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$_2$Cl$_2$ + 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$_2$H$_3$C(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$_2$I)$_2$C=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$_3$CHOO and (CH$_3$)$_2$COO 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$_2$H$_3$C(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$_2$H$_3$C(CH$_3$)IOO was also observed.

On employing a quantum-cascade laser coupled with a Herriot cell, we recorded spectra of CH$_2$OO in regions 880–932 and 1280–1330 cm$^{-1}$ at resolution 0.002 cm$^{-1}$. In addition to improved rotational parameters, perturbation was observed at many rotational levels of CH$_2$OO [3]. Kinetic investigations based on this new experimental scheme has been applied to the reaction of CH$_2$OO with NO$_2$ [4] and HCl. If time permits, we will also discuss the emission of the products from the reaction CH$_2$I + O$_2$, initiated by photolysis of a mixture of CH$_2$I$_2$ + O$_2$ at 308 or 248 nm and detected by a step-scan FTIR [5]. At 308 nm, only the small-\nu component of CO was observed and assigned to be from decomposition of HCOOH. In contrast, at 248 nm, an additional large-\nu 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

References:


