

INFRARED SPECTRUM OF (Z)-3-IODO-BUT-2-EN-1-YL [$\bullet\text{CH}_2\text{CHC}(\text{CH}_3)\text{I}$] PRODUCED UPON PHOTODISSOCIATION OF (Z)-1,3-DIIODO-BUT-2-ENE [$(\text{CH}_2\text{I})\text{HC} = \text{C}(\text{CH}_3)\text{I}$] IN SOLID *para*-HYDROGEN

KAROLINA ANNA HAUPA, *Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan;*
YUAN-PERN LEE, *Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.*

Isoprene is the most abundant volatile organic compound (VOC) in the Earth's atmosphere after methane. Ozonolysis of isoprene, with the production of the Criegee intermediate methyl vinyl ketone oxide (MVKO), plays an important role in atmospheric chemistry. Recently, Barber *et al.*^a photolyzed 1,3-diiodo-but-2-ene [$(\text{CH}_2\text{I})\text{HC} = \text{C}(\text{CH}_3)\text{I}$] in the presence of O_2 with UV light and identified the Criegee intermediate *syn-trans*-MVKO as the main reaction product. However, the detailed mechanism for the production of MVKO is unexplored. It was assumed that photolysis of $(\text{CH}_2\text{I})\text{HC} = \text{C}(\text{CH}_3)\text{I}$ at 248 nm results in preferential dissociation of the weaker allylic $\text{C}_{(1)}\text{-I}$ bond, rather than the vinylic (sp^2 -hybridized) $\text{C}_{(3)}\text{-I}$ bond. Addition of O_2 to the $\text{C}_{(3)}$ atom, followed by breaking the $\text{C}_{(3)}\text{-I}$ bond, produces the Criegee intermediate MVKO.

In this work we took the advantage of the diminished cage effect of solid *para*-hydrogen (*p*- H_2) as a matrix host to study the UV photodissociation of (Z)- $(\text{CH}_2\text{I})\text{HC} = \text{C}(\text{CH}_3)\text{I}$. We report the formation and infrared identification of (Z)-3-iodo-but-2-en-1-yl [$\bullet\text{CH}_2\text{CHC}(\text{CH}_3)\text{I}$] radical intermediate upon photodissociation of (Z)- $(\text{CH}_2\text{I})\text{HC} = \text{C}(\text{CH}_3)\text{I}$ in solid *p*- H_2 at 3.3 K with light at 280 nm. Lines at 3115.6, 2025.2, 3001.2, 2933.2, 2880.3, 2835.8, 1474.9, 1409.6, 1406.7, 1375.5, 1265.3, 1061.8, 1018.5, 1008.6, 922.0, 913.7, and 792.5 cm^{-1} are assigned to (Z)- $\bullet\text{CH}_2\text{CHC}(\text{CH}_3)\text{I}$. The assignments were derived according to behavior on secondary photolysis and comparison of the vibrational wavenumbers and the IR intensities of the observed lines with values predicted with the B2PLYP-D3/cc-pVTZ-pp method. No evidence of breakage of the $\text{C}_{(3)}\text{-I}$ bond to form $\bullet\text{C}(\text{CH}_3) = \text{C}(\text{CH}_2\text{I})\text{H}$ was observed.

^aV. P. Barber *et al.* J. Am. Chem. Soc., **140**, 10866-10880 (2018).