

S2

Matrix Isolation Study of the Vacuum Ultraviolet Photolysis of Methyl Mercaptan. Spectroscopic Evidence for Thioformaldehyde

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H_2CS has been trapped in argon and nitrogen matrices at 14 K as a product of the ultraviolet or vacuum ultraviolet photolysis of CH_3SH . A small concentration of H_2CS has also been observed upon vacuum ultra-violet photolysis of a mixture of CH_4 and H_2S in an argon matrix. The isotopic data support the assignment of absorptions at 993 and at 1063 cm^{-1} to the out-of-plane deformation and the $\text{C}=\text{S}$ stretching fundamentals of H_2CS in an earlier gas-phase study [1] were confirmed in the matrix experiments. The formation of substantial concentrations of both HDCS and D_2CS on vacuum ultraviolet photolysis of CD_3SH suggests that photolytic rupture of a $\text{C}-\text{D}$ bond followed by rapid intramolecular rearrangement of CD_2SH to CHD_2S may occur on exposure of the sample to radiation of wavelength shorter than 2500 \AA . Subsequent photolysis of this intermediate by vacuum ultraviolet or ultraviolet radiation leads to the formation of thioformaldehyde.

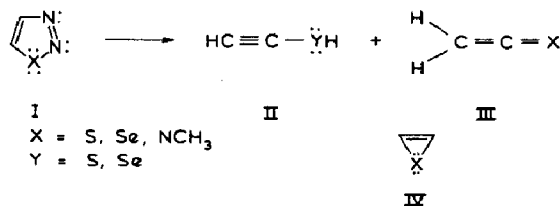
1 J. W. C. Johns and W. B. Olson, *J. Mol. Spectrosc.*, **39** (1971) 479.

S3

Photolysis of Matrix-isolated 5-Membered Heterocycles

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The photodecomposition of 1,2,3-thiadiazole I ($\text{X} = \text{S}$) in inert gas matrices at 8 K using Pyrex filtered light leads to thioketene and ethynyl mercaptan. The photodecomposition of 1,2,3-selenadiazole I ($\text{X} = \text{Se}$) under the same conditions produces selenaketene and ethynyl selenol as well as acetylene. Photolysis of the



N-methyltriazole I ($\text{X} = \text{N}-\text{CH}_3$) gives the hetero *N*-methyl ketenimine, apparently free of ethynyl amine. Labeling experiments designed to detect potential anti-aromatic intermediates IV will be described.

S4

Radiative and Radiationless Processes Involving the Second Excited Singlet State of Thiocarbonyl Compounds

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Recent evidence [1, 2, 3] indicates that both fluorescence and photochemical processes may originate from the second excited singlet state of thiocarbonyl compounds. In the present paper experimental evidence that fluorescence is obtained in high yield from S_2 of thiophosgene, Cl_2CS , and other thiocarbonyl compounds is presented and discussed.

The S_2-S_0 adsorption, emission and excitation spectra of thiophosgene vapour have been measured and the observed single vibronic transitions assigned. Comparison of the absorption and excitation spectra reveals that emission is excited only when transitions to the upper state terminate in $3^m 4^n$ [4], m or $n = 0$ or 1, and that the upper state is depopulated by rapid radiationless processes when higher vibrational levels are populated. The most prominent bands in the emission spectrum are those in which the transitions terminate in $1_p 3_q 4_r$ [4] with $1 < p < 10$, $1 < q < 5$ and $1 < r < 4$. All three types of spectra are consistent with a pyramidal excited state in which equilibrium internuclear distances are substantially greater than those of the ground state. The implications of this fluorescence anomaly with respect to the nature of radiationless