Sulfur Atom Abstraction from Episulfides and Carbonyl Sulfide by Methyl Radicals

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Abstract: In the gas-phase reactions of methyl radicals with ethylene episulfide, propylene episulfide, and *cis*-2-butene episulfide, the major step is concerted sulfur atom transfer accompanied by less efficient hydrogen atom abstractions. Arrhenius parameters of both reactions were measured for ethylene episulfide and propylene episulfide. Methyl radicals as well as sulfur atoms abstract sulfur from carbonyl sulfide and the rate parameters of these reactions have also been determined. Potential energies of activation and lower limits to the frequency factors have been computed from EHMO and transition state theories and compared with experimentally measured values.

Metathetical reactions of methyl radicals involving the transfer of an atom of hydrogen or the halogens have been widely investigated.[1–5] In addition to these "normal" reactions, group transfer reactions of methyl radicals such as

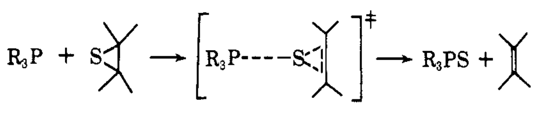
$$CH_3 + CH_3COCOCH_3 \longrightarrow CO(CH_3)_2 + CH_3CO$$

$$CH_3 + CH_3ONO \longrightarrow CH_3NO + CH_3O$$

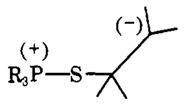
$$CH_3 + CD_3SH \longrightarrow CH_3SH + CD_3$$

are also known.[6–8] The present study reports a unique type of reaction in which the monovalent methyl radical abstracts a divalent sulfur atom from bridged sulfur-containing molecules (episulfides) and carbonyl sulfide.

In an earlier study of the *tert*-butyl peroxide initiated free-radical reaction of propylene episulfide, abstraction of hydrogen both α and β to the sulfur atom was observed[9] but sulfur atom abstraction resulting in the production of propylene was not detected. Nucleophilic attack upon episulfides by organolithium compounds,[10,11] triethyl phosphite,[11–13] and triphenyl-[12,14] or tributylphosphine[14] has been shown to occur readily with the production of the aryllithium mercaptide, triethyl thiophosphonate, triphenyl- or tributylphosphine sulfide, and the corresponding olefin. Using *cis*- and *trans*-2-butene, the reactions were shown to follow a stereospecific pathway suggesting a concerted, single-step attack upon the sulfur atom *via* a symmetrical transition state



The alternative mechanism implicating the ionic intermediate



was considered less probable.

The present article reports the results of detailed kinetic studies on the CH_3 + ethylene episulfide (EES), CH_3 + propylene episulfide (PES), CH_3 + COS, and $S(^3P)$ + COS systems, along with those of preliminary studies on the stereochemical aspect of the CH_3 + *cis*-2-butene episulfide reaction. The experimental reaction rate parameters are also compared with those estimated by the modified bond-energy–bond-order (BEBO) method[15] and Benson's method[16] of obtaining lower limits of the *A* factor.

Experimental Section

The reactors used for the study of the temperature dependence of the methyl radical reactions consisted of 5 × 6 and 5 × 10 cm cylindrical quartz cells enclosed in aluminum block furnaces connected to a conventional high vacuum system *via* Hoke valves. Temperature readings were made with standardized iron–constantan thermocouples. Hanovia medium-pressure mercury arcs were used in conjunction with Kodak Wratten No. 18A filters ($\lambda > 3150$ Å). At each temperature, control experiments with episulfides were made in order to correct for thermal decomposition.

A circulating system (700 cc vol) was used in the relative rate measurements of $S(^3P)$ atoms with ethylene and carbonyl sulfide using a Hanovia medium-pressure mercury arc equipped with a Vycor 7910 filter ($\lambda > 2250$ Å).

Low-temperature distillations, gas chromatography, and mass spectrometry were employed to separate and analyze the products. Nitrogen, CO, and CH_4 were analyzed on an 8-ft molecular sieves column operated at 25°. In experiments using azomethane-d_6 and EES the isotopic composition of the methane fraction was determined by mass spectrometry using an AEI-MS10 instrument. Ethane, ethylene, and propylene were analyzed on a 15-ft medium activity silica gel column at 25° and heavier molecular weight products were separated on silicone gum rubber SE-30, TCP, and mineral oil columns.

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Table I. Reactions of Methyl Radicals with EES[a]

Temp, °C	[EES][b]	$[(CH_3N)_2]$[b]	R_{N_2}[c]	$R_{C_2H_6}$[d]	$R_{C_2H_4}$[c,e]	$k_5/k_2^{1/2} \times 10^1$
31	5.02	0.37	12.80	103.80	3.67	2.71
60	4.86	0.40	7.58	24.95	4.45	6.03
89	6.26	0.39	10.12	18.36	11.44	13.49
120	6.30	0.40	11.42	4.61	17.51	40.89
145	3.76	0.38	14.33	15.40	17.74	37.99
165	3.83	0.40	14.48	4.41	22.25	87.45
205	3.93	0.38	15.37	1.59	21.19	133.89

Temp, °C	[EES][b]	$[(CD_3N)_2]$[b]	R_{N_2}[c]	$R_{C_2D_6}$[d]	R_{CD_3H}[d]	$R_{C_2H_4}$[c,e]	$k_6/k_2^{1/2} \times 10^1$	$k_5/k_2^{1/2} \times 10^1$
30	5.29	1.55	5.37	56.50	0.71	2.75	0.06	2.19
50	7.78	1.31	6.95	42.85	2.17	6.84	0.14	4.25
84	9.36	1.15	17.28	29.10	14.74	37.45	0.92	23.46
105	6.50	1.22	12.88	12.03	8.52	17.80	1.19	25.02
130	8.20	1.07	21.70	10.36	37.90	30.34	4.53	36.35
178	6.67	1.01	21.50	3.51	33.30	30.98	8.34	77.51
204	6.48	1.32	29.66	3.12	74.04	44.25	20.44	122.22

[a] Photolysis times between 7 and 30 min. [b] Values $\times 10^6$ mol/cc. [c] Values $\times 10^{12}$ mol/(cc sec). [d] Values $\times 10^{13}$ mol/(cc sec). [e] Corrected for excess C_2H_4 at higher temperatures.

Carbonyl sulfide (Matheson) was purified by a previously described procedure.[17] Carbon monoxide and nitrogen were Airco reagent grades and were used without further purification. Phillips research grade hydrocarbons were the calibration standards. Methane-d_3, methane-d_4, azomethane, and azomethane-d_6 were from Merck. The azo compounds were purified before each experiment by trap-to-trap vacuum distillation from −112° and collected at −139°. Methanethiol, dimethyl sulfide, dimethyl disulfide, and dimethylmercury (Eastman) were purified by vacuum distillation. Episulfides were prepared by warming mixtures of potassium thiocyanate with the appropriate carbonate[18,19] and isolating them from the distillate by glc.

Results

The photolytic decomposition of azomethane has been shown to take place *via* the following processes.[20,21]

$$CH_3N{=}NCH_3 + h\nu \xrightarrow{\Phi\,=\,0.993} 2CH_3 + N_2 \quad (1a)$$

$$\xrightarrow{\Phi\,=\,0.007} C_2H_6 + N_2 \quad (1b)$$

Secondary free-radical processes are those of combination, addition, and abstraction

$$2CH_3 \longrightarrow C_2H_6 \quad (2)$$

$$CH_3N{=}NCH_3 + CH_3 \longrightarrow (CH_3)_2N\dot{N}CH_3 \quad (3)$$

$$\longrightarrow \cdot CH_2N{=}NCH_3 + CH_4 \quad (4)$$

for which elementary rate constants have been determined. In the presence of a substance containing a labile species, rate constants for the competing reaction

$$CH_3 + RX \longrightarrow CH_3X + \cdot R$$

can be measured from comparative product yields.

Reactions of Methyl Radicals with Episulfides. Photolysis of azomethane in the presence of EES gave rise to N_2, C_2H_4, CH_3SCH_3, and CH_3SSCH_3 along with smaller amounts of CH_4, C_2H_6, and methylethyldiimide. Data concerning the principal reaction products obtained at different temperatures are given in Table I. It was also observed that small amounts of NO had a suppressing effect on the yields of C_2H_4 and the sulfides, indicating that these products originate from free-radical precursors. Thus the overall reaction can be adequately described in terms of the elementary processes 1–10.[22]

$$CH_3 + EES \longrightarrow CH_3S + C_2H_4 \quad \Delta H = -12.4 \text{ kcal/mol} \quad (5)$$

$$\longrightarrow CH_4 + C_2H_3S \quad (6)$$

$$CH_3 + CH_3S \longrightarrow CH_4 + CH_2S \quad \Delta H = -56.9 \text{ kcal/mol} \quad (7)$$

$$\longrightarrow (CH_3)_2S \quad \Delta H = -72 \text{ kcal/mol} \quad (8)$$

$$2CH_3S \longrightarrow CH_3SH + CH_2S \quad \Delta H = -39.5 \text{ kcal/mol} \quad (9)$$

$$\longrightarrow (CH_3S)_2 \quad \Delta H = -63.7 \text{ kcal/mol} \quad (10)$$

As the temperature is increased the $C_2H_4/2N_2$ ratio increases and that of the total CH_3S to C_2H_4 decreases. These trends suggest that at elevated temperatures ethylene is produced by additional reactions, the most probable of which is abstraction of sulfur atom from EES by the methyl thiyl radical

$$CH_3S + EES \longrightarrow CH_3S_2 + C_2H_4 \quad \Delta H = -12.6 \text{ kcal/mol} \quad (11)$$

The principal reaction product was ethylene in a temperature-dependent yield. Further evidence in favor of reaction 11 comes from auxiliary studies in which dimethyl disulfide was photolyzed in the vapor phase in the presence of EES. The major reaction product was ethylene, the yields being temperature dependent. The data in Table I were therefore corrected with the assumption that the C_2H_4 produced in (11) is given by $2C_2H_6 + CH_4 + (CH_3)_2S + C_2H_4 + C_2H_5N{=}NCH_3 - 2N_2$.

Using the relation

$$k_5/k_2^{1/2} = [R_{C_2H_4}/R_{C_2H_6}{}^{1/2}][EES]^{-1}$$

and taking the value $\log k_2$ (cc mol^{-1} sec^{-1})[23] = 13.34, least-mean-squares treatment of the data yields

$$\log k_5 = 10.85 \pm 0.48 - (6700 \pm 800/RT) \text{ (cc mol}^{-1}\text{ sec}^{-1})$$

and

$$\log k_5 = 10.77 \pm 0.64 - (6500 \pm 1000/RT) \text{ (cc mol}^{-1}\text{ sec}^{-1})$$

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Table II. Reaction of Methyl Radicals with PES[a]

Temp, °C	$[\mathrm{PES}]$[b]	$[(\mathrm{CH_3N})_2]$[b]	$R_{\mathrm{N_2}}$[c]	$R_{\mathrm{C_2H_6}}$[c]	$R_{\mathrm{CH_4}}$[c]	$R_{\mathrm{C_3H_6}}$[c]	$k_{13}/k_2^{1/2} \times 10^1$	$k_{14}/k_2^{1/2} \times 10^1$
66	1.83	0.35	42.71	19.81	3.14	19.88	7.80	0.94
87	1.67	0.52	73.69	19.55	8.11	26.72	11.42	2.47
110	1.61	0.45	71.43	11.15	14.23	54.81	32.11	
129	1.75	0.51	82.58	5.57	14.21	60.55	46.48	7.83
135	1.80	0.35	59.15	3.55	11.49	53.97	50.18	8.42
138	1.76	0.47	66.89	4.08	14.72	37.14	33.03	9.75
153	1.74	0.41	42.52	2.79	13.55	54.05	58.88	10.68
162	5.77	1.18	32.48	7.00	100.72	522.41	108.40	16.18

[a] Photolysis time, 45 min. [b] Values $\times 10^6$ mol/cc. [c] Values $\times 10^{13}$ mol/(cc sec).

for the reaction of the CH_3 and CD_3 radical, respectively.

Similarly the rate equation for hydrogen abstraction from EES, reaction 6, $\log k_6 = 11.34 \pm 0.60 - (9540 \pm 1000/RT)$ (cc mol^{-1} sec^{-1}), was derived by the relation $[k_6/k_2^{1/2} = R_{\mathrm{CD_3H}}/R_{\mathrm{C_2H_6}}^{1/2}][\mathrm{EES}]^{-1}$ from experiments using azomethane-d_6 as a source of CD_3 radicals.

Finally, Arrhenius parameters for reaction 11 could be estimated by the relation

$$k_{11}/k_{10}^{1/2} = [R_{\mathrm{C_2H_4(excess)}}/R_{\mathrm{(CH_3S)_2}}^{1/2}][\mathrm{EES}^{-1}]$$

using $\log k_{10} = 13.40$ (cc mol^{-1} sec^{-1}).[24] The data show considerable scatter and yield approximate values for $\log A_{11}$ (cc mol^{-1} sec^{-1}) ~ 11.5 and $E_{11} \sim 8.8$ kcal mol^{-1}.

The reactions of methyl radicals with PES were studied less extensively. The major products were nitrogen, methane, ethane, propylene, dimethyl sulfide, methylethyldiimide, and dimethyl disulfide. The overall reaction can be interpreted by the mechanism considered for the EES reaction except that steps 5 and 6 are replaced by

$$\mathrm{CH_3 + PES \longrightarrow CH_3S + C_3H_6} \quad \Delta H = -11.1 \text{ kcal/mol} \quad (12)$$

$$\mathrm{\longrightarrow CH_4 + C_3H_5S} \quad (13)$$

The PES reactions were carried out using lower episulfide concentrations and under these conditions the excess olefin was less readily estimated, and corrections in the kinetic treatment for reactions such as

$$\mathrm{CH_3S + PES \longrightarrow CH_3S_2 + C_3H_6}$$

could not be applied. Product yields are listed in Table II. The reaction parameters for (12) and (13) were calculated by

$$k_{12}/k_2^{1/2} = [R_{\mathrm{C_3H_6}}/R_{\mathrm{C_2H_6}}^{1/2}][\mathrm{PES}]^{-1}$$

and

$$k_{13}/k_2^{1/2} = \{R_{\mathrm{CH_4}}/R_{\mathrm{C_2H_6}}^{1/2} - k_4/k_2^{1/2}[(\mathrm{CH_3N})_2]\}[\mathrm{PES}]^{-1}$$

from which $\log k_{12} = 11.33 \pm 0.92 - (7450 \pm 1660/RT)$ (cc mol^{-1} sec^{-1}) and $\log k_{13} = 11.00 \pm 0.48 - (8260 \pm 870/RT)$ (cc mol^{-1} sec^{-1}). It should be noted that the parameters for reaction 5, uncorrected for C_2H_4 produced in (11), $\log A = 11.35$ (cc mol^{-1} sec^{-1}) and $E_a = 7.4$ kcal mol^{-1}, are identical with those for (12) and therefore the corrected values should be similar as well; also, we have ignored the possibility of the additional CH_4 producing reaction (7), in computing the rate parameters for reaction 13.

An attempt was also made to measure the approximate kinetic parameters for the reactions of CF_3 radicals with EES. However, when hexafluoroazomethane (HFA) was irradiated at $\lambda > 3100$ Å in a system containing added EES, $C_2H_4/2N_2$ ratios as high as 6 were obtained, leading us to suspect the possibility of a sensitized decomposition reaction of the type[25,26]

$$\mathrm{HFA} + h\nu \longrightarrow \mathrm{HFA}^*$$

$$\mathrm{HFA}^* + \mathrm{EES} \longrightarrow \mathrm{HFA} + \mathrm{EES}^*$$

$$\mathrm{EES}^* \longrightarrow \mathrm{S} + \mathrm{C_2H_4}$$

Reactions of CD_3 Radicals with COS. Product yields for the reaction

$$\mathrm{CD_3 + COS \longrightarrow CD_3S + CO} \quad \Delta H = 1.4 \text{ kcal/mol} \quad (14)$$

as a function of temperature are presented in Table III.

Table III. Reactions of CD_3 Radicals with COS[a]

Temp, °C	$[\mathrm{COS}]$[b]	$[(\mathrm{CD_3N})_2]$[b]	$R_{\mathrm{N_2}}$[c]	$R_{\mathrm{C_2D_6}}$[c]	R_{CO}[c]	$k_{15}/k_2^{1/2} \times 10^2$
81	30.28	2.41	40.60	28.56	1.16	0.715
105	37.74	3.22	52.51	23.02	4.45	2.457
125	22.15	1.99	36.09	11.54	3.86	5.131
146	40.13	4.32	69.52	10.25	1.23	9.566
171	10.59	0.84	15.86	2.64	3.65	21.171
203	11.22	1.11	22.27	1.27	6.50	51.336
217	20.96	1.85	37.70	1.39	16.19	65.554

[a] Photolysis times between 30 and 40 min. [b] Values $\times 10^6$ mol/cc; 6×5 cm cell. [c] Values $\times 10^{12}$ mol/(cc sec); 6×5 cm cell.

The rate parameters for (14) can be calculated by the relation

$$k_{14}/k_2^{1/2} = [R_{\mathrm{CO}}/R_{\mathrm{C_2H_6}}^{1/2}][\mathrm{COS}]^{-1}$$

which leads to the expression

$$\log k_{14} = 11.58 \pm 0.25 - (11350 \pm 350/RT) \text{ (cc mol}^{-1}\text{ sec}^{-1}\text{)}$$

Reactions of $S(^3P)$ Atoms with COS. The photolysis of COS in the presence of a large excess of CO_2 is a convenient source of $S(^3P)$ atoms.[27] When ethylene is present the ratio of rate constants for the two competing reactions

$$\mathrm{S(^3P) + COS \longrightarrow CO + S_2} \quad \Delta H = -29.3 \text{ kcal/mol} \quad (15)$$

and

$$\mathrm{S(^3P) + C_2H_4 \longrightarrow EES} \quad \Delta H = -58.6 \text{ kcal/mol} \quad (16)$$

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[26] $\Phi_{\mathrm{N_2}} = 1.0$ (3660 Å) at low pressures and decreases to ~ 0.25 at 1 atm: E. C. Wu and O. K. Rice, *J. Phys. Chem.*, 72, 542 (1968).

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can be determined using the kinetic expression

$$\frac{k_{16}}{k_{15}} = \frac{P_{\mathrm{COS}}}{P_{\mathrm{C_2H_4}}}\left(\frac{R_{\mathrm{CO}}{}^0/2}{R_{\mathrm{CO}} - R_{\mathrm{CO}}{}^0/2} - 1\right)$$

where R_{CO} and $R_{\mathrm{CO}}{}^0$ are the rates of formation of CO with and without added C_2H_4, respectively. In order to obtain precise data, correction must be made for the secondary reaction (eq 17) which may occur to a minor

$$\mathrm{S(^3P) + EES \longrightarrow S_2 + C_2H_4} \qquad (17)$$

extent. Table IV lists the product yields and k_{16}/k_{15} ratios from which, taking $k_{16} = 8.9 \times 10^{11}$ cc mol^{-1} sec^{-1},[28] $k_{15} = 1.1 \times 10^{10}$ cc mol^{-1} sec^{-1}. This value is probably correct to within a factor of 2.

Table IV. Reactions of $S(^3P)$ Atoms with C_2H_4 and COS[a]

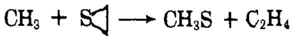
$P_{\mathrm{C_2H_4}}$, Torr	R_{CO}, $\times 10^{-6}$ mol/min	k_{16}/k_{15}[b]
0.00	0.24	
0.29	0.18	100
0.48	0.17	74
0.73	0.16	78
0.96	0.16	71
1.16	0.15	94
	Av =	83

[a] P_{COS} = 51 Torr, $P_{\mathrm{CO_2}}$ = 1243 Torr; radiation time = 10 min at 25°. [b] Corrected for reaction 17, taking $k_{17} = 5 \times 10^{13}$ cc mol^{-1} sec^{-1};[28-30] each value is the average of two determinations.

Discussion

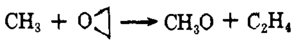
The CH_3 + episulfide system provides a unique example of an abstraction reaction wherein a divalent atom is abstracted by a monovalent radical. This is in striking contrast to the analogous systems CH_3, H, or CF_3 + epoxide, where only H-atom transfer has been observed.[31-34] The dissimilarity in the chemical reactivity of these molecules is not restricted to their reactions with free radicals; they exhibit characteristic differences in their thermal and photochemical decompositions as well. Ethylene episulfide decomposes thermally[35] or photochemically[36] to yield ethylene and sulfur, whereas the principal mode of decomposition of ethylene epoxide involves a unimolecular rearrangement to acetaldehyde which subsequently decomposes *via* a free-radical route.[37-39]

Among the factors influencing reactivities, enthalpy changes associated with the reactions appear to have a greater influence on the thermal and photochemical decompositions than on the reactions with free radicals. The difference in the enthalpy change of the two reactions



ΔH = −12.4 kcal/mol (5)

and

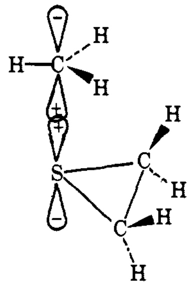


ΔH = −7.3 kcal/mol (18)

is only 5 kcal/mol, unlikely to be sufficient to account for the difference in reactivities. It will be shown below, on the other hand, that BEBO calculations predict a significantly larger value for the potential energy of activation of the epoxide than episulfide reaction which would explain satisfactorily why reaction 18 has not been observed.

An additional, important factor influencing the chemistry of these molecules is the intrinsic reactivity of the nonbonding p orbitals of the heteroatom. The nonbonding 3p orbital of sulfur is more nucleophilic than the nonbonding 2p orbital of oxygen and has a higher aptitude for valence shell expansion. This tends to stabilize the activated complex and thereby decreases the activation energy of the episulfide reactions.

In the CH_3 + EES system we propose a reaction path where the initial interaction involves the π orbital of the CH_3 radical with the nonbonding 3p orbital of the S atom



which then leads to a symmetrical transition state. The complex may be further stabilized by back donation of charge from the carbon to the sulfur d orbital. Decomposition of this complex occurs preferentially *via* a single-step concerted process resulting in the transfer of the S atom to the methyl radical without the intermediacy of the $\cdot CH_2CH_2SCH_3$ radical. This conclusion is based on a number of kinetic and stereochemical observations on the CH_3 + episulfide and related systems.

The photoinitiated addition of thiols to olefins is nonstereospecific and the intermediacy of thioalkyl radicals is well documented.[40-46] For example, Skell and Allen[44] have shown that the reaction of CH_3SD with *cis*- or *trans*-butene at −70° produces a mixture of *erythro*- and *threo*-3-deuterio-2-methylthiobutane starting with either olefin (Scheme I). In the presence of added DBr, the overall reaction was found to be stereospecific with the *cis*- and *trans*-butenes yielding the *threo*- and *erythro*-3-deuterio-2-methylthiobutanes,

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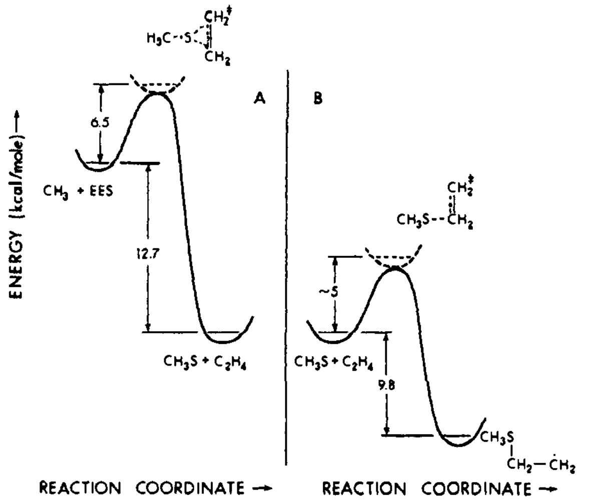
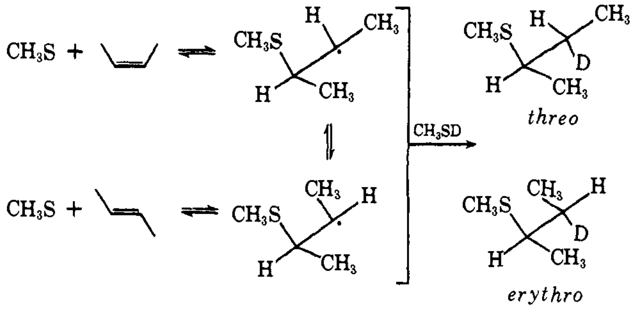


Figure 1. Schematic potential energy diagram: A, CH_3 + EES → $CH_3S + C_2H_4$; B, $CH_3S + C_2H_4 \rightarrow CH_3SCH_2\text{-}\dot{C}H_2$.

respectively. Steric control of mercaptan addition in this instance was suggested to occur by the rapid reaction of diastereomerically related 3-methylthio-2-butyl radicals with DBr, which was faster than the radical isomerization process. For unconjugated olefins, the overall addition process required an activation energy of about 3 kcal mol^{-1} when carried out in solution.[45] In the gas phase, however,[24] it was observed to have a negative activation energy requirement of −5.3 to −11.7 kcal mol^{-1}. Cis ⇄ trans isomerization of 2-butene and 1,2-ethylene-d_2 was also detected, suggesting that the thiyl radical attack on the double bonds of these molecules was reversible and probably responsible for the negative temperature coefficient of the overall reaction.

Scheme I



Preliminary experiments in which azomethane was photolyzed in the presence of *cis*-2-butene episulfide yielded 80% *cis*-butene indicating that the desulfurization reaction is largely stereospecific, as is the case in the nucleophilic attack on episulfides by organolithium or trisubstituted organophosphine or phosphite compounds.[11,14] Therefore, the activated complex in the CH_3 + episulfide system as in the above nucleophilic reactions must decompose predominantly *via* a single-step concerted abstraction of the sulfur atom.

Figure 1 is a potential energy diagram for the forward and reverse processes of the CH_3 + EES system. The potential energy profile for the CH_3 + *cis*-2-butene episulfide system should not be appreciably different. Now if the $CH_3SCH(CH_3)\dot{C}HCH_3$ radical is an intermediate, its rate constant with respect to the unimolecular decomposition to 2-butene + CH_3S can be estimated to be $k_d \sim 10^{13}[(29 - 15)/29]^{22} \sim 5 \times 10^5$ sec^{-1} and therefore owing to the long lifetime of the radical the stereospecificity of the reaction should be lost. This low value of k_d would also lead to efficient collisional stabilization of the intermediate radical altering the course of the reaction altogether, contrary to experimental observations. We are therefore forced to conclude that the abstraction of sulfur atom from episulfides by alkyl radicals predominantly follows a reaction path which corresponds to a single-step concerted reaction without the intermediacy of the thioalkyl radical.

Potential Energies of Activation. We have carried out calculations for the activation energies of the processes reported in this paper within the framework of the extended BEBO method.[15] Calculations have also been performed on some of the analogous reactions of the ethylene oxide molecule.

The potential energy, V, of transition-state formation of a bimolecular multivalent transfer reaction

$$AX + B \longrightarrow \underset{n1}{A\cdots}X\underset{n2}{\cdots B} \longrightarrow A + XB$$

is given by

$$V = (D_{e,AX} - D_{1,AX}n_1^{q'}) - D_{2,XB}n_2^{q''} + V_r \quad \text{(A)}$$

where $D_{e,AX}$ is the bond dissociation energy of A–X, D_1 and D_2 are the single bond dissociation energies, n_1 and n_2 are the bond orders, V_r is the triplet repulsion term, and q' and q'' are given by

$$q' = [\log (D_{e,AX}/D_1)]/\log n_{AX}$$

$$q'' = [\log (D_{e,AX}/D_2)]/\log n_{XB}$$

for $n > 1$. The bond orders n_1 and n_2 are related by

$$n_2 = (n_{XB}/n_{AX})(n_{AX} - n_1)$$

where n_{AX} and n_{XB} are the initial bond orders of the reactant and product, respectively. Expression A was evaluated as a function of n and the value of n_2 which corresponds to the maximum in V was determined. Whenever n_1 or n_2 was less than unity, q in expression A was replaced by p calculated for the bond-order region below 1 by Johnston's method.[47] Input data employed in the computations are given in Table V.

It was reported by Mayer[15] that good agreement between the calculated and observed activation energies for the abstraction of O atoms from molecules such as $CO_2(^1\Sigma)$ and $N_2O(^1\Sigma)$ by $O(^3P)$, $H(^2S)$, or $OH(^2\Pi)$ could only be obtained if the O atom abstracted was considered to be in its lowest excited $^1D_2$ state. This was attributed to the requirement of maintaining spin angular momentum throughout the reaction and was formally accomplished by adding 45.4 kcal, the excitation energy of the $^1D_2$ state of the O atom, to the bond dissociation energy of the bond being formed and broken in the process.

The results of these calculations are presented in Table VI, and for convenience a summary of all the rate parameters obtained in the present study along with the relevant literature data is given in Table VII.

It is seen that the computed value of V for the attack of the $S(^3P)$ atom on $COS(^1\Sigma)$ is in fair agreement with the observed E_a when correction for spin conservation

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(47) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966, p 339.

Table V. Input Data to the Potential Energy Calculations[a]

	OC=S			S—CH$_3$	O—CH$_3$	S=S	O=O
Dissociation energy, D_e, kcal/mol	74	60	85	70	90	103	120
Bond energy, B_e, kcal/mol	166	118[b]	144[b]	70	90	103	120
Bond order	2	2	2	1	1	2	2
Ground state	$^1\Sigma$	^{1}A	^{1}A	$^2\Pi$	$^2\Pi$	$^3\Sigma_g^-$	$^3\Sigma_g^-$
Single bond values used							
D_1,[c] kcal/mol	32	37	47	70	90	65	35
r_1, Å	1.81	1.81	1.43	1.81	1.43	2.04	1.47
B_1, kcal/mol	73	73	80	70	90	65	35

[a] The main sources of data are ref 16 and B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules," *Nat. Bur. Stand.* (*U. S.*), NSRDS-NBS 31 (1970). [b] Estimated using the C–C bond energy of 106 kcal/mol in $\mathrm{H_2\dot{C}\text{–}\dot{C}H_2}$; see ref 16, p 51. [c] For polyatomic molecules $D_1/B_1 = D_e/B_e$.

Table VI. Activation Energies

Reaction	E_a- (exptl), kcal/mol	V, kcal/mol[a]	
		x	y
$\mathrm{S(^3P) + COS(^1\Sigma) \longrightarrow S_2(^3\Sigma_g^-) + CO(^1\Sigma)}$	~5	4	0
$\mathrm{S(^3P) + S\lhd(^1A) \longrightarrow S_2(^3\Sigma_g^-) + \underset{CH_2}{\overset{CH_2}{\Vert}}\ (^1A)}$	0	0	0
$\mathrm{O(^3P) + O\lhd(^1A) \longrightarrow O_2(^3\Sigma_g^-) + \underset{CH_2}{\overset{CH_2}{\Vert}}\ (^1A)}$		48	3
$\mathrm{CH_3(^2\Pi) + COS(^1\Sigma) \longrightarrow CH_3S(^2\Pi) + CO(^1\Sigma)}$	11	33	7
$\mathrm{CH_3(^2\Pi) + S\lhd(^1A) \longrightarrow CH_3S(^2\Pi) + \underset{CH_2}{\overset{CH_2}{\Vert}}\ (^1A)}$	6	14	0
$\mathrm{CH_3(^2\Pi) + O\lhd(^1A) \longrightarrow CH_3O(^2\Pi) + \underset{CH_2}{\overset{CH_2}{\Vert}}\ (^1A)}$		40	0

[a] Columns x and y give the values computed with and without the addition of 26.4 and 45.4 kcal/mol, the difference in singlet and triplet state S atom and O atom, respectively, to D_e.

in the transition state is applied.[48] It is to be noted that the rate constant of this reaction at 25° is identical with that for the reaction of O(^{3}P) with COS, Table VII. Intuitively, one would expect the latter reaction to be faster in view of its considerably higher exothermicity (S(^{3}P) + COS, $\Delta H = -29.3$ kcal/mol; O(^{3}P) + COS, $\Delta H = -51.4$ kcal/mol).

For the S(^{3}P) + EES(^{1}A) system the calculation predicts $V \sim 0$ regardless of spin state and, indeed, the measured rate constant is within a few tenths of the collision frequency and the activation energy has been estimated from experiment to have a value of 0.3 kcal.[49]

For the reaction of CH$_3$ with COS and EES the measured values of the activation energies lie between the computed V's with and without applying correction for spin conservation in the transition state. This (if a physical rationalization is permissible) can be ascribed to a partial relaxation of the spin angular momentum selection rule owing to heavy atom perturbation. The selection rule is more stringent in the case of oxygen and for this reason the actual values of activation energies for the

$$\mathrm{O + O\lhd \longrightarrow O_2 + C_2H_4,\quad CH_3 + O\lhd \longrightarrow CH_3O + C_2H_4} \qquad (19)$$

reactions should be close to the higher limit of the computed V's, 48 and 40 kcal/mol, respectively, Table VI, which explains the nonoccurrence of these reactions. In conclusion it would appear that within the context of the BEBO method for the calculation of potential energies of activation, the high activation energy and the consequent nonoccurrence of the reactions (19) are due to their somewhat lower exothermicity and more stringent adherence to the spin conservation rule than of the episulfides and also to the considerably higher excitation energy of the ^{1}D$_2$ state of the oxygen than sulfur atoms.

Arrhenius *A* Factors. The method[16] used here to compute the lower limits to A factors is based on the assumption that in a reaction such as CH$_3$ + COS, we can consider the transition state to be a rigid complex thus allowing its entropy to be calculated by comparison with analogous molecules. Since there are no close analogs of the activated complexes for the reactions of present interest, we will use the entropy of COS and EES corrected for the extra S atom or CH$_3$ radical. The entropy contribution due to an extra CH$_3$ group is taken to be 4.3 gibbs/mol ($S°((\mathrm{CH_3})_2\mathrm{S}) - S°(\mathrm{CH_3S})$) and that of an S atom to be 6.5 gibbs/mol ($S°(\mathrm{CS_2}) - S°(\mathrm{CS})$). Spin will contribute R ln 2 and R ln 3 terms to the entropy of the [CH$_3$ + substrate]‡ and [S + substrate]‡ complexes. A contribution of about 2 gibbs/mol has been estimated for the increased principal moments of inertia of the activated complex from bond length considerations. At 300°K, tentative assignment of degenerate bending modes C–S–C at 200 cm^{-1} and C–S–S at 150 cm^{-1} in the transition state gives

$$S°^{\ddagger}(\mathrm{COSS}) \geqslant S°(\mathrm{COS}) + 7.5 + 2.2 + 2.2 + 5.4$$

and

$$S°^{\ddagger}(\mathrm{COSCH_3}) \geqslant S°(\mathrm{COS}) + 4.3 + 1.4 + 2.0 + 4.4$$

in units of gibbs/mol with reference to a standard state of 1 atm. Thus

$$\Delta S^{\ddagger}(\mathrm{COSS}) \geqslant S°(\mathrm{COS}) + 16.1 - S°(\mathrm{COS}) - S°(\mathrm{S}) \geqslant -24.1$$

and

$$\Delta S^{\ddagger}(\mathrm{COSCH_3}) \geqslant S°(\mathrm{COS}) + 11.3 - S°(\mathrm{COS}) - S°(\mathrm{CH_3}) \geqslant -34.0$$

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(48) Computed V's do not include the contribution from triplet term V_t. It has been shown[15] that in O-atom transfer reactions its magnitude is only about 2 kcal/mol and is usually counterbalanced by the zero-point energy corrections. Since the S atom has low-lying vacant d orbitals, these will modify V_t. The magnitude of this effect, however, cannot be assessed at present.

(49) O. P. Strausz, W. B. O'Callaghan, E. M. Lown, and H. E. Gunning, *J. Amer. Chem. Soc.*, **93**, 559 (1971).

Table VII. Arrhenius Parameters for Some Atom Transfer Reactions

Reaction	Log A (cc mol^{-1} sec^{-1})	E_a, kcal mol^{-1}	Ref
$H + (CH_2)_2O \rightarrow H_2 + C_2H_3O$		8.5	34
$CH_3 + (CH_2)_2O \rightarrow CH_4 + C_2H_3O$		9.0	31
$CH_3 + (CH_2)_2O \rightarrow CH_4 + C_2H_3O$		9.6	32
$CF_3 + (CH_2)_2O \rightarrow CF_3H + C_2H_3O$	12.50	11.0	34
$O(^3P) + (CH_2)_2O \rightarrow$?	10.20	1.8	*d*
$O(^3P) + COS \rightarrow CO + SO$	14.08	5.8	*e*
$O(^3P) + COS \rightarrow CO + SO$	13.81	5.5	*f*
$O(^3P) + COS \rightarrow CO + SO$	13.28	4.5	*g*
$S(^3P) + EES \rightarrow S_2(^3\Sigma_g^-) + C_2H_4$	~14	~0	28,29
$S(^3P) + PES \rightarrow S_2(^3\Sigma_g^-) + C_3H_6$			
	This Work[a]		
$CH_3 + EES \rightarrow CH_3S + C_2H_4$	10.85 ± 0.48	6.7 ± 0.8	
	(11.35 ± 0.51)	(7.4 ± 0.9) (uncorrected)	
$CD_3 + EES \rightarrow CD_3S + C_2H_4$	10.77 ± 0.64	6.5 ± 1.1	
	(11.10 ± 0.70)	(7.1 ± 1.2) (uncorrected)	
$CD_3 + EES \rightarrow CD_3H + C_2H_3S$[b]	11.34 ± 0.60	9.54 ± 1.00	
$CH_3 + PES \rightarrow CH_3S + C_3H_6$	11.33 ± 0.92	7.45 ± 1.66	
$CH_3 + PES \rightarrow CH_4 + C_3H_5S$[b]	11.00 ± 0.48	8.26 ± 0.87	
$CD_3 + COS \rightarrow CD_3S + CO$[b]	11.58 ± 0.25	11.35 ± 0.35	
$CH_3S + EES \rightarrow CH_3S_2 + C_2H_4$	~11.5	~8.8	
$S(^3P) + COS \rightarrow CO + S_2$[c]	~13.7 (assumed)	~5	

[a] Arrhenius parameters were obtained from a least-mean-squares treatment of the data in Tables I, II, and III. [b] Errors quoted are statistical with activation energy errors based on a 90% confidence limit. [c] E_a estimated assuming A factor similar to $O(^3P)$ + COS reaction. [d] G. Marsh and J. Heicklen, *J. Phys. Chem.*, **71**, 250 (1967). [e] K. Hoyermann, H. G. Wagner, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*, **71**, 603 (1967). [f] K. H. Homann, G. Krome, and H. G. Wagner, *ibid.*, **72**, 998 (1968). [g] A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, **50**, 707 (1969).

Transformation to molarity units gives $\Delta S_c^{\ddagger}(COSS) \geqslant -15.8$ and $\Delta S^{\ddagger}(COSCH_3) \geqslant -25.7$. Using the expression

$$A = (ekT/h)e^{\Delta S_c^{\ddagger}/R}$$

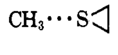
to calculate the preexponential factor of the bimolecular transfer reactions we obtain $A(COS + S) \geqslant 6 \times 10^{12}$ and $A(COS + CH_3) \geqslant 4 \times 10^{10}$ cc mol^{-1} sec^{-1}. The observed A factor for the reaction of CH_3 with COS is larger than the computed value indicating that there is more looseness in the transition state. Inclusion of the low rocking modes of the CH_3 group in the calculation of $\Delta S^{\ddagger}$ would probably improve the agreement. The A factor of the CH_3 + EES reaction is lower than that of the CH_3 + COS reaction because the bending and rocking modes in the latter will presumably have lower frequencies than the former. It should be pointed out that generally the frequency factors for the abstraction reactions of atoms are larger than for the analogous reactions of alkyl radicals since the entropy contributions to $\Delta S^{\ddagger}$ by the atomic species are usually smaller than the radicals; for example, the preexponential factors reported for hydrogen abstractions by H atoms are larger than those by alkyl radicals.[16] Further studies are in progress and will be reported at a later date.

Addendum

After submission of our original manuscript, a semiempirical MO calculation was carried out on the reaction paths of the S + EES and CH_3 + EES systems. Potential energies were computed by the EHMO method[50] for the approach of the radical along with X, Y, and Z axes using Slater-type atomic orbitals[51] as in previous studies[52] and literature values for the molecular geometries.[53] The calculated potential energy curves are presented in Figures 2 and 3 for the S + EES and CH_3 + EES system, respectively.

The lowest energy path for the S + EES reaction lies in the Z direction, that is, when the attack occurs from above the ring plane. This has a calculated activation energy of ~1 kcal/mol, which is in agreement with the experimental estimate.[49] Attack along the Y and X axes has computed activation energies of 7.5 and 10 kcal/mol, respectively. The computed value of enthalpy change, −44.5 kcal/mol, also agrees with the thermochemical datum, −43.4 kcal/mol.

For the CH_3 + EES system the situation is more complex. The initial approach is along attractive surfaces from the Z and Y directions. The depth of the potential wells representing loose



complexes is quite sizable, 7–11 kcal/mol, with the Z conformation lying lowest. As the reaction progresses the order of stability changes and in the activated complex the lowest energy barrier obtains for the Y complex with an activation energy of zero. The activation energy for the Z and X complexes are higher having values of 3.5 and 14.5 kcal/mol, respectively. This shift in stability is probably due to the increase in steric repulsion between the methyl and ring hydrogens

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(50) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(51) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2626 (1963).

(52) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 2412 (1966).

(53) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11** (1958); *Suppl.*, **No. 18** (1965).

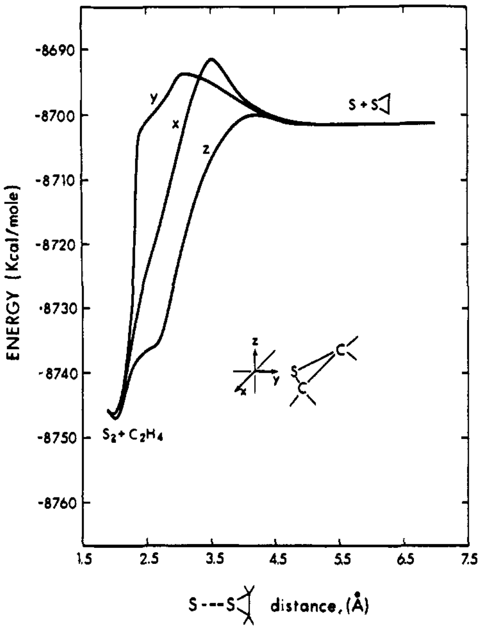

Figure 2. EHMO potential energy curves for the reaction of sulfur atom with EES. The curves labeled *Y*, *Z*, and *X* indicate potential energy variations with respect to the progress parameter S–S distance, for the approach of the sulfur atom along the *Y*, *Z*, and *X* axes, respectively.

as the structure tightens in the activated complex. There appears to be two possible ways to reconcile the computational results with the experimental activation energy, 6.7 kcal/mol. Thus, the reaction may follow the lowest energy path and the computations systematically underestimate the heights of energy barriers or, owing to the orienting effect of the loose complex, the reaction does not follow the lowest energy path. It should be noted in this regard that the calculated enthalpy change of the reaction, −16.7 kcal/mol, compares favorably with the thermochemical value of −12.4 kcal/mol.

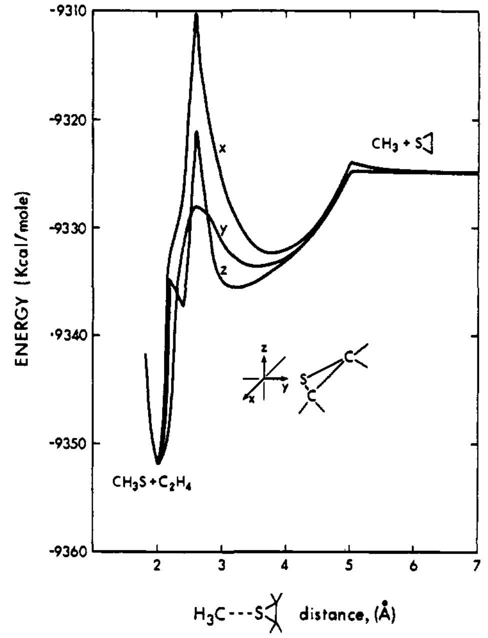

Figure 3. EHMO potential energy curves for the reaction of methyl radical with EES. The curves labeled *Y*, *Z*, and *X* indicate potential energy variations with respect to the progress parameter H_3C–S distance, for the approach of the methyl radical along the *Y*, *Z*, and *X* axes, respectively.

It should also be mentioned that in a recent communication Klabunde and Skell[54] reported the analogous desulfurization reaction of *cis–trans*-butene-2 episulfides by carbon atoms to yield CS and *cis-* and *trans-*butene-2 in a ratio of 4.5.

Acknowledgments. We thank the National Research Council of Canada for financial support.

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(54) K. J. Klabunde and P. S. Skell, *J. Amer. Chem. Soc.*, **93**, 3807 (1971).