Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Catalyzed Reaction of Isocyanates (RNCO) with Water: Supplementary Information

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Extended Methods

A benchmark is performed to justify the reliability of the results obtained with the composite methods as the size and lack of symmetry of these structures preclude a pure coupled cluster treatment with a large basis set. Using the reactants (H_2O + HNCO), hydrolysis transition states (**TS1**, **TS2**) and respective products (**M1**, **M2**), as well as the transition state connecting the two hydrolysis products (**TS3**), we benchmark this composite method against the CCSD(T)/cc-pVQZ geometries obtained from CFOUR 2.0. The MP2[TZ,QZ] + ΔCCSD(T)/DZ method exhibited a RMSE of 0.0020 Å for bond lengths and a RMSE of 0.172° for bond angles, slightly outperforming conventional CCSD(T)/cc-pVTZ (RMSE = 0.0022 Å , 0.528°) and significantly outperforming CCSD(T)/cc-pVDZ (RMSE = 0.0112 Å , 1.746°), therefore justifying the reliability of geometries obtained via composite methods for this system. CCSD(T)/CBS single points are obtained on top of these composite geometries and likely sufficiently capture the correlation energy of each stationary point given the small CCSDT and CCSDT(Q) corrections obtained in the focal point tables for the parent case. In the catalyzed sections, CCSD(T)/aug-cc-pV(T+d)Z single points are run on the optimized geometries and not extrapolated due to the cost of the larger systems and the additional augmented functions.

The Cartesian coordinates for all optimized structures can be found in the accompanying files labeled: "Coupled Cluster Geometries" for the uncalatlyzed high level geometries, "Uncatalyzed Substituent Geometries" for the substituted RNCO + H_2O geometries, and "Catalyzed Geometries" for the water and RNCO catalyzed structures.

Additional Figures

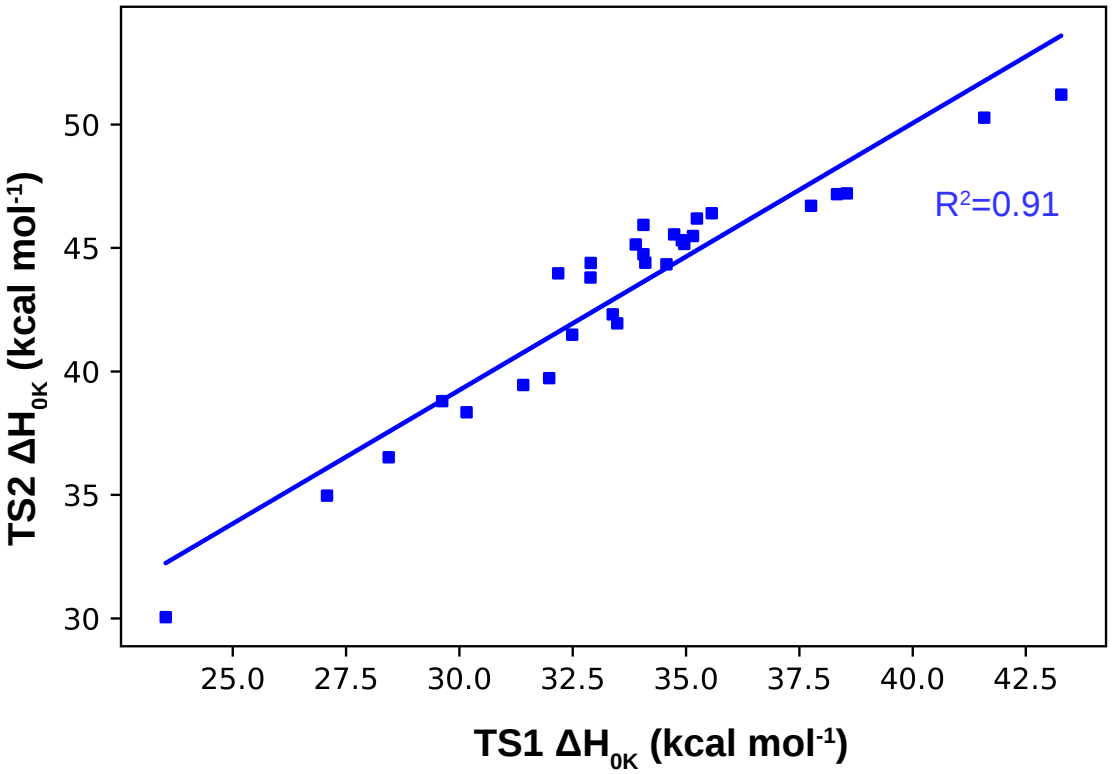

Figure 1: Scatter plot of the **TS1** vs **TS2** ΔH_{0K} values at the CCSD(T)/CBS//MP2[TZ,QZ] + ΔCCSD(T)/cc-pV(D+d)Z level of theory.

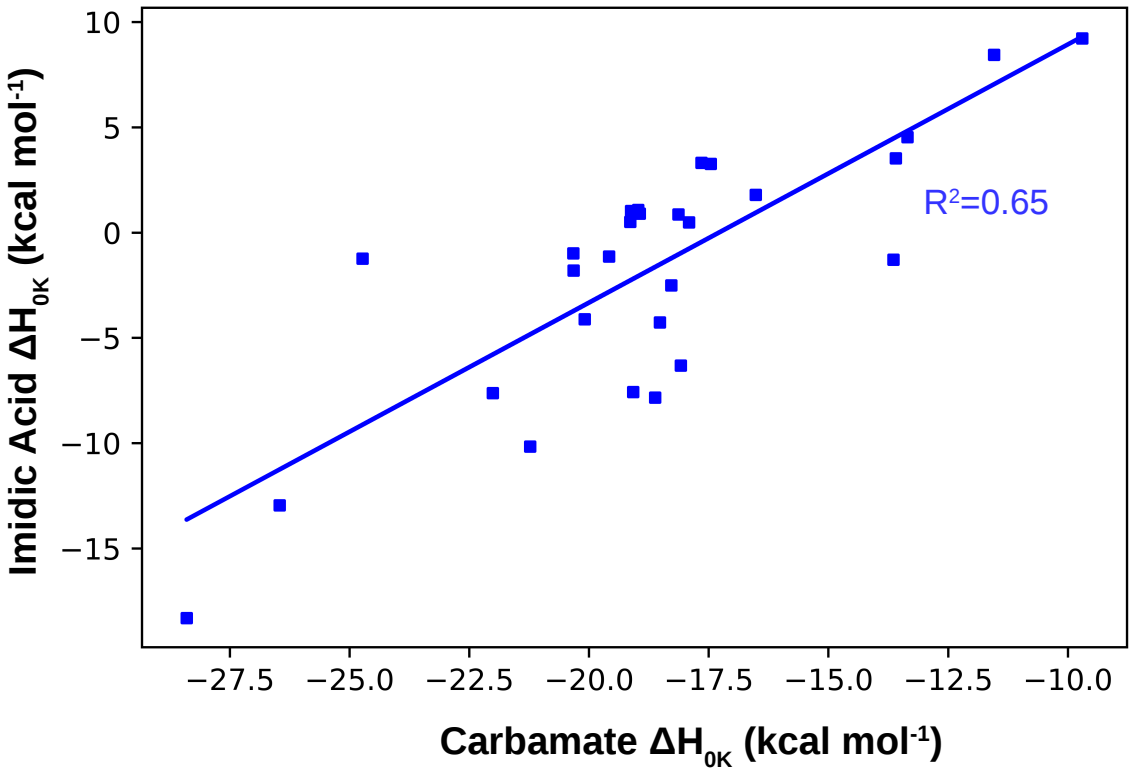

Figure 2: Scatter plot of the **M1** vs **M2** ΔH_{0K} values at the CCSD(T)/CBS//MP2[TZ,QZ] + ΔCCSD(T)/cc-pV(D+d)Z level of theory.

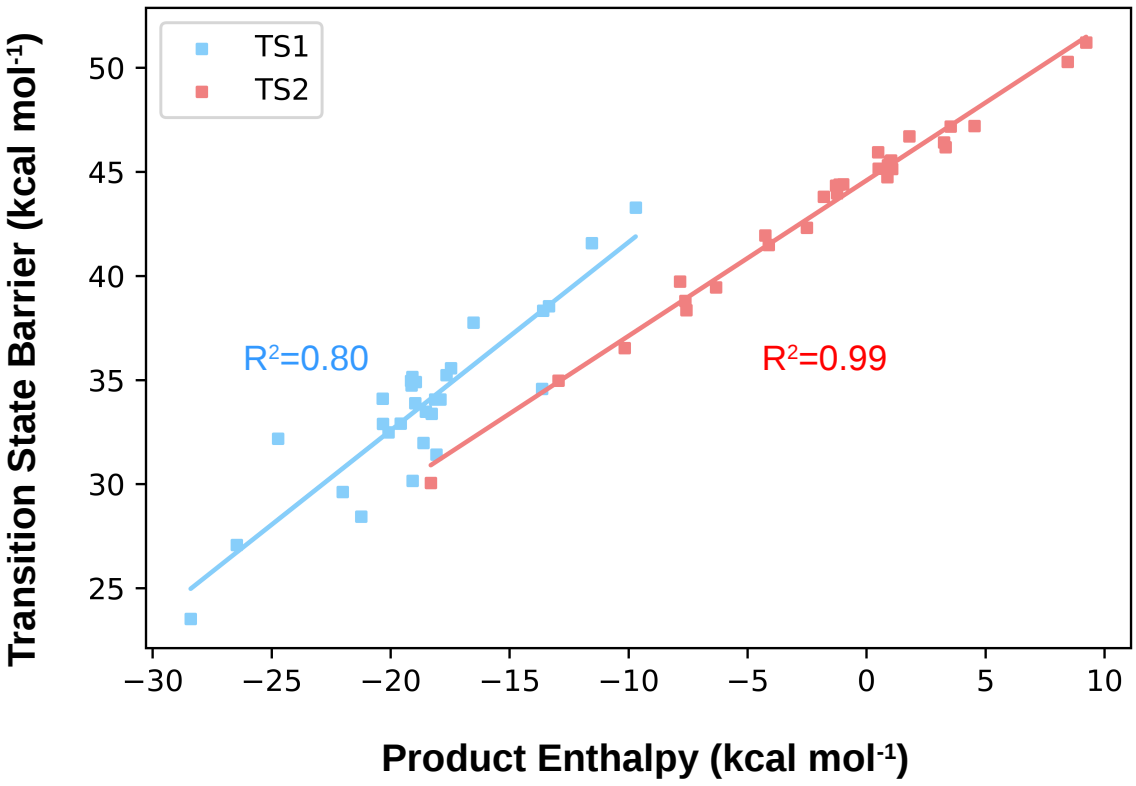

Figure 3: Bell-Evans-Polanyi plot of the product relative enthalpies vs the transition state barrier heights for **TS1** (Blue) and **TS2** (Red). ΔH_{0K} values are obtained at the CCSD(T)/CBS//MP2[TZ,QZ] + ΔCCSD(T)/cc-pV(D+d)Z level of theory.

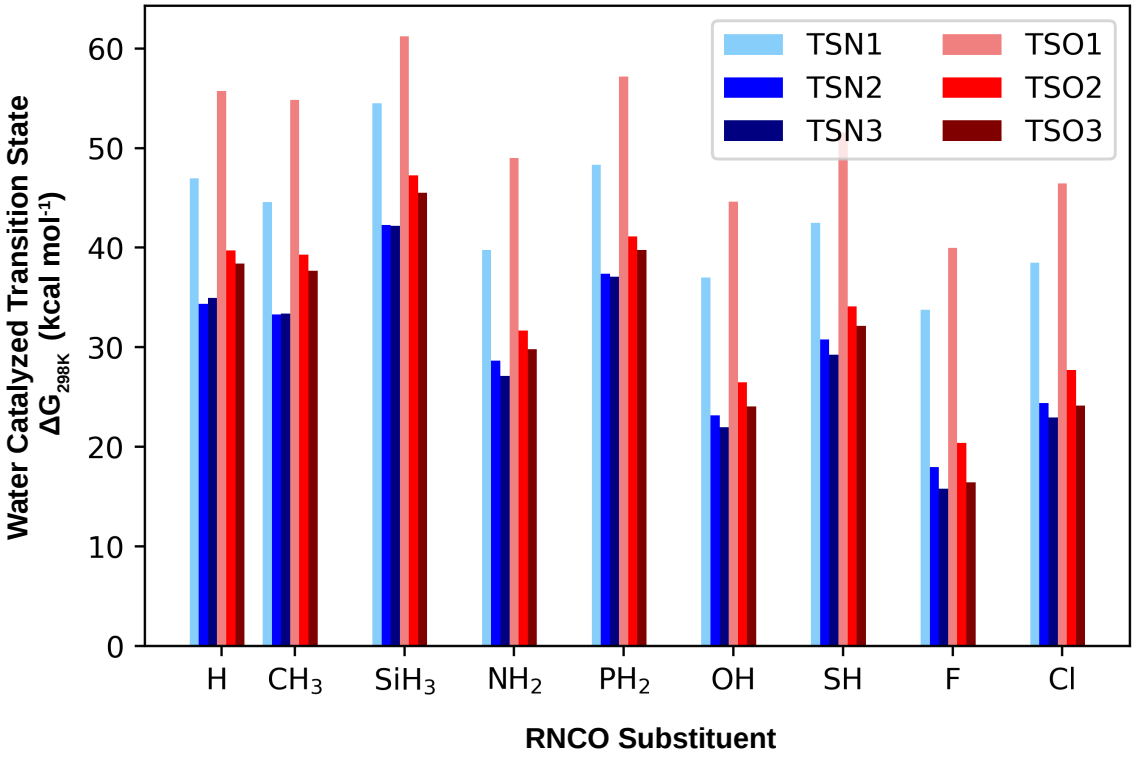

Figure 4: ΔG_{298K} barrier heights relative to separated products for the uncatalyzed and RNCO catalysed cases at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + ΔCCSD(T)/6-31+G** level of theory.

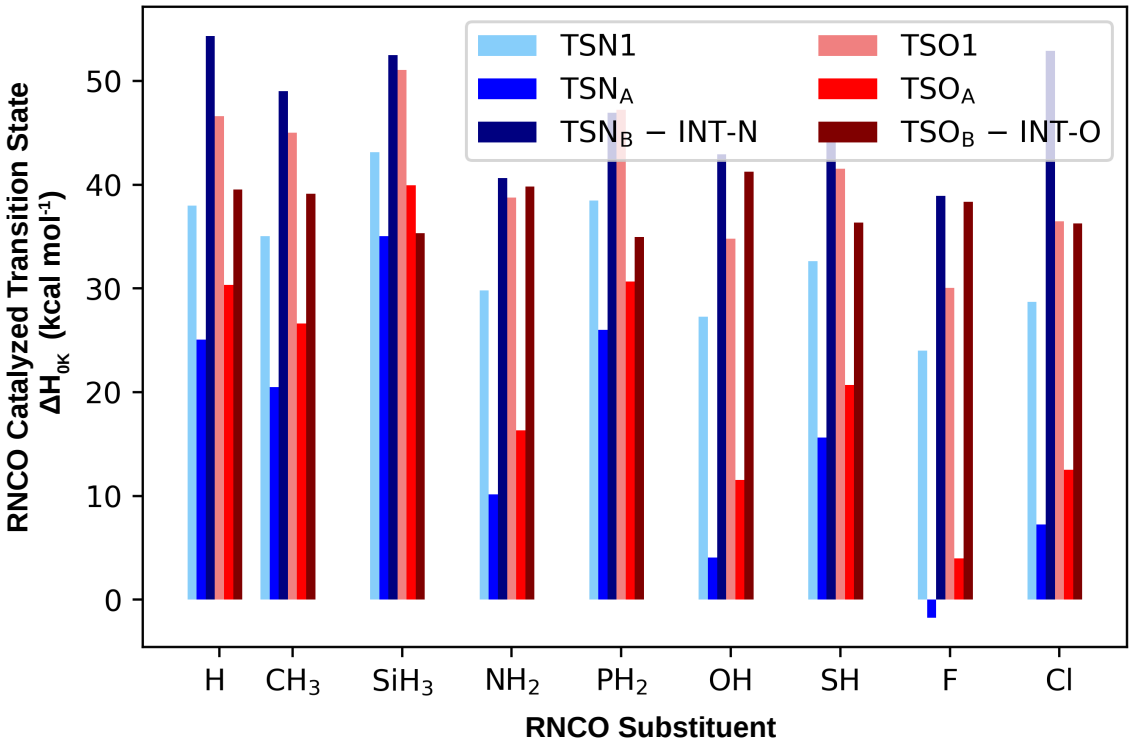

Figure 5: ΔH_{0K} barrier heights relative to separated products for the uncatalyzed (**TSN1** and **TSO1**) and RNCO catalysed cases at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + ΔCCSD(T)/6-31+G** level of theory. The barrier with the A subscript corresponds to the initial transition state forming the intermediate species and the second barrier corresponds to the hydrogen transfer process from the intermediate to the final produce. See SI Figure 8.

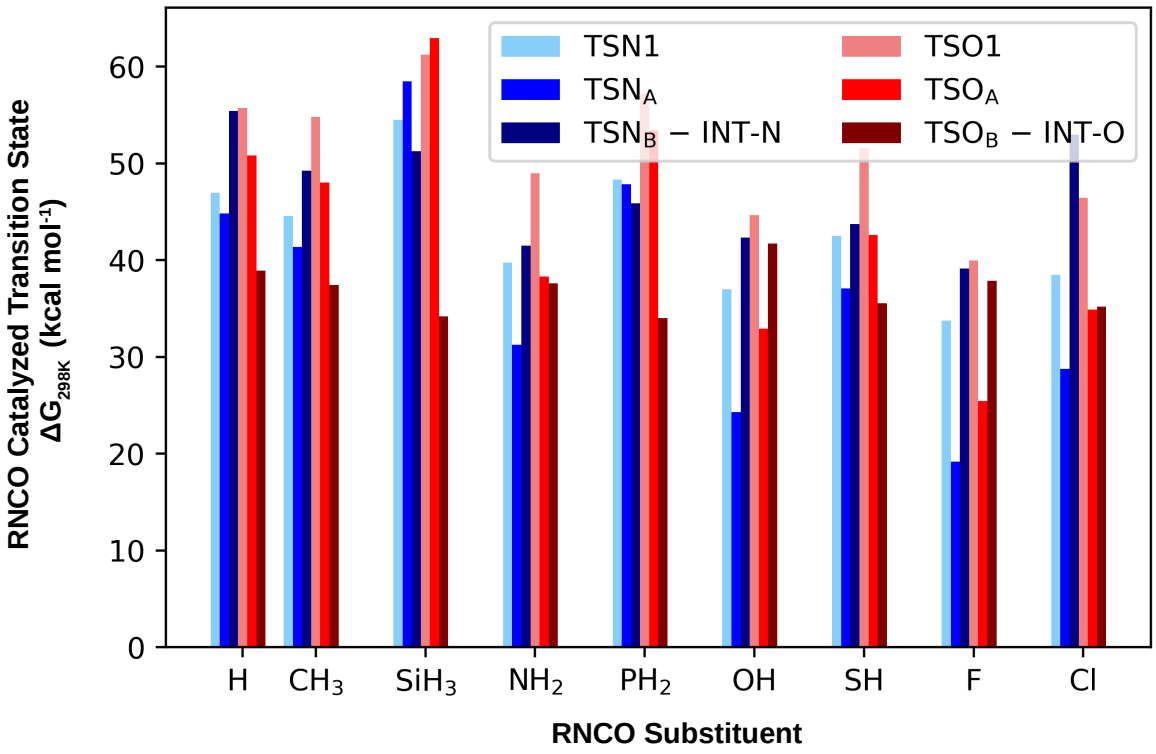

Figure 6: ΔG_{298K} barrier heights relative to separated products for the uncatalyzed (**TSN1** and **TSO1**) and RNCO catalysed cases at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + ΔCCSD(T)/6-31+G** level of theory. The barrier with the A subscript corresponds to the initial transition state forming the intermediate species and the second barrier corresponds to the hydrogen transfer process from the intermediate to the final produce. See SI Figure 8.

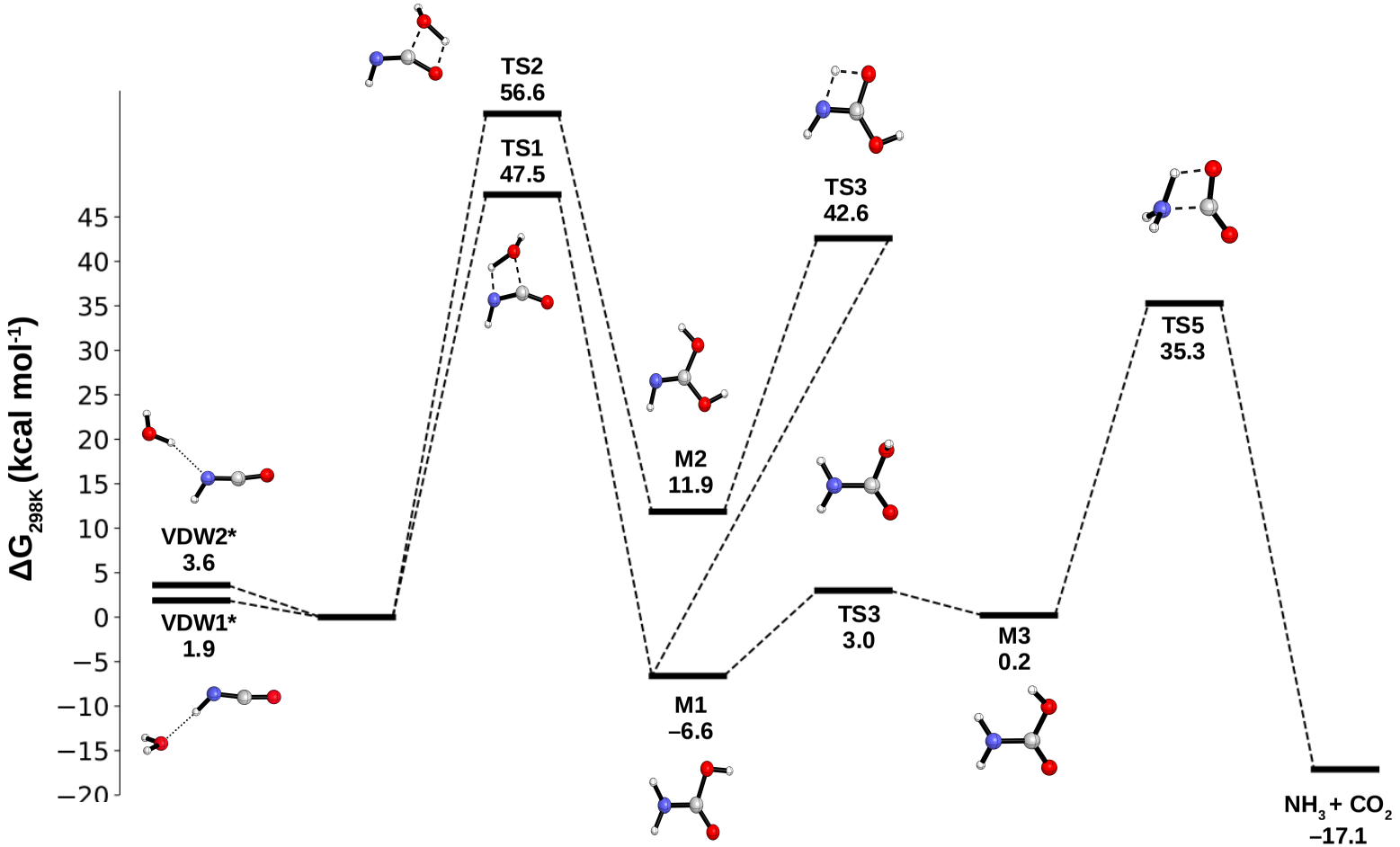

Figure 7: Predicted 298 K Gibbs energies for stationary points on the HNCO + H_2O potential energy surface. All values are in kcal mol^{-1} and target the CCSDT(Q)/CBS limit. Structures denoted with an asterisk are computed using augmented basis functions.

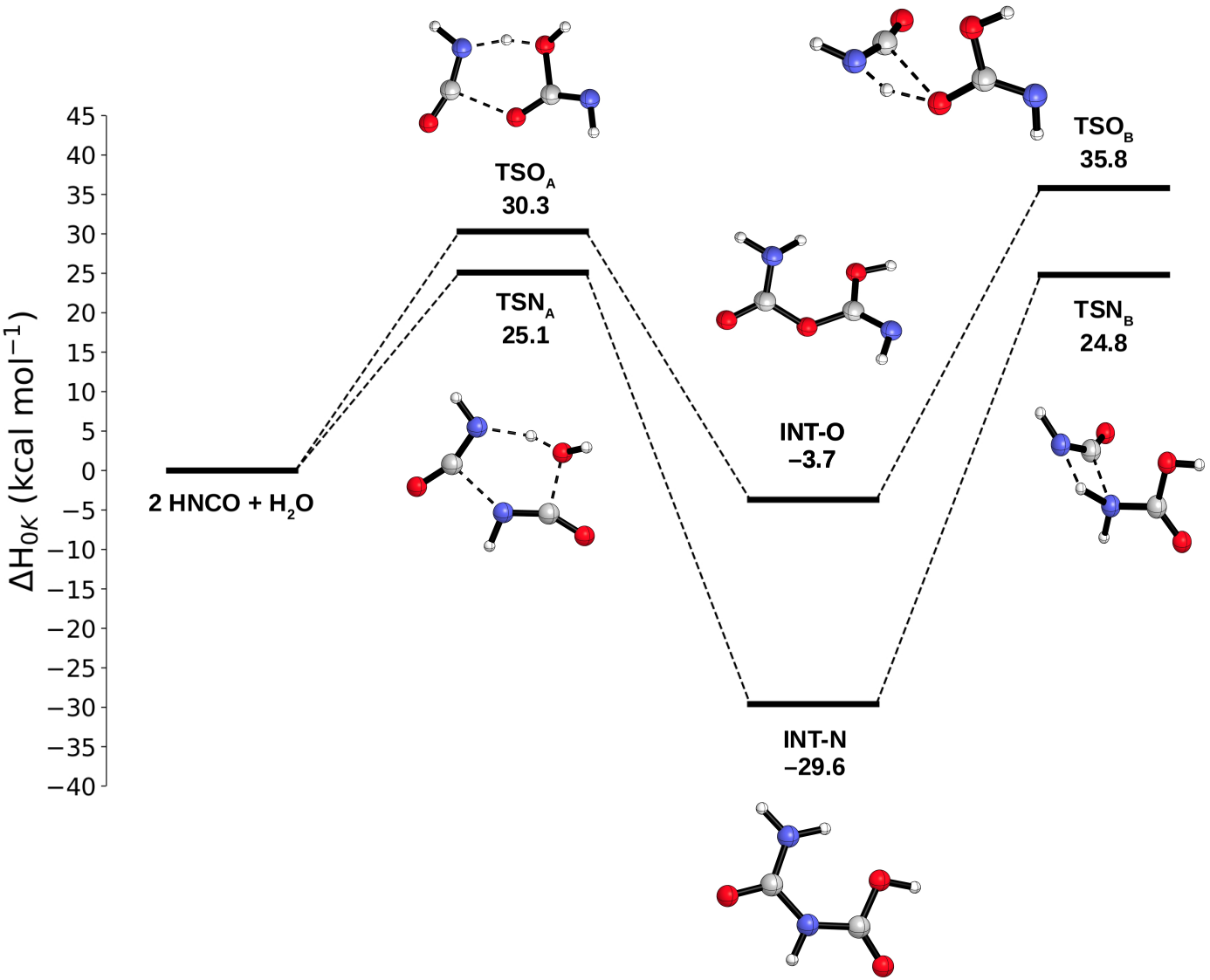

Figure 8: Predicted ΔH_{0K} energies for stationary points on the 2HNCO + H_2O potential energy surface. All values are in kcal mol^{-1} and are obtained at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + ΔCCSD(T)/6-31+G** level of theory.

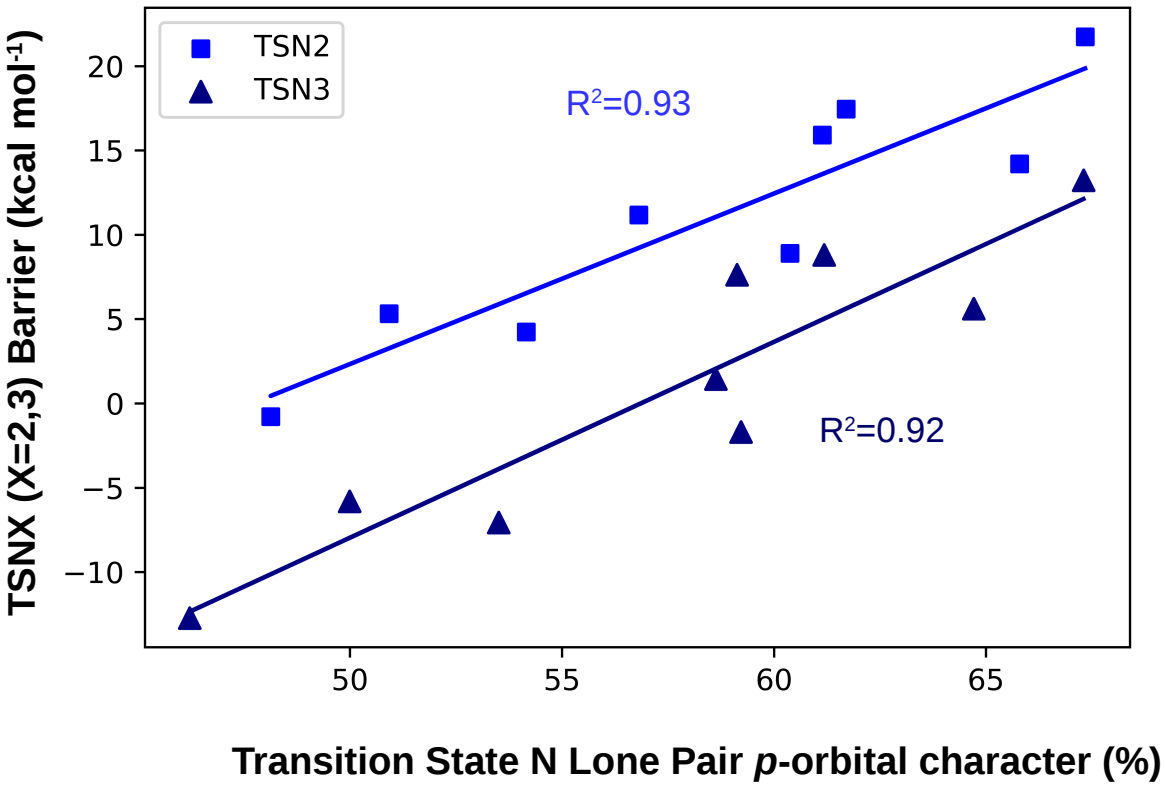

Figure 9: Scatterplot of ΔH_{0K} barrier heights at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + ΔCCSD(T)/6-31+G** level of theory versus the *p*-orbital character of the nitrogen lone pair in the **TSN2** and **TSN3** transition states.

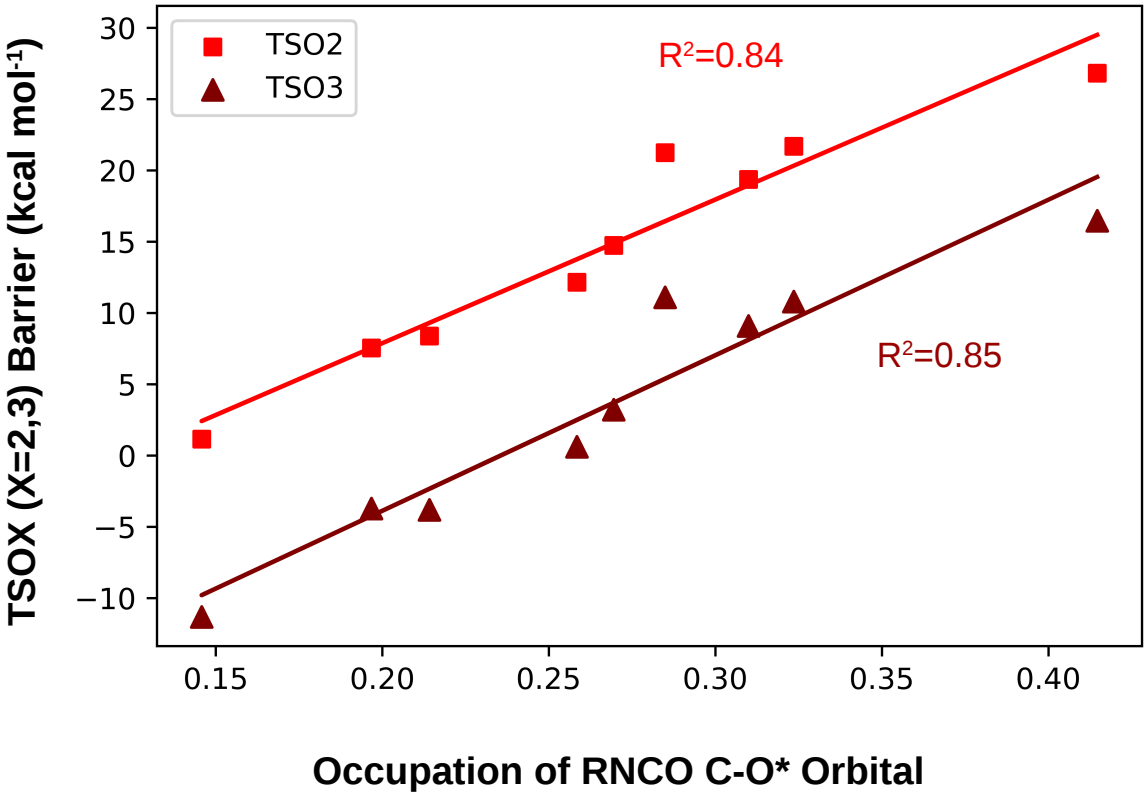

Figure 10: Scatterplot of ΔH_{0K} barrier heights at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + ΔCCSD(T)/6-31+G** level of theory of **TSO2** and **TSO3** versus the C-O* occupancy in the RNCO species.

Energetic Data

Table 1: Reactant data for RNCO structures at the CCSD(T)/CBS//MP2[TZ,QZ] + Δ CCSD(T)/cc-pV(D+d)Z level of theory. The CCSD(T)/CBS energies are in hartree and all other values are in kcal mol^{-1}. The final two columns are the ZPVE and Gibbs energy corrections.

Substituent	CCSD(T)/CBS Energy (hartree)	ZPVE (kcal/mol)	Gibbs Correction (kcal/mol)
Water	-76.37451504	13.45	1.97
H	-168.5125432	13.31	-1.09
F	-267.5823254	8.28	-7.97
Cl	-627.6254199	8.04	-8.84
Br	-2740.697359	7.84	-9.81
OH	-243.5943375	16.23	-0.18
SH	-566.2526638	13.72	-3.61
SeH	-2568.726513	12.86	-5.45
NH_2	-223.7575312	24.52	7.35
PH_2	-510.0436352	19.50	1.74
AsH_2	-2403.679436	18.29	-0.32
CH_3	-207.7588253	31.84	14.67
SiH_3	-458.8220168	24.30	5.59
GeH_3	-2245.437783	23.51	3.81
CH_2CH_3	-247.0202977	49.83	31.06
$CH(CH_3)_2$	-286.2831192	67.42	47.58
$CH_2CH_3CH_{3A}$	-286.2789689	67.81	48.03
$CH_2CH_3CH_{3B}$	-286.2786727	67.70	47.40
$C(CH_3)_3$	-325.5461258	84.64	63.88
C_6H_5	-399.2229168	64.55	44.10
$CHCH_{2A}$	-245.7869241	34.72	16.89
$CHCH_{2B}$	-245.7880954	34.60	16.85
COH_A	-281.7191908	20.26	2.76
COH_B	-281.717051	20.03	2.55
CF_3	-505.329789	17.65	-2.17
$COOH_A$	-356.9146381	23.94	5.47
$COOH_B$	-356.9133746	23.82	5.31
$COOH_C$	-356.9113867	23.82	5.32
SO_2Cl	-1175.764373	15.68	-4.91
CN	-260.6169319	13.23	-3.73

Table 2: Transition state data for **TS1** structures at the CCSD(T)/CBS//MP2[TZ,QZ] + Δ CCSD(T)/cc-pV(D+d)Z level of theory. The CCSD(T)/CBS energies are in hartree and all other values are in kcal mol^{-1}. The final two columns are the 0 K enthalpies and 298 K Gibbs energies relative to water plus RNCO.

Substituent	CCSD(T)/CBS	ZPVE	Gibbs Correction	ΔH_{0K}	ΔG_{298K}
H	-244.8287516	27.92	11.43	37.76	47.13
F	-343.9210018	22.76	5.18	23.52	33.67
Cl	-703.9555678	22.10	3.89	28.44	38.60
Br	-2817.024493	21.72	2.76	30.16	40.32
OH	-319.9270006	30.50	12.76	27.08	37.23
SH	-642.5758392	27.45	9.16	32.49	43.01
SeH	-2645.047793	26.28	7.16	33.38	44.04
NH_2	-300.086129	38.78	20.89	29.62	40.38
PH_2	-586.3571232	32.98	14.57	38.33	49.15
AsH_2	-2479.992573	31.77	11.97	38.55	48.83
CH_3	-284.0781844	45.64	27.19	34.96	45.16
SiH_3	-535.127442	37.68	17.59	43.28	53.38
GeH_3	-2321.745813	36.83	16.04	41.58	51.97
CH_2CH_3	-323.3391955	63.53	43.28	35.15	45.15
$CH(CH_3)_2$	-362.6012946	81.09	60.45	35.57	46.25
$CH_2CH_3CH_A3$	-362.5981755	81.46	60.49	34.91	45.20
$CH_2CH_3CH_{3B}$	-362.5976352	81.03	60.97	34.74	46.45
$C(CH_3)_3$	-401.8648262	98.30	76.85	35.24	46.02
C_6H_5	-475.5437995	78.40	56.89	34.06	44.47
$CHCH_{2A}$	-322.1082346	48.67	29.79	33.89	44.31
$CHCH_{2B}$	-322.1091209	48.59	29.65	34.10	44.40
COH_A	-358.0399829	34.06	15.24	34.06	44.22
COH_B	-358.0412747	34.11	15.33	32.18	42.38
CF_3	-581.6515997	31.51	10.61	33.48	43.88
$COOH_A$	-433.2370571	37.61	18.33	32.90	43.58
$COOH_B$	-433.2359372	37.55	18.28	32.89	43.60
$COOH_C$	-433.231119	37.46	18.15	34.57	45.24
SO_2Cl	-1252.088853	29.15	8.15	31.41	42.49
CN	-336.9415025	27.32	8.89	31.98	41.99

Table 3: Transition state data for **TS2** structures at the CCSD(T)/CBS//MP2[TZ,QZ] + Δ CCSD(T)/cc-pV(D+d)Z level of theory. The CCSD(T)/CBS energies are in hartree and all other values are in kcal mol^{-1}. The final two columns are the 0 K enthalpies and 298 K Gibbs energies relative to water plus RNCO.

Substituent	CCSD(T)/CBS	ZPVE	Gibbs Correction	ΔH_{0K}	ΔG_{298K}
H	-244.8150062	28.24	11.90	46.71	56.23
F	-343.9109923	23.01	5.63	30.05	40.39
Cl	-703.943128	22.37	4.38	36.53	46.90
Br	-2817.011946	22.03	3.31	38.35	48.75
OH	-319.9149665	30.83	13.26	34.97	45.27
SH	-642.5618673	27.68	9.49	41.49	52.11
SeH	-2645.034135	26.64	7.66	42.31	53.11
NH_2	-300.0717896	38.96	21.48	38.80	49.96
PH_2	-586.3433179	33.17	14.81	47.18	58.06
AsH_2	-2479.978563	31.65	12.51	47.21	58.17
CH_3	-284.0621398	45.77	28.23	45.16	56.27
SiH_3	-535.1150897	37.85	17.98	51.21	61.52
GeH_3	-2321.732256	37.01	16.39	50.28	60.83
CH_2CH_3	-323.3230821	63.76	43.89	45.49	55.87
$CH(CH_3)_2$	-362.5844575	81.36	61.04	46.41	57.41
$CH_2CH_3CH_{3A}$	-362.5819633	81.70	60.89	45.32	55.77
$CH_2CH_3CH_{3B}$	-362.5813915	81.65	60.42	45.55	56.10
$C(CH_3)_3$	-401.8477692	98.55	77.40	46.19	57.27
C_6H_5	-475.5271148	78.63	57.12	44.75	55.17
$CHCH_{2A}$	-322.0906486	48.89	29.97	45.14	55.53
$CHCH_{2B}$	-322.0930109	48.78	29.94	44.40	54.80
COH_A	-358.0212365	34.17	14.77	45.94	55.51
COH_B	-358.0224206	34.06	15.86	43.97	54.73
CF_3	-581.638544	31.79	11.30	41.95	52.76
$COOH_A$	-433.2186297	37.53	17.87	44.39	54.69
$COOH_B$	-433.2185062	37.53	18.28	43.80	54.61
$COOH_C$	-433.2162209	37.88	18.15	44.34	54.26
SO_2Cl	-1252.076479	29.42	8.57	39.45	50.67
CN	-336.9295628	27.58	9.30	39.73	49.89

Table 4: Data for **M1** structures at the CCSD(T)/CBS//MP2[TZ,QZ] + Δ CCSD(T)/cc-pV(D+d)Z level of theory. The CCSD(T)/CBS energies are in hartree and all other values are in kcal mol^{-1}. The final two columns are the 0 K enthalpies and 298 K Gibbs energies relative to water plus RNCO.

Substituent	CCSD(T)/CBS	ZPVE	Gibbs Correction	ΔH_{0K}	ΔG_{298K}
H	-244.9223369	32.37	15.94	-16.52	-7.08
F	-344.0104823	27.00	9.51	-28.40	-18.15
Cl	-704.0413428	26.24	8.15	-21.23	-10.97
Br	-2817.109632	25.90	7.09	-19.08	-8.77
OH	-320.0194913	35.00	17.38	-26.46	-16.19
SH	-642.6667584	31.91	13.41	-20.09	-9.80
SeH	-2645.137434	30.87	11.41	-18.28	-7.96
NH_2	-300.175309	43.11	25.18	-22.01	-11.30
PH_2	-586.4470794	37.52	18.61	-13.59	-3.26
AsH_2	-2480.082129	36.07	15.67	-13.35	-3.66
CH_3	-284.1714021	50.03	31.46	-19.14	-9.07
SiH_3	-535.219224	42.29	23.55	-9.70	1.74
GeH_3	-2321.837858	41.47	21.94	-11.54	0.12
CH_2CH_3	-323.4327719	68.01	48.56	-19.09	-8.29
$CH(CH_3)_2$	-362.6928146	85.49	64.93	-17.46	-6.70
$CH_2CH_3CH_{3A}$	-362.6910781	85.91	65.11	-18.94	-8.48
$CH_2CH_3CH_{3B}$	-362.6911861	85.88	65.00	-19.11	-8.22
$C(CH_3)_3$	-401.9561566	102.73	82.40	-17.65	-5.75
C_6H_5	-475.6339218	82.77	61.21	-18.13	-7.77
$CHCH_{2A}$	-322.1999121	53.34	34.52	-18.97	-8.49
$CHCH_{2B}$	-322.2028075	52.95	34.13	-20.33	–9.91
COH_A	-358.1297526	38.42	19.68	-17.91	-7.67
COH_B	-358.1391052	38.58	20.03	-24.73	-14.32
CF_3	-581.7408786	35.53	14.93	-18.52	-7.82
$COOH_A$	-433.3276372	41.96	22.27	-19.58	-9.32
$COOH_B$	-433.3280236	42.13	22.48	-20.32	-9.98
$COOH_C$	-433.3144565	41.55	21.68	-13.64	-3.53
SO_2Cl	-1252.174745	33.55	12.30	-18.08	-7.26
CN	-337.0281872	31.11	12.58	-18.62	-8.72

Table 5: Data for **M2** structures at the CCSD(T)/CBS//MP2[TZ,QZ] + Δ CCSD(T)/cc-pV(D+d)Z level of theory. The CCSD(T)/CBS energies are in hartree and all other values are in kcal mol^{-1}. The final two columns are the 0 K enthalpies and 298 K Gibbs energies relative to water plus RNCO.

Substituent	CCSD(T)/CBS	ZPVE	Gibbs Correction	ΔH_{0K}	ΔG_{298K}
H	-244.8928581	32.19	15.83	1.80	11.30
F	-343.9936087	26.49	9.06	-18.31	-8.02
Cl	-704.0233283	26.01	8.04	-10.16	0.23
Br	-2817.090977	25.71	7.03	-7.57	2.88
OH	-319.996893	34.33	16.73	-12.95	-2.66
SH	-642.6407336	31.56	13.28	-4.11	6.41
SeH	-2645.111934	30.64	11.56	-2.51	8.19
NH_2	-300.1515626	42.60	24.97	-7.62	3.40
PH_2	-586.4193259	37.22	18.63	3.53	14.18
AsH_2	-2480.053357	35.90	16.52	4.54	15.24
CH_3	-284.1393282	49.55	30.58	0.51	10.18
SiH_3	-535.1885146	41.95	22.75	9.23	20.21
GeH_3	-2321.805411	41.09	21.39	8.45	19.93
CH_2CH_3	-323.4001512	67.62	48.21	0.98	11.83
$CH(CH_3)_2$	-362.6593198	85.19	65.09	3.26	14.48
$CH_2CH_3CH_{3A}$	-362.6588153	85.51	64.82	0.90	11.48
$CH_2CH_3CH_{3B}$	-362.6584223	85.46	64.66	1.03	12.00
$C(CH_3)_3$	-401.922214	102.40	81.48	3.32	14.64
C_6H_5	-475.6029005	82.30	60.77	0.87	11.26
$CHCH_{2A}$	-322.1666475	52.52	33.51	1.08	11.38
$CHCH_{2B}$	-322.1712841	52.51	33.70	-0.98	9.44
COH_A	-358.0998243	38.04	19.23	0.49	10.66
COH_B	-358.1005879	37.90	19.82	-1.24	9.65
CF_3	-581.7181383	35.52	15.34	-4.26	6.86
$COOH_A$	-433.2978517	41.71	21.78	-1.14	8.88
$COOH_B$	-433.2978517	41.71	21.78	-1.80	8.25
$COOH_C$	-433.2950816	41.75	21.94	-1.28	8.89
SO_2Cl	-1252.156086	33.60	12.54	-6.32	4.69
CN	-337.0112838	31.28	13.05	-7.84	2.36

Table 6: Electronic Energies of water catalyzed transition states at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + Δ CCSD(T)/6-31+G* level of theory in units of hartree.

Substituent	TSN1	TSN2	TSN3	TSO1	TSO2	TSO3
H	-244.7299225	-321.11195	-397.4720773	-244.7166555	-321.1042313	-397.4673102
F	-343.7834132	-420.1699453	-496.5353876	-343.7741942	-420.1673929	-496.533823
Cl	-703.8261242	-780.2103513	-856.5746171	-703.8141246	-780.2060733	-856.5721726
OH	-319.7986074	-396.1827096	-472.5474073	-319.7871743	-396.1773712	-472.5421348
SH	-642.4542413	-718.8347154	-795.197708	-642.4406524	-718.8303508	-795.1952002
NH_2	-299.9658781	-376.3456907	-452.7092074	-299.9521234	-376.3413361	-452.7062571
PH_2	-586.2412929	-662.6211356	-738.9820406	-586.2277139	-662.6153609	-738.9793609
CH_3	-283.964123	-360.3438706	-436.703493	-283.9485841	-360.3359537	-436.6989573
SiH_3	-535.014325	-611.3953131	-687.7556607	-535.0021096	-611.3879234	-687.7515707

Table 7: ZPVE corrections of the water catalyzed transition states at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + Δ CCSD(T)/6-31+G* level of theory in units of kcal mol^{-1}.

Substituent	TSN1	TSN2	TSN3	TSO1	TSO2	TSO3
H	28.01	44.28	60.58	28.31	44.75	61.06
F	22.83	39.19	55.17	23.07	39.53	55.60
Cl	22.16	38.49	54.56	22.41	38.88	55.03
OH	30.59	47.20	63.35	30.92	47.16	63.38
SH	27.60	43.50	60.17	27.97	44.32	60.37
NH_2	38.86	54.92	71.05	39.21	55.44	71.51
PH_2	33.16	49.13	65.54	33.38	49.74	65.86
CH_3	45.70	61.77	77.46	45.92	61.96	78.09
SiH_3	37.65	53.95	70.16	37.91	54.40	70.83

Table 8: 298 K Gibbs energy corrections of the water catalyzed transition states at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + Δ CCSD(T)/6-31+G* level of theory in units of kcal mol^{-1}.

Substituent	TSN1	TSN2	TSN3	TSO1	TSO2	TSO3
H	11.54	26.19	40.31	11.98	26.73	40.78
F	5.26	19.58	34.26	5.69	20.39	33.92
Cl	3.98	18.55	33.21	4.42	19.20	32.87
OH	12.89	27.62	42.83	13.35	27.61	41.59
SH	9.08	23.64	37.43	9.63	24.22	38.76
NH_2	20.99	35.78	49.91	21.60	36.05	50.71
PH_2	14.27	29.20	42.94	14.60	29.33	43.93
CH_3	27.28	41.84	55.12	27.78	42.90	56.60
SiH_3	19.06	33.45	47.03	18.11	33.79	47.78

Table 9: Electronic energies of the RNCO catalyzed transition states at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + Δ CCSD(T)/6-31+G* level of theory in units of hartree.

Substituent	TSN_A	INT-N	TSN_B	TSO_A	INT-O	TSO_B
H	-413.202777	-413.2966795	-413.204246	-413.1926975	-413.2549686	-413.1848742
F	-611.3072504	-611.38562	-611.3178039	-611.2981323	-611.3637812	-611.2956689
Cl	-1331.39357	-1331.467287	-1331.376764	-1331.382973	-1331.44117	-1331.376764
OH	-563.3381657	-563.4283122	-563.353249	-563.3266384	-563.3980269	-563.3249864
SH	-1208.64858	-1208.731445	-1208.653818	-1208.639777	-1208.700815	-1208.636545
NH_2	-523.6714178	-523.7567986	-523.686666	-523.660973	-523.7276022	-523.6571952
PH_2	-1096.225175	-1096.305785	-1096.224111	-1096.215638	-1096.271357	-1096.209557
CH_3	-491.6688729	-491.7641649	-491.6796428	-491.6572195	-491.7223581	-491.6536195
SiH_3	-993.773049	-993.8587526	-993.767101	-993.7630792	-993.8176374	-993.7555198

Table 10: ZPVE corrections of the RNCO catalyzed transition states at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + Δ CCSD(T)/6-31+G* level of theory in units of kcal mol^{-1}.

Substituent	TSN_A	INT-N	TSN_B	TSO_A	INT-O	TSO_B
H	45.20	49.47	45.81	44.11	49.2	44.73
F	34.37	38.11	34.46	34.37	37.9	33.48
Cl	33.24	36.75	32.82	31.88	36.5	32.34
OH	49.52	54.19	50.03	49.77	53.9	49.28
SH	43.86	48.23	43.72	43.40	47.8	43.86
NH_2	66.31	70.33	66.96	65.95	70.2	65.88
PH_2	55.24	59.23	54.92	53.94	59.0	55.16
CH_3	80.42	84.93	80.89	79.24	84.2	80.15
SiH_3	65.09	69.22	64.20	63.74	68.4	64.78

Table 11: 298 K Gibbs corrections of RNCO catalyzed transition states at the CCSD(T)/aug-cc-pV(T+d)Z//MP2/jul-cc-pV([TZ,QZ]+d)Z + Δ CCSD(T)/6-31+G* level of theory in units of kcal mol^{-1}.

Substituent	TSN_A	INT-N	TSN_B	TSO_A	INT-O	TSO_B
H	25.12	29.16	26.58	24.76	29.4	24.30
F	11.75	16.38	12.97	12.29	16.0	11.14
Cl	9.90	13.93	10.11	9.40	13.4	8.12
OH	25.97	32.55	27.75	27.37	31.7	27.54
SH	19.61	25.17	20.20	19.59	24.2	19.36
NH_2	42.84	47.47	44.94	43.35	49.1	42.54
PH_2	30.63	36.04	30.67	30.22	34.5	29.76
CH_3	56.49	61.96	58.15	55.84	61.9	56.15
SiH_3	39.66	45.18	38.93	37.87	43.3	38.54

Table 12: Focal point analyses for the CCSD(T)/cc-pVQZ transition states. Below each table the CCSDT(Q)/CBS energy is printed followed by the ZPVE correction, frozen core correction, scalar relativistic correction, and the DBOC. Units are kcal mol $^{-1}$.

TS1

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	49.263	-16.692	3.394	-2.052	0.037	-0.160	33.790
cc-pVTZ	52.518	-18.058	4.017	-2.757	[0.037]	[-0.160]	[35.596]
cc-pVQZ	53.668	-18.072	3.978	-2.877	[0.037]	[-0.160]	[36.575]
cc-pV5Z	54.078	-17.988	3.879	-2.889	[0.037]	[-0.160]	[36.958]
cc-pV6Z	54.176	[-17.950]	[3.835]	[-2.894]	[0.037]	[-0.160]	[37.044]
CBS	[54.197]	[-17.899]	[3.775]	[-2.901]	[0.037]	[-0.160]	[37.049]

$E_{CCSDT(Q)/CBS+\Delta}$ =37.05+1.26+0.24+0.00$_4$–0.02 = **38.54**

TS2

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	57.665	-13.752	1.418	-1.414	0.086	-0.084	43.919
cc-pVTZ	59.574	-15.228	1.970	-2.068	[0.086]	[-0.084]	[44.251]
cc-pVQZ	60.690	-15.179	1.919	-2.156	[0.086]	[-0.084]	[45.276]
cc-pV5Z	61.021	-15.087	1.809	-2.156	[0.086]	[-0.084]	[45.589]
cc-pV6Z	61.102	[-15.046]	[1.760]	[-2.156]	[0.086]	[-0.084]	[45.662]
CBS	[61.120]	[-14.990]	[1.693]	[-2.155]	[0.086]	[-0.084]	[45.669]

$E_{CCSDT(Q)/CBS+\Delta}$ =45.67+1.55+0.32+0.00$_1$–0.03 = **47.51**

TS3

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	37.920	-8.822	0.412	-0.494	0.091	-0.018	29.089
cc-pVTZ	41.231	-10.701	0.840	-1.092	[0.091]	[-0.018]	[30.350]
cc-pVQZ	42.343	-10.911	0.723	-1.179	[0.091]	[-0.018]	[31.049]
cc-pV5Z	42.6717	-10.967	0.605	-1.192	[0.091]	[-0.018]	[31.190]
cc-pV6Z	42.753	[-10.992]	[0.552]	[-1.197]	[0.091]	[-0.018]	[31.189]
CBS	[42.771]	[-11.026]	[0.480]	[-1.205]	[0.091]	[-0.018]	[31.095]

$E_{CCSDT(Q)/CBS+\Delta}$ = 31.10+2.21+0.11+0.08–0.03= **33.47**

TS4

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	-15.566	4.551	-2.787	1.472	0.058	0.286	-11.986
cc-pVTZ	-13.274	3.219	-2.924	1.221	[0.058]	[0.286]	[-11.414]
cc-pVQZ	-12.449	3.028	-3.195	1.171	[0.058]	[0.286]	[-11.102]
cc-pV5Z	-12.151	3.042	-3.3897	1.171	[0.058]	[0.286]	[-10.983]
cc-pV6Z	-12.070	[3.048]	[-3.474]	[1.171]	[0.058]	[0.286]	[-10.981]
CBS	[-12.051]	[3.056]	[-3.592]	[1.171]	[0.058]	[0.286]	[-11.071]

$E_{CCSDT(Q)/CBS+\Delta}$ = –11.07+4.79+0.04+0.11–0.01= **–6.13**

TS5

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	33.063	-13.569	1.741	-1.389	0.059	-0.055	19.850
cc-pVTZ	35.835	-14.068	2.059	-1.864	[0.059]	[-0.055]	[21.966]
cc-pVQZ	36.960	-13.892	1.923	-1.921	[0.059]	[-0.055]	[23.073]
cc-pV5Z	37.354	-13.790	1.781	-1.915	[0.059]	[-0.055]	[23.435]
cc-pV6Z	37.440	[-13.744]	[1.719]	[-1.912]	[0.059]	[-0.055]	[23.506]
CBS	[37.459]	[-13.682]	[1.633]	[-1.909]	[0.059]	[-0.055]	[23.505]

$E_{CCSDT(Q)/CBS+\Delta}$ =23.51+2.43+0.25+0.01–0.01 = **26.19**

Table 13: Focal point analyses for the CCSD(T)/cc-pVQZ minima. Below each table the CCSDT(Q)/CBS energy is printed followed by the ZPVE correction, frozen core correction, scalar relativistic correction, and the DBOC. Units are kcal mol $^{-1}$.

M1

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	-26.966	4.817	-2.451	1.545	0.088	0.289	-22.678
cc-pVTZ	-24.267	3.542	-2.665	1.325	[0.088]	[0.289]	[-21.688]
cc-pVQZ	-23.352	3.322	-2.974	1.282	[0.088]	[0.289]	[-21.345]
cc-pV5Z	-23.035	3.301	-3.170	1.280	[0.088]	[0.289]	[-21.247]
cc-pV6Z	-22.950	[3.292]	[-3.256]	[1.279]	[0.088]	[0.289]	[-21.258]
CBS	[-22.929]	[3.279]	[-3.375]	[1.277]	[0.088]	[0.289]	[-21.371]

$E_{CCSDT(Q)/CBS+\Delta}$ =–21.37+5.62+0.01+0.12–0.02 = **−15.64**

M2

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	-6.097	3.783	-3.473	1.408	0.098	0.257	-4.026
cc-pVTZ	-3.575	2.025	-3.438	1.073	[0.098]	[0.257]	[-3.561]
cc-pVQZ	-2.721	1.947	-3.676	1.055	[0.098]	[0.257]	[-3.040]
cc-pV5Z	-2.449	2.002	-3.858	1.070	[0.098]	[0.257]	[-2.881]
cc-pV6Z	-2.377	[2.026]	[-3.939]	[1.077]	[0.098]	[0.257]	[-2.859]
CBS	[-2.360]	[2.059]	[-4.050]	[1.086]	[0.098]	[0.257]	[-2.911]

$E_{CCSDT(Q)/CBS+\Delta}$ = –2.91+5.47+0.13+0.10–0.02= **2.77**

M3

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	-18.908	4.087	-2.700	1.404	0.060	0.286	-15.771
cc-pVTZ	-16.498	2.796	-2.825	1.154	[0.060]	[0.286]	[-15.027]
cc-pVQZ	-15.696	2.693	-3.101	1.125	[0.060]	[0.286]	[-14.633]
cc-pV5Z	-15.386	2.738	-3.298	1.133	[0.060]	[0.286]	[-14.467]
cc-pV6Z	-15.309	[2.758]	[-3.384]	[1.136]	[0.060]	[0.286]	[-14.453]
CBS	[-15.291]	[2.786]	[-3.504]	[1.141]	[0.060]	[0.286]	[-14.522]

$E_{CCSDT(Q)/CBS+\Delta}$ = –14.52+5.53+0.08+0.10–0.00$_7$= **−8.83**

CO_2 + NH_3

	HF	+δ MP2	+δ CCSD	+δ (T)	+δ T	+δ (Q)	NET
cc-pVDZ	-25.854	-0.261	0.277	-0.004	0.037	0.022	-25.784
cc-pVTZ	-24.249	1.891	-0.072	0.214	[0.037]	[0.022]	[-22.156]
cc-pVQZ	-23.713	2.533	-0.281	0.306	[0.037]	[0.022]	[-21.097]
cc-pV5Z	-23.495	2.813	-0.416	0.352	[0.037]	[0.022]	[-20.688]
cc-pV6Z	-23.435	[2.937]	[-0.476]	[0.372]	[0.037]	[0.022]	[-20.543]
CBS	[-23.420]	[3.107]	[-0.558]	[0.400]	[0.037]	[0.022]	[-20.412]

$E_{CCSDT(Q)/CBS+\Delta}$ =–20.41+2.07+0.11–0.07+0.05 = **−18.27**

Table 14: Focal point analyses for the CCSD(T)/aug-cc-pVTZ van der Waals complexes. Below each table the CCSDT(Q)/CBS energy is printed followed by the ZPVE correction, frozen core correction (Obtained at the CCSD(T)/aug-cc-pCVTZ level of theory), scalar relativistic correction (obtained using the decontracted aug-cc-pCVTZ basis set), and the DBOC (at the SCF/aug-cc-pVTZ level of theory). Units are kcal mol $^{-1}$.

VDW1							
	HF	$+\delta$ MP2	$+\delta$ CCSD	$+\delta$ (T)	$+\delta$ T	$+\delta$ (Q)	NET
aug-cc-pVDZ	-4.596	-1.965	0.518	-0.354	0.037	-0.008	-6.367
aug-cc-pVTZ	-4.380	-2.088	0.485	-0.334	[0.037]	[-0.008]	[-6.289]
aug-cc-pVQZ	-4.335	-2.005	0.504	-0.330	[0.037]	[-0.008]	[-6.137]
aug-cc-pV5Z	-4.306	[-1.976]	[0.510]	[-0.328]	[0.037]	[-0.008]	[-6.070]
aug-cc-pV6Z	[-4.295]	[-1.963]	[0.513]	[-0.327]	[0.037]	[-0.008]	[-6.042]
CBS	[-4.290]	[-1.945]	[0.517]	[-0.326]	[0.037]	[-0.008]	[-6.015]
$E_{CCSDT(Q)/CBS+\Delta}$ =–6.02+1.72–0.07++0.02–0.02 = **−4.36**							

VDW2							
	HF	$+\delta$ MP2	$+\delta$ CCSD	$+\delta$ (T)	$+\delta$ T	$+\delta$ (Q)	NET
aug-cc-pVDZ	-2.014	-1.683	0.282	-0.256	0.010	-0.001	-3.662
aug-cc-pVTZ	-1.844	-1.673	0.281	-0.244	[0.010]	[-0.001]	[-3.471]
aug-cc-pVQZ	-1.802	-1.552	0.310	-0.240	[0.010]	[-0.001]	[-3.276]
aug-cc-pV5Z	-1.779	[-1.509]	[0.320]	[-0.239]	[0.010]	[-0.001]	[-3.198]
aug-cc-pV6Z	[-1.771]	[-1.490]	[0.325]	[-0.238]	[0.010]	[-0.001]	[-3.165]
CBS	[-1.767]	[-1.464]	[0.331]	[-0.238]	[0.010]	[-0.001]	[-3.128]
$E_{CCSDT(Q)/CBS+\Delta}$ =–3.17+1.43–0.03+0.00$_1$–0.01 = **−1.73**							