INFRARED EMISSION FROM UV-IRRADIATED MIXTURES OF CH_2I_2 AND O_2 PROBED WITH A STEP-SCAN FTIR SPECTROMETER

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The Criegee intermediates, carbonyl oxides proposed by Criegee in 1949 as key intermediates in the ozonolysis of alkenes, play important roles in organic chemistry and atmospheric chemistry. The simplest Criegee intermediate is CH_2OO. In the reaction of O_3 with C_2H_4, some CH_2OO thus produced are internally excited so that they decompose to form OH, CO, CO_2, and other compounds. Recently a new scheme for production of CH_2OO in laboratories, ultra-violet (UV) irradiation of diiodomethane (CH_2I_2) in O_2, has enabled direct detection of CH_2OO with various methods and stimulated active research on Criegee intermediates. Even though $\sim 25\%$ of CH_2OO was reported to decompose at pressure smaller than 60 Torr,[a] and infrared absorption of internally excited CO and CO_2 was reported,[b] no investigation on the dynamics of the decomposition products in the reaction CH_2I + O_2 has been reported.

We employed a step-scan Fourier-transform infrared (FTIR) spectrometer to record temporally resolved emission upon irradiation of mixtures of CH_2I_2, O_2, and Ar at 248 and 308 nm. IR emission of CO, CO_2, OH, CH_2I, and H_2CO in the region $1860 - 4900\ cm^{-1}$was recorded. At total pressure 8 Torr and irradiation wavelength 248 nm, rotationally resolved lines of CO ($v \leq 11$, $J \leq 19$) in region $1860 - 2300\ cm^{-1}$were observed; the rotational distribution is Boltzmann with temperature near 300 K, but the vibrational distribution is bimodal, with two components having averaged vibrational energies of 99 and 18 kJ mol^{-1}. Emission of OH ($v \leq 3$, $J \leq 5.5$) in region $2980 - 3600\ cm^{-1}$was observed with ambient rotational distribution and average vibrational energy of 41 kJ mol^{-1}. The branching ratio of CO : OH is 60:40. Emission of highly internally excited CO_2 was also observed; its average internal energy was estimated. The effects of pressure and irradiation wavelength on the emission of these species will be discussed.

[a] W.-L. Ting, C.-H. Chang, Y.-F. Lee, H. Matsui, Y.-P. Lee, and J. J.-M. Lin, *J. Chem. Phys.* 2014, **141**, 104308.

[b] Y. T. Su, H.-Y. Lin, R. Putikam, H. Matsui, M. C. Lin, and Y. P. Lee, *Nat. Chem.* 2014, **6**, 477.