INFRARED IDENTIFICATION OF THE CRIEGEE INTERMEDIATE $(CH_3)_2COO$

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The Criegee intermediates are carbonyl oxides that play critical roles in ozonolysis of alkenes in the atmosphere. We reported previously the mid-infrared spectra of the simplest Criegee intermediate CH_2OO.[a, b] and the methyl-substituted intermediate CH_3CHOO.[c] Here we report the transient infrared spectrum of $(CH_3)_2COO$, produced on UV photolysis of a mixture of $(CH_3)_2CI_2$, N_2, and O_2 in a flow reactor, using a step-scan Fourier-transform spectrometer. Guided by results of quantum-chemical calculations, rotational contours of the four observed bands are simulated successfully and provide definitive identification of $(CH_3)_2COO$. Although all observed bands of $(CH_3)_2COO$ contain hot bands from four vibrational modes of low energy, we were able to simulate the spectra satisfactorily. Observed bands with origins near 887, 1040, 1368, and 1422 cm^{-1} agree satisfactorily with corresponding anharmonic vibrational wavenumbers at 903, 1061, 1364, and 1422 cm^{-1} predicted with the B3LYP/aug-cc-pVTZ method. Furthermore, we could also estimate the rate coefficient of the self-reaction of $(CH_3)_2COO$. The direct infrared detection of $(CH_3)_2COO$ should prove useful for future field measurements and laboratory investigations of this Criegee intermediate.

[a] Y.-T. Su, Y.-H. Huang, H. A. Witek, Y.-P. Lee, *Science* **340**, 174 (2013).

[b] Y.-H. Huang, J. Li, H. Guo, Y.-P. Lee, *J. Chem. Phys.* **142**, 214301 (2015).

[c] H.-Y. Lin, Y.-H. Huang, X. Wang, J. M. Bowman, Y. Nishimura, H. A. Witek, Y.-P. Lee, *Nat. Comm.* **6**, 7012 (2015).