

Spectroscopy and Reactions of Criegee Intermediates

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The Criegee intermediates, a carbonyl oxide proposed to be produced in reactions of ozone with unsaturated hydrocarbons, play important roles in formation of OH and organic acids in the atmosphere but have eluded its direct detection until recently^[1] when the reaction of $\text{CH}_2\text{I} + \text{O}_2$ was employed to produce CH_2OO . We reported previously the transient IR absorption spectrum of CH_2OO using a step-scan FTIR spectrometer^{[2], [3]}. Here, we report the IR absorption spectra of CH_2OO at resolution 0.25 cm^{-1} , showing partially rotationally resolved structures^[4]. With the analysis of the vibration-rotational spectra, we provide a definitive assignment of these bands to CH_2OO . Previously assigned ν_5 mode near 1330 cm^{-1} turned out to be $2\nu_9$ at 1233.5 cm^{-1} , and the true ν_5 mode lies at 1213.0 cm^{-1} . At high pressure ($P > 100 \text{ Torr}$) four bands near 1233.8 , 1221 , 1087 , and 923 cm^{-1} were identified as ICH_2OO , the adduct of $\text{CH}_2\text{I} + \text{O}_2$. With direct detection of both CH_2OO and ICH_2OO , we determined the pressure dependence of the yield of CH_2OO ; the value near one atmosphere is greater than previous reports and might have significant impact in atmospheric chemistry.

Methyl substitution of CH_2OO induces two conformers of CH_3CHOO and consequently complicates the infrared spectrum. We report the transient infrared spectrum of both *syn*- and *anti*- CH_3CHOO , produced from $\text{CH}_3\text{CHI} + \text{O}_2$ in a flow reactor, using a step-scan Fourier-transform spectrometer^[5]. Guided and supported by high-level full-dimensional quantum calculations, rotational contours of the four observed bands are simulated successfully and provide definitive identification of both conformers. Furthermore, *anti*- CH_3CHOO shows a reactivity greater than *syn*- CH_3CHOO toward NO/NO_2 ; at the later period of reaction, the spectrum can be simulated with only *syn*- CH_3CHOO . Without NO/NO_2 , *anti*- CH_3CHOO also decays much faster than *syn*- CH_3CHOO .

If time permits, results of IR spectra of $(\text{CH}_3)_2\text{CHOO}$ and reaction products of $\text{CH}_2\text{OO} + \text{SO}_2$ and $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ will also be presented.

References

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