Electronic Supplementary Information

Characterization of Electrophilicity and Oxidative Potential of Atmospheric Carbonyls

Jin Y. Chen,[a§] Huanhuan Jiang,[b§] Stacy Jy Chen,[b] Cody Cullen,[c] C. M. Sabbir Ahmed,[a] and Ying-Hsuan Lin[*ab]

[a] Environmental Toxicology Graduate Program, University of California, Riverside, California 92521, United States

[b] Department of Environmental Sciences, University of California, Riverside, California 92521, United States

[c] Department of Chemical Engineering, University of California, Riverside, California 92521, United States

[§]Authors contributed equally to this study

[*] Corresponding author

Email: ying-hsuan.lin@ucr.edu (Y.-H. L.) Tel: (951)-827-3785 Fax: (951)-827-4652

Pages: 18
Tables: 5
Figures: 2

Table of Contents

Table S1: The chemical reactivity descriptors EHOMO, ELUMO, μ, η and ω) of carbonyl compounds calculated in gas phase.

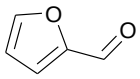
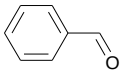
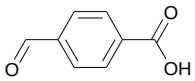
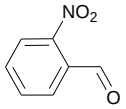
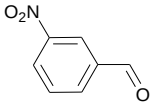
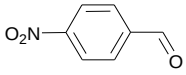
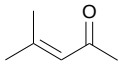
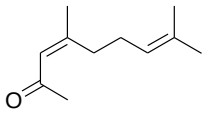
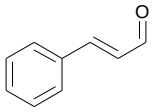
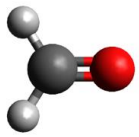
Compound	Structure	E_{HOMO} eV	E_{LUMO} eV	μ eV	η eV	ω eV
Simple carbonyl						
Formaldehyde (FM)		-7.667	-1.746	-4.707	5.921	1.87
2-Furaldehyde (2-FA)		-7.207	-2.155	-4.681	5.052	2.17
Benzaldehyde (BA)		-7.340	-2.176	-4.758	5.164	2.19
4-Formylbenzoic acid (4-FBA)		-7.632	-2.870	-5.251	4.762	2.90
2-Nitrobenzaldehyde (2-NBA)		-7.768	-3.303	-5.536	4.465	3.43
3-Nitrobenzaldehyde (3-NBA)		-7.908	-3.323	-5.616	4.585	3.44
4-Nitrobenzaldehyde (4-NBA)		-7.963	-3.565	-5.764	4.398	3.78
α,β-unsaturated carbonyl						
Mesityl oxide (MPO)		-6.763	-1.610	-4.187	5.153	1.70
Citral (CTR)		-6.706	-1.824	-4.265	4.882	1.86
trans-Cinnamaldehyde (*t*-CA)		-6.959	-2.517	-4.738	4.442	2.53

Table S2: Optimized geometry of carbonyls in gas phase and in water solvent from the Gaussian 09 program.

Gaussian Optimized Geometry, Gas Phase:

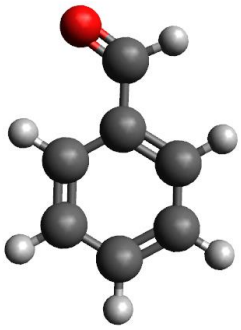
Formaldehyde
E(RB3LYP) = -114.541577701 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

C	0.00000	0.52742	0.00000
O	0.00000	-0.67430	0.00000
H	-0.00001	1.11493	0.93973
H	-0.00001	1.11493	-0.93973



Benzaldehyde
E(RB3LYP) =-345.666239183 Hartree(Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

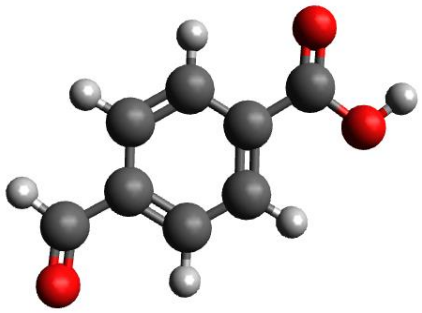
C	-1.99189	0.46358	0.00005
C	-0.53400	0.20655	0.00008
C	0.35492	1.28690	0.00001
C	1.72933	1.06367	-0.00009
C	2.21651	-0.24269	-0.00007
C	1.33257	-1.32598	0.00006
C	-0.03833	-1.10446	0.00012
O	-2.84864	-0.39249	-0.00024
H	-2.27063	1.53915	0.00097
H	-0.03461	2.30040	0.00004
H	2.41747	1.90105	-0.00022
H	3.28638	-0.41923	-0.00014
H	1.71866	-2.33893	0.00012
H	-0.74281	-1.92794	0.00016



4-Formylbenzoic acid

E (RB3LYP) = -534.295211516 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

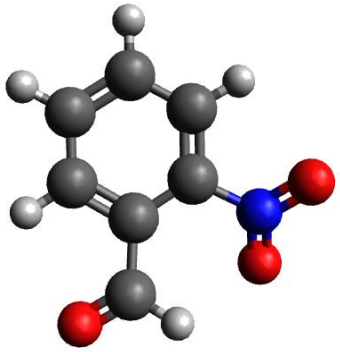
C	-3.23113	0.30439	-0.00003
O	-3.98513	-0.64116	0.00033
C	-1.74968	0.20387	-0.00008
C	-0.98081	1.37289	-0.00006
C	0.40626	1.29788	-0.00014
C	1.03309	0.04777	-0.00024
C	2.52354	0.01713	-0.00034
O	3.23205	0.99515	0.00035
O	3.02541	-1.24221	0.00021
C	0.26520	-1.12622	-0.00024
C	-1.11952	-1.04708	-0.00012
H	-3.62426	1.34258	0.00036
H	-1.47336	2.33993	0.00003
H	1.01854	2.19080	-0.00013
H	3.99070	-1.16232	0.00065
H	0.76000	-2.08826	-0.00032
H	-1.73201	-1.94077	-0.00014



2-Nitrobenzaldehyde

E (RB3LYP) = -550.212689420 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

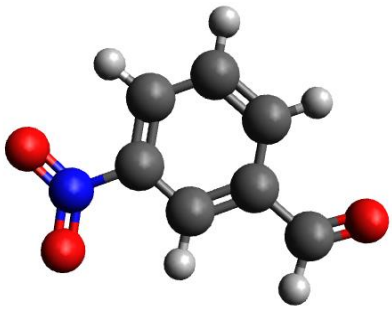
N	1.83296	-0.08103	0.03635
O	2.63301	-0.86133	-0.45962
O	2.12797	0.97566	0.58284
C	0.40030	-0.45191	-0.00568
C	-0.60112	0.52981	-0.05137
C	-0.36342	2.00300	-0.22224
O	-1.23679	2.81585	-0.02765
C	-1.93005	0.09177	-0.02279
C	-2.24238	-1.26077	0.05397
C	-1.22405	-2.21312	0.08571
C	0.10657	-1.80927	0.04920
H	0.63290	2.31205	-0.56903
H	-2.70753	0.84452	-0.07073
H	-3.27943	-1.57385	0.08181
H	-1.46182	-3.26855	0.14274
H	0.91658	-2.52549	0.07540



3-Nitrobenzaldehyde

E (RB3LYP) = -550.224223249 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

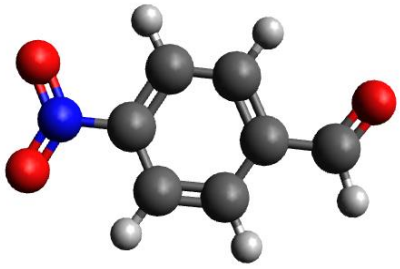
N	2.30133	-0.48159	0.00001
O	2.38668	-1.70232	0.00058
O	3.25248	0.28780	-0.00071
C	0.94209	0.10894	0.00005
C	-0.15853	-0.73867	-0.00003
C	-1.43571	-0.17735	-0.00003
C	-2.62350	-1.07085	-0.00018
O	-3.76774	-0.68204	-0.00015
C	-1.59012	1.21616	0.00012
C	-0.47364	2.04368	0.00022
C	0.80806	1.49313	0.00016
H	-0.01170	-1.81166	-0.00009
H	-2.38897	-2.15505	-0.00023
H	-2.59319	1.62612	0.00014
H	-0.59255	3.12038	0.00035
H	1.69383	2.11363	0.00018



4-Nitrobenzaldehyde

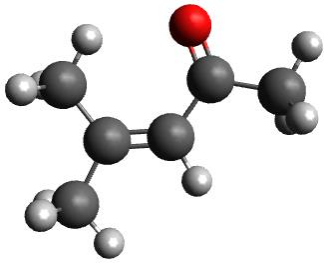
E (RB3LYP) = -550.223245374 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

N	-2.52393	-0.09984	0.00002
O	-3.16777	0.94050	0.00140
O	-3.00698	-1.22348	-0.00129
C	-1.04335	0.01008	-0.00001
C	-0.46916	1.27606	-0.00048
C	0.91822	1.36848	-0.00056
C	1.70472	0.21213	-0.00009
C	3.18690	0.33573	-0.00012
O	3.94913	-0.60174	0.00029
C	1.09852	-1.05105	0.00042
C	-0.28415	-1.15900	0.00041
H	-1.10187	2.15255	-0.00074
H	1.39329	2.34382	-0.00099
H	3.56628	1.37836	-0.00055
H	1.72631	-1.93378	0.00081
H	-0.78168	-2.11887	0.00070



Mesityl oxide

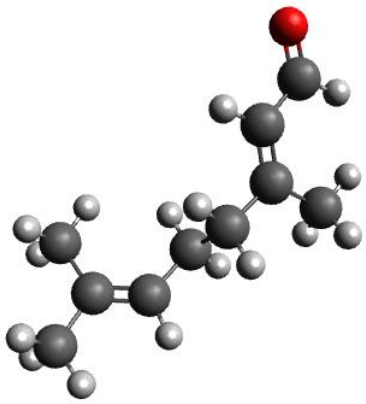
E (RB3LYP) = -309.962942241 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):



C	-1.53337	1.34384	0.04939
C	-1.20502	-0.12162	0.00165
C	0.04081	-0.63904	-0.02994
C	1.33307	0.08906	-0.01653
C	2.56623	-0.79824	0.04634
O	1.44556	1.30389	-0.05586
C	-2.40005	-1.03805	-0.01364
H	-2.01063	1.64096	-0.89279
H	-2.26714	1.53506	0.84028
H	-0.65381	1.96230	0.19919
H	0.13259	-1.72198	-0.05680
H	2.53706	-1.43105	0.93935
H	2.59604	-1.46729	-0.82005
H	3.46322	-0.18110	0.06241
H	-3.05672	-0.79399	-0.85637
H	-2.11766	-2.08934	-0.08670
H	-2.99737	-0.90034	0.89480

Citral

E (RB3LYP) = -466.002393482 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

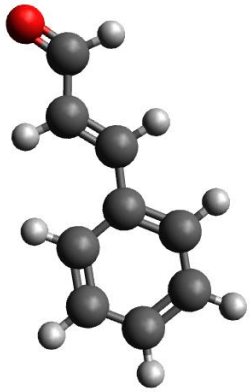


C	-2.98931	-1.66773	0.55963
C	-3.16763	-0.26054	0.04795
C	-4.54945	0.03863	-0.48046
C	-2.21477	0.68125	0.04499
C	-0.79279	0.57140	0.52159
C	0.22287	0.70312	-0.64573
C	1.66308	0.67274	-0.19056
C	2.17030	1.94664	0.43249
C	2.39320	-0.45065	-0.35563
C	3.78410	-0.65597	0.04947
O	4.38298	-1.70091	-0.12376
H	-3.68720	-1.86781	1.38103
H	-3.22240	-2.39239	-0.22894
H	-1.98173	-1.87596	0.91805
H	-5.30712	-0.11405	0.29716
H	-4.63401	1.06562	-0.84102
H	-4.80790	-0.63626	-1.30490
H	-2.48069	1.65729	-0.36031

H	-0.60316	1.36590	1.25321
H	-0.61272	-0.37339	1.03811
H	0.04071	-0.10638	-1.35677
H	0.02882	1.64477	-1.17385
H	1.52256	2.25386	1.25948
H	3.18816	1.87850	0.81090
H	2.13523	2.75502	-0.30652
H	1.93998	-1.31506	-0.83405
H	4.30003	0.19426	0.53603

trans-Cinnamaldehyde

E (RB3LYP) = -423.083192755 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):



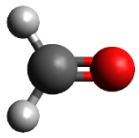
C	3.35775	-0.28859	0.00013
C	1.99490	0.24280	-0.00007
C	0.93371	-0.58683	0.00054
C	-0.48549	-0.23876	0.00028
C	-1.43620	-1.27341	-0.00008
C	-2.79963	-0.99575	-0.00042
C	-3.23974	0.32608	-0.00031
C	-2.30780	1.36679	0.00014
C	-0.94735	1.08978	0.00039
O	4.36337	0.39221	-0.00064
H	3.42717	-1.39833	0.00139
H	1.90193	1.32380	-0.00087
H	1.14233	-1.65628	0.00132
H	-1.09637	-2.30393	-0.00015
H	-3.51648	-1.80878	-0.00073
H	-4.30096	0.54709	-0.00054
H	-2.64645	2.39658	0.00029
H	-0.23901	1.90956	0.00082

Gaussian Optimized Geometry, Water Solvent:

Formaldehyde

E(RB3LYP) = -114.546525343 Hartree (Eh)
Hartree Electronic state: 1-A
Cartesian Coordinates (Angstroms):

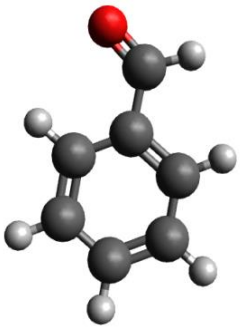
C	0.00000	-0.53129	0.00000
O	0.00000	0.67678	0.00000
H	-0.00001	-1.11325	0.93844
H	-0.00001	-1.11325	-0.93844



Benzaldehyde

E (RB3LYP) = -345.189785981 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

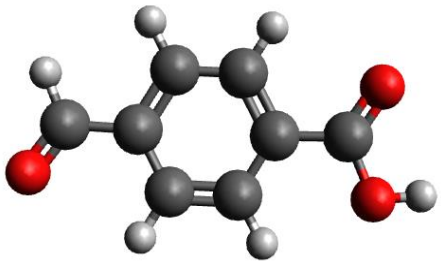
C	-1.98644	0.46404	0.00016
C	-0.53560	0.20142	0.00015
C	0.35009	1.28710	0.00004
C	1.72528	1.06767	-0.00015
C	2.21713	-0.23785	-0.00013
C	1.33739	-1.32599	0.00008
C	-0.03440	-1.10945	0.00019
O	-2.85400	-0.39182	-0.00039
H	-2.26320	1.53582	0.00108
H	-0.04206	2.29889	0.00010
H	2.41016	1.90728	-0.00031
H	3.28733	-0.41060	-0.00025
H	1.72762	-2.33701	0.00016
H	-0.72850	-1.94144	0.00031



4-Formylbenzoic acid

E (RB3LYP) = -534.307733963 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

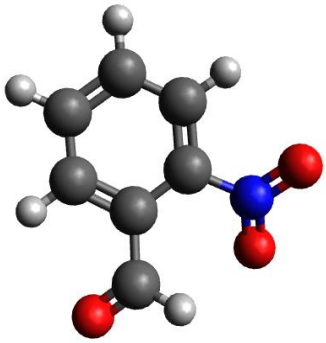
C	3.22644	0.30767	0.00013
O	3.98916	-0.63914	-0.00034
C	1.74987	0.19977	0.00011
C	0.98361	1.37163	0.00014
C	-0.40376	1.29749	0.00016
C	-1.03379	0.04870	0.00015
C	-2.52478	0.01394	0.00016
O	-3.23261	0.99868	-0.00044
O	-3.02308	-1.23741	0.00006
C	-0.26793	-1.12739	0.00011
C	1.11668	-1.05074	0.00003
H	3.61699	1.34239	-0.00027
H	1.47577	2.33797	0.00014
H	-1.00658	2.19628	0.00019
H	-3.99143	-1.17845	-0.00028
H	-0.75966	-2.09065	0.00010
H	1.71904	-1.95085	0.00001



2-Nitrobenzaldehyde

E (RB3LYP) = -550.224630179 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

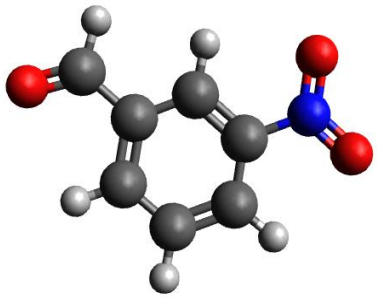
N	1.79783	-0.25294	0.03803
O	2.54425	-1.11526	-0.40839
O	2.18437	0.79812	0.54450
C	0.34673	-0.49561	-0.01497
C	-0.55506	0.58045	-0.07126
C	-0.15941	2.00775	-0.26947
O	-0.87982	2.93103	0.04892
C	-1.91948	0.27681	-0.03930
C	-2.36143	-1.04068	0.04602
C	-1.44164	-2.08718	0.08983
C	-0.07637	-1.81676	0.05642
H	0.80341	2.19318	-0.76569
H	-2.62785	1.09318	-0.10283
H	-3.42363	-1.25074	0.07128
H	-1.78139	-3.11301	0.15776
H	0.65437	-2.61186	0.10938



3-Nitrobenzaldehyde

E (RB3LYP) = -550.236789568 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

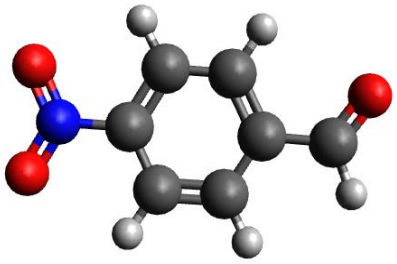
N	-2.29157	-0.48030	0.00004
O	-2.38731	-1.70321	-0.00139
O	-3.25280	0.28131	0.00155
C	-0.94042	0.10871	-0.00004
C	0.16082	-0.73908	0.00015
C	1.43662	-0.17400	0.00008
C	2.61559	-1.07146	0.00038
O	3.76822	-0.68852	0.00030
C	1.58768	1.22078	-0.00028
C	0.47055	2.04766	-0.00050
C	-0.80914	1.49480	-0.00033
H	0.02359	-1.81255	0.00039
H	2.37943	-2.15149	0.00067
H	2.58610	1.64067	-0.00038
H	0.58733	3.12384	-0.00081
H	-1.69050	2.12057	-0.00047



4-Nitrobenzaldehyde

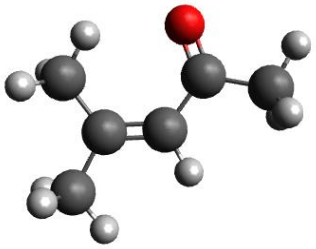
E (RB3LYP) = -550.235866482 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

N	-2.51565	-0.09780	-0.00004
O	-3.16971	0.93918	0.00222
O	-3.01121	-1.21924	-0.00190
C	-1.04215	0.01018	-0.00006
C	-0.46684	1.27655	-0.00075
C	0.92006	1.36790	-0.00085
C	1.70378	0.20868	-0.00018
C	3.18201	0.33918	-0.00026
O	3.95081	-0.60057	0.00056
C	1.09647	-1.05458	0.00056
C	-0.28542	-1.16161	0.00060
H	-1.09021	2.15894	-0.00125
H	1.39396	2.34272	-0.00148
H	3.55993	1.37763	-0.00050
H	1.71515	-1.94299	0.00113
H	-0.77578	-2.12443	0.00112



Mesityl oxide

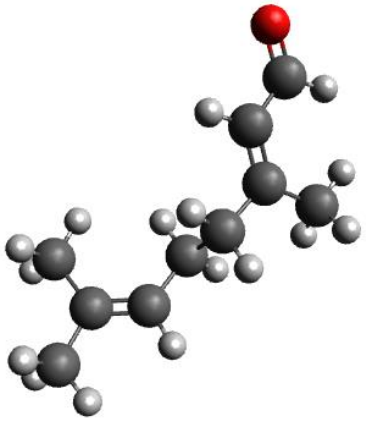
E (RB3LYP) = -309.970343628 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):



C	-1.52906	1.34092	0.11698
C	-1.20267	-0.12107	0.00213
C	0.04399	-0.64002	-0.06456
C	1.32954	0.08268	-0.03782
C	2.55762	-0.79446	0.10874
O	1.44287	1.30250	-0.13657
C	-2.39672	-1.03492	-0.03577
H	-1.83686	1.72329	-0.86432
H	-2.38091	1.48289	0.78831
H	-0.68259	1.93353	0.45264
H	0.13500	-1.72114	-0.11976
H	2.48450	-1.40602	1.01317
H	2.62450	-1.48578	-0.73754
H	3.45719	-0.18165	0.14969
H	-3.07531	-0.73526	-0.84218
H	-2.11743	-2.07905	-0.18136
H	-2.96716	-0.94960	0.89579

Citral

E (RB3LYP) = -466.012217419 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):

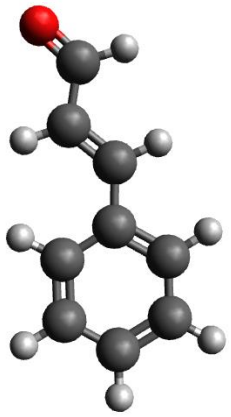


C	-2.98626	-1.68734	0.49855
C	-3.16476	-0.25827	0.05068
C	-4.55161	0.06803	-0.44956
C	-2.20758	0.68042	0.07707
C	-0.78133	0.54561	0.53598
C	0.22043	0.70054	-0.64239
C	1.66137	0.67578	-0.19565
C	2.17609	1.95779	0.39628
C	2.38551	-0.45899	-0.34565
C	3.76854	-0.64851	0.05468
O	4.38147	-1.70005	-0.10344
H	-3.68106	-1.92210	1.31330
H	-3.22703	-2.37406	-0.32106
H	-1.97661	-1.91283	0.84048
H	-5.30038	-0.11565	0.32998
H	-4.63555	1.10951	-0.76660
H	-4.82180	-0.57297	-1.29697
H	-2.47181	1.67353	-0.28573

H	-0.57542	1.32150	1.28204
H	-0.60375	-0.41396	1.02505
H	0.03883	-0.10249	-1.36071
H	0.01776	1.64979	-1.15095
H	1.50865	2.30293	1.19138
H	3.18256	1.89008	0.80301
H	2.16791	2.73710	-0.37366
H	1.91981	-1.32709	-0.80531
H	4.28373	0.20673	0.52329

trans-Cinnamaldehyde

E (RB3LYP) = -423.093761553 Hartree (Eh)
Electronic state: 1-A
Cartesian Coordinates (Angstroms):



C	3.34476	-0.28972	0.00011
C	1.99525	0.24948	0.00001
C	0.93263	-0.58488	0.00042
C	-0.48392	-0.23640	0.00023
C	-1.43196	-1.27567	-0.00006
C	-2.79616	-0.99931	-0.00033
C	-3.23759	0.32335	-0.00023
C	-2.30783	1.36767	0.00013
C	-0.94627	1.09355	0.00022
O	4.36576	0.38663	-0.00052
H	3.41223	-1.39510	0.00097
H	1.89813	1.33014	-0.00054
H	1.14101	-1.65351	0.00100
H	-1.08954	-2.30493	-0.00010
H	-3.51216	-1.81284	-0.00059
H	-4.29910	0.54266	-0.00040
H	-2.64914	2.39638	0.00027
H	-0.24093	1.91572	0.00054

Table S3: The nanomoles of carbonyls added to the DTT assay.

Carbonyl	**nmol**
Formaldehyde	6.71×10^{4}—3.36×10^{5}
2-Furaldehyde	2.39×10^{2}—1.20×10^{3}
Benzaldehyde	9.70×10^{3}—4.85×10^{4}
4-Formylbenzoic acid	3.26×10^{1}—1.63×10^{2}
2-Nitrobenzaldehyde	6.85×10^{0}—1.37×10^{2}
3-Nitrobenzaldehyde	6.48×10^{0}—1.30×10^{2}
4-Nitrobenzaldehyde	6.79×10^{0}—1.36×10^{2}
Citral	1.11×10^{2}—5.57×10^{2}
trans-Cinnamaldehyde	3.78×10^{1}—1.89×10^{2}
Mesityl oxide	3.53×10^{3}

Table S4. The comparisons of DTTr of carbonyls in this study with other compounds and aerosol systems reported previously.

Compounds or aerosols system	DTT_r (nmol/min/μg)	Reference
Pure compound		
Formaldehyde	8.50×10^{-6}	This study
2-Furaldehyde	9.39×10^{-5}	This study
Benzaldehyde	1.53×10^{-5}	This study
4-Formylbenzoic acid	1.67×10^{-4}	This study
2-Nitrobenzaldehyde	6.67×10^{-4}	This study
3-Nitrobenzaldehyde	2.13×10^{-4}	This study
4-Nitrobenzaldehyde	3.65×10^{-4}	This study
Mesityl oxide	1.02×10^{-4}	This study
Citral	1.53×10^{-4}	This study
trans-Cinnamaldehyde	1.51×10^{-3}	This study
Isoprene epoxydiol (IEPOX)	$7.00\pm1.39\times10^{-5}$	Kramer et al.[1]
2-Methyltetrol	$4.44\pm0.92\times10^{-5}$	Kramer et al.[1]
Methacrylic acid epoxide (MAE)	$9.84\pm0.97\times10^{-5}$	Kramer et al.[1]
2-Methylglyceric acid	$2.51\pm0.37\times10^{-4}$	Kramer et al.[1]
2-Hydroperoxy-2-methyl-but-3-en-1-ol (ISOPOOH)	$4.90\pm2.20\times10^{-1}$	Kramer et al.[1]
Methacrolein	$3.26\pm0.10\times10^{-2}$	Jiang et al.[2]
9,10-Phenanthraquinone	25.46 ± 1.00	Jiang et al.[2]
1,2-Naphthoquinone	9.07 ± 0.29	Jiang et al.[2]
1,4-Naphthoquinone	2.92 ± 0.12	Jiang et al.[2]
tert-Butyl hydroperoxide	$1.17\pm0.19\times10^{-2}$	Jiang et al.[3]
Ambient PM		
Ambient PM	$\sim10^{-3}$–10^{-2}	Fang et al.[4]
Ambient PM	$\sim (2–6) \times10^{-2}$	Verma et al.[5]
Primary aerosol		
Accord diesel	$2.3\pm0.2\times10^{-2}$	Cheung et al.[6]
DPF-Accord diesel	$1.9\pm0.2\times10^{-2}$	Cheung et al.[6]
Corolla gasoline	$1.2\pm0.1\times10^{-2}$	Cheung et al.[6]
Golf diesel	$1.8\pm0.3\times10^{-2}$	Cheung et al.[6]
Golf biodiesel	$2.5\pm0.3\times10^{-2}$	Cheung et al.[6]
Wood smoke	$2.5\pm0.1\times10^{-2}$	Jiang et al.[2]
Secondary organic aerosol		
Naphthalene SOA	$11.8\pm1.4\times10^{-2}$	McWhinney et al.[7]
Toluene SOA	$(3.7–8.2) \times10^{-2}$	Jiang et al.[2, 3]
1,3,5-Trimethylbenzene SOA	$(1.4–2.5) \times10^{-2}$	Jiang et al. [2, 3]
Isoprene SOA	$(1.6–5.3) \times10^{-2}$	Jiang et al. [2, 3]
α-Pinene SOA	$(0.9–1.3) \times10^{-2}$	Jiang et al. [2, 3]
Isoprene SOA	$\sim10^{-2}$	Tuet et al.[8]
α-Pinene SOA	$\sim (2–3) \times10^{-2}$	Tuet et al.[8]
β-caryophyllene SOA	$\sim2\times10^{-2}$	Tuet et al. [8]
Pentadecane SOA	$\sim (1.5–2) \times10^{-2}$	Tuet et al. [8]
m-xylene SOA	$\sim (2–4) \times10^{-2}$	Tuet et al. [8]
Naphthalene SOA	~0.1-0.2	Tuet et al. [8]
Isoprene SOA	$2.10\pm0.22\times10^{-3}$	Kramer et al.[1]
Methacrolein SOA	$2.30\pm0.27\times10^{-3}$	Kramer et al. [1]
IEPOX-derived SOA	$1.79\pm0.16\times10^{-3}$	Kramer et al. [1]
MAE-derived SOA	$3.13\pm0.30\times10^{-3}$	Kramer et al. [1]

Table S5. Local selectivity indexes computed for the tested *α,β*-unsaturated carbonyls based on the condensed Fukui function using UCA-FUKUI software.[9]

***α,β*-Unsaturated carbonyl**	**Atom**	**f-**	**f+**	**f0**	**Dual-Descriptor**
Citral	C_{10}	-0.0001	0.2674	0.1336	0.2673
	C_7	0.0000	0.2384	0.1192	0.2383
trans-Cinnamaldehyde	C_3	0.0272	0.1893	0.1082	0.1621
	C_1	-0.018	0.1258	0.0539	0.1078
Mesityl oxide	C_4	0.0077	0.2319	0.1198	0.2242
	C_2	0.1363	0.2248	0.1805	0.0886

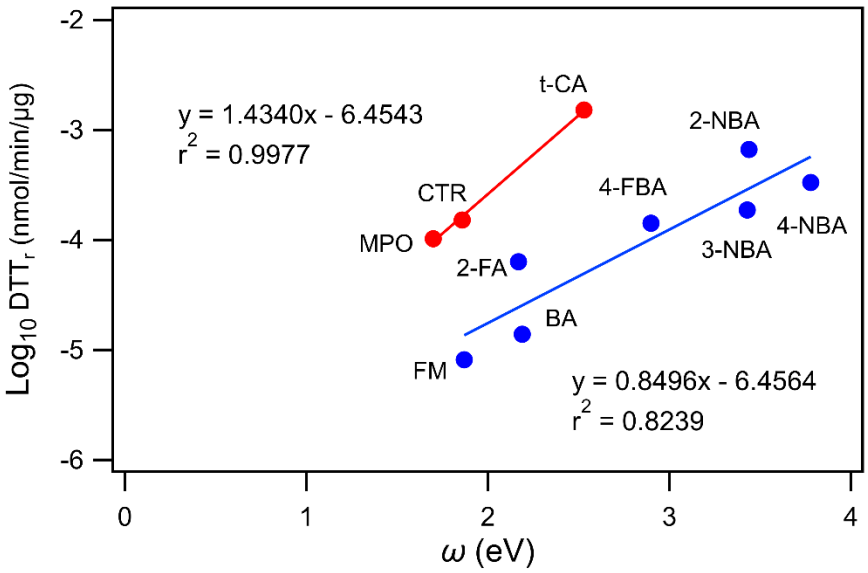


Fig. S1: Comparison between the calculated electrophilicity index in gas phase and the measured Log_{10}(DTT activity) (nmol DTT consumed per reaction incubation minute per µg of sample). The r^2 values of simple (blue) and *α,β*-unsaturated (red) carbonyls are 0.8239 and 0.9977, respectively.

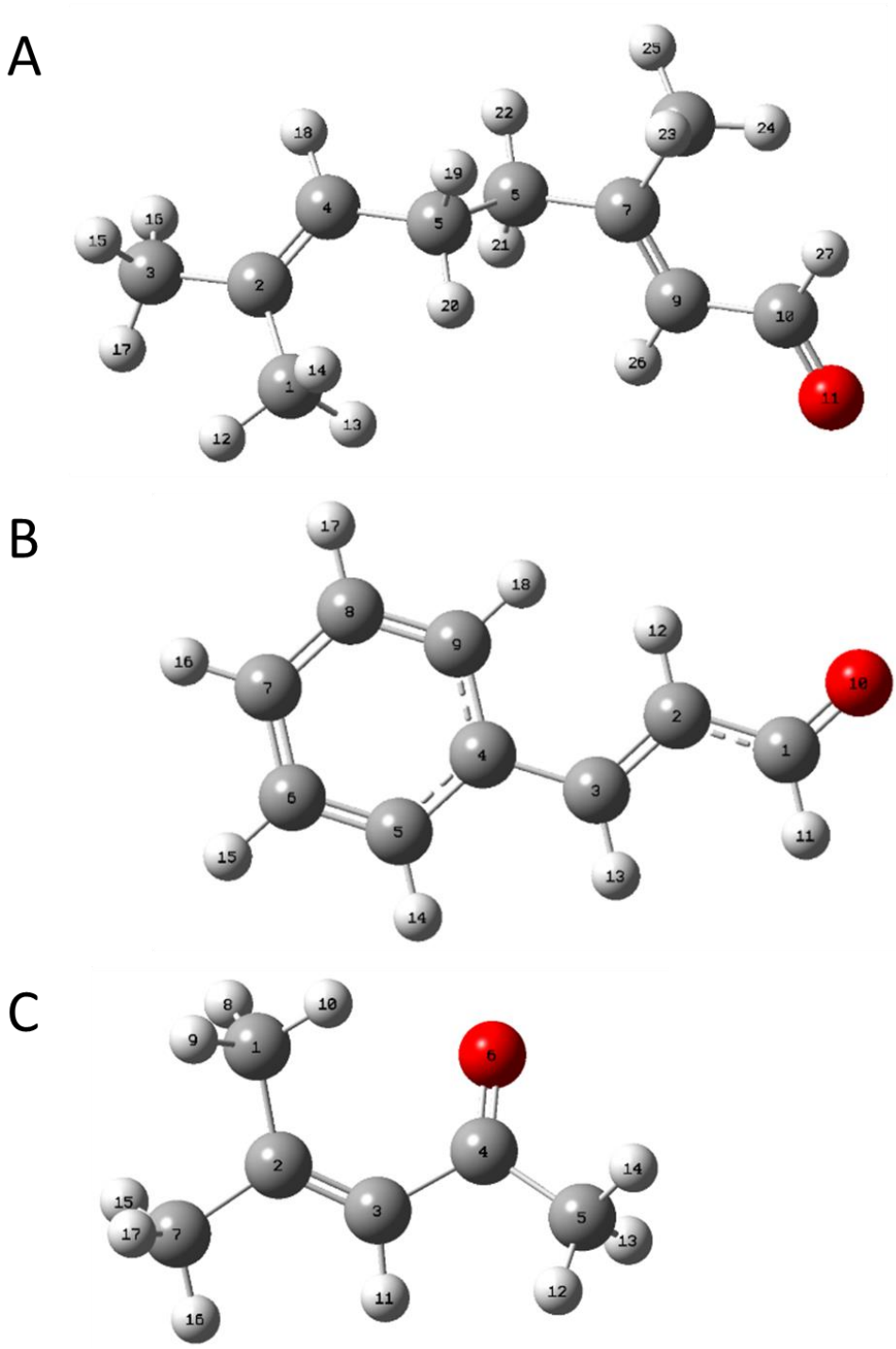


Fig. S2: Molecular geometries showing atom labels for (A) citral, (B) *trans*-cinnamaldehyde and (C) mesityl oxide.

Reference

1. A. Kramer, W. Rattanavaraha, Z. Zhang, A. Gold, J. Surratt and Y. Lin, Assessing the oxidative potential of isoprene-derived epoxides and secondary organic aerosol, *Atmos. Environ.*, 2016, **130**, 211-218.

2. H. Jiang, M. Jang, T. Sabo-Attwood and S. E. Robinson, Oxidative potential of secondary organic aerosols produced from photooxidation of different hydrocarbons using outdoor chamber under ambient sunlight, *Atmos. Environ.*, 2016, **131**, 382-389.

3. H. Jiang, M. Jang and Z. Yu, Dithiothreitol activity by particulate oxidizers of SOA produced from photooxidation of hydrocarbons under varied NO_x levels, *Atmos. Chem. Phys.*, 2017, **17**, 9965-9977.

4. T. Fang, V. Verma, H. Guo, L. E. King, E. S. Edgerton and R. J. Weber, A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE), *Atmos. Meas. Tech.*, 2015, **8**, 471-482.

5. V. Verma, T. Fang, H. Guo, L. King, J. T. Bates, R. E. Peltier, E. Edgerton, A. G. Russell and R. J. Weber, Reactive oxygen species associated with water-soluble $PM_{2.5}$ in the southeastern United States: spatiotemporal trends and source apportionment, *Atmos. Chem. Phys.*, 2014, **14**, 12915-12930.

6. K. L. Cheung, A. Polidori, L. Ntziachristos, T. Tzamkiozis, Z. Samaras, F. R. Cassee, M. Gerlofs and C. Sioutas, Chemical characteristics and oxidative potential of particulate matter emissions from gasoline, diesel, and biodiesel cars, *Environ. Sci. Technol.*, 2009, **43**, 6334-6340.

7. R. D. McWhinney, S. Zhou and J. P. D. Abbatt, Naphthalene SOA: redox activity and naphthoquinone gas–particle partitioning, *Atmos. Chem. Phys.*, 2013, **13**, 9731-9744.

8. W. Y. Tuet, Y. Chen, L. Xu, S. Fok, D. Gao, R. J. Weber and N. L. Ng, Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds, *Atmos. Chem. Phys.*, 2017, **17**, 839-853.

9. J. Sánchez-Márquez, D. Zorrilla, A. Sánchez-Coronilla, M. Desireé, J. Navas, C. Fernández-Lorenzo, R. Alcántara and J. Martín-Calleja, Introducing "UCA-FUKUI" software: reactivity-index calculations, *J. Mol. Model.*, 2014, **20**, 2492.