Photochemistry of Isothiazole Isolated in Solid Ar Matrices

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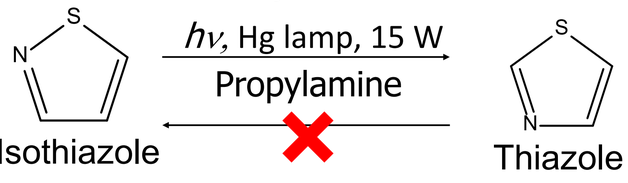
Introductions

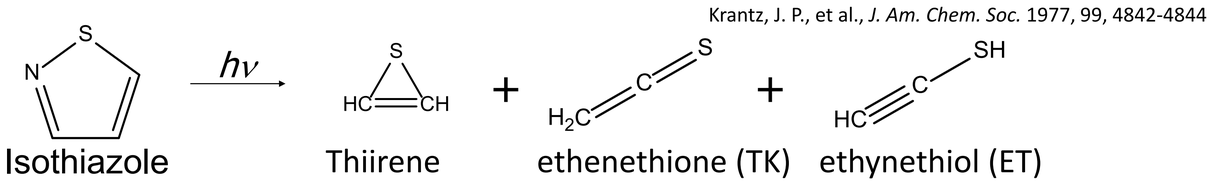
Photochemistry of Isothiazole



Isothiazole is converted to thiazole by UV irradiation, while the reverse reaction is not occurred.

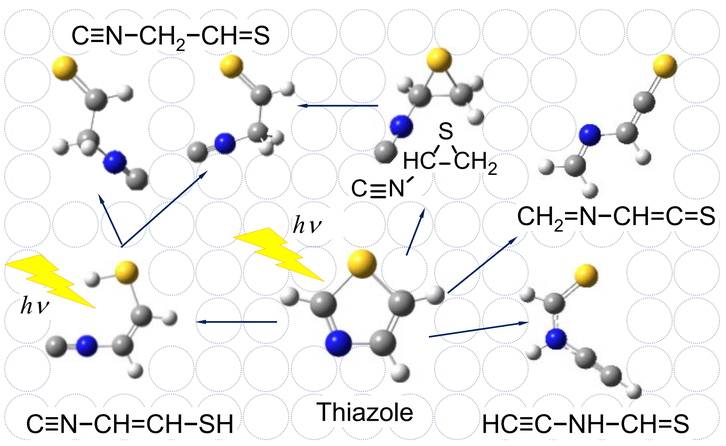
Catteaum, J. P., et al., *J. Chem. Soc., Chem. Commun.* 1969, 1018

Matrix-isolation Study of Isothiazole (as precursor of thiirene)



Krantz, J. P., et al., *J. Am. Chem. Soc.* 1977, 99, 4842-4844

Photochemistry of Thiazole in a low-temperature Ar matrix



- ✓ Photoproducts: Newly recognized 6 type molecules including 4 type isocyano compounds.
- ✓ Photodecomposition products: ethynethiol (ET), ethenethione (TK), hydrogen cyanide (HC≡N), and acetylene (HC≡CH).

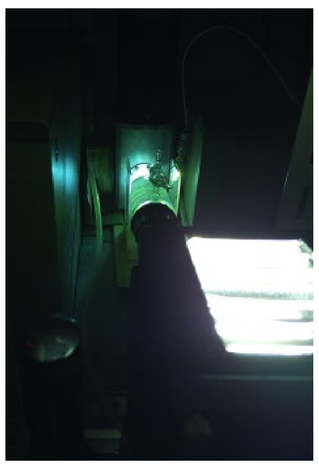
Miyazaki, J., et al. *RSC Adv*. 2017, **7**, 4960-4974

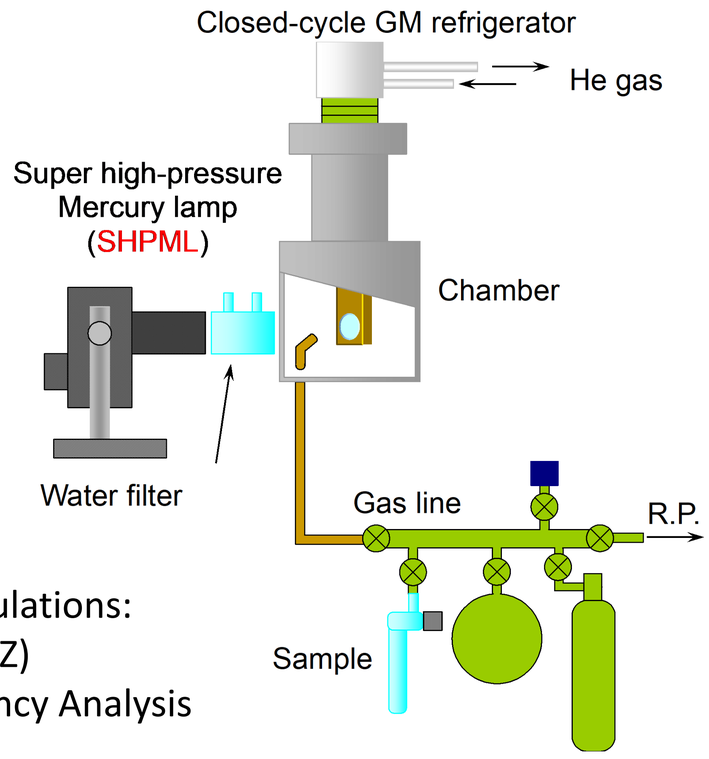
- ✓ Using high-power UV irradiation, three types of hydrogen-bonded complexes between HS−C≡CH and HC≡N are produced.

Miyazaki, J., et al, *J. Mol. Struct*., 2019, **1175**, 900-905

Experimental setup

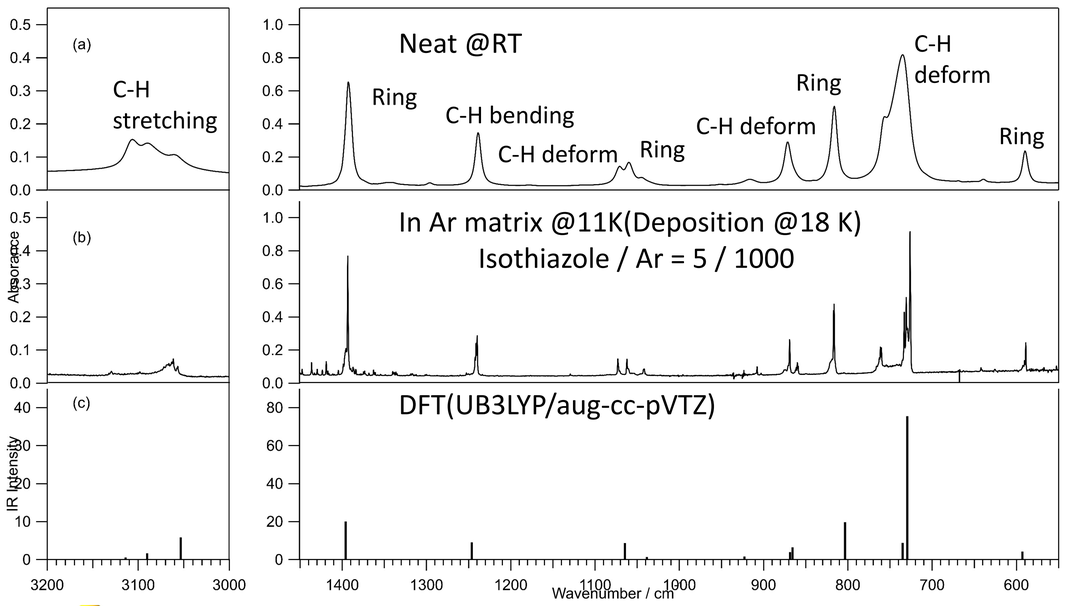
- ➢Matrix-Isolation: Isothaizole was isolated in solid argon matrices at 11 K.
- ➢Infrared Spectroscopy
- ➢UV-light Irradiation (Super High Pressure Mercury Lamp)

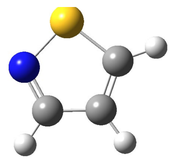




- ➢Density Functional Theory Calculations:
  Gaussian03 (UB3LYP/aug-cc-pVTZ)
  Geometry Optimization, Frequency Analysis

Infrared spectra of isothiazole





Isothiazole

Scaling factors of 0.96, 0.97 and 0.98 were applied to the regions over 2800 cm^{-1}, between 2800 to 1900 cm^{-1}, and below 1900 cm^{-1}, respectively.

Reference of peak assignments: Califano, S., et al, *Spectrochim. Acta*, 1964, **20**, 339-344

Purpose

UV photochemistry of isothiazole isolated in solid Ar matrices was investigated using IR spectroscopy and DFT calculations in order to clarify the photochemical reaction mechanism of isothiazole.

Conclusions

- Photochemical reaction of isothiazole isolated in solid argon matrices using super-high-pressure mercury lamp was observed.
- Thiirene was detected in Ar matrix as initial photoproducts of isothiazole, and ethenethione (TK), ethynethiol (ET), H≡CN, and HC≡CH were also detected.
- Though isocyano compounds observed in thiazole experiments were observed, cyano compounds were rarely observed.
- Further investigation with lower wavelength UV radiation is necessary to understand the photochemical mechanism of isothiazole in isolated system.

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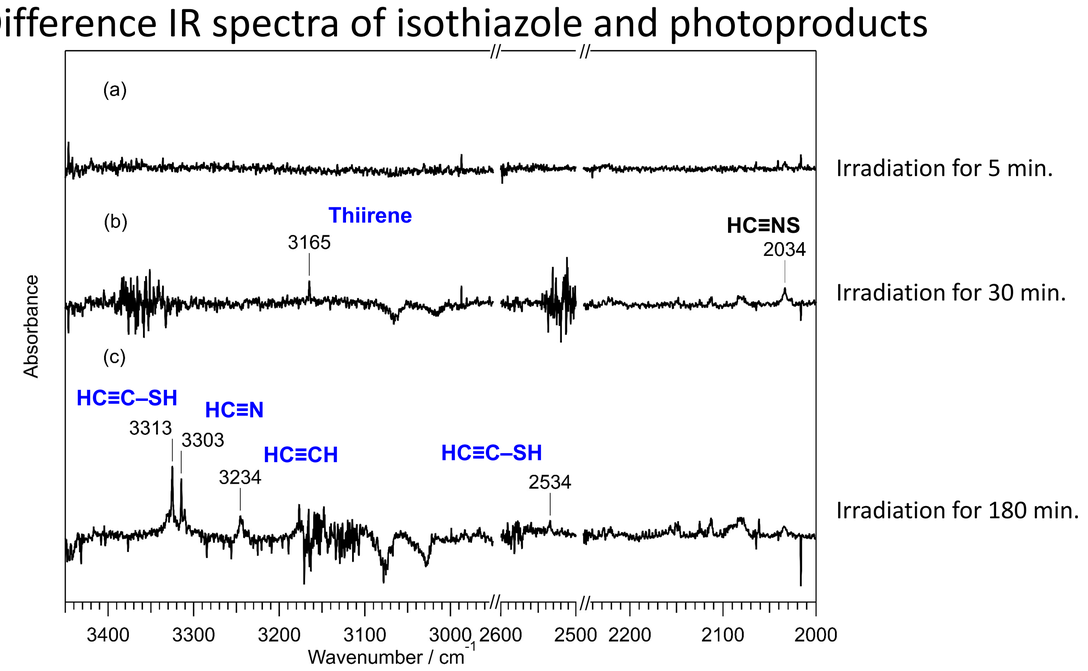
Results and Discussion

Infrared spectra of isothiazole in low-temperature Ar matrices

Difference IR spectra of isothiazole and photoproducts



Difference IR spectra of isothiazole and photoproducts.
(Power of radiation source is higher than above.)