ELECTRONIC SUPPORTING INFORMATION

Quantitative kinetics of the atmospheric reaction between isocyanic acid and hydroxyl radical: post-CCSD(T) contribution, anharmonicity, recrossing effects, torsional anharmonicity, and tunneling

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Note on spin-orbit coupling

All calculations in the full text and SI include the spin-orbit coupling, which raises the barrier height, enthalpy of activation, and reaction energy by 0.20 kcal/mol.

Electronic partition functions

The rate constants include the ratio of electronic partition functions $\frac{g_{TS1}}{g_{HNCO}\, g_{OH}}$. To calculate the electron partition functions, we used 0.4 kcal/mol as the energy difference between the two spin-orbit splitting states of OH($^2\Pi$). For other species, we treat the electronic partition function as the electronic degeneracy of the ground state. The results of these treatments are as follows:

$$g_{TS1} = 2$$

$$g_{HNCO} = 1$$

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

Table S1. Scale factors applied to vibrational frequencies.

Methods	Scale Factor
CCSD(T)-F12a/cc-pVTZ-F12	0.984
CCSD(T)-F12a/cc-pVDZ-F12	0.983
CCSD(T)-F12b/jun'-cc-pVDZ	0.981
M08-HX/MG3S	0.973
M05-2X/aug-cc-pVTZ	0.964

Table S2. Energies (classical barrier heights) of the HNCO + OH reaction and mean unsigned deviations at the different theoretical methods.[a] (kcal/mol)

Methods	$\Delta V^{\ddagger}$		
	TS1	TS2	MUD
W2X//CCSD(T)-F12a/cc-pVTZ-F12	6.81	6.85	0.00
W2X//CCSD(T)-F12a/cc-pVDZ-F12	6.80	6.86	0.00
W2X//CCSD(T)-F12b/jun'-cc-pVDZ	6.80	6.86	0.01

[a]All reactant energies used to compute barrier heights and enthalpies in this table include a spin-orbit contribution of -0.20 kcal/mol, and this raised all reported barrier heights and enthalpies of activation by 0.20 kcal/mol.

Table S3. The relative zero-point vibrational energies of the HNCO + OH reaction and mean unsigned deviations at the different theoretical methods. (kcal/mol)

Methods	($\Delta E_{ZPE}^{\ddagger}$)		
	TS1	TS2	MUD
CCSD(T)-F12a/cc-pVTZ-F12	-0.88	2.26	0.00
CCSD(T)-F12a/cc-pVDZ-F12	-0.65	2.26	0.12
CCSD(T)-F12b/jun'-cc-pVDZ	-0.63	2.27	0.13

Table S4. The enthalpy of activation at 0 K for OH reaction with HNCO (kcal/mol).

Method	$\Delta H_0^{\ddagger}$	
	TS1	TS2
GMM(P).L//CCSD(T)-F12a/cc-pVTZ-F12[a]	5.05	8.22
GMM(P).L//CCSD(T)-F12a/cc-pVTZ-F12 [b]	4.67	8.12
Effect of scale factor	-0.38	-0.11

[a] The enthalpy of activation at 0 K calculated with harmonic zero-point vibration energy without a scale factor.

[b] The enthalpy of activation at 0 K calculated with anharmonic zero-point vibration energies using the reaction-specific scale factors calculated by using the MPW1K/MG3S method.

Table S5. The rate constant (cm^3 $molecule^{-1}$ s^{-1}) of the TS1.

T(K)	$\kappa_{HL}^{TST\,a}$	Γ_{LL}^{b}	$k_{LL}^{SCT\,c}$	$F_{act}^{MS-T\,d}$	$k_1^{\,e}$
190	3.06E-18	0.826	1.62E+03	0.44	1.80E-15
200	5.72E-18	0.830	8.39E+02	0.44	1.76E-15
210	1.01E-17	0.834	4.73E+02	0.44	1.75E-15
220	1.70E-17	0.837	2.86E+02	0.44	1.79E-15
230	2.73E-17	0.839	1.84E+02	0.44	1.86E-15
240	4.24E-17	0.842	1.24E+02	0.44	1.96E-15
250	6.35E-17	0.844	8.78E+01	0.44	2.08E-15
260	9.25E-17	0.845	6.43E+01	0.44	2.22E-15
270	1.31E-16	0.847	4.86E+01	0.44	2.39E-15
280	1.82E-16	0.848	3.79E+01	0.44	2.59E-15
290	2.47E-16	0.850	3.02E+01	0.44	2.81E-15
298	3.11E-16	0.850	2.56E+01	0.44	3.00E-15
300	3.29E-16	0.851	2.46E+01	0.44	3.05E-15
310	4.30E-16	0.851	2.04E+01	0.45	3.33E-15
320	5.55E-16	0.852	1.72E+01	0.45	3.62E-15
330	7.06E-16	0.853	1.47E+01	0.45	3.95E-15
340	8.86E-16	0.853	1.27E+01	0.45	4.30E-15

350	1.10E-15	0.854	1.12E+01	0.45	4.69E-15
390	2.37E-15	0.855	7.24E+00	0.45	6.56E-15
440	5.19E-15	0.854	4.88E+00	0.45	9.75E-15
490	9.93E-15	0.853	3.67E+00	0.45	1.40E-14
540	1.72E-14	0.851	2.96E+00	0.45	1.96E-14
590	2.77E-14	0.848	2.51E+00	0.46	2.68E-14
640	4.20E-14	0.845	2.20E+00	0.46	3.57E-14
690	6.08E-14	0.842	1.98E+00	0.46	4.66E-14
740	8.49E-14	0.838	1.82E+00	0.46	5.98E-14
790	1.15E-13	0.835	1.70E+00	0.46	7.55E-14
840	1.52E-13	0.831	1.60E+00	0.47	9.41E-14
890	1.96E-13	0.828	1.52E+00	0.47	1.16E-13
940	2.49E-13	0.824	1.46E+00	0.47	1.41E-13
990	3.10E-13	0.821	1.41E+00	0.47	1.69E-13
1040	3.82E-13	0.818	1.37E+00	0.47	2.02E-13
1090	4.64E-13	0.814	1.33E+00	0.48	2.39E-13
1140	5.57E-13	0.811	1.30E+00	0.48	2.80E-13
1190	6.63E-13	0.808	1.27E+00	0.48	3.26E-13
1240	7.82E-13	0.804	1.25E+00	0.48	3.78E-13
1290	9.14E-13	0.801	1.23E+00	0.48	4.34E-13
1340	1.06E-12	0.798	1.21E+00	0.49	4.97E-13
1390	1.22E-12	0.795	1.19E+00	0.49	5.65E-13
1440	1.40E-12	0.792	1.18E+00	0.49	6.39E-13
1490	1.60E-12	0.789	1.17E+00	0.49	7.19E-13
1540	1.81E-12	0.787	1.16E+00	0.49	8.07E-13
1590	2.04E-12	0.784	1.15E+00	0.49	9.00E-13
1640	2.29E-12	0.781	1.14E+00	0.49	1.00E-12
1690	2.56E-12	0.779	1.13E+00	0.49	1.11E-12
1740	2.85E-12	0.776	1.12E+00	0.49	1.23E-12
1790	3.16E-12	0.774	1.11E+00	0.49	1.35E-12
1840	3.50E-12	0.771	1.11E+00	0.50	1.48E-12
1890	3.85E-12	0.769	1.10E+00	0.50	1.62E-12
1940	4.23E-12	0.767	1.10E+00	0.50	1.77E-12
1990	4.64E-12	0.764	1.09E+00	0.50	1.92E-12
2040	5.07E-12	0.762	1.09E+00	0.50	2.09E-12
2090	5.52E-12	0.760	1.08E+00	0.50	2.26E-12
2140	6.00E-12	0.758	1.08E+00	0.50	2.44E-12
2190	6.51E-12	0.756	1.07E+00	0.50	2.64E-12
2240	7.04E-12	0.754	1.07E+00	0.50	2.84E-12
2290	7.60E-12	0.752	1.07E+00	0.50	3.05E-12
2340	8.19E-12	0.750	1.07E+00	0.50	3.27E-12
2390	8.81E-12	0.748	1.06E+00	0.50	3.50E-12
2440	9.46E-12	0.746	1.06E+00	0.50	3.74E-12

2490	1.01E-11	0.745	1.06E+00	0.50	3.99E-12
2540	1.08E-11	0.743	1.06E+00	0.50	4.24E-12
2590	1.16E-11	0.741	1.05E+00	0.50	4.51E-12
2640	1.24E-11	0.740	1.05E+00	0.50	4.79E-12
2690	1.32E-11	0.738	1.05E+00	0.50	5.08E-12
2740	1.40E-11	0.736	1.05E+00	0.50	5.37E-12
2790	1.49E-11	0.735	1.05E+00	0.50	5.68E-12
2840	1.58E-11	0.733	1.04E+00	0.50	6.01E-12
2890	1.67E-11	0.732	1.04E+00	0.50	6.34E-12
2940	1.77E-11	0.730	1.04E+00	0.50	6.68E-12
2990	1.87E-11	0.729	1.04E+00	0.50	7.03E-12
3000	1.89E-11	0.729	1.04E+00	0.50	7.10E-12

[a] k_{HL}^{TST} is the conventional transition state theory rate constant calculated with the high level.

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

[c] The k_{LL}^{SCT} is the LL tunneling coefficient.

[d] $F_{act}^{MS-T} = \frac{F_{TS}^{MS-T}}{F_{OH}^{MS-T} F_{HNCO}^{MS-T}}$, where F_{OH}^{MS-T} is 1, F_{HNCO}^{MS-T} and F_{TS}^{MS-T} are calculated using the multi-structural method with torsional anharmonicity based on a coupled torsional potential.

[e] rate constant of the HNCO + OH reaction using variational transition state theory with small-curvature tunneling and torsional anharmonicity.

Here, it is worth noting that where HL denote higher level with GMM(P).L//CCSD(T)-F12a/cc-pVTZ-F12 level, and LL denote lower level with M08-HX/MG3S level.

Table S6. The rate constant (cm^3 molecule^{-1} s^{-1}) of the TS2.

T(K)	k_{HL}^{TST} [a]	Γ_{LL}^{b}	k_{LL}^{SCT} [c]	F_{act}^{MS-T}	k_2
190	9.72E-23	0.986	4.33E+00	0.85	3.54E-22
200	2.77E-22	0.986	3.60E+00	0.85	8.38E-22
210	7.14E-22	0.986	3.10E+00	0.85	1.86E-21
220	1.69E-21	0.986	2.75E+00	0.85	3.89E-21
230	3.72E-21	0.986	2.48E+00	0.85	7.71E-21
240	7.67E-21	0.986	2.27E+00	0.85	1.46E-20
250	1.49E-20	0.986	2.11E+00	0.85	2.63E-20
260	2.77E-20	0.986	1.98E+00	0.84	4.55E-20

270	4.91E-20	0.986	1.87E+00	0.84	7.62E-20
280	8.36E-20	0.986	1.78E+00	0.84	1.23E-19
290	1.37E-19	0.986	1.71E+00	0.84	1.94E-19
298	2.00E-19	0.985	1.65E+00	0.84	2.73E-19
300	2.19E-19	0.985	1.64E+00	0.84	2.96E-19
310	3.38E-19	0.985	1.59E+00	0.84	4.42E-19
320	5.10E-19	0.985	1.54E+00	0.84	6.45E-19
330	7.50E-19	0.985	1.50E+00	0.83	9.22E-19
340	1.08E-18	0.985	1.46E+00	0.83	1.29E-18
350	1.53E-18	0.984	1.43E+00	0.83	1.78E-18
390	5.13E-18	0.983	1.33E+00	0.83	5.55E-18
440	1.75E-17	0.982	1.25E+00	0.83	1.77E-17
490	4.74E-17	0.980	1.19E+00	0.82	4.57E-17
540	1.09E-16	0.978	1.15E+00	0.83	1.01E-16
590	2.20E-16	0.976	1.13E+00	0.83	2.01E-16
640	4.05E-16	0.974	1.11E+00	0.83	3.63E-16
690	6.89E-16	0.972	1.09E+00	0.84	6.12E-16
740	1.10E-15	0.970	1.08E+00	0.84	9.76E-16
790	1.68E-15	0.968	1.07E+00	0.85	1.48E-15
840	2.46E-15	0.966	1.06E+00	0.86	2.16E-15
890	3.48E-15	0.964	1.05E+00	0.87	3.06E-15
940	4.77E-15	0.962	1.05E+00	0.87	4.19E-15
990	6.37E-15	0.960	1.04E+00	0.88	5.62E-15
1040	8.32E-15	0.958	1.04E+00	0.89	7.38E-15
1090	1.07E-14	0.956	1.04E+00	0.90	9.50E-15
1140	1.35E-14	0.954	1.03E+00	0.91	1.20E-14
1190	1.67E-14	0.953	1.03E+00	0.92	1.50E-14
1240	2.05E-14	0.951	1.03E+00	0.93	1.85E-14
1290	2.48E-14	0.949	1.03E+00	0.93	2.25E-14
1340	2.97E-14	0.947	1.02E+00	0.94	2.71E-14
1390	3.53E-14	0.946	1.02E+00	0.95	3.24E-14
1440	4.15E-14	0.944	1.02E+00	0.96	3.83E-14
1490	4.84E-14	0.942	1.02E+00	0.97	4.50E-14
1540	5.61E-14	0.941	1.02E+00	0.98	5.24E-14
1590	6.45E-14	0.939	1.02E+00	0.98	6.06E-14
1640	7.38E-14	0.937	1.02E+00	0.99	6.97E-14
1690	8.39E-14	0.936	1.01E+00	1.00	7.97E-14
1740	9.49E-14	0.934	1.01E+00	1.01	9.07E-14
1790	1.07E-13	0.933	1.01E+00	1.02	1.03E-13
1840	1.20E-13	0.931	1.01E+00	1.02	1.16E-13
1890	1.34E-13	0.930	1.01E+00	1.03	1.30E-13
1940	1.48E-13	0.928	1.01E+00	1.04	1.45E-13
1990	1.64E-13	0.927	1.01E+00	1.05	1.61E-13

2040	1.81E-13	0.925	1.01E+00	1.05	1.79E-13
2090	2.00E-13	0.924	1.01E+00	1.06	1.98E-13
2140	2.19E-13	0.923	1.01E+00	1.07	2.18E-13
2190	2.39E-13	0.921	1.01E+00	1.08	2.39E-13
2240	2.61E-13	0.920	1.01E+00	1.08	2.62E-13
2290	2.84E-13	0.919	1.01E+00	1.09	2.86E-13
2340	3.08E-13	0.917	1.01E+00	1.10	3.12E-13
2390	3.33E-13	0.916	1.01E+00	1.10	3.39E-13
2440	3.60E-13	0.915	1.01E+00	1.11	3.68E-13
2490	3.88E-13	0.914	1.01E+00	1.11	3.98E-13
2540	4.18E-13	0.913	1.01E+00	1.12	4.30E-13
2590	4.48E-13	0.911	1.01E+00	1.13	4.63E-13
2640	4.81E-13	0.910	1.01E+00	1.13	4.98E-13
2690	5.14E-13	0.909	1.01E+00	1.14	5.35E-13
2740	5.50E-13	0.908	1.01E+00	1.14	5.73E-13
2790	5.86E-13	0.907	1.01E+00	1.15	6.14E-13
2840	6.25E-13	0.906	1.01E+00	1.15	6.55E-13
2890	6.64E-13	0.905	1.00E+00	1.16	6.99E-13
2940	7.06E-13	0.904	1.00E+00	1.16	7.45E-13
2990	7.49E-13	0.902	1.00E+00	1.17	7.92E-13
3000	7.60E-13	0.902	1.00E+00	1.17	8.05E-13

Table S7. The total rate constant (cm^3 $molecule^{-1}$ s^{-1}) of the HNCO + OH reaction.

T(K)	k_1	k_2	k_{total}	E_a
190	1.80E-15	3.54E-22	1.80E-15	-0.06
200	1.76E-15	8.38E-22	1.76E-15	-1.20
210	1.75E-15	1.86E-21	1.75E-15	-1.04
220	1.79E-15	3.89E-21	1.79E-15	-0.89
230	1.86E-15	7.71E-21	1.86E-15	-0.74
240	1.96E-15	1.46E-20	1.96E-15	-0.59
250	2.08E-15	2.63E-20	2.08E-15	-0.45
260	2.22E-15	4.55E-20	2.22E-15	-0.31
270	2.39E-15	7.62E-20	2.39E-15	-0.18
280	2.59E-15	1.23E-19	2.59E-15	-0.05
290	2.81E-15	1.94E-19	2.81E-15	0.07
298	3.00E-15	2.73E-19	3.00E-15	0.17
300	3.05E-15	2.96E-19	3.05E-15	0.19
310	3.33E-15	4.42E-19	3.33E-15	0.31

320	3.62E-15	6.45E-19	3.62E-15	0.42
330	3.95E-15	9.22E-19	3.95E-15	0.52
340	4.30E-15	1.29E-18	4.31E-15	0.62
350	4.69E-15	1.78E-18	4.69E-15	0.72
390	6.56E-15	5.55E-18	6.56E-15	1.07
440	9.75E-15	1.77E-17	9.77E-15	1.42
490	1.40E-14	4.57E-17	1.41E-14	1.71
540	1.96E-14	1.01E-16	1.97E-14	1.96
590	2.68E-14	2.01E-16	2.70E-14	2.16
640	3.57E-14	3.63E-16	3.61E-14	2.32
690	4.66E-14	6.12E-16	4.72E-14	2.47
740	5.98E-14	9.76E-16	6.08E-14	5.63
790	7.55E-14	1.48E-15	7.70E-14	5.86
840	9.41E-14	2.16E-15	9.63E-14	6.15
890	1.16E-13	3.06E-15	1.19E-13	6.47
940	1.41E-13	4.19E-15	1.45E-13	6.80
990	1.69E-13	5.62E-15	1.75E-13	7.15
1040	2.02E-13	7.38E-15	2.09E-13	7.50
1090	2.39E-13	9.50E-15	2.48E-13	7.85
1140	2.80E-13	1.20E-14	2.92E-13	8.19
1190	3.26E-13	1.50E-14	3.41E-13	8.54
1240	3.78E-13	1.85E-14	3.96E-13	8.88
1290	4.34E-13	2.25E-14	4.57E-13	9.21
1340	4.97E-13	2.71E-14	5.24E-13	9.54
1390	5.65E-13	3.24E-14	5.97E-13	9.86
1440	6.39E-13	3.83E-14	6.77E-13	10.18
1490	7.19E-13	4.50E-14	7.64E-13	10.50
1540	8.07E-13	5.24E-14	8.59E-13	10.80
1590	9.00E-13	6.06E-14	9.61E-13	11.11
1640	1.00E-12	6.97E-14	1.07E-12	11.41
1690	1.11E-12	7.97E-14	1.19E-12	11.70
1740	1.23E-12	9.07E-14	1.32E-12	11.99
1790	1.35E-12	1.03E-13	1.45E-12	12.28
1840	1.48E-12	1.16E-13	1.60E-12	12.56
1890	1.62E-12	1.30E-13	1.75E-12	12.84
1940	1.77E-12	1.45E-13	1.91E-12	13.12
1990	1.92E-12	1.61E-13	2.09E-12	13.39
2040	2.09E-12	1.79E-13	2.27E-12	13.66
2090	2.26E-12	1.98E-13	2.46E-12	13.93
2140	2.44E-12	2.18E-13	2.66E-12	14.20
2190	2.64E-12	2.39E-13	2.88E-12	14.46
2240	2.84E-12	2.62E-13	3.10E-12	14.72
2290	3.05E-12	2.86E-13	3.33E-12	14.98

2340	3.27E-12	3.12E-13	3.58E-12	15.24
2390	3.50E-12	3.39E-13	3.84E-12	15.49
2440	3.74E-12	3.68E-13	4.11E-12	15.75
2490	3.99E-12	3.98E-13	4.39E-12	16.00
2540	4.24E-12	4.30E-13	4.67E-12	16.25
2590	4.51E-12	4.63E-13	4.97E-12	16.50
2640	4.79E-12	4.98E-13	5.29E-12	16.74
2690	5.08E-12	5.35E-13	5.61E-12	16.99
2740	5.37E-12	5.73E-13	5.95E-12	17.23
2790	5.68E-12	6.14E-13	6.29E-12	17.48
2840	6.01E-12	6.55E-13	6.67E-12	17.72
2890	6.34E-12	6.99E-13	7.04E-12	17.96
2940	6.68E-12	7.45E-13	7.43E-12	18.20
2990	7.03E-12	7.92E-13	7.83E-12	18.44
3000	7.10E-12	8.05E-13	7.90E-12	18.49

Table S8. The conventional transition state theory (TST) rate constants (cm^3 $molecule^{-1}$ s^{-1}) without a transmission coefficient for HNCO + OH reaction.

T(K)	$k_1{}^a$	$k_1{}^{'b}$	$k_2{}^a$	$k_2{}^{'b}$	$f_1{}^c$	$f_2{}^c$
190	3.06E-18	1.02E-18	9.72E-23	6.8E-23	3.01	1.43
200	5.72E-18	2.00E-18	2.77E-22	1.97E-22	2.86	1.41
210	1.01E-17	3.71E-18	7.14E-22	5.16E-22	2.73	1.38
220	1.70E-17	6.50E-18	1.69E-21	1.24E-21	2.61	1.36
230	2.73E-17	1.09E-17	3.72E-21	2.77E-21	2.51	1.35
240	4.24E-17	1.75E-17	7.67E-21	5.77E-21	2.43	1.33
250	6.35E-17	2.70E-17	1.49E-20	1.14E-20	2.35	1.31
260	9.25E-17	4.06E-17	2.77E-20	2.13E-20	2.28	1.30
270	1.31E-16	5.91E-17	4.91E-20	3.81E-20	2.22	1.29
280	1.82E-16	8.41E-17	8.36E-20	6.54E-20	2.16	1.28
290	2.47E-16	1.17E-16	1.37E-19	1.08E-19	2.11	1.27
298	3.11E-16	1.50E-16	2.00E-19	1.58E-19	2.07	0.94
300	3.29E-16	1.59E-16	2.19E-19	1.74E-19	2.07	1.26
310	4.3E-16	2.13E-16	3.38E-19	2.71E-19	2.02	1.25
320	5.55E-16	2.80E-16	5.10E-19	4.11E-19	1.99	1.24
330	7.06E-16	3.62E-16	7.50E-19	6.08E-19	1.95	1.23
340	8.86E-16	4.62E-16	1.08E-18	8.81E-19	1.92	1.23
350	1.10E-15	5.83E-16	1.53E-18	1.25E-18	1.89	1.22
390	2.37E-15	1.32E-15	5.13E-18	4.29E-18	1.79	1.20
440	5.19E-15	3.06E-15	1.75E-17	1.49E-17	1.70	1.17

490	9.93E-15	6.11E-15	4.74E-17	4.10E-17	1.63	1.16
540	1.72E-14	1.09E-14	1.09E-16	9.52E-17	1.57	1.14
590	2.77E-14	1.80E-14	2.20E-16	1.95E-16	1.53	1.13
640	4.20E-14	2.80E-14	4.05E-16	3.60E-16	1.50	1.12
690	6.08E-14	4.13E-14	6.89E-16	6.18E-16	1.47	1.12
740	8.49E-14	5.86E-14	1.10E-15	9.96E-16	1.45	1.11
790	1.15E-13	8.05E-14	1.68E-15	1.53E-15	1.43	1.10
840	1.52E-13	1.07E-13	2.46E-15	2.24E-15	1.41	1.10
890	1.96E-13	1.40E-13	3.48E-15	3.18E-15	1.40	1.09
940	2.49E-13	1.79E-13	4.77E-15	4.37E-15	1.39	1.09
990	3.10E-13	2.26E-13	6.37E-15	5.86E-15	1.38	1.09
1040	3.82E-13	2.79E-13	8.32E-15	7.68E-15	1.37	1.08
1090	4.64E-13	3.41E-13	1.07E-14	9.87E-15	1.36	1.08
1140	5.57E-13	4.12E-13	1.35E-14	1.25E-14	1.35	1.08
1190	6.63E-13	4.93E-13	1.67E-14	1.55E-14	1.35	1.08
1240	7.82E-13	5.84E-13	2.05E-14	1.91E-14	1.34	1.07
1290	9.14E-13	6.85E-13	2.48E-14	2.31E-14	1.33	1.07
1340	1.06E-12	7.98E-13	2.97E-14	2.78E-14	1.33	1.07
1390	1.22E-12	9.23E-13	3.53E-14	3.30E-14	1.33	1.07
1440	1.40E-12	1.06E-12	4.15E-14	3.88E-14	1.32	1.07
1490	1.60E-12	1.21E-12	4.84E-14	4.54E-14	1.32	1.07
1540	1.81E-12	1.38E-12	5.61E-14	5.26E-14	1.31	1.07
1590	2.04E-12	1.56E-12	6.45E-14	6.06E-14	1.31	1.06
1640	2.29E-12	1.75E-12	7.38E-14	6.94E-14	1.31	1.06
1690	2.56E-12	1.96E-12	8.39E-14	7.90E-14	1.31	1.06
1740	2.85E-12	2.19E-12	9.49E-14	8.94E-14	1.30	1.06
1790	3.16E-12	2.43E-12	1.07E-13	1.01E-13	1.30	1.06
1840	3.50E-12	2.69E-12	1.20E-13	1.13E-13	1.30	1.06
1890	3.85E-12	2.97E-12	1.34E-13	1.26E-13	1.30	1.06
1940	4.23E-12	3.27E-12	1.48E-13	1.40E-13	1.30	1.06
1990	4.64E-12	3.58E-12	1.64E-13	1.55E-13	1.29	1.06
2040	5.07E-12	3.92E-12	1.81E-13	1.71E-13	1.29	1.06
2090	5.52E-12	4.27E-12	2.00E-13	1.89E-13	1.29	1.06
2140	6.00E-12	4.65E-12	2.19E-13	2.07E-13	1.29	1.06
2190	6.51E-12	5.04E-12	2.39E-13	2.26E-13	1.29	1.06
2240	7.04E-12	5.46E-12	2.61E-13	2.47E-13	1.29	1.06
2290	7.60E-12	5.90E-12	2.84E-13	2.69E-13	1.29	1.06
2340	8.19E-12	6.37E-12	3.08E-13	2.92E-13	1.29	1.06
2390	8.81E-12	6.85E-12	3.33E-13	3.16E-13	1.29	1.05
2440	9.46E-12	7.36E-12	3.60E-13	3.42E-13	1.28	1.05
2490	1.01E-11	7.90E-12	3.88E-13	3.68E-13	1.28	1.05
2540	1.08E-11	8.46E-12	4.18E-13	3.96E-13	1.28	1.05
2590	1.16E-11	9.04E-12	4.48E-13	4.26E-13	1.28	1.05

2640	1.24E-11	9.65E-12	4.81E-13	4.56E-13	1.28	1.05
2690	1.32E-11	1.03E-11	5.14E-13	4.89E-13	1.28	1.05
2740	1.40E-11	1.09E-11	5.50E-13	5.22E-13	1.28	1.05
2790	1.49E-11	1.16E-11	5.86E-13	5.57E-13	1.28	1.05
2840	1.58E-11	1.23E-11	6.25E-13	5.94E-13	1.28	1.05
2890	1.67E-11	1.31E-11	6.64E-13	6.32E-13	1.28	1.05
2940	1.77E-11	1.39E-11	7.06E-13	6.71E-13	1.28	1.05
2990	1.87E-11	1.47E-11	7.49E-13	7.12E-13	1.28	1.05
3000	1.89E-11	1.48E-11	7.60E-13	7.20E-13	1.28	1.05

[a] k_1 and k_2 are the conventional transition state theory rate constants calculated using the specific-reaction scale factors.

[b] $k_1^{'}$ and $k_2^{'}$ are the conventional transition state theory rate constants calculated using the scale factors obtained by the standard method.

[c] f_1 and f_2 are equal to $k_1/k_1^{'}$ and $k_2/k_2^{'}$ respectively.

Table S9. Absolute energies (Hartree) and the Cartesian coordinates (Å) of the optimized geometries.

(a) by CCSD(T)-F12a/cc-pVTZ-F12

species	Absolute energies	Cartesian coordinates			
OH	-75.674101	O	0.0000000000	0.0000000000	0.1080069596
		H	0.0000000000	0.0000000000	-0.8625469596
HNCO	-168.511459	C	0.0078532480	0.0445787126	0.0000000000
		O	-0.3670205795	1.1485223621	0.0000000000
		N	0.2410710237	-1.1502686006	0.0000000000
		H	1.1741183078	-1.5237844742	0.0000000000
TS1	-244.175237	C	-0.8182306315	0.1472788647	0.0031858264
		O	-1.7748344663	-0.5188358602	-0.0010636888
		N	0.1124306872	0.9510521047	0.0337956306
		H	1.1847122868	0.5380590300	-0.1917543780
		H	2.0455841336	-0.5288590516	0.8482346742
		O	1.9157359902	-0.4463360876	-0.1092560643
TS2	-244.175133	C	0.4318203696	-0.1651781984	-0.0244269571
		O	1.3810261484	0.5056337872	-0.0076287275
		N	-0.2486341090	-1.2288213610	0.1202338607
		H	-0.9064952649	-1.4349502181	-0.6221362980
		H	-1.5012951113	0.7565171809	0.8157192594
		O	-1.1913670328	0.7825428092	-0.1018351375

NCO	-167.825323	C	0.0000000000	0.0000000000	-0.0381971211
		N	0.0000000000	0.0000000000	-1.2677076313
		O	0.0000000000	0.0000000000	1.1393457525
H_2O	-76.374113	H	0.7575842167	-0.4649772311	0.0000000000
		H	-0.7575827122	-0.4649830468	0.0000000000
		O	-0.0000015045	0.1226092779	0.0000000000
P2	-244.223985	C	-0.0472138727	0.1026143564	0.0067644772
		O	-0.5952444592	1.1770277299	-0.0268936184
		N	-0.7392491636	-1.1056529178	-0.1011562686
		H	-1.6032703366	-1.0082282254	0.4354561666
		H	1.5003595225	-0.9635654864	-0.0430820436
		O	1.2859773096	-0.0265254568	0.0393962868

(b) by CCSD(T)-F12a/cc-pVDZ-F12

species	Absolute energies	Cartesian coordinates			
OH	-75.663803	O	0.0000000000	0.0000000000	0.1080720808
		H	0.0000000000	0.0000000000	-0.8626120808
HNCO	-168.491147	C	0.0083644972	0.0441899232	0.0000000000
		O	-0.3665371036	1.1488159607	0.0000000000
		N	0.2397972676	-1.1520146993	0.0000000000
		H	1.1743973388	-1.5219431846	0.0000000000
TS1	-244.144401	C	-0.8129977676	0.1460527704	0.0044286340
		O	-1.7690306305	-0.5215756944	-0.0030964562
		N	0.1158035350	0.9536973908	0.0402788152
		H	1.1850881575	0.5401280492	-0.1976787347
		H	2.0406080797	-0.5245414385	0.8483833989
		O	1.9059266260	-0.4514020774	-0.1091736572
TS2	-244.144726	C	0.4321826054	-0.1659569116	-0.0247959500
		O	1.3825360898	0.5042084468	-0.0088109072
		N	-0.2496252273	-1.2297348605	0.1224628721
		H	-0.9031209270	-1.4346241130	-0.6243066845
		H	-1.5020910883	0.7581731772	0.8169631352
		O	-1.1948264528	0.7836782612	-0.1015864657
NCO	-167.805926	C	0.0000000000	0.0000000000	-0.0384214242
		N	0.0000000000	0.0000000000	-1.2684685127
		O	0.0000000000	0.0000000000	1.1403309369
H_2O	-76.363197	H	0.7573402916	-0.4650872813	0.0000000000
		H	-0.7573387874	-0.4650930961	0.0000000000
		O	-0.0000015042	0.1228293774	0.0000000000
P2	-244.193323	C	-0.0472897457	0.1028237918	0.0067860742

		O	-0.5959512830	1.1776988031	-0.0266757472
		N	-0.7393925879	-1.1074657338	-0.1015842031
		H	-1.6029987420	-1.0073747170	0.4355513031
		H	1.4997972926	-0.9638009037	-0.0428999802
		O	1.2871940661	-0.0262112404	0.0393075533

(c) by CCSD(T)-F12b/$jun^{'}$-cc-pVDZ

species	Absolute energies	Cartesian coordinates			
OH	-75.648890	O	0.0000000000	0.0000000000	0.1077725725
		H	0.0000000000	0.0000000000	-0.8623125725
HNCO	-168.460631	C	0.0081127181	0.0433003586	0.0000000000
		O	-0.3645814662	1.1474373581	0.0000000000
		N	0.2376798814	-1.1528919584	0.0000000000
		H	1.1748108667	-1.5187977583	0.0000000000
TS1	-244.099234	C	-0.8171450677	0.1481664031	0.0035873175
		O	-1.7751388269	-0.5145956943	-0.0127866640
		N	0.1143036363	0.9502493539	0.0504477148
		H	1.1747872253	0.5290162950	-0.1972355892
		H	2.0615401606	-0.5106361033	0.8474373262
		O	1.9070508724	-0.4598412544	-0.1083081052
TS2	-244.098622	C	0.4294503708	-0.1668343385	-0.0238513435
		O	1.3773477512	0.5056818836	-0.0064187873
		N	-0.2483110176	-1.2323617000	0.1232495129
		H	-0.9026565924	-1.4316884141	-0.6256911659
		H	-1.4926844517	0.7604563394	0.8174592584
		O	-1.1980910602	0.7804902295	-0.1048214746
NCO	-167.777768	C	0.0000000000	0.0000000000	-0.0382888509
		N	0.0000000000	0.0000000000	-1.2673677575
		O	0.0000000000	0.0000000000	1.1390976084
H_2O	-76.346009	H	0.7571497526	-0.4647806366	0.0000000000
		H	-0.7571482463	-0.4647864464	0.0000000000
		O	-0.0000015063	0.1222160830	0.0000000000
P2	-244.149175	C	-0.0467630501	0.1022558917	0.0069878892
		O	-0.5958245847	1.1759682922	-0.0258847007
		N	-0.7360862891	-1.1087488393	-0.0992111044
		H	-1.6029305480	-1.0046251125	0.4332890973
		H	1.4974519430	-0.9632028763	-0.0435917295
		O	1.2855115290	-0.0259773559	0.0388955482

(d) by M08-HX/MG3S

species	Absolute energies	Cartesian coordinates			
OH	-75.7272	O	0.00000000	0.00000000	0.10779100
		H	0.00000000	0.00000000	-0.86233100
HNCO	-168.678	C	0.00000000	0.04827500	0.00000000

		O	-0.37140400	1.14412200	0.00000000
		N	0.25730100	-1.12821300	0.00000000
		H	1.17012500	-1.54513600	0.00000000
C1	-244.411995	C	1.19153300	0.06442800	0.00000000
		O	2.27913600	-0.33889600	0.00000000
		N	0.11668900	0.59849700	0.00000000
		H	-0.80636600	0.18840100	0.00000100
		H	-3.37058800	0.43802300	-0.00000400
		O	-2.75276900	-0.31141200	0.00000000
TS1	-244.393	C	-0.84585500	0.15279100	0.00077900
		O	-1.80397400	-0.49641800	-0.00403000
		N	0.09856800	0.91888400	0.02798000
		H	1.19493900	0.51906000	-0.18492300
		H	2.07882100	-0.53128800	0.84715100
		O	1.94289900	-0.42067000	-0.10381500
TS2	-244.392	C	0.43432600	-0.16806000	-0.02186000
		O	1.36852400	0.50763400	-0.00324500
		N	-0.23926700	-1.22589600	0.10663400
		H	-0.91370200	-1.44095900	-0.61776100
		H	-1.50186200	0.76781200	0.81440300
		O	-1.18296400	0.77521300	-0.09824500
NCO	-167.986	C	0.00000000	0.00000000	-0.03774800
		N	0.00000000	0.00000000	-1.25697600
		O	0.00000000	0.00000000	1.12816500
H_2O	-76.428	H	0.76321900	-0.46134000	0.00000000
		H	-0.76321900	-0.46134700	0.00000000
		O	0.00000000	0.11533600	0.00000000
P2	-244.442	C	-0.04529800	0.10336400	0.01011300
		O	-0.59363300	1.16855700	-0.01974100
		N	-0.73112700	-1.11268600	-0.07034000
		H	-1.62528800	-0.99788800	0.41110900
		H	1.51565900	-0.95763700	-0.04911000
		O	1.28104600	-0.02804000	0.02845400

Table S10. Absolute energies in Hartree (1 Hartree = 1.a.u.)

Species	Methods	Total energies (a.u.)
HNCO	GMM(P).L //CCSD(T)-F12a/cc-pVTZ-F12	-168.79315388
	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-168.8008449
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-168.51095823
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-168.79931
	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-168.7992887

	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-168.7992987
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-168.7917492
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-168.7917186
OH	GMM(P).L //CCSD(T)-F12a/cc-pVTZ-F12	-75.79147194
	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-75.79360552
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-75.674100415
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-75.79360552
	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-75.79360514
	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-75.79360651
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-75.79102264
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-75.79098531
C1	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-244.19142476
TS1	GMM(P).L //CCSD(T)-F12a/cc-pVTZ-F12	-244.57517562
	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-244.5853091
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-244.1747843
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-244.5823815
	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-244.5823697
	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-244.5823862
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-244.5719894
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-244.5718919
TS2	GMM(P).L //CCSD(T)-F12a/cc-pVTZ-F12	-244.5750747
	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-244.5852808
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-244.1539414
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-244.582311
	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-244.5822868
	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-244.5822869
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-244.571893
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-244.571791
NCO	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-168.1148729
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-167.8249162
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-168.1125304
	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-168.1125109
	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-168.1125358
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-168.1049138
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-168.1048898
H_2O	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-76.49443363
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-76.37405896
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-76.49395354

	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-76.49395331
	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-76.4939565
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-76.49135252
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-76.4912975
P2	W3X-L//CCSD(T)-F12a/cc-pVTZ-F12	-244.6333005
	CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S	-244.1632679
	W2X//CCSD(T)-F12a/cc-pVTZ-F12	-244.6310548
	W2X//CCSD(T)-F12a/cc-pVDZ-F12	-244.6310257
	W2X//CCSD(T)-F12b/$jun^{'}$-cc-pVDZ	-244.6310512
	MW2-F12//CCSD(T)-F12a/cc-pVTZ-F12	-244.62069
	MW2-F12.L//CCSD(T)-F12a/cc-pVTZ-F12	-244.6206113

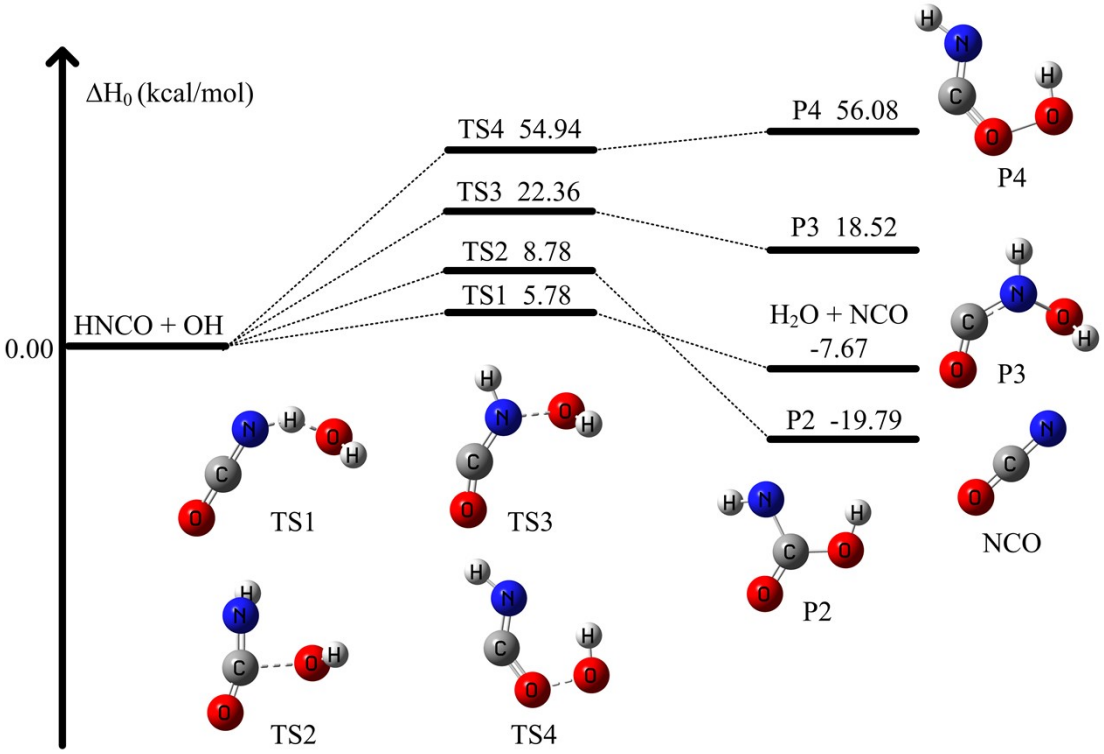

Figure S1. The enthalpy profile of the OH reaction with HNCO at 0 K as calculated by CCSD(T)-F12a/cc-pVTZ-F12//M08-HX/MG3S.

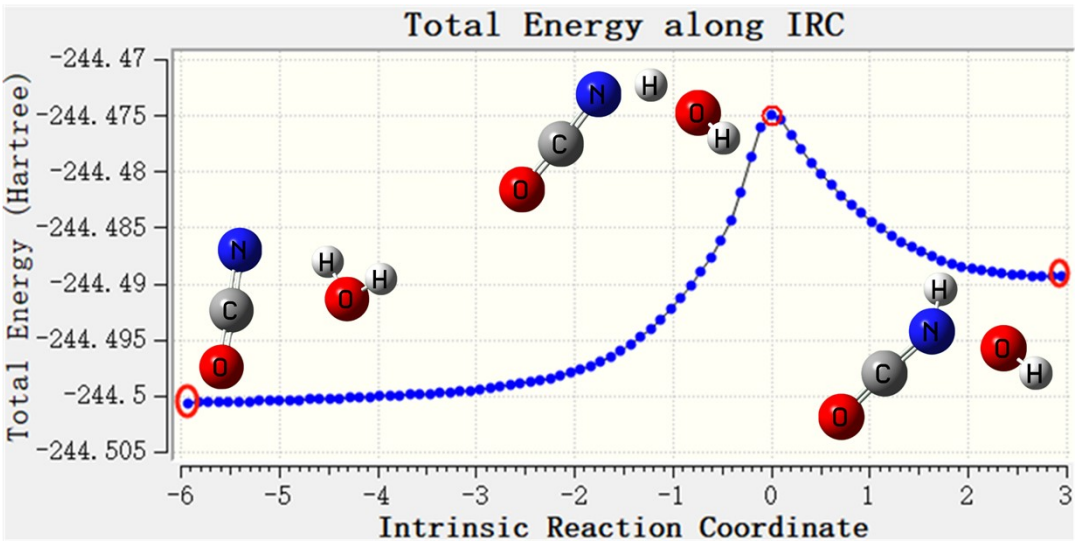

Figure S2. Intrinsic Reaction Coordinate (IRC) calculations for TS1.

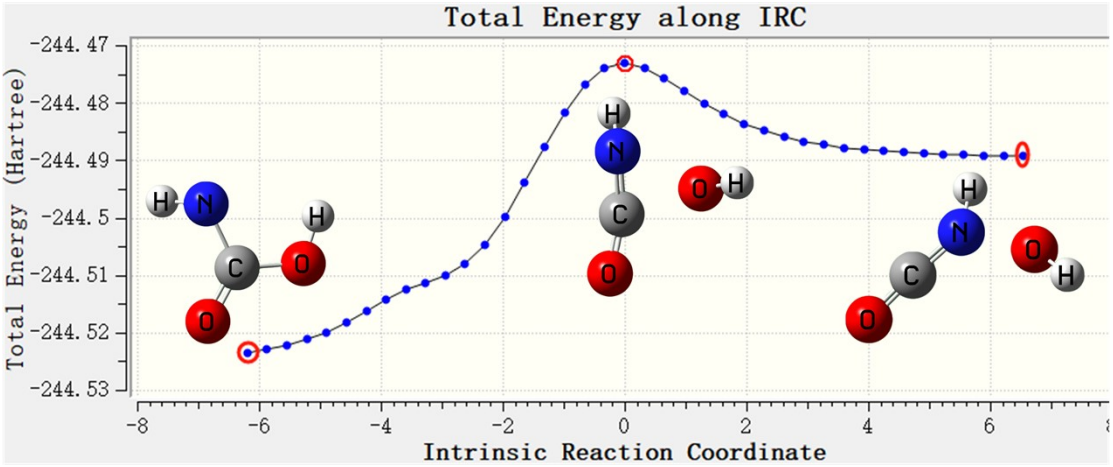

Figure S3. Intrinsic Reaction Coordinate (IRC) calculations for TS2.