

Supporting Information

Degradation Mechanisms and Substituent Effects of *N*-Chloro- α -Amino Acids: A Computational Study

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Text SI-1

Calculation Details of Validation of Calculation Method on the Unimolecular Decomposition of N-Cl-Gly

Regarding the unimolecular decomposition of *N*-Cl-Gly, as stated in the introduction subsection, previously calculated activation barriers are in the range of 1~45 kcal/mol with different *ab initio* and DFT methods, which are definitely not consistent with the experimental rate constant k of $\sim 10^{-6}$ s⁻¹. Therefore, the first and most important thing is to obtain a relatively accurate calculation method. To obtain a suitable method for this research work, three basis sets 6-31+G(d), 6-311+G(d), and 6-311++G(d,p), six DFT methods M06-2X, B3LYP, CAM-B3LYP, B1B95, BMK, and M05-2X along with implicit CPCM and SMD solvent models have been tested for the unimolecular decomposition of *N*-Cl-Gly, and the calculated results are listed in Table S1.

As shown in Table S1 that the activation free energies (ΔG^\ddagger) calculated with M06-2X functional method at the above three basis sets along with SMD solvent model are in the range of 21~23 kcal/mol whereas those with CPCM model are 15~17 kcal/mol, and the estimated ΔG^\ddagger based on the experimental rate constant $k=2.3\sim 1.67\times 10^{-6}$ s⁻¹ are around 25 kcal/mol. It is clear that the results calculated with SMD model are significantly better than those from CPCM model. Furthermore, it can also be found that the ΔG^\ddagger calculated with 6-311+G(d) basis set are very similar or the same as those with 6-311++G(d,p), which means that 6-311+G(d) basis set is good enough. Table S1 also shown that no matter which functional was chosen from

the six DFT functionals, ΔG^\ddagger after correction with CCSD(T) method are very close to each other in the range of 22.9~23.4 kcal/mol, of course ΔG^\ddagger from M06-2X and M05-2X are closer to that calculated at CCSD(T) level than those from other functionals. As discussed above, it can be concluded that the activation free energies obtained with single point calculation of CCSD(T) and optimization by using M06-2X along with 6-311+G(d) basis set and the SMD solvent model are in great agreement with the experimental results.

Table S1. Activation free energies (at 298 K and 1 atm, in kcal/mol) calculated with different methods for unimolecular decomposition of *N*-Cl-Gly under base-free neutral conditions.

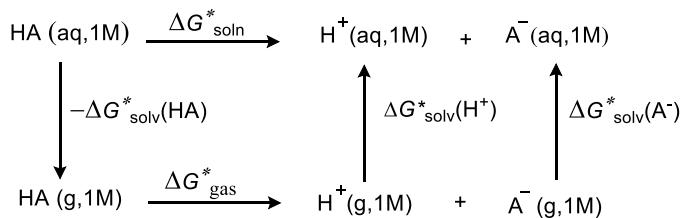
methods	SMD			CPCM		
	6-31+G*	6-311+G*	6-311++G**	6-31+G*	6-311+G*	6-311++G**
M06-2X	23.2	21.8	21.6	16.7	15.4	15.3
CCSD(T) //M06-2X	6-31+G*	25.2	25.5	25.5	18.8	19.0
	6-311+G*	23.1	23.4	23.4	17.1	17.3
	6-311++G**	23.0	23.3	23.3	17.0	17.2
^a CCSD(T)//B3LYP		24.0(12.4)			--	
^a CCSD(T)//CAM-B3LYP		20.7(20.7)			--	
^a CCSD(T)//B1B95		23.4(16.3)			--	
^a CCSD(T)//BMK		22.9(18.3)			--	
^a CCSD(T)//M05-2X		23.4(22.9)			--	

^a basis set is 6-311+G*; values in the parentheses calculated with DFT method.

Text SI-2

Quantum Chemical LFER for Estimation of pK_a Values

It is known that, all continuum solvent pK_a can be obtained via a thermodynamic cycle (Scheme S1) through Eq. 1, in which solution-phase reaction free energies are calculated as the sum of the corresponding gas-phase free energy and the free energy of solvation as expressed in Eq. 2.¹



Scheme S1 pK_a calculation via the direct method

$$pK_a = \frac{\Delta G_{\text{solv}}^*}{RT \ln(10)} \quad (1)$$

$$\Delta G_{\text{solv}}^* = \Delta G_{\text{gas}}^* - \Delta G_{\text{solv}}^*(\text{HA}) + \Delta G_{\text{solv}}^*(\text{H}^+) + \Delta G_{\text{solv}}^*(\text{A}^-) \quad (2)$$

where the superscript * denotes a standard state of 1 mol/L. It is notable that there is a free energy change of 1 mol of an ideal gas from 1 atm (0.04087 M) to 1 M at 298 K with the value of $-RT\ln(0.04087/1) = 1.89$ kcal/mol. Based upon previous work,^{2,3} a benchmark value of $\Delta G_{\text{solv}}^*(\text{H}^+)$ was recommended as -265.9 kcal/mol and it was reproduced to within 0.2 kcal/mol by using the cluster pair approximation.⁴ Moreover, CBS-QB3 method was found to give very accurate results for the gas-phase free energy (ΔG_{gas}^*).^{5,6} Therefore, in this study, ΔG_{gas}^* were calculated with the CBS-QB3 method, and solvation free energies ($\Delta G_{\text{solv}}^*(\text{HA})$ and $\Delta G_{\text{solv}}^*(\text{A}^-)$) were obtained at the M05-2X-SMD/6-31G(d)//CBS-QB3 level.

The correlation between the experimental pK_a values and the uncorrected quantum

chemical pK_a values for the $-NH^+$ moiety in seven amines have been established in this study. As illustrated in Figure S1, the squared correlation coefficients for the above system is $R^2 = 0.98$. Based on the obtained quantum chemical linear free energy relationship (LFER), pK_a of amino alcohols were calculated and their values are demonstrated in Table S2.

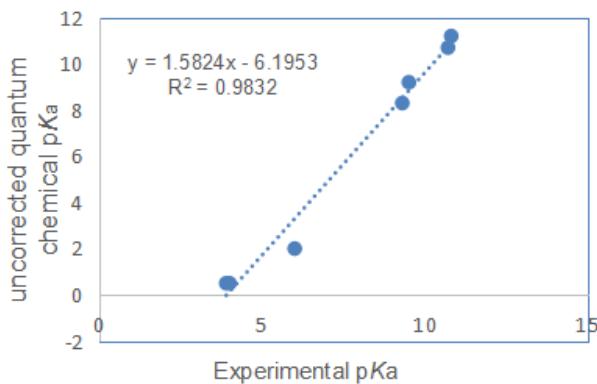


Figure S1. The correlation between the experimental pK_a values and uncorrected quantum chemical pK_a values for seven amines.

Table S2. pK_a values of some amines and amino alcohols involved in the degradation of *N*-monochloro- α -amino acids calculated by using LFER.

Amines	pK_a (experimental)	pK_a (uncorrected quantum chemical)	pK_a (quantum chemical LFER estimate)
Known experimental pK_a data			
NH_3	9.3	8.3	9.2
CH_3NH_2	10.7	10.7	10.7
$CH_3CH_2NH_2$	10.8	11.2	11.0
$OH-CH_2CH_2-NH_2$	9.5	9.2	9.7
$Cl-C_6H_5-NH_2$	4	0.5	4.2
$OH-NH_2$	6	2	5.2
$Br-C_6H_5-NH_2$	3.9	0.5	4.2
Unknown experimental pK_a data			
amino alcohols	<i>N</i> -Cl-Gly	--	4.9
	<i>N</i> -Cl-Ala	--	5.6
	<i>N</i> -Cl-Val	--	6.2
			7.0
			7.5
			7.8

pK_a values of imines were obtained from the Chemical Abstract (CA) database, which were calculated by using Advanced Chemistry Development Software, and

those of aldimine carboxylic acids were deduced based on the effect of carboxyl group. All the above pK_a values are illustrated in Table S3.

Table S3. pK_a values of imines and aldimine carboxylic acids.

Substance	pK_a
methanimine	(9.86±0.7) ^a
ethanimine	(10.49±0.7) ^a
2-methylpropan-1-imine	(10.21±0.7) ^a
aldimine carboxylic acids	$N\text{-Cl-Gly}$ $N\text{-Cl-Ala}$ $N\text{-Cl-Val}$
	<4

^a pK_a of imines were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2019 ACD/Labs).

Reference:

- (1) Ho, J. M.; Coote, M. L. A universal approach for continuum solvent pK_a calculations: are we there yet? *Theor. Chem. Acc.* **2010**, *125* (1-2), 3-21.
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- (5) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Kaylor, W. H.; Ringhand, H. P. The Proton's Absolute Aqueous Enthalpy and Gibbs Free Energy of Solvation from Cluster-Ion Solvation Data. *J. Phys. Chem. A.* **1998**, *102* (40), 7787-7794.
- (6) Liptak, M. D.; Shields, G. C. Accurate pK_a calculations for carboxylic acids using complete basis set and Gaussian-n models combined with CPCM continuum solvation methods. *J. Am. Chem. Soc.* **2001**, *123* (30), 7314-7319.

Table S4

Table S4. Activation free energies (ΔG^\ddagger) for the degradation of the various substituted *N*-chloro- α -amino acid anions via the CGF and the β -E pathways.

R/R'	CGF		β -E	
	α -carbon	<i>N</i> -terminal	α -carbon	<i>N</i> -terminal
H	21.8	--	15.8	--
CH ₃	18.4	20.3	17.8	16.2
CH ₂ CH ₃	15.3	20.0	22.2	18.6
CH(CH ₃) ₂	16.8	18.8	23.4	18.6
C(CH ₃) ₃	16.1	19.1	--	18.1
CH ₂ OH	17.8	18.6	20.0	16.4
OH	16.3	10.2	19.5	7.7
OCH ₃	15.8	7.7	20.2	4.9
NH ₂	14.6	5.7	19.5	--
NHCH ₃	11.9	6.2	18.2	--
F	19.1	17.9	18.3	14.6
Cl	20.2	17.9	17.3	11.7
CF ₃	18.7	21.6	10.6	14.5
CN	17.9	20.4	7.4	12.8
R=R'=CH ₃		15.6		--
R=R'=OCH ₃		7.5		--
tri-substituted (CH ₃)		14.3		--
tri-substituted (OCH ₃)		7.2		--

Figure S2

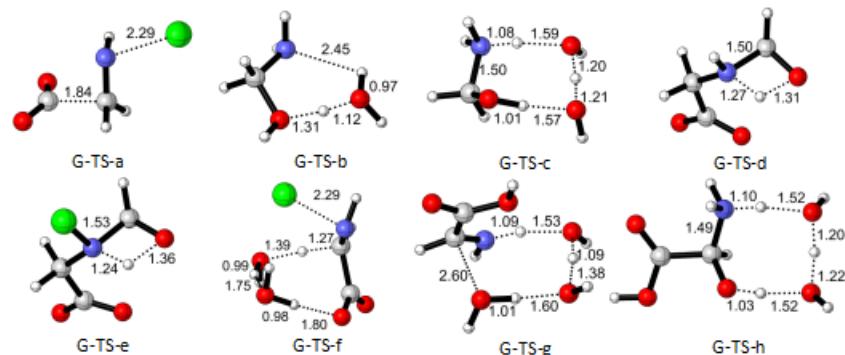


Figure S2. Structures of transition states and important geometric parameters calculated at the M06-2X/6-311+G(d) level involved in each elementary step of *N*-Cl-Gly decomposition pathways under base-free neutral conditions (atoms in green color represent chlorine atom, atoms in blue color represent nitrogen atom; atoms in red represent oxygen atom, atoms in white represent hydrogen atom; atoms in grey color represent carbon atom).

Figure S3

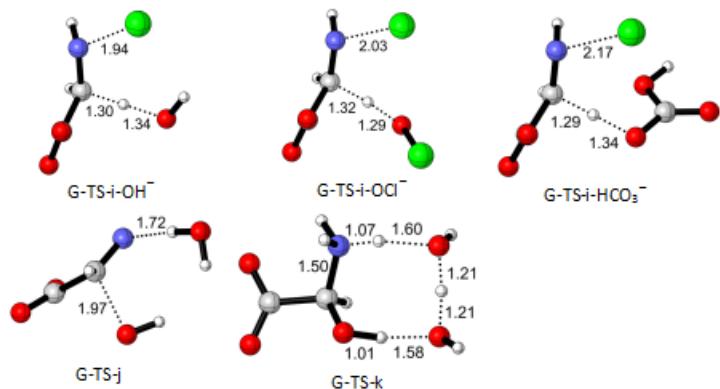


Figure S3. Structures of transition states and important geometric parameters calculated at the M06-2X/6-311+G(d) level involved in each elementary step of *N*-Cl-Gly decomposition pathways under very alkaline conditions and in the presence of OCl⁻ and HCO₃⁻ (atoms in green color represent chlorine atom, atoms in blue color represent nitrogen atom; atoms in red represent oxygen atom, atoms in white represent hydrogen atom; atoms in grey color represent carbon atom).

Figure S4

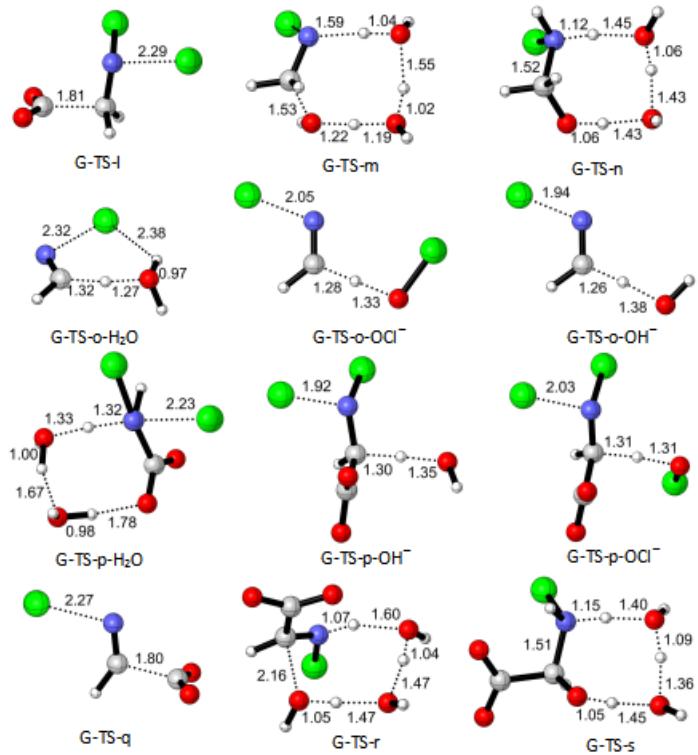


Figure S4. Structures of transition states and important geometric parameters calculated at the M06-2X/6-311+G(d) level involved in each elementary step of *N,N*-Cl-Gly decomposition pathways (atoms in green color represent chlorine atom, atoms in blue color represent nitrogen atom; atoms in red represent oxygen atom, atoms in white represent hydrogen atom; atoms in grey color represent carbon atom).

Standard orientation of G-TS-a

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-a

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -637.62 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-0.432388	-0.012650	-0.451065
2	1	0	-0.490548	1.007973	-0.477279
3	6	0	0.218818	-0.385700	0.661097
4	6	0	1.879549	0.045039	-0.001524
5	1	0	0.182167	0.236060	1.556119
6	1	0	0.269069	-1.455221	0.835584
7	8	0	2.056430	1.239726	0.052678
8	8	0	2.463752	-0.969364	-0.297320
9	17	0	-2.687390	0.010636	-0.044546

Standard orientation of G-TS-b

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-b

State=1-A

Charge = 1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -204.77 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-0.024276	1.137678	-0.111105
2	1	0	1.039992	0.423279	-0.063812
3	1	0	-2.045355	0.816497	-0.055896
4	6	0	-1.152936	0.310314	0.306558
5	7	0	-1.004484	-1.029167	-0.179070
6	1	0	-1.176811	-1.707023	0.552940
7	1	0	-0.153984	1.449300	-1.018208
8	1	0	-1.623137	-1.222843	-0.956749
9	8	0	1.912092	-0.302497	-0.031607
10	1	0	2.392420	-0.239226	0.807817
11	1	0	1.534131	-1.195132	-0.101941
12	1	0	-1.120778	0.335982	1.391690

Standard orientation of Step G-TS-c

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-c

State=1-A

Charge = 0 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1157.76 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.436069	-0.306636	0.423955
2	1	0	1.037880	-0.282400	1.443194
3	7	0	1.172592	1.080832	-0.143989
4	1	0	1.662716	1.800194	0.389738
5	1	0	1.502349	1.127311	-1.108501
6	8	0	0.857869	-1.264961	-0.372951
7	1	0	0.099502	1.286110	-0.118840
8	8	0	-1.663096	-1.098069	-0.015883
9	1	0	-2.007288	-1.444755	0.813257
10	1	0	-0.156035	-1.284677	-0.202859
11	8	0	-1.443820	1.309694	-0.093528
12	1	0	-1.839729	1.767640	0.655047
13	1	0	-1.648679	0.173744	0.000917
14	1	0	2.517091	-0.442487	0.451131

Standard orientation of G-TS-d

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-d

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1794.98 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.705606	0.194480	0.654294
2	8	0	-2.242452	-0.857593	-0.101586
3	7	0	-0.879456	0.796704	-0.437894
4	6	0	0.537078	1.067377	-0.167441
5	1	0	0.638358	1.672877	0.735551
6	1	0	0.944661	1.646941	-0.997102
7	6	0	1.382401	-0.201352	-0.017570
8	8	0	2.572872	-0.004225	0.335038
9	8	0	0.855165	-1.308312	-0.266743
10	1	0	-1.045723	-0.128969	1.465841
11	1	0	-2.448811	0.901607	1.031405
12	1	0	-1.361199	-0.288462	-0.894298
13	1	0	-1.339007	1.617094	-0.825512

Standard orientation of G-TS-e

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-e

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1691.31 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.791669	1.154787	0.826876
2	8	0	0.981610	2.064665	-0.202443
3	7	0	0.599216	-0.065933	-0.068119
4	6	0	-0.572926	-0.928401	0.175672
5	1	0	-0.539653	-1.299827	1.200602
6	1	0	-0.524050	-1.776267	-0.508076
7	6	0	-1.894794	-0.187022	-0.083776
8	8	0	-2.913470	-0.811005	0.290798
9	8	0	-1.851340	0.922292	-0.655899
10	1	0	-0.136136	1.285283	1.393527
11	1	0	1.640389	1.011216	1.499228
12	17	0	2.061425	-1.018182	-0.190833
13	1	0	0.642625	0.906419	-0.836569

Standard orientation of G-TS-f

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-f

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1183.50 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.609594	-1.058287	0.304264
2	1	0	0.827735	-1.831627	1.044050
3	1	0	0.206401	-0.094588	1.026112
4	6	0	1.834909	-0.267269	-0.207850
5	8	0	1.657699	0.581933	-1.111892
6	8	0	2.901367	-0.546244	0.373141
7	7	0	-0.332994	-1.318000	-0.621464
8	8	0	-0.203536	1.047141	1.698749
9	1	0	-0.464791	1.606373	0.925899
10	1	0	0.600539	1.435629	2.071172
11	8	0	-0.671347	2.016477	-0.762070
12	1	0	0.133006	1.534258	-1.045881
13	1	0	-1.412083	1.421449	-0.948550
14	17	0	-2.408541	-0.556281	-0.025858
15	1	0	-0.755138	-2.229835	-0.444868

Standard orientation of G-TS-g

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-g

State=1-A

Charge = 0 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -124.96 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.990348	-0.754198	0.915404
2	7	0	0.119478	-1.348902	1.077647
3	8	0	-0.312293	1.759464	0.841776
4	1	0	2.192055	-0.040590	-0.372972
5	1	0	-0.227376	1.975069	1.776347
6	8	0	2.184521	-1.120443	-0.486646
7	1	0	0.927645	-1.365189	0.344112
8	8	0	2.072105	1.307948	-0.125426
9	1	0	0.619858	1.611338	0.486276
10	1	0	2.185390	1.800238	-0.944801
11	1	0	2.955298	-1.472396	-0.028683
12	1	0	-1.705284	-0.681033	1.727865
13	6	0	-1.431128	-0.207066	-0.414282
14	8	0	-0.473298	-0.218628	-1.317956
15	8	0	-2.569252	0.142847	-0.583820
16	1	0	0.325828	-1.720326	2.003364
17	1	0	-0.795165	0.133283	-2.165192

Standard orientation of G-TS-h

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-h

State=1-A

Charge = 0 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1166.74 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.340767	-0.000064	-0.171287
2	1	0	-0.046177	-0.128409	-1.219351
3	7	0	0.180165	1.328391	0.252427
4	1	0	-0.042507	1.494469	1.235880
5	8	0	0.160237	-0.993290	0.643628
6	1	0	1.265861	1.319086	0.106869
7	8	0	2.530588	-1.340554	-0.188575
8	1	0	3.080269	-1.748462	0.488187
9	1	0	1.110772	-1.225947	0.330802
10	8	0	2.746882	1.059420	-0.129825
11	1	0	3.017589	1.403139	-0.987428
12	1	0	2.721693	-0.138613	-0.179544
13	1	0	-0.235719	2.082905	-0.296577
14	6	0	-1.863162	0.027376	-0.112247
15	8	0	-2.375209	-1.184500	-0.261602
16	8	0	-2.507947	1.036685	0.023874
17	1	0	-3.345769	-1.142863	-0.244611

Standard orientation of G-TS-i-OH⁻

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-i-OH⁻

State=1-A

Charge = -2 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1342.27 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.411128	-0.057387	0.763911
2	1	0	-0.046150	1.105004	0.313549
3	7	0	0.614087	-1.025285	0.638678
4	6	0	-1.622318	-0.303999	-0.077953
5	8	0	-1.503620	-0.927089	-1.170217
6	8	0	-2.707032	0.211361	0.332319
7	8	0	0.316345	2.293294	-0.178580
8	1	0	1.165299	2.114055	-0.598503
9	17	0	2.208257	-0.324127	-0.207575
10	1	0	1.036396	-1.161042	1.554190
11	1	0	-0.639379	0.176935	1.804873

Standard orientation of G-TS-i- OCl^-

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-i- OCl^-

State=1-A

Charge = -2 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1328.72 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.002313	1.062433	-0.747149
2	1	0	-0.134039	-0.245783	-0.895784
3	7	0	1.234697	1.456317	-0.243427
4	6	0	-1.187474	1.334315	0.128345
5	8	0	-1.024825	1.517248	1.364790
6	8	0	-2.313579	1.314769	-0.452132
7	8	0	-0.400546	-1.485906	-1.104934
8	17	0	2.426083	-0.115638	0.230617
9	1	0	1.828665	1.739878	-1.020262
10	1	0	-0.148101	1.305041	-1.801466
11	17	0	-0.847662	-2.128051	0.397180

Standard orientation of G-TS-i-HCO₃⁻

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-i-HCO₃⁻

State=1-A

Charge = -2 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1370.53 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.147521	0.032311	0.738733
2	1	0	0.228874	-0.566904	0.065608
3	7	0	0.931441	1.376989	0.776603
4	6	0	2.322150	-0.444582	-0.096011
5	8	0	2.707551	0.262888	-1.057512
6	8	0	2.791804	-1.565856	0.234362
7	17	0	-0.884346	1.994237	-0.248900
8	1	0	0.479721	1.615309	1.659228
9	1	0	0.986263	-0.504705	1.676723
10	6	0	-1.868518	-1.010219	-0.175678
11	8	0	-2.925364	-0.963577	-0.801022
12	8	0	-1.872878	-0.904658	1.182323
13	1	0	-2.777589	-0.734617	1.478913
14	8	0	-0.702412	-1.180684	-0.669109

Standard orientation of G-TS-j

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-j

State=1-A

Charge = -2 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -314.49 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.021164	-0.098943	-0.402456
2	7	0	0.815668	-1.070055	-0.043777
3	8	0	0.207848	1.468051	0.770611
4	6	0	-1.482589	-0.133896	-0.144494
5	8	0	-1.903376	-0.910306	0.749696
6	8	0	-2.194856	0.612677	-0.863524
7	1	0	1.095092	1.251679	1.080743
8	1	0	0.361883	-1.633535	0.675366
9	8	0	3.341971	-0.107193	-0.252612
10	1	0	3.238260	0.807338	0.031394
11	1	0	2.439787	-0.529731	-0.160909
12	1	0	0.311166	0.485828	-1.271819

Standard orientation of G-TS-k

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-k

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1153.93cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.399241	-0.055688	-0.142969
2	1	0	-0.058233	-0.041807	-1.184126
3	7	0	0.084042	1.229163	0.455574
4	1	0	-0.107716	1.232037	1.458882
5	8	0	0.138321	-1.119453	0.560863
6	1	0	1.137514	1.315275	0.279889
7	8	0	2.556343	-1.257531	-0.328141
8	1	0	3.138862	-1.688794	0.305306
9	1	0	1.086308	-1.269529	0.241615
10	8	0	2.688588	1.137555	-0.066483
11	1	0	2.908030	1.559015	-0.903599
12	1	0	2.688673	-0.059137	-0.218939
13	1	0	-0.417253	2.015487	0.039789
14	6	0	-1.945714	-0.067100	-0.147942
15	8	0	-2.502902	-1.179329	-0.065045
16	8	0	-2.492193	1.052512	-0.283989

Standard orientation of G-TS-1

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-1

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -638.60cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-0.369070	-0.115232	-0.344983
2	6	0	0.362197	-0.649781	0.662925
3	6	0	2.037770	-0.391813	0.029672
4	1	0	0.356764	-0.172959	1.641224
5	1	0	0.285176	-1.732964	0.667091
6	8	0	2.501649	0.631759	0.476528
7	8	0	2.362894	-1.322874	-0.672800
8	17	0	-2.529754	-0.749414	0.043583
9	17	0	-0.492281	1.601828	-0.189397

Standard orientation of G-TS-m

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-m

State=1-A

Charge = 0 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -891.66 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.358576	-1.183209	0.823997
2	7	0	-0.756009	0.142651	0.852156
3	8	0	0.556624	-1.587718	-0.332362
4	1	0	2.091385	0.764721	-0.179631
5	1	0	0.059618	-1.565987	-1.162677
6	8	0	1.150574	1.870704	0.354060
7	1	0	0.362553	1.231668	0.564549
8	8	0	2.463530	-0.127094	-0.501139
9	1	0	1.545949	-0.873914	-0.425306
10	1	0	3.178088	-0.401962	0.088112
11	1	0	0.870777	2.461952	-0.353524
12	1	0	0.275876	-1.366324	1.691885
13	1	0	-1.150054	-1.933369	0.758516
14	17	0	-1.950382	0.384517	-0.473852

Standard orientation of G-TS-n

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-n

State=1-A

Charge = 0 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -111.88 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.117836	-1.224387	0.731789
2	1	0	1.436177	-0.942902	-0.481210
3	8	0	1.114312	1.742429	0.119149
4	1	0	1.434169	2.273325	0.856936
5	1	0	0.000323	0.910867	0.534350
6	8	0	2.616056	-0.135117	-0.484045
7	1	0	3.191651	-0.394217	0.242435
8	1	0	1.846668	1.013186	-0.112816
9	1	0	-0.897470	-1.961046	0.920634
10	8	0	0.507296	-1.449904	-0.462796
11	7	0	-0.782009	0.139638	0.744196
12	17	0	-2.004466	0.298239	-0.480788
13	1	0	-1.226455	0.304977	1.651966
14	1	0	0.570624	-1.164650	1.582532

Standard orientation of G-TS-o-H₂O

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-o-H₂O

State=1-A

Charge = 0 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1390.07 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.005556	-1.278998	-0.008428
2	1	0	-1.406038	-0.017664	-0.041169
3	7	0	0.169098	-1.538475	0.018118
4	17	0	1.378857	0.440946	0.003305
5	8	0	-1.577851	1.236263	-0.093934
6	1	0	-2.103930	1.518130	0.670068
7	1	0	-0.686708	1.620123	-0.000996
8	1	0	-1.771430	-2.063468	-0.008878

Standard orientation of G-TS-o-OCI⁻

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-o-OCI⁻

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1183.38 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.492201	0.928881	0.000462
2	1	0	-0.789863	0.971132	0.000174
3	7	0	0.938756	-0.220881	-0.000124
4	17	0	2.984232	-0.250546	-0.000082
5	8	0	-2.120573	1.007793	-0.000478
6	17	0	-2.562185	-0.627201	0.000125
7	1	0	1.055151	1.861113	0.001024

Standard orientation of G-TS-o-OH⁻

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-o-OH⁻

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1236.95 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.631873	0.488597	-0.000006
2	1	0	-1.861350	0.203881	0.000031
3	7	0	0.130369	-0.500496	0.000119
4	17	0	2.011761	-0.008007	-0.000026
5	8	0	-3.225354	-0.007710	0.000064
6	1	0	-0.304958	1.529354	-0.000175
7	1	0	-3.352147	-0.963542	-0.000721

Standard orientation of G-TS-p-H₂O

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-p-H₂O

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1387.58 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.069658	0.114564	-0.831072
2	1	0	-0.348634	0.066528	-1.837776
3	1	0	1.092135	-0.724388	-0.854429
4	6	0	0.743217	1.434111	-0.468638
5	8	0	1.221004	1.550243	0.688860
6	8	0	0.785031	2.285848	-1.380395
7	7	0	-0.624869	-0.441954	0.193067
8	8	0	2.178361	-1.483034	-0.817265
9	1	0	2.493657	-1.295556	0.108390
10	1	0	2.824012	-1.108619	-1.432599
11	8	0	2.557657	-0.639634	1.645926
12	1	0	2.004646	0.148539	1.456221
13	1	0	2.075782	-1.177772	2.283478
14	17	0	-1.483387	-1.854799	-0.337653
15	17	0	-2.315507	0.924535	0.668623

Standard orientation of G-TS-p-OH⁻

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-p-OH⁻

State=1-A

Charge = -2 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1341.13 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.500622	0.228625	-0.413538
2	1	0	0.956390	1.396241	-0.077413
3	7	0	-0.660124	0.059366	0.381266
4	6	0	1.622635	-0.704390	-0.045646
5	8	0	1.647244	-1.227618	1.098786
6	8	0	2.521890	-0.842200	-0.922928
7	8	0	1.494325	2.589385	0.244761
8	1	0	2.390749	2.381201	0.533493
9	17	0	-1.844503	1.273457	-0.095379
10	1	0	0.317721	0.257761	-1.489811
11	17	0	-1.513804	-1.611852	-0.036679

Standard orientation of G-TS-p-OCI⁻

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-p-OCI⁻

State=1-A

Charge = -2 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -1258.67 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.089433	0.323279	-0.194274
2	1	0	-1.020000	0.006180	0.423852
3	7	0	1.053333	-0.440241	0.457951
4	6	0	0.184580	1.809984	0.050491
5	8	0	0.843987	2.233208	1.031337
6	8	0	-0.481414	2.523651	-0.749105
7	8	0	-2.207332	-0.219529	0.941186
8	17	0	0.769261	-2.136258	0.113673
9	1	0	-0.110329	0.066699	-1.236824
10	17	0	-3.231891	-0.461046	-0.388098
11	17	0	2.866805	-0.113837	-0.391301

Standard orientation of G-TS-q

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-q

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -582.76 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	0.498581	-0.000469	-0.542296
2	6	0	-0.175400	0.000662	0.450855
3	6	0	-1.918264	-0.000038	0.013572
4	8	0	-2.295995	-1.140868	-0.049568
5	8	0	-2.296641	1.140528	-0.050252
6	17	0	2.697493	0.000035	0.016515
7	1	0	-0.044370	0.001659	1.527307

Standard orientation of G-TS-r

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-r

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -236.71 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.583676	-0.983594	0.087089
2	7	0	0.541606	-0.725468	-0.481945
3	8	0	-0.697743	0.271491	1.846224
4	1	0	1.068368	1.961574	-0.391827
5	1	0	-0.203162	-0.190739	2.533030
6	8	0	1.280055	1.635506	-1.359241
7	1	0	0.737831	0.170464	-1.031994
8	8	0	0.700187	2.189015	1.017076
9	1	0	-0.115430	1.082908	1.531976
10	1	0	0.201526	3.007123	1.110085
11	1	0	2.236574	1.653070	-1.472870
12	1	0	-0.679010	-1.853813	0.724128
13	6	0	-1.841644	-0.286445	-0.458748
14	8	0	-1.651894	0.769852	-1.084862
15	8	0	-2.901239	-0.886746	-0.209391
16	17	0	1.981121	-1.468531	0.054270

Standard orientation of G-TS-s

Cartesian coordinates of all the transition states optimized at the M06-2X/6-311+G(d) level:

Standard orientation of transition state of G-TS-s

State=1-A

Charge = -1 Multiplicity = 1

Lowest Harmonic Vibrational Frequency (LHVF) = -396.65 cm⁻¹

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.263053	-0.557118	-0.174579
2	1	0	0.032297	-0.469445	-1.223962
3	7	0	0.105706	0.759970	0.472059
4	1	0	-0.290146	0.770939	1.417990
5	8	0	0.430867	-1.535629	0.505048
6	1	0	1.245868	0.868289	0.450015
7	8	0	2.750160	-1.473040	-0.421071
8	1	0	3.361524	-1.989412	0.113531
9	1	0	1.407405	-1.595150	0.124096
10	8	0	2.631835	0.860852	0.290982
11	1	0	2.906335	1.469581	-0.403949
12	1	0	2.798632	-0.163166	-0.050213
13	6	0	-1.778353	-0.810639	-0.014420
14	8	0	-2.284372	-1.574793	-0.862163
15	8	0	-2.331738	-0.275990	0.971113
16	17	0	-0.560438	2.116701	-0.380541