Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

for

Ammonia as an efficient catalyst for decomposition of carbonic acid: A quantum chemical investigation

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Table S1 Relative energies (in kcal mol^{-1}) of all species with respect to the isolated reactants involved in decomposition of carbonic acid calculated at the three different levels of theory. Here CA-X, TS_x and CW-X stands for the pre-reactive complex, transition state and post-reactive complex of X-catalyzed reaction (X = WM and WD, AM, AD and FA)

Catalyst	Species	M06-2X/ aug-cc-pVTZ	MP2/ aug-cc-pVTZ	CCSD(T)/ aug-cc-pVTZ
None	CA	0.0	0.0	0.0
	TS	44.9	40.8	43.9
	CW	-3.7	-10.1	-7.4
WM	CA-WM	-9.5	-9.3	-9.3
	TS_{WM}	15.8	15.2	17.9
	CW-WM	-11.6	-17.7	-15.1
WD	CA-WD	-13.7	-13.7	-13.5
	TS_{WD}	6.0	6.6	9.4
	CW-WD	-16.5	-22.1	-19.4
AM	CA-AM	-12.2	-12.3	-12.0
	TS_{AM}	10.2	7.7	10.6
	CW-AM	-12.3	-18.8	-16.0
AD	CA-AD	-18.7	-19.4	-18.9
	TS_{AD}	-3.8	-4.5	-2.0
	CW-AD	-19.3	-25.9	-22.9
FA	CA-FA	-12.2	-12.6	-12.6
	TS_{FA}	4.1	3.9	6.1
	CW-FA	-14.3	-19.9	-17.4

Table S2 Optimized geometries in Cartesian coordinates and normal mode frequencies of all species calculated at MP2/aug-cc-pVTZ level of theory

Species	Cartesian coordinate (Å)			Vibrational frequencies (cm^{-1})		
CA	C	-0.060696	-0.133494	-0.000032		
	O	-0.779495	-1.093599	0.000009	496.39	544.653	572.237
	O	1.276931	-0.194607	0.000008	605.857	790.357	967.833
	H	1.624839	0.706962	0.000007	1159.568	1270.334	1409.041
	O	-0.474827	1.158895	0.000004	1879.919	3796.856	3804.288
	H	-1.441538	1.128493	0.000022			
CW	C	0.894344	0.003275	-0.000036			
	O	0.899596	1.173203	0.000114	4.168	97.016	111.372
	O	0.924155	-1.166187	-0.000052	150.911	165.096	648.601
	H	-2.478377	-0.760632	0.001668	662.712	1328.626	1627.289
	O	-1.878007	-0.009492	-0.000193	2404.378	3818.824	3944.670
	H	-2.453637	0.760782	-0.000407			
TS	C	0.348400	0.084792	-0.006743			
	O	1.360754	-0.514254	-0.000946	-1684.612	397.487	501.476
	O	-0.182545	1.233878	0.023464	626.211	723.315	789.505
	H	-1.198507	0.536527	0.032401	940.464	1264.748	1302.201
	O	-1.130663	-0.695968	-0.107208	1985.134	2190.221	3780.694
	H	-1.272262	-1.234526	0.685580			
CA-WM	C	0.897095	-0.072478	0.002330			
	O	2.097991	-0.126568	0.019310	77.2246	117.8669	184.6784
	O	0.081851	-1.113392	-0.009694	213.2577	294.7233	433.9362
	H	-0.854308	-0.809426	-0.027224	556.8863	570.9267	628.0678
	O	0.198469	1.109400	-0.005222	790.9354	854.2377	958.3307
	H	0.877672	1.798099	-0.004558	1189.4082	1345.0185	1466.6503
	H	-3.079343	-0.156448	0.595981	1623.2309	1874.2634	3435.1441
	H	-2.075731	0.868397	0.047999	3789.2477	3793.4974	3918.3785
	O	-2.409668	-0.027659	-0.082667			
CW-WM	C	-1.354702	-0.465616	0.003664			
	O	-2.275819	0.243184	-0.087294	32.6045	99.3577	102.8496
	O	-0.462254	-1.221977	0.094274	123.5066	148.4672	181.0786
	H	1.652469	-1.038870	-0.045305	197.6712	217.6134	280.7546
	O	0.495865	1.579862	0.120828	482.9014	638.4357	645.3031
	H	0.632797	2.444502	-0.274183	661.1433	1331.5448	1628.3157
	H	3.044127	-0.761895	0.519569	1648.5028	2408.9585	3685.7272
	H	1.335481	1.107348	0.004885	3787.5944	3913.0525	3918.8378
	O	2.425126	-0.470743	-0.156178			
TS_{WM}	C	0.826834	-0.202595	-0.020493			
	O	1.986682	0.024672	0.171306	-1101.2445	109.0828	369.3814
	O	0.061049	-1.179895	-0.134735	429.6843	506.8299	547.6224
	H	-1.275754	-0.751812	-0.049005	591.4968	640.3274	691.9895
	O	-0.037714	1.114600	-0.192845	767.1696	785.5810	1057.6822
	H	0.440293	1.833169	0.240391	1187.5310	1343.5991	1409.8946
	H	-2.470630	-0.115912	0.901973	1602.8425	1802.4251	1999.2702
	H	-1.214871	0.776863	0.028843	2304.6912	3815.8149	3841.8385
	O	-2.065023	-0.025220	0.031370			

CA-WD	C 1.418115 -0.025101 -0.013876 O 2.587680 -0.299661 -0.075719 O 0.890580 1.155780 -0.241517 H -0.090812 1.185997 -0.080857 O 0.463829 -0.968910 0.316025 H 0.978851 -1.767911 0.500173 H -2.025534 1.878717 0.891808 H -2.181062 0.590299 0.043657 H -1.405953 -1.321759 -0.091777 H -2.661800 -1.597456 -0.936914 O -1.716371 1.449187 0.089231 O -2.366014 -1.188557 -0.118375	25.7033 81.9801 120.8444 150.0192 217.0661 220.6850 258.8435 294.0054 300.8475 432.8798 536.2812 561.1737 612.6177 633.8700 789.5171 830.3265 947.1864 984.0237 1208.2882 1348.8029 1434.8871 1629.3514 1652.8300 1872.9531 3229.6173 3555.2837 3715.2530 3778.2743 3893.9150 3901.4827
CW-WD	C -1.956598 0.204981 -0.267200 O -2.637770 -0.733803 -0.128127 O -1.302694 1.164954 -0.418872 H 1.018235 2.022339 0.142117 O 0.317317 -1.050326 0.936817 H 0.230963 -1.801780 1.529374 H 1.075263 0.762362 0.988626 H 2.319487 0.100811 -0.566645 H 1.015382 -1.292513 0.299479 H 3.258445 -1.053468 -0.976079 O 2.331543 -0.804217 -0.933607 O 1.644331 1.427437 0.567079	11.7840 29.9614 78.0064 82.6306 100.8991 171.9167 189.7089 199.8796 222.7317 226.4127 274.7306 323.9979 388.6173 474.7628 603.0356 643.7374 649.6029 663.3766 870.4335 1329.7097 1640.0060 1648.3376 1670.9791 2406.4572 3553.6631 3613.4894 3694.0579 3885.1085 3901.4793 3902.7252
TS_{WD}	C -1.322973 -0.214637 -0.026772 O -2.490865 -0.053486 0.235706 O -0.555482 -1.173196 -0.213682 H 0.917330 -1.260842 -0.111070 O -0.577251 1.118773 -0.194451 H -1.211154 1.788661 0.094697 H 2.188038 -1.690126 0.767955 H 2.007728 0.124666 0.123871 H 0.724997 1.254030 0.019007 H 2.242394 1.640017 -0.590508 O 1.816794 1.218309 0.165605 O 1.940367 -1.181472 -0.011092	-602.6739 40.4332 59.5854 123.0983 366.5743 396.6156 409.5121 478.4765 510.8520 548.9359 564.1045 584.7943 696.2055 744.0625 777.3313 998.7670 1060.4564 1120.4571 1315.8492 1390.4042 1504.0335 1621.1677 1721.0448 1781.9006 1912.6723 1946.6823 2678.1400 3797.8525 3841.6421 3866.7790
CA-AM	C 0.000000 0.932890 0.000000 O 0.042728 2.137673 0.000000 O 1.042330 0.126809 0.000000 H 0.751783 -0.833964 0.000000 O -1.178967 0.230547 0.000000 H -1.866071 0.911163 0.000000 N 0.235767 -2.464579 0.000000 H 0.494179 -3.005375 0.815904 H 0.494179 -3.005375 -0.815904 H -0.773164 -2.371966 0.000000	50.884 77.949 102.101 241.7131 299.5776 377.2078 568.4981 572.5081 634.8974 798.93 963.307 1058.656 1122.743 1194.641 1360.140 1499.472 1665.855 1670.321 1860.181 3053.060 3498.978 3642.161 3646.36 3793.994
CW-AM	C -1.428414 -0.461571 0.000020 O -2.347598 0.257659 0.005305 O -0.539282 -1.225693 -0.005148 H 1.850320 -1.127834 0.004590 O 0.450428 1.516319 -0.006018 H 0.690032 2.445926 0.012775 N 2.562453 -0.405934 0.003598 H 3.142805 -0.559357 -0.811483 H 3.145367 -0.559473 0.816813 H 1.296411 1.025424 -0.001099	29.6956 84.4920 90.0713 104.6744 120.0685 130.1069 205.5288 219.3456 253.7383 512.4337 643.2068 662.1362 756.0715 1098.058 1330.487 1644.765 1674.348 1679.667 2406.495 3493.030 3530.013 3635.474 3647.592 3906.964

TS_{AM}	C	0.909348	-0.227252	-0.025889		
	O	2.036271	0.108305	0.227857	-614.091	78.7365	234.4123
	O	0.203548	-1.218484	-0.179407	267.7703	373.9783	424.8637
	H	-1.584444	-0.882721	0.015534	432.1462	539.4310	610.0797
	O	-0.042424	1.102730	-0.243949	707.9513	757.6924	914.0791
	H	0.454224	1.833308	0.145187	1059.377	1279.305	1378.643
	N	-2.165191	-0.036342	0.148869	1571.522	1605.748	1699.753
	H	-2.620676	-0.047858	1.052269	1841.963	2000.875	3244.595
	H	-2.852283	0.054021	-0.588586	3570.111	3654.266	3816.085
	H	-1.275737	0.720749	0.052834		
CA-AD	C	-1.421406	-0.066824	-0.033150		
	O	-2.541033	-0.476912	-0.219494	24.4868	74.0686	99.1858
	O	-0.913596	1.043092	-0.510494	109.9298	139.8731	164.2814
	H	0.036100	1.215181	-0.178369	190.5739	244.9819	270.6929
	O	-0.509270	-0.759769	0.735566	334.3417	392.8406	535.2545
	H	-1.010115	-1.521841	1.059377	569.7160	591.6747	643.8864
	N	1.567830	1.584030	0.268110	799.9383	953.9550	1092.807
	H	1.642030	1.784015	1.258084	1144.330	1190.245	1201.535
	H	1.972331	2.369468	-0.226712	1364.674	1510.731	1656.179
	H	2.135788	0.756600	0.074633	1671.083	1681.347	1700.875
	N	2.479420	-1.266341	-0.355755	1856.211	2748.002	3393.325
	H	1.517596	-1.426669	-0.073563	3484.145	3576.605	3622.137
	H	3.060079	-1.900220	0.179152	3641.407	3642.474	3785.156
	H	2.555076	-1.550706	-1.324818		
CW-AD	C	-1.767654	0.226591	-0.390186		
	O	-2.689588	-0.161195	0.213782	23.6668	29.7038	71.9535
	O	-0.874405	0.637493	-1.027967	88.5027	107.6367	127.9603
	H	1.121995	2.147882	-0.076733	144.6423	163.2405	174.7847
	O	0.125833	-0.927075	1.268145	216.3126	241.6950	246.1339
	H	-0.000831	-1.678463	1.853228	311.0812	345.3892	416.4948
	N	1.777416	1.602590	0.469825	581.3941	639.9217	663.8051
	H	1.220467	1.025303	1.093824	852.0325	1098.009	1138.489
	H	2.300910	2.253846	1.041148	1327.665	1644.303	1657.245
	H	2.209368	-0.220824	-0.632608	1680.775	1684.866	1694.072
	N	1.959540	-1.190869	-0.828625	2402.401	3380.706	3427.594
	H	0.765885	-1.227359	0.581895	3476.847	3585.752	3612.309
	H	2.815674	-1.726016	-0.899559	3645.384	3645.686	3897.252
	H	1.519048	-1.209743	-1.740162		
TS_{AD}	C	1.280104	-0.163849	-0.108649		
	O	2.501627	-0.180388	-0.130939	-891.688	39.3660	53.1655
	O	0.388576	-0.781770	-0.744390	103.9378	227.0484	267.6999
	H	-0.993175	-1.258799	0.070442	304.3318	315.5491	416.9752
	O	0.687600	0.776589	0.844502	482.7888	551.9605	576.6371
	H	1.459889	1.185897	1.257378	615.8916	635.0976	688.8294
	N	-1.967152	-1.121773	0.438565	771.9404	812.2707	823.2697
	H	-1.963352	-1.221386	1.446076	1169.809	1253.371	1292.099
	H	-2.597557	-1.806800	0.042075	1328.802	1561.932	1579.438
	H	-2.031346	0.129906	-0.000261	1676.230	1705.590	1758.211
	N	-1.690152	1.247124	-0.461198	1787.333	1831.371	2965.067
	H	-0.800928	1.410192	0.038507	3242.188	3544.896	3556.150
	H	-2.325464	2.027942	-0.357772	3638.846	3649.350	3791.628
	H	-1.449984	1.123233	-1.439503		

CA-FA	C 1.650339 -0.039414 0.000011 O 2.837783 0.133909 0.000001 O 1.033094 -1.199755 -0.000109 H 0.049782 -1.101657 -0.000038 O 0.756377 1.019870 0.000098 H 1.312444 1.812561 0.000165 C -2.398640 -0.155261 0.000023 H -3.485431 -0.245791 0.000182 O -1.653008 -1.118721 0.000092 O -2.018299 1.111545 -0.000121 H -1.034566 1.128152 -0.000196	34.2422 78.0045 158.3823 168.1746 195.1214 214.2816 542.5487 567.0864 629.4547 685.2033 779.7491 841.5931 885.5253 937.3153 1082.167 1185.959 1239.343 1340.757 1383.534 1431.794 1459.329 1757.473 1887.032 3148.316 3353.524 3490.574 3778.820
CW-FA	C 2.070470 -0.556747 -0.000022 O 3.096051 -0.004942 -0.000012 O 1.068825 -1.168628 -0.000036 H -0.868032 -1.046197 0.000098 O 0.628488 1.678208 0.000049 H 0.797373 2.623692 0.000142 C -2.545403 -0.165236 -0.000018 H -3.609483 -0.410216 -0.000059 O -1.816300 -1.277528 0.000080 O -2.118576 0.969787 -0.000074 H -0.338168 1.589442 0.000011	23.3688 30.2958 48.4185 108.1472 128.2577 145.9832 155.7004 156.3189 202.7544 392.5414 575.4994 638.9665 654.2358 658.6611 777.4881 1076.213 1181.053 1333.092 1343.219 1420.784 1648.823 1774.667 2412.110 3131.075 3641.472 3686.055 3910.909
TS_{FA}	C -1.522536 -0.211338 -0.013146 O -2.670520 0.024502 -0.254747 O -0.760898 -1.194128 0.035242 H 0.564560 -1.096670 0.122803 O -0.716527 1.071860 0.384578 H -1.262437 1.827355 0.123633 C 2.197104 0.020164 -0.098310 H 3.281608 0.015401 -0.191776 O 1.661952 -1.111849 0.123763 O 1.605671 1.121442 -0.217602 H 0.411437 1.106345 0.044199	-922.953 65.5086 79.0000 179.2671 292.9209 385.8963 420.9905 557.5026 629.2966 655.3851 756.7068 768.4932 851.1535 1057.410 1078.907 1250.476 1311.002 1352.851 1379.826 1422.369 1568.048 1676.131 1742.372 1796.123 2029.362 3174.895 3785.808
WM	O 0.000000 0.000000 0.118189 H 0.000000 0.758025 -0.472754 H 0.000000 -0.758025 -0.472754	1627.7612 3824.7050 3950.6090
WD	O -1.385097 0.000601 0.110496 H -1.746597 -0.763119 -0.349950 H -1.747854 0.758911 -0.357831 O 1.512857 -0.000695 -0.121976 H 0.559405 0.000611 0.048517 H 1.912972 0.004353 0.751104	127.0098 147.1099 154.9316 184.1613 360.4078 630.2965 1629.3162 1650.2617 3718.7825 3813.9011 3915.1798 3935.2566
AM	N -0.000001 0.000024 -0.113458 H -0.813306 0.468039 0.264760 H 0.812092 0.470150 0.264756 H 0.001222 -0.938358 0.264690	1031.0862 1668.1686 1668.278 3507.0037 3654.7632 3654.842
AD	N -1.566861 -0.000104 -0.049447 H -1.370764 0.000065 0.944511 H -2.143019 -0.811868 -0.234205 H -2.141135 0.812853 -0.234957 N 1.665929 -0.000114 0.100349 H 2.126024 -0.810612 -0.294555 H 0.709620 -0.000019 -0.243743 H 2.125797 0.811106 -0.293365	49.2407 61.3644 109.2828 140.4679 240.9353 392.8552 1059.5477 1073.0278 1660.610 1670.2760 1674.2890 1692.332 3467.4939 3496.9773 3609.572 3640.714 3645.350 3646.330

FA	C	0.000000	0.422392	0.000000			
	H	-0.376774	1.447695	0.000000	625.952	674.778	1058.557
	O	1.163418	0.108154	0.000000	1130.131	1301.324	1408.906
	O	-1.034994	-0.439528	0.000000	1794.039	3125.306	3741.349
	H	-0.650614	-1.331055	0.000000			

Table S3 Absolute energies (in Hartree) of all species involved in decomposition of carboxylic acid calculated at the three different levels of theory. Here CA-X, TS_x and CW-X stands for the pre-reactive complex, transition state and post-reactive complex of X-catalyzed reaction (X = WM and WD, AM, AD and FA)

Catalyst	Species	M06-2X/ aug-cc-pVTZ	MP2/ aug-cc-pVTZ	CCSD(T)/ aug-cc-pVTZ
None	CA	-265.02377660	-264.63907576	-264.6759148
	TS	-264.95220347	-264.57406173	-264.6060256
	CW	-265.02961886	-264.6551204	-264.6876492
WM	CA-WM	-341.4690336	-340.9828534	-341.0329751
	TS_{WM}	-341.4287493	-340.9439045	-341.0422798
	CW-WM	-341.4723741	-340.9962466	-340.9897759
WD	CA-WD	-417.9140456	-417.3271415	-417.390438
	TS_{WD}	-417.8826278	-417.2947286	-417.3998065
	CW-WD	-417.9185268	-417.3404721	-417.3539439
AM	CA-AM	-321.59616703	-321.11927572	-321.1755954
	TS_{AM}	-321.56050389	-321.08737878	-321.1395183
	CW-AM	-321.59637830	-321.12964709	-321.1820193
AD	CA-AD	-378.15944730	-377.59104371	-377.6670727
	TS_{AD}	-378.13571087	-377.56733222	-377.6401674
	CW-AD	-378.16045247	-377.60140657	-377.673548
FA	CA-FA	-454.8128131	-454.1458856	-454.2137132
	TS_{FA}	-454.7868756	-454.1195708	-454.1840052
	CW-FA	-454.8161326	-454.1574632	-454.2213483