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Reactions of S Atoms with Dimethyl Sulfide and Thietane

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Abstract: $S(^1D)$ atoms react with CH_3SCH_3 to generate elemental sulfur and CH_3SSCH_3 as major primary products along with small amounts of C_2H_6, and with $\overline{\mathrm{CH_2(CH_2)_2S}}$ to give $\overline{\mathrm{CH_2(CH_2)_2SS}}$ and C_2H_4 in comparable yields. The reactions of ground-state $S(^3P)$ atoms with these substrates afford the same products, but the overall product recoveries are smaller, and in the case of $\overline{\mathrm{CH_2(CH_2)_2S}}$, the $C_2H_4/\overline{\mathrm{CH_2(CH_2)_2SS}}$ ratio is decreased. It is proposed that the primary adducts are vibrationally hot S_0 and T_1 state thiosulfoxides which then may isomerize to the corresponding disulfide, fragment via C–S cleavage, or undergo collisional deactivation to the ground state. Bimolecular reactions between two thermalized ground-state thiosulfoxide molecules and/or a thiosulfoxide molecule and an S_2–S_7 radical lead to regeneration of the substrate and to the formation of S_3–S_8 which ends up as elemental sulfur. The latter reactions predominate for the case of $S(^3P)$ addition to both substrates. From competitive experiments in the presence of C_3H_6 the following rate parameters have been derived: $k(S(^3P) + CH_3SCH_3) = (5.0 \pm 1.2) \times 10^{10} \exp[(0.84 \pm 0.24)/RT]$ $M^{-1}\,s^{-1}$ and $k(S(^3P) + \overline{\mathrm{CH_2(CH_2)_2S}}) = (8.2 \pm 1.9) \times 10^{10} \exp[(0.75 \pm 0.20)/(RT)]$ $M^{-1}\,s^{-1}$. The characteristic C–H insertion reaction with $S(^1D)$ atoms was not observed.

The ($\lambda > 240$ nm) photolysis of gaseous COS has been shown to generate metastable $S(^1D)$ and ground-state $S(^3P)$ atoms in a ratio of approximately 2:1.[1,2] The overall quantum yield of CO formation is 1.8 and the relevant reactions are

$$COS + h\nu \rightarrow \underset{67\%}{S(^1D)} + \underset{33\%}{S(^3P)} + CO \qquad (1)$$

$$S(^1D) + COS \rightarrow S_2 + CO \qquad (2a)$$

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

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

Thus, when a reactive substrate is present the CO yields serve as direct measure of the extent of competition between the substrate and COS for S atoms. In the presence of a ~15-fold excess of CO_2, the $S(^1D)$ atoms generated in the primary steps are largely deactivated to the ground state,

$$S(^1D) + CO_2 \rightarrow S(^3P) + CO_2^*$$

and therefore the COS/CO_2 system is an excellent source for the exclusive study of $S(^3P)$ atom reactions.

The reactions of S atoms with hydrocarbons have been extensively studied.[3] Thus, it has been shown that $S(^1D)$ atoms insert into paraffinic C–H bonds to yield the corresponding thiols in a fast and indiscriminate reaction and undergo stereoselective cycloaddition to the double bonds of alkenes, yielding thiiranes. The reaction with alkynes generates thiirene adducts which then react with a substrate molecule to yield thiophenes as one of the principal end products;[4] for the case of acetylene, thiophene accounts for only a few percent of the overall reaction, which is polymerization, but the corresponding thiophene yields increase with increasing CF_3 substitution in the alkyne. $S(^3P)$ atoms on the other hand are incapable of insertion and, like $S(^1D)$ atoms, have been shown to add stereoselectively to the double bonds of alkenes and the triple bonds of alkynes to generate thiiranes and thioketocarbenes, respectively. Absolute rate parameters are now available for a variety of $S(^3P)$ + alkene[5,6] and $S(^3P)$ + alkyne[7] reactions and clearly point to an electrophilic mode of attack: the activation energies decrease with increasing alkyl substitution on the unsaturated carbon atoms. For the $S(^1D,^3P)$ + alkane or alkene systems, product recoveries are high, in terms of the amount of S atoms produced, at short conversions.

The reactions of S atoms with other substrates have only been examined in a qualitative manner. $S(^1D)$ atoms have been shown to insert into the B–H bonds of diborane[8] and into the Si–H bond of monomethyl- and trimethylsilane,[9] and the latter reaction appears to be at least 25 times faster than the rate of insertion into C–H bonds. $S(^3P)$ atoms are inert with respect to Si–H insertion.

In view of the recent upsurge of interest in the reactions of atomic and radical species with organosulfur molecules,[10] we decided to carry out a study on the reactions of S atoms with this class of substrates. Other than the S + COS reactions, only the $S(^3P)$ + thiirane systems had been examined, using flash photolysis–resonance fluorescence[11] and flash photolysis–kinetic spectroscopy techniques.[12] The overall reaction is desulfurization, e.g.,

$$S(^3P) + \overline{\mathrm{CH_2CH_2S}} \rightarrow C_2H_4 + S_2(^3\Sigma_g^-)$$

and for parent thiirane $E_a \sim 0$.[11] Since the room temperature rate constants increase with increasing alkyl substitution,[12] it is

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possible that the activation energies become correspondingly negative.

The substrates chosen for the present investigation were the simplest sulfide, CH_3SCH_3, and the four-membered cyclic sulfide, $\overline{CH_2(CH_2)_2S}$. The results, which will be presented, clearly point to the intermediacy of unstable thiosulfoxides in both the $S(^1D)$ and $S(^3P)$ reactions with these molecules.

Experimental Section

Photolyses were carried out in a 10 × 5 cm quartz cell equipped with Suprasil windows. The cell was enclosed in a 6.5 cm thick cylindrical aluminum block furnace, 16 cm in length and insulated with a 1-in. layer of fiberglass. The ends were sealed with 2 mm thick quartz plates. The furnace was heated by means of four 10 cm long 150-W pencil heaters in axial positions connected to an API 2-mode temperature controller. Cell temperatures (±1 °C) were measured by using an iron–constantan thermocouple. The light source was a Hanovia medium-pressure mercury arc operated in conjunction with three 2-mm Vycor 7910 filters for the case of CH_3SCH_3 and one 2-mm Vycor 7910 together with a 240-nm interference filter for the case of $\overline{CH_2(CH_2)_2S}$.

Carbonyl sulfide (Matheson) was purified as described previously.[13] Dimethyl sulfide (Terochem) was distilled in vacuo at −98 °C; prior to each experiment further purification was achieved by GC on a 6 ft × 4 mm (i.d.) column packed with 12% tricresyl phosphate on chromosorb WAW-DMCS (80/100 mesh) followed by degassing at −115 °C. Thietane (API-USBM standard sample, stated purity 99.95%) was purified on a 3 ft × 4 mm (i.d.) column packed with 10% squalane on chromosorb W,HP (80/100 mesh) at 50 °C then degassed at −105 °C. NO (Matheson) and C_3H_6 (Matheson) were distilled at −183 and −139 °C, respectively, O_2 and CO_2 (Airco assayed reagents) were used as such.

Volatile materials (CO, CH_4, C_2H_6, SO_2, COS, and CO_2) were removed from the reaction mixture by degassing at the appropriate temperature and the total remaining condensible portion (<−139 °C) was transferred to the GC inlet for analysis. The columns were used as follows: CO, CH_4, 3 ft × 2 mm i.d. 80/100 mesh molecular sieve 5A; C_2H_6, 6 ft × 2 mm i.d. 80/100 mesh porapak N; CO_2, H_2O, SO_2, 5 ft × 2.5 mm i.d. (Teflon) 80/100 mesh porapak QS. CH_3SCH_3, CH_3SSCH_3, CH_3SH mixture, 4 ft × 4 mm i.d. 80/100 mesh chromosorb WAW-DMCS coated with 10% tricresyl phosphate operated at 30 °C; a careful search for CH_3SSSCH_3 and $CH_3SSSSCH_3$, on a 2 ft × 2.5 mm i.d. Teflon column packed with 80/100 mesh chromosorb W, HP coated with 3% OV-101, showed that these compounds were not present in the photolyzate; $\overline{CH_2(CH_2)_2S}$, $\overline{CH_2(CH_2)_2SS}$ mixture, same column as used above for $\overline{CH_2(CH_2)_2S}$ purification. The detector was a homemade block, fitted with a pair of Gow-Mac 13-502 thermistors, operated at 30 °C. Because of the instability of $\overline{CH_2(CH_2)_2SS}$, its molar response was estimated by assuming that the addition of a sulfur atom to $\overline{CH_2(CH_2)_2S}$ causes the same molar response change as for the case of CH_3SCH_3.

Mass spectra were obtained on an AEI MS-12 instrument at 70 eV and NMR spectra on either a Bruker WH-400 or WH-200 spectrometer. Microwave discharge experiments were carried out with a Baird Atomic Inc. Hg-Microwave Exciter Series No. EY1-55.

Results

(1) S + CH_3SCH_3 Reaction. Blank experiments with CH_3SCH_3 indicated that a small amount of decomposition into CH_3SSCH_3, C_2H_6, and CH_4 takes place under the conditions employed. However, from the measured extinction coefficient, it was determined that for a COS/CH_3SCH_3 ratio of 10, 97% of the incident radiation at $\lambda > 240$ nm is absorbed by COS at 25 °C and direct photolysis of CH_3SCH_3 in the presence of COS is negligible.

Photolysis of COS in the presence of CH_3SCH_3 led to the formation of CH_3SSCH_3 as the sole major condensible product. Lesser amounts of C_2H_6 and CH_4 were also formed, along with trace quantities of CH_3SH which were too small and erratic to be determined quantitatively. $CH_3S_4CH_3$ was demonstrably absent. A solid yellowish residue was visible on the cell walls.

Experiments were carried out at various exposure times, and the results are summarized in Table I.

One notable feature is the low product recovery, approximately 20% at low conversion, in terms of the total amount of sulfur atoms reacting with CH_3SCH_3. This is in marked contrast with the S + alkane or alkene systems, where it is possible to achieve 78% and 90% product recovery, respectively.[3] In order to ascertain whether this product loss could be accounted for in terms of involatile polymer, the following experiments were performed on a mixture consisting of 300 torr of COS and 30 torr of CH_3SCH_3:

Table I. Effect of Exposure Time on the Product Yields in the $COS–CH_3SCH_3$ System[a]

time, min	products, μmol				% recovery[b]
	CO	CH_3SSCH_3	C_2H_6	CH_4	
1.5	0.682	0.064	0.006	0	18
5	2.45	0.209	0.024	0.010	22
10	4.57	0.389	0.040	0.037	19
15	7.08	0.570	0.071	0.079	20
22	10.2	0.828	0.080	0.141	21
30	13.4	1.09	0.101	0.210	19
37	16.7	1.37	0.118	0.310	20
45	20.8	1.65	0.151	0.431	22

[a] $P(COS) = 300$, $P(CH_3SCH_3) = 30$ torr. [b] % recovery = $R(CH_3SSCH_3 + 1.5CH_4 + C_2H_6)/R(CO° - CO) \times 100$, where $R°(CO) = 0.711$ μmol min^{-1}. Cf. Discussion.

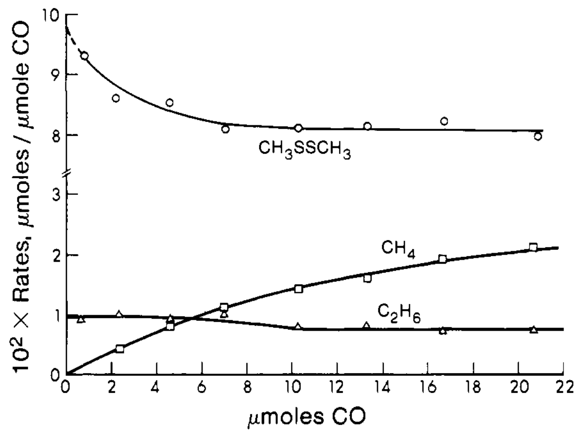

Figure 1. Rates of product formation vs. CO yield in the $COS–CH_3SCH_3$ system. $P(COS) = 300$ torr, $P(CH_3SCH_3) = 30$ torr. Photolysis times, 1.5–45 min.

(1) After a 30-min photolysis, which corresponded to a product loss of 9.8 μmol, the cell was evacuated, filled with 220 μmol of oxygen, and subjected to microwave discharge for 2 h in order to oxidize the residue to gaseous products. After careful removal of oxygen through three traps at −183 °C the remaining volatile material was found to consist solely of SO_2 (~3 μmol). Several control experiments with CH_3SCH_3 as substrate showed that CO_2 could be recovered quantitatively but that SO_2 probably reacted with Hg in the system and could only be detected in erratic and small amounts (of up to ~30%).

(2) Several high conversion runs were carried out (60, 90 min). After each experiment the cell was evacuated, cut off, and rinsed 3 times with 1-mL portions of $CHCl_3$. The solvent was evaporated, and the yellow solid remaining was redissolved in $CDCl_3$ and subjected to NMR (200 MHz) analysis. No signals were observed, even though the estimated product losses (19–31 μmol) would have been more than sufficient to generate a signal had the substance contained hydrogen. Finally, 1300 torr of CO_2 was added to the mixture, and after a 127-min photolysis the cell was rinsed with $CHCl_3$ and subsequently with CCl_4. The combined washings were treated and analyzed as above, and, again, no signal was observed. (Under similar operative conditions ~1.5 μmol of C_4H_6S generated a spectrum amenable to analysis.)

(3) The solvents for the NMR samples were evaporated and the solid residues were analyzed by MS using the direct probe. The spectra was very simple and consisted of multiples of 32, up to 256.

It can thus be concluded that most, if not all, of the mass imbalance in both the $S(^1D)$ and $S(^3P)$ + CH_3SCH_3 systems is due to the formation of elemental sulfur.

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Table II. Effects of Added CO_2 and NO in the COS–CH_3SCH_3 System

pressure, torr					μmol				
CH_3SCH_3	COS	CO_2	NO	time, min	CO	CH_4	C_2H_6	CH_3SSCH_3	% recovery[a]
	100			30	17.3				
	100	770		30	16.1				
10	100			30	11.5	0.314	0.161	1.111	30
10	100	770		30	9.22	0.062	0.118	0.667	11
10	100	1300		30	8.94	0.073	0.110	0.596	10
10	100		<0.1	15	5.77	0.013	0.032	0.370	nd[b]
10	100		1.86	15	5.63	nil	nil	0.139	nd
30	300			7.15	5.76	0.062	0.057	0.501	nd
30	300		3.98	7.15	5.60	nil	nil	0.104	nd

[a] % recovery = $[R(CH_3SSCH_3 + 1.5CH_4 + C_2H_6)/R(CO^\circ - CO)]100$. [b] Not determined.

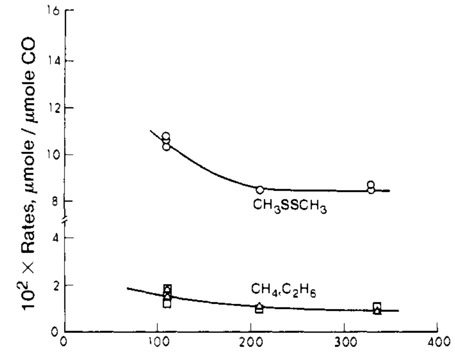

Figure 2. Rates of product formation vs. total pressure in the COS–CH_3SCH_3 system. $COS/CH_3SCH_3 = 10$. Exposure times: 15 min (110 torr); 9.16 min (220 torr); 7.15 min (330 torr).

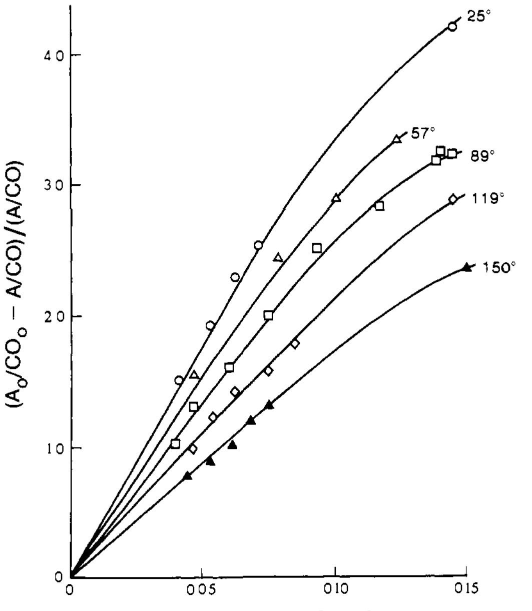

Figure 3. $(A_o/CO_o - A/CO)/(A/CO)$ vs. $[CH_3SCH_3]/[C_3H_6]$.

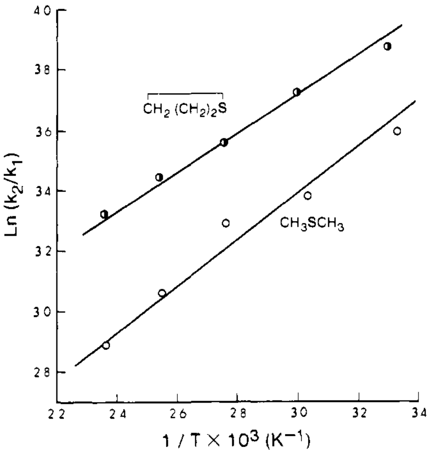

Figure 4. Arrhenius plots for the $S(^3P) + CH_3SCH_3$ and C_3H_6 and $S(^3P) + \overline{CH_2(CH_2)_2S}$ and C_3H_6 systems. k_1 refers to the $S(^3P) + C_3H_6$ reaction, k_2 to the $S(^3P) + CH_3SCH_3$ or $\overline{CH_2(CH_2)_2S}$ reaction.

The data in Table I are plotted in the form of product rates per μmol of CO formed in Figure 1 where it is seen that CH_4 behaves as if it were a secondary product, and there is a slight decrease in the rate of the apparent primary products, CH_3SSCH_3 and C_2H_6, with increasing conversion.

The product yields as a function of total pressure are illustrated in Figure 2. There is a significant suppressing effect on the formation of CH_3SSCH_3, and CH_4 and C_2H_6 also exhibit a similar, but more moderate, trend.

In order to delineate the reactivity of $S(^3P)$ atoms, experiments were carried out in the presence of excess CO_2. The results, listed in Table II, show that $S(^3P)$ atoms react in the same manner as $S(^1D)$ atoms but the overall product recoveries are lower.

The effects of added NO are also shown in Table II. CH_4 and C_2H_6 are completely suppressible, but it appears that CH_3SSCH_3 is not.

In order to measure rate parameters for the $S(^3P) + CH_3SCH_3$ reaction, competitive experiments were performed in the presence of C_3H_6 and ~1300 torr of CO_2. The two competing reactions are

$$S(^3P) + C_3H_6 \rightarrow CH_3\overline{CHCH_2S} \qquad (4)$$

$$S(^3P) + CH_3SCH_3 \rightarrow CH_3S(\text{-}S\cdot)CH_3 \qquad (5)$$

Because of the low product recoveries from reaction 5, relative rate constants had to be measured on the basis of the decrease in C_3H_6S yields with increasing CH_3SCH_3 pressure since reaction 4 is essentially quantitative at low conversions. If A_o and CO_o are the C_3H_6S and CO yields in the absence of CH_3SCH_3 and A and CO the C_3H_6S and CO yields in the presence of CH_3SCH_3, then

$$\frac{k_5}{k_4} = \frac{[(A_o/CO_o) - (A/CO)]}{A/CO}\ \frac{[C_3H_6]}{[CH_3SCH_3]}$$

where division of the As corrects for random fluctuations in the lamp intensity. Possible sources of error include (a) incomplete quenching of $S(^1D)$ atoms by CO_2, (b) secondary decomposition of C_4H_8S, and (c) some minor free radical reactions producing CO from COS via unknown mechanisms. It is assumed, however, that these complications do not affect the relative yields of C_4H_8S measured. Experiments were carried out at fixed C_3H_6 concentrations and at various concentrations of CH_3SCH_3 at 25, 57, 89, 119, and 150 °C. The results are summarized in Table III and the resulting plots of $(A_o - A)/A$ vs. $[CH_3SCH_3]/[C_3H_6]$ are illustrated in Figure 3. Some curvature is apparent for $[CH_3SCH_3]/[C_3H_6]$ ratios above ~0.1 but for smaller ratios the plots are linear. (One possible explanation for the nonlinear behavior of $(A_o - A)/A$ is sulfur atom transfer, $CH_3S(=S)CH_3$

Table III. Product Yields as a Function of Temperature and the $[CH_3SCH_3]/[C_3H_6]$ Ratio[a]

$P(CH_3SCH_3)$, torr	$[CH_3SCH_3]^b/[C_3H_6]$	products, μmol			$[(A_0/CO_0 - A/CO)/(A/CO)] \cdot \{[C_3H_6]/[CH_3SCH_3]\}$
		CO	C_3H_6S	CH_3SSCH_3	
			25 °C, 14 min		
0		2.93	1.98		0.0
2.77	0.0418	2.88	0.776	0.0247	36.1
3.49	0.0527	2.90	0.670	0.0360	36.5
4.14	0.0624	2.88	0.590	0.0442	36.8
4.67	0.0706	2.81	0.535	0.0496	36.0
9.61	0.145	2.86	0.355	0.125	30.6
			57 °C, 13 min		
0		3.18	2.11		0.0
3.01	0.0463	3.16	0.816	0.0240	33.7
5.05	0.0778	3.15	0.607	0.0475	31.2
6.49	0.100	3.11	0.528	0.0699	29.0
7.99	0.123	3.12	0.473	0.0751	27.4
			89 °C, 11.5 min		
0		3.31	2.16		0.0
3.08	0.0466	3.18	0.895	0.026	28.3
3.97	0.063	3.19	0.797	0.057	27.0
4.89	0.0741	3.13	0.676	0.054	27.3
0		3.17	2.08		0.0
2.69	0.0403	3.14	0.980	0.019	27.0
6.18	0.0932	3.06	0.569	0.058	27.0
7.72	0.117	3.03	0.515	0.072	24.3
9.61	0.145	3.05	0.472	0.129	22.3
			119 °C, 8 min		
0		3.14[c]	2.08[c]		0.0
3.02	0.0465	2.43	0.790	0.035	22.4
3.45	0.0533	2.44	0.728	0.036	22.9
4.00	0.0619	2.46	0.671	0.040	23.1
4.83	0.0745	2.49	0.636	0.043	21.4
5.46	0.0845	2.44	0.579	0.055	21.2
9.37	0.145	2.42	0.411	0.092	20.0
			150 °C, 8 min		
0		3.07[d]	2.00[d]		0.0
2.89	0.0436	2.93	1.07	0.031	17.8
3.49	0.0529	2.83	0.978	0.044	16.8
4.02	0.0608	2.88	0.899	0.049	18.0
4.48	0.0680	2.80	0.823	0.053	17.9
4.94	0.0750	2.77	0.775	0.067	17.8
9.79	0.149	2.75	0.534	0.102	15.9

[a] $P(COS) = 100$ torr, $P(CO_2) \simeq 1300$ torr, $P(C_3H_6) = 66.5$ torr. [b] For subsequent experiments at each temperature $[C_3H_6]$ has been corrected for depletion. [c] 10-min exposure time. [d] 8.5-min exposure time.

$+ C_3H_6 \rightarrow CH_3\overline{CHCH_2S} + CH_3SCH_3$, a phomenon that we have observed before.) Least mean squares analyses of the linear portions were carried out and the resulting slopes, Table IV, are plotted in the Arrhenius form in Figure 4 from which

$$E_4 - E_5 = 1.34 \pm 0.06 \text{ kcal mol}^{-1}$$

and

$$A_5/A_4 = 3.83 \pm 0.17$$

(2) The S + $\overline{CH_2(CH_2)_2S}$ Reaction. $\overline{CH_2(CH_2)_2S}$ absorbs strongly below 230 nm and features a second, much less intense absorption band centered around 260 nm. With the use of a high COS/substrate ratio (≥20:1) and the 240-nm interference filter, however, it was estimated that 99% of the incident radiation was absorbed by COS.

Photolysis of COS in the presence of $\overline{CH_2(CH_2)_2S}$ resulted in the formation of two retrievable products, C_2H_4 and a condensible product of mass 106, corresponding to the molecular formula $C_3H_6S_2$. Trace quantities of C_3H_6 were detected in a GC/MS cross scan of the volatile fraction. A yellowish residue was observed, but in much smaller quantities than for the cases where CH_3SCH_3 was the substrate.

The NMR ($CDCl_3$) spectrum of the M_r 106 product shows a triplet at δ 3.19 (4 H) and a quintet at δ 2.35 (2 H) with a J = 7.5 Hz. Assignment of the spectrum to 1,2-dithiolane (1,2-DT) is straightforward by comparison with the NMR spectra of thietane (δ 3.29, triplet 4 H, 2.97 quintet 2 H; J = 6.5 Hz) and of tetramethylene sulfide (δ 2.80, m 4 H, 1.90, m 4 H) obtained under identical conditions. In all these cases the methylenes adjacent to the sulfur atom resonate at lower fields.[14] Compared to thietane, the expected shift to lower field in 1,2-DT due to the presence of two sulfur atoms is offset by the larger upfield shift due to ring expansion analogous to the one observed on going from thietane to tetramethylene sulfide and, in general, from a four- to five-membered ring.[15] The four-membered ring structure thietane thiosulfoxide can be ruled out because in the absence of ring expansion the signals should show a small but downfield shift with respect to thietane.

Solution-phase syntheses of 1,2-DT have been reported in the literature[14,16] along with the observation that it is unstable with respect to polymerization.[16] In the gas phase, 1,2-DT polymerized as a brown film upon warming a sample from −196 °C to room temperature, and more than half could be decomposed in a 15-min photolysis at $\lambda > 240$ nm. The presence of mercury enhanced the rate of thermal decomposition. For these reasons distillations of the photolyzate and transfers to the GC inlet were done in the

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(14) The NMR spectrum of 1,2-dithiolane has been reported (Harpp, D. N.; Gleason, J. G. *J. Org. Chem.* **1970**, *35*, 3259); δ 2.30 (t, 2 H), 1.35 (m, 4 H). The latter assigment is, however, difficult to rationalize.

(15) Chamberlain, N. F. "The Practice of NMR Spectroscopy"; Plenum Press: New York, 1974; p 90.

(16) Barltrop, J. A.; Hayes, P. M.; Calvin, M. *J. Am. Chem. Soc.* **1954**, *76*, 4348.

Table IV. Product Yields as a Function of Temperature and the $[CH_2(CH_2)_2S]/[C_3H_6]$ Ratio[a]

$P(CH_2(CH_2)_2S)$, torr	$[CH_2(CH_2)_2S]$[b]/$[C_3H_6]$	products, μmol CO	products, μmol C_3H_6S	$[(A_0/CO_0 - A/CO)/(A/CO)] \cdot \{[C_3H_6]/[CH_2(CH_2)_2S]\}$
	25 °C, 35 min			
0		2.46	1.78	0.0
1.70	0.0261	2.43	0.767	49.7
2.56	0.0392	2.38	0.584	49.9
3.14	0.0481	2.44	0.522	49.7
3.78	0.0580	2.39	0.467	46.7
	60 °C, 35 min			
0		2.71	1.95	0.0
1.16	0.0176	2.64	1.09	41.9
1.87	0.0284	2.62	0.863	41.8
2.33	0.0356	2.60	0.752	41.9
3.11	0.0475	2.61	0.633	41.5
	90 °C, 35 min			
0		2.98	2.11	0.0
1.10	0.0165	2.83	1.26	35.8
1.69	0.0253	2.76	1.04	34.9
2.30	0.0345	2.78	0.890	34.9
3.18	0.0478	2.73	0.716	35.6
	120 °C, 32.5 min			
0		2.93	2.05	0.0
1.21	0.0180	2.73	1.22	31.4
1.61	0.0245	2.76	1.09	31.9
2.22	0.0331	2.73	0.937	31.6
2.96	0.0442	2.76	0.816	31.1
	150 °C, 30 min			
0		2.98	2.04	0.0
1.50	0.0227	2.78	1.15	27.7
2.07	0.0316	2.80	1.02	27.8
2.42	0.0367	2.70	0.913	27.9
3.03	0.0462	2.72	0.816	27.7

[a] $P(COS)$ = 100 torr, $P(CO_2) \simeq 1300$ torr, $P(C_3H_6)$ = 65.5 torr. [b] For subsequent experiments at each temperature, $[C_3H_6]$ has been corrected for depletion.

dark, as much as possible, and analyses were carried out without delay, but, nevertheless, product losses were unavoidable.

At low conversions the yields of 1,2-DT and C_2H_4 were comparable in magnitude, and the total product recovery extrapolated to zero time was estimated to be ~85%. With increasing conversion, however, the rate of formation of 1,2-DT decreased substantially, owing to secondary photolysis and thermal decay.

Ten experiments were carried out at total pressures ranging from 102.9 to 508.4 torr, at a fixed COS/C_3H_6S ratio of 34.4 and constant conversion (~2.44 μmol of CO). The rates of formation of 1,2-DT and C_2H_4 were found to be independent of total pressure, 0.162 ± 0.021 and 0.158 ± 0.008 μmol/μmol of CO, respectively.

The effects of CO_2 pressure on the product distribution are seen in Figure 5. As in the case of CH_3SCH_3, $S(^3P)$ atoms react with $CH_2(CH_2)_2S$ to yield the same products as $S(^1D)$ atoms, and there is an overall suppression of the total product recovery, ~40% in the presence of 1200 torr of CO_2 compared to ~60% in the absence of CO_2 under the same conditions. Unlike the S + CH_3SCH_3 system, however, the $S(^3P) + CH_2(CH_2)_2S$ reaction exhibits a change in the product distribution: the yield of 1,2-DT increases and that of C_2H_4 decreases with increasing CO_2 pressure and 1,2-DT/C_2H_4 ≃ 1.0 and 7.5 in the absence and presence of 1200 torr of CO_2, respectively.

Rate parameters for the

$$S(^3P) + CH_2(CH_2)_2S \rightarrow CH_2(CH_2)_2SS\cdot \qquad (6)$$

reaction were determined relative to reaction 4, in the same manner as described above for the case of CH_3SCH_3. The data listed in Table IV are plotted in Figure 6 from which the slopes are tabulated in Table V. The Arrhenius plot, shown in Figure 4, gives

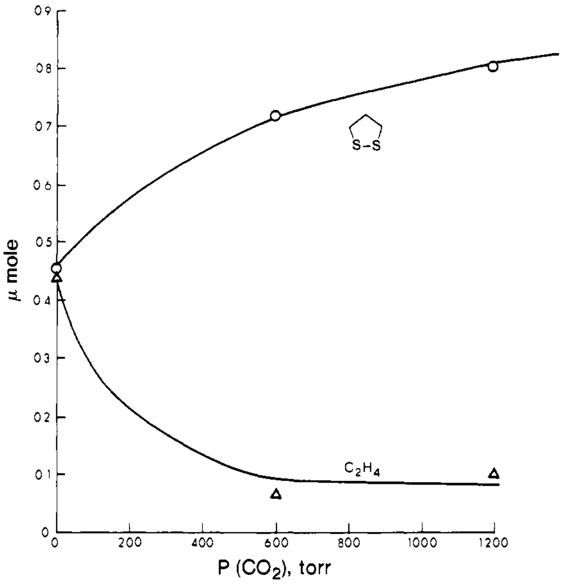

Figure 5. Product yields as a function of CO_2 pressure in the S + $CH_2(CH_2)_2S$ system. $P(COS)$ = 100 torr, $P(CH_2(CH_2)_2S)$ = 2.8 torr, exposure time, 35 min.

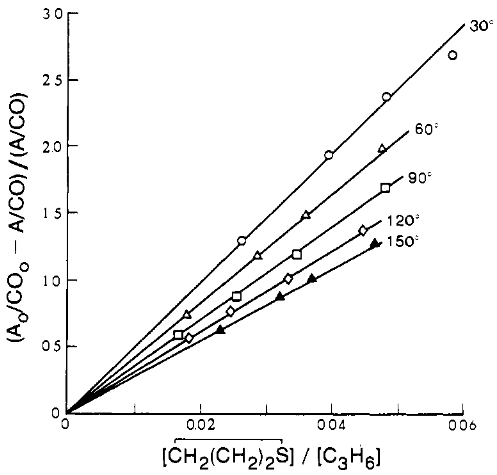

Figure 6. $(A_o/CO_o - A/CO)/(A/CO)$ vs. $[CH_2(CH_2)S]/[C_3H_6]$.

Table V. Slopes of the Plots in Figures 3 and 5

temp, °C	slope $(k(CH_3SCH_3)/k(C_3H_6))$	temp, °C	slope $(k(CH_2(CH_2)_2S)/k(C_3H_6))$
25	36.33 ± 0.44	25	48.01 ± 1.17
57	29.30 ± 1.85	60	41.60 ± 0.16
89	26.89 ± 0.67	90	35.33 ± 0.30
119	21.38 ± 0.85	120	31.40 ± 0.22
150	17.79 ± 0.44	150	27.77 ± 0.07

[a] The errors are standard deviations. The correlation coefficients are ⩾0.996.

$$A_6/A_4 = 6.30 \pm 0.25$$

and

$$E_4 - E_6 = 1.25 \pm 0.03 \text{ kcal mol}^{-1}$$

Discussion

Since $S(^3P)$ atoms are incapable of insertion, the only mode by which they can react with the sulfide molecules is via (spin and symmetry) allowed addition to the sulfur atom to give vibrationally excited lowest triplet state thiosulfoxides:

$$\mathrm{S(^3P) + CH_3SCH_3 \rightarrow CH_3\underset{\cdot}{S}(\text{–}S\cdot)CH_3(T_1)^\dagger} \quad (5)$$

and

$$\mathrm{S(^3P) + \overline{CH_2(CH_2)_2S} \rightarrow \overline{CH_2(CH_2)_2\underset{\cdot}{S}}\underset{\cdot}{S}(T_1)^\dagger} \quad (6)$$

The enthalpy change of the reaction

$$\mathrm{S(^3P) + CH_3SCH_3 \rightarrow CH_3S({=}S)CH_3(S_0)}$$

is -53 ± 4 kcal mol,[17] which sets an upper limit for the excitation energy of the T_1 state, the exact value of which is not known. The enthalpy change for the analogous reaction

$$\mathrm{S(^3P) + \overline{CH_2(CH_2)_2S} \rightarrow \overline{CH_2(CH_2)_2S}{=}S(S_0)}$$

is not known either but should be close to -53 kcal/mol, and the T_1 state should lie below that.

For the reaction involving $S(^1D)$ atoms more than one reaction channel is possible. Parallel to the spin- and symmetry-allowed addition to give the highly vibrationally excited ground-state thiosulfoxides,

$$\mathrm{S(^1D) + CH_3SCH_3 \rightarrow}$$
$$\mathrm{CH_3S({=}S)CH_3(S_0)^\dagger} \quad \Delta H \simeq -79 \pm 4 \text{ kcal mol}^{-1} \quad (7)$$

$$\mathrm{S(^1D) + \overline{CH_2(CH_2)_2S} \rightarrow}$$
$$\mathrm{\overline{CH_2(CH_2)_2S}{=}S(S_0)^\dagger} \quad \Delta H \simeq -79 \pm 4 \text{ kcal mol}^{-1} \quad (8)$$

insertion into the C–H bonds to give the corresponding hot ground state thiols is also a possibility:

$$\mathrm{S(^1D) + CH_3SCH_3 \rightarrow}$$
$$\mathrm{CH_3SCH_2SH(S_0)^\dagger} \quad \Delta H \simeq 81 \text{ kcal mol}^{-1}$$

$$\mathrm{S(^1D) + \overline{CH_2(CH_2)_2S} \rightarrow}$$
$$\mathrm{H_2\overline{CCH_2SHC}SH(S_0)^\dagger} \quad \Delta H \simeq -80 \text{ kcal mol}^{-1}$$

$$\mathrm{S(^1D) + \overline{CH_2(CH_2)_2S} \rightarrow}$$
$$\mathrm{H_2\overline{CSH_2CHC}SH(S_0)} \quad \Delta H \simeq -80 \text{ kcal mol}^{-1}$$

These thiols should be moderately stable ((methylthio)-methanethiol has been prepared for characterization by microwave spectroscopy[18]), yet the GC (and GC/MS cross scan) traces did not indicate the presence of compounds other than the products identified above and hence C–H insertion appears to be, at most, of minor importance under the conditions employed (vide infra). Direct insertion into the C–S bonds,

$$\mathrm{S(^1D) + CH_3SCH_3 \rightarrow CH_3SSCH_3(S_0)^\dagger}$$

$$\mathrm{S(^1D) + \overline{CH_2(CH_2)_2S} \rightarrow \overline{CH_2(CH_2)_2SS}(S_0)^\dagger}$$

is not compatible with the results, as will be shown.

The existence of branched forms of alkyl polysulfide molecules has long been discussed in the literature, although no spectral evidence could be obtained for their existence.[19] With the successful isolation and characterization of FS(=S)F in 1963,[20] however, it became evident that some thiosulfoxides could exist perhaps as short-lived transient intermediates. By the 1970's strong kinetic and mechanistic arguments were presented to the effect that thiosulfoxides are intermediates in the thermal racemization and isomerization of allylic disulfides[21] and in the elemental sulfur + allylic sulfide reaction which yields the corresponding disulfide.[22] The reduction of sulfoxides by P_4S_{10} was also believed to proceed via thiosulfoxide intermediates[23] and Baechler and co-workers[24] have recently shown that milder reducing agents such as B_2S_3 effect the conversion of sulfoxides into disulfides, as well as to monosulfides: the presence of the disulfide products constitutes the most compelling evidence to date for the intermediacy of thiosulfoxides in these systems.

On the basis of the product distributions obtained upon oxidation and reduction of various substituted diaryldisulfides Stepanov et al.[25] concluded that strongly electron-withdrawing substituents stabilize the thiosulfoxide form. Accordingly, the only thiosulfoxides that have been synthesized to date are those possessing strongly electron-withdrawing groups such as F[20] and O[26] bound to the S=S moiety. In the absence of such substituents thiosulfoxides undergo facile loss of sulfur, reverting to the sulfide.[21]

It will be shown that the nature of the observed products and the kinetics of their formation are consistent with the primary formation of dimethyl thiosulfoxide (Me_2TSO) and thietane thiosulfoxide (TTSO), both novel intermediates which have not been reported before. Not only are they the first examples of alkyl-substituted thiosulfoxides, but they are the first thiosulfoxides to be prepared in the gas phase.

The S + CH_3SCH_3 System. For the T_1 state Me_2TSO formed in step 5 the following reaction channels are energetically available:[17,27]

$$\mathrm{CH_3\underset{\cdot}{S}(\text{–}S\cdot)CH_3(T_1)^\dagger \xrightarrow{ISC} CH_3S({=}S)CH_3(S_0)^\dagger \rightarrow}$$
$$\mathrm{CH_3SSCH_3{}^*} \ (E_{\text{excess}} \leq 63 \text{ kcal mol}^{-1}) \quad (9a)$$

$$\mathrm{CH_3\underset{\cdot}{S}(\text{–}S\cdot)CH_3(T_1)^\dagger \rightarrow}$$
$$\mathrm{CH_3SS + CH_3} \ (E_{\text{excess}} \leq 6 \text{ kcal mol}^{-1}) \quad (9b)$$

$$\mathrm{CH_3\underset{\cdot}{S}(\text{–}S\cdot)CH_3(T_1)^\dagger + M \rightarrow CH_3S({=}S)CH_3(S_0) + M^*} \quad (9c)$$

where M can be COS, CH_3SCH_3, or CO_2. Dissociation of $Me_2TSO(T_1)^\dagger$ to $2CH_3S$ is ~9 kcal mol^{-1} endothermic.

Similarly, the hot ground-state Me_2TSO formed in step 7 may undergo analogous reactions:

$$\mathrm{CH_3S({=}S)CH_3(S_0)^\dagger \rightarrow}$$
$$\mathrm{CH_3SSCH_3{}^*} \ (E_{\text{excess}} \leq 89 \text{ kcal mol}^{-1}) \quad (10a)$$

$$\mathrm{CH_3S({=}S)CH_3(S_0)^\dagger \rightarrow}$$
$$\mathrm{CH_3SS + CH_3} \ (E_{\text{excess}} \leq 32 \text{ kcal mol}^{-1}) \quad (10b)$$

$$\mathrm{CH_3S({=}S)CH_3(S_0)^\dagger + M \rightarrow CH_3S({=}S)CH_3(S_0) + M^*} \quad (10c)$$

$(S_0)^\dagger$ Me_2TSO may also fragment into CH_3S radicals:

$$\mathrm{CH_3S({=}S)CH_3(S_0)^\dagger \rightarrow 2CH_3S} \ (E_{\text{excess}} \leq 21 \text{ kcal mol}^{-1}) \quad (10d)$$

Since most, if not all, of the "hot" CH_3SSCH_3 formed in reaction 10a is expected to fragment to $2CH_3S$ (vide infra), paths 10a and 10d are indistinguishable.

Step 7 is more exothermic than step 5 by 26 kcal mol^{-1}, the excitation energy of the $S(^1D)$ atom, and this difference in excess energy is carried over to the subsequent steps. Therfore, reactions

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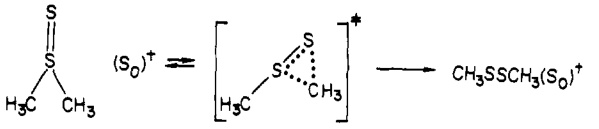
10a and 10b will be faster than (9a) and (9b), respectively. Also, reaction 9a features an intersystem crossing step prior to isomerization while reaction 10a is spin allowed. The suppressing effect of pressure on the singlet reaction, Figure 2, is due to the competition between (10a), (10b), and (10d) on the one hand and (10c) on the other.

The proposed thiosulfoxide–disulfide isomerization, steps 9a and 10a, are analogous to those postulated in the 2,3-sigmatropic rearrangements of allyl disulfides[21] and the B_2S_3 reduction of sulfoxides[24] and may be visualized as proceeding via the hypothetical transition state:



Although they could not be chemically trapped, phenyl-substituted dithiiranes have be postulated as transient intermediates in some interconversions.[28]

The final products from the triplet reaction then arise from the combination/disproportionation reactions of CH_3 and CH_3S_2 radicals,

$$2CH_3 \rightarrow C_2H_6 \tag{11}$$

$$2CH_3S_2 \rightarrow CH_3SSCH_3 + S_2 \tag{12}$$

$$CH_3S_2 + CH_3 \rightarrow CH_3SSCH_3 \tag{13}$$

collisional stabilization of the hot CH_3SSCH_3 formed in reaction 9a,

$$CH_3SSCH_3^* + M \rightarrow CH_3SSCH_3 + M \tag{14}$$

and the slow disproportionation reaction of thermalized Me_2TSO,

$$2CH_3S({=}S)CH_3(S_0) \rightarrow 2CH_3SCH_3 + S_2(^3\Sigma_g^-) \tag{15}$$

The sole fate of CH_3S_2 radicals in solution phase appears to be recombination.[29] However, the gas-phase disproportionation of HS_2 radicals, analogous to (12), has been observed to give $S_2(^1\Delta_g)$;[30] with thermalized CH_3S_2 radicals only ground-state $(^3\Sigma_g^-)S_2$ can form in an approximately thermoneutral reaction.

Reaction 15 has an enthalpy change of zero within the uncertainty of the >S=S bond dissociation energy,[17] 53 ± 4 kcal mol^{-1}, and is largely responsible for the low yield of the recoverable products, CH_4, C_2H_6, and CH_3SSCH_3, from the triplet reaction. An alternative and/or parallel mode of desulfurization of Me_2TSO is reaction with sulfur radicals (always present in the system).

$$CH_3S({=}S)CH_3 + S_{2-7} \rightarrow CH_3SCH_3 + c\text{-}S_{3-8} \quad \Delta H \leq -10 \text{ kcal mol}^{-1} \tag{16}$$

From the data in Table II it is seen that only ~10% of the $S(^3P)$ atoms that reacted with CH_3SCH_3 yielded retrievable products and the rest reverted to CH_3SCH_3 via steps 15 and 16. From the yield of C_2H_6 and CH_4 $\{[(C_2H_6 + {}^1/_2CH_4)/CH_3SSCH_3]100\}$ it can be estimated that ~24% of the disulfide was formed via the disproportionation step 12 and 76% through reaction 13 and 14. The overall yields from the triplet reaction are about one-third of those from the singlet reaction under similar conditions, Table II.

In the singlet reaction the observable products CH_4, C_2H_6, and CH_3SSCH_3 arise through steps 10a and 10b in competition with (10c). Step 10a is followed by

$$CH_3SSCH_3^* \rightarrow 2CH_3S \ (E_{excess} \leq 34 \text{ kcal mol}^{-1}) \tag{17a}$$

$$CH_3SSCH_3^* + M \rightarrow CH_3SSCH_3 + M^* \tag{17b}$$

Nitric oxide does not scavenge $S(^1D)$ atoms since the CO yields are unaffected (Table II). From the rate constant values for the $S(^3P) + NO + M$[31] and $S(^3P) + CH_3SCH_3$ (vide infra) reactions it can be shown that under the present conditions the $S(^3P)$ atom concentration is similarly unchanged in the presence of a few torr of NO. Hence the suppression of the CH_3SSCH_3 yields in the presence of NO, Table II, is caused by scavenging of the CH_3S radicals. It has been shown,[32] however, that at the NO/substrate concentrations used in this work not all the CH_3S can be scavenged and hence the residual CH_3SSCH_3 cannot be entirely ascribed to the molecular rearrangement–stabilization steps 10a and 17b. CH_4 and C_2H_6 are completely suppressed, consequently they must form from CH_3 radicals.

The intervention of CH_3S radicals from steps 10d and 17a leads to the disproportionation reactions

$$CH_3S_2 + CH_3S \rightarrow CH_3SCH_3 + S_2 \quad \Delta H = -30 \text{ kcal mol}^{-1} \tag{18}$$

$$CH_3S + CH_3S \rightarrow CH_3SH + CH_2S \tag{19a}$$

and the combination steps

$$2CH_3S \rightarrow CH_3SSCH_3 \tag{19b}$$

$$CH_3S + CH_3 \rightarrow CH_3SCH_3 \tag{20}$$

Reactions 18 and 20, reforming the substrate, are additional causes of the inherent low yields of the overall reaction while (19a), which is about 5% of the combination reaction 19b,[33] yields new products, both of which are good hydrogen donors.

Other sources of CH_3S radicals, with increasing conversion, include the secondary photolysis of the disulfide product

$$CH_3SSCH_3 + h\nu \rightarrow 2CH_3S \tag{21}$$

and the efficient exchange reaction[34]

$$CH_3SSCH_3 + CH_3 \rightarrow CH_3SCH_3 + CH_3S \tag{22}$$

Steps 21 and 22 may be responsible for the slight decrease in the yield of CH_3SSCH_3 with increasing photolysis time, Table I and Figure 1, to a near photostationary level. As CH_3SH and CH_2S, both of which contain labile hydrogen atoms, accumulate in the system the following abstraction reactions become increasingly important:

$$CH_3 + CH_3SH \rightarrow CH_4 + CH_3S \tag{23}$$

$$CH_3 + CH_2S \rightarrow CH_4 + CHS \tag{24}$$

$$CH_3 + CHS \rightarrow CH_4 + CS \tag{25}$$

$$CH_3S + CHS \rightarrow CH_3SH + CS \tag{26}$$

The observations that the CH_4 yields increase with increasing photolysis time, that CH_3SH is only formed in trace amounts, and that hydrogen could not be detected in the solid polymer are consistent with the occurrence of steps 23–26.

In the triplet reactions (Table II) the suppression of the CH_4/C_2H_6 ratio is a consequence of the fact that the CH_3S radical concentration is greatly reduced, thus affecting the rate of production of the hydrogen donors via reaction 19a.

The rate parameters for the reaction

$$S(^3P) + CH_3SCH_3 \rightarrow CH_3\underset{\cdot}{S}(-S\cdot)CH_3(T_1)^\dagger \tag{5}$$

were determined relative to the addition reaction to propene,

$$S(^3P) + CH_3CH{=}CH_2 \rightarrow CH_3\overline{CHCH_2S} \tag{4}$$

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Table VI. Rate Parameters for the Reactions of Some Atomic and Radical Species with CH_3SCH_3 and $\overline{CH_2(CH_2)_2S}$

reagent	substrate	k(25 °C) × 10^{-10}, $M^{-1}\ s^{-1}$	A × 10^{-9}, $M^{-1}\ s^{-1}$	E_a, kcal mol^{-1}	ref
$S(^3P)$	$\overline{CH_2(CH_2)_2S}$	29	82	−0.75	this work
$O(^3P)$	$\overline{CH_2(CH_2)_2S}$	10			37
$S(^3P)$	CH_3SCH_3	21	50	−0.84	this work
$O(^3P)$	CH_3SCH_3	3.1	6.7	−0.92	38
$O(^3P)$	CH_3SCH_3	3.3	12	−0.61	39
$O(^3P)$	CH_3SCH_3	2.9	8.6	−0.73	40
$O(^3P)$	CH_3SCH_3	3.0	7.7	−0.80	41
$H(^1S)$	CH_3SCH_3	0.021	17	2.6	42
$H(^1S)$	CH_3SCH_3	0.015	15	2.7	43
$OH(^2\Pi)$	CH_3SCH_3	0.60	3.3	−0.36	44
$OH(^2\Pi)$	CH_3SCH_3	0.26	4.1	0.27	45
$OH(^2\Pi)$	CH_3SCH_3	0.57	3.7	−0.27	46

For the latter reaction two sets of values have been reported, one by Klemm and Davis[6] who used flash photolysis with resonance fluorescence and the other by van Roodselaar[5] who used flash photolysis with kinetic absorption spectroscopy. The two sets,

$$E_a = 0.4 \pm 0.1\ \text{kcal mol}^{-1} \qquad A = (3.6 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$$

$$E_a = 0.5 \pm 0.2\ \text{kcal mol}^{-1} \qquad A = (1.3 \pm 0.3) \times 10^{10}\ M^{-1}\ s^{-1}$$

respectively, show good agreement in the value of the activation energy, but the preexponential factors differ significantly. Moreover, it has been pointed out[35] that, for the case of $O(^3P)$ + alkene reactions, the flash photolysis–resonance fluorescence technique consistently yields A and E_a values that are lower than those obtained by either flash photolysis–chemiluminescence, phase shift, or competitive methods. We therefore prefer to use van Roodselaar's data for the reference reaction with propene, and from the data presented in Tables III and V and Figures 3 and 4, we obtain

$$k_5 = (5.0 \pm 1.2) \times 10^{10} \exp[(0.84 \pm 0.24)/(RT)]\ M^{-1}\ s^{-1}$$

Thus the room temperature rate constant, $k_2 = 2.1 \times 10^{11}$, is quite high and close to the collision frequency. The rate constant of the $S(^1D)$ reaction must be at least of this magnitude. In comparison, the rate constant for insertion $S(^1D) + RH \rightarrow RSH$ may be as much as an order of magnitude lower ($k \geqslant (1.3–0.3) \times 10^{10}$ $M^{-1}\ s^{-1}$) and features a small activation energy.[3] This and the relatively low concentration of the $S(^1D)$ atoms owing to the high COS/CH_3SCH_3 ratios employed[36] could be the reasons why no evidence for the occurrence of insertion reactions could be found.

The analogous reaction of $O(^3P)$ atoms,

$$O(^3P) + CH_3SCH_3 \rightarrow CH_3\underset{\bullet}{S}(-O\cdot)CH_3(T_1)^\dagger$$

also features a small negative activation energy, as seen from the data in Table VI. Cvetanovic, Singleton, and Irwin[47] carried out careful product analysis of this system and reported the major products to be C_2H_6 and $(CH_3)_2S{=}O$ (Me_2SO) in a ratio ~3:1, respectively, in combined yields of ~35% in terms of the $O(^3P)$ atoms produced. The overall mechanism is postulated to be:

$$O(^3P) + CH_3SCH_3 \rightarrow CH_3\underset{\bullet}{S}(-\dot{O})CH_3(T_1)^\dagger$$

$$CH_3\underset{\bullet}{S}(-O\cdot)CH_3(T_1)^\dagger \xrightarrow{>90\%} CH_3SO\cdot + CH_3\cdot$$

$$CH_3\underset{\bullet}{S}(-O\cdot)CH_3(T_1)^\dagger \xrightarrow{?} CH_3S\cdot + CH_3O\cdot$$

$$2CH_3\cdot \rightarrow C_2H_6$$

$$CH_3\cdot + CH_3SO\cdot \rightarrow CH_3S({=}O)CH_3$$

$$CH_3\cdot + CH_3SO\cdot \rightarrow CH_3SOCH_3$$

In contrast to the S atom reaction, fragmentation appears to be the sole mode of decay of the primary adduct. Unfortunately, CH_3SOCH_3 is unknown and its possible intermediacy in this system cannot be evaluated.

The S + $\overline{CH_2(CH_2)_2S}$ Reaction. The reaction of $S(^1D)$ atoms with thietane affords C_2H_4 and 1,2-dithiolane (1,2-DT) as major products. By analogy with the $S(^1D) + CH_3SCH_3$ reaction the primary adduct is postulated to be the vibrationally hot S_0 state thietane thiosulfoxide (TTSO) with an excess vibrational energy of ca. 79 kcal mol^{-1}.

This adduct may then undergo C–S bond cleavage to form a biradical or be collisionally stabilized:

$$\overline{CH_2(CH_2)_2S}{=}S(S_0)^\dagger \rightarrow \cdot CH_2(CH_2)_2S_2\cdot \qquad (27a)$$

$$\overline{CH_2(CH_2)_2S}{=}S(S_0)^\dagger \xrightarrow{M} \overline{CH_2(CH_2)_2S}{=}S(S_0) \qquad (27b)$$

The biradical formed in (27a) can undergo ring closure, fragment via C–C, and, to a minor extent, C–S bond cleavage:

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow \overline{CH_2(CH_2)_2SS} \qquad (28a)$$

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow C_2H_4 + CH_2S_2 \qquad (28b)$$

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow C_3H_6 + S_2(^3\Sigma_g^-, {}^1\Delta_g) \qquad (28c)$$

The CH_2S_2 species formed in fragmentation step 28b may exist in three isomeric forms:

$$H_2C{=}S{=}S \qquad H_2\overline{CSS} \qquad HC({=}S)SH$$

The first two isomers have never been observed, although there is some evidence in support of the transient existence of some phenyl-substituted isomers.[28] Dithioformic acid, on the other hand, has been produced by the pyrolysis of $HC(SH)_3$ for microwave

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[36] From the data in Table II the total amount of S atoms produced in the photolysis of 300 torr of COS is CO°/2 = 0.356 μmol min^{-1}, of which 0.239 and 0.117 μmol are (^1D) and (^3P), respectively.[2] Since k_3 is small, 2 × 10^6 $M^{-1}s^{-1}$ (Klemm, R. B.; Davis, D. D. *J. Phys. Chem.* **1974**, *78*, 1137), this step can be ignored when CH_3SCH_3 is present and the measured CO yield comes from the primary step 1 and the abstraction reaction by $S(^1D)$ atoms, step 2a. Hence the yield of the abstraction reaction 2a = CO–CO°/2 = 0.099 (for the 1.5-min photolysis). Since $k_{2a}/k_{2b} \sim 2^2$ the yield of step 2b = 0.099/2 = 0.050. Hence the total amount of $S(^3P)$ atoms reacting with CH_3SCH_3 = 0.117 + 0.050 = 0.167 μmol. Because the combined amount $S(^1D) + S(^3P)$ reacting = (total sulfur produced) − (yield of 2a) = 0.356 − 0.099 = 0.257, it follows that only 0.090, or ~35%, are in the $S(^1D)$ state. This must be viewed as an estimate, however, since direct, more reliable measurements of the branching ratio in step 1 and the rate constant ratio k_{2a}/k_{2b} are not available.

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spectroscopic studies.[48] The thiosulfine and dithiirane structures, however, are more compatible with the proposed fragmentation.

1,2-**DT** is a highly unstable molecule which readily undergoes thermal, surface-catalytic, and photolytic reactions, and for this reason its quantitative measurement is difficult. Nevertheless, the product yields obtained are high and under favorable conditions at very low conversions would be approximately 85%. This indicates that the ring-opening reaction (27a) is highly facile owing to relief of ring strain (~19.4 kcal mol^{-1} [27]) and, in the pressure range studied, up to 508 torr, is complete.

$S(^3P)$ atoms also react with thietane to yield 1,2-DT and C_2H_4. The percent recovery of 1,2-DT is similar to the $S(^1D_2)$ case but that of C_2H_4 is drastically reduced (Figure 5) resulting in a higher 1,2-DT/C_2H_4 ratio (7.5 vs. 1.0 for $S(^1D_2)$). The triplet state TTSO formed in reaction 6 may undergo the following triplet-state analogues of steps 27 and 28

$$\overline{CH_2(CH_2)_2\underset{\cdot}{S}}S\cdot(T_1)^\dagger \rightarrow \cdot CH_2(CH_2)_2S_2\cdot \qquad (29a)$$

$$\overline{CH_2(CH_2)_2\underset{\cdot}{S}}S\cdot(T_1)^\dagger \rightarrow \overline{CH_2(CH_2)_2S}{=}S(S_0) \qquad (29b)$$

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow \overline{CH_2(CH_2)_2SS} \qquad (30a)$$

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow \overline{CH_2(CH_2)_2S}{=}S(S_0) \qquad (30b)$$

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow C_2H_4 + CH_2S_2 \qquad (30c)$$

$$\cdot CH_2(CH_2)_2S_2\cdot \rightarrow C_3H_6 + S_2 \qquad (30d)$$

and desulfurization of ground state TTSO can then take place

$$\overline{CH_2(CH_2)_2S}{=}S(S_0) \xrightarrow[S_2\text{–}S_7]{\overline{CH_2(CH_2)_2S}{=}S(S_0)} \overline{CH_2(CH_2)_2S} + S_2(S_3\text{–}S_8) \qquad (31)$$

The energy content of TTSO(T_1) is lower than that of TTSO$(S_0)^\dagger$ by 26 kcal mol^{-1}, which explains the lower observed yield of the fragmentation product. The biradical produced by C–S cleavage in step 29a may be viewed as a double doublet, in which case there are no spin restrictions on the subsequent modes of decay of this species. The low overall product recovery (~40%) in the $S(^3P)$ + thietane system indicates that desulfurization (step 31), probably preceded by intersystem crossing (step 29b), is the major reaction occurring. The recoveries of 1,2-DT from $S(^1D)$ and $S(^3P)$ addition were estimated to be 44% and 36%, respectively.

$O(^3P)$ atoms react with thietane to yield C_2H_4 and c-C_3H_6 in a ratio of 3.3.[37] The following mechanism has been proposed:

$$O(^3P) + \overline{CH_2(CH_2)_2S} \rightarrow \overline{CH_2(CH_2)_2\underset{\cdot}{S}}\underset{\cdot}{O}(T_1)$$

$$\overline{CH_2(CH_2)_2\underset{\cdot}{S}}\underset{\cdot}{O}(T_1) \xrightarrow[\text{cleavage}]{\text{C–C}} C_3H_6 + SO(^3\Sigma_g)$$

$$CH_2(CH_2)_2\underset{\cdot}{S}\underset{\cdot}{O}(T_1) \xrightarrow[\text{cleavage}]{\text{C–S}} C_2H_4 + CH_2SO$$

$$CH_2(CH_2)_2\underset{\cdot}{S}\underset{\cdot}{O}(T_1) \xrightarrow{M} \overline{CH_2(CH_2)_2S}{=}O$$

Isomerization to $\overline{CH_2(CH_2)_2SO}$ can account for, at most, 10% of the overall reaction.

In their reactions with thiiranes, the only cyclic sulfides studied to date apart from thietane, $S(^3P)$ atoms afford C_2H_4 and elemental sulfur, as the only retrievable products.[49] Since neither spectroscopic nor kinetic studies revealed any evidence for the intervention of any transient intermediate, it was proposed that the overall reaction is direct abstraction of the S atom from thiirane:[11,12]

$$S(^3P) + \overline{CH_2CH_2S} \rightarrow C_2H_4 + S_2(\tilde{X}^3\Sigma_g^-) \quad \Delta H = -43 \text{ kcal mol}^{-1}$$

Thus, one is forced to conclude that thiirane thiosulfoxides are both thermodynamically and kinetically unstable with respect to decomposition to alkenes and S_2.

Rate parameters for the reaction

$$S(^3P) + \overline{CH_2(CH_2)_2S} \rightarrow \overline{CH_2(CH_2)_2\underset{\cdot}{S}}S\cdot(T_1)^\dagger \qquad (6)$$

were determined in a manner analogous to the $S(^3P) + CH_3SCH_3$ reaction, and from the data in Tables IV and V, Figure 6, the derived rate expression is

$$k_6 = (8.2 \pm 1.9) \times 10^{10} \exp[(0.75 \pm 0.20)/(RT)] \text{ M}^{-1} \text{ s}^{-1}$$

Thus, the addition reactions of $S(^3P)$ atoms to CH_3SCH_3 and $\overline{CH_2(CH_2)_2S}$ are extremely fast, occurring at rates near to gas kinetic collision frequencies[50] and feature small negative activation energies. The A factors correspond to $\Delta S^\ddagger(CH_3SCH_3) = -21.90$ and $\Delta S^\ddagger(\overline{CH_2(CH_2)_2S}) = -20.92$ eu; the close similarity in these values implies similar transition states, consistent with the proposed mechanism. We believe that negative activation energies result when the potential energy surface of the loose adduct intersects the product surface on the repulsive part at a point below the level of the separated reactants, although other explanations have also been advanced.[35]

From the present results it can be concluded that the reactions of $S(^1D,^3P)$ atoms with simple thioethers generally feature attack at the sulfur nonbonding ^{3}p orbitals leading to the formation of thiosulfoxides. $O(^3P)$ atoms react similarly to yield the corresponding sulfoxide, and by analogy, the remaining group 6A atoms, Se and Te, probably form the corresponding unstable adducts. From the few studies reported in the literature, it appears that the high reactivity of the S nonbonding 3p orbital toward atom and radical attack is not limited only to divalent species: most atoms and radicals also preferentially attack at the sulfur site.

Rate parameters for the reactions of $S(^3P)$, $O(^3P)$, $H(^1S)$, and $OH(^2\Pi)$ with CH_3SCH_3 and $\overline{CH_2(CH_2)_2S}$ are summarized in Table VI. For the CH_3SCH_3 substrate, the A factor for the $S(^3P)$ addition is larger than that for the $O(^3P)$ addition (even if we adopt the lower A value for the reference reaction) although both reactions exhibit negative E_a's and similar temperature dependences. The larger A factor is partly a consequence of the greater size and polarizability of the sulfur atom. The H + CH_3SCH_3 reaction possesses a high A factor but the activation energy is positive, reflecting the less electrophilic nature of the H atoms. The OH radical is somewhat less reactive than $S(^3P)$ and $O(^3P)$, which is surprising in view of its higher reactivity with alkenes,[52] and this is probably associated with the structure of the transition state.

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Registry No. S, 7704-34-9; CH_3SCH_3, 75-18-3; $\overline{CH_2(CH_2)_2S}$, 287-27-4; CH_3SSCH_3, 624-92-0; $\overline{CH_2(CH_2)_2SS}$, 557-22-2.

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