Supporting Information
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Rate Coefficients of C1 and C2 Criegee Intermediate Reactions with Formic and Acetic Acid Near the Collision Limit: Direct Kinetics Measurements and Atmospheric Implications**
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Supplementary information

Experimental and Modeling Details

Experiment. Pulsed-laser photolysis of a diiodoalkane precursor (CH₂I₂ or CH₂CHI₂) at 351 nm or 266 nm forms α-iodoalkyl radicals, which subsequently react with O₂ and form CIs. The HCOOH or CH₃COOH reactants are introduced from dilute premixes, whose concentration is calculated accounting for dimerization.¹ MPIMS experiments (298 K and 4 Torr) used the Sandia multiplexed chemical kinetics reactor, as in previous kinetics studies of CH₂OO² and CH₃CHOO³ reactions. The reacting mixture is analyzed using time-resolved photoionization mass spectrometry with vacuum ultraviolet (VUV) photoionization. The VUV source was either a H₂ discharge (principally Lyman-a (10.2 eV)) or beamline 9.0.2 of the Advanced Light Source providing tunable synchrotron radiation. Conformer-dependent kinetics of CH₃CHOO was probed at 9.35 eV and 10.5 eV: at 9.35 eV, only the anti-conformer is ionized, whereas at 10.5 eV signal is dominated by syn-CH₃CHOO.³

Direct UV absorption probing of CH₂OO reactions with HCOOH and CH₃COOH (298 K and 5 Torr) took place in a time-resolved broadband cavity-enhanced absorption spectrometer.⁴ The apparatus consists of an uncoated slow-flow quartz reactor, integrated into a broadband optical resonator cavity, operated over the 300 – 450 nm wavelength range. Here 266-nm photolysis was chosen to reduce scattered-laser interference in the probe spectral region. A Xe arc lamp provides continuous probe radiation, and the average effective path length of the pump-probe overlap region is ~50 m over the probe wavelength range. A custom-built spectrometer (2 nm resolution (FWHM)) acquires the complete temporal evolution (120 μs resolution) of the full absorption spectrum for each laser shot, averaged for 120 - 540 shots. Transient absorption is obtained from the difference between photolysis ON and photolysis OFF spectra.

Initial number densities (in cm⁻³) for the data in Figure 1 were [O₂] = 1.0 × 10¹⁶ and [CH₂I₂] = 1.7 × 10¹³, [CH₂OO] ~ 4 × 10¹¹ or [CH₃CHI₂] = 4.0 × 10¹³, [CH₃CHOO] ~ 1 × 10¹². Initial number densities (in cm⁻³) for the data in Figure 2 were: [CH₂I₂] = 3.2 × 10¹³, [CH₂OO] ~ 5 × 10¹¹, and [O₂] = 8.2 × 10¹⁵.

Model. The STOCHEM-CRI global atmospheric model has been described in detail elsewhere.⁵ In the integrations presented here, reactions between the CIs CH₂OO, CH₃CHOO and larger CIs (≥ C3) with organic acids have been included, although for simplicity only the HCOOH fields are presented. Results are calculated for a base case⁶ that treats CI reactions with acids as negligible (case 1) and two scenarios using the present rate coefficients and two assumptions for reactions of larger CIs: Case 2, \( k(\text{other CI} + \text{HCOOH}) = 1.1 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \); Case 3, \( k(\text{other CI} + \text{HCOOH}) = 2.5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \) (see Table S1).
Table S1: Rate coefficients for CI reactions in the model scenarios

|                          | Base scenario (case 1) | Case 2       | Case 3       |
|--------------------------|------------------------|--------------|--------------|
| CI + H₂O                 | $1 \times 10^{-16}$ cm³ s⁻¹ | $1 \times 10^{-16}$ cm³ s⁻¹ | $1 \times 10^{-16}$ cm³ s⁻¹ |
| CI unimolecular loss     | 150 s⁻¹                | 150 s⁻¹      | 150 s⁻¹      |
| CH₂OO + acids            | –                      | $1.1 \times 10^{-10}$ cm³ s⁻¹ | $1.1 \times 10^{-10}$ cm³ s⁻¹ |
| CH₃COO + acids           | –                      | $2.5 \times 10^{-10}$ cm³ s⁻¹ | $2.5 \times 10^{-10}$ cm³ s⁻¹ |
| Other CI + acids         | –                      | $1.1 \times 10^{-10}$ cm³ s⁻¹ | $2.5 \times 10^{-10}$ cm³ s⁻¹ |
**Table S2:** Percentage loss rates for Criegee intermediates via reactions (7-9) using $k_8 = 100$ s$^{-1}$ and a variety of other assumed rate coefficients, at two temperatures and two [H$_2$O].

| Temp./K | $k$ / cm$^3$ molecule$^{-1}$ s$^{-1}$ | RH | [H$_2$O] cm$^3$ | [Acid] ppb | % loss rxn. 7 | % loss rxn. 8 | % loss rxn. 9 |
|---------|--------------------------------------|----|----------------|-------------|---------------|---------------|---------------|
| 283     | $k_7 = 1 \times 10^{-16}$ $k_9 = 1 \times 10^{-10}$ | 50% | $1.57 \times 10^{-1}$ | 1 | 13.3 | 84.6 | 2.1 |
|         | $k_7 = 1 \times 10^{-17}$ $k_9 = 1 \times 10^{-10}$ | 50% | $1.57 \times 10^{-1}$ | 1 | 1.5 | 96.1 | 2.4 |
|         | $k_7 = 1 \times 10^{-16}$ $k_9 = 1 \times 10^{-10}$ | 100% | $3.14 \times 10^{-1}$ | 1 | 23.5 | 74.7 | 1.8 |
|         | $k_7 = 1 \times 10^{-17}$ $k_9 = 1 \times 10^{-10}$ | 100% | $3.14 \times 10^{-1}$ | 1 | 3.0 | 94.7 | 2.3 |
| 298     | $k_7 = 1 \times 10^{-16}$ $k_9 = 1 \times 10^{-10}$ | 50% | $3.85 \times 10^{-1}$ | 1 | 27.3 | 70.9 | 1.8 |
|         | $k_7 = 1 \times 10^{-17}$ $k_9 = 1 \times 10^{-10}$ | 50% | $3.85 \times 10^{-1}$ | 1 | 3.6 | 94.0 | 2.4 |
|         | $k_7 = 1 \times 10^{-16}$ $k_9 = 1 \times 10^{-10}$ | 100% | $7.7 \times 10^{-1}$ | 1 | 42.9 | 55.7 | 1.4 |
|         | $k_7 = 1 \times 10^{-17}$ $k_9 = 1 \times 10^{-10}$ | 100% | $7.7 \times 10^{-1}$ | 1 | 7.0 | 90.7 | 2.3 |
|         | $k_7 = 1 \times 10^{-16}$ $k_9 = 1 \times 10^{-10}$ | 100% | $7.7 \times 10^{-1}$ | 10 | 40.6 | 52.8 | 6.6 |
|         | $k_7 = 1 \times 10^{-17}$ $k_9 = 5 \times 10^{-10}$ | 100% | $7.7 \times 10^{-1}$ | 10 | 6.4 | 83.2 | 10.4 |

**Table S3.** A summary of the calculated vapor pressures for assumed products of CI reactions with organic acids. Vapor pressures were calculated using the Nannoolal et al.\textsuperscript{[6]} vapor pressure estimation method. Vapor pressures above 4.0 Pa will not partition to the aerosol phase.\textsuperscript{[7]}

| R group (carbon chain length) | Adduct product from RCOOH + CH$_2$O | Adduct product from RCOOH + CH$_3$CHO | Ring opening product from RCOOH + CH$_2$O | Ring opening product from RCOOH + CH$_3$CHO |
|------------------------------|-------------------------------------|----------------------------------------|---------------------------------------------|--------------------------------------------|
| 0                            | 7170.0                              | 5281.6                                  | 214.3                                      | 132.1                                      |
| 1                            | 3639.1                              | 2691.5                                  | 126.2                                      | 76.5                                       |
| 2                            | 1067.4                              | 815.0                                   | 39.5                                       | 24.1                                       |
| 3                            | 321.6                               | 252.9                                   | 12.5                                       | 7.7                                        |
| 4                            | 99.2                                | 80.1                                    | 4.0                                        | 2.5                                        |
| 5                            | 31.2                                | 25.8                                    | 1.3                                        | 0.8                                        |
| 6                            | 10.0                                | 8.4                                     | 0.4                                        | 0.3                                        |
| 7                            | 3.2                                 | 2.8                                     | 0.1                                        | 0.1                                        |
Products of the CH$_2$OO + HCOOH reaction

The synchrotron photoionization spectra show product species that produce ions at $m/z = 31$ (CH$_3$O, appearance energy (AE) ~ 10.8 eV) and $m/z = 64$ (CH$_4$O$_2$, AE ~ 10.3 eV). These product signals were observed only when HCOOH was present. No product signal appears at the parent mass of a CH$_2$OO-HCOOH adduct ($m/z = 92$) or FAN ($m/z = 74$). Because the photoionization spectra of HPMF and FAN are unknown, the experiments do not necessarily rule out their formation, particularly if low-lying dissociative ionization channels exist. CBS-QB3 calculations$^8$ using Gaussian09$^9$ place the adiabatic ionization energy (AIE) of HPMF at 10.22 eV. As this energy is lower than the AEs of the $m/z = 31$ and $m/z = 64$ signals, it is possible that the $m/z = 31$ and $m/z = 64$ cations arise from dissociative ionization of HPMF. The chemical formula of FAN (C$_2$H$_2$O$_3$) rules out formation of the $m/z = 31$ (CH$_3$O) and $m/z = 64$ (CH$_4$O$_3$) signals via dissociative ionization of FAN; no evidence of FAN formation is observed under the present conditions.

The calculated AIE of hydroperoxymethanol (HPM, HOOCH$_2$OH), another plausible product at $m/z = 64$, is 9.90 eV, lower than the 10.3 eV observed AE. However, the HPM cation has an elongated C–OOH bond (1.61 Å vs 1.40 Å in the neutral), which could cause the apparent onset to be higher than the calculated AIE. Moreover, the thermodynamic appearance energy is 10.76 eV for the CH$_2$OH fragment ion from HPM (corresponding to HO$_2$ loss), similar to the ~ 10.8 eV onset observed for the $m/z = 31$ product signal. As a consequence, the observed product spectrum is consistent with HPM product as well as with a stabilized CH$_2$OO-HCOOH adduct, possibly HPMF. Further analysis of the products from the CH$_2$OO + HCOOH reaction would require the photoionization spectra for parent and fragment ions of potential products, which is outside the scope of the present study.
Figure S1: Kinetics results from the MPIMS experiments for C.I. reactions with acetic acid. Dependence of the decay constant of CH\textsubscript{2}OO (black; taken with a H\textsubscript{2} discharge), anti-CH\textsubscript{3}CHOO (blue; taken using 9.35 eV synchrotron radiation), and syn-CH\textsubscript{3}CHOO (red; taken using 10.5 eV synchrotron radiation) on [CH\textsubscript{3}COOH]. The solid lines are fits to the experimental data. The slopes are the second order rate coefficients for the C.I. + acetic acid reactions. Error bars shown are the 1\textsigma uncertainties from the fits of the experimental time profiles. Initial number densities (in cm\textsuperscript{-3}) were [O\textsubscript{2}] = 1.0 \times 10\textsuperscript{16} and [CH\textsubscript{2}I\textsubscript{2}] = 1.6 \times 10\textsuperscript{13}, [CH\textsubscript{2}OO] \sim 4 \times 10\textsuperscript{11} or [CH\textsubscript{3}CHI\textsubscript{2}] = 3.0 \times 10\textsuperscript{13}, [CH\textsubscript{3}CHOO] \sim 7 \times 10\textsuperscript{11}.
Figure S2: Kinetics results from the UV absorption experiments for the CH$_2$OO + HCOOH reaction at 295 K and 5.1 Torr: Dependence of the decay constant of CH$_2$OO on [HCOOH] (dots). The solid line is a fit to the experimental data with the slope as the second order rate coefficient for the CH$_2$OO + CH$_3$COOH reaction. Error bars shown are 15% of the nominal value as estimated from repeated experiments at identical conditions. Initial number densities (in cm$^{-3}$) were: [CH$_2$I$_2$] = 3.2 × 10$^{13}$, [CH$_2$OO] = 5 × 10$^{11}$, and [O$_2$] = 8.6 × 10$^{15}$. 

$$k_{\text{fit}} = (1.10 \pm 0.14) \times 10^{-10} \text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$$
Figure S3. Absolute modeled mixing ratios for formic acid under the three scenarios (Table S1).
Supplementary References

[1] A. Winkler, P. Hess, *J. Am. Chem. Soc.* 1994, **116**, 9233-9240.

[2] a) C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, D. L. Osborn, E. P. F. Lee, J. M. Dyke, D. W. K. Mok, D. E. Shallcross, C. J. Percival, *Phys. Chem. Chem. Phys.* **2012**; b) O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross, C. A. Taatjes, *Science* **2012**, 335, 204-207.

[3] C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke, D. K. W. Mok, D. L. Osborn, C. J. Percival, *Science* **2013**, 340, 171-180.

[4] a) L. Sheps, *J. Phys. Chem. Lett.* 2013, 4201-4205; b) L. Sheps, D. W. Chandler, Sandia National Laboratories, 2013, p. 26.

[5] a) A. T. Archibald, M. C. Cooke, S. R. Utembe, D. E. Shallcross, R. G. Derwent, M. E. Jenkin, *Atmos. Chem. Phys.* **2010**, **10**, 8097-8118; b) C. Percival, O. Welz, A. J. Eskola, J. D. Savee, D. L. Osborn, D. O. Topping, D. Lowe, S. Utembe, A. Bacak, G. McFiggans, M. Cooke, A. T. Archibald, M. Jenkin, R. G. Derwent, I. Riipinen, D. Mok, E. P. F. Lee, J. Dyke, C. A. Taatjes, D. E. Shallcross, *Faraday Discuss.* **2013**, **165**, 45-73; c) S. R. Utembe, M.C.Cooke, A. T. Archibald, M. E. Jenkin, R. G. Derwent, D. E. Shallcross, *Atmos. Environ.* **2010**, **44**, 1609-1622.

[6] a) Y. Nannoolal, J. Rarey, D. Ramjugernath, *Fluid Phase Equilib.* **2008**, **269**, 117-133; b) Y. Nannoolal, J. Rarey, D. Ramjugernath, W. Cordes, *Fluid Phase Equilib.* **2004**, 226, 45-63.

[7] a) M. H. Barley, G. McFiggans, *Atmos. Chem. Phys.* **2010**, **10**, 749-767; b) A. M. Booth, M. H. Barley, D. O. Topping, G. Mcfiggans, A. Garforth, C. J. Percival, *Atmos. Chem. Phys.* **2010**, **10**, 4879-4892.

[8] a) J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **1999**, **110**, 2822-2827; b) J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, **112**, 6532-6542.

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Revision A.1 ed., Gaussian, Inc, Wallingford CT, 2009.