Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

The Role of Ammonia oxide in the Reaction of Hydroxylamine with Carboxylic Esters

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1. Minima and transition state structures were obtained at CPCM/X3LYP/6-31(+)G(d) level

MS1a

Total Energy: -591.5949602323 a.u.

Atom	X	Y	Z
C	0.4205180373	1.6717578943	-1.6838928778
C	1.1940183921	0.5245018059	-1.4936765276
C	2.5325129901	0.5016930116	-1.8884658213
C	3.0914531730	1.6415036384	-2.4679225793
C	2.3268043765	2.7903006126	-2.6727850345
C	0.9882029576	2.8012967789	-2.2762857578
O	4.4125487415	1.6174975958	-2.9225058275
N	6.7013730020	1.4648006424	-2.7804506974
C	5.4423626013	1.8709484369	-1.9647182022
O	5.4165222884	1.0229371326	-0.8972061194
C	5.5170400808	3.3263541400	-1.5587630021
O	6.9753188122	0.1218574807	-2.6231989504
H	-0.6210162962	1.6838913870	-1.3766789307
H	0.7555459107	-0.3599851175	-1.0405360341
H	3.1406912587	-0.3860763568	-1.7554699767
H	2.7769800482	3.6580404265	-3.1443160043
H	0.3903187097	3.6940064672	-2.4349633451
H	6.5179867344	1.6915389622	-3.7657176664
H	7.4932813345	2.0326253032	-2.4552841071
H	5.9055690782	0.2158607202	-1.2471231118
H	6.3520660845	3.4866732439	-0.8719733629
H	5.6381353102	3.9633722527	-2.4402880261
H	4.5922033744	3.6105025411	-1.0507600372

MS1b

Total Energy: -591.6038637889 a.u.

Atom	X	Y	Z
C	3.4829217096	-0.3547019853	0.1603653849
C	3.1165635057	0.8561178324	-0.4324980935
C	1.7721347206	1.1613050479	-0.6374249440
C	0.7844503305	0.2467708734	-0.2587769110
C	1.1395497690	-0.9749326335	0.3220773480
C	2.4906340527	-1.2607744751	0.5350647400
C	-1.6275780571	0.3502800121	0.3000032412
O	-2.6587363304	1.1632875236	-0.1899354522
C	-1.3699192244	0.7275907052	1.7496027255
N	-1.9654914549	-1.0750257752	0.2158220436
O	-2.5410149960	-1.3242464854	-1.0812797515
O	-0.5172154645	0.6177441900	-0.5644696512
H	4.5302142409	-0.5887892597	0.3258373172
H	3.8779162473	1.5714643580	-0.7304563049
H	1.4726887710	2.1012155549	-1.0906971086
H	0.3709618793	-1.6860566229	0.5970722069
H	2.7633562442	-2.2080243264	0.9918080223
H	-2.9131662771	0.8002100529	-1.0593139430
H	-2.2663066837	0.5439422389	2.3477294107
H	-1.1307184089	1.7926604189	1.7986713282
H	-0.5395792983	0.1558752546	2.1660762199
H	-2.7443146271	-1.2471766958	0.8526898534
H	-1.8844789108	-1.8856092328	-1.5266989421

MS2

Total Energy: -591.6088664238a.u.

Atom	X	Y	Z
C	0.6687406090	0.1317578773	0.2711983238
C	1.1903415860	-0.9482683363	-0.4483823268
C	2.5746242642	-1.0658438975	-0.5916463030
C	3.4358013124	-0.1316000563	-0.0133551391
C	2.9039331833	0.9330255150	0.7171751518
C	1.5231854692	1.0702529247	0.8560972831
O	-0.6892919131	0.3081212649	0.5043648682
C	-1.6281436893	0.2630581943	-0.5821605213
O	-2.8245663726	0.7846771403	-0.0279968349

O	-1.8126783912	-1.0410027221	-1.0263454392
C	-1.2423787268	1.1622450575	-1.7386809052
N	-3.3925483305	-0.1767523448	0.8854446493
H	0.5225406192	-1.6786195692	-0.8879412388
H	2.9798702381	-1.9009011415	-1.1563507909
H	4.5108155688	-0.2340108115	-0.1277530254
H	3.5631745121	1.6657851278	1.1737525453
H	1.0934286882	1.8979126360	1.4116390786
H	-0.2965555798	0.8312041605	-2.1715324112
H	-1.1337469083	2.1905511891	-1.3865914535
H	-2.0186379043	1.1200935008	-2.5051143954
H	-2.2752718064	-1.4989004623	-0.2930733192
H	-4.3875717830	-0.1542473154	0.6610196236
H	-3.2874563147	0.2460916951	1.8084536181

TS1

Total Energy: -591.5810975633 a.u.

Atom	X	Y	Z
C	-2.8339164545	-0.5296116321	1.1249343594
C	-1.4778432059	-0.2559096706	1.2987738426
C	-0.7517310992	0.4360433427	0.3082287794
C	-1.4310460666	0.8357736899	-0.8612938814
C	-2.7855100406	0.5508500177	-1.0287752862
C	-3.4974819869	-0.1339030894	-0.0396507511
O	0.5532931285	0.7148987186	0.4624703364
C	1.9053335902	-0.2969385930	-0.7718449951
C	1.3202569856	-1.6704401243	-0.6647799514
O	2.0933337409	0.3496667326	-1.7775706780
H	-3.3752624853	-1.0578086600	1.9061268431
H	-0.9654308440	-0.5664431722	2.2064235855
H	-0.8781119517	1.3750357945	-1.6250454057
H	-3.2887867260	0.8682270176	-1.9388883268
H	-4.5537827711	-0.3496316653	-0.1711133692
H	1.2360865262	-2.0088600661	0.3675598500
H	1.9641627712	-2.3594709684	-1.2233291152
H	0.3319090283	-1.6639066815	-1.1288386732
N	2.9214476925	0.0513553436	0.3888583716
O	2.4471212690	-0.2078630864	1.6825349573
H	3.1273239610	1.0529291383	0.2898081174

H	3.7913988295	-0.4806627482	0.2704675314
H	1.4818019194	0.1470204330	1.5402508794

TS2a

Total Energy: -591.5908724306 a.u.

Atom	X	Y	Z
C	0.8121929756	0.5570101079	3.0440528030
C	0.5727135431	-0.7857404246	2.7420375265
C	0.0807229377	-1.1527013875	1.4884055601
C	-0.1601528833	-0.1610597136	0.5349295527
C	0.0686906396	1.1842627583	0.8267628374
C	0.5546331818	1.5397879810	2.0862536856
O	-0.7061403166	-0.4869779054	-0.7061149800
C	0.1624365529	-1.1327872788	-1.6565894601
O	0.5135150062	-2.3721496902	-1.3632324413
C	1.2677325914	-0.2116532012	-2.1365088059
H	1.1901023992	0.8363603034	4.0229754988
H	0.7609109763	-1.5532767286	3.4873485217
H	-0.1183575389	-2.1886248827	1.2408777405
H	-0.1390326784	1.9369655591	0.0726299438
H	0.7313336408	2.5866337419	2.3160105472
H	1.8281571576	-0.6959374425	-2.9404707503
H	0.8722432759	0.7468231231	-2.4866998394
H	1.9554331196	-0.0192598485	-1.3086521549
N	-0.9283300890	-1.3389046954	-2.8621856032
O	-1.0342923451	-2.7036335183	-3.0541752088
H	-1.8202756198	-0.9438654514	-2.5454734146
H	-0.6359238384	-0.8721901395	-3.7258000834
H	-0.2216436879	-2.9225542667	-2.1496074757

TS2b

Total Energy: -591.5747141189a.u.

Atom	X	Y	Z
C	3.5461824254	-0.1530830001	-0.3835821440
C	2.8341069295	-1.2432375517	0.1241466057
C	1.5156892832	-1.0955241729	0.5528160399
C	0.8670051183	0.1600067179	0.4933220657
C	1.5961682110	1.2495399733	-0.0369460956

C	2.9148766921	1.0925496666	-0.4591694566
O	-0.3871601334	0.2990242654	0.9275179850
N	-2.8428207931	0.4871843799	0.2172967801
C	-2.0757161859	-0.5053110654	-0.2709817445
O	-2.2631965820	-1.7330171140	0.1687116184
C	-1.4112391152	-0.4128195542	-1.5956042700
O	-2.2792740418	1.7595439072	0.1143844684
H	4.5736043981	-0.2708719786	-0.7157806113
H	3.3085565050	-2.2198071146	0.1873820299
H	0.9636627928	-1.9422726631	0.9522422637
H	1.1127445629	2.2220623349	-0.0984037254
H	3.4540835741	1.9502242518	-0.8549322481
H	-3.2766061082	0.3480385812	1.1295349758
H	-2.6830675210	-1.7663520536	1.0493880276
H	-2.0524620636	-0.9180653905	-2.3279226189
H	-1.2675050742	0.6240982907	-1.8920882427
H	-0.4489598238	-0.9277026008	-1.5608331512
H	-1.3436152755	1.5464851324	0.4681183343

TS3

Total Energy: -591.5844767868 a.u.

Atom	X	Y	Z
C	2.4019601620	0.4797617227	-1.9600053185
C	2.3508828791	0.5869970975	-0.4606295784
O	2.0818600167	1.5988620358	0.1815469883
N	3.1726022705	-0.5595293319	1.4027486938
O	3.4845171484	-0.2491738951	0.0659798973
H	1.4590690373	0.8503211596	-2.3681243091
H	3.2142058942	1.1132928051	-2.3344629213
H	2.5626781725	-0.5486315588	-2.2829854074
H	3.3489741197	0.2419874037	2.0200779597
H	2.1426202206	-0.8075153428	1.3352660612
H	3.7482748578	-1.3616109859	1.6705930789
O	1.1118951974	-0.7423985879	-0.0220113039
C	-0.1628827087	-0.3096186220	0.0854240197
C	-0.6732791729	0.1716862144	1.3054767212
C	-2.0005423464	0.5927948283	1.4044451421
C	-2.8434040178	0.5506344759	0.2915872173
C	-2.3429855928	0.0804384929	-0.9267904499

C	-1.0201480675	-0.3458419249	-1.0317596343
H	-0.0214202357	0.2087227484	2.1743065379
H	-2.3758382555	0.9575137980	2.3573388047
H	-3.8760585313	0.8773633090	0.3723050098
H	-2.9898449724	0.0377061455	-1.7995229927
H	-0.6332620754	-0.7248199876	-1.9733022163

TS4a

Total Energy: -591.5918274794 a.u.

Atom	X	Y	Z
C	0.7729828980	0.1166828637	0.3910039148
C	1.2370391608	-1.1165549040	-0.0776989502
C	2.5941122288	-1.2759367940	-0.3627181308
C	3.4884213083	-0.2199373526	-0.1705165447
C	3.0182415853	1.0065546821	0.3035031298
C	1.6613194294	1.1784278208	0.5833128622
O	-0.5561853643	0.2881703688	0.7525105150
C	-1.5270790842	0.3974985493	-0.3324459901
O	-1.6109300337	-0.6654613061	-1.0971351105
C	-1.4120541065	1.7458056285	-1.0168315982
H	0.5336907752	-1.9294974738	-0.2119802580
H	2.9547428434	-2.2345258046	-0.7254507077
H	4.5444787947	-0.3526490831	-0.3867189036
H	3.7065851583	1.8327886396	0.4578134464
H	1.2819505468	2.1254019717	0.9551080369
H	-2.1749655752	1.8235387236	-1.7950536846
H	-0.4255864652	1.8377600891	-1.4801283538
H	-1.5396562297	2.5602352774	-0.2986475568
O	-2.8318249236	0.4815087193	0.5050694323
N	-3.4796601014	-0.7445903233	0.3036891956
H	-2.7054493912	-1.1414225486	-0.5103947850
H	-4.4233413719	-0.5675123796	-0.0459091964
H	-3.5144838702	-1.2745313374	1.1765472695

TS4b

Total Energy: -591.5569619291a.u.

Atom	X	Y	Z
C	3.6103881999	-0.0434869895	-0.5171161201
C	2.9529513734	-1.1205665876	0.0827629209
C	1.7471796495	-0.9308153608	0.7590483440
C	1.1707091196	0.3502377309	0.8539617005
C	1.8437217401	1.4323848403	0.2518887004
C	3.0455748442	1.2320580410	-0.4274582224
O	-0.0041431805	0.5189223304	1.5001624325
H	4.5470964304	-0.1958064162	-1.0454775238
H	3.3790044622	-2.1191228560	0.0219900803
H	1.2315898959	-1.7679990140	1.2221707105
H	1.4123667679	2.4272414973	0.3290348958
H	3.5455866439	2.0807696020	-0.8880288624
O	-2.8018246651	0.4944304774	0.1027582690
C	-2.6153133936	-0.5660205622	-0.5691895202
O	-3.5277747707	-1.4997779480	-0.4652197110
C	-1.4653568312	-0.8111366652	-1.4585403935
H	-4.2433571501	-1.2395773552	0.1524860765
H	-1.6203808234	-1.7262496069	-2.0283530271
H	-1.3396319529	0.0558322841	-2.1148923194
H	-0.5483636778	-0.8935822924	-0.8624531009
N	-1.7565508909	1.5371295785	0.0202684459
H	-2.2628990897	2.2718562894	0.5232008739
H	-0.7921601133	1.0562162429	0.8338313009

2. Analysis of dipolar isomers stability in aqueous solution

TABLE S1. Thermodynamics data of equilibrium between normal and dipolar isomers for each species in aqueous solution [a]

	MP2(1)	MP2(2)	MP4(1)	MP4(2)[b]	$\Delta G^*_{g[c]}$	$\Delta\Delta G^*_{solv[d]}$	$\Delta G^*_{sol[e]}$
H_2N-NH_2 H_3N-NH ⟶	46.43	45.64	45.74	44.95	44.00	-18.26	25.74
$HO-OH$ H_2O-O ⟶	48.75	51.11	45.46	47.81	47.87	-17.48	30.39
H_2N-OH H_3N-O ⟶	23.36	26.28	23.01	25.93	26.37	-23.38	2.98

[a]Energies in kcal/mol, T=298.15 and P=1 atm; (1) and (2) were carried out with the 6-31(+)G(d), TZVPP+diff basis set, respectively; [b]Energies obtained by the additivity approximation; [c]Gas-phase free energies at 1 mol L^{-1} standard state; [d]Solvation free energy contribution obtained at the SM8/B3LYP3/6-31G(d) level; [e]Solution phase (water) free energies at 1 mol L^{-1} standard state.