Supporting Information

Experimental and theoretical investigations of isomerization reactions of ionized acetone and its dimer

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S1. The charge distribution

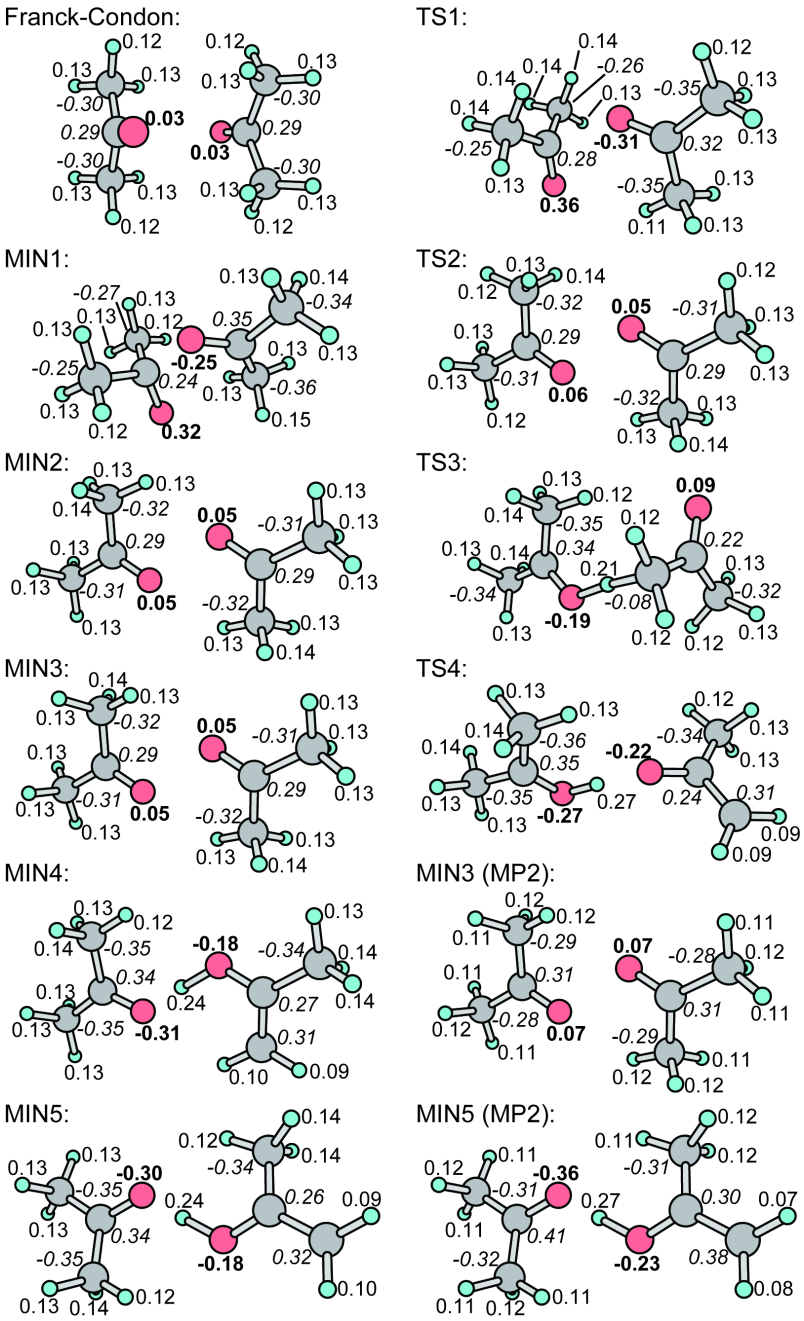

Figure S1. The natural charge distribution (UPBE1PBE/6-311+G(2d,2p) for all structures and MP2/6-311+G(2d,2p) for MIN1 and MIN3) in the cationic state (the total charge is unity) at the Franck-Condon structure and the dimer cation structures (optimized at the UPBE1PBE/6-311+G(2d,2p) level). Charges on H atoms, C atoms, and O atoms are presented with regular, italic, and bold characters, respectively.

S2. Cartesian coordinates for the Franck-Condon structure and the dimer cation structures

Franck-Condon:

C	-2.000546	-1.279683	0.375760
C	-1.658179	-0.000076	-0.336140
C	-2.001298	1.279204	0.375986
O	-1.103955	0.000175	-1.413001
H	-1.791537	-2.133730	-0.264119
H	-3.048765	-1.286631	0.681521
H	-1.396081	-1.345942	1.284385
H	-1.791461	2.133553	-0.263215
H	-3.049951	1.286023	0.680290
H	-1.398118	1.345020	1.285487
C	1.658179	0.000069	0.336140
C	2.001206	-1.279179	-0.376089
C	2.000636	1.279709	-0.375658
O	1.103957	-0.000232	1.413002
H	1.791330	2.133736	0.264149
H	1.396510	1.345911	-1.284510
H	3.048971	1.286753	-0.681027
H	1.791671	-2.133547	0.263187
H	3.049742	-1.285901	-0.680791
H	1.397682	-1.345052	-1.285360

MIN1:

C	0.387594	2.664670	0.710578
C	0.540192	1.299452	0.168935
C	1.802269	0.940687	-0.518513
O	-0.424662	0.524260	0.339265
H	-0.509816	2.765707	1.313812
H	1.279422	2.931654	1.283815
H	0.352167	3.363762	-0.132348
H	1.669209	0.226329	-1.326828
H	2.295960	1.840480	-0.879914
H	2.464328	0.471849	0.218581
C	-0.483775	-1.082729	-0.102405
C	-1.101246	-1.035980	-1.494645
C	-1.403274	-1.615704	0.999646
O	0.674602	-1.612011	-0.047829
H	-0.404673	-0.621220	-2.220093
H	-1.345788	-2.057600	-1.782339
H	-2.008209	-0.435974	-1.455723
H	-0.902755	-1.577368	1.964263
H	-2.304468	-1.006164	1.016695
H	-1.647805	-2.647579	0.754425

MIN2:

C	-3.257494	-0.770039	0.005005
C	-1.969976	-0.005374	-0.006408
C	-2.017514	1.483432	0.003704
O	-0.928689	-0.642642	-0.012691
H	-3.090835	-1.831919	0.159752
H	-3.909548	-0.359213	0.778373
H	-3.748527	-0.605865	-0.958551
H	-1.077116	1.919129	-0.314402
H	-2.848122	1.830475	-0.610307
H	-2.227034	1.790707	1.033782
C	1.969956	0.005355	-0.006457
C	3.257392	0.770173	0.005112
C	2.017681	-1.483438	0.003678
O	0.928598	0.642493	-0.012963
H	3.090585	1.832018	0.159948
H	3.909464	0.359359	0.778466
H	3.748485	0.606179	-0.958444
H	1.077177	-1.919284	-0.313900
H	2.847964	-1.830326	-0.610879
H	2.227964	-1.790728	1.033590

MIN3:

C	-2.019177	-1.483371	-0.005715
C	-1.970726	0.005492	-0.002826
C	-3.258012	0.770708	0.000874
O	-0.929137	0.642145	0.007681
H	-1.073802	-1.917342	-0.311063
H	-2.839357	-1.824798	-0.636727
H	-2.246846	-1.798603	1.018074
H	-3.092541	1.831337	0.165214
H	-3.739034	0.614077	-0.968952
H	-3.918224	0.354483	0.764364
C	1.970726	-0.005492	0.002826
C	2.019176	1.483371	0.005717
C	3.258013	-0.770708	-0.000875
O	0.929137	-0.642146	-0.007682
H	3.092542	-1.831336	-0.165217
H	3.739034	-0.614078	0.968952
H	3.918225	-0.354481	-0.764364
H	1.073800	1.917342	0.311066
H	2.246844	1.798605	-1.018072
H	2.839357	1.824798	0.636729

MIN4:

C	2.112449	1.474353	-0.028249
C	2.168545	0.050319	0.001773
C	3.467154	-0.656648	0.017437
O	1.110086	-0.639824	0.015402
H	0.131995	-0.089672	0.004011
H	1.160631	1.989222	-0.039351
H	3.027520	2.050026	-0.039951
H	3.324953	-1.733101	0.045465
H	4.047311	-0.379307	-0.867329
H	4.052013	-0.333492	0.883195
C	-2.079961	0.010667	-0.002065
C	-2.209185	-1.468878	-0.022736
C	-3.309031	0.837444	0.021206
O	-0.977399	0.572419	-0.004713
H	-3.086013	1.883083	-0.171587
H	-3.765013	0.742431	1.012486
H	-4.043151	0.456189	-0.690613
H	-1.263629	-1.974390	0.157244
H	-2.590674	-1.762662	-1.006081
H	-2.957271	-1.792630	0.702816

MIN5:

C	3.383587	0.814358	-0.022792
C	2.187794	0.044741	-0.004337
C	2.242883	-1.437738	0.032029
O	1.098829	0.683587	-0.019066
H	0.121357	0.087059	-0.007417
H	3.318820	1.893649	-0.047975
H	4.350558	0.331019	-0.011775
H	1.254374	-1.888984	0.027513
H	2.816513	-1.801250	-0.824621
H	2.786712	-1.757172	0.925323
C	-2.055648	-0.022419	0.001663
C	-3.275799	-0.860786	-0.024265
C	-2.196147	1.455340	0.031126
O	-0.948635	-0.577415	-0.000710
H	-1.255792	1.969654	-0.150449
H	-2.575106	1.739641	1.018304
H	-2.951050	1.776474	-0.688449
H	-3.042189	-1.904739	0.165091
H	-3.731663	-0.767150	-1.015832
H	-4.014108	-0.488549	0.687948

TS1:

C	-2.850833	-0.946927	0.006073
C	-1.652534	-0.057763	0.001861
C	-1.888112	1.417731	-0.012872
O	-0.527126	-0.542806	0.011526
H	-2.566878	-1.985013	0.155188
H	-3.557632	-0.629490	0.775511
H	-3.370855	-0.844822	-0.950954
H	-0.970387	1.981531	-0.154463
H	-2.607952	1.675584	-0.792030
H	-2.347880	1.710380	0.935406
C	1.691047	0.129343	-0.004933
C	1.900103	-0.602764	-1.307441
C	1.899123	-0.568065	1.319376
O	1.656079	1.343460	-0.014748
H	1.592498	0.006101	-2.152316
H	2.973227	-0.809216	-1.362628
H	1.336848	-1.531652	-1.252978
H	1.600953	0.066707	2.148362
H	1.323471	-1.490696	1.289881
H	2.970190	-0.783980	1.374413

TS2:

C	-3.267110	-0.727201	-0.004278
C	-1.956740	-0.009101	-0.001338
C	-1.936677	1.483189	0.013467
O	-0.935603	-0.679415	-0.012097
H	-3.139083	-1.805291	-0.019414
H	-3.826204	-0.416382	0.882645
H	-3.835884	-0.392348	-0.876134
H	-1.405322	1.837610	-0.871314
H	-2.944419	1.887865	0.033392
H	-1.374692	1.822682	0.884633
C	1.943237	-0.000975	-0.005282
C	3.220135	0.780731	-0.003185
C	2.011302	-1.488617	0.006942
O	0.893300	0.623296	-0.005627
H	3.040330	1.840943	0.148279
H	3.881813	0.381805	0.768290
H	3.709139	0.619327	-0.968249
H	1.076613	-1.937700	-0.309500
H	2.846226	-1.826289	-0.606354
H	2.225032	-1.791426	1.037562

TS3:

C	1.899994	-0.079897	-0.005431
C	3.210351	-0.659635	-0.369363
C	1.684711	1.380904	-0.127730
O	1.019587	-0.857493	0.403877
H	3.295371	-1.693587	-0.047569
H	4.016473	-0.048687	0.042674
H	3.309925	-0.604370	-1.459295
H	0.632613	1.649795	-0.194828
H	2.235669	1.778233	-0.979755
H	2.113012	1.850541	0.765917
C	-2.038408	0.125701	-0.022557
C	-2.670758	-1.095900	-0.610872
C	-1.264799	0.047142	1.222609
O	-2.186221	1.236858	-0.497154
H	-3.571139	-1.326178	-0.035190
H	-2.949675	-0.919139	-1.646239
H	-1.992044	-1.944985	-0.526054
H	-1.013142	1.005418	1.671789
H	-1.598049	-0.710661	1.928663
H	-0.072480	-0.381196	0.706167

TS4:

C	3.034839	-1.091958	0.648076
C	2.276967	-0.053349	0.021936
C	2.988991	1.010138	-0.744843
O	1.037961	-0.042961	0.140877
H	-0.317417	-0.376415	-0.282213
H	2.519073	-1.856218	1.213049
H	4.112777	-1.124325	0.566295
H	2.283067	1.707738	-1.186950
H	3.673259	1.550049	-0.085107
H	3.603288	0.559314	-1.528101
C	-2.202991	-0.031571	-0.030655
C	-1.960790	0.945375	1.044777
C	-3.565180	-0.345153	-0.482873
O	-1.259766	-0.634623	-0.597860
H	-0.926588	1.279319	1.080617
H	-2.206242	0.449993	1.992440
H	-2.647829	1.787436	0.953999
H	-3.589470	-1.243794	-1.093255
H	-3.915851	0.504996	-1.081134
H	-4.244634	-0.418323	0.367719