

A Theoretical Study of Ozonolysis of Ethylene

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Abstract

The classic reaction of ozone with ethylene, which produces the simplest Criegee intermediate and plays an important role in the atmosphere, has been studied using coupled-cluster calculations and modern techniques of chemical kinetics (steady-state two-dimensional master equation). The calculated results show that about 40% of nascent carbonyl oxide is cool, in excellent agreement with (indirect) experimental measurements; the remaining fraction is vibrationally hot (see Figure 1). The latter fraction of Criegee product has a short lifetime; it rapidly isomerizes to dioxirane/formic acid and then subsequently forms different products such as $\text{H}_2\text{O} + \text{CO}$, $\text{H}_2 + \text{CO}_2$, so on (see Scheme 1). The ultimate fate of cool Criegee in the atmosphere is believed to be through reaction with water dimer to form hydroxyl-methyl-hydroperoxide, HOCH_2OOH . In addition, yields of HO and HO_2 radical products are predicted to be $13 \pm 6\%$ and $17 \pm 6\%$, respectively. In the kinetic simulation, the HO radical product is produced mostly from the stepwise decomposition mechanism of primary ozonide rather than from dissociation of hot CH_2OO .

