Unimolecular Isomerization of Chemically Activated Thiirane to Vinylthiol

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Abstract: Excited $S(^1D_2)$ atoms from the in situ UV photolysis of COS react with ethylene to yield thiirane and vinylthiol in 100% yield. The relative yields of these two products are pressure dependent and the proportion of vinylthiol decreases with increasing total pressure while the sum remains constant. From detailed kinetic studies it is concluded that thiirane forms via pressure stabilization of the hot ground state cycloadduct thiirane, which at sufficiently high pressure is completely stabilized, and vinylthiol forms via direct insertion into the C–H bonds and also by unimolecular isomerization of the chemically activated ground-state thiirane. The isomerization reaction is complete at zero pressure. This novel rearrangement reaction is the formal analogue of the cyclopropane → propylene rearrangement, and like this reaction it proceeds concertedly through a bicyclic activated complex. The isomerization rate constant and preexponential factor could be satisfactorily reproduced with theoretical rate computations. The distribution of products is influenced by the wavelength of light employed for the photolysis of COS: at short wavelength the relative yield of $S(^1D_2)$ atom formation increases at the expense of $S(^3P_J)$ atom formation and the $S(^1D_2)$ atom carries increasing amounts of translational energy. $S(^3P_J)$ atoms react with ethylene to yield only thiirane. Rate-constant values for the various elementary steps involved in the reaction sequence have been derived.

Introduction

The chemistry of the group 6A atoms has been investigated in considerable depth in the past 2 decades. Studies on oxygen,[2-5] sulfur,[6] selenium,[7] and tellurium[8] atom reactions have shown these atoms to be highly reactive in their ground ^3P_J and lowest excited $^1D_2$ states. $O(^3P_J)$ and $O(^1D_2)$ atoms react with paraffins, olefins, and acetylenes; however, $S(^3P_J)$ and $Se(^3P_J)$ atoms, while highly reactive with olefins and acetylenes, are inert with respect to paraffins. $S(^1D_2)$ atoms react with all three families of organic molecules: with paraffins via concerted indiscriminate C–H bond insertion to yield the corresponding thiols, with olefins through simultaneous, competing cycloaddition to give the corresponding vibrationally excited singlet ground-state thiiranes and C–H insertion, and with acetylenes to give singlet ground-state thiirenes. Thus, $S(^3P_J)$ atoms at room temperature in the gas phase react with ethylene to yield thiirane in high yield as the sole product while $S(^1D_2)$ atoms react with ethylene to give thiirane and vinylthiol in comparable yields. The vinylthiol to thiirane ratios found for propylene[9] and the higher olefins are disproportionately lower and are more in line with those reported for the analogous products from the reaction of singlet methylene with olefins.[10] The inference was that vinylthiol in the ethylene reaction forms via a dual mechanism[11] that involves direct insertion into the vinylic C–H bonds, and unimolecular isomerization of the chemically activated ground-state thiirane having an excess vibrational energy >85 kcal/mol. The analogous reaction for the case of the other group 6A atoms has not been reported and, in the case of the most thoroughly investigated member of the group, oxygen, the enthalpy change of the reaction would be so excessive (ca. 130 kcal/mol) that in the pressure region where the isomerization is expected to occur it would be obscured by extensive fragmentation of the nascent product. Fragmentation of the hot adduct is difficult to suppress even in the $O(^3P_J) + C_2H_4$ reaction where the total excess energy is 46 kcal/mol lower.

Earlier studies have also shown that the vinylthiol to thiirane ratio is markedly decreased in the condensed phase relative to the gas phase, suggesting that isomerization in the condensed phase is effectively suppressed by collisional stabilization of the hot thiirane molecule.[9] In the case of propylene the product yields were not as markedly affected because in this case the isomerization of methylthiirane is slower or absent even in the gas phase because of the larger number of effective internal degrees of freedom in the molecule whereby the lifetime of the hot adduct is prolonged.

The present study was undertaken with the aim of elucidating the mechanism of the reaction of $S(^1D_2)$ atoms with ethylene and specifically to clarify whether the hypothetical isomerization reaction of the chemically activated ground-state thiirane to vinylthiol indeed takes place in the gas phase and, if this is the case, to examine the kinetic details of this novel reaction.

$S(^1D_2)$ atoms were produced by the in situ photolysis of carbonyl sulfide which, as has been shown before, is an excellent source of $S(^1D_2)$ atoms at effective wavelengths of ~254, 229, and 214 nm.

Experimental Section

The high-vacuum apparatus and procedures employed were similar to those described in previous reports from this laboratory.[11]

The light sources employed were (a) a Hanovia medium-pressure mercury arc equipped with a 6-mm Vycor 7910 filter (λ 254 nm) and (b) unfiltered Osram cadmium (λ 229 nm) and zinc (λ 214 nm) lamps.

Photolyses were carried out in cylindrical quartz cells 10.0 cm long, 5.0 cm in diameter, connected through Ace Teflon plug valves or Hoke TY 440 valves to a conventional grease-free vacuum system.

Reagents were measured in calibrated volumes and distilled into the reaction cell through traps kept at −139 °C to remove mercury vapor. After the reaction, the cell contents were slowly distilled through traps at −139 and −210 °C. The noncondensable gas was found to be pure CO and was measured in a gas buret. The fraction condensing at −210 °C contained only unreacted reagents while the −139 °C fraction consisted of thiirane and vinylthiol with less volatile materials present in significant amounts only in experiments of relatively high conversion.

The product fraction was distilled into an evacuated gas chromatograph sample loop and passed through a 2 mm i.d. × 122 cm glass column containing 60/80 mesh Diatoport S coated with 10% tricresyl phosphate maintained at ca. 22 °C. A microthermistor cell fitted with Gow-Mac 13-502 thermistors was employed as a detector and was operated at 26 °C with a bridge current of 8.0 mA. Helium was used as the carrier at a flow rate of 25 cm^3 min^{-1}. Retention times for vinylthiol and thiirane under these conditions were 2.5 and 5.0 min, respectively.

All parts of the chromatograph through which products passed were constructed either of glass or of Teflon except for the detector block itself in order to reduce the decomposition of vinylthiol which takes

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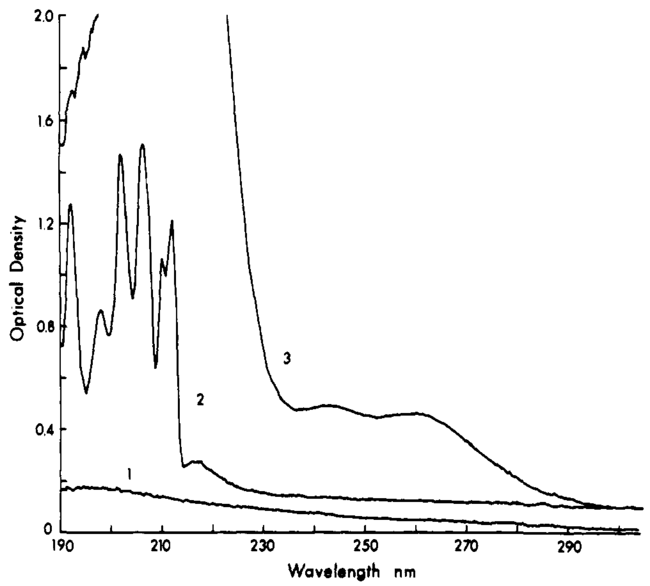

Figure 1. UV spectra of "low" and "high" concentration thiirane (Th) gas samples: (1) base line of 32.4-mL quartz cell (10-cm path length); (2) "low" concentration Th, P = 1.02 Torr; (3) "high" concentration Th, P = 32.33 Torr.

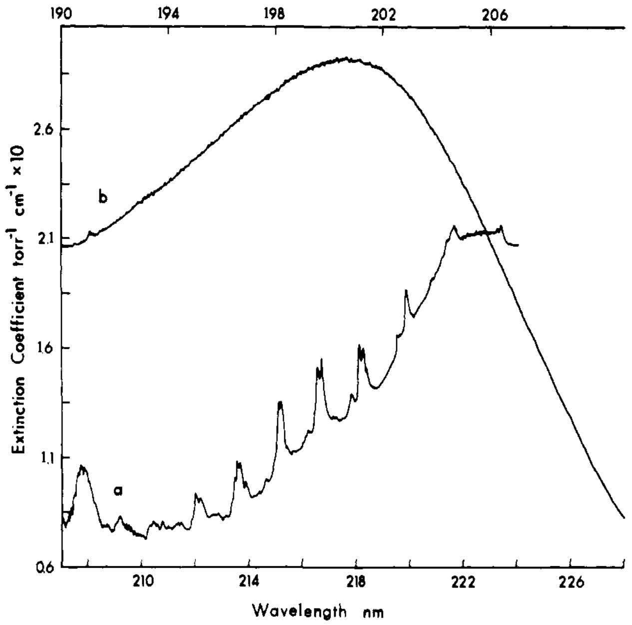

Figure 2. UV spectrum of vinylthiol. Upper scale refers to spectrum (a), lower scale refers to spectrum (b).

place on some surfaces (vide infra). Care was also taken to avoid leaving the products in contact with surfaces for longer periods than absolutely necessary during the course of the analytical procedure.

Traps were located downstream from the detector to allow effluent components to be trapped for identification and/or for purification purposes.

UV spectra were recorded on a Unicam 1800 spectrometer using a 10-cm long by 0.8-cm diameter quartz cell.

Properties of Vinylthiol. The first synthesis of vinylthiol (VT) was achieved by reacting S($^1D_2$) atoms in the gas and liquid phases with ethylene. Prior to this synthesis vinylthiol, like vinyl alcohol, was assumed to be nonexistent. Subsequently VT was prepared on a preparative scale for spectral characterization by the photoinitiated chain addition of hydrogen sulfide in the liquid phase at low temperature to acetylene. At room temperature VT is a highly reactive molecule, but under appropriate conditions the lifetime may be extended sufficiently to allow spectral (IR, UV, NMR, etc.) characterization.

In the present study it was found that VT readily reacts with metal surfaces. A 3.0 mm i.d. × 10 cm long glass column, packed with clean copper filings and placed between the sample loop and the chromatographic column quantitatively removed VT from a mixture. Stainless steel was less reactive and could be significantly deactivated by repeated passes of VT over the surface. In neither case could any volatile products be observed, which suggests that polymeric products are formed.

The reactivity of VT on quartz and Pyrex surfaces was also investigated. Experimentally significant amounts of VT were lost from a sample exposed to clean Pyrex surfaces for less than 1 h. The rate of loss decreased if the surface was cooled to liquid nitrogen temperature. "Curing" of the surfaces by exposure to VT vapor for about 2 days greatly reduced the surface activity.

Quartz surfaces, freshly flamed in the presence of air, caused only slight losses in the VT samples. "Cured" or unflamed quartz exhibited negligible activity.

In order to minimize the loss of VT by surface reactions, the gas chromatograph was constructed of glass and Teflon except for the detector block. The column and the detector were maintained at room temperature and at 26 °C, respectively. Under these conditions, trapping of the VT eluted from the column followed by rechromatography resulted in a decrease of the VT peak by some 15%. A good part of this loss was due to reaction with metal downstream from the thermistor and/or to inefficiency in the trapping system. Calibration of the chromatograph with pure samples gave a value of 0.98 ± 0.03 for the ratio of molar responses of VT and thiirane (Th) (i.e., R_{VT}/R_{Th}). Since the compounds are isomers, one would expect their molar responses to be approximately equal. It is clear, then, that the chromatographic technique employed was suitable for reliable analyses of VT and Th.

Table I. Light Absorption by the Reaction Components

	λ, nm	ϵ Torr^{-1} cm^{-1}	pressure, Torr	OD
VT	253.7	1.56×10^{-2}	0.020	3.0×10^{-4}
	228.8	8.6×10^{-2}		1.7×10^{-3}
	213.9	2.36×10^{-1}		4.7×10^{-3}
Th	253.7	1.18×10^{-3}	0.018	2.2×10^{-5}
	228.8	2.37×10^{-3}		4.3×10^{-5}
	213.9	1.95×10^{-2}		3.5×10^{-4}
COS	253.7	2.3×10^{-4}	41.20	9.0×10^{-3}
	228.8	3.42×10^{-3}		1.4×10^{-1}
	213.9	3.42×10^{-3}		1.4×10^{-1}

In order to estimate the effect of secondary photolysis of Th and VT in the COS–ethylene reaction, UV spectra were obtained and are reproduced in Figures 1 and 2. Extinction coefficients determined at 214, 229, and 254 nm are given in Table I.

These results suggest that secondary photolysis of the products, especially of VT, could readily occur in the photolysis of COS–ethylene mixtures.

Materials. COS (Matheson) was purified as described previously[11] and C_2H_4 (Matheson) by low-temperature degassing followed by trap-to-trap distillation.

Results and Discussion

As in earlier studies,[6,9,11] S($^1D_2$) atoms were generated by the UV photolysis of COS in the presence of ethylene. The latter molecule is completely transparent in the wavelength region employed, 254–214 nm, and under these conditions it is estimated that 67–74% of sulfur atoms are produced in the $^1D_2$ state and the rest in the ground ^3P_J state.[12] The reaction products were carbon monoxide, vinylthiol, thiirane, and, in longer exposure experiments, elemental sulfur and possibly some solid organosulfur polymer. Preliminary experiments have shown that the ratio of the two principal products VT and Th was exposure time dependent as expected from the UV spectra given in Figures 1 and 2 and Table I. Moreover, the absolute rates of formation of both VT and Th tended to decrease with increasing exposure time, the former more rapidly than the latter. Therefore, in order to obtain kinetically meaningful results representative of primary product yields, it was necessary in each case to carry out an exposure time study of product yields and extrapolate them to zero exposure time. Some illustrative examples of the exposure time depen-

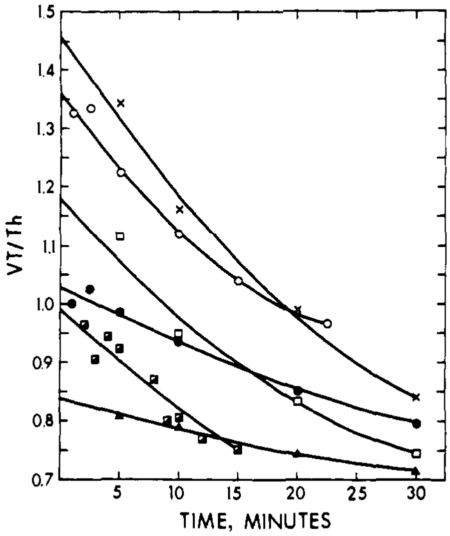

Figure 3. The dependence of VT/Th on exposure time: X, 253 Torr; ○, 852 torr; □, 1680 Torr; ●, 336 Torr; ▨, 660 Torr; ▲, 1272 Torr.

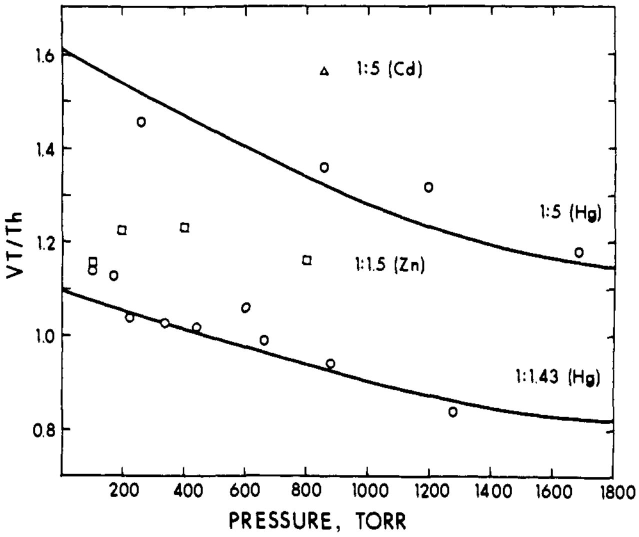

Figure 4. The dependence of VT/Th on total pressure. The solid curves have been calculated by eq 1.

dence of VT/Th using λ 254 nm radiation for the photolysis of COS are shown in Figure 3.

From earlier experimental[13] and theoretical studies[14] it was concluded that $S(^1D_2)$ atoms add concertedly to ethylene to yield singlet ground-state thiirane with $\Delta H = 85.0$ kcal/mol. If this chemically activated thiirane molecule indeed undergoes unimolecular isomerization in the system then the product yield ratio VT/Th should be dependent on total pressure at a given ratio of reactant concentrations. For this reason a series of exposure-time studies was performed to determine the yield ratio $[VT/Th]_0$ at zero exposure time for two C_2H_4/COS ratios, 1.43 and 5.0, as a function of total pressure. From the results presented in Figure 4 it is seen that indeed $[VT/Th]_0$ is pressure dependent and gradually decreases with increasing pressure as expected. The $[VT/Th]_0$ values are also affected by the C_2H_4/COS ratios; the higher the ratio the higher the value of $[VT/Th]_0$ at a given total pressure.

In some experiments the CO yields were also measured in addition to those of VT and Th. The data obtained are tabulated in Tables II–V. From these it can be seen that at low conversions the scavenging of sulfur atoms by COS and C_2H_4 is complete and the combined yield of VT, Th, and CO from the reaction of sulfur atoms is 100% within experimental error.

The formation and distribution of the observed reaction products can be accounted for in terms of the following set of elementary reactions.

$$COS + h\nu \rightarrow CO + S(^1D_2) \quad 67\% \qquad (1a)$$

$$COS + h\nu \rightarrow CO + S(^3P_J) \quad 33\% \qquad (1b)$$

$$COS + S(^1D_2) \rightarrow CO + S_2 \qquad (2a)$$

$$C_2H_4 + S(^1D_2) \rightarrow C_2H_3\text{-}SH \qquad (3a)$$

$$C_2H_4 + S(^1D_2) \rightarrow C_2H_4S^* \qquad (3b)$$

$$C_2H_4S^* \rightarrow C_2H_3\text{-}SH \qquad (4)$$

$$C_2H_4S^* + M \rightarrow C_2H_4S + M \qquad (5)$$

$$C_2H_4 + S(^3P_J) \rightarrow C_2H_4S \qquad (6)$$

M stands for the quenching gases COS and C_2H_4. $C_2H_4S^*$ represents a vibrationally excited singlet ground state Th molecule with an excess vibrational energy content of 91 kcal/mol, which corresponds to the enthalpy change of the reaction + the excess translational energy of the $S(^1D_2)$ atom produced in the mercury lamp photolysis. This energy is ample to bring about the unimolecular isomerization, reaction 4.

Steady-state treatment of this mechanism gives the following expression for VT/Th:

$$\frac{R_{VT}}{R_{Th}} = \frac{k_3k_4 + k_{3a}k_5[M]}{\tfrac{1}{2}k_3k_4 + \alpha k_4\dfrac{[COS]}{[C_2H_4]} + \left(\alpha\dfrac{[COS]}{[C_2H_4]} + \beta\right)k_5[M]} \qquad (I)$$

where $k_3 = k_{3a} + k_{3b}$, $\alpha = \tfrac{1}{2}k_{2a} + \tfrac{3}{2}k_{2b}$, $\beta = \tfrac{1}{2}k_{3a} + \tfrac{3}{2}k_{3b}$, and $[M] = [COS] + [C_2H_4]$. Equation I at $[M] = 0$ and $[M] = \infty$ reduces to

$$\left[\frac{R_{VT}}{R_{Th}}\right]_{p=0} = \frac{k_3}{\tfrac{1}{2}k_3 + \alpha\dfrac{[COS]}{[C_2H_4]}} \qquad (II)$$

$$\left[\frac{R_{VT}}{R_{Th}}\right]_{p=\infty} = \frac{k_{3a}}{\alpha\dfrac{[COS]}{[C_2H_4]} + \beta} \qquad (III)$$

respectively. In addition to eq I–III the following relationships should also hold:

$$\frac{\text{VT (from rearrangement)} + \text{VT (from insertion)}}{\text{Th}} = \left[\frac{\text{VT}}{\text{Th}}\right]_{p=0} \qquad (IV)$$

since at zero pressure all the hot Th molecules undergo isomerization, and at infinite pressure

$$\frac{\text{VT (from insertion)}}{\text{VT (from rearrangement)} + \text{Th}} = \left[\frac{\text{VT}}{\text{Th}}\right]_{p=\infty} \qquad (V)$$

since under this condition all $C_2H_4S^*$ are stabilized to Th. The experimental values of IV and V at $[COS]/[C_2H_4] = 0.20$ are 1.62 and 1.48, and at $[COS]/[C_2H_4] = 0.70$ they are 1.10 and 0.38, respectively. The data extrapolated to infinite pressure are in agreement with the value of 0.44 obtained in a liquid-phase mixture of ethylene and carbonyl sulfide at room temperature.[9]

In eq I–III, the only rate constant that has been estimated is k_{2a}. From flash photolysis studies, Donovan, Kirsch, and Husain[15] reported a minimum value of $k_{2a} = 4.0 \times 10^{10}$ L

Table II. Variation in the Zero Exposure Time Extrapolated Value of VT/Th as a Function of Total Pressure

pressure, Torr	$[COS/C_2H_4]$	$[VT/Th]_0$
253	0.2	1.46
852	0.2	1.36
1196	0.2	1.32
1680	0.2	1.18
100	0.7	1.14
162	0.7	1.13
220	0.7	1.04
336	0.7	1.03
440	0.7	1.02
600	0.7	1.06
660	0.7	0.99
880	0.7	0.94
1272	0.7	0.84

Table III. Product Yields of the Photolysis at 220 Torr Total Pressure[a]

time,	yield, μmol				product[b]
min	CO	VT	Th	VT/Th	recovery, %
3.0	2.46	0.80	0.81	0.99	97.6
5.0	4.23	1.24	1.30	0.96	97.4
7.0	5.79	1.43	1.66	0.86	91.3
9.0	7.49	1.77	2.06	0.86	90.5
12.0	9.82	2.08	2.57	0.81	86.8
15.0	12.32	2.28	2.99	0.76	84.4

[a] $COS:C_2H_4 = 1:1.43$. [b] Product recovery = $[(CO + VT + Th)/(R^0_{CO} \times \text{time})] \times 100$; $R^0_{CO} = 1.39$ μmol/min.

Table IV. Product Yields of the Photolysis at 440 Torr Total Pressure[a]

time,	yield, μmol				product[b]
min	CO	VT	Th	VT/Th	recovery, %
4.0	4.26	1.35	1.43	0.95	94.5
6.0	6.48	1.90	2.08	0.92	93.7
8.0	8.42	2.30	2.63	0.88	89.7
15.0	15.32	3.27	4.28	0.76	82.0
19.9	21.69	3.43	5.20	0.66	81.9

[a] $COS:C_2H_4 = 1:1.43$. [b] Product recovery = $[(CO + VT + Th)/(R^0_{CO} \times \text{time})] \times 100$; $R^0_{CO} = 1.86$ μmol/min.

$\text{mol}^{-1}\,\text{s}^{-1}$. Since deactivation occurs parallel to insertion, step 2b also takes place with a relative rate constant of $k_{2a}/k_{2b} \simeq 2$ (vide infra). The total estimated value of k_2, $(2 + 4 = 6) \times 10^{10}\ \text{L mol}^{-1}\,\text{s}^{-1}$, is less than the gas kinetic collision frequency only by a factor of about 2 and therefore it should well approximate the true value. Accepting the above value for k_{2a} and the value of 33% for the extent of $S(^3P_J)$ atom formation in primary step 1b it is possible to evaluate the values of the rate constants k_{2b}, k_{3a}, and k_4 from the present data.

From the results presented in Tables II-V and with the aid of eq VI-VIII one can calculate the percentage of $S(^1D_2)$ atoms consumed in reactions 2a and 2b and that consumed in reactions 3a and 3b:

$$\frac{R(CO) - R^0(CO)/2}{R^0(CO)/2} \times 100 = 17\%, \text{ step 2a} \qquad \text{(VI)}$$

$$\frac{[VT]_{p=0}}{R^0(CO)/2} \times 100 = 1.7 \times \frac{110}{210} \times \frac{1}{2.08} \times 100 = 43\%, \text{ step 3} \qquad \text{(VII)}$$

$$\text{step 1a} - (\text{step 2a} + \text{step 3}) = \text{step 2b} \qquad \text{(VIII)}$$

$$67 - (17 + 43) = 7\%$$

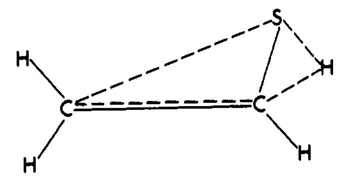

Figure 5. Assumed structure of the activated complex.

Table V. Product Yields of the Photolysis at 660 Torr Total Pressure[a]

time,	yield, μmol				product[b]
min	CO	VT	Th	VT/Th	recovery, %
2.0	2.43	0.84	0.86	0.97	99.3
3.0	3.80	1.22	1.34	0.91	101.1
4.0	5.06	1.65	1.74	0.95	101.6
5.1	6.46	2.05	2.22	0.92	101.2
8.0	9.78	2.85	3.28	0.87	95.6
9.1	11.10	2.90	3.63	0.80	93.1
10.0	12.40	3.19	3.96	0.81	94.0
12.0	14.60	3.50	4.56	0.77	90.8
15.0	17.74	3.98	5.31	0.75	86.6

[a] $COS:C_2H_4 = 1:1.43$. [b] Product recovery = $[(CO + VT + Th)/(R^0_{CO} \times \text{time})] \times 100$; $R^0_{CO} = 2.08$ μmol/min.

Thus, the relative rate constants computed are $k_{2a}/k_{2b} = 17/7 = 2.4$ and $k_{2a}/k_3 = (17/43)[C_2H_4]/[COS] = 0.40 \times 1.43 = 0.57$. By iteration and curve fitting from eq I-V and assuming a gas kinetic collision frequency for the deactivation of $C_2H_4S^*$, $\sigma(COS) = 4.13$ Å, $\sigma(C_2H_4) = 4.23$ Å, and $\sigma(C_2H_4S) = 5.2$ Å, the following absolute values were obtained for rate constants 2-5:

$$k_{2b} = 1.8 \times 10^{13}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$k_{3a} = 4.2 \times 10^{13}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$k_{3b} = 3.8 \times 10^{13}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

$$k_4 = 5.0 \times 10^{10}\ \text{s}^{-1}$$

$$k_5 = 2.3 \times 10^{14}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

We have also computed the value of the rate constant for the unimolecular isomerization of the chemically activated thiirane by RRKM theory. The value of k_4 was calculated from the expression[16]

$$k(E^*) = \frac{\lambda}{h} \frac{\sum P(E^{\ddagger})}{N(E^*)}$$

where $\Sigma P(E^{\ddagger})$ and $N(E^*)$ represent the sum of states and the density of states, respectively, and λ is the degeneracy of the reaction path. The sum of states and the density of states have been computed by direct count with the aid of an algorithm developed by Rabinovitch.[17]

The energy $\langle E^* \rangle$ of the chemically activated thiirane molecule can be obtained from the equation

$$\langle E^* \rangle = \Delta H_f{}^\circ(C_2H_4) + \Delta H_f{}^\circ(S(^1D_2)) - \Delta H_f{}^\circ(C_2H_4S) + \Delta E_{tr}$$

where ΔE_{tr} is the excess photolysis energy carried by the $S(^1D_2)$ atom. Substitution of the values[18,19] $\Delta H_f{}^\circ(C_2H_4) = 12.5$ kcal/mol, $\Delta H_f{}^\circ(S(^1D_2)) = 92.0$ kcal/mol, $\Delta H_f{}^\circ(C_2H_4S) = 19.3$ kcal/mol, and $\Delta E_{tr} = 6.0$ kcal/mol gives 91.2 kcal/mol for $\langle E^* \rangle$.

For RRKM calculations it is necessary to adopt a set of frequencies for the internal degrees of freedom of the activated complex. We assumed that the intramolecular hydrogen migration proceeds through a bicyclic structure which is depicted in Figure 5. The experimental value for the preexponential

Table VI. Vibrational Frequencies (cm^{-1}) of the Thiirane Molecule and the Activated Complex

ν_1	3018.5	ν_8	890.2
ν_2	1466.0	ν_9	3010.4
ν_3	1107.1	ν_{10}	1431.9
ν_4	1023.5	ν_{11}	1060.2
ν_5	633.3	ν_{12}	645.9
ν_6	3109.2	ν_{13}	3100.6
ν_7	1160.3	ν_{14}	947.1
ν_{15}	820.5		
3000 (3)		700 (1)	
1500 (1)		600 (2)	
1000 (3)		500 (1)	
900 (2)		150 (1)	

factor is not available and the set of vibrational frequencies assigned to the activated complex corresponds to an estimated A factor of $1 \times 10^{14}\ s^{-1}$, or an activation entropy of $\Delta S^{\ddagger} = 3.5$ eu. The rather low value of the computed A factor reflects the rigid structure of the activated complex. From preliminary studies on the thermal rearrangement of thiirane to vinylthiol it has been estimated that the activation energy of the process lies in the range of 55-65 kcal/mol.

According to ab initio molecular orbital calculations[14] on the ring distortion potential of thiirane, the 62 kcal/mol value for E_a can bring about an increase in the C-C-S bond angle from the 65° equilibrium value to about 120° in the activated complex. This would greatly facilitate intramolecular insertion of the sulfur atom into the C-H bond.

The vibrational frequencies assigned to the activated complex, together with the frequencies of the stable thiirane molecule,[20] are listed in Table VI.

The rate constant computed from RRKM theory has a value of $7.6 \times 10^{10}\ s^{-1}$, which compares favorably with the value of $5.0 \times 10^{10}\ s^{-1}$ derived from experimental kinetics. Thus, the lifetime of the hot thiirane molecule is short ($\approx 1.3 \times 10^{-11}$ s), but collisional relaxation by COS or C_2H_4 is highly efficient and could occur on every collision.

Extensive studies on the sulfur atom-olefin system[9] have shown that vinylthiol forms only when the olefin contains at least one unsubstituted carbon. In the case of propylene, small quantities of propene-2-thiol have been detected and indications are that the rearrangement of hot methylthiirane to methylvinylthiol does occur. However, owing to the large number of internal degrees of freedom this process is considerably slower than in the case of thiirane and its kinetics could only be studied at low total pressures where secondary photolysis and other losses in the unstable vinylthiols would cause severe complications. The absence of alkene-2-thiols among the reaction products from more highly substituted olefins is due to the nonoccurrence of the thiirane → vinylthiol rearrangement and to the steric hindrance exerted by the substituent to the insertion of the $S(^1D_2)$ atom into the $R(CH_2)C-H$ bond.

The novel thiirane → vinylthiol rearrangement described here is the analogue of the cyclopropane → propylene rearrangement in the sense that both reactions proceed concertedly via a bicyclic intermediate.[10,21] However, it should be mentioned that for the latter reaction an alternative two-step reaction path involving a diradical intermediate has also been proposed.[22] Similar rearrangements are likely to occur in the reactions of $O(^1D_2)$ and $Se(^1D_2)$ atoms with ethylene, and with oxygen probably even with higher olefins because of the higher energy content of the initial hot adduct, but these could not be detected because of the inherent instability of the resultant vinyl alcohol.

A few experiments were also performed using shorter wavelength radiation for the photolysis of COS, namely, λ 229 nm and λ 214 nm. The values extrapolated to zero exposure time for the vinyl thiol to thiirane ratios are given in Figure 4. Here, the extrapolation to zero exposure time became more troublesome especially at low COS concentrations owing to the smaller quantities of vinylthiol involved and also because in these experiments a different gas chromatograph was used in which the loss of vinylthiol due to surface effects was more extensive. As seen from the data, values of [VT/Th] obtained in either the 229- or 214-nm photolyses are higher than those in the 254-nm photolysis and in fact $[VT/Th]_{p=0}$ at λ 229 nm is higher than the zero pressure extrapolated values in the 254-nm photolysis. At low pressures the apparent fall-off in the 214-nm photolysis ratios is due to analytical errors.

The increase in the relative yield of vinylthiol can be due to either/or any combination of three factors. Firstly, the relative yields of primary steps 1a and 1b may be wavelength dependent. Indeed, in earlier studies on the reaction of $S(^1D_2)$ atoms with paraffins it has been shown that at λ 229 nm step 1a comprises 74% of step 1. Secondly, the excess translational energy of the $S(^1D_2)$ atom increases with increasing photonic energy with approximate values of 6, 12, and 16 kcal/mol at λ 254, 229, and 214 nm, respectively. Since most of the excess energy would still be present at the moment of reaction the energy content of $C_2H_4S^*$ should increase with decreasing wavelength of radiation, altering the lifetime of the hot cycloadduct. Also, the amount of excess translational energy could affect the relative rates of C-H insertion and addition to the double bond, but, since the rate constants for these reactions are high, about one-half of the gas kinetic collision frequency, the activation energies involved must be very low and their differences negligible. From the calculated unimolecular isomerization rate constants from RRKM theory as a function of total energy (at 229 nm, $k_a = 1.9 \times 10^{11}\ s^{-1}$; at 214 nm, $k_a = 3.4 \times 10^{11}\ s^{-1}$) and assuming that the relative rate constants for other reactions remain unaltered, a few percent decrease in the initial amount of $S(^3P_J)$ formation could be estimated from the experimental data.

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References and Notes

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