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Photolysis of Thietane and Thietane-d_6 in Argon Matrix: Infrared Spectra of Matrix-Isolated Thioformaldehyde and Thioformaldehyde-d_2

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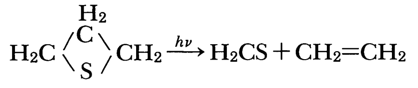
Synopsis. Argon-matrix isolated thietane at 10 K decomposed by irradiation (λ>290 nm) to form ethylene and thioformaldehyde. The photolysis of thietane under these conditions has been shown to be a clean source of thioformaldehyde. The CH_2S and CD_2S molecules generated this way are indefinitely stable and their infrared spectra could be recorded.

Thioformaldehyde easily polymerizes to a cyclic trimer (trithiane) under normal conditions. It has been generated by pyrolysis or photolysis of various precursors for spectroscopic investigations.[1] Recently infrared spectrum of thioformaldehyde generated by photolysis of matrix isolated methylene trithiocarbonate has been fully analyzed.[2]

Pyrolysis or photolysis in general results in formation of by-products that obscure frequently parts of spectrum of an aimed species in infrared studies. Haines et al.[3] reported that thietane decomposed by the action of light to form only ethylene as a gaseous product and a white solid which was probably a trimer of thioformaldehyde. We expected that photolysis of thietane in the argon matrix would produce thioformaldehyde in a monomeric form and ethylene,



$$H_2C\langle{}^{H_2}_{C}{}_{S}\rangle CH_2 \xrightarrow{h\nu} H_2CS + CH_2{=}CH_2$$

and the infrared spectrum of thioformaldehyde would be obtained by subtraction of absorptions of ethylene from the spectrum of the photolysis products.

Experimental

Thietane (Tokyo Kasei Kogyo Co.) was distilled under vacuum before use. Thietane-d_6 was prepared from 1,3-dibromopropane-d_6 (MSD ISOTOPES, Montreal) by the method similar to the procedure of Bordwell and Pitt[4] for preparation of thietane, and purified by trap-to-trap distillation. Ethylene-d_4 was prepared by dehydration of ethanol-d_6 (MSD ISOTOPES, Montreal) with sulfuric acid-d_2.

A mixture of thietane or thietane-d_6 with argon gas (Ar : thietane=200 : 1 in a mole ratio) was prepared using standard manometric procedure. The mixture was deposited within 2 h on a CsI plate cooled at 20 K by a CTI Cryogenics Cryodyne Cryocooler Model 21 closed-cycle helium refrigerator. The argon-matrix isolated precursor cooled down to 10 K was exposed to radiation from a high-pressure mercury lamp (Ushio Denki) through a water filter (10 cm) fitted with quartz windows. Since this irradiation experiment resulted in complicated fragmentation, a cut-off filter was used. The irradiation through a UV-29 filter (Toshiba Glass) gave favorably clean infrared spectra, though it took a long exposure time to decompose the precursor completely.

Infrared spectra (4000—250 cm^{-1}) were recorded on a Hitachi Model 260-50 grating spectrometer, which was calibrated with standard gases.[5]

Results and Discussion

Irradiation (λ>290 nm) of argon-matrix isolated thietane and thietane-d_6 for 8 h resulted in the disappearance of the initial infrared spectra, Figs. 1(a) and 2(a), and the appearance of new absorptions, Figs. 1(b) and 2(b). The absorptions due to ethylene and ethylene-d_4 in Figs. 1(b) and 2(b) could be identified by comparing them with the spectra of argon-matrix isolated ethylene and ethylene-d_4 (Figs. 3(a) and 3(b)). By the agreement with the absorptions observed previously,[2] the remaining spectra could be evidently identified as those of CH_2S and CD_2S. The observed frequencies were collected in Table 1 together with the results of Torres et al.[2]

Three absorptions remained at 3019(vw), 2956(m), and 2863(w) cm^{-1} after elimination of the CH_2 stretchings of ethylene in the CH stretching region, in agreement with previous observations, and in the CD stretching region two absorptions were observed at 2277(vw) and 2149(m) cm^{-1} aside from the CD_2 stretch-

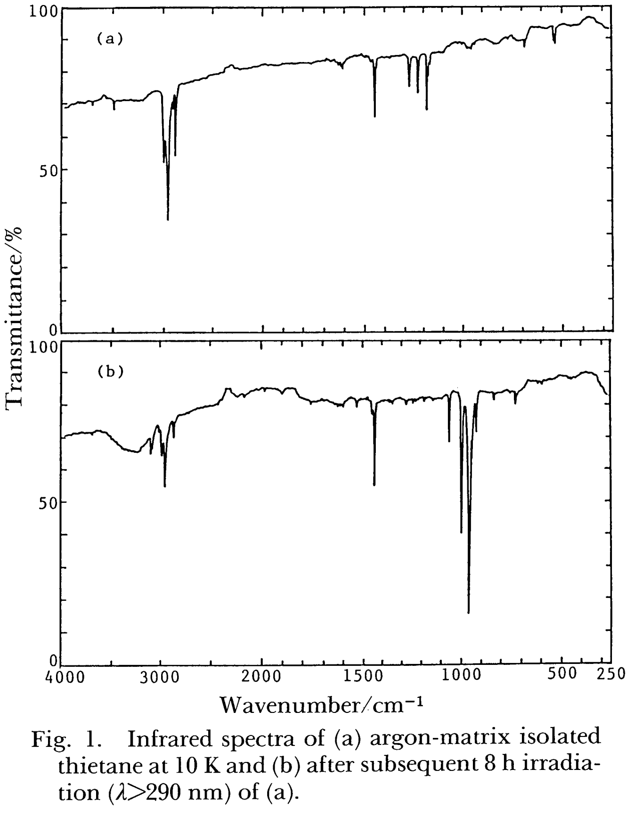


Fig. 1. Infrared spectra of (a) argon-matrix isolated thietane at 10 K and (b) after subsequent 8 h irradiation (λ>290 nm) of (a).

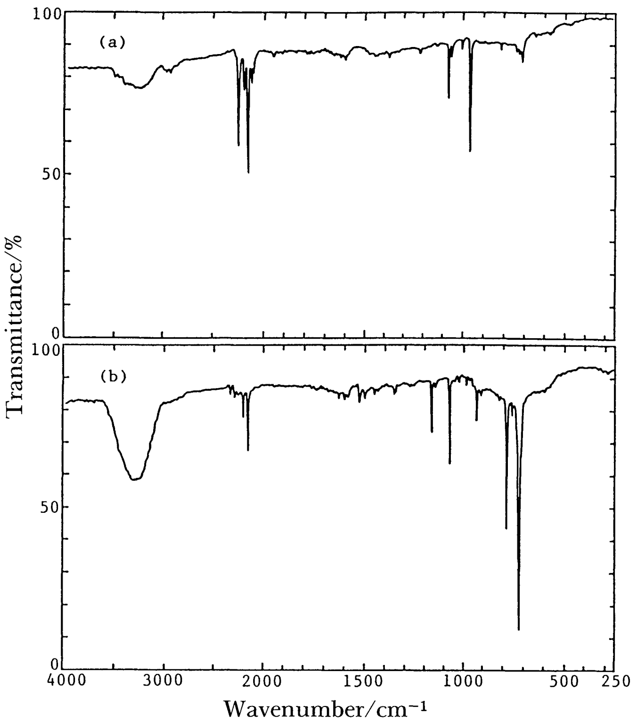


Fig. 2. Infrared spectra of (a) argon-matrix isolated thietane-d_6 at 10 K and (b) after subsequent 8 h irradiation (λ>290 nm) of (a).

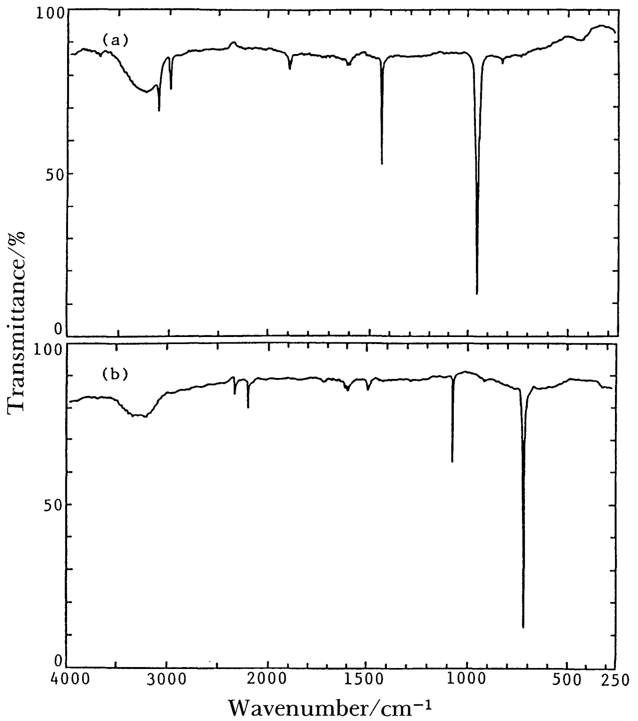


Fig. 3. Infrared spectra of argon-matrix isolated ethylene (a) and ethylene-d_2 (b) at 10 K.

Table 1. Observed Frequencies (cm^{-1}) of CH_2S and CD_2S

CH_2S		CD_2S		Assignment
This work	Torres[a)]	This work	Torres[a)]	
3019 (vw)	3017	2277 (w)	2280	ν_5 $CH_2(CD_2)$ stretch
2956 (m)	2965	2149 (m)	2155	ν_1 $CH_2(CD_2)$ stretch
2863 (w)	2869			$2\nu_2$
1436[b)]	1447	1162 (m)	1167	ν_2 $CH_2(CD_2)$ sym def
1052 (m)	1052	934 (m)	932	ν_3 C=S stretch
994 (s)	988	783 (s)	779	ν_6 $CH_2(CD_2)$ wag
990 (sh)	980	779 (sh)	773	ν_4 $CH_2(CD_2)$ rock

a) Photolysis of matrix isolated methylene trithiocarbonate, Ref. 2. b) Overlaps with the symmetric CH_2 deformation of ethylene.

ings of ethylene-d_4 also in agreement with the previous observations. The 2863 cm^{-1} band has been assigned to $2\nu_2$,[2)] whereas $2\nu_2$ of CD_2 must overlap with the 2327 cm^{-1} band of ethylene-d_4, if would appear.

Torres et al. assigned the symmetric CH_2 deformation to the absorption at 1447 cm^{-1} and it was observed to be slightly stronger than the C=S stretch (1052 cm^{-1}).[2)] In Fig. 1(b), there is a very weak absorption at 1449 cm^{-1}, but it is too weak as compared with the C=S stretch (1052 cm^{-1}). On the other hand, the symmetric CD_2 deformation of CD_2S is distinguishable from the symmetric CD_2 deformation (1071 cm^{-1}) of ethylene-d_4 (Fig. 2(b)). Thus the symmetric CH_2 deformation of CH_2S must accidentally overlap with the symmetric CH_2 deformation of ethylene.

For the out-of-plane and in-plane CH_2 deformations, there is only a prominent absorption at 994 cm^{-1}, which is accompanied with a shoulder at 990 cm^{-1}. There is often observed a vibrational mode as splitting into various bands in a matrix spectrum. However, on the basis of no splittings for the other bands, these should be interpreted to be due to different modes and we tentatively assinged the strong band at 994 cm^{-1} to the out-of-plane CH_2 deformation and the shoulder at 990 cm^{-1} to the in-plane in accordance with the interpretation of Torres et al.[2)] Two bands of CD_2S at 783(s) and 779 (shoulder) cm^{-1} were assigned similarly.

The exclusive photolysis product of ethylene and the good agreement of the remaining spectrum with the CH_2S absorptions previously reported shows that thietane is a clean source compound for the photochemical generation of thioformaldehyde.

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