Supporting Information

(Total pages: 11)

Amide-Imide Tautomerism of Acetohydroxamic Acid in Aqueous Solution: Quantum Calculation and SMD Simulations

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Table S1. Calculated thermodynamic data (in aqueous solution at 298.15 K, reported in atomic units unless otherwise indicated) for the stationary points considered in this study.

	M06-2X-SMD/6-311++G(d,p)		**MP2-PCM/6-311++G(d,p)**						**QCISD-PCM/cc-pVDZ// MP2-PCM/6-311++G(d,p)**
(au)	ΔG°_f	ΔH°_f	ΔG°_f (gas)	ΔG°_f	ΔH°_f	TCG [a]	TCH [b]	ΔG_{sol} [c]	E [d]
EA	-284.31350	-284.27817	-283.67181	-283.68286	-283.64739	0.05004	0.08551	-6.9	-283.64686
TS1	-284.24502	-284.21096	-283.60948	-283.61832	-283.58257	0.04415	0.07990	-5.6	-283.57405
EI	-284.30317	-284.26786	-283.66669	-283.67426	-283.63809	0.04875	0.08492	-4.7	-283.63724
EAW	-360.73493	-360.69152	-359.94043	-359.95398	-359.91022	0.06956	0.11332	-8.5	-359.90362
TS2	-360.70585	-360.66658	-359.91148	-359.92446	-359.88488	0.06522	0.10481	-8.2	-359.86852
EIW	-360.72558	-360.68298	-359.93625	-359.94835	-359.90363	0.06811	0.11283	-7.6	-359.89754
ZA	-284.31549	-284.28000	-283.67097	-283.68470	-283.64861	0.04956	0.08565	-8.6	-283.64593
TS3	-284.28917	-284.25478	-283.65085	-283.66156	-283.62708	0.04967	0.08415	-6.8	-283.62667
TS4	-284.29612	-284.26172	-283.65103	-283.66550	-283.63141	0.04693	0.08102	-9.0	-283.62203
$Z^{\pm}$	-284.29779	-284.26342	-283.64953	-283.66439	-283.62974	0.05055	0.08520	-9.3	-283.62359
TS5	-284.22671	-284.19129	-283.59014	-283.59909	-283.56400	0.04406	0.07914	-5.6	-283.55180
ZI	-284.30689	-284.27212	-283.67175	-283.67912	-283.64400	0.05005	0.08517	-4.6	-283.64319
ZAW	-360.73663	-360.69212	-359.93742	-359.95670	-359.91009	0.06636	0.11297	-12.1	-359.89844
TS6	-360.71927	-360.67611	-359.91838	-359.93968	-359.89605	0.06549	0.10912	-13.4	-359.87748
$ZW^{\pm}$	-360.72062	-360.67942	-359.92218	-359.93974	-359.89556	0.06924	0.11342	-13.8	-359.88105
TS7	-360.69046	-360.65090	-359.89406	-359.90925	-359.86962	0.06657	0.10620	-9.5	-359.84965
ZIW	-360.73087	-360.68735	-359.93963	-359.95339	-359.90916	0.06902	0.11325	-8.6	-359.90111

[a] Thermal correction to the Gibbs free energy; [b] Thermal correction to the enthalpy; [c] In kcal/mol; [d] Uncorrected energy.

Table S2. Enthalpy changes (in kcal/mol) along the reaction profile of the five transformations studied from electronic structure calculations in solution.

		M06-2X-SMD	MP2-PCM	QCISD-PCM// MP2-PCM
(a)	EA	0.0	0.0	0.0
	TS1	42.2	40.7	42.2
	EI	6.5	5.8	5.7
(b)	EAW	0.0	0.0	0.0
	TS2	15.6	15.9	16.7
	EIW	5.4	4.1	3.5
(c)	ZA	0.0	0.0	0.0
	TS3	15.8	13.5	11.1
	EA	1.1	0.8	-0.7
	TS1	43.3	41.4	41.5
	EI	7.6	6.6	5.0
(d)	ZA	0.0	0.0	0.0
	TS4	11.5	10.8	12.1
	$Z^{\pm}$	10.4	11.8	13.7
	TS5	55.7	53.1	55.0
	ZI	4.9	2.9	1.4
(e)	ZAW	0.0	0.0	0.0
	TS6	10.0	8.8	10.7
	$ZW^{\pm}$	8.0	9.1	11.2
	TS7	25.9	25.4	26.4
	ZIW	3.0	0.6	-1.5

Table S3. Equilibrium constants (K) calculated in the gas phase and in solution for each of the Imide $\rightleftharpoons$ Amide elementary steps and global processes studied at 298.15 K.

		MP2	M06-2X	QCISD-PCM// MP2-PCM	MP2-PCM	M06-2X-SMD	SMD
(a)	EI $\rightleftharpoons$ EA (TS1)	$2.3{\cdot}10^{2}$	94	$6.8{\cdot}10^{3}$	$9.0{\cdot}10^{3}$	$5.6{\cdot}10^{4}$	$4.4{\cdot}10^{5}$
(b)	EIW $\rightleftharpoons$ EAW (TS2)	83	33	$1.3{\cdot}10^{2}$	$3.9{\cdot}10^{2}$	$2.0{\cdot}10^{4}$	57
(c)	EA $\rightleftharpoons$ ZA (TS3)	0.41	$7.94{\cdot}10^{-2}$	0.62	7.0	8.2	68
	EI $\rightleftharpoons$ ZA	93	7.4	$4.2{\cdot}10^{3}$	$6.4{\cdot}10^{4}$	$4.6{\cdot}10^{5}$	$3.0{\cdot}10^{7}$
	EIW $\rightleftharpoons$ ZAW	3.4	37	17	$7.0{\cdot}10^{3}$	$1.2{\cdot}10^{5}$	
(d)	ZI $\rightleftharpoons$ $Z^{\pm}$ (TS5)	$6.0{\cdot}10^{-11}$	$2.74{\cdot}10^{-11}$	$5.7{\cdot}10^{-10}$	$1.7{\cdot}10^{-7}$	$6.5{\cdot}10^{-5}$	$4.5{\cdot}10^{-6}$
	$Z^{\pm}$ $\rightleftharpoons$ ZA (TS4)	$7.2{\cdot}10^{9}$	$1.23{\cdot}10^{9}$	$5.4{\cdot}10^{10}$	$2.2{\cdot}10^{9}$	$1.4{\cdot}10^{8}$	$3.4{\cdot}10^{9}$
	ZI $\rightleftharpoons$ ZA	0.44	$3.38{\cdot}10^{-2}$	31	$3.7{\cdot}10^{2}$	$8.9{\cdot}10^{3}$	$1.5{\cdot}10^{4}$
(e)	ZIW $\rightleftharpoons$ $ZW^{\pm}$ (TS7)	$9.4{\cdot}10^{-9}$	$2.98{\cdot}10^{-12}$	$4.7{\cdot}10^{-10}$	$5.1{\cdot}10^{-7}$	$1.9{\cdot}10^{-5}$	$2.3{\cdot}10^{-6}$
	$ZW^{\pm}$ $\rightleftharpoons$ ZAW (TS6)	$1.0{\cdot}10^{7}$	$1.95{\cdot}10^{12}$	$2.1{\cdot}10^{9}$	$6.5{\cdot}10^{7}$	$2.3{\cdot}10^{7}$	$2.7{\cdot}10^{8}$
	ZIW $\rightleftharpoons$ ZAW	$9.7{\cdot}10^{-2}$	5.80	1.0	33	$4.5{\cdot}10^{2}$	$6.1{\cdot}10^{2}$

Table S4. Calculated tunneling factors (κ) and data used for these calculations at 298.15 K.[a]

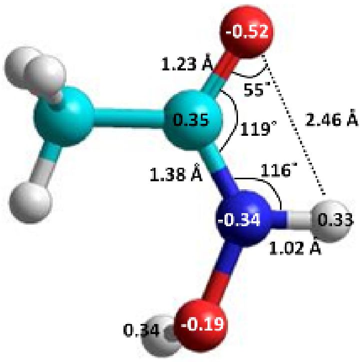
	MP2-PCM/6-311++G(d,p)				M06-2X- SMD/6-311++G(d,p)				QCISD-PCM/cc-pVDZ// MP2-PCM/6-311++G(d,p)		
	$\Delta H^{\neq}$	ΔH	$\nu^{\neq}$	κ	$\Delta H^{\neq}$	ΔH	$\nu^{\neq}$	κ	$\Delta H^{\neq}$	ΔH	κ
EA → EI (TS1)	40.67	5.83	1842.0	4677.27	42.18	6.47	-1903.0	12820.54	42.17	5.67	6261.80
EAW → EIW (TS2)	15.90	4.14	-1666.0	38.18	15.65	5.35	-1100.0	4.07	16.68	3.50	44.90
ZA → $Z^{\pm}$ (TS4)	10.79	11.84	-964.0	1.00	11.47	10.40	-1232.0	2.01	12.09	13.74	1.00
$Z^{\pm}$ → ZI (TS5)	41.25	-8.95	-1771.0	4778.43	45.26	-5.46	-1848.0	25160.31	41.24	-12.33	5.00
ZAW → $ZW^{\pm}$ (TS6)	8.81	9.10	-1103.0	1.00	10.05	7.97	-1297.0	3.28	10.74	11.19	1.00
$ZW^{\pm}$ → ZIW (TS7)	16.30	-8.51	-1230.0	7.10	17.90	-4.98	-753.0	1.86	15.18	-12.68	7.10

[a] Standard enthalpy of activation ($\Delta H^{\neq}$) and enthalpy change (ΔH) of the forward reaction (in kcal/mol), imaginary frequency of the TS ($\nu^{\neq}$, in cm^{-1}).

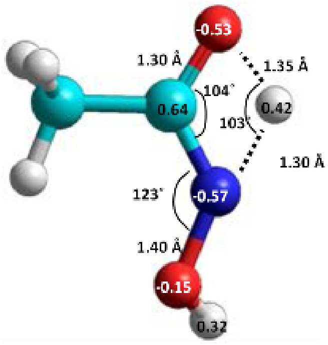
Section S1

MP2-PCM/6-311++G(d,p) Cartesian coordinates of the optimized stationary points considered in this study.

EA
C,0,-0.584055,-0.139875,0.016390
O,0,-1.564885,-0.875196,-0.047779
N,0,0.670720,-0.699719,0.166461
H,0,0.762655,-1.646006,-0.189906
O,0,1.770845,0.093509,-0.188251
H,0,2.275293,0.169757,0.630701
C,0,-0.648533,1.363570,0.017826
H,0,-0.169447,1.753667,-0.883595
H,0,-0.116461,1.771996,0.879668
H,0,-1.694579,1.665498,0.043558



TS1
C,0,-0.981835,1.322801,0.013036
H,0,-1.512716,1.521382,-0.920810
H,0,-0.141752,2.010327,0.113928
H,0,-1.681798,1.460417,0.840386
C,0,-0.503748,-0.080062,0.016104
O,0,-1.252956,-1.140926,-0.030091
N,0,0.723938,-0.547451,0.075604
H,0,0.010145,-1.621195,-0.050009
O,0,1.847117,0.253497,-0.135166
H,0,2.394942,0.098511,0.645828



EI
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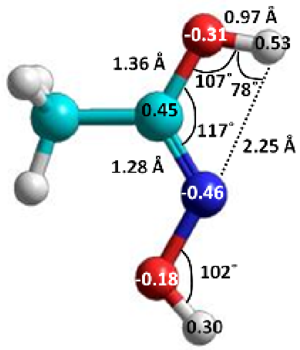
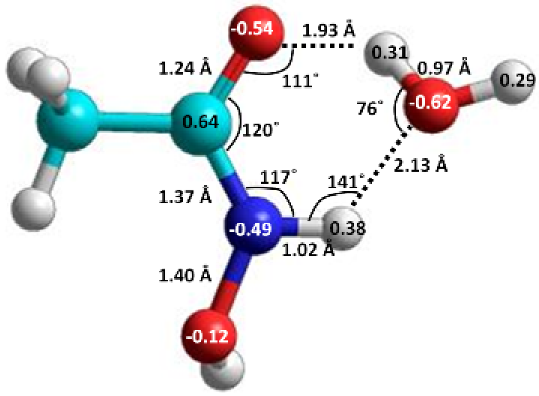
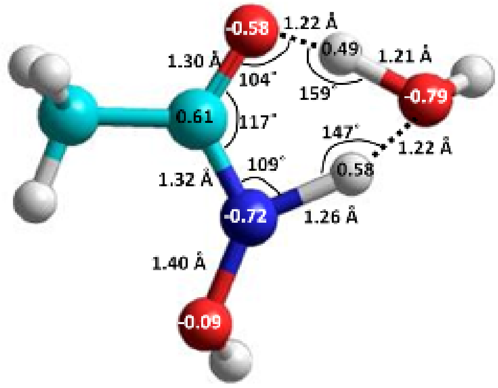
H,0,-0.334159,1.869241,-0.448310
H,0,1.441866,1.691847,-0.559645
C,0,0.412767,-0.077880,-0.011954
O,0,1.596204,-0.743092,0.000297
N,0,-0.664085,-0.779070,-0.005548
H,0,1.394782,-1.689639,0.044450
O,0,-1.811052,0.046436,0.022900
H,0,-2.520240,-0.595212,-0.092081



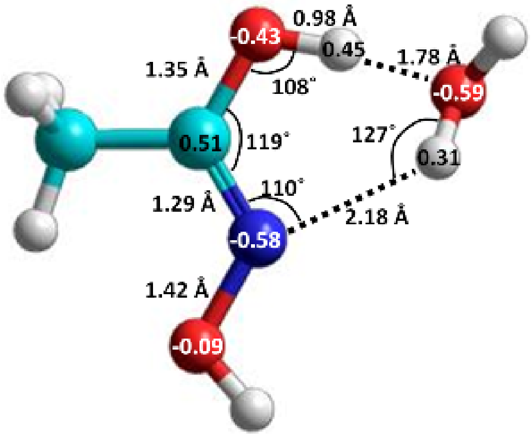
EAW
C,0,1.869108,-0.979903,0.141871
H,0,2.212648,-0.589516,1.103135
H,0,2.512003,-0.561250,-0.635273
H,0,1.933077,-2.066974,0.137659
C,0,0.435522,-0.585543,-0.081999
O,0,-0.493404,-1.397733,-0.153424
N,0,0.182751,0.747441,-0.269939
H,0,-0.773435,1.058699,-0.109862
O,0,1.141050,1.662386,0.176169
H,0,1.433960,2.107635,-0.628686
O,0,-2.735180,0.278582,0.208046
H,0,-2.200181,-0.509068,0.017482
H,0,-3.488931,0.203075,-0.383798



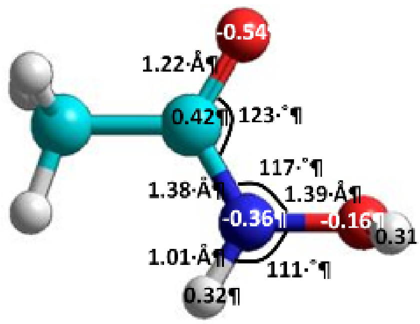
TS2
C,0,1.800632,-0.944719,0.031084
H,0,2.182386,-0.756036,1.038461
H,0,2.413128,-0.376953,-0.670519
H,0,1.862384,-2.010960,-0.183430
C,0,0.369878,-0.514776,-0.047869
O,0,-0.571117,-1.409950,-0.053159
N,0,0.009542,0.749239,-0.092184
H,0,-1.247464,0.823858,0.027856
O,0,1.034407,1.683802,0.106010
H,0,0.911485,2.313299,-0.615828
O,0,-2.301798,0.215290,0.152110
H,0,-1.593862,-0.754826,0.016559
H,0,-2.875795,0.345202,-0.612267



EIW
C,0,1.884488,-0.951370,0.033875
H,0,2.225885,-0.991917,1.072816
H,0,2.546195,-0.283384,-0.517300
H,0,1.924776,-1.956390,-0.387250
C,0,0.478693,-0.450087,-0.017557
O,0,-0.464674,-1.415448,-0.029041
N,0,0.099667,0.782386,-0.028146
H,0,-1.347794,-0.984166,-0.012788
O,0,1.214221,1.653151,0.028642
H,0,0.803080,2.511854,-0.118403
O,0,-2.701667,0.175424,-0.060048
H,0,-2.073328,0.904665,0.048088
H,0,-3.349091,0.302521,0.640891



ZA
C,0,1.763801,-0.561565,0.014572
H,0,1.648179,-1.633605,-0.152850
H,0,2.229136,-0.396960,0.989656
H,0,2.416759,-0.143445,-0.753359
C,0,0.449945,0.184785,-0.014037
O,0,0.365703,1.405584,-0.000701
N,0,-0.643937,-0.644696,-0.124906
H,0,-0.564964,-1.584636,0.245320
O,0,-1.893490,-0.091483,0.153357
H,0,-2.330974,-0.056065,-0.705787



TS3
C,0,1.094509,1.163899,-0.050418
H,0,2.034746,1.139909,-0.600184
H,0,1.265407,1.568301,0.953007
H,0,0.371689,1.810950,-0.552255
C,0,0.527482,-0.221506,0.084936
O,0,1.110184,-1.240139,-0.212755
N,0,-0.835094,-0.319244,0.616890
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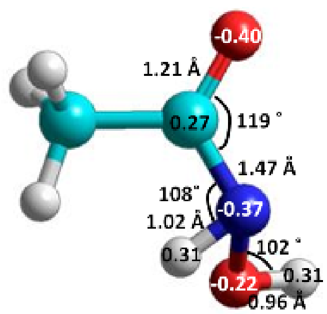

TS4
C,0,1.844478,-0.296317,-0.000047
H,0,2.327514,0.120022,0.886812
H,0,2.327569,0.120077,-0.886848
H,0,1.959784,-1.381371,-0.000070
C,0,0.410229,0.077202,-0.000082
O,0,-0.025252,1.302750,-0.000335
N,0,-0.586672,-0.779556,0.000177
H,0,-0.515543,-1.790390,0.000396
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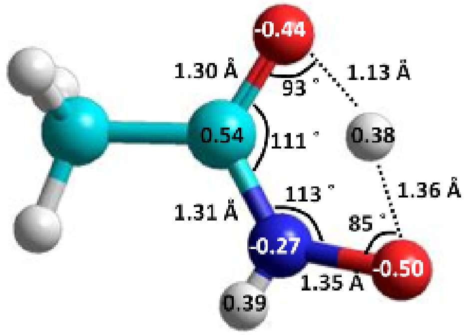
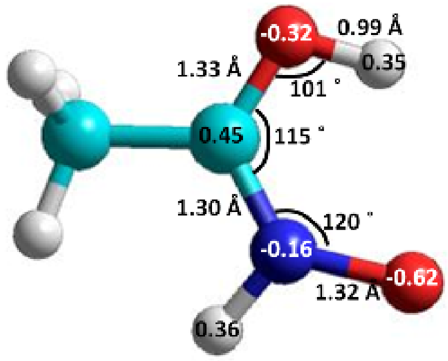


$Z^{\pm}$
C,0,1.805846,-0.419411,-0.000022
H,0,1.840982,-1.510061,-0.000079
H,0,2.320420,-0.043081,0.887513
H,0,2.321121,-0.042668,-0.886859
C,0,0.401682,0.052711,-0.000007
O,0,0.131284,1.352629,-0.000053
N,0,-0.646534,-0.723255,0.000058
H,0,-0.544231,-1.737030,-0.000665
O,0,-1.855751,-0.196595,0.000037
H,0,-0.861986,1.347557,-0.000010



TS5
C,0,1.843425,-0.402827,0.011042
H,0,2.327230,-0.013502,0.910063
H,0,2.358974,0.003020,-0.863011
H,0,1.903256,-1.490933,-0.000221
C,0,0.423411,0.023363,-0.006164
O,0,0.123509,1.306916,0.003022
N,0,-0.566458,-0.813710,-0.108909
H,0,-1.410587,-1.317526,0.424443
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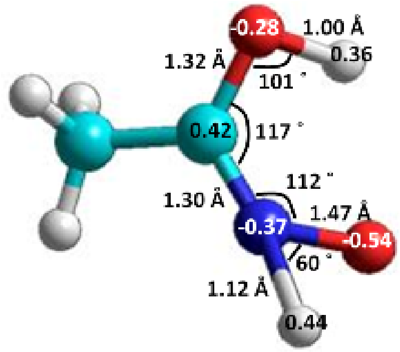
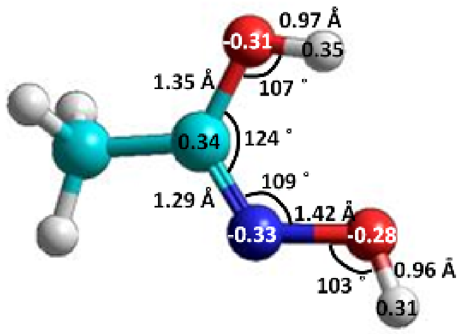
H,0,-0.874923,1.276392,0.049258



ZI
C,0,0.486752,1.805250,0.007019
H,0,1.576315,1.824943,0.010181
H,0,0.107724,2.306423,0.901252
H,0,0.114980,2.340341,-0.870645
C,0,0.006251,0.396005,-0.021339
O,0,-1.333644,0.245748,-0.025538
H,0,-1.505162,-0.709870,0.012921
N,0,0.845400,-0.583847,-0.048924
O,0,0.120059,-1.805967,-0.115963
H,0,0.775543,-2.459594,0.151033



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H,0,2.613293,-0.855166,1.349153
H,0,3.236429,-0.414058,-0.250132
C,0,1.207946,0.101451,0.084426
O,0,1.166789,1.275783,0.452719
N,0,0.104357,-0.462807,-0.504006
H,0,0.245462,-1.139873,-1.246245
O,0,-0.901113,0.451584,-0.850760
H,0,-0.498187,1.303199,-0.584906
O,0,-3.250249,-0.286079,0.634273
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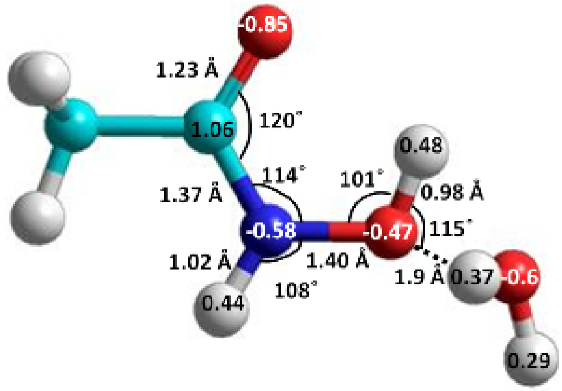
H,0,-3.650159,-0.987999,0.114390



TS6
C,0,-2.44445,0.695935,0.345954
H,0,-2.36484,1.747179,0.065927
H,0,-2.64458,0.617658,1.416761
H,0,-3.27253,0.235001,-0.197005
C,0,-1.19135,-0.031289,0.030832
O,0,-1.00015,-1.289339,0.261796
N,0,-0.12981,0.523634,-0.517375
H,0,-0.02567,1.478802,-0.837671
O,0,0.875523,-0.369504,-0.716242
H,0,0.06545,-1.25777,-0.182307
O,0,3.232528,0.242185,0.581028
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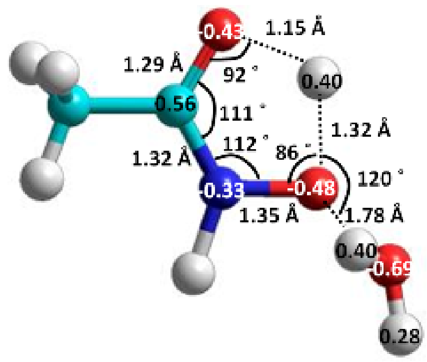
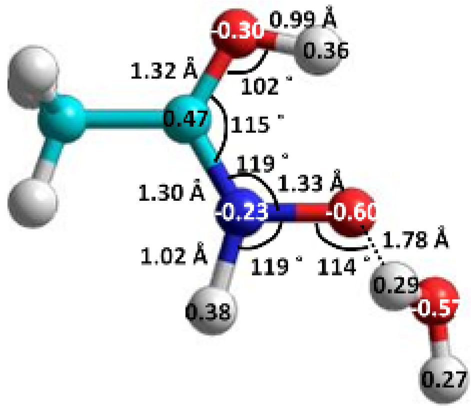
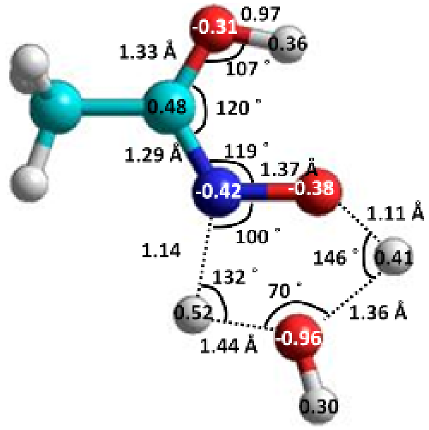


ZW±
C,0,-2.377097,-0.841066,0.263258
H,0, -2.172825,-1.878052,-0.007213
H,0,-3.217263,-0.470838,-0.328990
H,0,-2.646398,-0.788858,1.320748
C,0,-1.187247,0.005834,0.015520
O,0,-1.224091,1.299921,0.290111
N,0,-0.058607,-0.427683,-0.469320
H,0,0.065053,-1.405834,-0.724256
O,0,0.938987,0.426071,-0.661247
H,0,-0.317030,1.595774,0.019428
O,0,3.274543,-0.254754,0.539980
H,0,2.428750,-0.032815,0.093928
H,0,3.740517,-0.784096,-0.111827

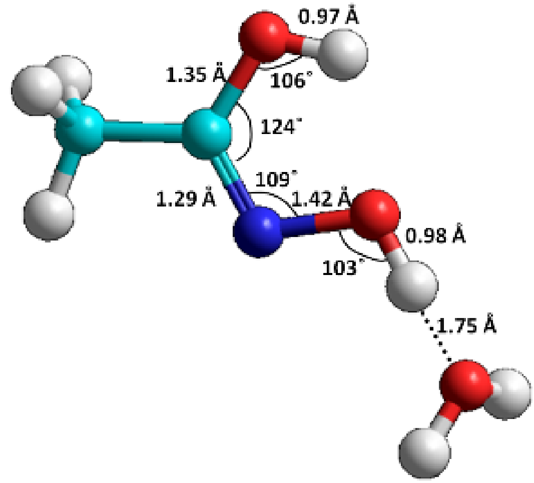


TS7

C,0,1.815871,1.260230,-0.008283
H,0,1.191927,2.152673,-0.048385
H,0,2.475639,1.234686,-0.878721
H,0,2.431187,1.280864,0.894086
C,0,0.972571,0.038484,0.002028
O,0,1.594838,-1.136314,0.051004
N,0,-0.312611,0.086942,-0.052502
H,0,-1.161113,0.840376,-0.020448
O,0,-1.025923,-1.085747,-0.035832
H,0,0.906497,-1.825236,0.083152
O,0,-2.578626,0.687905,0.145420
H,0,-1.987926,-0.529111,0.033439
H,0,-3.105978,0.921494,-0.624657



ZIW
C,0,2.129669,1.515199,-0.044417
H,0,2.847986,1.419107,-0.862986
H,0,2.685639,1.559015,0.895762
H,0,1.555091,2.432514,-0.172148
C,0,1.211843,0.342461,-0.035329
O,0,1.809620,-0.858063,0.124264
N,0,-0.061722,0.492747,-0.181589
H,0,-3.763897,0.377159,-0.316332
O,0,-0.682436,-0.779295,-0.171859
H,0,1.086970,-1.508197,0.158918
O,0,-3.333973,-0.283002,0.237065
H,0,-1.624136,-0.566909,-0.014690
H,0,-3.631525,-0.067505,1.126921



Section S2

Using MP2-PCM/6-311++G(d,p) results:

(a) EA ✂ EI $k = 6.03e\text{-}14\ s^{-1}$

(b) EAW ✂ EIW $k = 6.26\ s^{-1}$

(c) ZA ✂ EA $k_1 = 141\ s^{-1}$ $K_1=0.14$
EA ✂ EI $k_2=6.03e\text{-}14\ s^{-1}$ $K_2=1.1e\text{-}4$

Since the first step is a fast equilibrium, the pre-equilibrium approximation can be applied:
$R = k_2\ [EA] = k_2\ K_1[ZA]$

$k_{eff} = k_2\ K_1 = 8.44e\text{-}15\ s^{-1}$

Estimate of water-assisted (c) mechanism:

ZAW ✂ EAW $k_1 < 141\ s^{-1}$ $K_1 = 5.63e\text{-}2$ (no RDS)
EAW ✂ EIW $k_2=6.26\ s^{-1}$ $K_2=2.6e\text{-}3$

(d) ZA ✂ $Z^{\pm}$ $k_1 = 9.11e3\ s^{-1}$ $K_1=4.6e\text{-}10$
$Z^{\pm}$ ✂ ZI $k_2=1.24e\text{-}23\ s^{-1}$ $K_2=5.9e6$

Since the first step is a fast equilibrium, the pre-equilibrium approximation can be applied
$R = k_2\ [Z^{\pm}] = k_2\ K_1[ZA]$

$k_{eff} = k_2\ K_1 = 5.70e\text{-}33\ s^{-1}$

(e) ZAW ✂ $ZW^{\pm}$ $k_1 = 9.22e4\ s^{-1}$ $K_1=1.5e\text{-}8$
$ZW^{\pm}$ ✂ ZIW $k_2=6.56e\text{-}9\ s^{-1}$ $K_2=2.0e6$

Since the first step is a fast equilibrium, the pre-equilibrium approximation can be applied

$k_{eff} = k_2\ K_1 = 9.84e\text{-}17\ s^{-1}$

Most favourable process from a kinetic point of view:
E-Amide ✂ E-Imide
Followed by: Z-Amide ✂ E-Imide