nificant only in the very last stages  $(t > 300 \ \mu sec)$  of the iodine and iodine monochloride formation shown in Figure 1.

Effect of Additives. We attempted to examine the effects of nitric oxide, oxygen, and ethylene on the flash photolysis to see if atom-scavenging reactions could be observed. These attempts failed because in all three cases a very rapid dark reaction occurred, consuming the iodine monochloride.

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# **Primary and Secondary Photolytic Processes in the** Photodecomposition of Thietane Vapor

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The photolysis of thietane vapor at 254 and 313 nm and at temperatures between 22 and 200° has been examined. The only primary photodecomposition forms ethylene and thioformaldehyde. Thioformaldehyde monomer is long lived and undergoes secondary photolysis to produce propylene in a sequence of reactions involving both the photoexcited monomer and a diradical. Photolysis of thioformaldehyde yields H<sub>2</sub> with a quantum yield  $\leq 0.08$  at temperatures less than 200° and is therefore much more resistant to photodecomposition than its oxygen analog.

Extensive investigations have yielded valuable information concerning the mechanism of the primary processes involved in the photolysis of the cyclic ketones,<sup>1</sup> the pyrazolines,<sup>2</sup> the cyclic ethers,<sup>3</sup> and the cyclic sulfides.<sup>4</sup> In particular, the question of diradical vs. molecular decomposition pathways has been thoroughly studied and, in the cases of the cyclic ketones and the pyrazolines, tentative identifications of the excited states involved have been made. For the cyclic ethers and sulfides, however, the nature of the excited states and the photodecomposition pathways are much less certain. In part this is due to the added complication that one or more of the primary products may absorb light strongly at the photolysis wavelength.

For the particular case of the cyclic ethers, some evidence that secondary photolysis may be important has been obtained.<sup>3</sup> The carbonyl-containing fragment produced in the primary step apparently undergoes secondary photodecomposition with the production of several additional products.

Previous reports of the photolysis of thietane<sup>4b</sup> vapor have indicated that ethylene is a major product, likely arising via the molecular scission of an excited molecule.

$$\Box_{\mathbf{S}} + h\nu \longrightarrow C_2 \mathbf{H}_4 + \mathbf{C} \mathbf{H}_2 \mathbf{S} \tag{1}$$

Other hydrocarbon products, cyclopropane and propylene, were thought to arise from the reaction of unidentified intermediates with the substrate. It was necessary to postulate the existence of at least four different excited states and three additional intermediates to explain the results

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obtained. No secondary photolysis processes were reported.

In this paper evidence that propylene is not a primary product of the photolysis of thietane vapor in its lowest energy absorption band is presented. Rather, it is demonstrated that propylene is very likely produced as a result of the secondary photolysis of monomeric thioformaldehyde. Conclusions regarding the nature of the likely primary processes in the photolysis of thioformaldehyde are also presented.

#### **Experimental Section**

Materials. Thietane (Eastman) was purified by preparative gas chromatography on a 10-ft dinonyl phthalate column. NO (Matheson) was purified by passing it through a 5-ft silica gel column at  $-78^{\circ}$  followed by degassing under vacuum at  $-210^{\circ}$ . It was distilled from

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**Figure 1.** Ratio of rate of  $C_3H_6$  to  $C_2H_4$  production vs. time of illumination in the 254-nm photolysis of 30.0 Torr of thietane at 200°.

 $-160^{\circ}$  prior to each run. H<sub>2</sub>S was purified by gas chromatography on a 10-ft Porapak Q column to remove traces of hydrocarbons. Ethylene and isopentane were subjected to rough fractionation and degassing under vacuum.

Apparatus. The reaction system was a typical mercurycontaining, grease-free high-vacuum system. Photolysis was carried out in a cylindrical quartz cell 20 cm in length and of 0.216 l. total volume mounted in an aluminum block furnace. The temperature of the oven was controlled to  $\pm 1^{\circ}$ .

In some runs a Hanovia medium-pressure lamp was used in conjunction with a Corning No. 7740 filter to isolate the  $\lambda > 300$ -nm region, and with a Barr and Stroud U2 interference filter to isolate the 254-nm region. In most experiments a PEK Model 715 500-W high-pressure mercury lamp was used in conjunction with a Bausch and Lomb high-intensity grating monochromator, adjusted for a 10-nm bandwidth. Intensity of irradiation was monitored using an RCA 935 phototube coated with sodium salicylate. Response of the phototube was linear with light intensity at both wavelengths.

Extinction coefficients were measured using a Cary 14 spectrophotometer and were found to be nearly invariant with temperature from 25 to 230° in the 330-240-nm region.

Analysis. Products from the photolysis were analyzed using a Gow-Mac 69-500 gas chromatograph modified to allow the direct sampling of gases. The fraction noncondensable at  $-130^{\circ}$  was separated on a 10-ft Porapak Q column, and the condensable products on a 10-ft 10% dinonyl phthalate on Gas-Chrom Z column. NO was measured using a molecular sieve 13X column using carrier gas purified by passage through a molecular sieve trap at  $-196^{\circ}$ . Identification of products was made by mass spectrometry and comparison of retention times with authentic samples.

#### Results

Thietane exhibits a broad, structureless absorption extending from about 240 to 330 nm. At the photolysis wavelengths of 254 and 313 nm the decadic molar extinction coefficients for thietane vapor were found to be 11.4 and 0.75  $M^{-1}$  cm<sup>-1</sup>, respectively, virtually independent of temperature and in excellent agreement with previous measurements.<sup>4b,5</sup>



Figure 2. Rate of  $C_3H_6$  production vs. temperature from the 313-nm photolysis of 10 Torr of thietane.

Photolysis of thietane vapor at either wavelength, at temperatures from 22 to 235° and at pressures from 1 to 40 Torr produces only ethylene (and thioformaldehyde) in substantial yield when the percentage decomposition of the substrate is sufficiently small. That propylene is in fact a secondary photolysis product may be observed from Figure 1, in which a typical graph of the ratio of the rate of  $C_3H_6$  to the rate of  $C_2H_4$  production is plotted as a function of exposure time. Because the rate of production of  $C_2H_4$  is nearly invariant with exposure time in these experiments, it is evident that at very small percentage decompositions the rate of  $C_3H_6$  falls to near zero. In order to show that the presence of ethylene was not necessary for the production of propylene, a similar series of experiments was carried out in which 10 Torr of thietane with 1 Torr added ethylene was photolyzed. The rate of  $C_3H_6$  production still fell to near zero at short exposure times. The rates of formation of cyclopropane and of all other minor products are less than 2% of the rate of C<sub>2</sub>H<sub>4</sub> formation for photolysis in this absorption band and were not measured routinely. When 10 Torr of thietane was photolyzed at 200° with 1 atm of Ar added no significant change in the yield of cyclopropane was observed.

In order to obtain some information regarding the nature of the secondary photolysis process, experiments were carried out in which the yield of  $C_3H_6$  from the photolysis of thietane to about 1% conversion was measured as a function of temperature. Figure 2 indicates that there are probably two processes producing propylene. One is dominant at temperatures less than about 200° and is responsible for the slow increase in the yield with increasing temperature. The second is responsible for the rapid increase in the yield at temperatures greater than about 200°. Blank runs showed that this rapid rise in yield was photochemically and not thermally initiated.

These results were confirmed by experiments in which the yield of  $C_3H_6$  was measured as a function of the pressure of added nitric oxide (Figure 3). At 205° only part of the propylene is scavengable with NO. As the temperature is lowered, the fraction of the  $C_3H_6$  which can be scavenged increases sharply and virtually all the propylene is scavengable at temperatures less than 175°.

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Figure 3. Yield of C3H6 vs. pressure of added NO from the 313nm photolysis of 10 Torr of thietane at 205°.

Table I<sup>a</sup>

P <sub>NO</sub> , Torr	Rate (C₂H₄), µmol/5 hr	Rate (C₃H <sub>6</sub> ), μmol/5 hr	$\Delta R(NO) / \Delta R(C_3H_6)$
0	1.75	0.150	
50	1.76		
10	1.73		
$2.32 \times 10^{-2}$		0.080	1.49
$3.74 \times 10^{-2}$		0.072	1.78
$5.53 \times 10^{-2}$		0.067	2.07
$8.40 \times 10^{-2}$		0.066	2.01
11.73 × 10 <sup>-2</sup>		0.066	2.06

 $^{a}$  T = 205°,  $\lambda$  = 313 nm,  $P_{\text{thietane}}$  = 10 Torr.

In order to show that NO was in fact scavenging radical- or diradical-precursors of propylene (and not just quenching some excited intermediate) experiments were carried out in which the amount of NO consumed was measured. All experiments were performed at 205° with 313-nm radiation. The results are presented in Table I. In these experiments the yields of ethylene (a primary product) were unchanged when up to 50 Torr of NO was added. Blank runs indicated that NO was not consumed on prolonged heating of mixtures of NO and thietane or NO, thietane, and its photolysis products. (Greater than 98% of the NO initially present was recovered in these blank runs.) At NO pressures for which scavenging of the scavengable precursor of  $C_3H_6$  was complete (>4 × 10<sup>-2</sup> Torr at 205°), the ratio of the amount of NO consumed to the amount of C<sub>3</sub>H<sub>6</sub> scavenged,  $\Delta R(NO)/\Delta R(C_3H_6)$ , was 2:1 within an experimental error of about  $\pm 7\%$ .

#### Discussion

The available evidence now indicates that the only primary products of the 254- and 313-nm photolysis of thietane vapor at temperatures from 22 to 200° are ethylene and monomeric thioformaldehyde. Propylene is a secondary photolysis product, one precursor of which is scavengable (at  $T < 175^{\circ}$ ) by nitric oxide. Other products (cyclopropane, CH<sub>4</sub>, and CS<sub>2</sub>) are present in trace amounts (<1% of the C<sub>2</sub>H<sub>4</sub> yield) and are not formed by a significant decomposition pathway.





Figure 4. Stern-Volmer plot of the ratio of the yield of scavengable  $C_3H_6$  with no added NO (Y<sup>0</sup>) to the yield of scavengable  $C_3H_6$  with NO added (Y) vs. concentration of added NO. Photolysis was at 313 nm and 205°.

The question of the nature of the secondary photolysis process and the mechanism of C<sub>3</sub>H<sub>6</sub> production is a particularly intriguing one. Two questions must be answered: first, what is the identity of the species which absorbs and thereby initiates the propylene-producing reactions, and second, what is the nature of the nitric oxide consuming species which is the propylene precursor?

Identity of Absorber. The light absorber responsible for the initiation of the propylene-producing reactions is very likely monomeric thioformaldehyde, produced in the primary process (reaction 1) in yield equal to that of ethylene. This process is analogous to that postulated by Margerum, et al.,<sup>3</sup> in the photolysis of oxetane vapor at  $\lambda$ <200 nm in which formaldehyde, a primary product, absorbed light in its  $(\pi,\pi^*)$  absorption band and decomposed to H, HCO, H<sub>2</sub>, and CO.

Thioformaldehyde is unstable in monomeric form and has been reported to undergo trimerization to trithiane,<sup>6</sup> a crystalline material of low volatility (mp 216°) which, if present, could not have been analyzed in our experiments. The rate of disappearance of the monomer is likely quite slow, however, and previous measurements<sup>7,8</sup> have indicated that the half-life of thioformaldehyde may be as long as several minutes in a static system. Because a "steady-state" concentration of thioformaldehyde monomer will only be achieved after a period of several monomer half-lives, it is evident that it may take several minutes for a steady state to be achieved in the photolysis system. This compares favorably with the observed time required for a steady state to be achieved in the rate of  $C_3H_6$  production (cf., Figure 1). One therefore may conclude that the production of monomeric thioformaldehyde is a necessary preliminary step in the production of  $C_3H_6$ . Reactions leading to propylene subsequent to the initial excitation of thioformaldehyde may easily occur in a time which is short in comparison with the time necessary to establish steady-state conditions in the photolysis system.

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Other evidence that thioformaldehyde monomer is the most logical choice for the secondary absorber comes from a consideration of the nature of the electronic absorption spectrum which such an absorber must have. If the absorption of light by the secondary absorber (assumed to be  $CH_2S$ ) produces  $C_3H_6$  with a maximum quantum yield of unity, then, when only a small percentage of the incident light is absorbed,  $([CH_2S]_{ss} \in (CH_2S)^{254})/([C_3H_6S])$  $\epsilon(C_3H_6S)^{254}) \geq (rate C_3H_6)/(rate C_2H_4)$  under steadystate conditions. The best fit of the data of Figure 1 gives a half-life for CH<sub>2</sub>S of about 3 min (in excellent agreement with previous measurements<sup>8</sup>) and a resultant steadystate concentration of CH<sub>2</sub>S of about  $2 \times 10^{-6}$  M, assuming that the monomer disappears by first-order or pseudofirst-order processes. Using this data, the previously determined value of  $\epsilon (C_3H_6S)^{254}$  11.4  $M^{-1}$  cm<sup>-1</sup> and a  $[C_3H_6S]$  of 1.61  $\times$  10<sup>-3</sup> M, one calculates that  $\epsilon$ (CH<sub>2</sub>S)<sup>254</sup>  $\geq 1.3 \times 10^3 M^{-1} \text{ cm}^{-1}$ .

Unfortunately the electronic absorption spectrum of thioformaldehyde has not been measured. However, in this reaction system only a  $(\pi,\pi^*)$  or a  $(n,\sigma^*)$  transition of a thiocarbonyl group is likely to have a molar extinction coefficient of the required magnitude. Furthermore, the existence of a  $(\pi,\pi^*)$  transition having a position near 254 nm and  $\epsilon^{254} \ge 1.3 \times 10^3 M^{-1} \text{ cm}^{-1}$  is not at all unreasonable. Previous measurements of the absorption spectra of aliphatic thio ketones<sup>9,10</sup> have shown that there are three adsorptions in the near uv-visible region; an intense  $(n,\sigma^*)$  absorption with  $\lambda_{max}$  near 215 nm (corresponding to the long-lived absorption observed by Callear, et al.,<sup>7</sup> in the flash photolysis of CH<sub>3</sub>SSCH<sub>3</sub>), an intense  $(\pi,\pi^*)$ absorption with  $\lambda_{max}$  near 240 nm, and a weak  $(n, \pi^*)$  absorption with  $\lambda_{max}$  about 500 nm. Since the aliphatic aldehvdes and ketones exhibit similar spectra<sup>11</sup> it is not unreasonable to expect that this aldehydes will have electronic absorption spectra similar to those of the thio ketones. Other possible light absorbers such as saturated sulfides and disulfides would not likely have large enough extinction coefficients at this wavelength. The conclusion that CH<sub>2</sub>S is the absorber responsible for the initiation of the sequence of reactions which result in the ultimate production of  $C_3H_6$  is compelling.

One interesting conclusion which may be drawn from these experiments is that photolysis of CH<sub>2</sub>S at wavelengths greater than 240 nm produces little atomic or molecular hydrogen. Careful analysis of the reaction products in runs in which a narrow band of wavelengths was employed produced no measurable amount of H<sub>2</sub> either in the photolysis at elevated temperatures of the substrate alone or in the presence of added  $H_2S$  and isopentane, commonly used as sources of readily abstractable hydrogen atoms. However, in experiments in which the full ( $\lambda$ >240 nm) spectrum of the high-pressure lamp was utilized  $H_2$  was produced with a yield of about 7-8% of that of propylene at 200°. Thus at temperatures less than 200° the quantum yield of  $H_2$  from the  $\lambda > 240$  nm photolysis of  $CH_2S$  must be less than about 0.08 since the maximum quantum yield of  $C_3H_6$  is unity. Thioformaldehyde would therefore appear to be much more resistant to photodecomposition than its oxygen analog.<sup>12</sup> One can conclude that other radiative and nonradiative pathways for dissipating the absorbed energy must be much more important than decomposition in the photolysis of  $CH_2S$  in its  $(\pi,\pi^*)$  or  $(n,\pi^*)$  absorption bands.

Nature of the Scavengable Precursor of  $C_3H_6$ . It is much more difficult to identify the scavengable intermediate which is the propylene precursor. The results presented do allow it to be partially characterized however.

A 2:1 ratio for  $\Delta R(NO)/\Delta R(C_3H_6)$  is consistent with either (1) the scavenging of a diradical precursor of  $C_3H_6$ by 2NO, or (2) the reaction of 1NO with each of two free radicals, one of which is a precursor of  $C_3H_6$ . The latter possibility may be eliminated on the grounds that there are no products present in significant yield which could have free radical origins. Moreover, the possibility that NO is consumed in reactions involving free S atoms can be ruled out since previous work<sup>4b</sup> has demonstrated that free S atoms are not formed in this system. It is conceivable that NO could react with excited CH<sub>2</sub>S to yield a product of formula ONCH<sub>2</sub>SNO but it is highly unlikely that this species would be stable even if such a reaction could occur. One therefore concludes that a diradical is the most likely C<sub>3</sub>H<sub>6</sub> precursor.

The diradical cannot be  $\cdot CH_2CH_2CH_2S$  because such a species would almost certainly decompose to C<sub>2</sub>H<sub>4</sub> and  $CH_2S$ , yet the  $C_2H_4$  yield is unaffected by nitric oxide. Trimethylene is also not likely involved because cyclopropane, a major product of trimethylene ring closure,<sup>2</sup> is not present in significant quantity either at low pressure or with high pressures of inert deactivator added. Rather, we suggest that the diradical must be formed from the reaction of electronically excited thioformaldehyde either with ground state CH<sub>2</sub>S, or with the substrate in a sequence of reactions which leads to the formation of polymer and propylene. The former process is analogous to the photodimerization of thiocarbonyls proposed by Ohno, et al.,12 but would require subsequent reactions with substrate before propylene could be produced. The latter process is also more likely because the substrate is present in a concentration which is about a thousand times larger than that of CH<sub>2</sub>S. A mechanism for the reaction below 175° which identifies the necessary overall reactions but which is likely quite incomplete follows.

$$CH_2S + h\nu \longrightarrow CH_2S^*$$
 (2)

$$CH_2S^* + \square_S \longrightarrow diradical (D)$$
 (3)

$$D \longrightarrow C_3 H_6 + C H_2 S_2 \tag{4}$$

$$D + \square_S \longrightarrow polymer$$
 (5)

$$D + 2NO \longrightarrow product$$
 (6)

The identity of the diradical, D, cannot be established at present because it was not possible to characterize the product of reaction 6. Either this product is unstable to gas chromatographic analysis or it is sufficiently involatile that it is impossible to remove it from the reaction cell. Some polymeric material is formed in the cell but neither photolysis nor thermolysis subsequent to its formation yields  $C_3H_6$  or  $C_2H_4$ . Any reaction in which a diradical decomposes to more than one C<sub>3</sub>H<sub>6</sub> can be ruled out since a  $\Delta R(NO)/\Delta R(C_3H_6)$  ratio of less than 2:1 would be obtained in such a process. Hence, any product of reaction 5 cannot yield more than one  $\mathrm{C}_3\mathrm{H}_6$  if it decomposes. Moreover, because  $\Delta R(NO)/\Delta R(C_3H_6) \simeq 2$  and because nei-

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ther  $N_2$  nor  $NO_2^{13}$  were produced in these experiments, further reaction of NO with the product of reaction 6 apparently does not occur.

At present the nature of the reactions which result in the formation of unscavengable  $C_3H_6$  at temperatures greater than 175° is unclear. This aspect of the work is under active investigation, however, and speculation regarding the possible results would seem to be unwarranted at present.

Finally, an estimate of the lifetime,  $\tau$ , of the scavengable diradical precursor to C<sub>3</sub>H<sub>6</sub> can be obtained from analysis of the data in Figure 3. Considering the scavengable portion of the C<sub>3</sub>H<sub>6</sub> only, a Stern-Volmer type of plot may be constructed (Figure 4). The slope of the graph gives  $\tau k = 4.3 \times 10^6 M^{-1}$ , where k is the rate constant for the scavenging reaction. An upper limit of  $k \leq 3.6 \times 10^{11}$   $M^{-1} \sec^{-1}$  is obtained for the case in which the scavenging reaction is diffusion controlled. Thus the average lifetime of D will be greater than  $1.2 \times 10^{-5} \sec at 205^{\circ}$ .

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# Kinetics of Particle Growth. I. Ammonium Nitrate from the Ammonia–Ozone Reaction<sup>1a</sup>

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 $NH_4NO_3$  particles were prepared from the reaction of  $NH_3$  and  $O_3$  at room temperature. The  $NH_3$  and initial  $O_3$  pressures ranged from 0.034 to 2.0 and from 0.020 to 0.10 Torr, respectively, their ratio being between 2 and 21.5. In all of the experiments N<sub>2</sub> was also present. The O<sub>3</sub> decay was monitored by ultraviolet absorption and obeyed the rate law  $-d[O_3]/dt = k[O_3]$ , where k is a function of [NH<sub>3</sub>] and [O<sub>3</sub>]<sub>0</sub> (the initial value of [O<sub>3</sub>]). One molecule of NH<sub>4</sub>NO<sub>3</sub> was presumed to be produced for every four molecules of O<sub>3</sub> consumed. The total number of particles greater than 200 or 1000 Å diameter was monitored as a function of reaction time. Initially there is a rapid production of particles in a short period of time (<10 min) until about 10<sup>5</sup> particles/cc are produced. Then particle production stops, as deduced from the fact that the number of particles between 200 and 1000 Å rapidly falls to zero. The larger particles grow, though the number, N, decays slowly according to the rate law  $N = N_0 \exp(-k't)$ . The number of particles is too small for coagulation to play any role, and the decay constant k' can be associated with diffusional loss to the wall. The number of particles at zero time,  $N_0$ , increases with the loss rate of  $O_3$ and with the N<sub>2</sub> pressure. The particles,  $C_l$  (l = integer), grow by reaction with the monomer, the average growth rate constant being  $\beta k[O_3]/4N$  where  $\beta$  is the fraction ( $\sim 3 \times 10^{-3}$ ) of NH<sub>4</sub>NO<sub>3</sub> monomers entering the gas phase. The loss of particles is entirely by diffusion to the walls, with a pressure-dependent rate constant  $k_{2,l}$ . For the simplified situation in which initially N<sub>0</sub> particles of r monomer units each are produced, and the particle growth rate constants are all considered identical, *i.e.*,  $\beta k[O_3]/4N$  (a nearly time-independent parameter since N and  $[O_3]$  decay at similar rates), then a simplified solution for the particle size distribution results,  $[C_l] = N_0 (\beta k [O_3] t/4N)^{l-r} \exp(-\alpha_l t)/(l-r)!$ , where  $\alpha_l = \beta k [O_3]/(l-r)!$  $4N + k_{2,l}$ . This distribution predicts a single maximum for  $[C_l]$  at  $\tau_{max} = (l - r)/\alpha_l$ .

### Introduction

In our laboratory, we have initiated a program to examine the kinetics of particle formation, *i.e.*, both the size distribution and growth rates, as a function of time for particles produced from gas-phase chemical reactions. As far as we know, such studies have not been made before under isothermal conditions, though particle formation has been observed in numerous laboratory studies and is important in polluted urban atmospheres.

A number of studies have been made of soot formation in flames and hydrocarbon pyrolysis. Soot formation in

- acetylene pyrolysis initiated at  $770-1070^{\circ}$ K and reaching 3000°K as a maximum has been discussed by Tesner.<sup>2</sup> He considered an initial distribution of carbon particles, corresponding to a commercial soot, and assumed that the particles grew upon every collision with a C<sub>2</sub>H<sub>2</sub> molecule until the C<sub>2</sub>H<sub>2</sub> was exhausted. The computed growth rate was about seven times that found experimentally, which
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