Low Temperature (550-700 K) Oxidation Pathways of Cyclic Ketones: Dominance of HO_2-Elimination Channels Yielding Conjugated Cyclic Coproducts

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Supplementary Material

Table S1. Initial concentrations (cm^{-3}) in the oxidation experiments for the compounds studied here. Helium was added to reach a total pressure of 4 or 8 Torr in all experiments.

	Temp (K)	Pressure (Torr)	$[Parent]_0$	$[O_2]$	$[Cl_2]$	$[Cl]_0$
CPO	550	8	9.8×10^{13}	2.9×10^{16}	2.0×10^{14}	6.0×10^{12}
CPO	650	8	8.3×10^{13}	2.5×10^{16}	1.7×10^{14}	5.1×10^{12}
CHO	550	8	5.0×10^{13}	2.8×10^{16}	5.6×10^{14}	1.6×10^{13}
CHO	700	4	4.0×10^{13}	1.1×10^{16}	2.2×10^{14}	6.6×10^{12}
2-Me-CPO	550	8	3.2×10^{13}	2.8×10^{16}	5.6×10^{14}	1.6×10^{13}

Concentrations in cm^{-3}

[a]The vapor pressure of 2-Me-CPO at 20 °C was estimated to be 4.3 Torr based on the vapor pressure at 25 °C of 5.8 Torr and using the Clausius Clapeyron equation. The enthalpy of vaporization of 2-Me-CPO was assumed to be equal to that of CHO (ΔH_{vap} = 11.0 kcal mol^{-1}).[1]

Table S1: Stationary point energies (0K) for small molecules computed in this work (CBS-QB3)

Small Molecules

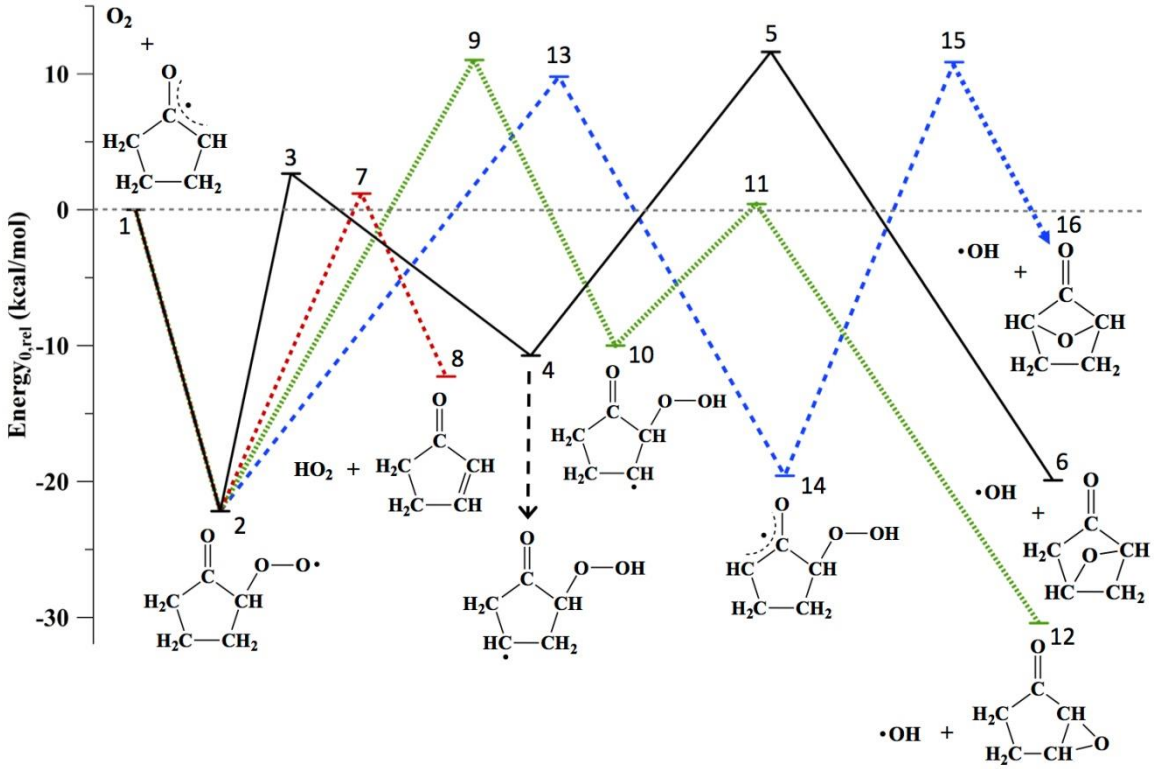
Species	Energy (Hartrees)
O_2	-150.164746
HO_2	-150.741102
OH	-75.649720

Table S2: Optimized stationary point geometries (0K) for small molecules computed in this work (CBS-QB3)

Small Molecules

O_2	O	1.214152	0.856009	-0.97843
	O	0.945073	1.930622	-0.50268
HO_2	O	2.048407	-0.976401	0.701909
	O	2.387916	-1.586283	-0.42797
	H	1.966058	-0.031512	0.474045
OH	O	2.054226	-0.968508	0.670989
	H	1.956918	-0.012814	0.503025

Tables S3-4: Stationary point energies and geometries (0K; CBS-QB3) for the CPO-2-yl + O_2 reaction in reference to the given potential energy surface replicated from the main text.



CPO-2-yl + O_2

Stationary Point	Energy (Hartrees)
1	-269.439274
2	-419.639386
3	-419.59978
4	-419.621126
5	-419.585495
6	-343.986047
7	-419.602128
8	-268.882468
9	-419.586437
10	-419.61995
11	-419.603353
12	-344.00279
13	-419.588421
14	-419.635218
15	-419.586704
16	No Stable Structure Converged

CPO-2-yl + O_2

Stationary Point				
1	C	1.344757	-0.683838	-0.000545
	C	1.369002	0.826799	0.367789
	H	2.020385	-1.288971	0.613106
	H	1.669662	-0.840454	-1.042097
	H	2.139509	1.373757	-0.177447
	H	1.587703	0.930239	1.433943
	C	-0.945195	0.08509	0.20119
	O	-2.167735	0.079473	0.300101
	C	-0.083737	-1.070263	0.14866
	C	-0.056955	1.332468	0.078715
	H	-0.464714	-2.083991	0.167557
	H	-0.150852	1.714874	-0.944576
	H	-0.399696	2.121186	0.750134
2	C	1.307978	-0.733383	-0.03443
	C	1.352385	0.727827	0.468503
	H	2.040659	-1.391568	0.433447
	H	1.47123	-0.770075	-1.116795
	H	2.170422	1.295001	0.023223
	H	1.49539	0.739207	1.552063
	C	-0.975158	0.089813	0.124609
	O	-2.172375	0.100635	0.037896
	C	-0.112806	-1.191171	0.25502
	C	-0.034224	1.292797	0.113788
	H	-0.489862	-2.017492	-0.345978
	H	-0.05095	1.708917	-0.900966
	H	-0.405033	2.071447	0.782609
	O	-0.263012	-1.58896	1.669022
	O	0.456512	-2.652969	1.953583
3	C	1.45292	-0.900699	-0.316878
	C	1.525988	0.522616	0.272498
	H	2.297559	-1.518966	-0.009135
	H	1.443824	-0.84282	-1.415566
	H	2.273556	1.195411	-0.144197
	C	0.113083	-1.341568	0.226959
	H	-0.209296	-2.376823	0.167978
	H	0.395286	-1.042073	1.547169
	O	1.849312	0.397954	1.658916
	O	0.745398	-0.204968	2.324011

	C	0.065571	1.039766	0.072159
	C	-0.843529	-0.197779	-0.03981
	H	-1.259913	-0.230864	-1.056767
	H	-1.682831	-0.122276	0.654919
	O	-0.25826	2.189371	-0.019083
4	C	1.111613	1.491661	-0.253918
	H	-3.063526	-0.714125	0.420624
	H	1.487035	2.505608	-0.260095
	C	0.954509	-0.864454	0.064433
	O	1.275175	-2.017945	0.140008
	C	-0.4145	-0.358652	-0.477643
	C	1.796609	0.35686	0.429703
	H	-0.81835	-1.045314	-1.226005
	H	2.841455	0.195507	0.134032
	H	1.807863	0.450931	1.527807
	O	-1.234448	-0.366111	0.690676
	O	-2.558911	0.103209	0.304338
	C	-0.126719	1.059598	-0.986038
	H	0.032909	1.039675	-2.076268
	H	-0.987885	1.712524	-0.816868
5	C	0.656007	0.376928	0.723141
	H	1.50598	0.470349	1.392853
	C	-0.866251	0.702145	-0.77001
	H	2.553365	-1.367741	-1.091595
	H	-1.087456	0.948201	-1.799471
	O	1.016016	-0.121536	-0.582436
	O	2.275975	-1.256186	-0.171656
	C	-0.121721	1.590709	0.198872
	H	0.535619	2.311652	-0.284609
	H	-0.758467	2.09427	0.939658
	C	-1.493562	-0.424739	-0.009958
	H	-1.5992	-1.347012	-0.584745
	H	-2.478376	-0.172339	0.406443
	C	-0.473413	-0.57531	1.149997
	O	-0.565299	-1.256664	2.129658
6	C	1.074392	-0.740922	0.414418
	C	1.39068	0.764668	0.262511
	H	1.822925	-1.483718	0.678936
	H	2.062191	1.124761	1.040781
	H	1.660498	1.158692	-0.720336

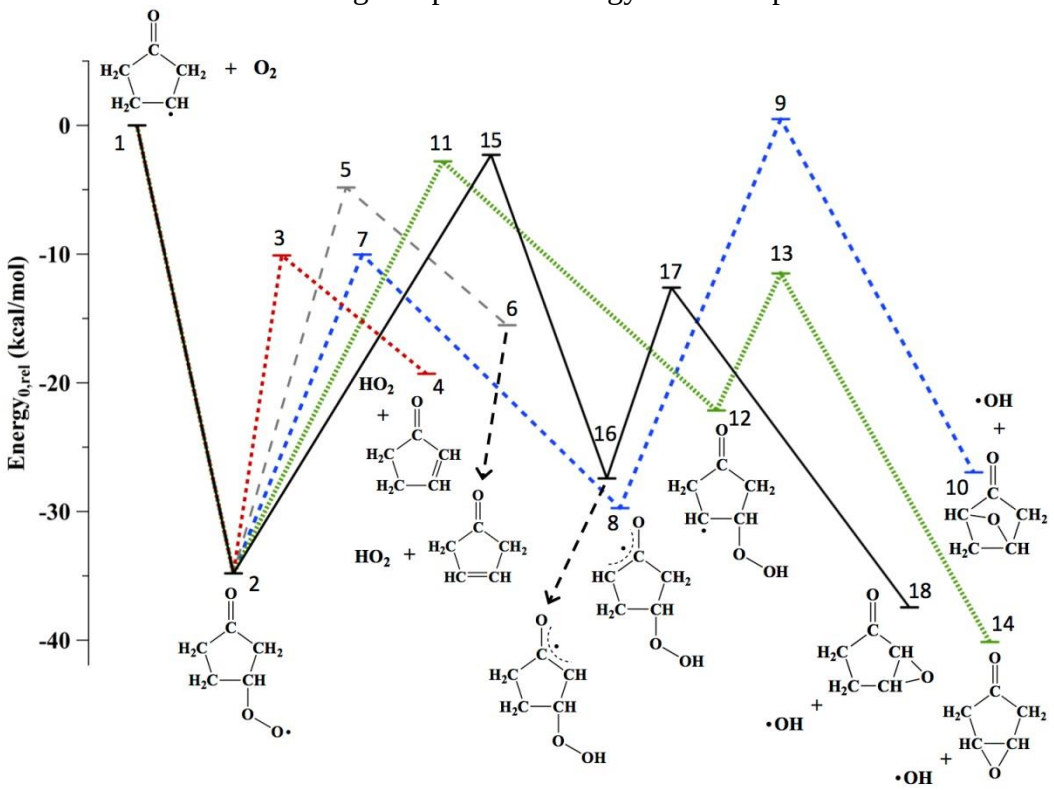
	C	-0.812699	0.198978	-0.480004
	O	-1.783246	0.57972	-1.07179
	C	0.073143	-1.046613	-0.713803
	C	-0.085593	0.819022	0.725414
	H	-0.480419	-1.969955	-0.534799
	H	-0.549986	1.644597	1.256841
	H	0.489577	-1.064443	-1.723811
	O	0.162258	-0.392241	1.518117
7	C	0.206593	0.804756	-0.868628
	C	1.342457	1.06204	0.141278
	H	-0.896593	1.005629	-0.191427
	H	0.048957	1.491851	-1.697795
	H	2.256842	1.329977	-0.395948
	H	1.116463	1.885819	0.821182
	C	1.50933	-0.287343	0.866199
	H	2.544106	-0.561512	1.074755
	H	0.970867	-0.303588	1.819583
	O	-1.847145	-0.648693	0.262952
	O	-1.957849	0.590105	0.463515
	C	0.021723	-0.568687	-1.027051
	H	-0.50416	-1.067409	-1.828745
	C	0.860513	-1.324538	-0.056768
	O	1.026041	-2.521079	-0.03407
8	C	1.211552	0.761217	0.19897
	C	1.367229	-0.735116	0.068634
	H	2.068847	1.417614	0.300911
	H	1.894057	-1.146539	0.936358
	H	1.978286	-0.986091	-0.805082
	C	-0.969896	-0.001178	0.023217
	O	-2.177848	0.014693	-0.033744
	C	-0.063806	1.16296	0.1743
	C	-0.078943	-1.252904	-0.04902
	H	-0.430521	2.177976	0.250082
	H	-0.357587	-1.935092	0.757406
	H	-0.273109	-1.774165	-0.989198
9	C	1.523704	0.555268	-0.187074
	H	2.269607	1.091091	0.403602
	C	0.046199	-1.410333	-0.279656
	C	0.083877	1.030821	-0.012715
	H	-0.229364	-2.306981	0.274837

	H	-0.114449	1.828777	0.699167
	H	0.205782	1.684478	-1.200968
	H	0.045166	-1.656914	-1.346201
	O	1.799933	0.672761	-1.608225
	O	1.092439	1.825419	-2.019875
	C	1.458973	-0.96051	0.082008
	C	-0.844821	-0.181188	0.008367
	H	-1.662141	-0.082561	-0.711879
	H	-1.315947	-0.267134	0.993588
	O	2.349183	-1.630034	0.52996
10	C	-0.215204	1.143853	-0.667931
	C	1.032749	1.624836	0.012269
	H	-3.054383	-1.089955	0.116869
	H	-0.928336	1.801373	-1.145574
	H	1.697935	2.128434	-0.702254
	H	0.813505	2.371636	0.786021
	C	0.97158	-0.815152	-0.06
	O	1.392788	-1.926531	-0.23112
	C	-0.423994	-0.312911	-0.517594
	C	1.696053	0.357005	0.592001
	H	-0.776774	-0.841387	-1.407889
	H	2.770968	0.284739	0.423923
	H	1.524275	0.277787	1.670833
	O	-1.288929	-0.660013	0.600424
	O	-2.636392	-0.229337	0.261179
11	C	-0.305368	1.094865	-0.686467
	C	0.913162	1.55537	0.053149
	H	-2.007928	-1.031347	2.18535
	H	-1.0022	1.747525	-1.192859
	H	1.613987	2.006017	-0.664036
	H	0.68168	2.337532	0.782524
	C	0.874109	-0.871372	-0.085613
	O	1.36167	-1.934748	-0.350425
	C	-0.50087	-0.363509	-0.560149
	C	1.517659	0.281383	0.686936
	H	-0.973427	-0.957917	-1.342905
	H	2.604001	0.223124	0.631765
	H	1.218836	0.184285	1.733766
	O	-1.326572	-0.046948	0.529682
	O	-1.541228	-1.496262	1.47613

12	C	1.38424	-0.659592	0.105764
	C	1.365898	0.859016	0.177576
	H	2.211278	-1.235305	0.509305
	H	2.096802	1.30033	-0.503935
	H	1.622865	1.175335	1.193118
	C	-0.926115	-0.005794	0.150891
	O	-2.090222	-0.039163	0.457783
	C	0.006671	-1.189772	0.093979
	C	-0.092468	1.242764	-0.163779
	H	-0.208109	1.469714	-1.227011
	H	-0.471983	2.093882	0.401248
	H	-0.294773	-2.164178	0.460143
	O	0.8169	-1.161299	-1.102818
13	C	1.427503	0.611087	0.375174
	H	2.306276	1.210449	0.143866
	C	0.073559	-1.302924	0.118754
	H	-0.240634	-2.300533	-0.172482
	H	0.521187	-1.334389	1.424496
	O	1.316135	0.49707	1.839533
	O	1.271153	-0.844606	2.245223
	C	-0.868856	-0.10961	0.073357
	H	-1.584584	-0.200202	-0.748869
	H	-1.457389	-0.026162	0.991887
	C	1.432795	-0.809065	-0.233609
	C	0.071935	1.130468	-0.094108
	H	0.137326	1.436674	-1.143487
	H	-0.255259	1.989293	0.492637
	O	2.326205	-1.355198	-0.828864
14	C	0.934641	1.57138	0.083557
	H	-3.100367	-0.960711	0.231505
	H	1.562577	2.361923	-0.33974
	H	0.544727	1.969385	1.032054
	C	0.92491	-0.844558	-0.041791
	O	1.264776	-2.021259	0.01964
	C	-0.458283	-0.341368	-0.537443
	C	1.684366	0.311251	0.333251
	H	-0.829013	-0.934752	-1.37716
	H	2.671476	0.241148	0.773741
	O	-1.306704	-0.524438	0.598108
	O	-2.649419	-0.105006	0.215899
	C	-0.22284	1.13842	-0.85552

	H	-1.132993	1.72278	-0.725268
	H	0.095064	1.23458	-1.897705
15	C	0.675036	0.402416	-0.773362
	H	1.523232	0.557029	-1.432917
	C	-0.869395	0.782675	0.737584
	H	2.535504	-1.136722	1.310273
	H	-1.219787	1.154273	1.694734
	O	1.06252	0.122369	0.590167
	O	2.162627	-1.283788	0.428929
	C	-1.358706	-0.474633	0.086995
	H	-1.326824	-1.318106	0.77969
	H	-2.402433	-0.356682	-0.230783
	C	-0.117586	1.596336	-0.243212
	C	-0.379438	-0.647086	-1.120645
	H	-0.856939	-0.442652	-2.082187
	H	0.063707	-1.641267	-1.143115
	O	-0.035539	2.789921	-0.400402

Tables S5-6: Stationary point energies and geometries (0K; CBS-QB3) for the CPO-3-yl + O_2 reaction in reference to the given potential energy surface replicated from the main text.



CPO-3-yl + O_2

Stationary Point	Energy (Hartrees)
1	-269.428065
2	-419.648304
3	-419.608919
4	-268.882468
5	-419.600515
6	-268.87645
7	-419.608799
8	-419.640219
9	-419.592027
10	-343.986047
11	-419.597257
12	-419.628127
13	-419.611141
14	-344.007053
15	-419.596457
16	-419.636542
17	-419.612885
18	-344.00279

CPO-3-yl + O_2

Stationary Point				
1	C	1.497993	-0.978714	-0.086648
	C	1.468847	0.51632	0.056083
	H	2.208943	-1.449364	0.60138
	H	1.826078	-1.272499	-1.096569
	H	2.360979	1.128337	0.06904
	C	-0.823386	-0.175379	0.001361
	O	-2.020657	-0.162692	-0.120445
	C	0.044351	-1.428283	0.15988
	C	0.084519	1.063606	0.025642
	H	-0.31233	-2.218712	-0.502236
	H	-0.139521	1.689106	-0.852121
	H	-0.174717	1.685847	0.895071
	H	-0.093924	-1.784584	1.186956
2	C	1.475595	-0.929243	-0.156076
	C	1.489615	0.558206	0.217083
	H	2.272793	-1.470077	0.35563
	H	1.649705	-1.020028	-1.231984
	H	2.276221	1.139842	-0.262815
	C	-0.826971	-0.168397	0.072518
	O	-2.028731	-0.15763	0.041513
	C	0.06239	-1.408304	0.211248
	C	0.077177	1.067362	-0.038064
	H	-0.320452	-2.227265	-0.398643
	H	-0.013172	1.470848	-1.052353
	H	-0.21844	1.858376	0.652144
	H	0.013198	-1.72856	1.257756
	O	1.789642	0.589603	1.664689
	O	1.781736	1.812224	2.148685
3	C	-0.05019	0.485066	0.975216
	C	-0.966303	1.219125	0.027061
	H	0.375471	0.982729	1.836285
	H	-0.45121	2.025006	-0.500317
	H	-1.765049	1.687396	0.615294
	C	-1.528695	0.122191	-0.89481
	H	-0.999482	0.090047	-1.852604
	H	-2.592635	0.21656	-1.111731
	C	-0.15921	-0.906411	0.839164
	H	0.97785	-1.043318	0.108249

	H	0.030026	-1.598036	1.65511
	O	2.007341	-0.506289	-0.408856
	O	1.776973	0.698897	-0.068412
	C	-1.24563	-1.196502	-0.156153
	O	-1.795351	-2.25211	-0.343657
4	C	1.211552	0.761217	0.19897
	C	1.367229	-0.735116	0.068634
	H	2.068847	1.417614	0.300911
	H	1.894057	-1.146539	0.936358
	H	1.978286	-0.986091	-0.805082
	C	-0.969896	-0.001178	0.023217
	O	-2.177848	0.014693	-0.033744
	C	-0.063806	1.16296	0.1743
	C	-0.078943	-1.252904	-0.04902
	H	-0.430521	2.177976	0.250082
	H	-0.357587	-1.935092	0.757406
	H	-0.273109	-1.774165	-0.989198
5	C	0.042069	0.536197	0.94046
	C	0.225899	-0.841963	0.804325
	H	-0.44941	1.001444	1.783325
	H	-0.943266	-1.048354	0.177443
	H	0.094243	-1.500199	1.659849
	C	1.315936	-1.121618	-0.227767
	H	1.045521	-1.839771	-1.005916
	H	2.240794	-1.486972	0.233531
	C	0.86196	1.320493	-0.035911
	H	0.284141	1.987137	-0.681767
	H	1.60339	1.947316	0.47795
	O	-2.026895	-0.656895	-0.37496
	O	-1.91462	0.586952	-0.135223
	C	1.597045	0.249507	-0.859278
	O	2.278953	0.456379	-1.826764
6	C	1.258862	0.694985	0.094293
	C	1.24445	-0.60698	-0.19758
	H	2.152933	1.304615	0.145411
	H	2.125223	-1.198795	-0.4158
	C	-1.031093	0.021089	0.163279
	O	-2.228447	0.00907	0.27601
	C	-0.14545	-1.18433	-0.193623
	H	-0.290729	-1.982624	0.543745

	H	-0.455019	-1.598794	-1.160307
	C	-0.118565	1.244558	0.350882
	H	-0.250469	1.65459	1.359131
	H	-0.414759	2.038421	-0.344921
7	C	1.475594	-0.917895	-0.306011
	C	1.492821	0.522215	0.270614
	H	2.3135	-1.517154	0.054341
	H	1.530657	-0.871779	-1.4024
	H	2.302416	1.149826	-0.099591
	C	-0.80491	-0.221628	-0.024854
	O	-2.00399	-0.25689	-0.158385
	C	0.123421	-1.376673	0.173008
	C	0.07853	1.042986	-0.013005
	H	-0.230664	-2.397536	0.072552
	H	0.035856	1.521395	-0.996084
	H	-0.277016	1.756672	0.730413
	H	0.3224	-1.06656	1.491543
	O	1.78476	0.371297	1.673809
	O	0.69533	-0.24254	2.31147
8	C	0.749301	0.377788	0.699837
	H	1.266077	0.6472	1.623922
	C	-1.370165	-0.44055	-0.169146
	O	-2.243612	-1.216168	-0.540953
	C	-1.191702	0.923331	-0.60041
	H	2.500325	-1.651662	-0.475006
	H	-1.85561	1.409914	-1.303607
	O	1.729748	0.054571	-0.294005
	O	2.557436	-1.012398	0.247842
	C	-0.282305	-0.742274	0.870742
	H	-0.73394	-0.714151	1.868892
	H	0.153389	-1.732686	0.741743
	C	-0.024873	1.560473	0.066941
	H	0.617471	2.128417	-0.613804
	H	-0.346245	2.266063	0.847354
9	C	0.668718	0.359426	0.609789
	H	1.596436	0.432184	1.170774
	C	-1.405022	-0.417117	-0.066776
	O	-2.38169	-1.065515	-0.356131
	C	-0.907192	0.805888	-0.757381
	H	2.227555	-1.400538	-1.539676

	H	-1.290962	1.139339	-1.713499
	O	0.910451	0.004083	-0.782752
	O	2.166855	-1.228172	-0.589274
	C	-0.382782	-0.659654	1.057839
	H	-0.810506	-0.468477	2.047053
	H	0.003937	-1.677897	1.018052
	C	-0.123213	1.61877	0.243607
	H	0.503532	2.382376	-0.214675
	H	-0.728507	2.057116	1.047352
10	C	1.074392	-0.740922	0.414418
	C	1.39068	0.764668	0.262511
	H	1.822925	-1.483718	0.678936
	H	2.062191	1.124761	1.040781
	H	1.660498	1.158692	-0.720336
	C	-0.812699	0.198978	-0.480004
	O	-1.783246	0.57972	-1.07179
	C	0.073143	-1.046613	-0.713803
	C	-0.085593	0.819022	0.725414
	H	-0.480419	-1.969955	-0.534799
	H	-0.549986	1.644597	1.256841
	H	0.489577	-1.064443	-1.723811
	O	0.162258	-0.392241	1.518117
11	C	1.535043	-0.962102	0.039181
	C	1.517288	0.535997	-0.230884
	H	2.132237	-1.515073	-0.68942
	H	1.932945	-1.190104	1.033285
	H	2.283005	1.12204	0.283191
	C	0.082151	1.020077	0.07677
	H	-0.073717	1.626803	0.965833
	H	0.21378	1.855152	-1.001307
	O	1.627614	0.714751	-1.658159
	O	1.030054	1.978685	-1.885999
	C	-0.833672	-0.152399	-0.155373
	H	-1.2112	-0.183414	-1.185837
	H	-1.698216	-0.209751	0.507288
	C	0.066301	-1.402291	-0.002474
	O	-0.330583	-2.53057	0.088934
12	C	-0.021397	1.532068	0.048081
	C	0.706679	0.382683	0.674845
	H	0.427339	2.508953	-0.068736

	H	1.210797	0.63819	1.612202
	C	-1.457368	-0.370586	-0.16939
	O	-2.310224	-1.118101	-0.569027
	C	-1.303851	1.105719	-0.572629
	H	-2.178818	1.671826	-0.221684
	H	2.55091	-1.665367	-0.397577
	H	-1.319707	1.193545	-1.668314
	O	1.723543	0.024869	-0.286742
	O	2.536407	-1.02929	0.329724
	C	-0.350325	-0.715678	0.828424
	H	-0.789901	-0.692783	1.832742
	H	0.046244	-1.718226	0.671058
13	C	-0.23769	1.032482	-0.788008
	C	0.817258	1.575953	0.103059
	H	-2.252512	-1.025711	1.898756
	H	-0.865168	1.613432	-1.447821
	H	1.602793	2.09723	-0.462884
	H	0.45547	2.292554	0.848458
	C	-0.417902	-0.429551	-0.57968
	H	-0.749764	-1.045392	-1.418111
	O	-1.459941	-0.046881	0.278754
	O	-2.043196	-1.494136	1.077904
	C	0.80541	-0.923217	0.18083
	H	1.541708	-1.390444	-0.483497
	H	0.526911	-1.64389	0.94978
	C	1.42571	0.336291	0.792315
	O	2.261743	0.37336	1.653948
14	C	1.311101	-0.771011	0.32948
	C	1.317727	0.704591	0.297173
	H	2.037697	-1.344055	0.895896
	H	2.049549	1.295332	0.838109
	C	-0.924309	-0.034673	-0.212684
	O	-2.068943	-0.037516	-0.577293
	C	-0.086869	-1.28886	0.098845
	C	-0.075584	1.224378	0.04382
	H	-0.154188	-1.997915	-0.729572
	H	-0.136697	1.897073	-0.81485
	H	-0.481301	1.754999	0.912707
	H	-0.497162	-1.777281	0.990043
	O	1.834666	-0.059998	-0.803517

15	C	0.281471	-0.52003	-0.590052
	H	0.419016	-1.095269	-1.510443
	C	-1.318263	0.785125	0.700931
	C	0.629454	0.947098	-0.75163
	H	-2.343201	1.155633	0.708994
	H	1.084526	1.339247	-1.656402
	H	1.82184	0.648677	-0.017686
	H	-0.97334	0.739356	1.739831
	O	1.171442	-1.075564	0.414497
	O	2.325515	-0.329812	0.399375
	C	-0.401867	1.752793	-0.063775
	C	-1.136907	-0.570294	-0.00616
	H	-1.852878	-0.676188	-0.825537
	H	-1.255271	-1.431063	0.655287
	O	-0.506299	2.96095	-0.089906
16	C	-0.045417	1.651587	0.165253
	C	0.767426	0.415122	0.607997
	H	0.566032	2.302145	-0.461594
	H	-0.325072	2.21682	1.057472
	H	1.347147	0.572089	1.520838
	C	-1.464329	-0.321102	0.013773
	O	-2.452897	-1.032489	-0.117471
	C	-1.297411	1.099613	-0.541307
	C	-0.242057	-0.679272	0.696568
	H	-2.20078	1.686552	-0.368973
	H	-0.06664	-1.65533	1.129582
	H	2.387625	-1.577696	-0.71151
	H	-1.156179	1.028353	-1.624263
	O	1.701638	0.160662	-0.47113
	O	2.582856	-0.909575	-0.040259
17	C	-0.167416	1.044107	0.97954
	H	-2.193719	-0.177601	-2.078029
	H	-0.736015	1.658306	1.662316
	C	-0.463531	-0.362464	0.619595
	H	-0.936906	-1.02854	1.341452
	O	-1.375316	0.265539	-0.248906
	O	-1.871206	-0.876265	-1.489651
	C	0.777566	-0.896552	-0.103492
	H	1.426888	-1.388629	0.626665
	H	0.483244	-1.624477	-0.858382
	C	0.98233	1.518274	0.190002

	C	1.455962	0.357082	-0.689178
	H	1.124602	0.55031	-1.71338
	H	2.54565	0.313734	-0.698618
	O	1.473698	2.625465	0.265121
18	C	1.38424	-0.659592	0.105764
	C	1.365898	0.859016	0.177576
	H	2.211278	-1.235305	0.509305
	H	2.096802	1.30033	-0.503935
	H	1.622865	1.175335	1.193118
	C	-0.926115	-0.005794	0.150891
	O	-2.090222	-0.039163	0.457783
	C	0.006671	-1.189772	0.093979
	C	-0.092468	1.242764	-0.163779
	H	-0.208109	1.469714	-1.227011
	H	-0.471983	2.093882	0.401248
	H	-0.294773	-2.164178	0.460143
	O	0.8169	-1.161299	-1.102818

Tables S7-S11: Absolute photoionization cross sections at the mass of the parent for the indicated species.

2-Cyclopentenone

Energy(eV)	Photoionization Cross Section (Mb)
9.200	0.06
9.225	0.08
9.250	0.10
9.275	0.12
9.300	0.35
9.325	0.29
9.350	2.31
9.375	2.43
9.400	3.51
9.425	3.49
9.450	4.12
9.475	4.56
9.500	6.08
9.525	5.73
9.550	5.48
9.575	6.59
9.600	6.80
9.625	7.17
9.650	7.31
9.675	7.37
9.700	7.85
9.725	8.06
9.750	8.35
9.775	9.02
9.800	9.47
9.825	9.46
9.850	9.20
9.875	9.54
9.900	10.24
9.925	10.91
9.950	10.45
9.975	11.17
10.000	11.78
10.025	11.72
10.050	11.89

3-Cyclopentenone

Energy(eV)	Photoionization Cross Section (Mb)
9.100	0.00
9.125	0.01
9.150	0.00
9.175	0.00
9.200	0.01
9.225	0.01
9.250	0.04
9.275	0.04
9.300	0.11
9.325	0.17
9.350	0.34
9.375	0.48
9.400	0.73
9.425	1.20
9.450	1.62
9.475	2.17
9.500	2.90
9.525	3.36
9.550	3.59
9.575	4.12
9.600	4.33
9.625	4.80
9.650	5.02
9.675	5.76
9.700	5.88
9.725	6.49
9.750	6.59
9.775	7.19
9.800	7.36
9.825	7.67
9.850	7.74
9.875	8.27
9.900	8.45
9.925	8.70
9.950	9.43

10.075	13.46	9.975	9.43
10.100	14.96	10.000	10.01
10.125	14.86	10.025	10.41
10.150	15.43	10.050	10.52
10.175	16.74	10.075	10.86
10.200	18.32	10.100	11.27
10.225	18.44	10.125	11.18
10.250	19.64	10.150	11.87
10.275	20.81	10.175	12.06
10.300	21.88	10.200	12.62
10.325	21.71	10.225	13.16
10.350	22.79	10.250	13.15
10.375	24.15	10.275	13.70
10.400	25.66	10.300	14.43
10.425	25.85	10.325	14.87
10.450	25.68	10.350	14.55
10.475	26.54	10.375	15.11
10.500	27.26	10.400	15.70
10.525	28.71	10.425	15.85
10.550	28.67	10.450	16.29
10.575	28.40	10.475	16.50
10.600	29.19	10.500	16.72
10.625	28.77	10.525	17.05
10.650	30.10	10.550	17.07
10.675	29.11	10.575	16.80
10.700	29.47	10.600	17.19
10.725	30.05	10.625	17.81
10.750	29.70	10.650	17.44
10.775	29.21	10.675	17.85
10.800	31.57	10.700	17.79
10.825	30.92	10.725	18.24
10.850	31.24	10.750	18.35
10.875	30.06	10.775	18.16
10.900	30.64	10.800	18.40
10.925	29.77	10.825	18.02
10.950	30.51	10.850	18.12
10.975	31.41	10.875	18.63
11.000	31.94	10.900	18.26
11.025	30.52	10.925	18.69
11.050	30.69	10.950	18.79
11.075	32.29	10.975	18.84
11.100	31.85	11.000	19.11
11.125	31.67	11.025	18.72

11.150	30.66
11.175	31.71
11.200	30.87
11.225	31.06
11.250	30.79
11.275	30.00
11.300	30.94
11.325	31.54
11.350	30.27
11.375	30.96
11.400	31.03
11.425	30.87
11.450	30.52
11.475	30.45
11.500	29.55
11.525	29.97
11.550	30.76
11.575	26.05
11.600	19.71
11.625	35.46
11.650	33.80
11.675	34.13
11.700	32.41

2-Cyclohexenone

Energy(eV)	Photoionization Cross Section (Mb)
8.915	0.00
8.940	0.00
8.965	0.01
8.990	0.01
9.015	0.01
9.040	0.01
9.065	0.05
9.090	0.10
9.115	0.12
9.140	0.19
9.165	0.28
9.190	0.83
9.215	1.53
9.240	1.92
9.265	2.37

2-Methyl-2-Cyclopentenone

Energy(eV)	Photoionization Cross Section (Mb)
8.915	0.02
8.940	0.00
8.965	0.00
8.990	0.00
9.015	0.00
9.040	0.02
9.065	0.00
9.090	0.00
9.115	0.06
9.140	0.14
9.165	0.12
9.190	0.92
9.215	1.93
9.240	2.32
9.265	2.67

9.290	2.71	9.290	3.80
9.315	3.63	9.315	3.89
9.340	4.24	9.340	4.46
9.365	4.12	9.365	4.72
9.390	4.32	9.390	5.13
9.415	5.05	9.415	4.85
9.440	5.51	9.440	5.74
9.465	5.70	9.465	5.54
9.490	5.71	9.490	6.61
9.515	5.97	9.515	6.12
9.540	6.04	9.540	6.92
9.565	6.46	9.565	6.71
9.590	6.59	9.590	7.39
9.615	6.43	9.615	7.91
9.640	7.13	9.640	8.09
9.665	7.08	9.665	8.93
9.690	7.20	9.690	9.35
9.715	7.80	9.715	9.50
9.740	7.71	9.740	10.91
9.765	8.16	9.765	10.51
9.790	8.26	9.790	11.69
9.815	8.75	9.815	11.64
9.840	8.63	9.840	11.96
9.865	9.26	9.865	12.55
9.890	9.69	9.890	12.74
9.915	9.83	9.915	14.64
9.940	10.54	9.940	14.43
9.965	11.24	9.965	15.15
9.990	11.88	9.990	16.01
10.015	12.44	10.015	16.98
10.040	13.07	10.040	16.82
10.065	13.65	10.065	18.09
10.090	14.30	10.090	18.61
10.115	14.77	10.115	18.85
10.140	16.02	10.140	19.90
10.165	16.10	10.165	20.28
10.190	16.41	10.190	20.37
10.215	17.67	10.215	21.79
10.240	17.99	10.240	22.26
10.265	17.92	10.265	22.56
10.290	18.06	10.290	22.20
10.315	18.73	10.315	25.45
10.340	19.28	10.340	25.04

10.365	20.08
10.390	19.57
10.415	19.85
10.440	19.86
10.465	20.13
10.490	19.91
10.515	20.10

10.365	25.50
10.390	27.30
10.415	26.91
10.440	27.14
10.465	28.19
10.490	28.68
10.515	29.04
10.540	29.72
10.565	30.88
10.590	30.44
10.615	31.26
10.640	31.24
10.665	31.18
10.690	31.95
10.715	32.30
10.740	33.48
10.765	32.97
10.790	32.39
10.815	33.93
10.840	33.44
10.865	35.14
10.890	33.47
10.915	34.37
10.940	34.30
10.965	33.48
10.990	34.27
11.015	34.76

Cyclohexanone

Energy(eV)	Photoionization Cross Section (Mb)
8.797	0.00
8.822	0.00
8.847	0.00
8.872	0.00
8.897	0.00
8.922	0.00
8.947	0.01
8.972	0.00
8.997	0.00
9.022	0.02

9.047	0.03
9.072	0.07
9.097	0.15
9.122	0.49
9.147	1.43
9.172	1.78
9.197	2.04
9.222	2.27
9.247	2.55
9.272	3.17
9.297	3.64
9.322	4.04
9.347	4.49
9.372	4.77
9.397	4.96
9.422	5.40
9.447	5.59
9.472	5.95
9.497	6.12
9.522	6.25
9.547	6.50
9.572	6.92
9.597	7.25
9.622	7.63
9.647	7.60
9.672	7.87
9.697	8.10
9.722	8.33
9.747	8.80
9.772	8.71
9.797	9.13
9.822	9.15
9.847	9.63
9.872	9.58
9.897	10.36
9.922	10.39
9.947	10.68
9.972	10.82
9.997	11.23
10.022	11.93
10.047	12.32
10.072	12.57
10.097	13.12

10.122	13.21
10.147	13.44
10.172	14.30
10.197	14.76
10.222	15.08
10.247	15.41
10.272	16.32
10.297	16.08
10.322	16.31
10.347	16.21
10.372	16.78
10.397	17.00
10.422	17.47
10.447	17.35
10.472	17.28
10.497	17.14
10.522	17.51
10.547	17.57
10.572	17.60
10.597	17.88
10.622	17.45
10.647	17.82
10.672	17.60
10.697	17.28
10.722	17.46
10.747	17.19
10.772	17.46
10.797	16.58
10.822	16.59
10.847	16.55
10.872	16.77
10.897	16.66
10.922	16.38
10.947	16.60
10.972	16.84
10.997	16.75

[1] J. S. Chickos and W. E. Acree, *J. Phys. Chem. Ref. Data*, 2003, **32**, 519-878.