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Spectroscopy, Kinetics, and Dynamics of Criegee Intermediates

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Abstract

Criegee intermediates, carbonyl oxides produced in ozonolysis of unsaturated hydrocarbons, play important roles in atmospheric chemistry. A new production scheme using photolysis of $R_2Cl_2 + O_2$ facilitated the production and direct detection of Criegee intermediates with various spectral techniques and has stimulated rapidly expanding research [1,2]. Methyl vinyl ketone oxide [MVKO, $C_2H_3C(CH_3)OO$] is an important Criegee intermediates in ozonolysis of isoprene; it is resonance stabilized by its allyl moiety. We photolyzed a mixture of 1,3-diiodo-but-2-ene [$(CH_2I)HC=C(CH_3)I$] and O_2 to produce MVKO and characterized the *syn-trans*- and *syn-cis*-conformers with transient infrared spectra recorded using a step-scan Fourier-transform spectrometer. The O–O stretching band at 948 cm^{-1} is much greater than the corresponding bands of *syn*- CH_3CHOO and $(CH_3)_2COO$ Criegee intermediates at 871 and 887 cm^{-1} , respectively, confirming a stronger O–O bond due to resonance stabilization. We observed also iodoalkenyl radical $C_2H_3C(CH_3)I$ upon photolysis of the precursor to confirm the fission of the terminal allylic C–I bond rather than the central vinylic C–I bond of the precursor. At high pressure, the adduct $C_2H_3C(CH_3)IOO$ was also observed.

On employing a quantum-cascade laser coupled with a Herriot cell, we recorded spectra of CH_2OO in regions $880\text{--}932$ and $1280\text{--}1330\text{ cm}^{-1}$ at resolution 0.002 cm^{-1} . In addition to improved rotational parameters, perturbation was observed at many rotational levels of CH_2OO [3]. Kinetic investigations based on this new experimental scheme has been applied to the reaction of CH_2OO with NO_2 [4] and HCl . If time permits, we will also discuss the emission of the products from the reaction $CH_2I + O_2$, initiated by photolysis of a mixture of $CH_2I_2 + O_2$ at 308 or 248 nm and detected by a step-scan FTIR [5]. At 308 nm, only the small- ν component of CO was observed and assigned to be from decomposition of $HCOOH$. In contrast, at 248 nm, an additional large- ν component of CO was observed and assigned to be due to secondary reaction of HCO with O_2 ; HCO is the coproduct of OH from the decomposition of $HCOOH$.

Keywords: Criegee intermediates, infrared spectroscopy, atmospheric chemistry

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