# Supplementary information

# Comparative time-based intermediates study of ozone oxidation of 4-chloro- and 4-nitrophenols followed by LCMS-TOF

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**Fig. 1S:** Mass spectrum of single hydroxylation intermediate (C6H5ClO2) of 4CP for pH 3 at 10 min



**Fig. 2S:** Mass spectrum of single hydroxylation intermediate (C6H5ClO2) of 4CP for pH 7 at 10 min



**Fig. 3S:** Mass spectrum of single hydroxylation intermediate (C6H5ClO2) of 4CP for pH 10 at 10 min



**Fig. 4S:** Mass spectrum for the identified isomer of single hydroxylation intermediate (C6H5ClO2) of 4CP for pH 10 at 40 min



**Fig. 5S:** Mass spectrum for the intermediate C6H5ClO4 (3-chloro-trans, trans-muconic acid) of 4CP for pH 3 at 20 min



**Fig. 6S:** Mass spectrum for the intermediate C6H4O4 (2,6-dihydroxybenzoquinone) of 4CP for pH 7 at 10 min



**Fig. 7S:** Mass spectrum for the intermediate C6H6O2 (hydroquinone) of 4CP for pH 10 at 30 min



**Fig. 8S:** Mass spectrum for the intermediate C6H6O2 (catechol) of 4CP for pH 10 at 20 min



**Fig. 9S:** Mass spectrum for the intermediate C12H8Cl2O2 (5,5’-dichloro-2,2’biphenyldiol) of 4CP for pH 10 at 10 min



**Fig. 10S:** Mass spectrum for the intermediate C12H8Cl2O3 of 4CP for pH 10 at 10 min

 **Fig. 11S:** Mass spectrum for the intermediate C12H8Cl2O4 of 4CP for pH 10 at 30 min



**Fig. 12S:** Mass spectrum for the intermediate C12H9ClO3 of 4CP for pH 10 at 30 min



**Fig. 13S:** Mass spectrum for the intermediate C12H7ClO4 of 4CP for pH 10 at 10 min



**Fig. 14S:** Mass spectrum for the intermediate C12H9ClO7 of 4CP for pH 3 at 30 min





**Fig. 15S:** Mass spectrum for the intermediate C5H3ClO5 of 4CP for pH 7 (top) and pH 10 (bottom) at 40 min

 **Fig. 16S:** Mass spectrum for the intermediate C5H4O4 of 4CP for pH 7 pH 10 at 30 min

 **Fig. 17S:** Mass spectrum for the intermediate C5H6O4 of 4CP for pH 3 at 30 min

 **Fig. 18S:** Mass spectrum for the intermediate C5H4O3 of 4CP for pH 3 at 10 min (top) and pH 7 at 40 min



**Fig. 19S:** Mass spectrum for the intermediate C4H3ClO of 4CP for pH 3 at 10 min

 **Fig. 20S:** Mass spectrum for the intermediate C4H3ClO of 4CP for pH 7 at 40 min

**Table 1S**: Intermediates of 4-chlorophenol ozonation at different pH identified from EIC/TIC chromatogram and mass spectra

| **Time**  **(min)** | **Acidic pH (3)** | | | **Dissolution pH (7)** | | | **Alkaline pH (10)** | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Formula | Mass | Retention time (min) | Formula | Mass | Retention time (min) | Formula | Mass | Retention time (min) |
| 0 min | C6H5ClO | 128.0036 | 23.306 | C6H5ClO | 128.0038 | 23.366 | C6H5ClO | 128.3200 | 23.235 |
| 10 min | C4H3ClO | 101.9872 | 17.696 | - | - | - | - | - | - |
| C5H4O3 | 112.0158 | 9.579 | - | - | - | - | - | - |
| C6H4O4 | 140.0108 | 13.472 | C6H4O4 | 140.0112 | 13.634 | - | - | - |
| C6H5ClO | 128.003 | 23.500 | C6H5ClO | 128.0032 | 23.263 | C6H5ClO | 128.0030 | 22.107 |
| C6H5ClO2 | 143.9985 | 19.986 | C6H5ClO2 | 143.9982 | 19.860 | C6H5ClO2 | 144.0021 | 20.107 |
| - | - | - | - | - | - | \*C6H5ClO2 | 143.998 | 18.939 |
| C12H8Cl2O2 | 253.9807 | 29.208 | C12H8Cl2O2 | 253.9838 | 28.827 | C12H8Cl2O2 | 253.9838 | 27.050 |
| \*C12H8Cl2O2 | 253.9908 | 23.456 | \*C12H8Cl2O2 | 253.9906 | 23.232 | \*C12H8Cl2O2 | 253.9908 | 22.791 |
| \*C12H8Cl2O2 | 253.9908 | 31.769 | - | - | - | \*C12H8Cl2O2 | 253.9904 | 29.605 |
| C12H8Cl2O3 | 269.9854 | 28.579 | - | - | - | C12H8Cl2O3 | 269.9856 | 25.309 |
| \*C12H8Cl2O3 | 269.9853 | 24.620 | - | - | - | \*C12H8Cl2O3 | 269.9855 | 23.889 |
| \*C12H8Cl2O3 | 269.9856 | 27.270 | - | - | - | - | - | - |
| - | - | - | C12H7ClO4 | 250.0036 | 27.529 | - | - | - |
| 20 min | C4H3ClO | 101.9874 | 17.990 | - | - | - | - | - | - |
| C6H4O4 | 140.0101 | 14.210 | C6H4O4 | 140.0109 | 13.993 | - | - | - |
| C6H5ClO | 128.0040 | 23.139 | C6H5ClO | 128.0034 | 23.377 | C6H5ClO | 128.0041 | 22.608 |
| \*C6H5ClO | 128.0028 | 15.511 | - | - | - | \*C6H5ClO | 128.0028 | 16.829 |
| C6H5ClO2 | 144.0008 | 20.035 | C6H5ClO2 | 143.9994 | 20.095 | C6H5ClO2 | 143.9979 | 19.050 |
| \*C6H5ClO2 | 143.9979 | 17.692 | \*C6H5ClO2 | 143.9980 | 17.725 | \*C6H5ClO2 | 143.9979 | 17.003 |
| C6H5ClO4 | 175.9871 | 17.148 | - | - | - | - | - | - |
| C12H8Cl2O2 | 253.9897 | 28.265 | C12H8Cl2O2 | 253.9909 | 28.865 | C12H8Cl2O2 | 253.9910 | 26.861 |
| \*C12H8Cl2O2 | 253.9906 | 23.089 | \*C12H8Cl2O2 | 253.9906 | 23.364 | \*C12H8Cl2O2 | 253.9908 | 22.601 |
| \*C12H8Cl2O2 | 253.9907 | 31.355 | - | - | - | \*C12H8Cl2O2 | 253.9903 | 29.109 |
| C12H8Cl2O3 | 269.9856 | 26.291 | - | - | - | C12H8Cl2O3 | 269.9857 | 25.131 |
| \*C12H8Cl2O3 | 269.9848 | 23.220 | - | - | - | \*C12H8Cl2O3 | 269.9856 | 23.71 |
| C12H9ClO3 | 236.0239 | 21.233 | - | - | - | C12H9ClO3 | 236.0240 | 20.865 |
| - | - | - | - | - | - | \*C12H9ClO3 | 236.0237 | 21.463 |
| - | - | - | - | - | - | \*C12H9ClO3 | 236.0234 | 21.911 |
| - | - | - | - | - | - | C12H8Cl2O4 | 285.9797 | 27.643 |
| - | - | - | C12H7ClO4 | 250.0036 | 27.572 | - | - | - |
| 30 min | C4H3ClO | 101.9874 | 18.364 | - | - | - | - | - | - |
| C5H4O3 | 112.0155 | 11.012 | - | - | - | - | - | - |
| C5H4O4 | 128.0110 | 8.797 | - | - | - | C5H4O4 | 128.0110 | 8.825 |
| \*C5H4O4 | 128.0104 | 7.968 | - | - | - | \*C5H4O4 | 128.0110 | 8.073 |
| C5H6O4 | 130.0252 | 7.541 | - | - | - | - | - | - |
| \*C5H6O4 | 130.262 | 6.382 | - | - | - | - | - | - |
| C6H4O4 | 140.0101 | 14.384 | C6H4O4 | 140.0112 | 13.951 | C6H4O4 | 140.0112 | 13.790 |
| C6H4O4 | 140.0107 | 12.478 | \*C6H4O4 | 140.0114 | 6.990 | \*C6H4O4 | 140.0110 | 6.830 |
| C6H5ClO | 128.0034 | 23.621 | C6H5ClO | 128.0030 | 23.393 | C6H5ClO | 128.0030 | 23.186 |
| C6H5ClO  (Isomer in EIC) | 128.0029 | 15.670 | \*C6H5ClO | 128.0030 | 15.407 | C6H5ClO (Isomer in EIC) | 128.0030 | 15.407 |
| C6H5ClO2 | 143.9983 | 20.569 | C6H5ClO2 | 143.9986 | 20.103 | C6H5ClO2 | 143.9998 | 20.032 |
| C6H5ClO4 | 175.9873 | 17.420 | - | - | - | - | - | - |
| C12H8Cl2O2 | 253.9911 | 27.313 | C12H8Cl2O2 | 253.9908 | 28.859 | C12H8Cl2O2 | 253.9906 | 28.566 |
| C12H9ClO3 | 236.0242 | 21.8390 | - | - | - | - | - | - |
| C12H8Cl2O3 | 269.9855 | 25.829 | C12H8Cl2O3 | 269.9851 | 26.325 | C12H8Cl2O3 | 269.0238 | 26.586 |
| C12H9Cl2O7 | 300.0040 | 16.480 | - | - | - | - | - | - |
| - | - | - | - | - | - | C12H8Cl2O4 | 285.9802 | 29.397 |
| 40 min | C4H3ClO | 101.9874 | 17.773 | C4H3ClO | 101.9875 | 17.754 | - | - | - |
| - | - | - | C5H3ClO5 | 177.9670 | 7.365 | C5H3ClO5 | 177.9671 | 7.853 |
| C5H4O4 | 128.0112 | 8.460 | C5H4O4 | 128.112 | 8.681 | C5H4O4 | 128.0110 | 9.025 |
| C5H4O3 | 112.0155 | 10.278 | C5H4O3 | 112.0160 | 10.874 | - | - | - |
| C6H4O4 | 140.0101 | 13.746 | C6H4O4 | 140.0111 | 14.074 | C6H4O4 | 140.0110 | 14.638 |
| C6H4O4 | 140.0109 | 6.467 |  |  |  |  |  |  |
| C6H5ClO  (Isomer in EIC) | 128.0026 | 15.326 | \*C6H5ClO | 128.0030 | 15.425 | C6H5ClO (Isomer in EIC) | 128.0030 | 15.829 |
| C6H5ClO | 128.0033 | 23.289 | C6H5ClO | 128.0033 | 23.271 | \*C6H5ClO (Main compound but no longer seen in EIC) | 128.0030 | 23.055 |
| C6H5ClO2 | 143.9982 | 19.989 | C6H5ClO2 | 143.9986 | 19.916 | C6H5ClO2 (Main product) | 143.9987 | 19.757 |
| \*C6H5ClO2 | 143.9979 | 17.597 | \*C6H5ClO2 | 143.9980 | 17.506 | C6H5ClO2 (Isomer) | 143.9982 | 17.33 |
| C6H5ClO4 | 175.9843 | 17.012 | - | - | - | - | - | - |
| C12H8Cl2O3 | 269.9781 | 26.682 | C12H8Cl2O3 | 269.9854 | 26.772 | C12H8Cl2O3 | 269.9856 | 26.205 |
| - | - | - | - | - | - | C12H8Cl2O4 | 285.9802 | 28.719 |
| C12H9ClO3 | 236.0241 | 21.371 | C12H9ClO3 | 236.0240 | 21.282 | - | - | - |
| C12H8Cl2O2 | 253.9908 | 28.697 | C12H8Cl2O2 | 253.9981 | 28.836 | - | - | - |

Intermediates/compounds in asterisk (\*) were only found in the qualitative analysis workflow data. They were included in the table for discourse purpose.



**Fig. 21S:** Mass spectrum for the intermediate C6H4N2O5 of 4NP for pH 10 at 20 min

 **Fig. 22S:** Mass spectrum for the intermediate C6H5NO5 of 4NP for pH 10 at 30 min



**Fig. 23S:** Mass spectrum for the intermediate C6H5O3 of 4NP for pH 10 at 30 min

**Table 2S:** Intermediates of 4-nitrophenol ozonation at different pH identified from EIC/TIC chromatogram and mass spectra

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Time**  **(min)** | **Acidic pH (3)** | | | **Dissolution pH (7)** | | | **Alkaline pH (10)** | | |
| Formula | Mass | Retention time (min) | Formula | Mass | Retention time (min) | Formula | Mass | Retention time (min) |
| 0 min | C6H5NO3 | 139.0274 | 20.758 | C6H5NO3 | 139.0268 | 20.846 | C6H5NO3 | 139.0273 | 20.669 |
| 10 min | C6H5NO3 | 139.0274 | 20.782 | C6H5NO3 | 139.0267 | 20.796 | C6H5NO3 | 139.0274 | 20.863 |
| C6H5NO4 | 155.0226 | 17.953 | C6H5NO4 | 155.0217 | 17.972 | C6H5NO4 | 155.0180 | 18.0102 |
| 20 min |  |  |  |  |  |  | C3H5NO5 | 135.0170 | 7.468 |
|  |  |  |  |  |  | \*C6H6O2 | 110.0363 | 14.310 |
| C6H5NO3 | 139.0273 | 20.900 | C6H5NO3 | 139.0270 | 20.829 | C6H5NO3 | 139.0274 | 20.818 |
| C6H5NO4 | 155.0227 | 17.936 | C6H5NO4 | 155.0213 | 17.952 | C6H5NO4 | 155.0222 | 17.550 |
|  |  |  | \*C6H5NO4 | 155.0219 | 15.950 | \*C6H5NO4 | 155.0219 | 14.894 |
|  |  |  |  |  |  | C6H4N2O5 | 184.0127 | 22.817 |
| 30 min |  |  |  | C4H6O3 | 102.0307 | 6.743 | C4H6O3 | 102.0318 | 7.711 |
|  |  |  |  |  |  | C6H5O3 | 125.0239 | 17.852 |
| C6H5NO3 | 139.0274 | 21.0880 | C6H5NO3 | 139.0270 | 20.829 | C6H5NO3 | 139.0274 | 20.818 |
|  |  |  |  |  |  | \*C6H5NO3 | 139.0273 | 18.120 |
| C6H5NO4 | 155.0226 | 17.929 | C6H5NO4 | 155.0213 | 17.952 | C6H5NO4 | 155.0222 | 17.852 |
|  |  |  | \*C6H5NO4 | 155.0219 | 15.950 | \*C6H5NO4 | 155.0218 | 14.625 |
|  |  |  |  |  |  | C6H5NO5 | 171.0172 | 14.470 |
|  |  |  |  |  |  | C6H4N2O5 | 184.0128 | 22.975 |
| 40 min |  |  |  |  |  |  | C4H6O3 | 102.0314 | 7.239 |
|  |  |  | C4H3N4O6 | 203.0043 | 6.714 |  |  |  |
|  |  |  |  |  |  | C6H5O3 | 125.0239 | 19.036 |
| C6H5NO3 | 139.0275 | 20.802 | C6H5NO3 | 139.0268 | 20.867 | C6H5NO3 | 139.0273 | 21.421 |
|  |  |  |  |  |  | \*C6H5NO3 | 139.0273 | 19.207 |
| C6H5NO4 | 155.0226 | 17.912 | C6H5NO4 | 155.0215 | 17.955 | C6H5NO4 | 155.0223 | 19.035 |
|  |  |  |  |  |  | C6H5NO5 | 171.0172 | 16.288 |
|  |  |  |  |  |  | \*C6H5NO5 | 171.172 | 17.713 |
|  |  |  |  |  |  | C6H4N2O5 | 184.0127 | 23.057 |
|  |  |  |  |  |  | \*C6H4N2O5 | 184.0128 | 20.607 |

Intermediates/compounds in asterisk (\*) were only found in the qualitative analysis workflow data. They were included in the table for discourse purpose

**Fig. 24S:** LCMS-TOF calibration curve for 4CP

**Fig. 25S:** LCMS-TOF calibration curve for 4NP