

INFRARED SPECTRA OF GASEOUS (Z)-3-iodo-but-2-en-1-yl [$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{I}$] RADICAL, METHYL VINYL KETONE OXIDE [$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$] CRIEGEE INTERMEDIATE, AND $\text{C}_2\text{H}_3\text{CI}(\text{CH}_3)\text{OO}$ PEROXY RADICAL 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 OXYGEN

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Methyl vinyl ketone oxide [MVKO, $\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$], an important Criegee intermediate in ozonolysis of isoprene, was recently identified in laboratories with near infrared action spectrum (to produce OH) using photolysis of a gaseous mixture of 1,3-diiodo-but-2-ene [$(\text{CH}_2\text{I})\text{HC}=\text{C}(\text{CH}_3)\text{I}$] and O_2 ,^a but its mid-infrared spectrum and the detailed mechanism of its formation remains unexplored. We employed a step-scan Fourier-transform infrared spectrometer to investigate the reaction intermediates. Upon irradiation at 248 nm of gaseous (Z)-1,3-diiodo-but-2-ene, the (Z)-3-iodo-but-2-en-1-yl [$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{I}$] radical was observed, indicating the fission of the terminal allylic C-I bond, not the central vinylic C-I bond. This radical is characterized by infrared absorption bands at 1406, 1261, 1109, 1019, 924, and 902 cm^{-1} . Upon irradiation at 248 nm of a gaseous mixture of (Z)-1,3-diiodo-but-2-ene and O_2 at 35 Torr, the Criegee intermediate MVKO, characterized by infrared absorption bands at 1416, 1383, 1346, 1060, 987, 948, and 908 cm^{-1} , was observed. At pressure 236 Torr, the reaction adduct 3-iodo-but-1-en-1-yl-peroxy [$\text{C}_2\text{H}_3\text{CI}(\text{CH}_3)\text{OO}$] radical, characterized by infrared absorption bands at 1375, 1296, 1213, 1161, 1108, 1063, 986, 934, and 885 cm^{-1} , was observed. These new spectra of $\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{I}$, $\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$, and $\text{C}_2\text{H}_3\text{CI}(\text{CH}_3)\text{OO}$ provide valuable information for the understanding of the formation mechanism of the Criegee intermediate MVKO from the source reaction of photolysis of $(\text{CH}_2\text{I})\text{HC}=\text{C}(\text{CH}_3)\text{I}$ in O_2 in laboratories.

^aV. P. Barber, S. Pandit, A. M. Green, N. Trongsiwat, P. J. Walsh, S. J. Klippenstein, M. I. Lester, *J. Am. Chem. Soc.* **140**, 10866 (2018).