



Criegee Intermediate-Carboxylic Acid Reactions, A Potential Source for Secondary Organic Aerosols in the Atmosphere

Rabi Chhantyal-Pun (1), Brandon Rotavera (2,3), Max McGillen (1), Anwar Khan (1), Arkke Eskola (2,4), Rebecca Caravan (2), Lucy Blacker (1), David Tew (1,5), David Osborn (2), Carl Percival (6), Craig Taatjes (2), Dudley Shallcross (1), and Andrew Orr-Ewing (1)

(1) School of Chemistry, University of Bristol, Bristol, UK, (2) Combustion Research Facility, Sandia National Laboratories, Livermore, USA, (3) School of Environmental, Civil, Agricultural, and Mechanical Engineering, University of Georgia, Athens, USA, (4) Department of Chemistry, University of Helsinki, Helsinki, Finland, (5) Department of Electronic Structure Theory, Max Planck Institute for Solid State Research, Stuttgart, Germany, (6) Jet Propulsion Laboratory, National Aeronautical and Space Administration, Pasadena, USA

Trace atmospheric concentrations of carboxylic acids have a potent effect upon the environment, where they modulate aqueous chemistry and perturb Earth's radiative balance.¹ Halogenated carboxylic acids are produced by the tropospheric oxidation of halocarbons, and are considered persistent pollutants because of their weak tropospheric and aqueous sinks.² However, recent studies reported rapid reactions between carboxylic acids and Criegee intermediates, which provide an efficient gas-phase removal process.^{3,4} Accordingly, absolute rate coefficients of two Criegee intermediates, CH_2OO and $(\text{CH}_3)_2\text{COO}$, with a suite of carboxylic acids (HCOOH , CH_3COOH , CClF_2COOH , $\text{CF}_3\text{CF}_2\text{COOH}$, and pyruvic acid) were measured with a view to develop a structure-activity relationship (SAR). This SAR is based upon the dipole-capture model and affords the prediction of the reactivity of any combination of Criegee intermediates and carboxylic acids. Complementary synchrotron-based photoionization mass spectrometry measurements demonstrate that these reactions produce stable adducts. For larger reactants, adducts are expected to have low vapor pressure and condense to form secondary organic aerosols (SOA). Inclusion of the Criegee intermediate reaction with formic and pinonic acids in a global atmospheric chemistry and transport model predicts peak SOA contributions of up to 0.1 and $1.0 \mu\text{g}/\text{m}^3$ in the forested regions around the world. Global models under-predict aerosol mass concentration,⁵ and inclusion of Criegee intermediate-carboxylic acid reactions should help better constrain the models.

Bibliography

1. Chebbi et al. Atmos. Environ. 1996, 30, 4233-4249
2. Burkholder et al. Chem. Rev. 2015, 115, 3704-3759
3. Welz et al. Angew. Chem. Int. Ed. 2014, 53, 4547-4550
4. Chhantyal-Pun et al. Angew. Chem. Int. Ed. 2017, 56, 9044-9047
5. Utembe et al. Atmos. Environ. 2011, 45, 1604-1614