Supporting Information: OH-Formation Following Vibrationally Induced Reaction Dynamics of H$_2$COO

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1 Geometrical Criteria for Structure Assignments

Structures in Figures 8 and 9 were assigned as follows. A total of $\sim 10^7$ structures was analyzed. Each of the 3 states (reactant, TS, product) was approximately identified through specific geometric criteria, starting with the product state, followed by the TS and ending with the reactant state.

For H-transfer, classification started by comparing with criteria for a product structure (HCOOH): $[1.5 < d(CH_A) < 2.3$ Å, $d(O_AO_B) < 1.7$ Å, and $d(H_AO_B) < d(CH_A)]$. If this test failed, criteria for the TS were applied: $[d(CH_A) < 1.7$ Å, $d(H_AO_B) < 1.5$ Å, $d(O_AO_B) < 1.7$ Å), $(d(CH_A) - d(O_AO_B)) < 0.35$ Å]. If this test was negative, criteria for a reactant structure were applied: $[d(CH_A) < 2.4$ Å, $d(CO_A) < 1.8$ Å, $d(H_AO_B) < 1.3$ Å, $d(O_AO_B) < 1.7$ Å].

For the dioxirane pathway, classification started by comparing with dioxirane: $[60° < CO_AO_B \leq 85°$, $d(CO_A) > 1.3$ Å, and $d(O_AO_B) > 1.45$ Å]; for the TS the criterion was: $[80° < CO_AO_B < 100°]$; and for the reactant: $[d(CH_A) < 2.4$ Å and $d(CO_A) < 1.9$ Å]. In both cases (H-transfer and dioxirane formation) a structure remained unclassified if it failed all tests. Of course, other and more refined criteria could be applied or the distributions could be smoothed. However, for the present purpose the approach outlined above was deemed sufficient.
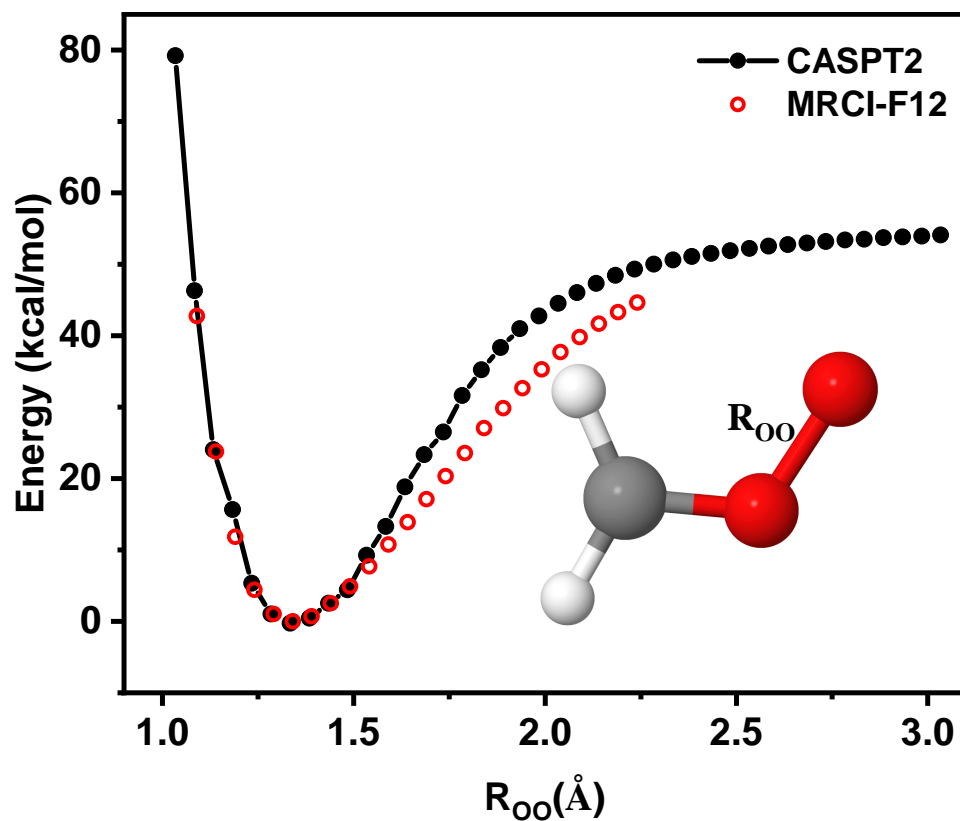
2   Additional Figures

Figure S1: One-dimensional cut at CASPT2 level of theory for the reactant along the O-O bond with other coordinates fixed at the equilibrium of H_2COO. The relaxed scan along the O-O bond (red open circle) at the MRCI-F12 level from Ref.[1] is included for comparison.
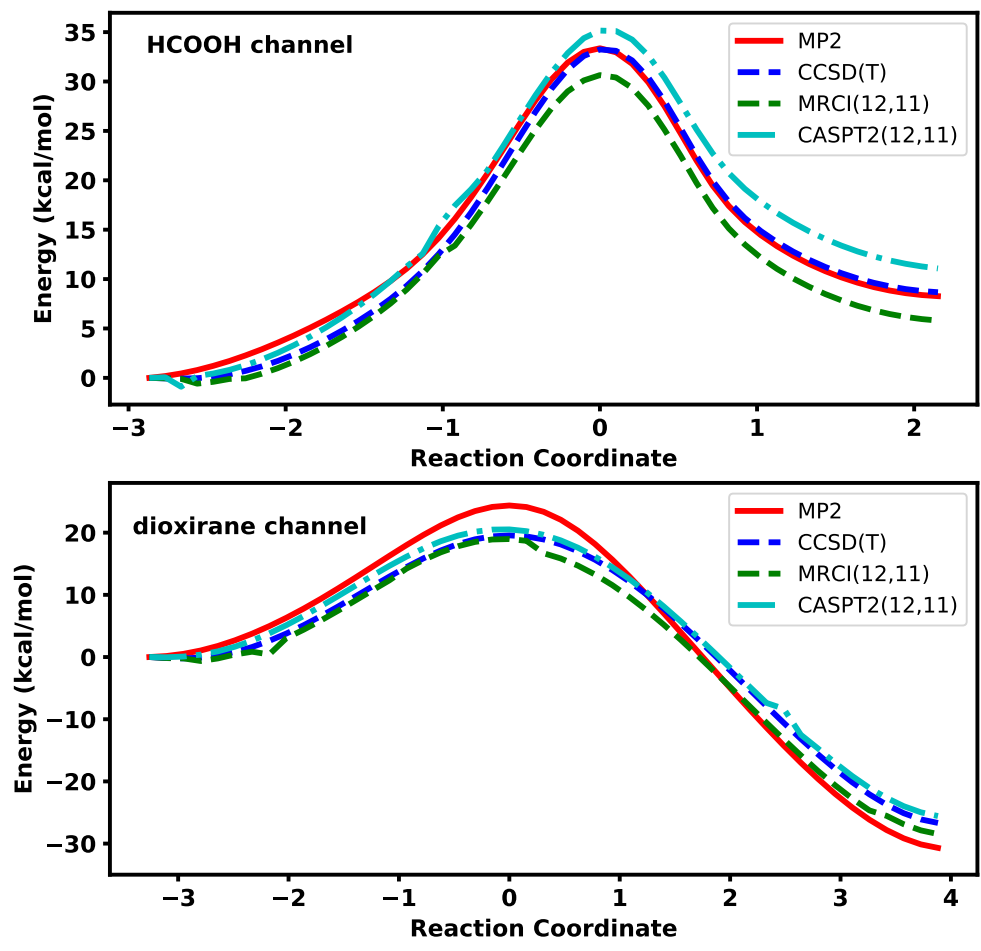
Figure S2: The energy profiles of H$_2$COO for the H-transfer channel (upper panel) and for the dioxirane channel (bottom panel). The performance of four different levels of theory (MP2, CCSD(T), MRCI, CASPT2) are included for comparison.
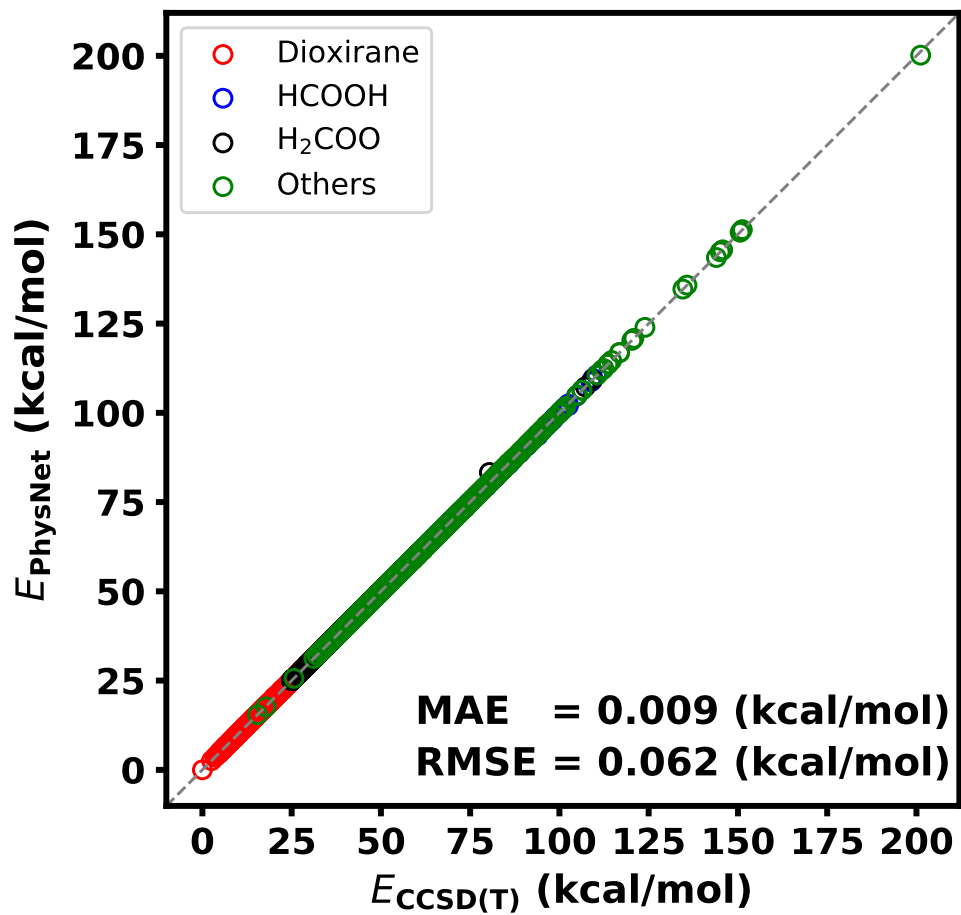
Figure S3: Correlation of 2962 (10%) *ab initio* energies and predicted energies on the test set from the PhysNet base model.
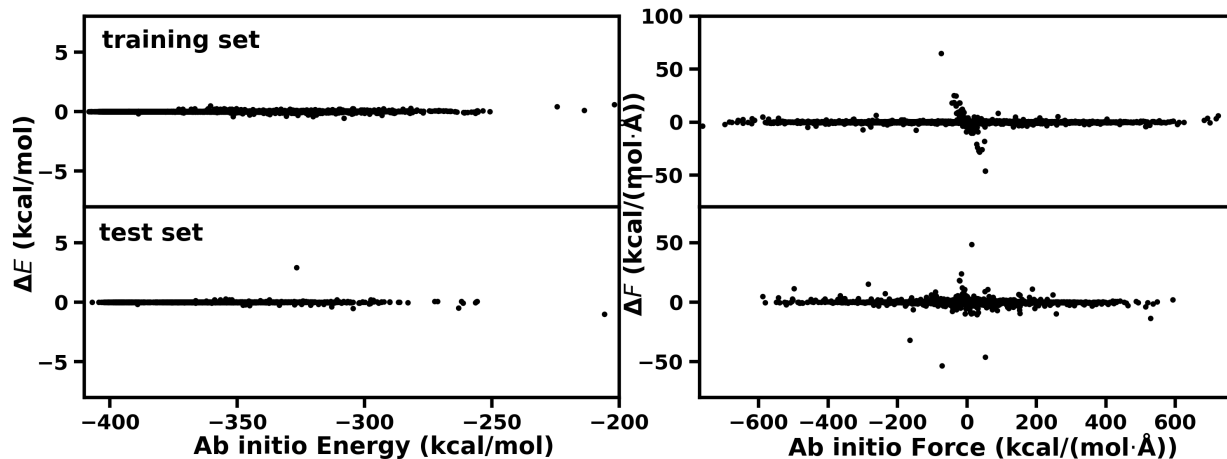
Figure S4: Comparison between reference CCSD(T)-F12a/aVTZ energies/forces and predicted energies/forces on the training and test sets from the PhysNet base model, from top to bottom. The performance of the best PhysNet base model for H_2OOC is shown. Here, $\Delta E = E_{\text{PhysNet}} - E_{\text{CCSD}}$, $\Delta F = F^{\alpha}_{\text{PhysNet}} - F^{\alpha}_{\text{CCSD}}$ where $\alpha = (x, y, z)$ are the three Cartesian components of the forces on each atom. On the energies for the base model, the $\text{MAE}_{\text{train}}(E)$ and $\text{MAE}_{\text{test}}(E)$ are 0.007, 0.009 kcal/mol, and the corresponding $\text{RMSE}_{\text{train}}(E)$ and $\text{RMSE}_{\text{test}}(E)$ are 0.019, 0.062 kcal/mol. The $\text{MAE}_{\text{train}}(F)$ and $\text{MAE}_{\text{test}}(F)$ on forces for the model are 0.022, 0.063 kcal/(mol·Å), and the corresponding $\text{RMSE}_{\text{train}}(F)$ and $\text{RMSE}_{\text{test}}(F)$ are 0.251, 0.597 kcal/(mol·Å).
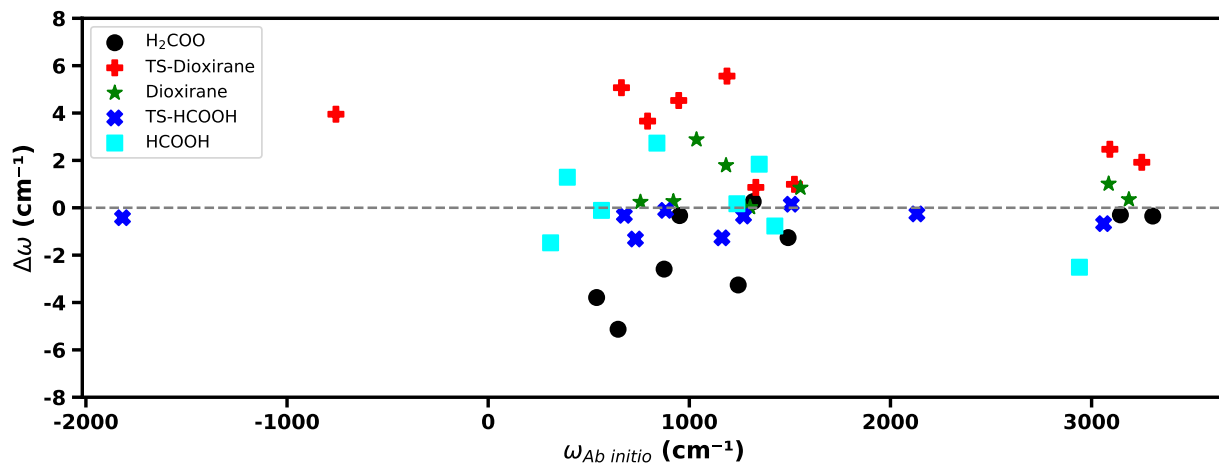
Figure S5: Accuracy of the harmonic frequencies from the PhysNet base model is shown, with respect to the appropriate reference *ab initio* values. Here, $\Delta \omega = \omega_{\text{Ab initio}} - \omega_{\text{PhysNet}}$. All absolute deviations of the harmonic frequencies are smaller than 6 cm^{-1}. The harmonic frequencies and their intensities (km/mol) at the MP2/6-311++G(2d,2p) level of theory for H_2COO are 535.5(19.4), 640.8(20.6), 872.2(41.5), 951.5(856.5), 1239.9(209.8), 1318.1(9.6), 1490.0(5.2), 3142.3(15.9), and 3303.2(2.4) cm^{-1}. The measured experimental (anharmonic) frequencies for H_2COO are 847.44, 909.26, 1213.30, 1285.90 and 1434.10 cm^{-1}.[2,3]

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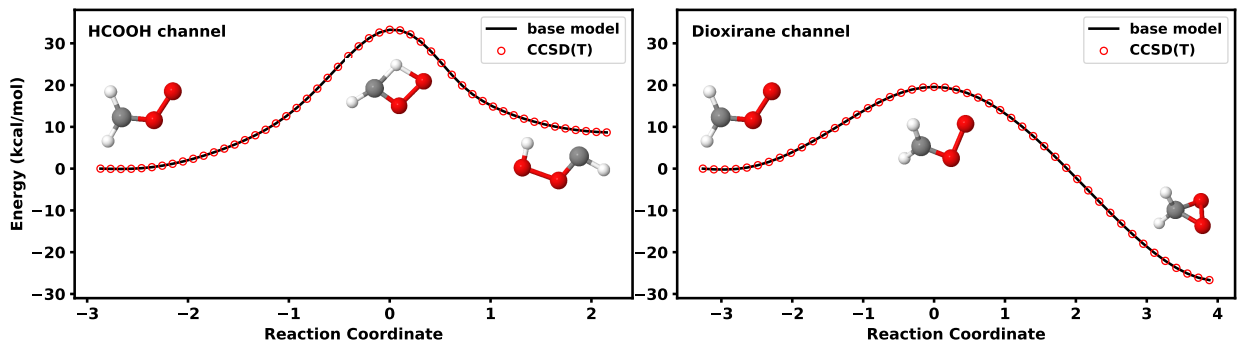
Figure S6: Energy profiles of the H-transfer channel (left panel) and the dioxirane formation channel (right panel). Here, the black solid line represents the energies from the PhysNet base model, and the red open circles refer to the reference CCSD(T)-F12a/aVTZ energies.
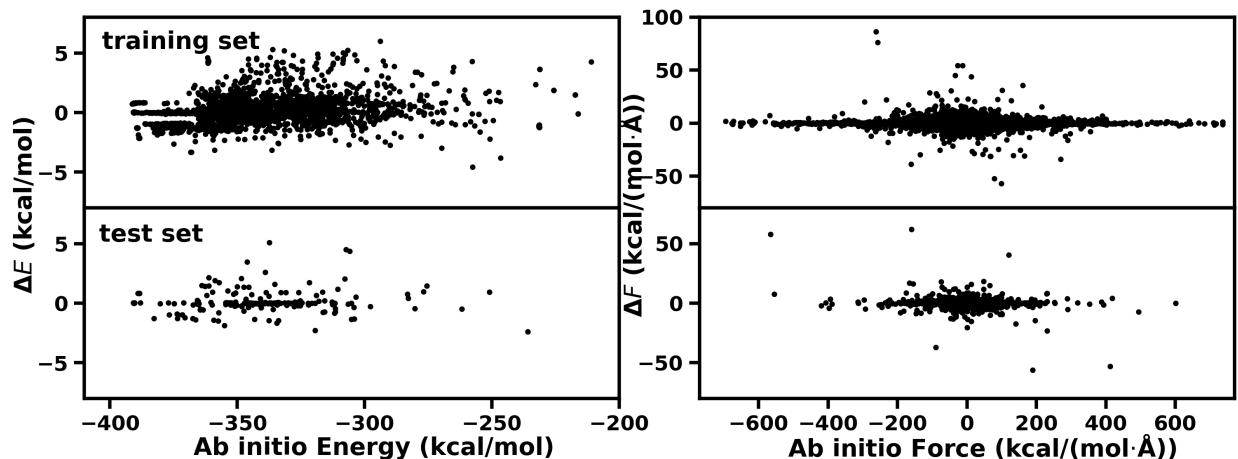
Figure S7: Comparison between reference CASPT2/aVTZ energies/forces and predicted energies/forces on the training and test sets from the PhysNet TL model, from top to bottom. The performance of the best PhysNet TL model for H_2OOC is shown. Here, $\Delta E = E_{\mathrm{PhysNet}} - E_{\mathrm{CCSD}}$, $\Delta F = F_{\mathrm{PhysNet}}^{\alpha} - F_{\mathrm{CCSD}}^{\alpha}$ where $\alpha = (x, y, z)$ are the three Cartesian components of the forces on each atom. On the energies for the TL model, the $\mathrm{MAE}_{\mathrm{train}}(E)$ and $\mathrm{MAE}_{\mathrm{test}}(E)$ are 0.43, 0.41 kcal/mol, and the corresponding $\mathrm{RMSE}_{\mathrm{train}}(E)$ and $\mathrm{RMSE}_{\mathrm{test}}(E)$ are 0.91, 0.85 kcal/mol. The $\mathrm{MAE}_{\mathrm{train}}(F)$ and $\mathrm{MAE}_{\mathrm{test}}(F)$ on forces for the model are 0.39, 0.75 kcal/(mol·Å), and the corresponding $\mathrm{RMSE}_{\mathrm{train}}(F)$ and $\mathrm{RMSE}_{\mathrm{test}}(F)$ are 1.46, 3.54 kcal/(mol·Å).
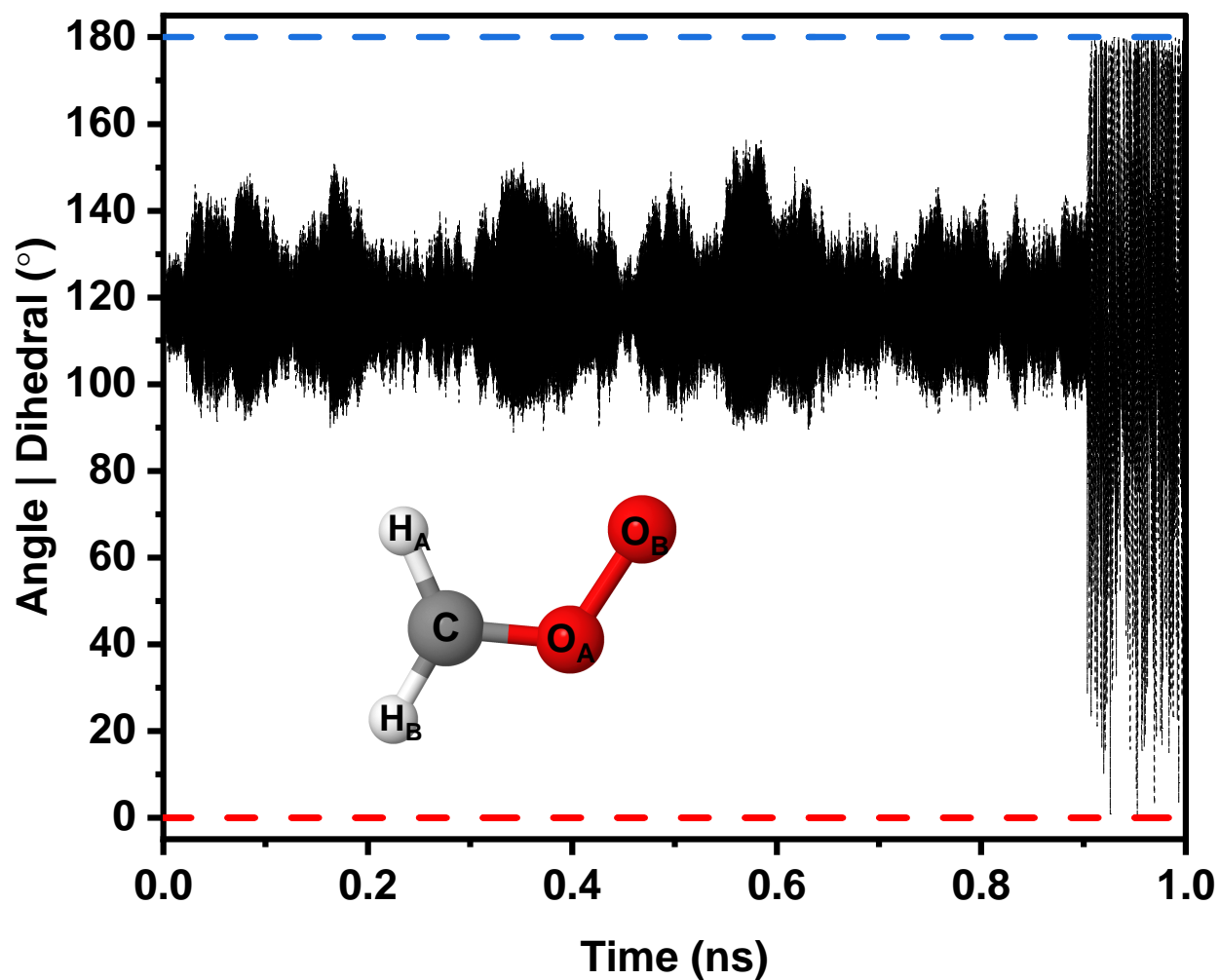
Figure S8: Time series for CO_AO_B valence angle (black) and $H_ACO_AO_B$ (red) and $H_BCO_AO_B$ dihedrals (blue) for a reactive trajectory for the H-transfer channel by exciting $\sim 4\nu_{CH}$ (32.0 kcal/mol) using the PhysNet TL PES. H-transfer occurs after ~ 0.9 ns. The molecule remains planar throughout the simulation.

3 Additional Tables

Table S1: The harmonic bond, Morse bond, valence angle and generalized van der Waals parameters for reactant(CH$_2$OO) and product(dioxirane). k_b in kcal/mol/Å^2, r_e in Å, D_e in kcal/mol, β in Å^{-1}, k_θ in kcal/mol/radian^2, θ_e in degree, k_d in kcal/mol, ϕ_d in degree, k_i in kcal/mol/radian^2, ϕ_i in degree, r in Å and ϵ in kcal/mol. Atom number code (see Figure S8): C(1), H$_A$(2), H$_B$(3), O$_A$(4), O$_B$(5).

	Reactant				Product			
Bond harmonic	k_b	r_e			k_b	r_e		
1 - 2	410.12	1.08			473.13	1.09		
1 - 3	410.12	1.08			473.13	1.09		
1 - 4	474.32	1.27			437.81	1.38		
4 - 5	203.53	1.34			242.86	1.52		
Bond Morse	D_e	r_e	β		D	r_e	β	
1 - 5	X	X	X		127.75	1.38	2.69	
Angle	k_θ	θ_e			k_θ	θ_e		
2 - 1 - 3	26.39	121.99			20.13	135.59		
2 - 1 - 4	46.27	116.96			54.50	118.82		
3 - 1 - 4	53.38	113.91			67.83	117.68		
1 - 4 - 5	39.38	121.72			67.78	120.94		
4 - 1 - 5	X	X			22.97	89.04		
2 - 1 - 5	X	X			82.66	106.65		
3 - 1 - 5	X	X			54.73	118.00		
1 - 5 - 4	X	X			40.18	98.21		
Dihedral	N	k_d	ϕ_d		N	k_d	ϕ_d	
2 - 1 - 4 - 5	2	4.02	180.00		X	X	X	
3 - 1 - 4 - 5	2	5.54	180.00		X	X	X	
Improper	N	k_i	ϕ_i		N	k_i	ϕ_i	
1 - 2 - 4 - 3	0	21.33	0.00		0	18.04	0.00	
1 - 5 - 4 - 2	0	X	X		0	15.26	0.00	
GVDW	r	ϵ	n	m	r	ϵ	n	m
1 - 5	1.76	0.72	6.19	12.82	X	X	X	X

Table S2: GAPO parameters for dioxirane channel: i labels the reactant, j labels the product, $V_{ij,k}^0$ is the center of the Gaussian function (in kcal/mol), $\sigma_{ij,k}$ is the width of the Gaussian (in kcal/mol) and a_{ij} is the polynomial coefficient in kcal/mol.

k	$V_{ij,k}^0$	$\sigma_{ij,k}$	$a_{ij,k0}$	$a_{ij,k1}$	$a_{ij,k2}$	$a_{ij,k3}$
1	-5.36605	3.91184	-2.86507	-0.43938	-0.20009	0.00187
2	13.43213	1.78751	-0.21920	0.27335		
3	5.14916	3.94423	-2.00850			

Table S3: The harmonic bond, Morse bond, angle and generalized van der Waals parameters for reactant(CH$_2$OO) and product(HCOOH). k_b in kcal/mol/Å^2, r_e in Å, D in kcal/mol, β in Å^{-1}, k_θ in kcal/mol/radian^2, θ_e in degree, k_d in kcal/mol, ϕ_d in degree, k_i in kcal/mol/radian^2, ϕ_i in degree, r in Å and ϵ in kcal/mol. **Atom number code(see Figure S8): C(1), H$_A$(2), H$_B$(3), O$_A$(4), O$_B$(5).**

	Reactant				Product			
Bond harmonic	k_b	r_e			k_b	r_e		
1 - 3	413.90	1.09			333.44	1.10		
1 - 4	719.68	1.28			388.47	1.23		
Bond Morse	D	r_e	β		D	r_e	β	
1 - 2	78.55	1.08	2.16		X	X	X	
5 - 2	X	X	X		67.21	0.96	1.98	
4 - 5	349.82	1.34	1.02		9.83	1.53	1.00	
Angle	k_θ	θ_e			k_θ	θ_e		
2 - 1 - 3	18.18	106.37			X	X		
2 - 1 - 4	50.22	115.51			X	X		
3 - 1 - 4	59.82	110.03			31.33	101.58		
1 - 4 - 5	99.54	120.17			92.80	111.12		
2 - 5 - 4	X	X			39.59	91.73		
Dihedral	N	k_d	ϕ_d		N	k_d	ϕ_d	
2 - 1 - 4 - 5	2	5.97	180.00		X	X	X	
3 - 1 - 4 - 5	2	7.37	180.00		X	X	X	
3 - 1 - 4 - 5	3	X	X		3	20.52	0.00	
1 - 4 - 5 - 2	2	X	X		2	7.43	180.00	
Improper	N	k_i	ϕ_i		N	k_i	ϕ_i	
1 - 2 - 4 - 3	0	35.41	0.00		X	X	X	
GVDW	r	ϵ	n	m	r	ϵ	n	m
5 - 2	3.32	1.3	6.90	13.8	X	X	X	X
1 - 2	X	X	X	X	4.61	1.35	6.95	12.86

Table S4: GAPO parameters for H-transfer channel: i labels the reactant, j labels the product, $V_{ij,k}^0$ is the center of the Gaussian function (in kcal/mol), $\sigma_{ij,k}$ is the width of the Gaussian (in kcal/mol) and a_{ij} is the polynomial coefficient in kcal/mol.

k	$V_{ij,k}^0$	$\sigma_{ij,k}$	$a_{ij,k0}$	$a_{ij,k1}$
1	-9.51488	28.24630	-5.64736	-0.11152
2	-0.48168	6.31526	-5.29915	
3	34.98611	15.02948	2.19718	

Table S5: Comparison of energies for 5 stationary points between the predicted energies and *ab initio* energies (in kcal/mol) from the PhysNet base model.

	H$_2$COO	TS-dioxirane	Dioxirane	TS-HCOOH	HCOOH
CCSD(T)	0.00	20.03	-26.15	33.86	9.15
base model	0.00	20.03	-26.15	33.86	9.15

References

(1) Dawes, R.; Jiang, B.; Guo, H. UV absorption spectrum and photodissociation channels of the simplest Criegee intermediate (CH$_2$OO). *J. Am. Chem. Soc.* **2015**, *137*, 50–53.

(2) Yu, H.-G.; Ndengue, S.; Li, J.; Dawes, R.; Guo, H. Vibrational energy levels of the simplest Criegee intermediate (CH$_2$OO) from full-dimensional Lanczos, MCTDH, and MULTIMODE calculations. *J. Chem. Phys.* **2015**, *143*, 084311.

(3) Huang, Y.-H.; Li, J.; Guo, H.; Lee, Y.-P. Infrared spectrum of the simplest Criegee intermediate CH$_2$OO at resolution 0.25 cm^{-1} and new assignments of bands 2ν_9 and ν_5. *J. Chem. Phys.* **2015**, *142*, 214301.