SUPPLEMENTARY MATERIALS
FEBRUARY 21, 2023

Reactions with Criegee Intermediates Are the Dominant Gas-Phase Sink for Formyl Fluoride in the Atmosphere

Yu Xia,[a] Bo Long,[a]* Ai Liu,[a] Donald G. Truhlar[b]*

[a]College of Materials Science and Engineering, Guizhou Minzu University, Guiyang 550025, China

[b]Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, USA

TABLE OF CONTENTS

* Corresponding author email addresses:
wwwltcommon@sina.com (Bo Long)
truhlar@umn.edu (Donald G. Truhlar)

Note on units

In the article and SI, all the energies and enthalpies are in kcal/mol (except for Table S16 which uses hartrees), all the frequencies are in cm^{-1}, all coordinates are in Å and deg, all concentrations are in molecules/cm^3, and all rate constants are in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.

Software

All the electronic structure calculations were performed using the *Gaussian 16*[1] and *MN-GFM*[2] software packages. The coupled cluster methods were performed by *Molpro 2019*[3] and *MRCC*.[4-5] Rate constants were calculated using *Polyrate 2017B*[6] and *Gaussrate 2017B*.[7]

Electronic partition functions

The rate constants include the ratio of electronic partition functions

$$\frac{g_{\mathrm{TS}}}{g_{\mathrm{FCHO}}\, g_{\mathrm{OH\ or\ Criegee\ intermediate}}}.$$

where TS denotes the transition state.

For the purpose of computing electronic partition functions, we used 0.4 kcal/mol for the energy difference of the two spin-orbit-split states of OH($^2\Pi$). For the other species, we take the electronic partition function to be the electronic degeneracy of the ground state. These treatments yield:

$g_{\mathrm{TS}} = 2$ for the reaction with OH and 1 for reactions of Criegee intermediates

$g_{\mathrm{FCHO}} = 1$

$g_{\mathrm{OH}} \approx 2 + 2\exp[-(0.4\ \mathrm{kcal/mol})/RT]$

$g_{\mathrm{Criegee\ intermediate}} = 1$

Computational details of the DL-MS-CVT/SCT calculations

The DL-MS-CVT rate constant is

$$k^{\mathrm{DL}}_{\mathrm{MS-CVT/SCT}}(T) = F^{\mathrm{MS-T}}_{\mathrm{fwd}} k^{\mathrm{DL}}_{\mathrm{SS-CVT/SCT}}(T) \quad (1)$$

where the single-structural CVT/SCT rate constant is defined as

$$k^{\mathrm{DL}}_{\mathrm{SS-CVT/SCT}}(T) = \kappa^{LL}_{SCT} \Gamma^{\mathrm{LL}}_{\mathrm{CVT}} k^{\mathrm{HL}}_{\mathrm{SS-TST}}(T) \quad (2)$$

in which κ^{LL}_{SCT} and $\Gamma^{\mathrm{LL}}_{\mathrm{CVT}}$ are the tunneling and recrossing transmission coefficients calculated by using canonical vibrational transition theory with small-curvature at the lower level (LL), and $k^{\mathrm{HL}}_{\mathrm{SS-TST}}$ is the rate constant obtained by using conventional transition state theory at the higher level (HL). The multistructural and torsional anharmonicity factor[8] of the forward reaction is defined as

$$F^{\mathrm{MS-T}}_{\mathrm{fwd}} = \frac{F^{\mathrm{MS-T}}(\mathrm{TS})}{F^{\mathrm{MS-T}}(\mathrm{R})} = \frac{Q^{\ddagger-\mathrm{MS-T}}/Q^{\ddagger-\mathrm{SSHO}}}{Q^{\mathrm{R-MS-T}}/Q^{\mathrm{R-SSHO}}} \quad (S3)$$

in which $Q^{\ddagger-\mathrm{MS-T}}$ and $Q^{\mathrm{R-MS-T}}$ are the multistructural partition functions for the saddle points and the reactants, respectively, and $Q^{\ddagger-\mathrm{SSHO}}$ and $Q^{\mathrm{R-SSHO}}$ are the single-structural harmonic-oscillator rovibrational partition functions for the lowest-energy saddle point and the reactant, respectively.

Details of the variable-reaction-coordinate rate calculations for the *anti*-CH_3CHOO + FCHO reaction

In eq 3 of the main text, k_{loose} denotes the rate constant of the formation of the precursor complex from the reactants. This was calculated by using variable-reaction-coordinate variational transition state theory (VRC-VTST).[9-11] We used two pivot points to produce a single-faceted dividing surface. One pivot point is located at a distance *d* from the center of mass (COM) of *anti*-CH_3CHOO, where the vector connecting the pivot point with *anti*-CH_3CHOO's COM is perpendicular to the *anti*-CH_3CHOO plane, and the other pivot point is located at a distance *d* from the COM of FCHO, where the vector connecting the pivot point with FCHO's COM is perpendicular to FCHO plane. The lengths of these vectors were fixed at 0.05 Å because our investigations showed that the best results for the CH_2OO + $HCHO/(H_2O)_2$ reaction were obtained with d = 0.05 Å.[12]

The reaction coordinate *s* is the distance between a pivot point on one reactant and a pivot point on the other reactant. The distance *s* between pivot points was varied from 4.3 to 8.4 Å with a 0.1 Å grid increment to find the optimum value. We used 1400 configurations for sampling the single-faceted dividing surfaces.

Computational details for the FCHO + OH reaction

The energies calculated for the FCHO + OH reaction are in Figure A1. The rate constant was calculated by the dual-level strategy[13-18] that uses W3X-L[19] //CCSD(T)-F12a[20]/jun-cc-pVDZ[21] (called W3X-L//junD for short) as the higher-level theory for conventional transition state theory without tunneling and that uses M08-HX/MG3S[22-23] as the lower-level theory for direct dynamics calculations of the recrossing transmission coefficient and the tunneling transmission coefficient by using canonical variational transition state theory with small curvature tunneling. The calculations for this reaction are single-structural.

Table S1. Abbreviations for the theoretical methods and basis sets used in the article[a]

Method	Ref.	Explanation
Electronic structure methods		
M11-L	[24]	Minnesota 2011 local density functional
CCSD(T)	[25]	Coupled cluster theory with single and double excitations and noniterative connected triple excitations
CCSD(T)-F12a	[20]	CCSD(T) with F12a explicit correlation
CCSDT(Q)	[26]	Coupled cluster theory with single, double, and triple excitations and noniterative connected quadruple excitations
W2X	[27]	Cost-effective approximation to CCSD(T)/CBS
MW2-F12	[28]	Cost-effective approximation to CCSD(T)/CBS with larger basis sets
W3X-L	[19]	Cost-effective approximation to CCSDT(Q)/CBS with the larger basis sets
MW3X-L	[15]	MW2-F12 plus beyond-CCSD(T) contributions from W3X-L
Basis sets		
MG3S	[23]	Modified G3 semidiffuse basis, which is the same as 6-311+G (2df, 2p) for H, C, O, and F (although not for all elements)
cc-pVTZ-F12	[29]	correlation-consistent polarized valence double zeta basis modified for use in F12 calculations
cc-pVDZ-F12	[29]	correlation-consistent polarized valence double zeta basis modified for use in F12 calculations
jun′-cc-pVDZ	new	Tables S1, S2, and S3 include some calculations labeled CCSD(T)-F12a/jun′-cc-pVDZ. These represent an improved way to carry out CCSD(T)-F12b calculations with the jun-cc-pVDZ basis set. The original CCSD(T)-F12b/jun-cc-pVTZ calculations were performed using “cc-pVTZ/JKfit”, “cc-VTZ/MP2fit”, and “cc-pVTZ/OptR1” as auxiliary basis sets. We define CCSD(T)-F12b/jun′-cc-pVTZ as a calculation using “aug-cc-pVDZ/JKfit”, “aug-cc-pVDZ/MP2fit”, and “aug-cc-pVDZ/OptR1” as auxiliary basis sets. The cost of CCSD(T)-F12b/jun′-cc-pVDZ is almost equal to that of CCSD(T)-F12a/jun-cc-pVDZ.
jun-cc-pVDZ	[21]	correlation-consistent polarized valence double zeta basis augmented with diffuse functions at the jun level
CBS	[30]	complete basis set (limit obtained by extrapolation)
Kinetics methods		
CVT	[31]	Canonical variational transition state theory
SCT	[32]	Small-curvature tunneling

[a]We use the standard notation by which A/B denotes geometries and energies calculated by method A and basis set B, and A/B//C/E denotes single-point energies by A/B at geometries optimized by C/E. For composite methods, A/B is replaced by the name of the composite method.

Table S2. The scale factors for vibrational frequencies

Method	Method abbreviation	Factor[33]
CCSD(T)-F12a/cc-pVTZ-F12	T	0.984
CCSD(T)-F12a/cc-pVDZ-F12	D	0.983
DF-CCSD(T)-F12b/jun-cc-pVDZ	junD	0.981
DF-CCSD(T)-F12b/jun′-cc-pVDZ	jun′D	0.981
M11-L/MG3S		0.985
M08-HX/MG3S		0.973

CH_2OO reaction

Table S3. Mean unsigned deviations of complexation energies, barrier heights, and reaction energies for the CH_2OO + FCHO reaction (in kcal/mol)

Methods	ΔE		$V^{\ddagger}$		ΔE		
	C1	C2	TS1	TS2	P1	P2	MUD-G
W2X//T	-8.19	-7.68	-6.32	-4.68	-48.08	-49.72	0.00
W2X//D	-8.22	-7.72	-6.28	-4.63	-48.12	-49.78	0.04
W2X//jun′D	-8.15	-7.65	-6.29	-4.64	-48.15	-49.82	0.05
W2X//junD	-8.14	-7.63	-6.29	-4.63	-48.16	-49.82	0.06

[a]ΔE is a reaction energy, $V^{\ddagger}$ is a barrier height. We use MUD-G for mean unsigned deviations due to geometry changes, so as not to confuse them with mean unsigned deviations (MUDs) of energies due to the method chosen for single-point energies.

[b]CX, TSX, and PX denote precursor complexes, transition states, and products of the CH_2OO + FCHO reaction.

Table S4. Mean unsigned deviations of relative zero-point vibrational energies for the CH_2OO + FCHO reaction (in kcal/mol)

Methods	ΔE_{ZPE}		$\Delta E_{ZPE}^{\ddagger}$		ΔE_{ZPE}		
	C1	C2	TS1	TS2	P1	P2	MUD-GF
T	1.73	1.72	2.50	2.55	5.69	5.76	0.00
D	1.66	1.48	2.49	2.53	5.67	5.74	0.06
junD	1.57	1.54	2.50	2.56	5.64	5.74	0.07
jun′D	1.58	1.45	2.51	2.57	5.67	5.77	0.08

[a]$\Delta E_{ZPE}^{\ddagger}$ and ΔE_{ZPE} are changes in zero-point vibrational energy in going from reactants to the transition state and the product, respectively. We use MUD-GF for mean unsigned deviations due to geometry and frequency changes, so as not to confuse them with mean unsigned deviations (MUDs) of energies due to the method chosen for single-point energies.

[b]The CX, TSX and PX denote precursor complexes, transition states, and products of the CH_2OO + FCHO reaction.

Table S5. The enthalpies of activation and reaction enthalpies for the CH_2OO + FCHO reaction at 0 K (in kcal/mol)

Methods	ΔH_0		$\Delta H_0^{\ddagger}$		ΔH_0		
	C1	C2	TS1	TS2	P1	P2	MUD-GF
W2X//T	-6.46	-5.97	-3.83	-2.12	-42.39	-43.95	0.00
W2X//D	-6.56	-6.23	-3.80	-2.09	-42.45	-44.03	0.09
W2X//jun′D	-6.57	-6.21	-3.79	-2.07	-42.48	-44.05	0.10
W2X//junD	-6.57	-6.09	-3.79	-2.07	-42.52	-44.08	0.10

[a]$\Delta H_0^{\ddagger}$ is the enthalpy of activations at 0 K and is given by $V^{\ddagger} + \Delta E_{ZPE}^{\ddagger}$, and ΔH_0 is the enthalpy of reaction at 0 K and is given by $\Delta E + \Delta E_{ZPE}$. We use MUD-GF for mean unsigned deviations due to geometry and frequency changes, so as not to confuse them with mean unsigned deviations (MUDs) of energies due to the method chosen for single-point energies.

[b]The CX, TSX and PX denote precursor complexes, transition states and products of the CH_2OO + FCHO reaction.

CH_2OO, *anti*-CH_3CHOO, and *syn*-CH_3CHOO reactions

Table S6. The enthalpies of activation (in kcal/mol) at 0 K for the reactions of FCHO with CH_2OO, *anti*-CH_3CHOO, and *syn*-CH_3CHOO

Method	$\Delta H_0^{\ddagger}$						
	TS1	TS2	a-TS1	a-TS2	s-TS1	s-TS2	MUD
MW3X-L//junD	-3.04	-1.26	-6.19	-4.67	-0.04	1.77	0.00
W3X-L//junD	-3.23	-1.46	-6.42	-4.90	-0.32	1.5	0.23
MW2-F12//junD	-3.59	-1.87	-6.79	-5.32	-0.59	1.19	0.59
M11-L/MG3S	-3.89	-2.02	-6.83	-5.31	-0.81	0.75	0.78
W2X//jun′D	-3.79	-2.07	-7.00	-5.53	-0.85	0.95	0.81
W2X/junD	-3.79	-2.07	-7.01	-5.54	-0.87	0.92	0.82

[a]$\Delta H_0^{\ddagger}$ is the enthalpy of activation at 0 K and is given by $V^{\ddagger} + \Delta E_{ZPE}^{\ddagger}$.

[b]TS1, TS2, a-TS1, a-TS2, s-TS1, and s-TS2 denote transition states of the reactions of FCHO with CH_2OO, *anti*-CH_3CHOO, and *syn*-CH_3CHOO, in which the prefixes “a” and “s” denote the “*anti*” and “*syn*” isomer, respectively.

Table S7. HPL rate constants (cm^3 $molecule^{-1}$ s^{-1}) and transmission coefficients (unitless) for the FCHO + CH_2OO reaction.

T/K	k_{TST}^{HL} [a]	Γ_{CVT}^{LL} [b]	κ_{SCT}^{LL} [c]	$k_{CVT/SCT}^{DL}$ [d]	F_{fwd}^{MS-T} [e]	$k_{1\,MS-CVT/SCT}^{DL}$ [f]
190	4.79E-12	9.21E-01	1.32E+00	5.80E-12	0.80	4.67E-12
200	3.10E-12	9.20E-01	1.28E+00	3.65E-12	0.81	2.95E-12
210	2.10E-12	9.19E-01	1.25E+00	2.41E-12	0.81	1.96E-12
220	1.48E-12	9.18E-01	1.22E+00	1.66E-12	0.81	1.35E-12
230	1.08E-12	9.17E-01	1.20E+00	1.18E-12	0.82	9.69E-13
240	8.05E-13	9.15E-01	1.18E+00	8.72E-13	0.82	7.18E-13
250	6.18E-13	9.14E-01	1.17E+00	6.60E-13	0.83	5.46E-13
260	4.86E-13	9.12E-01	1.15E+00	5.12E-13	0.83	4.25E-13
270	3.90E-13	9.11E-01	1.14E+00	4.05E-13	0.84	3.39E-13
280	3.18E-13	9.09E-01	1.13E+00	3.27E-13	0.84	2.75E-13
290	2.64E-13	9.07E-01	1.12E+00	2.68E-13	0.85	2.27E-13
298	2.30E-13	9.05E-01	1.11E+00	2.32E-13	0.85	1.97E-13
300	2.22E-13	9.05E-01	1.11E+00	2.24E-13	0.85	1.90E-13
310	1.90E-13	9.03E-01	1.11E+00	1.89E-13	0.86	1.62E-13
320	1.64E-13	9.01E-01	1.10E+00	1.62E-13	0.86	1.39E-13
330	1.43E-13	8.99E-01	1.09E+00	1.40E-13	0.87	1.21E-13
340	1.26E-13	8.97E-01	1.09E+00	1.23E-13	0.87	1.07E-13
350	1.12E-13	8.95E-01	1.08E+00	1.08E-13	0.88	9.49E-14

[a] k_{TST}^{HL} is the higher-level calculation by conventional transition state theory without a transmission coefficient.

[b] Γ_{CVT}^{LL} is the lower-level recrossing transmission coefficient, which equals $k_{CVT}^{LL}/k_{TST}^{LL}$.

[c] κ_{SCT}^{LL} is the lower-level tunneling transmission coefficient calculated by the small-curvature tunneling approximation.

[d] The nonfinal high-pressure-limit (HPL) rate constant $k_{CVT/SCT}^{DL}$ is calculated by the dual-level CVT/SCT method, by which it equals k_{TST}^{HL} κ_{SCT}^{LL} Γ_{CVT}^{LL}, where HL is MW3X-L//T, and LL is M11-L/MG3S for TS1 of the CH_2OO + FCHO reaction.

[e] F_{fwd}^{MS-T} is the multistructural and torsional anharmonicity factor of the CH_2OO + FCHO forward reaction.

[d] $k_{1\,MS-CVT/SCT}^{DL}$ is the rate constant of CH_2OO + FCHO reaction.

Table S8. HPL rate constants (cm^3 $molecule^{-1}$ s^{-1}) and transmission coefficients (unitless) for the *anti*-CH_3CHOO + FCHO reaction

T/K	$k_{\mathrm{TST}}^{\mathrm{HL}}$ [a]	$\Gamma_{\mathrm{CVT}}^{\mathrm{LL}}$ [b]	$\kappa_{\mathrm{SCT}}^{\mathrm{LL}}$ [c]	$k_{\mathrm{CVT/SCT}}^{\mathrm{DL}}$ [d]	$k_{\text{VRC-TST}}$ [e]	$F_{\mathrm{fwd}}^{\mathrm{MS-T}}$ [f]	$k_{2_{\mathrm{CUS}}}^{\mathrm{DL}}$ [g]
190	1.15E-08	9.09E-01	1.19E+00	1.24E-08	8.69E-10	0.63	7.82E-10
200	4.97E-09	9.08E-01	1.17E+00	5.26E-09	8.48E-10	0.64	6.76E-10
210	2.34E-09	9.06E-01	1.15E+00	2.44E-09	8.28E-10	0.64	5.41E-10
220	1.18E-09	9.05E-01	1.14E+00	1.22E-09	8.08E-10	0.64	3.97E-10
230	6.37E-10	9.04E-01	1.12E+00	6.47E-10	7.72E-10	0.65	2.71E-10
240	3.62E-10	9.02E-01	1.11E+00	3.63E-10	7.41E-10	0.65	1.79E-10
250	2.16E-10	9.00E-01	1.10E+00	2.14E-10	7.15E-10	0.65	1.17E-10
260	1.34E-10	8.98E-01	1.09E+00	1.32E-10	6.93E-10	0.66	7.72E-11
270	8.68E-11	8.96E-01	1.09E+00	8.46E-11	6.73E-10	0.66	5.16E-11
280	5.80E-11	8.94E-01	1.08E+00	5.61E-11	6.56E-10	0.67	3.53E-11
290	3.99E-11	8.92E-01	1.08E+00	3.83E-11	6.42E-10	0.67	2.46E-11
298	3.02E-11	8.90E-01	1.07E+00	2.88E-11	6.31E-10	0.67	1.88E-11
300	2.83E-11	8.90E-01	1.07E+00	2.69E-11	6.29E-10	0.67	1.76E-11
310	2.05E-11	8.88E-01	1.07E+00	1.94E-11	6.17E-10	0.68	1.28E-11
320	1.52E-11	8.85E-01	1.06E+00	1.43E-11	6.07E-10	0.68	9.57E-12
330	1.15E-11	8.83E-01	1.06E+00	1.07E-11	5.98E-10	0.69	7.26E-12
340	8.84E-12	8.81E-01	1.05E+00	8.21E-12	5.91E-10	0.69	5.60E-12
350	6.93E-12	8.78E-01	1.05E+00	6.39E-12	5.83E-10	0.69	4.40E-12

[a] $k_{\mathrm{TST}}^{\mathrm{HL}}$ is the higher-level calculation by conventional transition state theory without a transmission coefficient.

[b] $\Gamma_{\mathrm{CVT}}^{\mathrm{LL}}$ is the lower-level recrossing transmission coefficient, which equals $k_{\mathrm{CVT}}^{\mathrm{LL}}/k_{\mathrm{TST}}^{\mathrm{LL}}$.

[c] $\kappa_{\mathrm{SCT}}^{\mathrm{LL}}$ is the lower-level tunneling transmission coefficient calculated by the small-curvature tunneling approximation.

[d] The nonfinal HPL rate constant $k_{\mathrm{CVT/SCT}}^{\mathrm{DL}}$ is calculated by the dual-level CVT/SCT method.

Therefore $k_{\mathrm{a-TS1}}^{\mathrm{DL}}$ equals $k_{\mathrm{TST}}^{\mathrm{L1}}\ \kappa_{\mathrm{SCT}}^{\mathrm{L2}}\ \Gamma_{\mathrm{CVT}}^{\mathrm{L2}}$, where L1 is MW3X-L//junD, and L2 is M11-L/MG3S for transition state 1 of the *anti*-CH_3CHOO + FCHO reaction.

[e] $k_{\text{VRC-TST}}$ is calculated by M11-L/MG3S for the loose transition state of the *anti*-CH_3CHOO + FCHO reaction.

[f] $F_{\mathrm{fwd}}^{\mathrm{MS-T}}$ is the multistructural and torsional anharmonicity factor of *anti*-CH_3CHOO + FCHO forward reaction.

[g] $k_{2_{\mathrm{CUS}}}^{\mathrm{DL}}$ is the rate constant of *anti*-CH_3CHOO + FCHO reaction, given by

$$k_{2_{\mathrm{CUS}}}^{\mathrm{DL}} = (F_{\mathrm{fwd}}^{\mathrm{MS-T}}\ k_{\mathrm{CVT/SCT}}^{\mathrm{DL}}\ k_{\text{VRC-TST}})/(F_{\mathrm{fwd}}^{\mathrm{MS-T}}\ k_{\mathrm{CVT/SCT}}^{\mathrm{DL}} + k_{\text{VRC-TST}}).$$

Table S9. HPL rate constants (cm^3 $molecule^{-1}$ s^{-1}) and transmission coefficients (unitless) for the *syn*-CH_3CHOO + FCHO reaction

T/K	k_{TST}^{HL} [a]	Γ_{CVT}^{LL} [b]	κ_{SCT}^{LL} [c]	$k_{CVT/SCT}^{DL}$ [d]	F_{fwd}^{MS-T} [e]	$k_{3\,MS-CVT/SCT}^{DL}$ [f]
190	5.37E-16	8.97E-01	1.29E+00	6.19E-16	0.91	5.61E-16
200	5.26E-16	8.96E-01	1.25E+00	5.91E-16	0.89	5.25E-16
210	5.18E-16	8.94E-01	1.23E+00	5.68E-16	0.87	4.96E-16
220	5.12E-16	8.93E-01	1.20E+00	5.50E-16	0.86	4.72E-16
230	5.09E-16	8.91E-01	1.18E+00	5.36E-16	0.84	4.53E-16
240	5.07E-16	8.89E-01	1.17E+00	5.26E-16	0.83	4.37E-16
250	5.07E-16	8.86E-01	1.15E+00	5.18E-16	0.82	4.23E-16
260	5.08E-16	8.84E-01	1.14E+00	5.12E-16	0.81	4.12E-16
270	5.10E-16	8.82E-01	1.13E+00	5.08E-16	0.79	4.03E-16
280	5.14E-16	8.79E-01	1.12E+00	5.05E-16	0.78	3.95E-16
290	5.18E-16	8.76E-01	1.11E+00	5.04E-16	0.77	3.89E-16
298	5.22E-16	8.74E-01	1.10E+00	5.04E-16	0.76	3.85E-16
300	5.23E-16	8.74E-01	1.10E+00	5.04E-16	0.76	3.84E-16
310	5.30E-16	8.71E-01	1.10E+00	5.06E-16	0.75	3.79E-16
320	5.37E-16	8.68E-01	1.09E+00	5.08E-16	0.74	3.76E-16
330	5.44E-16	8.65E-01	1.08E+00	5.11E-16	0.73	3.73E-16
340	5.53E-16	8.62E-01	1.08E+00	5.14E-16	0.72	3.71E-16
350	5.62E-16	8.59E-01	1.07E+00	5.19E-16	0.71	3.70E-16

[a] k_{TST}^{HL} is the higher-level calculation by conventional transition state theory without a transmission coefficient.

[b] Γ_{CVT}^{LL} is the lower-level recrossing transmission coefficient, which equals $k_{CVT}^{L2}/k_{TST}^{L2}$.

[c] κ_{SCT}^{LL} is the lower-level tunneling transmission coefficient calculated by the small-curvature tunneling approximation.

[d] The nonfinal high-pressure-limit (HPL) rate constant $k_{CVT/SCT}^{DL}$ is calculated by the dual-level CVT/SCT method, by which it equals k_{TST}^{HL} κ_{SCT}^{LL} Γ_{CVT}^{LL}, where HL is MW3X-L//junD, and LL is M11-L/MG3S for transition state 1 of the *syn*-CH_3CHOO + FCHO reaction.

[e] F_{fwd}^{MS-T} is the multistructural and torsional anharmonicity factor of the *syn*-CH_3CHOO + FCHO forward reaction.

[f] $k_{3\,MS-CVT/SCT}^{DL}$ is the rate constant of *syn*-CH_3CHOO + FCHO, equal to $k_{CVT/SCT}^{DL}$ F_{fwd}^{MS-T}.

Table S10. Fitting parameters of high-pressure-limit rate constants for forward reaction

	ln A (A in s^{-1})	n (unitless)	E (kcal/mol)	T_0 (K)
CH_2OO + FCHO	-27.09	-4.75	3.54	-88.42
anti-CH_3CHOO + FCHO	-103.43	46.99	-63.24	-48.04
syn-CH_3CHOO + FCHO	-37.53	1.58	-1.29	-10.24

CH_2OO, OH, and HO_2 reactions

Table S11. The ratio between CH_2OO + FCHO and FCHO + OH reaction rates for various concentrations in molecules/cm^3

T	k_1	k_{OH}	v_1^a					
			[CH_2OO]=10^4			[CH_2OO]=10^5		
			[OH] =10^4	[OH] =10^5	[OH] =10^6	[OH] =10^4	[OH] =10^5	[OH] =10^6
190	4.67E-12	1.30E-16	3.60E+04	3.60E+03	3.60E+02	3.60E+05	3.60E+04	3.60E+03
200	2.95E-12	1.80E-16	1.64E+04	1.64E+03	1.64E+02	1.64E+05	1.64E+04	1.64E+03
210	1.96E-12	2.44E-16	8.04E+03	8.04E+02	8.04E+01	8.04E+04	8.04E+03	8.04E+02
220	1.35E-12	3.24E-16	4.17E+03	4.17E+02	4.17E+01	4.17E+04	4.17E+03	4.17E+02
230	9.69E-13	4.24E-16	2.29E+03	2.29E+02	2.29E+01	2.29E+04	2.29E+03	2.29E+02
240	7.18E-13	5.45E-16	1.32E+03	1.32E+02	1.32E+01	1.32E+04	1.32E+03	1.32E+02
250	5.46E-13	6.91E-16	7.90E+02	7.90E+01	7.90E+00	7.90E+03	7.90E+02	7.90E+01
260	4.25E-13	8.64E-16	4.92E+02	4.92E+01	4.92E+00	4.92E+03	4.92E+02	4.92E+01
270	3.39E-13	1.07E-15	3.17E+02	3.17E+01	3.17E+00	3.17E+03	3.17E+02	3.17E+01
280	2.75E-13	1.31E-15	2.10E+02	2.10E+01	2.10E+00	2.10E+03	2.10E+02	2.10E+01
290	2.27E-13	1.58E-15	1.44E+02	1.44E+01	1.44E+00	1.44E+03	1.44E+02	1.44E+01
298	1.97E-13	1.83E-15	1.08E+02	1.08E+01	1.08E+00	1.08E+03	1.08E+02	1.08E+01
300	1.90E-13	1.89E-15	1.01E+02	1.01E+01	1.01E+00	1.01E+03	1.01E+02	1.01E+01
310	1.62E-13	2.25E-15	7.19E+01	7.19E+00	7.19E-01	7.19E+02	7.19E+01	7.19E+00
320	1.39E-13	2.66E-15	5.25E+01	5.25E+00	5.25E-01	5.25E+02	5.25E+01	5.25E+00
330	1.21E-13	3.11E-15	3.90E+01	3.90E+00	3.90E-01	3.90E+02	3.90E+01	3.90E+00
340	1.07E-13	3.62E-15	2.95E+01	2.95E+00	2.95E-01	2.95E+02	2.95E+01	2.95E+00
350	9.49E-14	4.19E-15	2.26E+01	2.26E+00	2.26E-01	2.26E+02	2.26E+01	2.26E+00

[a] $v_1 = \frac{v}{v_{\mathrm{OH}}} = \frac{k_1[\mathrm{FCHO}][CH_2\mathrm{OO}]}{k_{\mathrm{OH}}[\mathrm{FCHO}][\mathrm{OH}]} = \frac{k_1[CH_2\mathrm{OO}]}{k_{\mathrm{OH}}[\mathrm{OH}]}$, where k_1 is the rate constant of CH_2OO + FCHO, and k_{OH} is the rate constant of FCHO + OH. Both k_1 and k_{OH} are from this work.

Table S12. Atmospheric lifetimes of FCHO for reaction with CH_2OO, OH, and HO_2 as functions of temperature

T (K)	τ_1[a,b](s)	τ_2[c](s)	τ_3[d](s)
220	7.40E+07	3.09E+09	2.35E+09
230	1.03E+08	2.36E+09	1.78E+09
240	1.39E+08	1.84E+09	1.37E+09
250	1.83E+08	1.45E+09	1.07E+09
260	2.35E+08	1.16E+09	8.51E+08
270	2.95E+08	9.37E+08	6.86E+08
280	3.64E+08	7.66E+08	5.60E+08
290	4.41E+08	6.33E+08	4.62E+08
298	**5.08E+08**	**5.47E+08**	**3.99E+08**
300	5.25E+08	5.28E+08	3.85E+08
310	6.18E+08	4.44E+08	3.24E+08
320	7.17E+08	3.76E+08	2.75E+08

[a] $\tau = \frac{1}{k_b[X]}$, where k_b is the rate constant for reaction with X, and [X] stands for the concentration of X, where X is CH_2OO, OH, or HO_2.

[b] τ_1 is the reaction-specific atmospheric lifetime for the FCHO + CH_2OO reaction, where the concentration of CH_2OO is 1×10^4 molecules/cm^3.

[c] τ_2 is the reaction-specific atmospheric lifetime for the FCHO + OH reaction, where the concentration of OH is 1×10^6 molecules/cm^3.

[d] τ_3 is the reaction-specific atmospheric lifetime for the FCHO + HO_2 reaction, where the concentration of HO_2 is taken to be 1.1×10^9 molecules/cm^3. The concentration of HO_2 varies greatly between day and night [Brasseur, G. P.; Solomon, S., *Aeronomy of the middle atmosphere: Chemistry and physics of the stratosphere and mesosphere*. Springer Science & Business Media: 2006; pp. 617-621], but this value is close to the maximum, which reached during the daytime [Lew, M. M.; Rickly, P. S.; Bottorff, B. P.; Reidy, E.; Sklaveniti, S.; Léonardis, T.; Locoge, N.; Dusanter, S.; Kundu, S.; Wood, E.; Stevens, P. S., OH and HO_2 radical chemistry in a midlatitude forest: measurements and model comparisons. *Atmos. Chem. Phys.* **2020***, 20*, 9209-9230.].

Geometries and absolute energies

Table S13. Cartesian coordinates (Å) of optimized structures

Species	Methods	Cartesian coordinates			
FCHO	D	O	-0.2449314424	1.1272032214	0.0000000000
		C	0.3803112035	0.1260065247	0.0000000000
		F	-0.1940302926	-1.0875129032	0.0000000000
		H	1.4664873714	0.0151688171	0.0000000000
	junD	O	-0.2499534360	1.1318226741	0.0000000000
		C	0.3803327150	0.1283125744	0.0000000000
		F	-0.1983647049	-1.0932995998	0.0000000000
		H	1.4758222658	0.0140300114	0.0000000000
	M11-L/MG3S	O	1.12470500	0.10445300	0.00000000
		C	0.00000000	0.38317200	0.00000000
		H	-0.44619300	1.39893700	0.00000000
		F	-0.95016100	-0.50373200	0.00000000
CH_2OO	D	C	1.0738898213	-0.2040618152	0.0000000000
		O	-0.0046664679	0.4706154646	0.0000000000
		O	-1.1647544521	-0.2048945578	0.0000000000
		H	1.0101594984	-1.2843811341	0.0000000000
		H	1.9777416003	0.3858980425	0.0000000000
	junD	C	1.0745904807	-0.2044064377	0.0000000000
		O	-0.0081258289	0.4706452826	0.0000000000
		O	-1.1695901229	-0.2018571835	0.0000000000
		H	1.0109079706	-1.2948993528	0.0000000000
		H	1.9845875005	0.3936936913	0.0000000000
	M11-L/MG3S	C	1.03953700	-0.21812800	0.00000000
		H	0.97611200	-1.31070200	0.00000000
		H	1.96189500	0.36313000	0.00000000
		O	0.00000000	0.45058600	0.00000000
		O	-1.14690400	-0.16854300	0.00000000
C1	D	C	-1.5995823444	0.6845030673	0.5686926670
		O	-1.6545667671	-0.2342636325	-0.2963944574
		O	-0.7667920618	-1.2557872763	-0.1534724487
		H	-0.9095103099	0.5913926577	1.3961081252
		H	-2.2884052235	1.5014942132	0.4086326928
		O	0.8037725762	1.1759849005	-0.4388828832
		C	1.2863245992	0.0884662970	-0.4446054742
		F	1.8958731971	-0.4130153036	0.6381012568
		H	1.3776283341	-0.5965269233	-1.2841224783
	junD	C	-1.6248334179	0.6902554940	0.5757118781
		O	-1.6580847551	-0.2295900756	-0.2944284116
		O	-0.7666250135	-1.2471500641	-0.1406587736
		H	-0.9400437912	0.5992695630	1.4213702167
		H	-2.3260876703	1.5073821286	0.4041214691
		O	0.8230713770	1.1732762830	-0.4362339945
		C	1.3099632284	0.0830486731	-0.4566269874
		F	1.9274138425	-0.4298266316	0.6279767393
		H	1.3999682000	-0.6044173705	1.3071751362
	M11-L/MG3S	C	-1.56667800	0.66847300	0.55568600
		O	-1.60834200	-0.22842300	-0.28741200
		O	-0.73450400	-1.21285600	-0.15373600

		H	-0.87506000	0.59321700	1.39956000
		H	-2.26829600	1.48926900	0.39249200
		O	0.75877700	1.14927900	-0.42450100
		C	1.24539100	0.08461800	-0.42716200
		F	1.81877200	-0.40796200	0.62785800
		H	1.37468200	-0.59336700	-1.28872800
C2	D	C	-1.7339281780	0.7265537684	-0.2068419663
		O	-1.4026009796	-0.4770249566	-0.3683532104
		O	-0.8348273859	-1.1011801178	0.6905935777
		H	-1.5943523045	1.1879024980	0.7629712781
		H	-2.1580865657	1.2025212675	-1.0813023851
		O	0.8609265225	1.2689139940	0.3270477418
		C	1.3137244835	0.1745656107	0.3936778301
		H	1.5470982867	-0.3974604206	1.2914241864
		F	1.6875461210	-0.4912976436	-0.6976360523
	junD	C	-1.7590028014	0.7343919767	-0.2054220596
		O	-1.4103239817	-0.4715082243	-0.3775154421
		O	-0.8367391907	-1.1028336411	0.6829081832
		H	-1.6280997819	1.1905905317	0.7775309669
		H	-2.1859146825	1.2152413614	-1.0860099232
		O	0.8688682091	1.2655580307	0.3093204232
		C	1.3378417327	0.1717314113	0.3984387694
		H	1.5736146266	-0.3953303209	1.3077826857
		F	1.7252558696	-0.5143471253	-0.6954526037
	M11-L/MG3S	C	-1.72862000	0.72269300	-0.17558900
		O	-1.39051700	-0.44123700	-0.39326700
		O	-0.79177500	-1.09017000	0.59165700
		H	-1.57045700	1.16008200	0.81419800
		H	-2.18988400	1.23404400	-1.02323400
		O	0.82194500	1.22260400	0.19739100
		C	1.29320500	0.16662300	0.37202600
		H	1.48985400	-0.33383900	1.33642700
		F	1.75174900	-0.54730600	-0.60802800
TS1	D	C	-1.3851398791	0.6287517021	0.5658011447
		O	-1.5114211181	-0.3491184139	-0.2287188276
		O	-0.4583646119	-1.2368438951	-0.1199863912
		H	-0.7313859596	0.5442067320	1.4211093333
		H	-2.0965212087	1.4302008113	0.4173843231
		O	0.4873747267	1.1591389641	-0.4556973036
		C	1.0451439010	0.0792712412	-0.4588876062
		F	1.7784138090	-0.2980065533	0.6084703211
		H	1.3246783409	-0.4892165884	-1.3407569938
	junD	C	-1.3881817273	0.6329600587	0.5665466724
		O	-1.5080755328	-0.3503019975	-0.2288317746
		O	-0.4435219906	-1.2272024860	-0.1141540789
		H	-0.7410144390	0.5460403040	1.4397802879
		H	-2.1101707349	1.4372767858	0.4106499282
		O	0.4844444698	1.1595294702	-0.4516033497
		C	1.0403967492	0.0713512141	-0.4645030360
		F	1.7847076234	-0.3097611747	0.6085695943
		H	1.3341935824	-0.4915081746	-1.3577362439
	M11-L/MG3S	C	-1.36166600	0.60731900	0.56162500
		O	-1.48506300	-0.33643700	-0.23012800

		O	-0.45326400	-1.19524300	-0.14079300
		H	-0.68436700	0.52546600	1.41425900
		H	-2.07715600	1.42398000	0.42996000
		O	0.46429600	1.13709500	-0.47799700
		C	1.01570800	0.07768600	-0.44307600
		F	1.69940400	-0.26641400	0.61762000
		H	1.33488600	-0.50506800	-1.32275200
TS2	D	C	-1.5955359747	0.5752348666	-0.1609440313
		O	-1.1966557092	-0.5994368607	-0.4104926439
		O	-0.4251922175	-1.1006514218	0.6281949616
		H	-1.6359315665	0.9232527069	0.8594003139
		H	-2.0540911033	1.0837201577	-0.9993054236
		O	0.4485485720	1.2715943621	0.1597180630
		C	1.0389557946	0.2289901330	0.3894221515
		H	1.4513688741	-0.0696717809	1.3492037073
		F	1.6764833303	-0.3964671631	-0.6200230983
	junD	C	-1.6001650886	0.5770755341	-0.1652893570
		O	-1.1921811579	-0.5995895680	-0.4113717338
		O	-0.4135847165	-1.0875840300	0.6312972036
		H	-1.6530751023	0.9282714283	0.8642988036
		H	-2.0644769757	1.0824273472	-1.0154330679
		O	0.4498177351	1.2748311401	0.1707473641
		C	1.0384011540	0.2231328901	0.3963333344
		H	1.4728199260	-0.0798683884	1.3566001136
		F	1.6703942257	-0.4021313536	-0.6320086603
	M11-L/MG3S	C	-1.58333600	0.55660700	-0.15993300
		O	-1.17094800	-0.58278500	-0.40714100
		O	-0.41275100	-1.05780500	0.60758700
		H	-1.60838600	0.92250800	0.86763700
		H	-2.05733000	1.06995700	-1.00280100
		O	0.44576600	1.25197800	0.15689700
		C	1.01765600	0.22191000	0.37911600
		H	1.44153100	-0.07969600	1.35287300
		F	1.63574800	-0.38610900	-0.59906100
P1	D	C	1.1567201087	-0.6451932152	0.3749562998
		O	1.3877622205	0.6895504982	0.0159624591
		O	0.0180962749	1.1766784789	-0.1080804785
		H	0.8469710113	-0.7279712660	1.4200060258
		H	2.0482556657	-1.2204883371	0.1432334697
		O	0.0997993656	-1.0352352006	-0.4857952174
		C	-0.7475829688	0.0402879744	-0.4538132473
		F	-1.6963115812	-0.1029895977	0.5181371485
		H	-1.2601490966	0.1699746650	-1.4033004595
	junD	C	1.1547105726	-0.6460968817	0.3779609274
		O	1.3914583145	0.6915288900	0.0251850376
		O	0.0196086233	1.1836747392	-0.1275376635
		H	0.8326034632	-0.7366939221	1.4280661915
		H	2.0564849529	-1.2228500940	0.1472997315
		O	0.1062189130	-1.0308898290	-0.4983808622
		C	-0.7450810263	0.0432286603	-0.4595462862
		F	-1.6830707170	-0.1066011531	0.5355203136
		H	-1.2793720960	0.1693135904	-1.4072613897

	M11-L/MG3S	C	1.14479100	-0.62823600	0.35647600
		O	1.33792000	0.66200600	-0.03713600
		O	0.00769600	1.12051000	-0.01073100
		H	0.90691900	-0.69663800	1.43686500
		H	2.03720500	-1.21368700	0.09988900
		O	0.07170100	-1.03291700	-0.41419900
		C	-0.74186100	0.03672000	-0.42725400
		F	-1.72368000	-0.07928000	0.44588100
		H	-1.18713000	0.17613600	-1.42848500
P2	D	C	1.3639310338	-0.4879496545	-0.0884695162
		O	1.0037729888	0.8107215243	-0.4817025962
		O	-0.0353060297	1.0722631707	0.5129323045
		H	1.9969273370	-0.4729069588	0.8017868370
		H	1.8399410756	-0.9674967666	-0.9406965014
		O	0.1338894413	-1.1312604279	0.2168759564
		C	-0.7672931071	-0.1083897861	0.4437204978
		H	-1.3123522036	-0.2212853012	1.3786993148
		F	-1.6661455360	-0.0704887999	-0.5754312966
	junD	C	1.3660847434	-0.4881551515	-0.0887137273
		O	1.0009420311	0.8109639243	-0.4816608846
		O	-0.0381831285	1.0736380024	0.5197515382
		H	2.0141220215	-0.4738381409	0.8020312734
		H	1.8354401987	-0.9696591103	-0.9549677110
		O	0.1363577741	-1.1320588350	0.2307040531
		C	-0.7681715770	-0.1083175481	0.4473087922
		H	-1.3295525661	-0.2188844792	1.3828391854
		F	-1.6596744973	-0.0704816617	-0.5895775194
	M11-L/MG3S	C	1.32834200	-0.47510500	-0.08602100
		O	0.97459900	0.78197100	-0.47872400
		O	-0.02357800	1.03950800	0.49931000
		H	1.96966100	-0.46364200	0.81843000
		H	1.83985100	-0.96064300	-0.93022400
		O	0.12980700	-1.10645700	0.18791200
		C	-0.74827400	-0.10639600	0.42607300
		H	-1.28510500	-0.22092300	1.38439200
		F	-1.62793800	-0.06510600	-0.55343300
anti-CH3CHOO	junD	C	0.3704518992	0.4184433374	-0.0000000761
		H	0.0911760199	1.4784462126	-0.0000009663
		O	-0.5888447874	-0.4152422930	0.0000008414
		O	-1.8591575291	0.0807745342	0.0000007607
		C	1.7611424524	-0.1042547661	-0.0000003224
		H	2.2981983851	0.2619546385	0.8885423023
		H	1.7550431272	-1.2011347933	0.0000006078
		H	2.2981974328	0.2619531298	-0.8885441473
	M11-L/MG3S	C	0.36745900	0.41173700	0.00000100
		H	0.10037500	1.47711000	0.00000000
		O	-0.56926600	-0.39831400	0.00000000
		O	-1.80367300	0.06492100	0.00000000
		C	1.72941400	-0.10117500	0.00000000
		H	2.28317200	0.26041200	0.87709600
		H	1.73555600	-1.19416000	0.00000100
		H	2.28317000	0.26040900	-0.87709900

syn-CH3CHOO	junD	C	0.4645323302	0.7116650091	-0.0000576727
		H	0.7819946006	1.7570510893	-0.0001240744
		O	-0.8067312833	0.5844127044	0.0000118267
		O	-1.2900137616	-0.6865312829	0.0000974961
		C	1.3442666820	-0.4720776540	-0.0000440486
		H	1.1015765248	-1.0938989883	-0.8776538241
		H	2.3993210190	-0.1761770526	-0.0001109210
		H	1.1016638882	-1.0938138251	0.8776502181
	M11-L/MG3S	C	0.45800100	0.69939300	-0.00005700
		H	0.77767500	1.74508000	-0.00012300
		O	-0.77870600	0.56788600	0.00001100
		O	-1.22442000	-0.67688100	0.00009400
		C	1.32705400	-0.45292600	-0.00004400
		H	1.07733600	-1.08735500	-0.86396700
		H	2.38224800	-0.17729600	-0.00011000
		H	1.07742200	-1.08727100	0.86396500
anti-C1	junD	C	1.3048149335	0.0299019969	0.4405024116
		O	0.9567633917	0.9686131892	-0.3314992745
		O	-0.2527527786	1.5744932770	-0.0331051970
		H	0.6688891545	-0.1543184637	1.3128229911
		O	-0.7794525206	-1.1939815740	-0.5334461952
		C	-1.6297688265	-0.3554860184	-0.4486811864
		F	-2.3484465930	-0.2048201272	0.6841531833
		H	-2.0179198297	0.2983596481	-1.2385556195
		C	2.5409849163	-0.7266019608	0.1279043775
		H	3.2309924041	-0.6813831520	0.9837394138
		H	2.2696773447	-1.7812540230	-0.0346071404
		H	3.0234224035	-0.3242187921	-0.7707857644
	M11-L/MG3S	C	1.26987300	0.03735500	0.43054500
		O	0.93187800	0.95622400	-0.32392800
		O	-0.24799300	1.53048500	-0.05001200
		H	0.63347600	-0.15423400	1.30335400
		O	-0.70229500	-1.15719500	-0.51626700
		C	-1.54937500	-0.35030600	-0.42155300
		F	-2.22817700	-0.20512600	0.67622500
		H	-1.96984200	0.27896900	-1.22346500
		C	2.47691900	-0.71002800	0.12365200
		H	3.16979500	-0.69858100	0.97386100
		H	2.21008400	-1.76143400	-0.04731900
		H	2.97286100	-0.31682500	-0.76665100
anti-C2	junD	C	-1.4402834312	0.0744433086	-0.3485109964
		O	-0.7811590142	0.9384159688	0.2973408571
		O	0.2036969375	1.6055217200	-0.4117306078
		H	-1.2205969876	-0.0150148863	-1.4172609581
		O	0.8531782856	-1.2052858494	-0.6913703059
		C	1.6596730559	-0.3816320991	-0.3726783965
		H	2.2656471112	0.2628475793	-1.0203389814
		F	2.0164652085	-0.2235477090	0.9179400993
		C	-2.4543879289	-0.7311224980	0.3737462578
		H	-3.4385662097	-0.6013248962	-0.1012172124
		H	-2.1768454716	-1.7934923124	0.2933762604
		H	-2.5010665555	-0.4372883263	1.4291289839

	M11-L/MG3S	C	-1.41165600	0.07763700	-0.33509700
		O	-0.77389900	0.90981100	0.31801700
		O	0.20722500	1.54805200	-0.33602600
		H	-1.17410800	-0.00818700	-1.40260400
		O	0.78387000	-1.18673700	-0.54712200
		C	1.60354800	-0.37219000	-0.34883800
		H	2.15158100	0.22858300	-1.09402900
		F	2.08114600	-0.16764700	0.83941100
		C	-2.42295100	-0.71529100	0.34237700
		H	-3.39864600	-0.60026300	-0.14606600
		H	-2.15854200	-1.77789200	0.26100300
		H	-2.50181300	-0.44335600	1.39739900
syn-C1	junD	C	1.7133928837	0.0907267354	0.4958400972
		O	1.2272500856	-1.0468862431	0.2056518591
		O	0.4296762237	-1.0956105536	-0.9126517949
		H	2.3138116861	0.0626321364	1.4095221633
		O	-1.1434812755	0.1661528115	1.2891110749
		C	-1.6578678299	-0.2515694674	0.2988013238
		F	-2.0150774206	0.5773313079	-0.7102503736
		H	-1.9640431057	-1.2795622089	0.0679856457
		C	1.5142164252	1.2730477614	-0.3651647596
		H	0.4450346437	1.5299221295	-0.3979663471
		H	2.1045502565	2.1194463896	0.0036091057
		H	1.7960604272	0.9981692011	-1.3950229944
	M11-L/MG3S	C	1.68933800	0.08051700	0.48096000
		O	1.18711700	-1.01388000	0.18624000
		O	0.41232700	-1.01128700	-0.90134900
		H	2.29661000	0.03238700	1.39075300
		O	-1.12501000	0.22312600	1.23532000
		C	-1.62446800	-0.23760700	0.28700800
		F	-1.99740800	0.49791900	-0.72022400
		H	-1.91513800	-1.28906300	0.11459200
		C	1.51406800	1.25451700	-0.34179800
		H	0.44945800	1.51894500	-0.38471000
		H	2.10412200	2.09693400	0.02079600
		H	1.77250700	0.99129200	-1.37812300
syn-C2	junD	C	-1.5726321506	-0.0699480615	-0.7026303299
		O	-0.7561803259	-1.0049689257	-0.4274915357
		O	-0.3865176042	-1.1219613884	0.8898203033
		H	-1.8013900890	-0.0224549746	-1.7709957149
		O	1.0280772449	1.3653410207	-0.0956479680
		C	1.6434761660	0.4536956857	0.3629187953
		H	1.8239316694	0.2155295860	1.4189624369
		F	2.2790262156	-0.4340479887	-0.4278893762
		C	-2.1494683942	0.7977758834	0.3419048993
		H	-1.3371907428	1.3642444909	0.8226552264
		H	-2.8948288009	1.4754910225	-0.0892332744
		H	-2.5876891883	0.1556946499	1.1233515381
	M11-L/MG3S	C	-1.56166500	-0.06155900	-0.69928600
		O	-0.76259400	-0.98082900	-0.46524300
		O	-0.37935600	-1.09772500	0.80786800
		H	-1.82610800	0.00467400	-1.75966100
		O	0.99675900	1.29757700	-0.20824700

		C	1.57640500	0.44973000	0.34577200
		H	1.68257900	0.30071800	1.43527100
		F	2.26533400	-0.44242400	-0.29443500
		C	-2.09373000	0.77819700	0.34733700
		H	-1.26559400	1.31699000	0.82767100
		H	-2.84174500	1.47604200	-0.03028600
		H	-2.50167100	0.13300000	1.13896400
anti-TS1	junD	C	1.1662337258	0.0479993823	0.4294412766
		O	0.8100715191	1.0402146330	-0.2811888344
		O	-0.5079354842	1.4181980597	-0.0263609101
		H	0.5627167296	-0.1788476938	1.3122005281
		O	-0.4907115336	-1.1080047106	-0.5717934843
		C	-1.4102124454	-0.3161170901	-0.4483550245
		F	-2.1576860600	-0.3355784641	0.6925432559
		H	-1.9712388784	0.1598591407	-1.2608908112
		C	2.4594993426	-0.6065296877	0.1253830194
		H	3.1187844271	-0.5524670629	1.0040283436
		H	2.2519048292	-1.6664121082	-0.0855449391
		H	2.9352788282	-0.1405363984	-0.7453414200
	M11-L/MG3S	C	1.15475400	0.05950800	0.42626400
		O	0.79866400	1.01912000	-0.27877900
		O	-0.47937400	1.38626100	-0.03429700
		H	0.54035300	-0.18180100	1.30009400
		O	-0.47326900	-1.08953400	-0.56622400
		C	-1.37486900	-0.32076100	-0.42785600
		F	-2.08488400	-0.33963900	0.67374200
		H	-1.94052900	0.16266600	-1.24206600
		C	2.41815700	-0.58986400	0.12580100
		H	3.08816200	-0.55664000	0.99279600
		H	2.21832700	-1.64828400	-0.08152600
		H	2.90121300	-0.13925400	-0.74382800
anti-TS2	junD	C	-1.3042870912	0.1480020784	-0.3378376574
		O	-0.6064315233	0.9704772366	0.3339188114
		O	0.5288939892	1.3824743039	-0.3732182058
		H	-1.1412190343	0.1153127650	-1.4169469974
		O	0.5131442368	-1.1664011014	-0.5654976751
		C	1.4187175118	-0.3651273751	-0.3743875514
		H	2.1346507798	-0.0046627481	-1.1237320082
		F	1.9640586060	-0.2835562813	0.8726085354
		C	-2.4082381356	-0.5602784654	0.3497895974
		H	-3.3661903232	-0.3005658945	-0.1246109070
		H	-2.2394236912	-1.6394128424	0.2162206336
		H	-2.4241943249	-0.3143806757	1.4178884246

	M11-L/MG3S	C	-1.29381000	0.15884500	-0.32899600
		O	-0.60251500	0.94792800	0.33494100
		O	0.49978000	1.35113400	-0.34933300
		H	-1.11106800	0.11103700	-1.40703900
		O	0.49916600	-1.15381100	-0.52044200
		C	1.38799300	-0.37003900	-0.35545100
		H	2.08188100	-0.00404600	-1.13343200
		F	1.94592400	-0.27860200	0.82619800
		C	-2.37656200	-0.54277000	0.33645800
		H	-3.33736300	-0.30921000	-0.13713300
		H	-2.21273000	-1.61936500	0.20581800
		H	-2.41121500	-0.30922000	1.40260600
syn-TS1	junD	C	1.4416965667	0.0231169643	0.3494152855
		O	1.0483672163	-1.1367155254	-0.0192856599
		O	-0.0730308992	-1.0931675944	-0.8416247655
		H	2.1752799349	-0.0583070274	1.1603021494
		O	-0.5796649525	0.2102495050	1.2722748609
		C	-1.2825571068	-0.2334263609	0.3705241030
		F	-1.7977106145	0.6353303976	-0.5617528118
		H	-1.9316251307	-1.1149411483	0.4438827114
		C	1.2898027599	1.2874994452	-0.4114227080
		H	1.0925279236	2.1068883976	0.2911267084
		H	2.2628669922	1.4735016336	-0.9002183478
		H	0.4920403100	1.2201063131	-1.1551475254
	M11-L/MG3S	C	1.44425900	0.01350400	0.32788800
		O	1.02126800	-1.11290000	-0.00245800
		O	-0.06686900	-1.05528200	-0.80311500
		H	2.19138400	-0.06940700	1.12954200
		O	-0.58476400	0.23137000	1.24176300
		C	-1.25592000	-0.20819700	0.35158200
		F	-1.75330300	0.61539400	-0.55723200
		H	-1.90756500	-1.09795300	0.43132000
		C	1.27185800	1.25757200	-0.39817900
		H	1.06585900	2.07146300	0.30095800
		H	2.23395800	1.48641500	-0.88432000
		H	0.47782800	1.18815600	-1.13967500
syn-TS2	junD	C	-1.3045162492	-0.1806935809	-0.6288280400
		O	-0.4922719953	-1.1419854702	-0.4060803166
		O	0.1655736365	-1.0241276989	0.8183703104
		H	-1.6182395744	-0.1767337074	-1.6797052047
		O	0.4183362814	1.2087227894	-0.3351094152
		C	1.1833809013	0.5174794428	0.3341874972
		H	1.4544036904	0.6978119881	1.3830776648
		F	2.2057755687	-0.1230282370	-0.3051179906
		C	-2.0624024395	0.5840328827	0.3909161674
		H	-2.1279904400	1.6331460697	0.0771243634
		H	-3.0809220113	0.1569773847	0.4069968621
		H	-1.5986603687	0.5032261368	1.3769041019
	M11-L/MG3S	C	-1.30994300	-0.20388400	-0.62026400
		O	-0.48078400	-1.11255200	-0.41687200
		O	0.15683000	-0.98932700	0.77576900
		H	-1.64693300	-0.20975500	-1.66675100
		O	0.40845600	1.20082700	-0.31585600

		C	1.14738600	0.51002300	0.33257700
		H	1.40767200	0.68226400	1.39533900
		F	2.14648000	-0.09185700	-0.27444900
		C	-2.01860800	0.57134000	0.38000100
		H	-2.07370200	1.61656200	0.06694200
		H	-3.05051200	0.18780900	0.42007400
		H	-1.54387500	0.49337800	1.35622600
anti-P1	junD	C	-0.9027251138	-0.1202079560	-0.3476597078
		O	-0.6272492229	1.2190206269	0.0011194921
		O	0.8297795870	1.1966049665	0.1336720405
		H	-0.6140770896	-0.3046556875	-1.3973918456
		O	-0.0234906079	-0.8462813244	0.5122683663
		C	1.1484137452	-0.1427606808	0.4498337666
		F	1.9527547135	-0.6094553332	-0.5665578894
		H	1.7173554108	-0.2171212267	1.3831128714
		C	-2.3410226540	-0.4364748792	-0.0453281301
		H	-2.9926494614	0.2006015161	-0.6584442774
		H	-2.5366898741	-1.4886271361	-0.2919004053
		H	-2.5430684328	-0.2611568856	1.0192287188
	M11-L/MG3S	C	-0.89536700	-0.10727400	-0.35497100
		O	-0.59757500	1.17292000	0.03508000
		O	0.80477800	1.12929600	0.00563500
		H	-0.65287500	-0.24378300	-1.43125100
		O	-0.01506600	-0.85879700	0.41786900
		C	1.12113600	-0.14967600	0.42445700
		F	1.99783300	-0.60791400	-0.45084800
		H	1.59463600	-0.17287200	1.42273900
		C	-2.30476000	-0.42907100	-0.02853800
		H	-2.98183400	0.21519400	-0.59537700
		H	-2.51836000	-1.46724400	-0.29438700
		H	-2.48521500	-0.29129300	1.04154500
anti-P2	junD	C	-1.0374328639	0.1687550702	-0.3925933118
		O	-0.3945528157	1.0776227052	0.4777077684
		O	0.9151972306	1.1624639788	-0.1708809979
		H	-1.3202515844	0.6808369365	-1.3285289695
		O	-0.0192672926	-0.7919265335	-0.7021412886
		C	1.1802837208	-0.1859293156	-0.3887225471
		H	1.9285416149	-0.2614068224	-1.1871477631
		F	1.6974738780	-0.7695610436	0.7388451646
		C	-2.1976491406	-0.4671416911	0.3253808007
		H	-2.9447288925	0.2996501111	0.5729127341
		H	-2.6586876314	-1.2146592222	-0.3342892225
		H	-1.8412152232	-0.9551371734	1.2418696327
	M11-L/MG3S	C	-1.00585800	0.15536300	-0.36746800
		O	-0.38261600	1.03239200	0.48415500
		O	0.87254300	1.12991700	-0.16346900
		H	-1.27762800	0.66825700	-1.31611500
		O	-0.02156600	-0.79184600	-0.63817600
		C	1.15133200	-0.18315200	-0.37493300
		H	1.87261600	-0.23831400	-1.20999100
		F	1.69594300	-0.74072700	0.68994100
		C	-2.17623000	-0.45441000	0.31249800
		H	-2.92775900	0.30768100	0.53606400

		H	-2.63226800	-1.20236000	-0.34104300
		H	-1.86079800	-0.93923400	1.24094900
syn-P1	junD	C	1.1078722325	-0.0606064373	0.4493798745
		O	0.8065395150	-1.2862272144	-0.1915540521
		O	-0.5516384142	-1.0365774275	-0.6654851468
		H	1.8696099270	-0.2980499866	1.2042606967
		O	-0.1088804844	0.2247447012	1.1439364471
		C	-1.1137471310	-0.1691501688	0.2990150927
		F	-1.6321077800	0.8930279791	-0.4059763261
		H	-1.9433999140	-0.6273304773	0.8502920309
		C	1.5244363519	1.0419026045	-0.5001589225
		H	1.6625185372	1.9736812607	0.0661415811
		H	2.4745797347	0.7636157564	-0.9773663267
		H	0.7603114252	1.1996564100	-1.2718399487
	M11-L/MG3S	C	1.07652500	-0.05584500	0.44687700
		O	0.75808300	-1.24541500	-0.16887200
		O	-0.50852000	-0.93327800	-0.69210300
		H	1.83463000	-0.29776200	1.21074400
		O	-0.11107700	0.26610400	1.09713400
		C	-1.09315100	-0.15571600	0.28513700
		F	-1.67126000	0.84407400	-0.35618100
		H	-1.87711700	-0.68572300	0.85815900
		C	1.52554400	1.01493000	-0.49287700
		H	1.67351800	1.95299100	0.05004100
		H	2.47180200	0.73247500	-0.96430300
		H	0.77711700	1.18185200	-1.27311100
syn-P2	junD	C	0.9671915321	-0.1890776270	-0.5395325809
		O	0.3349013512	1.0822047006	-0.5739330801
		O	-0.4887826752	1.0073576462	0.6359379426
		H	1.1646727421	-0.4384440644	-1.5921279356
		O	-0.0444087333	-1.0698045647	-0.0332080709
		C	-1.0316774175	-0.2622304385	0.4920629949
		H	-1.3777195065	-0.6001791653	1.4762371287
		F	-2.1061889331	-0.2400310134	-0.3587905320
		C	2.1991268407	-0.2311362674	0.3338265949
		H	2.5883401836	-1.2585607293	0.3665426694
		H	2.9678151412	0.4343405641	-0.0833678428
		H	1.9475984747	0.0943189590	1.3523897118
	M11-L/MG3S	C	0.94385800	-0.18244300	-0.54493100
		O	0.32239700	1.04673600	-0.58364300
		O	-0.44284600	0.97475000	0.61078900
		H	1.17723800	-0.42836300	-1.59650200
		O	-0.04814000	-1.04356700	-0.08081600
		C	-0.99100100	-0.25726100	0.47489200
		H	-1.29360000	-0.60093900	1.47976800
		F	-2.05577300	-0.22966000	-0.30413400
		C	2.14823100	-0.22767900	0.33658600
		H	2.53968200	-1.24792100	0.39036200
		H	2.93329500	0.42628600	-0.05468700
		H	1.88752800	0.09881900	1.34835300

Table S14. Absolute energies in hartrees

Species	Method	Energy (a.u.)
FCHO	MW3X-L//D	-213.9470187
	W3X-L//D	-213.955548
	M11-L/MG3S	-213.757748
	MW2-F12//D	-213.9458461
	W2X//D	-213.9543754
	W2X//junD	-213.9541235
CH_2OO	MW3X-L//D	-189.714624
	W3X-L//D	-189.7225695
	M11-L/MG3S	-189.55266
	MW2-F12//D	-189.7116541
	W2X//D	-189.7195996
	W2X//junD	-189.7195993
C1	MW3X-L//D	-403.6741383
	W3X-L//D	-403.690813
	M11-L/MG3S	-403.320589
	MW2-F12//D	-403.6703989
	W2X//D	-403.6870743
	W2X//junD	-403.6864699
C2	MW3X-L//D	-403.6733737
	W3X-L//D	-403.6900454
	M11-L/MG3S	-403.319727
	MW2-F12//D	-403.6695996
	W2X//D	-403.6862713
	W2X//junD	-403.6856505
TS1	MW3X-L//D	-403.6705435
	W3X-L//D	-403.6872673
	M11-L/MG3S	-403.316603
	MW2-F12//D	-403.6672627
	W2X//D	-403.6839865
	W2X//junD	-403.6835141
TS2	MW3X-L//D	-403.6678238
	W3X-L//D	-403.6845351
	M11-L/MG3S	-403.313627
	MW2-F12//D	-403.6646344
	W2X//D	-403.6813457
	W2X//junD	-403.6808787
P1	MW3X-L//D	-403.7359573
	W3X-L//D	-403.7526299
	M11-L/MG3S	-403.37632
	MW2-F12//D	-403.7339807
	W2X//D	-403.7506533
	W2X//junD	-403.7502350
P2	MW3X-L//D	-403.738569
	W3X-L//D	-403.7552611
	M11-L/MG3S	-403.379725
	MW2-F12//D	-403.736605

	W2X//D	-403.7532971
	W2X//junD	-403.7528908
anti-CH3CHOO	W3X-L//junD	-229.0662367
	W2X//junD	-229.0629202
	M11L	-228.859419
syn-CH3CHOO	W3X-L//junD	-229.0719368
	W2X//junD	-229.0688182
	M11L	-228.86518
anti-C1	W3X-L//junD	-443.0370553
	W2X//junD	-443.0330725
	M11L	-442.711006
anti-C2	W3X-L//junD	-443.0360668
	W2X//junD	-443.0320502
	M11L	-442.70978
syn-C1	W3X-L//junD	-443.0393362
	W2X//junD	-443.0353167
	M11L	-442.713306
syn-C2	W3X-L//junD	-443.0385853
	W2X//junD	-443.0345358
	M11L	-442.712574
anti-TS1	W3X-L//junD	-443.0354134
	W2X//junD	-443.0318443
	M11L	-442.709256
anti-TS2	W3X-L//junD	-443.0330693
	W2X//junD	-443.0295854
	M11L	-442.706836
syn-TS1	W3X-L//junD	-443.0313219
	W2X//junD	-443.027889
	M11L	-442.705659
syn-TS2	W3X-L//junD	-443.0284046
	W2X//junD	-443.0250121
	M11L	-442.703116
anti-P1	W3X-L//junD	-443.0960068
	W2X//junD	-443.0937171
	M11L	-442.767317
anti-P2	W3X-L//junD	-443.0985224
	W2X//junD	-443.0962458
	M11L	-442.770487
syn-P1	W3X-L//junD	-443.0931434
	W2X//junD	-443.0908429
	M11L	-442.764427
syn-P2	W3X-L//junD	-443.0968098
	W2X//junD	-443.094528
	M11L	-442.768434

Figures

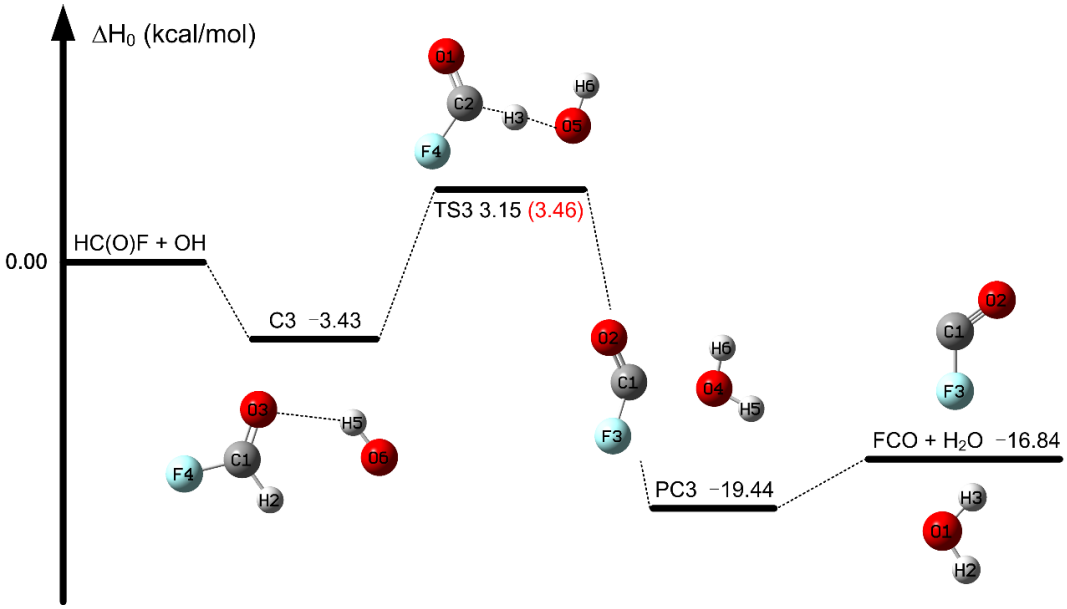

Figure S1. Enthalpies for the FCHO + OH reaction at 0 K.
In black: Enthalpy profile calculated by M08-HX/MG3S.
In red: Enthalpy of activation calculated by W3X-L//CCSD(T)-F12b/jun-cc-pVDZ.

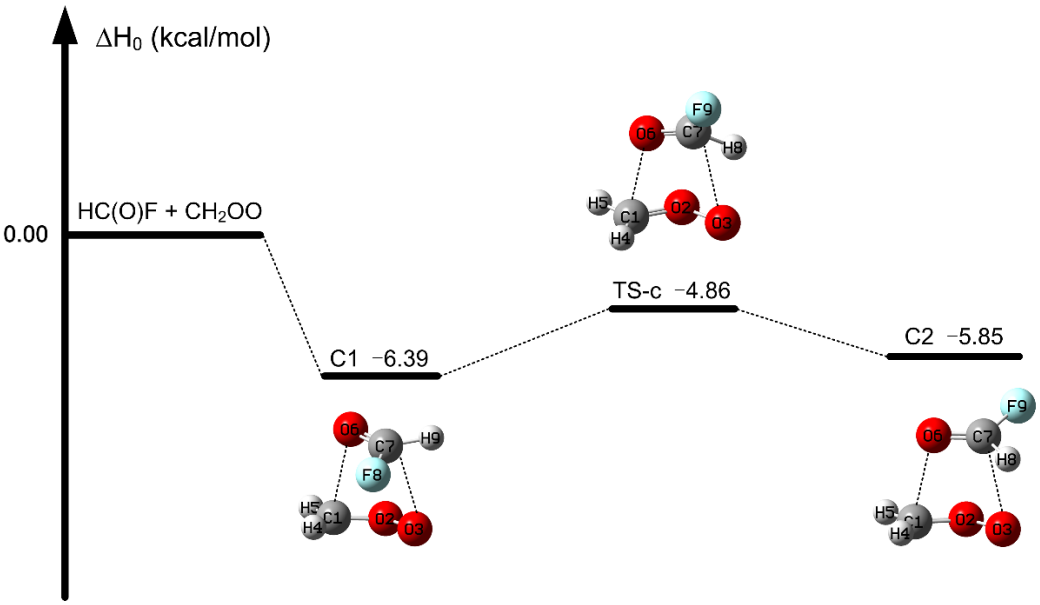

Figure S2. Enthalpy profile at 0 K for the conversion of C1 to C2 as calculated by M11-L/MG3S.

References

[1]. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

[2]. Y. Zhao, R. Peverati, K. Tang, S. Luo, H. Yu, X. He, D. Truhlar, MN-GFM 6.7; Department of Chemistry. University of Minnesota: Minneapolis, MN 55455-0431 (2015).

[3]. H.-J. K. Werner, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györffy, W.; Kats, D.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Shamasundar, K. R.; Adler, T. B.; Amos, R. D.; Bennie, S. J.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Lee, S. J. R.; Liu, Y.; Lloyd, A. W.; Ma, Q.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Miller, T. F.; Mura, M. E.; Nicklaß, A.; O'Neill, D. P.; Palmieri, P.; Peng, D.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Welborn, M, Molpro: a general-purpose quantum chemistry program package. WIREs Comput. Mol. Sci. 2 (2012) 242-253.

[4]. M. Kállay, P. R. Nagy, D. Mester, et al., The MRCC program system: Accurate quantum chemistry from water to proteins. J. Chem. Phys. 152 (2020) 074107.

[5]. M. N. Kállay, P. R.; Mester, D.; Rolik, Z.; Samu, G.; Csontos, J.; Csóka, J.; Szabó, P. B.; Gyevi-Nagy, L.; Hégely, B.; Ladjánszki, I.; Szegedy, L.; Ladóczki, B.; Petrov, K.; Farkas, M.; Mezei, P. D.; Ganyecz, Á, MRCC, a string-based quantum chemical program suite. www.mrcc.hu.

[6]. J. Zheng, J. Bao, R. Meana-Pañeda, et al., Polyrate, version 2017-C. University of Minnesota, Minneapolis, MN (2018).

[7]. J. Zheng, L. Bao, S. Zhang, J. Corchado, Y. Chuang, E. Coitiño, B. Ellingson, D. Truhlar, Gaussrate, version 2017-B. University of Minnesota: Minneapolis (2018).

[8]. J. L. Bao, D. G. Truhlar, Variational transition state theory: theoretical framework and recent developments. Chem. Soc. Rev. 46 (2017) 7548-7596.

[9]. Y. Georgievskii, S. J. Klippenstein, Variable reaction coordinate transition state theory: Analytic results and application to the $C_2H_3 + H \rightarrow C_2H_4$ reaction. J. Chem. Phys. 118 (2003) 5442-5455.

[10]. J. Zheng, S. Zhang, D. G. Truhlar, Density Functional Study of Methyl Radical Association Kinetics. J. Phys. Chem. A 112 (2008) 11509-11513.

[11]. J. L. Bao, X. Zhang, D. G. Truhlar, Barrierless association of CF2 and dissociation of C2F4 by variational transition-state theory and system-specific quantum Rice–Ramsperger–Kassel theory. Proc. Natl. Acad. Sci. USA. 113 (2016) 13606-13611.

[12]. B. Long, Y. Wang, Y. Xia, X. He, J. L. Bao, D. G. Truhlar, Atmospheric Kinetics: Bimolecular Reactions of Carbonyl Oxide by a Triple-Level Strategy. J Am Chem Soc. 143 (2021) 8402-8413.

[13]. B. Long, J. L. Bao, D. G. Truhlar, Unimolecular reaction of acetone oxide and its reaction with water in the atmosphere. Proc. Natl. Acad. Sci. USA. 115 (2018) 6135-6140.

[14]. B. Long, J. L. Bao, D. G. Truhlar, Atmospheric Chemistry of Criegee Intermediates: Unimolecular Reactions and Reactions with Water. J. Am. Chem. Soc. 138 (2016) 14409-14422.

[15]. B. Long, J. L. Bao, D. G. Truhlar, Kinetics of the Strongly Correlated CH3O + O2 Reaction: The Importance of Quadruple Excitations in Atmospheric and Combustion Chemistry. J. Am. Chem. Soc. 141 (2019) 611-617.

[16]. X.-F. Tan, B. Long, D.-S. Ren, W.-J. Zhang, Z.-W. Long, E. Mitchell, Atmospheric chemistry of CH_3CHO: the

hydrolysis of CH_3CHO catalyzed by H_2SO4. Phys. Chem. Chem. Phys. 20 (2018) 7701-7709.

[17]. X.-F. Tan, L. Zhang, B. Long, New mechanistic pathways for the formation of organosulfates catalyzed by ammonia and carbinolamine formation catalyzed by sulfuric acid in the atmosphere. Phys. Chem. Chem. Phys. 22 (2020) 8800-8807.

[18]. B. Long, Y. Wang, Y. Xia, X. He, J. L. Bao, D. G. Truhlar, Atmospheric Kinetics: Bimolecular Reactions of Carbonyl Oxide by a Triple-Level Strategy. J. Am. Chem. Soc. 143 (2021) 8402-8413.

[19]. B. Chan, L. Radom, W3X: A Cost-Effective Post-CCSD(T) Composite Procedure. J. Chem. Theory Comput. 9 (2013) 4769-4778.

[20]. G. Knizia, T. B. Adler, H.-J. Werner, Simplified CCSD(T)-F12 methods: Theory and benchmarks. J. Chem. Phys. 130 (2009) 054104.

[21]. E. Papajak, J. Zheng, X. Xu, H. R. Leverentz, D. G. Truhlar, Perspectives on Basis Sets Beautiful: Seasonal Plantings of Diffuse Basis Functions. J. Chem. Theory Comput. 7 (2011) 3027-3034.

[22]. Y. Zhao, D. G. Truhlar, Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. J. Chem. Theory Comput. 4 (2008) 1849-1868.

[23]. B. J. Lynch, Y. Zhao, D. G. Truhlar, Effectiveness of Diffuse Basis Functions for Calculating Relative Energies by Density Functional Theory. J. Phys. Chem. A 107 (2003) 1384-1388.

[24]. R. Peverati, D. G. Truhlar, M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics. J. Phys. Chem. Lett. 3 (2012) 117-124.

[25]. K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, A fifth-order perturbation comparison of electron correlation theories. Chem. Phys. Lett. 157 (1989) 479-483.

[26]. Y. J. Bomble, J. F. Stanton, M. Kállay, J. Gauss, Coupled-cluster methods including noniterative corrections for quadruple excitations. J. Chem. Phys. 123 (2005) 054101.

[27]. B. Chan, L. Radom, W2X and W3X-L: Cost-Effective Approximations to W2 and W4 with kJ mol^{-1} Accuracy. J. Chem. Theory Comput. 11 (2015) 2109-2119.

[28]. N. Sylvetsky, K. A. Peterson, A. Karton, J. M. Martin, Toward a W4-F12 approach: Can explicitly correlated and orbital-based ab initio CCSD (T) limits be reconciled? J. Chem. Phys. 144 (2016) 214101.

[29]. K. A. Peterson, T. B. Adler, H.-J. Werner, Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B–Ne, and Al–Ar. J. Chem. Phys. 128 (2008) 084102.

[30]. A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, Basis-set convergence in correlated calculations on Ne, N_2, and H_2O. Chem. Phys. Lett. 286 (1998) 243-252.

[31]. D. G. Truhlar, B. C. Garrett, Variational transition-state theory. Acc. Chem. Res. 13 (1980) 440-448.

[32]. Y. P. Liu, G. C. Lynch, T. N. Truong, D. H. Lu, D. G. Truhlar, B. C. Garrett, Molecular modeling of the kinetic isotope effect for the [1,5]-sigmatropic rearrangement of cis-1,3-pentadiene. J. Am. Chem. Soc. 115 (1993) 2408-2415.

[33]. I. Alecu, J. Zheng, Y. Zhao, D. G. Truhlar, Computational thermochemistry: scale factor databases and scale factors for vibrational frequencies obtained from electronic model chemistries. J Chem Theory Comput. 6 (2010) 2872-2887.