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The charging of neutral dimethylamine and dimethylamine–sulfuric acid clusters using protonated acetone

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Cluster	Delta E (kcal/mol)	Delta H (kcal/mol)	Delta G (kcal/mol)	Delta S (kcal/mol)
$H^+(Ac)_1(DMA)_1$*	-24.33	-23.18	-15.11	-27.08
$H^+(DMA)_1$*	-	-	-	-
$H^+(DMA)_2$*,a	-26.33	-25.68	-16.89	-29.45
$H^+(SA)_1(DMA)_2$*,b	-65.60	-61.47	-44.58	-56.64
$H^+(SA)_1(DMA)_3$*,a	-98.15	-91.60	-61.05	-102.45
$H^+(Ac)_2(DMA)_1$*	-43.92	-41.30	-25.51	-52.97
$(SA)_1(DMA)_1$c	-27.22	-24.65	-15.40	-31.01
$(Ac)_1(SA)_1$	-15.67	-14.27	-4.03	-34.36
$(Ac)_1(DMA)_1$	-6.47	-4.95	3.92	-29.74
$H^+(Ac)_1$	30.09	28.11	28.13	-0.07
$H^+(Ac)_2$	-4.35	-6.84	3.07	-33.22
$H^+(Ac)_3$	-18.21	-18.03	0.26	-61.36
$H^+(DMA)_3$a	-46.41	-43.77	-25.80	-60.28
$H^+(SA)_1(DMA)_1$b	-19.29	-18.19	-10.83	-24.68
$H^+(SA)_1(Ac)_2$	-19.54	-20.25	-0.79	-65.27
$H^+(Ac)_1(DMA)_2$	-46.16	-43.68	-25.71	-60.28
$H^+(SA)_1(Ac)_1(DMA)_1$	-43.55	-42.40	-25.75	-55.86
$H^+(SA)_1(Ac)_2(DMA)_1$	-64.66	-61.57	-33.20	-95.14

*Cluster types listed in Figure 3c in the main article.

a)Previously published in Almeida et al. (2013) at a different temperature.

b)Previously published in Kupiainen et al. (2012).

c)Published previously by Ortega et al. (2012).

Table S1. The Gibbs free energies of formation for the allowed cluster types. For these energies, $H^+(DMA)_1$ is considered a monomer, which is why no energies are listed for its formation. This also means that the Delta G for e.g. $H^+(DMA)_2$ is calculated from the Gibbs

free energies of $H^+(DMA)_1$ and $(DMA)_1$. The energies of $H^+(Ac)_1$ are for the proton transfer reaction $H^+(DMA)_1 + (Ac)_1 \rightarrow (DMA)_1 + H^+(Ac)_1$. Thus, the energies reported for the formation of clusters containing acetone also include this proton transfer energy.

Cluster	Dipole moment (D)	Polarizability (Å^3)
$(SA)_1$	2.96[a]	6.2[b]
$(DMA)_1$	1.01[c]	6.37[c]
$(Ac)_1$	2.88[c]	6.33[c]
$(SA)_1(DMA)_1$	8.76[d]	9.37[d]
$(Ac)_1(SA)_1$	4.72[e]	10.10[e]
$(Ac)_1(DMA)_1$	2.62[e]	10.45[e]

[a)]Sedo et al. (2008).

[b)]Nadykto and Yu (2003).

[c)]CRC Handbook of Chemistry and Physics (Lide, 2010).

[d)]Previously published in Almeida et al. (2013).

[e)]Values obtained from simulation at the B3LYP/CBSB7 level of theory.

Table S2. Dipole moments and polarizabilities for the neutral clusters and monomers.

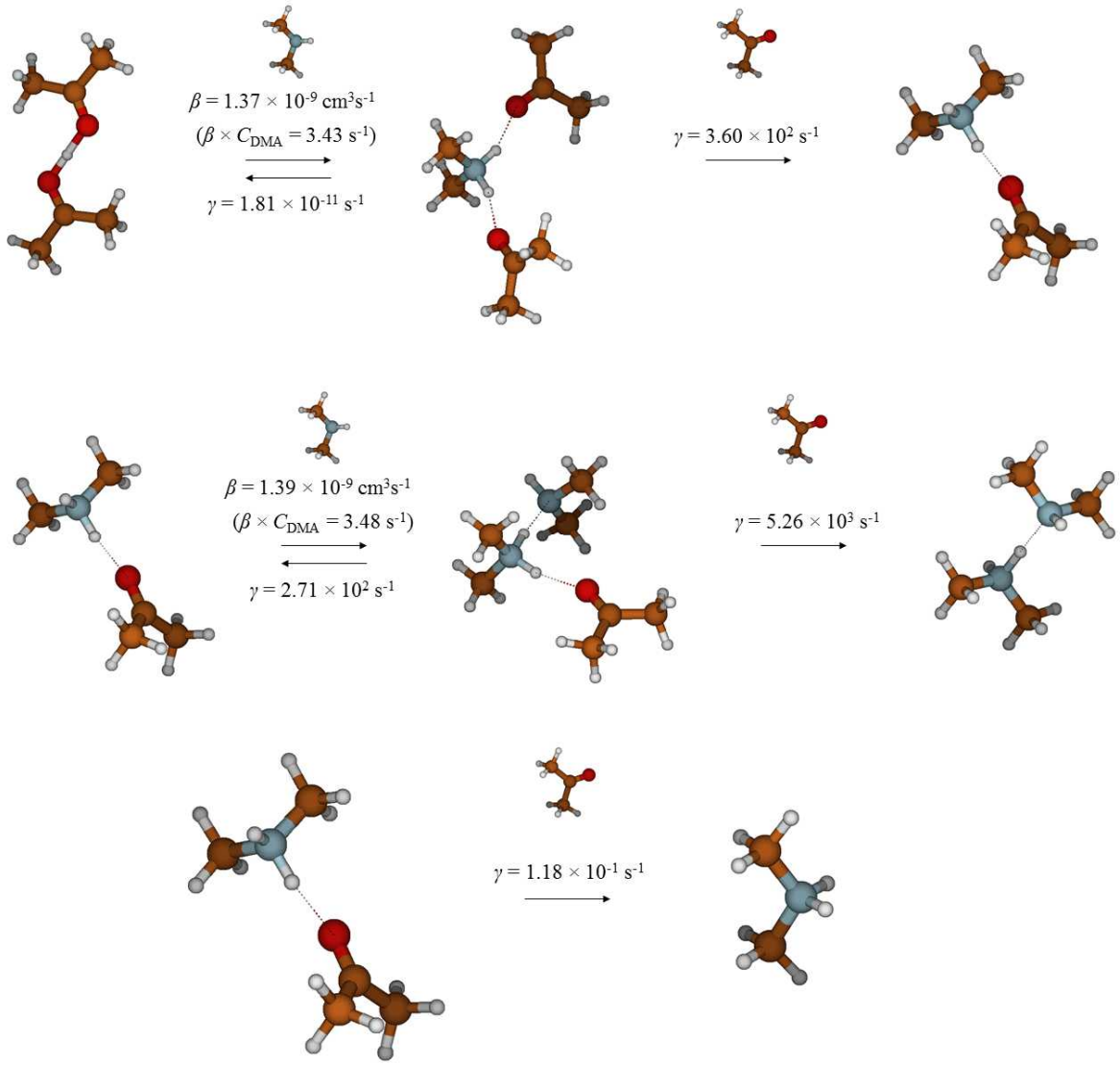

Figure S1. The dominant reaction paths leading to the formation of the cluster types (from top to bottom) $H^+(Ac)_1(DMA)_1$, $H^+(DMA)_2$ and $H^+(DMA)_1$. In the figure, γ is the evaporation coefficient and β is the collision coefficient. The values in parentheses are example values calculated assuming [DMA]=100 ppt. Collisions with neutral acetone monomers are not included, since the initial neutral acetone monomer concentration was assumed to be zero in the simulations.

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Cartesian coordinates for the most stable structure of each cluster, optimized at the B3LYP/CBSB7 level.

Neutral:

$(H_2SO_4)_1$

S	0.000000	0.000000	0.165252
O	0.000000	1.262812	0.826069
O	0.000000	-1.262812	0.826069
O	1.247362	-0.047261	-0.851640
O	-1.247362	0.047261	-0.851640
H	-1.456139	-0.860946	-1.117451
H	1.456139	0.860946	-1.117451

$((CH_3)_2NH)_1$

N	0.000000	0.563912	-0.148594
C	1.215453	-0.222523	0.020305
C	-1.215453	-0.222523	0.020305
H	0.000001	1.329114	0.517154
H	1.282780	-0.965827	-0.780467
H	2.089686	0.427944	-0.061159
H	1.275377	-0.765224	0.981298
H	-1.282775	-0.965832	-0.780462
H	-1.275381	-0.765218	0.981301
H	-2.089687	0.427943	-0.061167

$(C_3H_6O)_1$

C	-0.000070	0.186391	-0.000129

C	1.291451	-0.613508	-0.001609
C	-1.291539	-0.613340	0.001621
O	0.000129	1.395491	0.000031
H	-1.376888	-1.187461	-0.926959
H	-1.301428	-1.334910	0.824231
H	-2.141469	0.061889	0.089311
H	2.141221	0.061763	-0.091149
H	1.377612	-1.185888	0.927951
H	1.300862	-1.336578	-0.822919

$(H_2SO_4)_1 \cdot ((CH_3)_2NH)_1$

H	1.202657	-0.116413	0.805505
S	-1.285655	-0.159813	0.012780
O	-1.799961	1.405256	0.038106
O	-0.439059	-0.259155	-1.202714
O	-2.469017	-0.979113	-0.010431
O	-0.456443	-0.215855	1.230045
H	-2.600799	1.438544	-0.501892
N	1.882601	-0.026869	0.007871
H	1.159416	-0.130108	-0.760163
C	2.856478	-1.140467	-0.007379
H	3.503993	-1.077114	0.867623
H	3.459129	-1.088258	-0.914467
H	2.305790	-2.079796	0.011578
C	2.459827	1.337301	-0.016143
H	3.093965	1.484705	0.858389
H	1.639041	2.052859	-0.000146
H	3.047081	1.470607	-0.924910

$(C_3H_6O)_1 \cdot (H_2SO_4)_1$

C	-3.769214	-0.543568	0.404276
C	-2.444458	-0.070755	-0.131568
C	-2.146690	1.406874	-0.087712
H	-1.448792	1.583855	0.737248
H	-3.042932	2.008381	0.064922
H	-1.638421	1.714004	-1.003357
H	-0.121198	-0.466957	-0.955708
O	-1.634978	-0.876314	-0.570012
S	1.664215	0.121459	0.090762
O	0.819400	0.648119	1.120021
O	2.855332	0.778661	-0.346400
O	0.814870	-0.183492	-1.199870
O	2.058371	-1.358446	0.610673
H	-3.915233	-0.167014	1.421569
H	-3.816180	-1.630985	0.394674
H	-4.579915	-0.129514	-0.204481
H	2.793439	-1.678646	0.067668

$(C_3H_6O)_1 \cdot ((CH_3)_2NH)_1$

C	-1.498973	-0.014566	0.249280
C	-1.780729	1.278894	-0.490325
C	-1.711181	-1.295261	-0.534004
O	-1.106138	-0.023502	1.395537
H	-1.629015	-2.154679	0.130249
H	-2.682051	-1.300531	-1.037537
H	-0.936082	-1.355425	-1.303900
H	-1.634885	2.127169	0.177088
H	-1.097722	1.357970	-1.341131
H	-2.801402	1.287914	-0.884778
H	1.827235	-2.083434	-0.466761

N	1.664125	0.004876	-0.625817
C	1.944072	1.232890	0.116522
C	1.982246	-1.193663	0.148793
H	2.210667	0.002293	-1.481038
H	1.269228	1.293310	0.974065
H	2.979360	1.297201	0.493953
H	1.306503	-1.254681	1.005616
H	3.017864	-1.213843	0.530112
H	1.757915	2.100847	-0.521111

Positively charged:

$(C_3H_7O)_1^+$

C	-0.005068	0.060159	-0.000139
C	1.229521	-0.745071	0.006681
C	-1.346019	-0.540740	-0.008219
O	0.029653	1.337259	-0.005069
H	2.115492	-0.177272	0.295791
H	1.110191	-1.624231	0.644851
H	1.373141	-1.128062	-1.015209
H	-1.567589	-0.843400	1.027691
H	-2.105908	0.169341	-0.330709
H	-1.361699	-1.456100	-0.604029
H	0.928543	1.715559	0.032231

$(C_3H_6O)_1 \cdot (C_3H_7O)_1^+$

C	2.140424	-0.009353	-0.004469
C	2.166367	1.480109	-0.014831
C	3.413255	-0.774738	0.011167
O	1.068649	-0.653441	-0.012306

H	1.199011	1.918939	0.223726
H	2.936699	1.851706	0.664705
H	2.462335	1.801517	-1.021725
H	3.828395	-0.718527	1.025951
H	3.247513	-1.819231	-0.245211
H	4.151947	-0.317670	-0.651326
H	0.070818	-0.081984	0.006771
C	-2.131935	0.008348	0.006144
C	-3.357814	0.855819	0.006648
C	-2.273057	-1.479542	-0.020677
O	-1.020383	0.564051	0.032192
H	-2.610034	-1.806742	0.970550
H	-3.052660	-1.777837	-0.725383
H	-1.336728	-1.982885	-0.257388
H	-3.120615	1.885383	0.266992
H	-3.791524	0.831955	-1.000799
H	-4.114735	0.446639	0.680162

$(C_3H_6O)_2 \cdot (C_3H_7O)_1^+$

C	-3.065048	1.013812	0.009180
C	-3.273373	1.484196	-1.410717
C	-3.915911	1.655590	1.077560
O	-2.244405	0.151800	0.280212
H	-3.816828	1.119629	2.020171
H	-3.593907	2.693140	1.218939
H	-4.965354	1.692523	0.773248
H	-4.247237	1.131851	-1.767629
H	-3.297990	2.575923	-1.463096
H	-2.492128	1.094335	-2.061681
C	3.318835	0.699358	0.033629
C	3.569592	0.794642	-1.442863
C	4.270139	1.385730	0.963417

O	2.362410	0.070492	0.494322
H	4.097499	1.074414	1.991705
H	5.305849	1.194308	0.671038
H	4.118254	2.468455	0.884170
H	2.705862	0.475094	-2.024854
H	3.857682	1.810364	-1.723157
H	4.420726	0.149474	-1.690348
C	-0.215367	-1.822646	-0.004154
C	-1.221344	-2.667680	-0.685877
C	-0.175247	-1.735514	1.472873
O	0.609430	-1.207635	-0.733564
H	-2.191834	-2.559586	-0.200419
H	-1.283195	-2.428211	-1.745122
H	-0.913059	-3.715013	-0.570031
H	-0.407796	-2.702845	1.921863
H	0.768958	-1.342929	1.846169
H	-0.986863	-1.045831	1.741592
H	1.348228	-0.647275	-0.228610

$((CH_3)_2NH_2)_1^+$

N	0.000000	0.000000	0.540852
C	0.000000	1.267957	-0.276150
C	0.000000	-1.267957	-0.276150
H	0.816156	-0.000007	1.159149
H	-0.816156	0.000007	1.159149
H	0.893134	1.276122	-0.897827
H	-0.893131	1.276124	-0.897834
H	0.893131	-1.276124	-0.897834
H	-0.893134	-1.276122	-0.897827
H	-0.000001	2.120753	0.400431
H	0.000001	-2.120753	0.400431

$(C_3H_6O)_1 \cdot ((CH_3)_2NH_2)_1^+$

C	1.800148	-0.026540	0.009395
C	2.379530	1.213149	-0.615568
C	2.757494	-1.041415	0.566484
O	0.588449	-0.215479	0.073074
H	3.275223	-1.534485	-0.264095
H	3.529494	-0.559154	1.171885
H	2.226511	-1.789703	1.151833
H	1.622739	1.773633	-1.163104
H	2.790855	1.848651	0.176817
H	3.212929	0.964047	-1.277135
N	-2.013161	0.326303	-0.299995
C	-2.511539	0.702411	1.062176
C	-2.487417	-1.013163	-0.776706
H	-2.292748	1.042801	-0.971900
H	-0.963257	0.306311	-0.273686
H	-3.600217	0.716132	1.058328
H	-2.146435	-0.035556	1.773755
H	-3.575896	-1.024769	-0.799172
H	-2.113582	-1.769052	-0.089341
H	-2.123603	1.686575	1.319369
H	-2.086777	-1.192370	-1.772869

$(C_3H_6O)_2 \cdot ((CH_3)_2NH_2)_1^+$

C	3.528822	-0.606586	-0.077946
C	3.342715	-2.100705	-0.136849
C	4.937913	-0.079474	-0.119990
O	2.576668	0.159511	-0.003260
H	4.938081	1.001224	-0.249918
H	5.442150	-0.329818	0.819951
H	5.510168	-0.559051	-0.918662

H	3.569127	-2.446091	-1.151813
H	4.042999	-2.610147	0.529721
H	2.319031	-2.377420	0.111997
N	0.004971	1.116142	0.124072
C	-0.008009	2.003563	-1.076744
C	0.038467	1.856906	1.419553
H	-0.848811	0.527815	0.098765
H	0.846783	0.512439	0.072622
H	-0.895158	2.632942	-1.041754
H	0.894503	2.612038	-1.076563
H	-0.844645	2.489647	1.490370
H	0.942535	2.461856	1.457744
H	-0.034590	1.381537	-1.969718
H	0.043308	1.136371	2.235850
C	-3.535551	-0.585047	-0.047553
C	-4.892712	-0.106090	-0.488609
C	-3.428164	-2.000284	0.458378
O	-2.563413	0.157318	-0.099566
H	-3.925085	-2.068488	1.432411
H	-3.949561	-2.693558	-0.206595
H	-2.386419	-2.298625	0.568401
H	-5.657113	-0.364803	0.248928
H	-4.881066	0.968496	-0.661529
H	-5.167956	-0.617692	-1.417529

$(H_2SO_4)_1 \cdot (C_3H_6O)_1 \cdot (C_3H_7O)_1^+$

C	-2.664430	-0.958104	-1.489532
C	-2.697962	-0.705493	-0.016346
C	-3.360945	-1.705798	0.871306
C	-0.108488	2.630624	1.443568
C	-0.000853	2.560728	-0.037627
C	1.022169	3.364663	-0.749246

O	-0.761081	1.843365	-0.728613
O	-2.196680	0.307711	0.492005
S	1.618536	-1.090483	0.030702
O	1.805777	0.268056	0.442803
O	0.348847	-1.597587	-0.383416
O	2.107454	-2.073162	1.186000
O	2.698595	-1.321933	-1.119277
H	-2.370203	-1.991331	-1.685969
H	-1.996020	-0.275324	-2.010470
H	-3.681356	-0.837571	-1.880864
H	2.533563	-2.168142	-1.566726
H	-3.575100	-1.276362	1.848250
H	-2.666675	-2.545694	0.997796
H	-4.266977	-2.107819	0.413491
H	0.887606	2.582721	1.887670
H	-0.748529	1.852703	1.854355
H	-0.523791	3.613349	1.700274
H	2.890490	-1.706602	1.628687
H	0.773710	3.473679	-1.803449
H	1.966759	2.811928	-0.664151
H	1.171198	4.335020	-0.272891
H	-1.451514	1.155859	-0.185986

$(C_3H_6O)_1 \cdot ((CH_3)_2NH) \cdot ((CH_3)_2NH_2)_1^+$

C	2.594692	0.320308	-0.019190
C	3.197555	1.699326	-0.010824
C	3.544579	-0.848747	-0.058699
O	1.379637	0.166011	0.003357
H	3.029162	-1.783579	0.158107
H	3.988993	-0.910125	-1.058428
H	4.371373	-0.705692	0.641475
H	2.435154	2.454351	-0.194098

H	3.653769	1.880886	0.968875
H	3.999750	1.781388	-0.748755
N	-2.475860	0.975931	0.050587
C	-2.265728	1.668840	-1.236444
C	-1.983866	1.769954	1.194871
H	-3.474001	0.823204	0.171702
H	-1.604297	-0.490986	0.031551
H	-2.699272	2.675420	-1.244126
H	-1.193196	1.757365	-1.424524
H	-2.398123	2.784538	1.207971
H	-0.895391	1.841563	1.136950
H	-2.716163	1.090738	-2.045326
H	-2.251990	1.274364	2.129805
N	-0.962633	-1.366082	0.023456
C	-1.174017	-2.144020	1.274686
C	-1.204097	-2.146975	-1.220487
H	0.001269	-0.985124	0.012083
H	-2.210632	-2.476399	1.322589
H	-0.513687	-3.010939	1.287507
H	-2.241229	-2.480518	-1.241960
H	-0.543251	-3.013174	-1.247605
H	-0.954187	-1.505888	2.129389
H	-1.006401	-1.510546	-2.081816

$(H_2SO_4)_1 \cdot (C_3H_6O)_1 \cdot ((CH_3)_2NH_2)_1^+$

C	3.808741	0.480503	-0.086259
C	4.010945	-0.016542	1.314509
C	5.012906	0.822717	-0.905575
O	2.685616	0.612089	-0.582142
H	5.446734	1.751652	-0.517676
H	5.782447	0.052943	-0.807094
H	4.739698	0.964506	-1.949320

H	4.394498	-1.042175	1.262997
H	4.772666	0.576307	1.826101
H	3.084343	-0.016413	1.886209
N	-3.572723	0.527093	-0.062656
C	-3.814739	1.885852	0.513570
C	-4.804290	-0.182897	-0.525158
H	-2.888953	0.590645	-0.830990
H	-3.059505	-0.057897	0.621531
H	-4.279202	2.515567	-0.243401
H	-4.472402	1.790382	1.375769
H	-5.285186	0.407669	-1.303185
H	-5.478616	-0.305998	0.320513
H	-2.859960	2.310262	0.818791
H	-4.519423	-1.157318	-0.917808
S	-0.455015	-0.644789	0.051071
O	-0.963042	-0.033634	-1.163759
O	-1.454909	-0.952409	1.050373
O	0.665358	0.142993	0.710047
H	1.557175	0.340855	0.109709
O	0.337557	-1.975241	-0.360540
H	-0.091034	-2.382204	-1.129040

$(H_2SO_4)_1 \cdot (C_3H_6O)_2 \cdot ((CH_3)_2NH_2)_1^+$

N	-2.830805	1.662870	0.355259
C	-3.009915	2.158282	1.750682
C	-3.567507	2.453803	-0.672812
H	-1.820499	1.666374	0.125122
H	-4.064928	2.104449	2.014661
H	-2.428566	1.528853	2.422346
H	-2.657671	3.186700	1.814879
H	-4.633661	2.412297	-0.456050
H	-3.217902	3.484916	-0.651967

H	-3.374445	2.019304	-1.652160
C	4.987471	-0.749527	0.405522
C	6.056831	-1.696760	-0.054374
C	5.328980	0.228738	1.495102
O	3.873238	-0.787589	-0.111811
H	5.882307	-0.263834	2.298280
H	5.993662	0.994496	1.079447
H	4.439649	0.714603	1.894229
H	7.002061	-1.170841	-0.211831
H	6.236079	-2.437392	0.733104
H	5.747446	-2.208980	-0.963381
S	0.809420	0.718978	-0.583538
O	-0.097413	1.776727	-0.208379
O	0.290829	-0.599387	-0.824342
O	1.940180	0.731178	0.468621
H	2.722263	0.088338	0.247965
O	1.546300	1.212114	-1.920969
H	1.610589	0.461267	-2.530564
C	-3.964532	-1.998519	0.128115
C	-5.190917	-2.871312	0.136819
C	-2.628892	-2.673020	-0.043609
O	-4.068158	-0.785362	0.265005
H	-6.062133	-2.301443	0.454662
H	-5.361634	-3.256739	-0.874517
H	-5.046285	-3.741145	0.783078
H	-2.677832	-3.444319	-0.816320
H	-1.840860	-1.957640	-0.276589
H	-2.377101	-3.186280	0.891823
H	-3.154556	0.671725	0.305888
