the thioaldehyde or thioketone structure, which in turn would escape detection since thiocarbonyls form solid trimers with very low vapor pressures.

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