Temperature-Dependence of the Rates of Reaction of Trifluoroacetic Acid with Criegee Intermediates

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Halogenated organic acids such as trifluoroacetic acid (TFA) form in the Earth's troposphere by oxidation of anthropogenically produced hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluoro-olefins (HFOs), and also have natural sources.[1,2] They react only slowly with hydroxyl radicals and do not photolyse at actinic wavelengths.[3] Current atmospheric models therefore incorporate surface deposition and rain-out as their main loss processes. Results of a recent kinetic study of Criegee intermediates reactions with TFA will be presented.[4] The rate coefficients for gas-phase reactions of two Criegee intermediates, formaldehyde oxide and acetone oxide, with TFA decrease with increasing temperature in the range 240 – 340 K. The rate coefficients $k(CH_2OO + TFA) = (3.4 \pm 0.3) \times 10^{-10}$ cm^3 s^{-1} and $k((CH_3)_2COO + TFA) = (6.1 \pm 0.2) \times 10^{-10}$ cm^3 s^{-1} at 294 K exceed estimates for collision-limited values, suggesting rate enhancement by capture mechanisms because of the large permanent dipole moments of the two reactants. The observed temperature dependence is attributed to competitive stabilization of a pre-reactive complex. Inclusion of these reactions in a global atmospheric and chemistry transport model shows that reaction with Criegee intermediate is the dominant sink for TFA in forested regions around the world.

Bibliography

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