Photolysis of Thietane Vapor

H. A. Wiebe and Julian Heicklen*

Contribution from the Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pennsylvania 16802.

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Abstract: Thietane vapor was photoexcited with 2139-, 2288-, and 2537-Å radiation and by mercury sensitization at 2537 Å. Experiments were done at 25 and 236° at various pressures and light intensities as well as in the presence of n-C_4H_{10}, i-C_4H_8, and O_2. In all cases the products were C_2H_4, C_3H_6, and polymer; with O_2 present, SO_2 was also produced. With 2537-Å radiation, some propylene episulfide was also formed for prolonged irradiation. The experiments with added i-C_4H_8 showed that sulfur atoms were not intermediates. The indications are that all four methods of excitation lead to different electronic levels. These states then decompose to either C_2H_4 and CH_2S or an intermediate which reacts with ground-state thietane to produce S_2 and the C_3 hydrocarbons. At 2188 and 2139 Å, some of the initially formed c-C_3H_6 is energized and can rearrange to C_3H_6 unless stabilized by collision.

The photochemical decomposition of cyclic compounds proceeds by two different primary photolytic processes. In systems where the quantum yields of products are independent of temperature, an intramolecular rearrangement followed by unimolecular dissociation gives the final products. Free radicals or diradicals may also be formed in the molecular fragmentation process. The electronic states from which the photodecomposition occurs have also been determined for several compounds.

The photochemistry of cyclic ketones has been widely investigated and discussions of the various modes for their photodecomposition have been included in several recent books and review articles.[1-4] Detailed photochemical investigations have been made for cyclobutanone and cyclopentanone in particular, and the mechanism for their decomposition is perhaps best understood. Although the formation of a diradical as the primary process for the photodecomposition of cyclopentanone has been proposed,[5] more recent results[6] indicated that the products (C_2H_4, c-C_4H_8, CO, and 4-pentenal) could arise by molecular scission of an electronically excited state. Since then Lee,[7] using photosensitization techniques, has shown that C_2H_4, c-C_4H_8, and CO come from the excited singlet state, whereas 4-pentenal comes from the triplet state. It has also been shown that the c-C_4H_8 is formed vibrationally energized and unless collisionally deactivated can undergo decomposition to C_2H_4.[8]

A somewhat more detailed mechanism has been obtained for the decomposition of photoexcited cyclobutanone.[9,10] The products are C_2H_4, CH_2CO, C_3H_6, c-C_3H_6, and CO. C_2H_4 and CH_2CO have been shown to arise from a vibrationally excited ground electronic state of cyclobutanone formed by an internal conversion process from the first electronically excited state.[10] Vibrationally excited c-C_3H_6 and CO are formed from a short-lived triplet state of cyclobutanone,[11] originating from an intersystem crossing process of the electronically excited singlet state. The vibrationally excited c-C_3H_6 then undergoes collisional deactivation or isomerization to propylene.[8,10,12,13]

The photochemistry of several oxygen-containing heterocycles has also been examined. A number of oxetanes were photodecomposed by a mercury arc and the products were olefins and carbonyl compounds,[14] indicating direct molecular fragmentation. On the other hand the photodecomposition of oxirane (ethylene oxide) proceeds through intramolecular rearrangement to give mainly $CH_3 + HCO$,[15,16] although H_2 and CH_2CO are also produced.[16] Furans, upon Hg $6(^3P_1)$ photosensitization or direct photolysis, undergo ring contraction to cyclopropenecarboxaldehyde intermediates which mainly decompose to CO and hydrocarbon products.[17,18] The selective isomerization of 2-alkylfurans to 3-alkylfurans observed in photosensitization and direct photolysis at 2537 Å was also postulated to proceed *via* a carboxaldehyde intermediate formed from an electronically excited state of the furan.[19] The photodecomposition of oxolane (tetrahydrofuran) can proceed *via* molecular fragmentation to produce formaldehyde and vibrationally excited c-C_3H_6 in one of the primary processes.[20] Similarly, the photodecomposition of 1,3-dioxolane leads to either $CH_2O + CH_3 + CO + H$ or $C_2H_4 + CO_2 + H_2$ (or 2H).[21]

The most complete investigations on the photochemistry of sulfur heterocycles have been made for the thio-

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* Address correspondence to this author.

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phenes. In solution it has been found that 2-arylthiophenes undergo irreversible photorearrangement to 3-arylthiophenes,[22] and the rearrangement has been postulated to proceed from an excited singlet state level.[23] The photodecomposition of thiophene vapor and the possible intermediates involved have also been reported.[24] In a brief study on the photolyses of

$$\overline{\mathrm{CH_2(CH_2)_{\mathit{n}}CH_2S}}$$

(n = 1–3), the gaseous decomposition products were given.[25] A more detailed study of the photodecomposition at 2537 Å of thiirane (ethylene episulfide) and thiolane (tetrahydrothiophene) was reported by Sidhu.[26] He reported results both in the presence and absence of foreign gases and discussed possible mechanisms.

The photolysis of several alkyl-1-pyrazolines has also been examined.[27] The mechanism for decomposition by direct and sensitized photolysis is believed to be loss of nitrogen and formation of hydrocarbon products *via* diradical intermediates.

In this article, the study of the photochemistry of thietane

$$\overline{\mathrm{CH_2CH_2CH_2S}}$$

is presented as an extension of the investigations of sulfur heterocycles. The effects of temperature, added gases, absorbed intensity, and energy of radiation were examined in order to determine the mechanism for decomposition.

Experimental Section

Materials. Thietane (Eastman Organic Chemicals) and 3-pentanone (Matheson Coleman and Bell) were purified by preparative gas chromatography on a 3-m tricresyl phosphate column. The gases (Matheson) were deaerated *in vacuo* at liquid nitrogen temperature before each experiment. N_2O and O_2 (extra-dry grade) were used directly without further purification. HBr was purified by distillation *in vacuo* at −130°, and the butane (instrument grade) and isobutylene (CP grade) were purified by gas chromatography on a 0.5-m Porapak R column to remove small amounts of propane and propylene.

Apparatus. The reaction cells, furnace, radiation sources, and construction of the vacuum systems employed have been described previously.[24] The low-pressure mercury lamp was used for both mercury-sensitized and direct photolysis experiments at 2537 Å. A mercury-free vacuum line, employing a calibrated vacuum gauge (Alphatron, NRC Type 530) and a Wallace-Tiernan, Inc. Model FA-160 pressure indicator to measure pressures, was used for direct photolysis studies at 2537 Å.

In the present investigation a Corning 9-30 filter was used in conjunction with the cadium lamp to remove the 2144-Å radiation and reduce the intensity of the 2265-Å emission to 6.5% of that of the 2288-Å spectral line. The filter also reduced the intensity at 2288 Å by a factor of 8. A second filter would have reduced the intensity to a value too small for convenient radiation times. The relative intensities of the 2265- and 2288-Å lines from the lamp–filter combination were determined by passing the radiation through a Jarrell-Ash Model 82-470 grating monochromator with 100-μ slit width. The radiation was detected by an RCA 935 phototube; the relative intensities were computed assuming equal spectral response of the phototube at the two wavelengths. The above monochromator–phototube combination was also used to measure extinction coefficients for HBr and thietane at 2139, 2265, and 2288 Å, employing the zinc and cadium lamps as radiation sources. The extinction coefficients for thietane and HBr were: 2.94×10^{-3}, 7.58×10^{-2}, and 0.108 $\mathrm{Torr^{-1}\ cm^{-1}}$ for thietane and 1.41×10^{-3}, 2.09×10^{-3}, and 6.61×10^{-3} $\mathrm{Torr^{-1}\ cm^{-1}}$ for HBr at 2288, 2265, and 2139 Å, respectively.

Analysis. The products from the photolysis of thietane were analyzed by gas chromatography. A 0.5-m column of 80–100 mesh Porapak Type R was used for measurement of the hydrocarbon products, and a 3-m column of 10% tricresyl phosphate on Chromosorb G for the sulfur-containing products, SO_2 and propylene episulfide. Identification of the products was made by mass spectrometry and comparison of gas chromatographic retention times with those of known samples.

Actinometry. The photolysis of 3-pentanone vapor at 125° was utilized as a chemical actinometer for direct photolysis experiments at 2537 Å. The quantum yield of CO is near unity for these conditions.[28] For mercury-sensitized studies at 2537 Å, N_2O was employed since $\Phi\{N_2\} = 1$, and HBr was used for photolysis with the zinc (2139 Å) and cadmium (2265, 2288 Å) lamps where $\Phi\{H_2\} = 1$.

Extinction coefficients (decadic) for thietane and 3-pentanone vapor were found to be 6.40×10^{-4} and 4.12×10^{-4} $\mathrm{Torr^{-1}\ cm^{-1}}$, respectively, as measured on a Cary 15 spectrophotometer at 2537 Å and room temperature.

The quantum yields of products were determined as described previously.[24] Corrections for the quantum yields of products from studies with the cadmium lamp were made at thietane pressures smaller than 2 Torr, since I_a at 2265 Å compared to that at 2288 Å is significant. These corrections were based on the relative light intensities at 2265 and 2288 Å and the relative extinction coefficients of HBr and thietane at these wavelengths.

Results

The ultraviolet absorption spectrum of thietane vapor consists of two regions of absorption, and the electronic transitions are believed to be non-Rydberg.[29] The first band, structureless and of low intensity, extends from 3000 to 2300 Å with a maximum at about 2600 Å. A second absorption band, from 2300 to 2060 Å, is much stronger and displays considerable structure. The electronic transition of the low-energy band involves excitation of a nonbonding electron of sulfur. In the high-energy band, two transitions are probable, one due to excitation of a nonbonding electron of sulfur and the other assigned to a transition in the C–S valence shell.

Thietane vapor was photolyzed directly with 2139-, 2288-, and 2537-Å radiation. Irradiation at 2139 and 2288 Å corresponds to absorption in the high-energy band, whereas photolysis at 2537 Å occurs in the low-energy band. The photodecomposition of thietane was also examined by mercury sensitization at 2537 Å.

The gas-phase products obtained from the mercury sensitization and direct photolysis at 2139 and 2288 Å were C_2H_4, C_3H_6, and c-C_3H_6. In addition to these products, direct photolysis at 2537 Å resulted in the formation of small amounts of propylene episulfide. A white polymer was also formed in all irradiations, which was removed by heating the reaction cell in the presence of air after each experiment.

The effects of pressure, light intensity, and temperature on the photolysis of thietane at 2139 and 2288 Å are given in Tables I and II, respectively. A dark run at 250° resulted in the formation of a small amount of ethylene (less that 1% of that of a photolytic experiment). At 350° a thermal reaction led to the formation of an appreciable amount of C_2H_4, C_3H_6, and c-C_3H_6

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Table I. Photolysis of Thietane at 2139 Å

[THT], Torr	$I_a \times 10^{-11}$, quanta/(cm^3 sec)	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
		Temp = 25°			
0.57	64.9	10.0	0.543	0.116	0.545
0.65	69.2	10.0	0.545	0.110	0.546
0.85	9.0	90.0	0.528	0.100	0.528
1.15	87.5	10.0	0.473	0.0835	0.520
1.57	10.8	91.0	0.477	0.0801	0.528
1.91	97.0	5.0	0.456	0.109	0.558
2.10	98.3	10.0	0.414	0.0667	0.518
2.55	99.9	10.0	0.455	0.0678	0.513
3.55	11.1	60.0	0.427	0.0657	0.575
3.82	105	10.0	0.430	0.0603	0.530
4.20	106	5.0	0.422	0.0566	0.547
7.0	11.5	60.0	0.400	0.0391	0.567
8.5	118	5.0	0.407	0.0456	0.584
10.3	11.8	60.0	0.375	0.0357	0.547
12.7	11.9	60.0	0.370	0.0301	0.537
16.8	118	5.0	0.360	0.0239	0.565
19.5	118	10.0	0.345	0.0236	0.507
21.2	12.2	65.0	0.328	0.0253	0.508
26.0	12.3	77.0	0.334	0.0216	0.515
35.8	12.3	60.0	0.331	0.0169	0.505
38.7	118	10.0	0.278	0.0152	0.472
46.0	12.3	60.0	0.318	0.0132	0.480
		Temp = 236°			
1.12	34.9	5.0	0.614	0.237	0.517
1.22	36.2	5.0	0.533	0.202	0.502
4.3	58.0	5.0	0.522	0.135	0.532
10.3	61.2	5.0	0.474	0.122	0.512
21.8	66.5	5.0	0.422	0.0815	0.532
39.5	66.5	5.0	0.390	0.0751	0.511

Table II. Photolysis of Thietane at 2288 Å

[THT], Torr	$I_a \times 10^{-11}$, quanta/(cm^3 sec)	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
		Temp = 25°			
0.57	2.20	92.0	0.745	0.0723	0.445
0.65	2.26	90.0	0.735	0.0715	0.441
0.66	2.26	20.0	0.715	0.0653	0.520
0.85	0.236	1065	0.705	0.0603	0.452
1.15	3.38	70.0	0.720	0.0602	0.476
1.57	0.317	360.0	0.704	0.0617	0.507
2.10	4.56	85.0	0.745	0.0543	0.426
2.55	5.20	60.0	0.650	0.0503	0.442
3.82	6.60	80.0	0.538	0.0402	0.407
8.5	11.4	20.0	0.551	0.0436	0.438
9.3	12.4	60.0	0.564	0.0370	0.348
10.3	1.24	182.0	0.530	0.0269	0.376
16.1	1.70	540.0	0.518	0.0223	0.357
16.8	17.2	30.0	0.492	0.0206	0.359
19.5	19.4	60.0	0.510	0.0207	0.347
26.0	1.79	180.0	0.462	0.0188	0.374
38.7	23.7	75.0	0.437	0.0128	0.342
		Temp = 236°			
10.7	7.73	30.0	0.661	0.142	0.517
22.0	9.05	30.0	0.587	0.095	0.462
30.0	10.8	30.0	0.582	0.110	0.435
41.0	12.3	30.0	0.567	0.092	0.372

(as well as H_2S and a yellow oil of low volatility). As a result the elevated-temperature study was carried out at 236°. The quantum yields were independent of the extent of decomposition which ranged from about 15% decomposition at low pressure to 0.5% at high pressure. The quantum yield of each product, as seen in Tables I and II, decreases continually with increasing pressure, but there is no discernible effect of I_a even when it is changed by a factor 10.

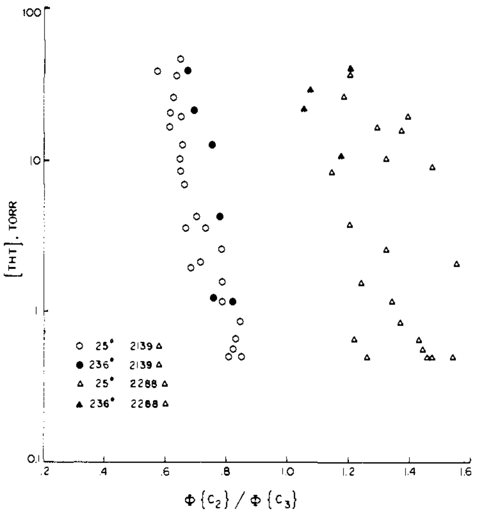

Figure 1. Plot of $\Phi\{C_2H_4\}/(\Phi\{c\text{-}C_3H_6\} + \Phi\{C_3H_6\})$ as a function of thietane pressure.

In Figure 1 the pressure, wavelength, and temperature dependence of the C_2/C_3 product ratio is shown. Although considerable scatter is present at 2288 Å, the increase in the ratio as the energy of photolysis decreases is apparent. At both wavelengths, the ratio drops as the pressure is enhanced. At 2139 Å the low-pressure limit is about 0.82, which drops to 0.62 at the high-pressure limit at both temperatures. However, the falloff occurs at higher pressures at the elevated temperature. With 2288-Å radiation the scatter is sufficient to mask any temperature differences or to ascertain the low- and high-pressure limiting values.

As the pressure increases, both $\Phi\{c\text{-}C_3H_6\}$ and $\Phi\{C_3H_6\}$ drop, but $\Phi\{C_3H_6\}$ drops much more rapidly and approaches zero. This suggests that C_3H_6 is formed by isomerization of vibrationally excited $c\text{-}C_3H_6$.

In order to determine whether reactive intermediates are formed in the primary process of the photodecomposition a number of experiments were carried out in the presence of $i\text{-}C_4H_8$ and $n\text{-}C_4H_{10}$ at 2139 and 2288 Å. The results are presented in Tables III and IV, respectively. No new products were formed upon addition

Table III. Photolysis of Thietane in the Presence of $i\text{-}C_4H_8$ at 25° and [THT] = 0.50 ± 0.02 Torr

[$i\text{-}C_4H_8$], Torr	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
λ = 2139 Å, I_a = 49.8 × 10^{11} quanta/(cm^3 sec), Irradiation Time = 5.0 min			
0	0.527	0.117	0.535
0	0.507	0.109	0.493
5.72	0.422	0.0537	0.488
13.3	0.378	0.0359	0.457
28.6	0.332	0.0227	0.471
42.5	0.294	0.0184	0.476
65.0	0.293		
88.0	0.329		
λ = 2288 Å, I_a = 1.35 × 10^{11} quanta/(cm^3 sec), Irradiation Time = 120.0 min			
0	0.672	0.0811	0.452
0	0.704	0.0753	0.408
8.38	0.525	0.0169	0.417
19.0	0.493	0.0119	0.424
28.3	0.484	0.00608	0.500
42.5	0.452	0.00453	0.456

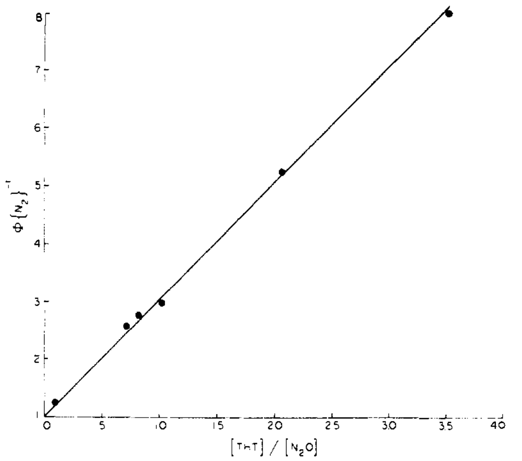

Figure 2. Plot of $\Phi\{N_2\}^{-1}$ *vs.* [THT]/[N_2O] in the Hg $6(^3P_1)$-sensitized photolysis of thietane–N_2O mixtures at 25°.

of either i-C_4H_8 or n-C_4H_{10}, indicating the absence of sulfur atoms. If sulfur atoms were formed episulfides should have been observed upon addition of i-C_4H_8.[30]

Table IV. Photolysis of Thietane in the Presence of n-C_4H_{10} at 25° and [THT] = 0.50 ± 0.02 Torr

[n-C_4H_{10}], Torr	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
λ = 2139 Å, I_a = 58.1 × 10^{11} quanta/(cm³ sec), Irradiation Time = 10.0 min			
0	0.490	0.115	0.494
5.53	0.366	0.0505	0.575
8.14	0.338	0.0378	0.567
25.0	0.298	0.0259	0.610
36.8	0.284	0.0220	0.592
47.0	0.315	0.0153	0.615
51.0	0.259		
64.5	0.242		
113.0	0.174		
λ = 2288 Å, I_a = 1.77 × 10^{11} quanta/(cm³ sec), Irradiation Time = 120.0 min			
0	0.720	0.0775	0.412
0	0.765	0.0821	0.415
4.68	0.582	0.0525	0.390
7.17	0.601	0.0445	0.425
20.2	0.494	0.0284	0.412
45.1	0.424	0.0216	0.381
52.0	0.387	0.0140	0.384

The variations of quantum yields with pressure of the added gases are the same as for thietane.

The results for decomposition of thietane by direct photolysis at 2537 Å are given in Table V. While the formation of C_2H_4 is the major process, smaller amounts of C_3H_6 and c-C_3H_6 are also present. At longer conversions trace amounts of propylene episulfide were also observed. The quantum yields of C_3H_6 and c-C_3H_6 are increased as the temperature is raised, while the C_2H_4 yields appear to be unaffected. C_3H_6 is the only product affected by pressure, the quantum yield decreasing with increasing pressure.

The results for the measurement of the relative quenching efficiencies of thietane and N_2O for Hg $6(^3P_1)$ are shown in Table VI. The pertinent reactions are

Table V. Photolysis of Thietane at 2537 Å

[THT], Torr	I_a × 10^{-11}, quanta/(cm³ sec)	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6]\}$
Temp = 25 ± 5°					
1.13	4.38	120.0	0.830	0.034	0.001
5.2	2.05	75.0	0.815	0.011	0.001
10.1	39.2	40.0	0.838	0.0073	0.001
19.8	76.7	10.0	0.942	0.0055	
45.4	176	10.0	0.827	0.0038	0.0008
Temp = 125°					
0.96	2.81	150.0	0.77	0.11	0.02
1.20	3.52	120.0	1.00	0.12	
1.35	3.94	30.0	0.97	0.11	
5.2	15.2	30.0	0.97	0.072	
10.2	29.8	20.0	0.96	0.053	
17.1	50.2	15.0	1.03	0.053	0.02
22.0	64.4	12.0	0.97	0.040	0.02
43.0	126	10.0	0.88	0.035	0.03

Table VI. Relative Quenching Efficiencies of Thietane and N_2O for Hg $6(^3P_1)$ at 52 ± 2° and I_a = 1.45 × 10^{13} quanta/(cm³ sec)

[THT], Torr	[N_2O], Torr	$\Phi\{N_2\}$
7.3	77.4	0.805
25.2	35.3	0.388
21.2	26.3	0.362
20.5	20.3	0.337
27.8	13.5	0.191
35.3	10.0	0.125

$$\mathrm{Hg}\ 6(^3P_1) + N_2O \longrightarrow \mathrm{Hg} + N_2 + O \qquad (1)$$

$$\mathrm{Hg}\ 6(^3P_1) + \mathrm{THT} \longrightarrow \text{not } N_2 \qquad (2)$$

where THT represents thietane. The reactions lead to the expression

$$\Phi\{N_2\}^{-1} = 1 + k_2[\mathrm{THT}]/k_1[N_2O] \qquad (\mathrm{I})$$

Figure 2 is a plot of $\Phi\{N_2\}^{-1}$ *vs.* [THT]/[N_2O] and yields $k_2/k_1 = 2.31$.

The results of the Hg $6(^3P_1)$-photosensitized decomposition of thietane are shown in Table VII. At low pressures all the incident radiation is not absorbed, and it is necessary to make corrections. The Lorentz broadening correction factors for C_3H_8 and three fluorinated ethylenes have been found to be almost identical,[31] and

Table VII. Hg $6(^3P_1)$-Sensitized Decomposition of Thietane at 25 ± 2° and I_a = 1.45 × 10^{13} quanta/(cm³ sec)

[THT], Torr	Irradiation time, min	$1/f^a$	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
1.08	1.5	1.95	0.98		
1.08	2.0	1.95	1.01		
5.5	3.0	1.55	0.83		
8.7	3.0	1.35		0.03	0.005
13.5	3.0	1.23	0.78		
17.5	3.0	1.19	0.71		
27.0	3.0	1.12	0.75		
30.0	3.0	1.10	0.70	0.02	0.004
42.5	3.0	1.01	0.72		
46.0	3.0	1.00	0.71	0.02	0.004
53.5	3.0	1.00	0.70		

[a] Lorentz broadening correction factor.[31]

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

(31) R. J. Norstrom, Ph.D. Thesis, University of Alberta, Edmonton, Alberta, 1966.

it was assumed that the factor for thietane would be similar. These factors at each pressure are listed in Table VII. All the reported quantum yields have been corrected by these factors. C_2H_4 is the major decomposition product, the C_3's being formed in only small amounts. While there appears to be a small pressure dependence on the quantum yield of C_2H_4, it is absent for the C_3 products.

The data in Tables VIII–XI give the results when the photodecomposition of thietane was carried out in the presence of O_2. At 2139 and 2288 Å (Tables VIII and IX, respectively) SO_2 is formed in addition to the hydrocarbon products. The SO_2 quantum yield increases with increasing O_2 pressure and there is a concomitant increase in the C_2H_4 and total C_3 quantum yields. The results of the direct photolysis of thietane at 2537 Å in the presence of O_2 are listed in Table X. In addition to the hydrocarbon products, small amounts of SO_2 are also formed. The SO_2 was not determined since it was present in quantities too small for accurate measurement. There is considerable scatter in the quantum yields of C_2H_4 which is probably due to loss of product when the O_2 was removed by pumping at −196°. Since the pumping loss appears to be irregular, no corrections were made and the quantum yield of C_2H_4 probably is unaffected by increasing pressure of O_2. There is, however, an increase in the quantum yields of the C_3 products as O_2 is added. The effect of O_2 on the Hg $6(^3P_1)$-photosensitized decomposition is shown in Table XI. In addition to the Lorentz broadening correction, a correction for the fraction of Hg $6(^3P_1)$ quenched by O_2 is also included.[32] The corrected quantum yields are not markedly affected by O_2, though $\Phi\{C_2H_4\}$ might be slightly enhanced.

Table VIII. Photolysis of Thietane at 2139 Å in the Presence of O_2 at 25°

$[O_2]$, Torr	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi[C_3H_6]$	$\Phi\{c\text{-}C_3H_6\}$	$\Phi\{SO_2\}$
$I_a = 58.1 \times 10^{11}$ quanta/(cm^3 sec), [THT] = 0.50 ± 0.02 Torr					
0	10.0	0.513	0.121	0.513	
7.42	10.0	0.575	0.101	0.592	
11.0	5.0	0.569	0.0866	0.628	
12.5	5.0				0.204
43.5	10.0	0.622	0.0511	0.705	
44.5	5.0				0.257
93.8	10.0	0.717	0.0319	0.766	
163.5	5.0	0.835	0.0204	0.810	
207	5.0				0.402
318	3.0				0.354
331	15.0				0.360
355	2.5				0.467
400	10.0				0.437
411	5.0	0.778	0.0126	0.842	
552	5.0	0.878	0.0101	0.805	
$I_a = 6.98 \times 10^{11}$ quanta/(cm^3 sec), [THT] = 0.50 ± 0.02 Torr					
0	30.0	0.538	0.130	0.549	
57.0	30.0				0.336
57.5	32.0	0.801	0.0438	0.863	
63.0	15.0	0.924	0.0495	0.932	
105	30.0				0.475
$I_a = 111 \times 10^{11}$ quanta/(cm^3 sec), [THT] = 10.0 ± 0.30 Torr					
0	5.0	0.348	0.0341	0.545	
0	5.0	0.326	0.0360	0.545	
86.0	5.0	0.398	0.0248	0.545	
283	3.0				0.101
374	5.0	0.486	0.0146	0.602	
557	5.0				0.227
591	5.0	0.568	0.0097	0.632	
777	3.0				0.282

Table IX. Photolysis of Thietane at 2288 Å in the Presence of O_2 at 25°

$[O_2]$, Torr	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$	$\Phi\{SO_2\}$
$I_a = 0.145 \times 10^{11}$ quanta/(cm^3 sec), [THT] = 0.50 ± 0.02 Torr					
0	1440.0	0.705	0.0790	0.415	
0	604.0	0.732	0.0675	0.476	
66.0	515.0				0.322
66.5	502.0	1.04	0.0359	0.740	
80.0	1170.0	1.09	0.0515	0.701	
123	720.0				0.544
153	1440.0	1.04	0.0260	0.685	
$I_a = 1.77 \times 10^{11}$ quanta/(cm^3 sec), [THT] = 0.50 ± 0.02 Torr					
0	181.0	0.710	0.0734	0.403	
0	180.0	0.775	0.0820	0.415	
6.85	240.0	0.660	0.0895	0.467	
10.1	75.0	0.654	0.0805	0.464	
36.5	60.0				0.328
49.0	120.0	1.01	0.0734	0.627	
83.5	180.0	0.945	0.0593	0.611	
168	75.0	1.01	0.0246	0.685	
213	60.0				0.567
254	135.0				0.780
265	165.0				0.715
270	45.0				0.615
335	75.0	1.01	0.0087	0.647	
451	75.0	1.01	0.002	0.630	
489	135.0				0.750
$I_a = 13.1 \times 10^{11}$ quanta/(cm^3 sec), [THT] = 10.0 ± 0.30 Torr					
0	45.0	0.530	0.0208	0.365	
0	45.0	0.512	0.0193	0.350	
75.0	45.0	0.550	0.0207	0.371	
231	30.0				0.152
458	45.0	0.705	0.0122	0.418	
463	45.0				0.206
646	30.0				0.219
732	45.0	0.625	0.00825	0.423	

Table X. Photolysis of 1.00 ± 0.03 Torr of Thietane at 2537 Å in the Presence of O_2 at 25° and $I_a = 3.00 \times 10^{11}$ quanta/(cm^3 sec)

$[O_2]$, Torr	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
0	50.0	0.80	0.04	
2.12	150.0	0.55	0.06	0.006
6.0	158.0	0.70	0.06	0.02
18.6	170.0	0.53		0.06
32.4	165.0	0.57	0.06	0.03
54.5	150.0	0.67	0.04	0.03
73.5	220.0	0.40	0.04	0.03

Table XI. Hg $6(^3P_1)$-Sensitized Decomposition of 30 Torr of Thietane in the Presence of O_2 at 25 ± 2° and $I_a = 1.45 \times 10^{13}$ quanta/(cm^3 sec)[a]

$[O_2]$, Torr	$1/Q$[b]	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
0.0	1.00	0.70	0.02	0.004
1.42	1.02	0.75	0.014	0.005
3.89	1.07	0.81	0.015	
5.75	1.10	0.83	0.018	0.005
9.62	1.17	0.84	0.019	0.007

[a] Lorentz broadening correction factor = 1.10.[31] [b] Correction for quenching by O_2 [Φ(uncorrected)/Q = Φ(corrected)].[32]

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(32) R. J. Cvetanović, *Progr. React. Kinet.*, 2, 39 (1964).

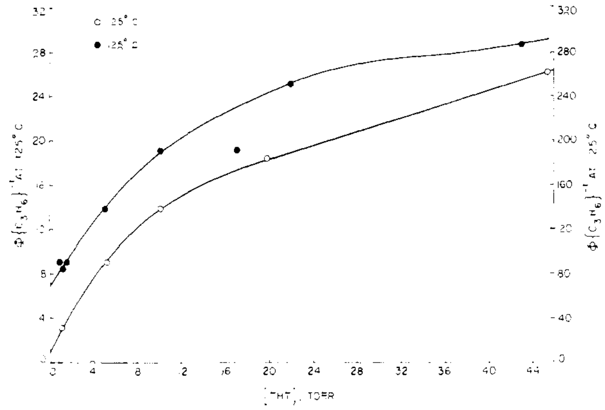

Figure 3. Plot of $\Phi\{C_3H_6\}^{-1}$ *vs.* thietane pressure in the direct photolysis of thietane at 2537 Å.

The increase in the product quantum yields at 2139 and 2288 Å when O_2 is added might be due to the formation of a reactive intermediate in the oxidation process. In order to detect the presence of an intermediate, the mixture was photolyzed in the presence of i-C_4H_8. The results are in Table XII and indicate that i-C_4H_8 has little, if any, effect.

Table XII. Photolysis of 10.0 ± 0.30 Torr of Thietane in the Presence of O_2 and i-C_4H_8 at 25°

$[O_2]$, Torr	$[i\text{-}C_4H_8]$, Torr	Irradiation time, min	$\Phi\{C_2H_4\}$	$\Phi\{C_3H_6\}$	$\Phi\{c\text{-}C_3H_6\}$
I_a = 111 × 10^{11} quanta/(cm^3 sec), λ = 2139 Å					
486	1.93	10.0	0.452	0.0126	0.622
475	6.68	5.0	0.448	0.0115	0.573
495	10.4	5.0	0.413	0.0098	0.578
0	10.4	5.0	0.292	0.0232	0.505
I_a = 13.1 × 10^{11} quanta/(cm^3 sec), λ = 2288 Å					
476	1.93	60.0	0.623	0.0095	0.393
482	6.68	60.0	0.604	0.0090	0.360
481	12.4	60.0	0.592	0.0089	0.367
0	12.4	60.0	0.467	0.0148	0.328

Discussion

2537 Å. In both the direct and mercury-sensitized photolysis at 2537 Å, the major product is C_2H_4 and its quantum yield is near unity. However, yields of the C_3 products are different in direct and sensitized decomposition, suggesting different electronic states as precursors.

The electronic state of thietane responsible for the direct photodecomposition at 2537 Å is probably an excited singlet which originates from excitation of a nonbonding electron of sulfur.[29] Presumably, mercury sensitization produces the corresponding triplet state.

The product quantum yields from Hg sensitization are nearly invariant to pressure changes. The small dependence for $\Phi\{C_2H_4\}$ in Table VII is uncertain, since incorrect Lorentz broadening correction factors may have been used. At pressures greater than 25 Torr, where pressure broadening is essentially complete, the quantum yields of C_2H_4 remain constant with increasing pressures as was observed in the direct photolysis. Thioformaldehyde was not observed, since thiocarbonyl compounds are unstable and undergo rapid polymerization.

The simplest mechanism is

$$\text{Hg }6(^3P_1) + \text{THT} \longrightarrow \text{Hg} + {}^3\text{THT} \quad (2)$$

$$^3\text{THT} \longrightarrow C_2H_4 + CH_2S \quad (3a)$$

$$^3\text{THT} \longrightarrow \text{THT} \quad (3b)$$

$$^3\text{THT} \longrightarrow I_{3c} \quad (3c)$$

$$I_{3c} + \text{THT} \longrightarrow C_3H_6 + S_2 \quad (4a)$$

$$\longrightarrow c\text{-}C_3H_6 + S_2 \quad (4b)$$

where I_{3c} represents some intermediate. Reaction 3a might proceed through upper vibrational levels of the ground singlet state or one of the products could be formed in a triplet state. Based on the above mechanism the results in Table VII suggest that $k_{4a}/k_{4b} \sim 2$, $k_{3a}/k_3 \sim 0.75$, $k_{3b}/k_3 \sim 0.24$, and $k_{3c}/k_3 \sim 0.01$, where $k_3 = k_{3a} + k_{3b} + k_{3c}$.

The addition of O_2 has little effect on the mercury-sensitized decomposition. This suggests that neither the triplet state of thietane, if indeed a triplet state is present, nor the intermediate I_{3c} is quenched by O_2. The small enhancement in the quantum yields as O_2 is increased probably reflects the fact that the excited O_2 intermediate formed from Hg sensitization transfers its energy like Hg $6(^3P_1)$. If the O_2 quenching corrections had not been made, quantum yields listed in Table XI would have been invariant to $[O_2]$.

The direct phototolysis at 2537 Å is most easily explained by the steps

$$\text{THT} + h\nu\ (2537\ \text{Å}) \longrightarrow {}^1\text{THT}_n \quad (5a)$$

$$\longrightarrow {}^1\text{THT}_0 \quad (5b)$$

$$^1\text{THT}_n \longrightarrow I_6 \quad (6)$$

$$^1\text{THT}_n + \text{M} \longrightarrow {}^1\text{THT}_0 + \text{M} \quad (7)$$

$$^1\text{THT}_0 \longrightarrow C_2H_4 + CH_2S \quad (8)$$

$$I_6 + \text{THT} \longrightarrow 2C_3H_6 + S_2 \quad (9)$$

where I_6 is some other intermediate, perhaps vibrationally excited I_{3c}, $^1\text{THT}_n$ represents upper vibrational levels of the excited singlet state of thietane, and $^1\text{THT}_0$ represents lower vibrational levels of the excited singlet state. The trace amount of c-C_3H_6 probably comes from an intermediate similar to I_{3c} produced from $^1\text{THT}_0$. The propylene episulfide seen on prolonged exposure may come from rearrangement and/or stabilization of I_6.

The mechanism predicts that

$$\Phi\{C_3H_6\}^{-1} = 1/2 + k_7[\text{M}]/2k_6 \quad (\text{II})$$

Figure 3 is a plot based on eq II. The graphs are not linear, indicating that the two-vibrational-level mechanism is a gross oversimplification. However, the falloff is apparent, it being more rapid at low temperatures than high temperatures, as expected.

In the presence of O_2, there may be some reduction in $\Phi\{C_2H_4\}$, though no trend is apparent within the scatter of the data. However, both $\Phi\{c\text{-}C_3H_6\}$ and $\Phi\{C_3H_6\}$ are greater than in the absence of O_2 for a corresponding pressure. Presumably some fraction of the upper singlet state can react with O_2 directly to produce C_3H_6 and c-C_3H_6.

2288 and 2139 Å. The photochemistry at 2288 and 2139 Å produces the same products, but the quantitative details are quite different, as shown in Figure 1. The C_2/C_3 product ratio depends markedly on the energy of the incident radiation. This dependence cannot be attributed to the energy difference between 2139 and 2288 Å, since a thietane molecule at 236° absorbing at 2288 Å contains much more energy than one at 25° absorbing at 2139 Å. Furthermore, even when the excess vibrational energy is quenched at high pressures, there is still a marked difference in results at the two wavelengths.

A possible explanation is that two electronic states are formed at both wavelengths,[29] but in different amounts. However, to simplify the discussion we will assume that one state is produced at 2139 and another at 2288 Å. Furthermore, since the only difference in the results is the quantitative details, the discussion will be based on one of the excited electronic states, designated THT*, but quantitative results given for both.

In formulating a mechanism from the results of Figure 1, it is necessary to realize that even at each wavelength the ratio of the C_2 to C_3 products changes with pressure. Thus two states are indicated at each wavelength. Furthermore, sulfur atoms are absent; yet at low pressure, the sum of the product quantum yields exceeds 1. The simplest mechanism consistent with the results at each wavelength is

$$\text{THT} + h\nu \longrightarrow \text{THT}^* \tag{10}$$

$$\text{THT}^* \longrightarrow C_2H_4 + CH_2S \tag{11a}$$

$$\longrightarrow \text{I} \tag{11b}$$

$$\text{THT}^* + \text{M} \longrightarrow \text{THT}^{**} + \text{M} \tag{12}$$

$$\text{THT}^{**} \longrightarrow C_2H_4 + CH_2S \tag{13a}$$

$$\longrightarrow \text{I} \tag{13b}$$

$$\text{THT}^{**} \longrightarrow \text{THT} \tag{14}$$

$$\text{I} + \text{THT} \longrightarrow 2c\text{-}C_3H_6 + S_2 \tag{15a}$$

$$\longrightarrow 2c\text{-}C_3H_6^* + S_2 \tag{15b}$$

$$c\text{-}C_3H_6^* \longrightarrow C_3H_6 \tag{16}$$

$$c\text{-}C_3H_6^* + \text{M} \longrightarrow c\text{-}C_3H_6 + \text{M} \tag{17}$$

In total, four excited states are required, THT* and THT** at 2288 Å and THT* and THT** at 2139 Å. The state THT** at each wavelength might be either the vibrationally deactivated THT* level or the corresponding triplet state. The intermediate I is different from that produced at 2537 Å since it leads to a different product distribution. However, as the analysis will show, it is thermalized before reaction, and after thermalization, it is the same at either 2288 or 2139 Å. Steps 15a and 15b are a two-step representation for a spectrum of energy distribution in the initially formed c-C_3H_6, the asterisk representing those molecules capable of rearrangement.

We have now introduced three unspecified intermediates I_{3c}, I_6, and I, with the already mentioned possibility that I_6 is just vibrationally excited I_{3c}. The most obvious possibility for any of these species is the diradical $CH_2CH_2CH_2S\cdot$, in either its singlet or triplet state. Another possibility is the thietane analog of Π-thiacyclopropane which was proposed[33] as an intermediate in the gas-phase pyrolysis of thiirane. In any event, the most energetic of the intermediates is I, since it can lead to energized c-C_3H_6, whereas I_{3c} and I_6 do not.

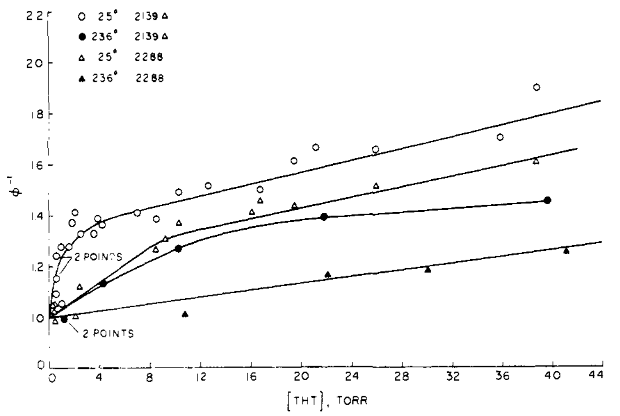

Figure 4. Plot of ϕ^{-1} *vs.* thietane pressure in the photolysis of thietane at 2288 and 2139 Å.

The mechanism predicts that the primary quantum yield, ϕ, is related to the product quantum yields by

$$\phi = \Phi\{C_2H_4\} + {}^1/_2\Phi\{C_3H_6\} + {}^1/_2\Phi\{c\text{-}C_3H_6\} \tag{III}$$

Furthermore, the pressure dependence of ϕ is given by

$$\phi^{-1} = 1 + k_{12}k_{14}[\text{M}]/(k_{11}k_{13} + k_{11}k_{14} + k_{12}k_{13}[\text{M}]) \tag{IV}$$

Figure 4 shows plots of ϕ^{-1} *vs.* [THT] at 25 and 236° at both 2288 and 2139 Å. The intercepts are all unity in conformance with the equation. At low pressures $k_{12}k_{13}$[THT] is small, the graphs are reasonably linear, and the slopes yield $k_{12}k_{14}/k_{11}(k_{13} + k_{14})$, which are listed in Table XIII. At the higher temperature at each wavelength, the slopes are smaller, indicating that k_{11} is enhanced as expected. For the same reason the breaks in the curves occur later at the higher temperature. In fact, the breaks in all four curves probably occur at about the same value of ϕ^{-1}, *i.e.*, 1.3. The breaks occur when $k_{12}k_{13}$[M] becomes important and the curves tend to flatten. They should reach an asymptotic value of $1 + k_{14}/k_{13}$.

Table XIII. Summary of Rate Constant Results

Ratio	Value	Units	Temp, °C	Energy	Source
k_2/k_1	2.31	None	25	Hg 6($^3P_1$)	Eq I, Figure 2
k_{3a}/k_3	~0.75	None	25	Hg 6($^3P_1$)	Table VII
k_{3b}/k_3	~0.24	None	25	Hg 6($^3P_1$	Table VII
k_{3c}/k_3	~0.01	None	25	Hg 6($^3P_1$)	Table VII
k_{4a}/k_{4b}	~2	None	25	Hg 6($^3P_1$)	Table VII
$\frac{k_{12}k_4/k_{11}}{(k_{13} + k_{14})}$	0.25	Torr^{-1}	25	2139 Å	Eq IV, Figure 4
$\frac{k_{12}k_4/k_{11}}{(k_{13} + k_{14})}$	0.026	Torr^{-1}	236	2139 Å	Eq IV, Figure 4
$\frac{k_{12}k_4/k_{11}}{(k_{13} + k_{14})}$	0.034	Torr^{-1}	25	2288 Å	Eq IV, Figure 4
$\frac{k_{12}k_4/k_{11}}{(k_{13} + k_{14})}$	0.007	Torr^{-1}	236	2288 Å	Eq IV, Figure 4
k_{15a}/k_{15b}	5.8	None	25		Eq V, Figure 5
k_{15a}/k_{15b}	2.9	None	236		Eq V, Figure 5
k_{17}/k_{16}	0.080	Torr^{-1}	25		Eq V, Figure 5
k_{17}/k_{16}	0.021	Torr^{-1}	236		Eq V, Figure 5

The breaks in the curves in Figure 4 correspond to the transition from decomposition from THT* to that

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[33] E. M. Lown, H. S. Sandu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, 90, 7164 (1968).

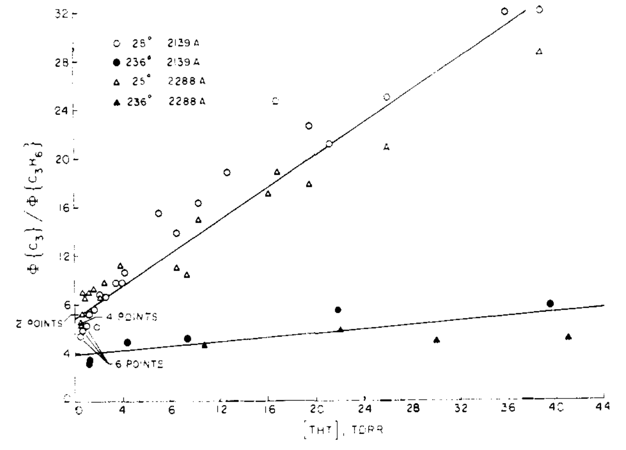

Figure 5. Plots of $(\Phi\{C_3H_6\} + \Phi\{c\text{-}C_3H_6\})/\Phi\{C_3H_6\}$ *vs.* thietane pressure in the photolysis of thietane at 2288 and 2139 Å.

from THT**, and the ratio of C_2 to C_3 products should change at the same place. Examination of Figure 1 shows that indeed this is the case. Particularly it should be noticed that the transition regions in Figures 1 and 4 lie at the same pressures for corresponding conditions. With 2139 Å, the transition pressure at 236° is about six times as large as at 25° in both figures. At 2288 Å it is not possible to make the comparison.

For the C_3 products, we have proposed that initially cyclopropane or excited cyclopropane is produced. The excited cyclopropane might be singlet trimethylene, which is indistinguishable in this system. However, triplet trimethylene is ruled out, since it would lead to some C_3H_6 even at infinite pressure.[34] Our results indicate the $\Phi\{C_3H_6\}$ approaches zero at infinite pressure. Furthermore reactions 15a and 15b represent a simple two step mechanism. Actually, all the initially formed $c\text{-}C_3H_6$ is energized, but with varying amounts of energy, and $c\text{-}C_3H_6^*$ does not represent a monoenergetic species. However, the two-step mechanism represents the major features to within our experimental uncertainty.

From the reaction steps 15a, 15b, 16, and 17 it can be deduced that

$$\Phi\{C_3\}/\Phi\{C_3H_6\} = (1 + k_{15a}/k_{15b})(1 + k_{17}[\mathrm{THT}]/k_{16}) \quad (\mathrm{V})$$

where $\Phi\{C_3\} \equiv \Phi\{c\text{-}C_3H_6\} + \Phi\{C_3H_6\}$. Figure 5 shows plots of $\Phi\{C_3\}/\Phi\{C_3H_6\}$ *vs.* [THT] at both temperatures and both wavelengths. The plots are reasonably linear in conformance with eq V. The results at each temperature were independent of the exciting wavelength, indicating both that I is the same at both wavelengths and that it is thermalized before disappearing by reaction 15. The plot at the elevated temperature has both a smaller intercept and smaller slope than the plot at room temperature. The former result indicates that a larger percentage of the initially formed cyclopropane is energized at the elevated temperature, the latter result that the energized cyclopropane isomerizes more easily at the elevated temperature. Both results conform to theory. The values for the appropriate rate constant ratios are listed in Table XIII.

The fact that the two-step model, reactions 15a and 15b, is oversimplified can be seen from the deviation from linearity at very low pressures in the low-temperature plot of Figure 5. In fact, all the initially formed cyclopropane is energized and the data points fall below the line at low pressure and should approach unity at zero pressure.

Values obtained for k_{17}/k_{16} from different systems will differ because the amount of excess energy in $c\text{-}C_3H_6^*$ will differ. Nevertheless, our values of 0.080 and 0.021 Torr^{-1} at 25 and 236°, respectively, compare favorably with values obtained in some other systems, where it might be expected that the excess energy would be comparable. Campbell and Schlag[13] found the ratio to vary between 0.1 and 2 Torr^{-1}, depending on the energy input, in the photolysis of cyclobutanone. Roquitte[20] examined the photolysis of oxolane at 1900–2100 Å and 120° and obtained $k_{17}/k_{16} \sim 0.16$ Torr^{-1}.

In the presence of O_2, the quantum yields of the hydrocarbons are enhanced and SO_2 is formed. The detailed mechanism is not clear, but certain aspects can be formulated. Surely the first step is the interaction of THT* with O_2 to form some species which can decompose an unexcited thietane molecule. The initial step in such a scheme might be

$$\mathrm{THT}^* + O_2 \longrightarrow C_2H_4 + CH_2S + O_2^* \quad (18a)$$

$$\longrightarrow C_2H_4 + CH_2S + O_2 \quad (18b)$$

Thus $\Phi\{C_2H_4\}$ should approach unity at high $[O_2]$, as it does at both wavelengths for [THT] = 0.50 Torr. At higher thietane pressures, reaction 18 competes with reaction 12 and $\Phi\{C_2H_4\}$ is reduced. The excited oxygen molecule, O_2^*, might react with thietane

$$O_2^* + \mathrm{THT} \longrightarrow SO_2 + c\text{-}C_3H_6^* \quad (19)$$

At 2288 Å, $\Phi\{C_3H_6\} + \Phi\{c\text{-}C_3H_6\}$ is less than $\Phi\{C_2H_4\}$ and approximately equal to $\Phi\{SO_2\}$ at high $[O_2]$, as would be expected. With 2139-Å radiation, THT* is more energetic and reaction 18b is negligible; $\Phi\{C_2H_4\} \sim \Phi\{C_3H_6\} + \Phi\{c\text{-}C_3H_6\}$ at high $[O_2]$. However, the mechanism fails in that $\Phi\{SO_2\}$ is considerably less than $\Phi\{C_3H_6\} + \Phi\{c\text{-}C_3H_6\}$. It is difficult to explain this discrepancy.

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