toxics

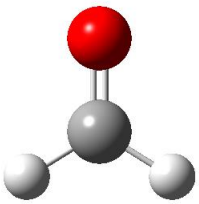
MDPI

# Supplementary Materials: Carbonyl Composition and Electrophilicity in Vaping Emissions of Flavored and Unflavored E-Liquids

Jin Y. Chen, Alexa Canchola, and Ying-Hsuan Lin

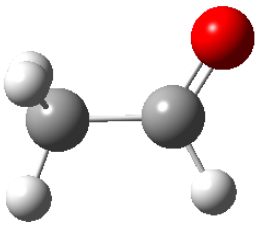
Table S1. Optimized geometries of target carbonyls calculated by DFT/B3LYP/6-311+G(d, p) level of theory and in water solvation using Gaussian 16W program.

| Formaldehyde | | | |
|---|---|---|---|
| Charge = 0 | | | |
| E(UB3LYP) = −114.432708094 Hartree (Eh) | | | |
| Electronic state: 1-A | | | |
| Cartesian Coordinates (Angstroms): | | | |
| O | −0.000041 | 0.676752 | 0.000000 |
| C | −0.000041 | −0.531376 | 0.000000 |
| H | −0.938433 | −1.112848 | 0.000000 |
| H | 0.939008 | −1.112912 | 0.000000 |



| | | | |
|---|---|---|---|
| Charge = −1 | | | |
| E(UB3LYP) = −114.624580950 Hartree (Eh) | | | |
| Electronic state: 1-A | | | |
| Cartesian Coordinates (Angstroms): | | | |
| O | −0.000009 | 0.727861 | 0.000000 |
| C | −0.000009 | −0.584091 | 0.000000 |
| H | −0.936931 | −1.159157 | 0.000000 |
| H | 0.937051 | −1.159186 | 0.000000 |
| Charge = +1 | | | |
| E(UB3LYP) = −114.160019523 Hartree (Eh) | | | |
| Electronic state: 1-A | | | |
| Cartesian Coordinates (Angstroms): | | | |
| O | −0.000105 | 0.663897 | 0.000000 |
| C | −0.000105 | −0.522196 | 0.000000 |
| H | −0.962402 | −1.089947 | 0.000000 |
| H | 0.963872 | −1.088057 | 0.000000 |

| Acetaldehyde | | | |
|---|---|---|---|
| Charge = 0 | | | |
| E(UB3LYP) = −153.354522985 Hartree (Eh) | | | |
| Electronic state: 1-A | | | |
| Cartesian Coordinates (Angstroms): | | | |
| C | 0.000000 | 0.471652 | 0.000000 |
| O | −1.207923 | 0.355997 | 0.000000 |
| C | 0.949642 | −0.693883 | 0.000000 |
| H | 0.452229 | 1.482132 | 0.000000 |
| H | 1.989744 | −0.367922 | 0.000000 |



| | | | |
|---|---|---|---|
| H | 0.761779 | −1.314399 | 0.881325 |
| H | 0.761779 | −1.314399 | −0.881325 |

Charge = −1

E(UB3LYP) = −153.370677836 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | 0.000000 | 0.497419 | 0.000000 |
| O | −1.293321 | 0.239851 | 0.000000 |
| C | 1.016429 | −0.611764 | 0.000000 |
| H | 0.360356 | 1.536615 | 0.000000 |
| H | 2.038719 | −0.214048 | 0.000000 |
| H | 0.924458 | −1.277656 | 0.878966 |
| H | 0.924458 | −1.277656 | −0.878966 |

Charge = +1

E(UB3LYP) = −153.102042126 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | 0.000000 | 0.451208 | 0.000000 |
| O | −1.192126 | 0.398092 | 0.000000 |
| C | 0.949359 | −0.730416 | 0.000000 |
| H | 0.434009 | 1.484123 | 0.000000 |
| H | 1.968672 | −0.358366 | 0.000000 |
| H | 0.719088 | −1.317621 | 0.893620 |
| H | 0.719088 | −1.317621 | −0.893620 |

## Acrolein

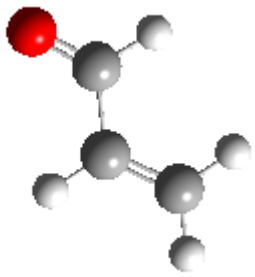
Charge = 0

E(UB3LYP) = −191.183387804 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | −1.214748 | 1.279427 | 0.000000 |
| C | 0.000000 | 0.719262 | 0.000000 |
| C | 0.148409 | −0.739513 | 0.000000 |
| O | 1.219144 | −1.322395 | 0.000000 |
| H | −2.112691 | 0.668793 | 0.000000 |
| H | −1.351926 | 2.354067 | 0.000000 |
| H | 0.910131 | 1.311027 | 0.000000 |
| H | −0.800630 | −1.309782 | 0.000000 |



Charge = −1

E(UB3LYP) = −191.208242254 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | −1.186351 | 1.404274 | 0.000000 |
| C | 0.000000 | 0.667011 | 0.000000 |
| C | 0.114150 | −0.735584 | 0.000000 |
| O | 1.208609 | −1.417489 | 0.000000 |
| H | −2.156618 | 0.915291 | 0.000000 |

| | | | |
|---|---|---|---|
| H | −1.178328 | 2.487565 | 0.000000 |
| H | 0.944178 | 1.215554 | 0.000000 |
| H | −0.844904 | −1.292697 | 0.000000 |

Charge = +1

E(UB3LYP) = −190.930698073 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | −0.923399 | 1.490212 | 0.000000 |
| C | 0.172970 | 0.709976 | 0.000000 |
| C | 0.000000 | −0.719132 | 0.000000 |
| O | 0.885347 | −1.559127 | 0.000000 |
| H | −1.930249 | 1.090204 | 0.000000 |
| H | −0.813474 | 2.568501 | 0.000000 |
| H | 1.188085 | 1.083768 | 0.000000 |
| H | −1.024564 | −1.155795 | 0.000000 |

## Benzaldehyde

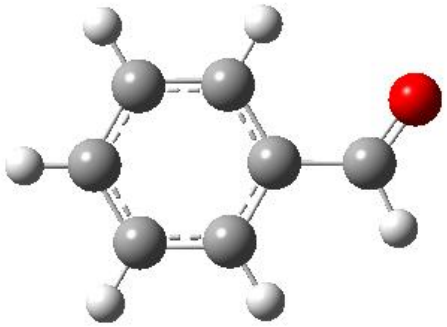
Charge = 0

E(UB3LYP) = −345.676360401 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| O | 2.854181 | −0.391611 | −0.000078 |
| C | 1.986641 | 0.463916 | 0.000076 |
| C | 0.535584 | 0.200982 | 0.000040 |
| C | 0.034053 | −1.109905 | 0.000036 |
| C | −0.349770 | 1.286844 | 0.000010 |
| C | −1.337636 | −1.325852 | 0.000002 |
| C | −1.725199 | 1.067938 | −0.000021 |
| C | −2.217196 | −0.237321 | −0.000027 |
| H | 2.262757 | 1.535775 | −0.000056 |
| H | 0.728135 | −1.941920 | 0.000060 |
| H | 0.042746 | 2.298463 | 0.000017 |
| H | −1.728700 | −2.336551 | 0.000000 |
| H | −2.409849 | 1.907725 | −0.000044 |
| H | −3.287394 | −0.410225 | −0.000052 |



Charge = −1

E(UB3LYP) = −345.763742749 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| O | 2.905663 | −0.399770 | −0.000288 |
| C | 1.972124 | 0.479781 | 0.000285 |
| C | 0.571895 | 0.221027 | 0.000170 |
| C | 0.032434 | −1.108894 | 0.000139 |
| C | −0.377215 | 1.294520 | 0.000046 |
| C | −1.336634 | −1.327406 | 0.000006 |
| C | −1.739152 | 1.059533 | −0.000084 |
| C | −2.249060 | −0.257790 | −0.000107 |
| H | 2.251592 | 1.550684 | −0.000317 |
| H | 0.718860 | −1.948297 | 0.000218 |

| | | | |
|---|---|---|---|
| H | −0.007260 | 2.317049 | 0.000055 |
| H | −1.710758 | −2.347931 | −0.000009 |
| H | −2.426349 | 1.900977 | −0.000163 |
| H | −3.317749 | −0.438952 | −0.000207 |

Charge = +1

E(UB3LYP) = −345.403731647 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| O | 2.820665 | −0.456620 | −0.000006 |
| C | 2.032758 | 0.460995 | 0.000007 |
| C | 0.555395 | 0.250624 | 0.000003 |
| C | 0.029491 | −1.077953 | 0.000004 |
| C | −0.313875 | 1.310038 | 0.000002 |
| C | −1.375061 | −1.320978 | −0.000001 |
| C | −1.725245 | 1.063451 | −0.000007 |
| C | −2.243289 | −0.258955 | 0.000003 |
| H | 2.360204 | 1.513283 | −0.000007 |
| H | 0.725059 | −1.909611 | −0.000001 |
| H | 0.044530 | 2.332454 | 0.000002 |
| H | −1.735073 | −2.341198 | −0.000013 |
| H | −2.406862 | 1.905372 | −0.000010 |
| H | −3.314216 | −0.410675 | 0.000011 |

*trans*-2-Hexenal

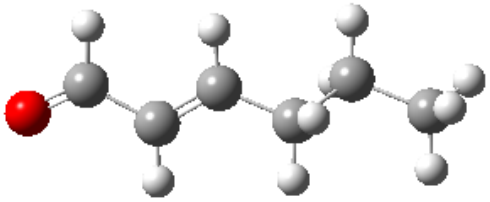
Charge = 0

E(UB3LYP) = −309.958896545 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | −2.638669 | 0.319521 | −0.003206 |
| C | −1.357376 | −0.374257 | 0.034723 |
| C | −0.244343 | 0.262892 | 0.436141 |
| C | 1.123625 | −0.329315 | 0.513109 |
| C | 2.148214 | 0.426447 | −0.358354 |
| C | 3.559730 | −0.152190 | −0.233532 |
| O | −3.695828 | −0.186820 | −0.351412 |
| H | −2.609234 | 1.380353 | 0.313763 |
| H | −1.342381 | −1.416907 | −0.270720 |
| H | −0.330353 | 1.310276 | 0.726660 |
| H | 1.459484 | −0.282706 | 1.557916 |
| H | 1.095248 | −1.385688 | 0.229712 |
| H | 1.823340 | 0.389462 | −1.403455 |
| H | 2.154769 | 1.483431 | −0.070627 |
| H | 4.264537 | 0.396518 | −0.863782 |
| H | 3.919126 | −0.096430 | 0.798560 |
| H | 3.584988 | −1.202335 | −0.540017 |



Charge = −1

E(UB3LYP) = −310.031522249 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | −2.672951 | 0.253138 | −0.140291 |
| C | −1.376611 | −0.190528 | 0.179681 |
| C | −0.218484 | 0.587608 | 0.257114 |
| C | 1.141394 | 0.052921 | 0.604013 |
| C | 2.185152 | 0.156002 | −0.529532 |
| C | 3.574874 | −0.343986 | −0.121547 |
| O | −3.744389 | −0.471509 | −0.209510 |
| H | −2.768165 | 1.337295 | −0.353498 |
| H | −1.280673 | −1.259051 | 0.391294 |
| H | −0.288957 | 1.655873 | 0.049252 |
| H | 1.558396 | 0.580524 | 1.478330 |
| H | 1.054235 | −0.999730 | 0.904042 |
| H | 1.825427 | −0.412510 | −1.395260 |
| H | 2.252955 | 1.201015 | −0.855850 |
| H | 4.290784 | −0.258109 | −0.944386 |
| H | 3.968415 | 0.231434 | 0.723064 |
| H | 3.542453 | −1.395604 | 0.182461 |

Charge = +1

E(UB3LYP) = −309.687393075 Hartree (Eh)

Electronic state: 1-A

Cartesian Coordinates (Angstroms):

| | | | |
|---|---|---|---|
| C | −2.585359 | 0.294347 | 0.004884 |
| C | −1.349933 | −0.406959 | 0.009250 |
| C | −0.239085 | 0.250077 | 0.441860 |
| C | 1.106798 | −0.350496 | 0.499560 |
| C | 2.133001 | 0.453198 | −0.344018 |
| C | 3.536416 | −0.145962 | −0.233474 |
| O | −3.682338 | −0.140600 | −0.344444 |
| H | −2.622612 | 1.354055 | 0.336706 |
| H | −1.347230 | −1.434081 | −0.332454 |
| H | −0.330998 | 1.285572 | 0.762097 |
| H | 1.426822 | −0.312376 | 1.550862 |
| H | 1.086097 | −1.397333 | 0.190107 |
| H | 1.808354 | 0.456420 | −1.388058 |
| H | 2.139440 | 1.493539 | −0.006288 |
| H | 4.241349 | 0.428485 | −0.839553 |
| H | 3.891547 | −0.134177 | 0.800658 |
| H | 3.554909 | −1.180531 | −0.586898 |

Table S2. Condensed Fukui parameters ($f_k^0$, $f_k^-$, $f_k^+$, and dual-descriptor) calculated using NPA data by UCA-Fukui software.

| Atom | NPA neutral | NPA anion | NPA cation | $f_k^-$ | $f_k^+$ | $f_k^0$ | Dual descriptor |
|---|---|---|---|---|---|---|---|
| | | | Formaldehyde | | | | |
| O | −0.5521 | −0.8986 | 0.0149 | 0.5670 | 0.3465 | 0.4568 | −0.2205 |
| C | 0.3153 | −0.2770 | 0.3305 | 0.0152 | 0.5923 | 0.3037 | 0.5771 |
| H | 0.1184 | 0.0878 | 0.3272 | 0.2088 | 0.0306 | 0.1197 | −0.1782 |
| H | 0.1184 | 0.0878 | 0.3274 | 0.2090 | 0.0306 | 0.1198 | −0.1785 |
| | | | Acetaldehyde | | | | |
| C | 0.4636 | −0.0180 | 0.4809 | 0.0172 | 0.4817 | 0.2494 | 0.4644 |
| O | −0.5898 | −0.9263 | −0.0454 | 0.5445 | 0.3365 | 0.4405 | −0.2080 |
| C | −0.6949 | −0.6606 | −0.6248 | 0.0702 | −0.0343 | 0.0179 | −0.0358 |
| H | 0.1196 | 0.0842 | 0.3307 | 0.2110 | 0.0354 | 0.1232 | −0.1756 |
| H | 0.2206 | 0.1893 | 0.2707 | 0.0501 | 0.0313 | 0.0407 | −0.0188 |
| H | 0.2405 | 0.1657 | 0.2940 | 0.0535 | 0.0747 | 0.0641 | 0.0212 |
| H | 0.2405 | 0.1657 | 0.2940 | 0.0535 | 0.0747 | 0.0641 | 0.0212 |
| | | | Acrolein | | | | |
| C | −0.2567 | −0.5583 | −0.0798 | 0.1769 | 0.3016 | 0.2392 | 0.1246 |
| C | −0.3109 | −0.3792 | −0.3171 | −0.0063 | 0.0684 | 0.031 | 0.0621 |
| C | 0.4033 | 0.1652 | 0.3788 | −0.0245 | 0.238 | 0.1068 | 0.2136 |
| O | −0.5864 | −0.8367 | −0.036 | 0.5504 | 0.2503 | 0.4003 | −0.3001 |
| H | 0.1989 | 0.169 | 0.2262 | 0.0272 | 0.0299 | 0.0286 | 0.0027 |
| H | 0.2086 | 0.1774 | 0.2371 | 0.0285 | 0.0313 | 0.0299 | 0.0028 |
| H | 0.2198 | 0.1766 | 0.2731 | 0.0534 | 0.0432 | 0.0483 | −0.0102 |
| H | 0.1233 | 0.0859 | 0.3177 | 0.1944 | 0.0374 | 0.1159 | −0.157 |
| | | | Benzaldehyde | | | | |
| O | −0.5885 | −0.8144 | −0.5189 | 0.0696 | 0.2260 | 0.1564 | −0.3404 |
| C | 0.4320 | 0.1894 | 0.4330 | 0.0010 | 0.2426 | 0.2416 | 0.1945 |
| C | −0.1804 | −0.1998 | −0.1452 | 0.0352 | 0.0194 | −0.0157 | 0.0129 |
| C | −0.1554 | −0.2622 | 0.1126 | 0.2681 | 0.1067 | −0.1614 | 0.0780 |
| C | −0.1572 | −0.2296 | −0.0936 | 0.0636 | 0.0724 | 0.0088 | 0.0173 |
| C | −0.2082 | −0.2243 | −0.1296 | 0.0786 | 0.0161 | −0.0625 | −0.0080 |
| C | −0.2122 | −0.2422 | 0.0807 | 0.2928 | 0.0300 | −0.2628 | 0.0203 |
| C | −0.1686 | −0.3120 | −0.1507 | 0.0179 | 0.1435 | 0.1256 | 0.0809 |
| H | 0.1267 | 0.0942 | 0.1546 | 0.0279 | 0.0325 | 0.0046 | −0.1421 |
| H | 0.2266 | 0.2038 | 0.2483 | 0.0217 | 0.0229 | 0.0012 | 0.0085 |
| H | 0.2217 | 0.1970 | 0.2554 | 0.0337 | 0.0247 | −0.0090 | 0.0042 |
| H | 0.2212 | 0.1993 | 0.2543 | 0.0331 | 0.0219 | −0.0112 | 0.0016 |
| H | 0.2219 | 0.2005 | 0.2437 | 0.0218 | 0.0215 | −0.0003 | 0.0024 |
| H | 0.2203 | 0.2004 | 0.2554 | 0.0352 | 0.0199 | −0.0153 | 0.0082 |
| | | | *trans*-2-Hexenal | | | | |
| C | 0.4029 | 0.1602 | 0.3721 | −0.0307 | 0.2426 | 0.1059 | 0.2119 |
| C | −0.3295 | −0.3857 | −0.3162 | 0.0133 | 0.0563 | 0.0348 | 0.0430 |
| C | −0.0420 | −0.3039 | 0.0912 | 0.1332 | 0.2619 | 0.1976 | 0.1287 |
| C | −0.4341 | −0.4094 | −0.4456 | −0.0116 | −0.0247 | 0.0181 | 0.0131 |
| C | −0.3755 | −0.3794 | −0.3722 | 0.0034 | 0.0039 | 0.0036 | 0.0005 |
| C | −0.5761 | −0.5803 | −0.5745 | 0.0016 | 0.0042 | 0.0029 | 0.0026 |
| O | −0.6050 | −0.8196 | −0.0606 | 0.5443 | 0.2146 | 0.3795 | −0.3298 |
| H | 0.1202 | 0.0676 | 0.3094 | 0.1892 | 0.0526 | 0.1209 | −0.1366 |
| H | 0.2142 | 0.1757 | 0.2647 | 0.0505 | 0.0385 | 0.0445 | −0.0120 |
| H | 0.2012 | 0.1615 | 0.2244 | 0.0233 | 0.0397 | 0.0315 | 0.0164 |
| H | 0.2236 | 0.1781 | 0.2559 | 0.0323 | 0.0455 | 0.0389 | 0.0132 |
| H | 0.2087 | 0.1871 | 0.2253 | 0.0166 | 0.0216 | 0.0191 | 0.0050 |
| H | 0.1961 | 0.1842 | 0.2054 | 0.0093 | 0.0120 | 0.0106 | 0.0027 |
| H | 0.1961 | 0.1847 | 0.2049 | 0.0088 | 0.0114 | 0.0101 | 0.0026 |
| H | 0.2048 | 0.1964 | 0.2127 | 0.0078 | 0.0084 | 0.0081 | 0.0006 |
| H | 0.1971 | 0.1914 | 0.2013 | 0.0042 | 0.0057 | 0.0050 | 0.0015 |
| H | 0.1973 | 0.1915 | 0.2018 | 0.0044 | 0.0058 | 0.0051 | 0.0014 |

Table S3. Condensed Fukui function, $f_k^-$, of carbonyl compounds calculated using UCA-FUKUI software.

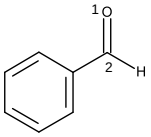
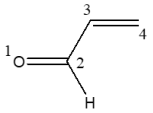
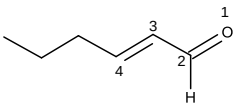
| | | $f_k^-$ (for electrophilic attack) | | | |
|---|---|---|---|---|---|
| **compound** | **structure** | **$O_{carbonyl}$[1]** | **$C_{carbonyl}$[2]** | **$C_\alpha$[3]** | **$C_\beta$[4]** |
| simple carbonyl | | | | | |
| formaldehyde |  | 0.567 | 0.0152 | n/a | n/a |
| acetaldehyde |  | 0.5445 | 0.0172 | n/a | n/a |
| benzaldehyde |  | 0.0696 | 0.0010 | n/a | n/a |
| α,β-unsaturated carbonyl | | | | | |
| acrolein |  | 0.5504 | −0.0245 | −0.0063 | 0.1769 |
| *trans*-2-hexenal |  | 0.5443 | −0.0307 | 0.0133 | 0.1332 |

Table S4. Condensed Fukui function, $f_k^0$, of carbonyl compounds calculated using UCA-FUKUI software.

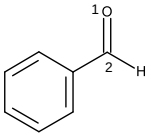
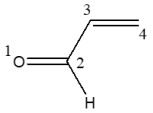
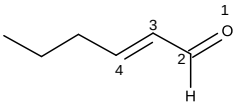
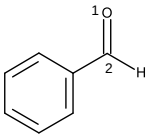
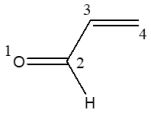
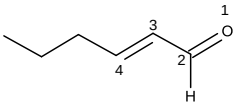
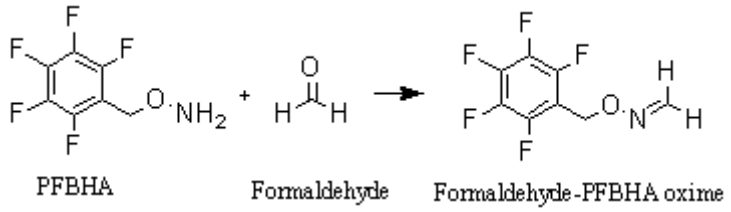
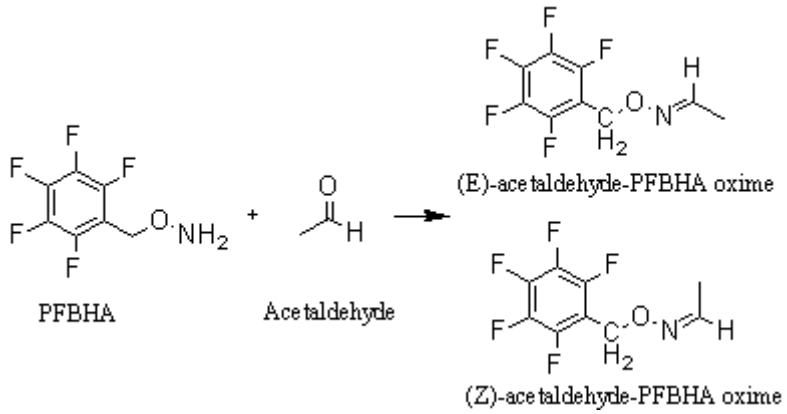
| | | $f_k^0$ (for neutral/radical attack) | | | |
|---|---|---|---|---|---|
| **compound** | **structure** | **$O_{carbonyl}$[1]** | **$C_{carbonyl}$[2]** | **$C_\alpha$[3]** | **$C_\beta$[4]** |
| simple carbonyl | | | | | |
| formaldehyde |  | 0.4568 | 0.3037 | n/a | n/a |
| acetaldehyde |  | 0.4405 | 0.2494 | n/a | n/a |
| benzaldehyde |  | 0.1564 | 0.2416 | n/a | n/a |
| α,β-unsaturated carbonyl | | | | | |
| acrolein |  | 0.4003 | 0.1068 | 0.031 | 0.2392 |
| *trans*-2-hexenal |  | 0.3795 | 0.1059 | 0.0348 | 0.1976 |

Table S5. Condensed Fukui function, dual-descriptor, of carbonyl compounds calculated using UCA-FUKUI software.

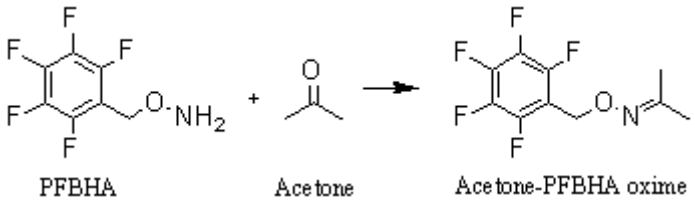
| | | dual-descriptor | | | |
|---|---|---|---|---|---|
| **compound** | **structure** | **$O_{carbonyl}$[1]** | **$C_{carbonyl}$[2]** | **$C_{\alpha}$[3]** | **$C_{\beta}$[4]** |
| simple carbonyl | | | | | |
| formaldehyde |  | −0.2205 | 0.5771 | n/a | n/a |
| acetaldehyde |  | −0.2080 | 0.4644 | n/a | n/a |
| benzaldehyde |  | −0.3403 | 0.1945 | n/a | n/a |
| α,β-unsaturated carbonyl | | | | | |
| acrolein |  | −0.3001 | 0.2136 | 0.0621 | 0.1246 |
| *trans*-2-hexenal |  | −0.3298 | 0.2119 | 0.0430 | 0.1287 |



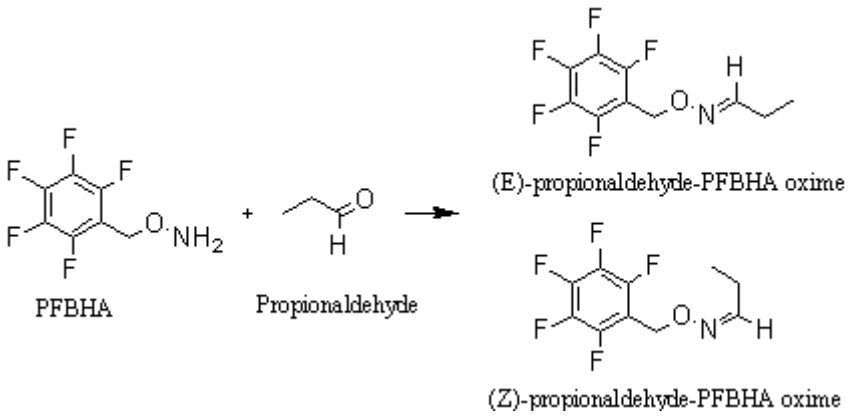

(A) Formaldehyde



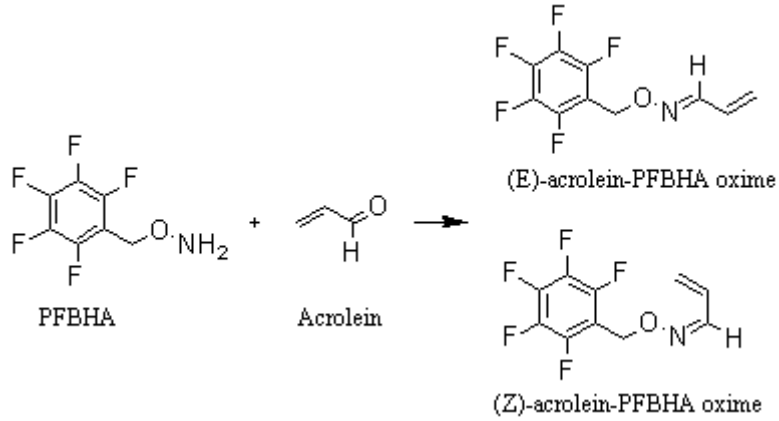

(B) Acetaldehyde



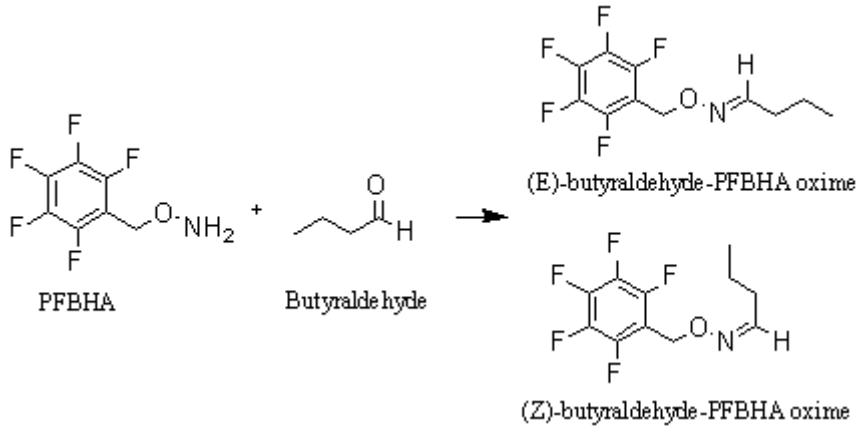

(C) Acetone



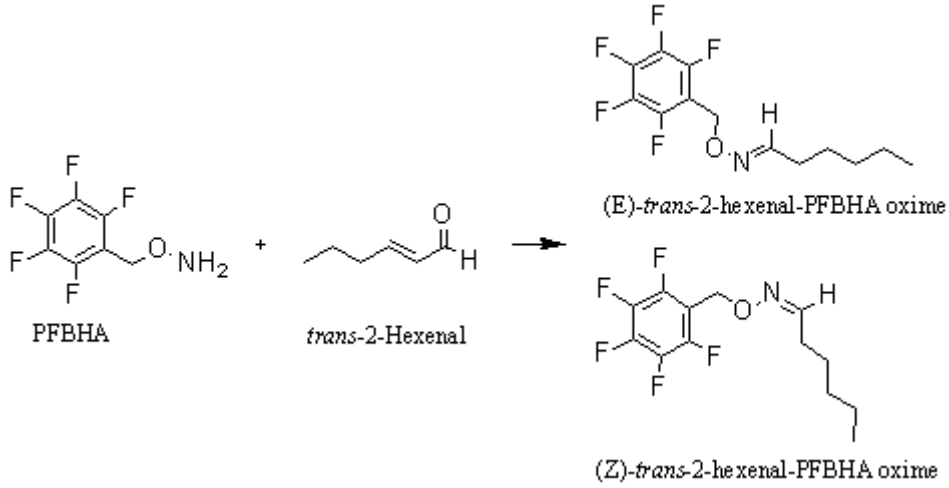

(D) Propionaldehyde



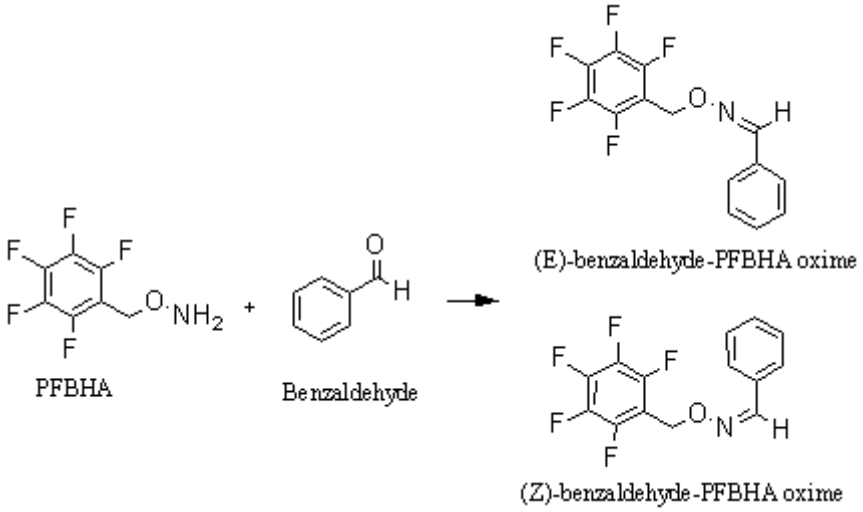

(E) Acrolein



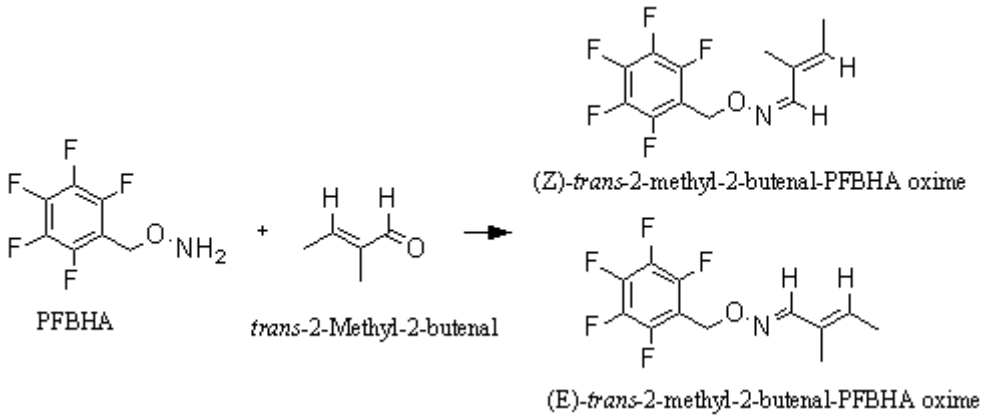

(F) Butyraldehyde



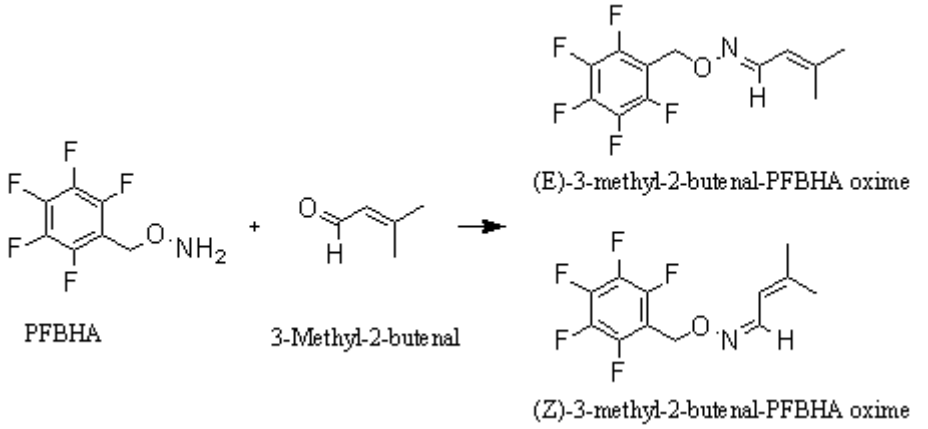

(G) *trans*-2-Hexenal



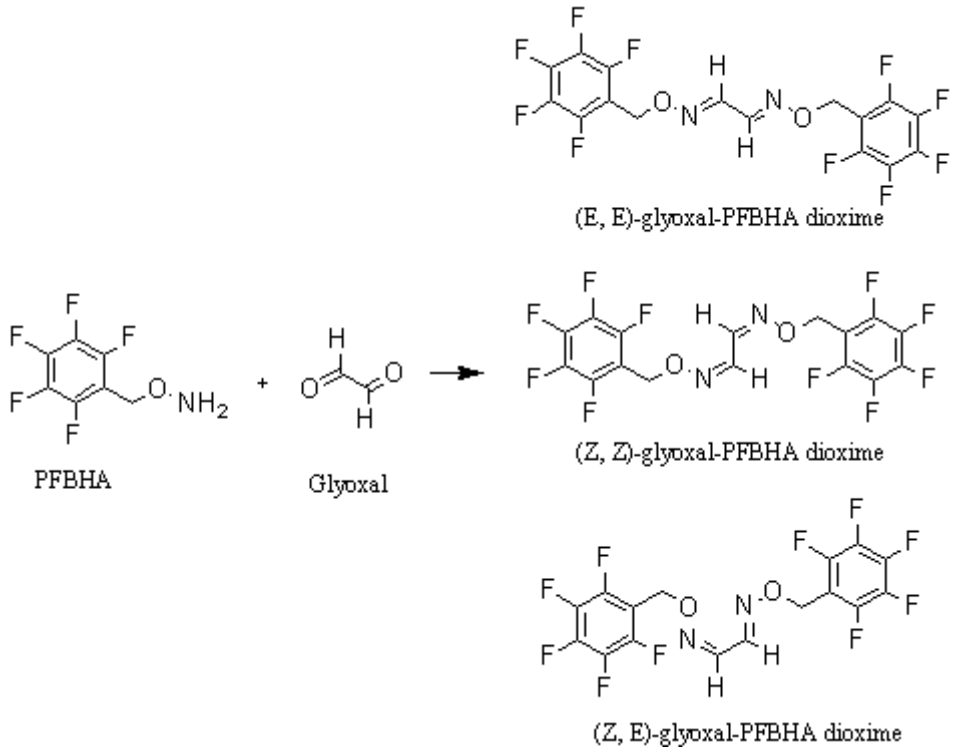

(H) Benzaldehyde



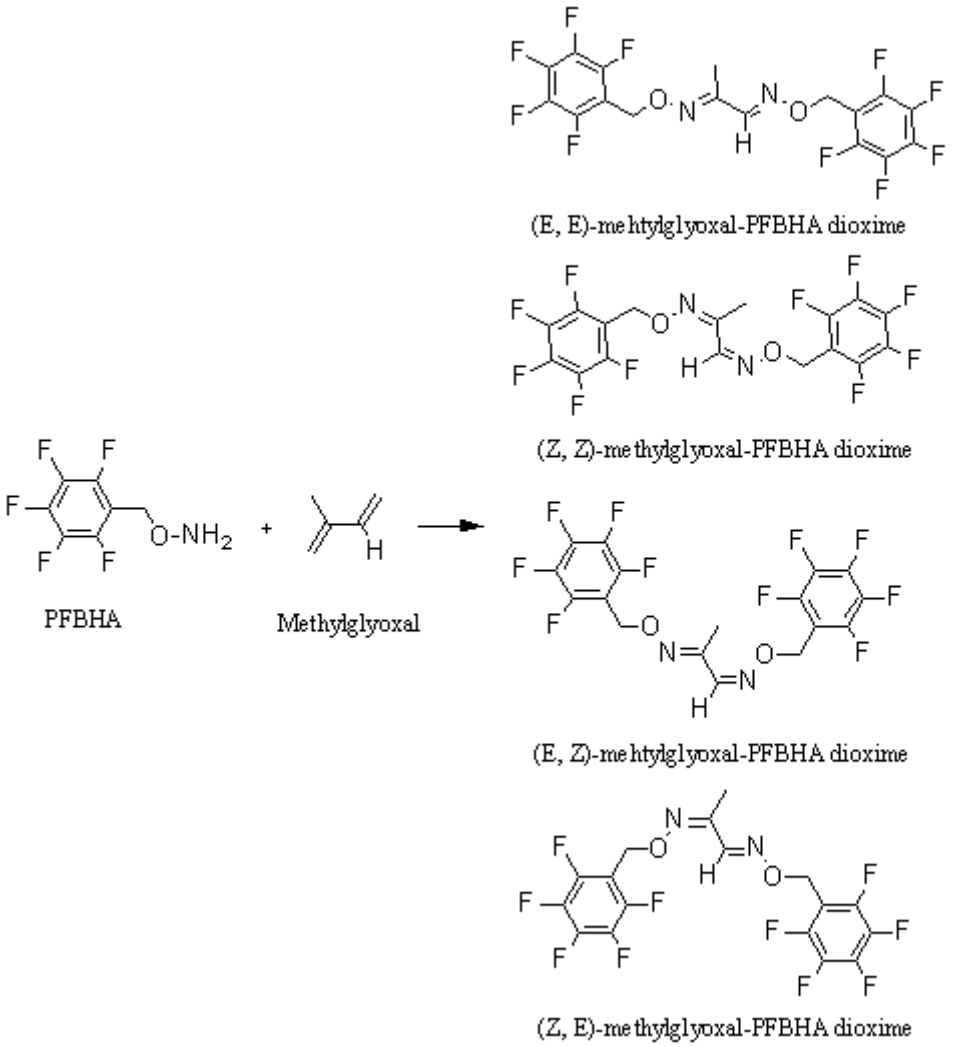

(I) *trans*-2-Methyl-2-butenal



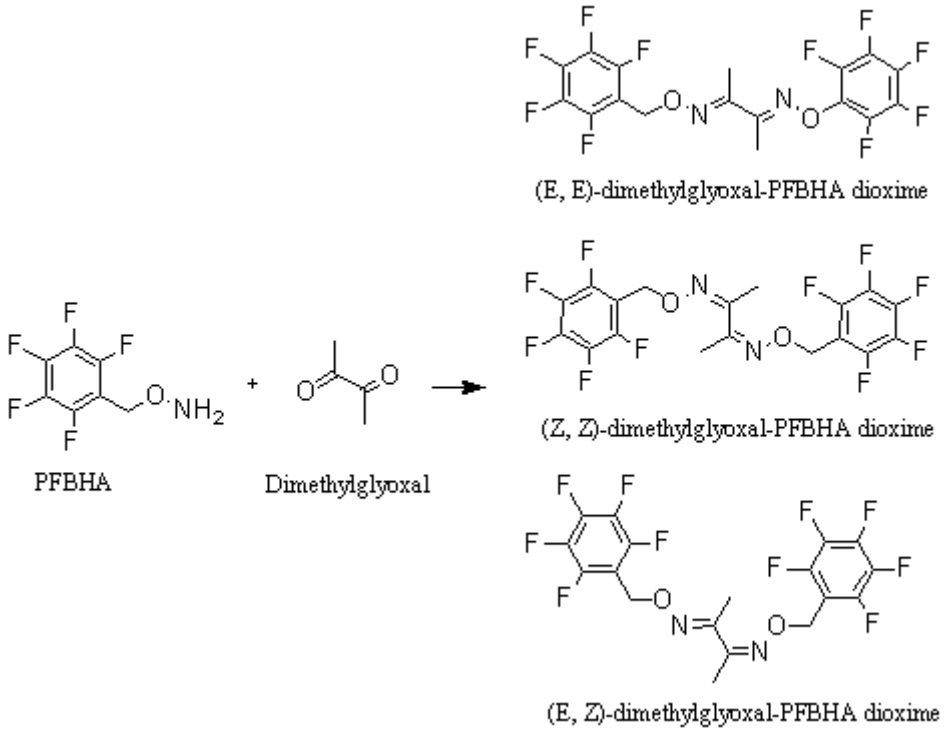

(J) 3-Methyl-2-butenal



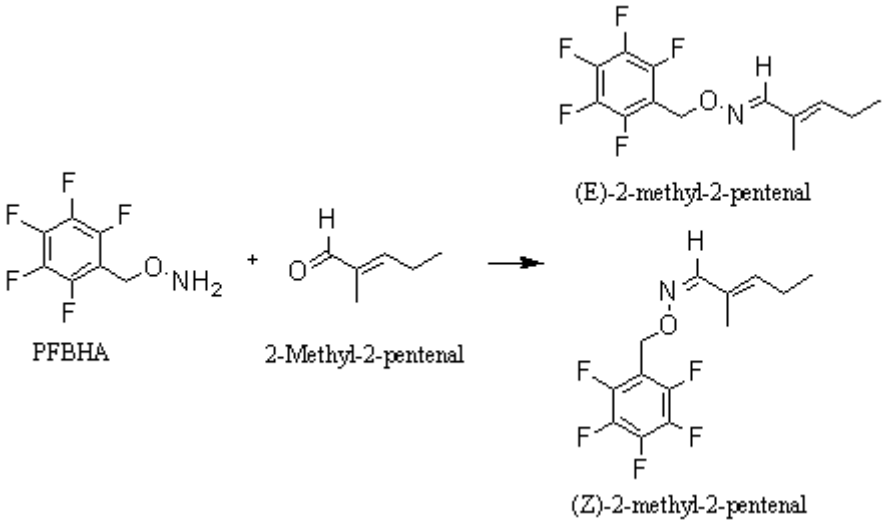

(K) Glyoxal




(L) Methylglyoxal




(M) Dimethylglyoxal




(N) 2-methyl-2-pentenal

**Scheme S1.** Derivatization between carbonyls (identified in Table 1) and PFBHA, and their oxime derivatives for **(A)** formaldehyde, **(B)** acetaldehyde, **(C)** acetone, **(D)** propionaldehyde, **(E)** acrolein, **(F)** butyraldehyde, **(G)** *trans*-2-hexenal, **(H)** benzaldehyde, **(I)** *trans*-2-methyl-2-butenal, **(J)** 3-methyl-2-butenal, **(K)** glyoxal, **(L)** methylglyoxal, **(M)** dimethyglyoxal, and **(N)** 2-methyl-2-pentenal.

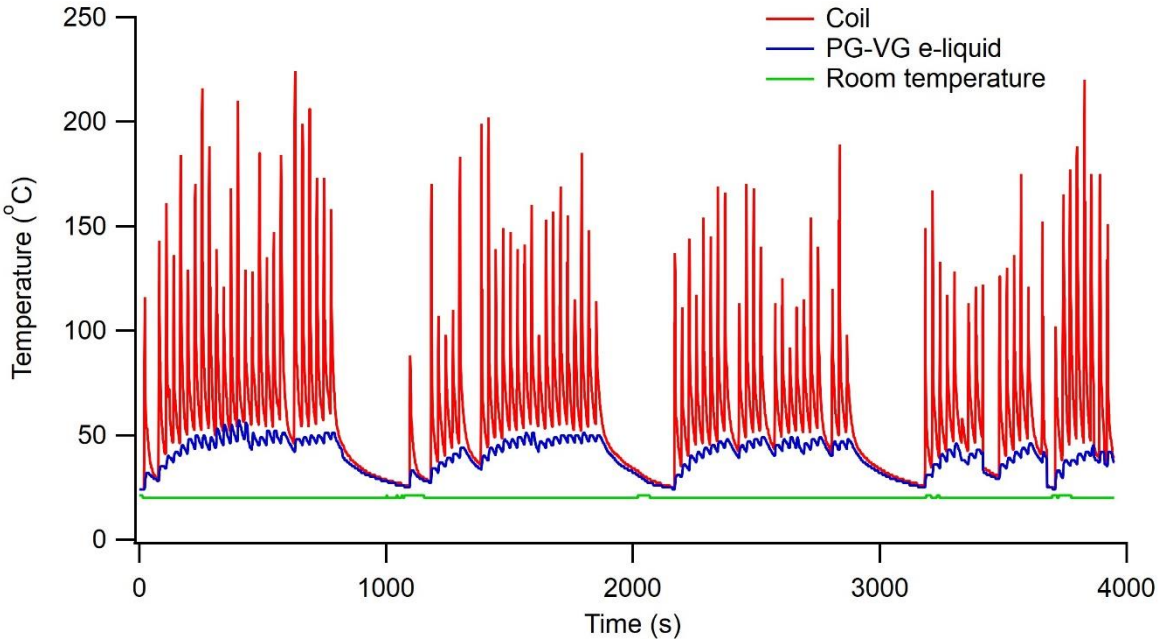



**Figure S1.** Temperature profile of the coil (red), PG-VG e-liquid (blue), and room temperature (green) measured by K-type thermocouple wires.