Supplemental Information: Formation of Highly Oxygenated Low-Volatility Products from Cresol Oxidation

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S1 Further Details on CF_3O^- CIMS Analysis

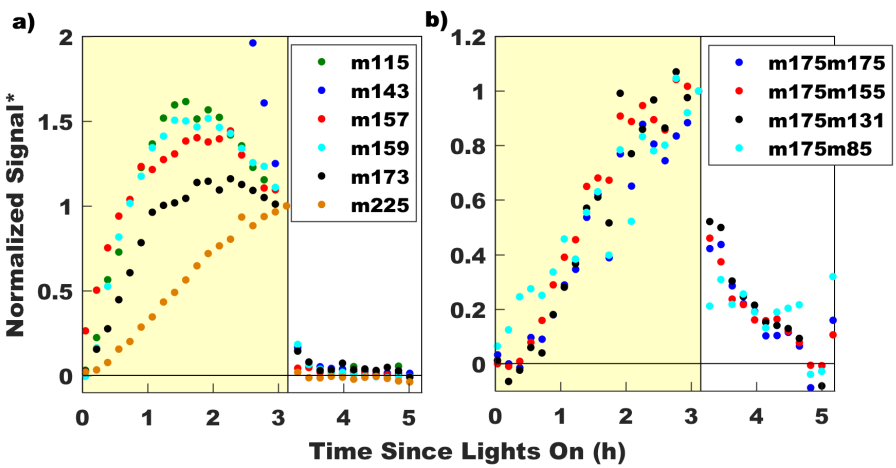


Figure S1. CIMS MS signals of 3-methyl catechol oxidation products (panel a) and MS/MS signals of tetrahydroxy toluene (panel b) for experiment 10. Desorption of compounds from instrument walls was measured by sampling photooxidation products generated in the chamber (yellow) and then immediately switching to purified air (white).*CIMS signal is normalized to time right before lights off.

Table S1: Estimated CIMS sensitivity factors

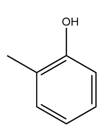
Compound	Structure	Polarizability ($\mathring{A}^3$) [a]	Dipole Moment (D) [b]	Sensitivity Factor [c]	Notes
Toluene Related Compounds					
o-Cresol		11.8	1.42	1	

Table S1: Estimated CIMS sensitivity factors

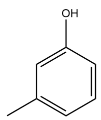
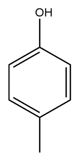
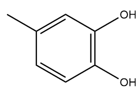
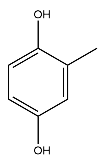
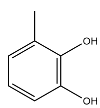
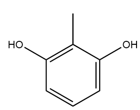
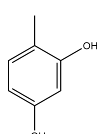
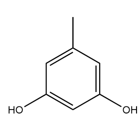
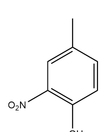
Compound	Structure	Polarizability (Å^3) [a]	Dipole Moment (D) [b]	Sensitivity Factor [c]	Notes
m-Cresol		13.1	1.53	1.07	
p-Cresol		13	1.53	1.06	
4-Methylcatechol		13.7	2.7	1.44	
Methyl hydroquinone		13.7	2.05	1.21	Assume same polarizability as 4-methyl catechol
3-Methylcatechol		13.7	2.42	1.34	Assume same polarizability as 4-methyl catechol
2-Methyl resorcinol		13.7	2	1.19	Assume same polarizability as 4-methyl catechol
4-Methyl resorcinol		13.7	1.81	1.13	Assume same polarizability as 4-methyl catechol
5-Methyl resorcinol		13.7	2.1	1.23	Assume same polarizability as 4-methyl catechol
4-Methyl-2-nitrophenol		16.2	3.49	1.69	

Table S1: Estimated CIMS sensitivity factors

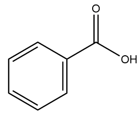
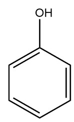
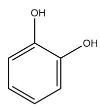
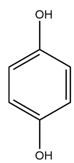
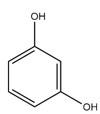
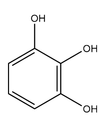
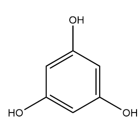
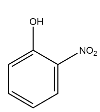
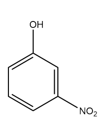
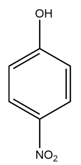
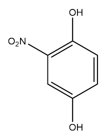
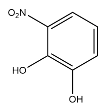
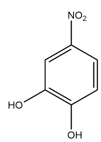
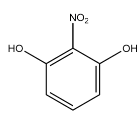
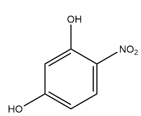
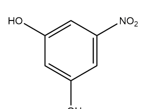
Compound	Structure	Polarizability ($\mathring{A}^3$) [a]	Dipole Moment (D) [b]	Sensitivity Factor [c]	Notes
Benzoic acid		11.3	1.26	0.92	
		Benzene Related Compounds			
Phenol		11.1	1.54	1	
Catechol		13.1	2.64	1.37	
Hydroquinone		13.1	1.78	1.08	Assume polarizability same as catechol.
Resorcinol		13.1	2.04	1.16	Assume polarizability same as catechol.
1,2,3-Benzene triol		11.1	3.17	1.47	
1,3,5-Trihydroxy benzene		11.1	2.7	1.32	Assume polarizability same as 1,2,3-benzene triol
o-Nitrophenol		14	3.12	1.48	
m-Nitrophenol		14	3.89	1.73	Assume polarizability same as *o*-nitrophenol

Table S1: Estimated CIMS sensitivity factors

Compound	Structure	Polarizability ($\AA^3$) [a]	Dipole Moment (D) [b]	Sensitivity Factor [c]	Notes
p-Nitrophenol		14	4.9	2.06	Assume polarizability same as *o*-nitrophenol
Nitrohydroquinone		14	3.5	1.60	Assume polarizability same as *o*-nitrophenol
3-Nitrocatechol		16.5	2.1	1.16	Assume polarity increases by same factor as phenol to catechol
4-Nitrocatechol		16.5	4.95	2.07	Assume polarity increases by same factor as phenol to catechol
2-Nitroresorcinol		16.5	2.18	1.19	Assume polarity increases by same factor as phenol to catechol
4-Nitroresorcinol		16.5	4.44	1.91	Assume polarity increases by same factor as phenol to catechol
5-nitroresorcinol		16.5	3.9	1.74	Assume polarity increases by same factor as phenol to catechol

[a] Polarizability was estimated using the refractive index of each compound reported in Lide (2001) as done by Dewar and Stewart (1984). [b] The reported dipole moment is the average of all values reported in McClellan (1974) for experiments using benzene as a solvent and taken between 20-30 °C. [c] The sensitivity factor equals the ion-molecule collision rate of the compound divided by the ion-molecule collision rate of *o*-cresol for toluene related compounds or phenol for benzene related compounds.

As done by Dewar and Stewart (1984), polarizability was estimated using the refractive index reported in (Lide, 2001) and the formula: $\bar{P} = (3/4\pi N)(M/d)[(n^2-1)/(n^2+2)] * 10^{24}$ where $\bar{P}$ is the average polarizability, n is the refractive index, N

Table S2. Water curve correction and sensitivity factors applied to each compound of interest

Compound	Water Curve Correction	Compound on which Sensitivity Factor is Based [a]
Cresol	*o*-cresol	Weighted *o*-,*m*-, and *p*-cresol [b]
Dihydroxy toluene	3-methyl catechol	3-methyl catechol
Trihydroxy toluene	3-methyl catechol	1,2,3 benzene triol
Tetrahydroxy toluene	3-methyl catechol	1,2,3 benzene triol
Hydroxy methyl benzoquinone	*o*-cresol	*o*-cresol
Dihydroxy methyl benzoquinone	3-methyl catechol	3-methyl catechol
Methyl nitrophenol	o-cresol	4-methyl-2-nitrophenol
Dihydroxy nitrotoluene	3-methyl catechol	3-nitrocatechol
Benzoic acid	*o*-cresol	benzoic acid
Peroxy benzoic acid	*o*-cresol	benzoic acid
Phenyl hydroperoxide	*o*-cresol	benzoic acid
Nitrosophenol	*o*-cresol	*o*-nitrophenol
Nitrophenol	*o*-cresol	*o*-nitrophenol
Dinitrophenol	*o*-cresol	*o*-nitrophenol

[a] The sensitivity factors are listed in Table S1. [b] The photooxidation isomer distribution reported by Klotz et al. (1998) was used to create a generalized cresol sensitivity factor.

is Avogadro's number, M is the molecular weight, and d is the density. The dipole moments measured in benzene and reported by McClellan (1974) were used to estimate the CIMS sensitivity. Dipole moments measured in air would be more accurate than those measured in benzene. However, very few dipole moments measured in air are available for the aromatic compounds of interest. For phenol, the CIMS sensitivity decreases by 7% when using the dipole moment measured in air (Pedersen et al., 1969) versus benzene (McClellan, 1974).

As noted in Table S1 when refractive index was unavailable, the polarizability for the closest related compound was used. The ion-molecule collision rate for each compound was estimated using the polarizabilities and dipole moments reported in Table S1 and the technique described in Su and Chesnavich (1982). The sensitivity is expected to be proportional to the ion-molecule collision rate. The sensitivity factor reported in Table S1 is the ratio of the ion-molecule collision rate for the compound to that of *o*-cresol for toluene related compounds and phenol for benzene related compounds.

As stated in the main text, the *o*-cresol or 3-methyl catechol water curve was used to determine the sensitivity of a compound with a correction for the ion-molecule collision rate. In Table S2, the water curve correction and the sensitivity factor used for each compound is reported. In some cases, as specified in Table S2 the polarizability and dipole moments were not available for toluene related compounds, so the benzene counterpart was used instead. Note that depending on the fraction of isomers of dihydroxy toluene that form from *o*-cresol oxidation, dihydroxy toluene may be underestimated. 3-methyl catechol has the highest sensitivity of all the isomers that could form from *o*-cresol oxidation (3-methyl catechol, 2-methyl resorcinol, 4-

methyl resorcionol, and methyl hydroquinone). Similarly, depending on the exact isomer distribution that forms from dihydroxy toluene oxidation, trihydroxy toluene may be underestimated. 1,3,5-trihydroxy benzene has a lower sensitivity factor (1.32) compared to that for 1,2,3 benzene triol (1.47). Polarizability and dipole moment measurements are not available for hydroxy methyl benzoquinone or dihydroxy methyl benzoquinone. Thus, we assume that hydroxy methyl benzoquinone behaves like *o*-cresol and dihydroxy methyl benzoquinone behaves like 3-methyl catechol.

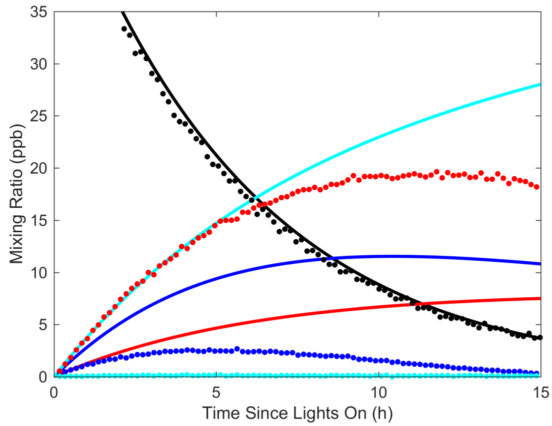


Figure S2. CIMS measurements (data points) compared to predictions from version 1 of kinetic model (lines) for benzaldehyde low-NO oxidation (experiment 10) for the following compounds benzaldehyde (black), peroxybenzoic acid (blue), benzoic acid (red), and phenyl hydroperoxide (cyan).

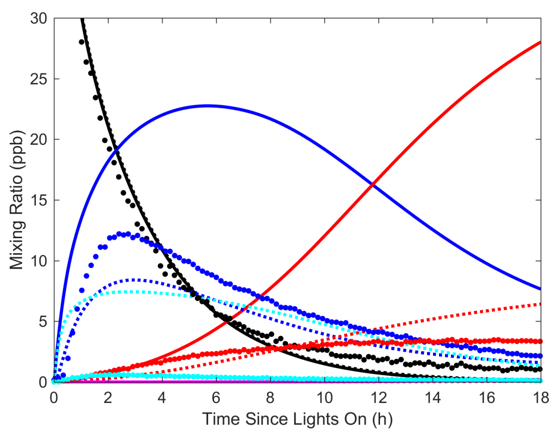


Figure S3. CIMS measurements (data points) compared to predictions from the kinetic model (solid lines version 1 and dotted lines version 3) for benzaldehyde oxidation under high-NO conditions (experiment 11) for the following compounds benzaldehyde (black), nitrophenol (blue), nitrosophenol (cyan), dinitrophenol (red), and maleic anhydride (magenta).

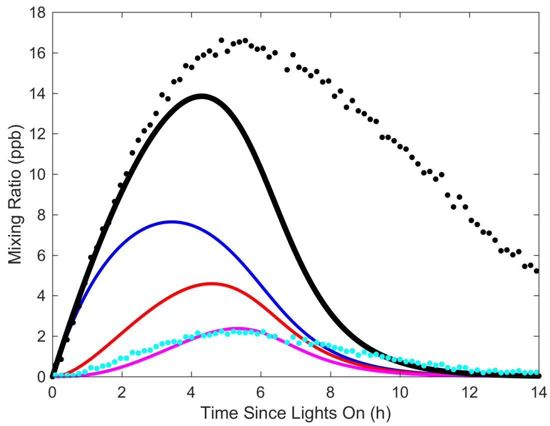


Figure S4. CIMS measurements (data points) compared to predictions from version 3 of the kinetic model (lines) for 3-methyl catechol oxidation under low-NO conditions for bicyclic intermediate products from all precursors (black), 3-methyl catechol (blue), trihydroxy toluene (red), tetrahydroxy toluene (magenta), and trihydroxy toluene or tetrahydroxy toluene tracers (cyan).

CIMS measurements and kinetic model results for products from low-NO oxidation of benzaldehyde are displayed in Figure S2. Benzoic acid is under-predicted by the kinetic model suggesting it is formed in a higher yield from RO_2 + RO_2 reactions, RO_2 + HO_2 reactions, or both. The low yield measured by the CIMS of peroxybenzoic acid, a product from only RO_2 + HO_2 reaction, could be caused by a variety of factors. For example, if the RO_2 + RO_2 reaction rate constant used in MCM v3.3.1 is too low, more RO_2 + HO_2 reactions would occur in the kinetic model producing an over-prediction of peroxybenzoic acid. Another possibility is that the branching ratio for the RO_2 + HO_2 reaction favors formation of benzoic acid more so than recommended by MCM v3.3.1. Because benzoic acid is a product from both RO_2 + RO_2 and RO_2 + HO_2 reactions further constraint is not possible.

Nitrosophernol is detected from benzaldehyde oxidation under high NO conditions (Figure S3). Previous studies have detected a product ($C_6H_5O(NO)$) from the reaction of phenoxy with NO (Tao and Li, 1999). The exact isomer that forms has not been experimentally confirmed. Based on theory, nitrosophenol is the most stable isomer (Yu et al., 1995). Two kinetic studies (Berho et al., 1998; Yu et al., 1995) proposed that phenyl nitrite is the dominant isomer given that nitrosophenol, which requires rearrangement, would not form at the timescales of their studies. $C_6H_5O(NO)$ was detected at the fluorine transfer at m/z (-) 142, implying that it is acidic like nitrosophenol. Possibly, nitrosophenol is over-predicted by version 3 of the kinetic model (Figure S3) because two isomers (nitrosophenol and phenyl nitrite) form and the CIMS is only sensitive to nitrosophenol. The reaction rate constant for C_6H_5O + NO measured by Berho et al. (1998) (1.65 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}) is used in the revised mechanism. The reaction of C_6H_5O + NO has been shown to be reversible, but not at temperatures relevant to this study (Berho et al., 1998; Yu et al., 1995).

m/z (-) 183, assumed to be a fragment of dinitrophenol, is possibly also maleic anhydride (cluster). Maleic anhydride is a decomposition product from dinitrophenol in MCM v3.3.1. However, the predicted amount of maleic anhydride formed in the kinetic mechanism (version 1 and 3) is ∼0.2 ppb after 18 hours of oxidation (Figure S3). Additionally, all nitro products detected by the CIMS have a corresponding fragment at the the F^- transfer minus 20 (hydroxy nitrotoluene, dihydroxy nitrotoluene, and nitrophenol). Thus, the m/z (-) 183 signal is attributed to dinitrophenol.

S2 Further Details on Kinetic Model

The initial conditions specified in Table 1 of the main text were used as input in the kinetic model. The kinetic model was run with 3 different versions. Version 1, the base case of the kinetic model, included reactions from MCM v3.3.1 for toluene and inorganic gas-phase chemistry and experimentally derived wall loss rates of *o*-cresol and 3-methyl catechol. Version 2 includes all reactions in Version 1 and photolysis of hydroxy nitrotoluene and dihydroxy nitrotoluene. Version 3 includes all reactions in Version 2 and oxidation products for 3-methyl catechol and benzaldehyde. The reactions and rate constants are listed in Table S3 and abbreviations are defined in Table S4. These reactions were included to test the chemistry proposed in the main text. Exact branching ratios and reaction rates for these reactions are unknown. Estimates based on known reactions of similar compounds were used.

Hydrogen abstraction from the hydroxy group of 3-methyl catechol, OH3TOL, and OH4TOL is assumed to form an intermediate that then reacts with NO_2 to from a nitro compound. Under low-NO conditions, there is no loss process for this intermediate in the kinetic model or MCM v3.1.1. In experiments 1 and 2, after all injections were complete, lights on was delayed for 2.5 h to estimate the wall loss of *o*-cresol. Wall loss of all other compounds is explained in section 4.2.1 in the main text.

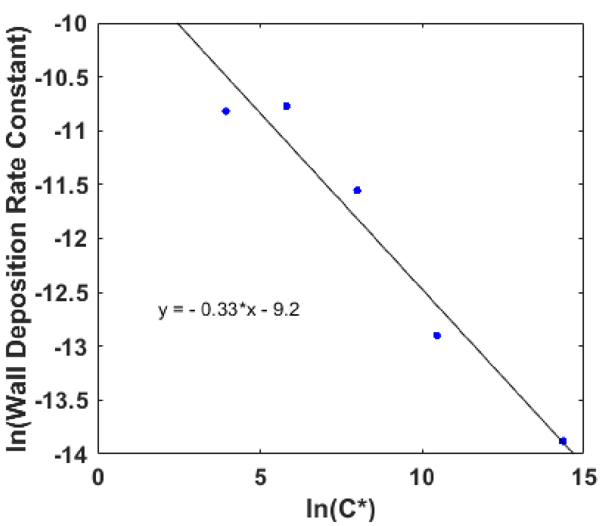


Figure S5. Linear fit to natural log of wall deposition rate constant versus natural log of C* used to estimate wall deposition of compounds that cannot be directly measured.

Table S3: Reactions and reaction rate constants added to chemistry in MCM v3.3.1 to test proposed chemistry.

New Reaction	New Reaction Rate [a]	Assumptions
	Version 1 – All reactions in MCM v 3.3.1 and those listed below.	
CRESOL → wall	9.4 x 10^{-7} s^{-1}	Measured in this study
MCATECHOL → wall	2.5 x 10^{-6} s^{-1}	Measured in this study
	Version 2 – All reactions in Version 1 and those listed below.	
TOL1OHNO2 + hv → products	1.73 x 10^{-4} s^{-1}	Assume similar to
MNCATECH + hv → products	1.73 x 10^{-4} s^{-1}	6-methyl-2-nitrophenol (Bejan et al., 2007)
	Version 3 – All reactions in Version 2 and those listed below.	
CRESOL + OH → BCRESOL	4.65 x 10^{-11} * 0.2 * 0.65	Assume missing products from
		Olariu et al. (2002) from bicyclic pathway.
MCATECHOL + OH → MCATEC1O	2.0 x 10^{-10} * 0.07	Assume same as *o*-cresol
MCATECHOL + OH → OHMBQN	2.0 x 10^{-10} * 0.07	oxidation from MCM v3.3.1
MCATECHOL + OH → OH3TOL	2.0 x 10^{-10} * 0.73	and (Olariu et al., 2002)
MCATECHOL + OH → BMCATECHOL	2.0 x 10^{-10} * 0.13	
OH3TOL + OH → OH3TOL1O	2.5 x 10^{-10} * 0.07	Assume same as *o*-cresol oxidation
OH3TOL + OH → OH2MBQN	2.5 x 10^{-10} * 0.07	from MCM v3.3.1 and (Olariu et al., 2002, 2000).
OH3TOL + OH → OH4TOL	2.5 x 10^{-10} * 0.73	Increased reaction rate constant due to additional
OH3TOL + OH → BOH3TOL	2.5 x 10^{-10} * 0.13	OH group to hard sphere collision rate limit.
OH4TOL + OH → OH4TOL1O	2.5 x 10^{-10} * 0.07	Assume same as o-cresol oxidation
OH4TOL + OH → OH3MBQN	2.5 x 10^{-10} * 0.07	from MCM v3.3.1 and Olariu et al. (2002, 2000).
OH4TOL + OH → OH5TOL	2.5 x 10^{-10} * 0.73	Increased reaction rate constant due to additional
OH4TOL + OH → BOH4TOL	2.5 x 10^{-10} * 0.13	OH group to hard sphere collision rate limit.
BCRESOL + OH → products	5.44 x 10^{-11}	Assume same as
BMCATECHOL + OH → products	5.44 x 10^{-11}	C5CO14OH from MCM v 3.3.1
BOH3TOL + OH → products	5.44 x 10^{-11}	
BOH4TOL + OH → products	5.44 x 10^{-11}	
OHMBQN + OH → products	2.3 x 10^{-11}	Assume same as
OH2MBQN + OH → products	2.3 x 10^{-11}	PTLQONE from MCM v 3.3.1
OH3TOL1O + NO_2 → products	2.08 x 10^{-12}	Assume same as
OH4TOL1O + NO_2 → products	2.08 x 10^{-12}	MCATEC1O from MCM v3.3.1
HOC6H4NO2 + *hv* → products	6.13 x 10^{-5} s^{-1}	Based on 2-nitrophenol measured

Table S3: Reactions and reaction rate constants added to chemistry in MCM v3.3.1 to test proposed chemistry.

New Reaction	New Reaction Rate [a]	Assumptions
		by Bardini (2006) reported by Chen et al. (2011)
C6H5O + NO → C6H5O(NO)	1.65×10^{-12}	Berho et al. (1998)
C6H5O(NO) + OH → products	9.0×10^{-13}	Assume same as
C6H5O(NO) + NO_3 → products	9.0×10^{-14}	HOC6H4NO2 from MCM v3.3.1
OH3TOL → wall	2.1×10^{-5} s^{-1}	Measured in this study
OH4TOL → wall	7.9×10^{-5} s^{-1}	Estimated in this study
OH5TOL → wall	5.0×10^{-4} s^{-1}	Estimated in this study
OHMBQN → wall	9.6×10^{-6} s^{-1}	Measured in this study
OH2MBQN → wall	2.0×10^{-5} s^{-1}	Measured in this study
OH3MBQN → wall	1.2×10^{-4} s^{-1}	Estimated in this study

[a] Reaction rate units are cm^3 $molec^{-1}$ s^{-1} unless otherwise noted.

Table S4. Abbreviations used in Table S3

Abbreviation	Description
BCRESOL	Tracer for products from the bicyclic intermediate pathway from cresol oxidation.
BMCATECHOL	Tracer for products from the bicyclic intermediate pathway from methyl catechol.
BOH3TOL	Tracer for products from the bicyclic intermediate pathway from trihydroxy toluene.
BOH4TOL	Tracer for products from the bicyclic intermediate pathway from tetrahydroxy toluene.
C5CO14OH	Acetyl acrylic acid (one of the bicyclic intermediate pathway products from o-cresol oxidation in MCM).
CRESOL	Cresol
HOC6H4NO2	Nitrophenol
MCATEC1O	Product from H-abstraction of OH group of methyl catechol
MCATECHOL	Methyl catechol
MNCATECH	Nitro dihydroxy toluene
OH2MBQN	Dihydroxy methyl benzoquinone
OH3MBQN	Trihydroxy methyl benzoquinone
OH3TOL	Trihydroxy toluene
OH3TOL1O	Product from H-abstraction of OH group of trihydroxy toluene
OH3TOL1O	Product from H-abstraction of OH group of tetrahydroxy toluene
OH4TOL	Tetrahydroxy toluene
OH5TOL	Pentahydroxy toluene
OHMBQN	Hydroxy methyl benzoquinone
PTLQONE	Methyl benzoquinone (one of the bicyclic intermediate pathway products from cresol oxidation in MCM)
TOL1OHNO2	Nitro hydroxy toluene

Table S5. Chamber conditions based on kinetic model (Version 1)

Expt	VOC-OH adduct rxn (%)		*o*-cresol rxn (%)		3-methyl catechol rxn (%)		RO_2 Reaction Partner (%)		
#	O_2	NO_2	OH	NO_3	OH	NO_3	RO_2	HO_2	NO
1	94	6	>31	<69	>41	<59	∼0	<1	>99
2	100	0	100	0	100	0	<12	>88	∼0
3	94	6	>44	<56	>44	<56	∼0	<1	>99
4	100	0	100	0	100	0	<6	>94	∼0
5	>99.9	<0.1	>96	<4	>91	<9	∼0	<1	>99
6	100	0	100	0	100	0	<1	>99	∼0
7	>99.9	<0.1	NA	NA	∼100	∼0	∼0	<2	>98
8	100	0	NA	NA	100	0	No RO_2 forms in MCM		
9	100	0	NA	NA	100	0	from low NO oxidation		
10	100	0	NA	NA	100	0	of methyl catechol.		
11	100	0	NA	NA	NA	NA	∼16[a]	∼84 [a]	∼0 [a]
12	97	3	NA	NA	NA	NA	∼0	<4	>96
13	100	0	100	0	100	0	<18	>82	∼0
14	90	10	>20	<80	>34	<66	∼0	<1	>99
15	>99.9	<0.1	>98	<2	>94	<6	∼0	<1	>99

[a] Throughout most of the experiment, the peroxy radical distribution was that stated. However, over the first hour there was exponential convergence to these steady state values from $RO_2 + RO_2$ = 100% and $RO_2 + HO_2$ = 0%.

S3 DART-MS Analysis Details and Product Identification

S3.1 DART-MS Analysis Details

A mass calibrant and an independent quality assurance/quality control (QA/QC) compound were run with each sample set to ensure mass accuracy to within 5 mDa. The mass calibrant used for positive mode was polyethylene glycol (average molecular weight of 600 amu, PEG-600; Acros Organics, Geel, Belgium), which was dissolved in methanol. The independent QA/QC compound used is reserpine, which was purchased from Sigma-Aldrich and diluted in methanol.

Tweezers were used to introduce the samples into the DART gas stream. Before analysis, the tweezers were rinsed with acetone, and were introduced into the gas stream to vaporize any contaminants. A strip (∼1 cm) was cut from each sample substrate for testing. The cutting was tested in triplicate, with each sampling being from a different are of the substrate.

In these studies, a solution of PEG-600 (50 μL in 10 mL of methanol) was used to calibrate (61-679 Da) the mass spectrometer for each run. Acceptable calibration was determined if the calibration Mass Center software produced a residual value of >9 x 10^{-12}. To ensure proper calibration, a solution of reserpine (5 mg in 10 mL of methanol) was analyzed subsequent to the PEG-600 in every sample run. Calibration was deemed sufficient if the m/z of reserpine fell within ± 0.005 Da of the theoretical value (609.281 Da).

The instrument used was a JEOL (Tokyo, Japan) AccuTOF™ mass spectrometer (JMS-T100LC) coupled with an IonSense (Saugus, MA, USA) DART® source. Ultra-pure helium was used as the ionizing gas with a flow rate of 1.75 L min^{-1}. For all analyses, the DART® source was set to a needle voltage of ±3.5 kV. Electrode 1 and electrode 2 voltages were both set to ±150 V. Mass spectrometer settings include: an orifice 1 voltage of ±20 V, orifice 2 voltage of ±5 V, a ring lens voltage of ±5 V, a peaks voltage of 1500 V, a mass range of 50 – 1500 m/z at 0.5 seconds per scan. A helium gas stream temperature of 325 °C was also employed.

S3.2 DART-MS Product Identification

Best available knowledge was used to assign the compounds displayed in Tables S6, S7, and S8. The smaller compounds could be fragmentation products. C_xH_yNO and $C_xH_yNO_2$ were assumed to be amines. These products could also be small nitro or nitroso compounds or fragmentation products of nitrates. Products that appeared to be fragmentation products (i.e., reasonable structures could not be drawn) were excluded from the list. The structure of each compound was necessary to estimate the vapor pressure. The most probable dominant isomer was selected in all cases, but there are likely many additional structural isomers that form as well. The abundances reported in Tables S6, S7, and S8 are not meant to be used quantitatively due to uncertainties in the vapor pressure estimation methods and centroid fitting algorithm. Often each m/z contained many over-lapping peaks and corrections were not made for isoptope effects.

Table S6. DART-MS data from low-NO toluene oxidation (experiment 13).

m/z (+) (Da)	Intensity (A.U.)	C	H	N	O	Δ (mDa) [a]	Smiles	Est. VP (atm) [b]	Abundance (R_f)
69.067377	6671.45	5	8	0	0	3.05	C=CC=CC	6.49E-01 (E)	3.42E-12
71.046739	11123.71	4	6	0	1	2.95	CC=CC=O	8.30E-02 (E)	4.46E-11
71.081281	3477.48	5	10	0	0	4.79	C=CCCC	6.49E-01 (E)	1.78E-12
73.064072	4280.44	4	8	0	1	1.27	CCCC=O	1.27E-01 (E)	1.12E-11
75.04371	5382.00	3	6	0	2	0.89	CC(CO)=O	6.92E-03 (E)	2.59E-10
80.048339	155429.63	5	5	1	0	1.69	C1=CC=CC=N1	3.46E-02 (N)	1.50E-09
83.082762	4393.36	6	10	0	0	3.31	C=CCCC=C	2.12E-01 (E)	6.89E-12
85.025484	4539.76	4	4	0	2	3.47	O=CC=CC=O	3.42E-03 (E)	4.41E-10
87.039802	7748.51	4	6	0	2	4.80	O=CCCC=O	6.19E-03 (E)	4.16E-10
97.026419	6180.71	5	4	0	2	2.53	O=CC1=CC=CO1	2.96E-03 (N)	6.95E-10
97.055251	2871.86	6	8	0	1	10.09	CC(C=CC=C)=O	8.87E-03 (E)	1.08E-10
97.101391	2954.88	7	12	0	0	0.33	CC1C=CCCC1	6.93E-02 (E)	1.42E-11
99.043366	9545.71	5	6	0	2	1.24	O=C(C)C=CC=O	1.12E-03 (E)	2.84E-09
99.072496	3758.17	6	10	0	1	8.49	CC(C=CCC)=O	8.87E-03 (E)	1.41E-10
101.057523	4501.87	5	8	0	2	2.73	O=C(C)CCC=O	2.02E-03 (E)	7.40E-10
109.035545	3507.03	6	4	0	2	-6.59	O=C1C=CC(C=C1)=O	2.48E-05 (E)	4.69E-08
109.096678	4467.03	8	12	0	0	5.05	C=CC=CC=CCC	2.27E-02 (E)	6.55E-11
111.043476	6721.86	6	6	0	2	1.13	O=CC1=CC=C(O1)C	1.25E-03 (N)	1.79E-09
111.11751	3129.72	8	14	0	0	-0.13	CCC=CC=CCC	2.27E-02 (E)	4.59E-11
113.019938	3471.30	5	4	0	3	3.93	O=C1C(C)=CC(O1)=O	7.03E-04 (E)	1.64E-09
113.05728	4021.97	6	8	0	2	2.97	O=CCCC=CC=O	4.92E-04 (E)	2.72E-09
115.038947	6483.21	5	6	0	3	0.57	O=C(C)C=CC(O)=O	6.57E-06 (E)	3.28E-07
115.064062	2955.96	6	10	0	2	11.84	O=CCCCCC=O	6.62E-04 (E)	1.49E-09
127.039667	5945.22	6	6	0	3	-0.15	O=C(C)C=CC(C=O)=O	1.64E-04 (E)	1.21E-08
127.112254	4155.67	8	14	0	1	0.04	O=CCCCCC=CC	1.45E-03 (E)	9.55E-10
129.053327	4254.59	6	8	0	3	1.84	O=C(C=CC(O)C=O)C	6.36E-05 (E)	2.22E-08
139.034538	5275.37	7	6	0	3	4.98	CC1=CC(C=C(O)C1=O)=O	5.26E-07 (E)	3.34E-06
141.050361	3122.55	7	8	0	3	4.81	CC1=CC=C(O)C(O)=C1O	5.97E-08 (N)	1.74E-05
155.034837	3399.08	7	6	0	4	-0.40	CC1=CC(C(O)=C(O)C1=O)=O	8.26E-09 (E)	1.37E-04
157.045695	8025.67	7	8	0	4	4.39	CC1=CC(O)=C(O)C(O)=C1O	3.28E-10 (N)	8.13E-03
161.091424	2838.46	11	12	0	1	5.22	O=CC=CC=CC=CC=CC=C	3.32E-05 (E)	2.85E-08
173.044149	3338.73	7	8	0	5	0.85	CC1=C(O)C(O)=C(C(O)=C1O)O	1.12E-12 (N)	9.92E-01
203.10019	3898.22	13	14	0	2	7.01	O=CC=CC=CC=CC=CC=CC(C)=O	1.46E-07 (E)	8.87E-06

[a] The difference between the measured and proposed compound exact mass. [b] Est. VP = Estimated vapor pressure. Estimation Method in parenthesis: E = EVAPORATION method and N = Nannoolal method.

Table S7: DART-MS data from high-NO *o*-cresol oxidation (experiment 15).

m/z (+) (Da)	Intensity [a]	C	H	N	O	Δ [b] (mDa)	Smiles	Est. VP (atm) [c]	Abundance (R_f)
69.06738	4799.51	5	8	0	0	3.05	C=CC=CC	6.49E-01 (E)	1.17E-11
71.04674	7360.97	4	6	0	1	2.95	CC=CC=O	8.30E-02 (E)	1.40E-10
73.06407	3055.72	4	8	0	1	1.27	CCCC=O	1.27E-01 (E)	3.82E-11
75.04371	3495.06	3	6	0	2	0.89	CC(CO)=O	6.92E-03 (E)	7.99E-10
76.0358	2830.61	2	5	1	2	4.06	OCC(N)=O	5.43E-08 (N)	8.25E-05
80.04834	2555.95	5	5	1	0	1.69	C1=CC=CC=N1	3.46E-02 (N)	1.17E-10
81.0676	2116.91	6	8	0	0	2.83	C=CC=CC=C	2.12E-01 (E)	1.58E-11
83.08276	2977.45	6	10	0	0	3.31	C=CCCC=C	2.12E-01 (E)	2.22E-11
85.02548	2862.51	4	4	0	2	3.47	O=CC=CC=O	3.42E-03 (E)	1.32E-09
85.06327	2015.80	5	8	0	1	2.07	CC(C=CC)=O	2.71E-02 (E)	1.17E-10
87.04526	4217.44	4	6	0	2	-0.66	O=CCCC=O	6.19E-03 (E)	1.08E-09
94.06261	2373.32	6	7	1	0	3.06	N1C=CC=CC=C1	2.04E-02 (N)	1.84E-10
95.08159	1934.09	7	10	0	0	4.49	CC1C=CCC=C1	6.93E-02 (E)	4.41E-11
97.02642	4443.40	5	4	0	2	2.53	O=CC1=CC=CO1	2.96E-03 (N)	2.38E-09
97.06102	3408.60	6	8	0	1	4.32	CC(C=CC=C)=O	8.87E-03 (E)	6.08E-10
97.09562	2367.86	7	12	0	0	6.10	CC1C=CCCC1	6.93E-02 (E)	5.40E-11
98.06128	2115.28	5	7	1	1	-0.69	NC(C=CC=C)=O	1.44E-06 (N)	2.33E-06
99.04337	5939.65	5	6	0	2	1.24	O=C(C)C=CC=O	1.12E-03 (E)	8.40E-09
99.07832	3689.73	6	10	0	1	2.67	CC(C=CCC)=O	8.87E-03 (E)	6.58E-10
100.0362	2821.45	4	5	1	2	3.65	O=CC=CC(N)=O	2.02E-07 (N)	2.21E-05
101.0222	2194.10	4	4	0	3	1.65	O=CC=CC(O)=O	2.01E-05 (E)	1.73E-07
101.0575	3823.68	5	8	0	2	2.73	O=C(C)CCC=O	2.02E-03 (E)	2.99E-09
102.0545	2971.25	4	7	1	2	1.54	NCC=CC(O)=O	2.92E-05 (N)	1.61E-07
104.0332	5611.42	3	5	1	3	1.60	CC=CON(=O)=O	2.60E-02 (E)	3.42E-10
109.1028	3360.34	8	12	0	0	-1.07	C=CC=CC=CCC	2.27E-02 (E)	2.34E-10
111.0435	4461.87	6	6	0	2	1.13	O=CC1=CC=C(O1)C	1.25E-03 (N)	5.64E-09
111.1175	2507.94	8	14	0	0	-0.13	CCC=CC=CCC	2.27E-02 (E)	1.75E-10
113.0262	1862.29	5	4	0	3	-2.29	O=C1C(C)=CC(O1)=O	7.03E-04 (E)	4.19E-09
113.0573	3145.91	6	8	0	2	2.97	O=CCCC=CC=O	4.92E-04 (E)	1.01E-08
114.0553	2382.57	5	7	1	2	0.17	C=C(C=CC(O)=O)N	1.45E-05 (N)	2.59E-07
115.0389	3284.56	5	6	0	3	0.57	O=C(C)C=CC(O)=O	6.57E-06 (E)	7.90E-07
115.0703	2005.33	6	10	0	2	5.56	O=CCCCCC=O	6.62E-04 (E)	4.79E-09
118.0469	2527.17	4	7	1	3	3.51	CCC=CON(=O)=O	8.50E-03 (E)	4.71E-10
120.0524	3185.49	4	9	1	3	13.66	CCCCON(=O)=O	8.50E-03 (E)	5.93E-10
126.0519	1896.52	6	7	1	2	3.58	OC1=CN=C(C)C(O)=C1	1.36E-05 (N)	2.20E-07

Table S7: DART-MS data from high-NO *o*-cresol oxidation (experiment 15).

m/z (+) (Da)	Intensity [a]	C	H	N	O	Δ [b] (mDa)	Smiles	Est. VP (atm) [c]	Abundance (R_f)
127.0397	3814.74	6	6	0	3	-0.15	O=C(C)C=CC(C=O)=O	1.64E-04 (E)	3.68E-08
127.0661	2199.51	7	10	0	2	9.84	O=C(C)CC=CCC=O	2.16E-04 (E)	1.61E-08
127.1123	3306.85	8	14	0	1	0.04	O=CCCCCC=CC	1.45E-03 (E)	3.61E-09
128.071	1864.39	6	9	1	2	0.14	O=C(C=CC=CCN)O	3.46E-06 (N)	8.52E-07
129.0533	2463.10	6	8	0	3	1.84	O=C(C=CC(O)C=O)C	6.36E-05 (E)	6.12E-08
130.0527	1871.23	5	7	1	3	-2.32	O=N(OC=CC=CC)=O	2.78E-03 (E)	1.07E-09
139.0414	2114.31	7	6	0	3	-1.92	CC1=CC(C=C(O)C1=O)=O	5.26E-07 (E)	6.36E-06
142.0463	2154.17	6	7	1	3	4.15	C=CC=CC(ON(=O)=O)=C	9.08E-04 (E)	3.75E-09
154.0524	1956.21	7	7	1	3	-2.01	OC1=C(N(=O)=O)C=CC =C1C	1.77E-05 (N)	1.75E-07
155.0348	3607.35	7	6	0	4	-0.40	CC1=CC(C(O)=C(O)C1=O) =O	8.26E-09 (E)	6.91E-04
157.0457	1941.16	7	8	0	4	4.39	CC1=CC(O)=C(O)C(O) =C1O	3.28E-10 (N)	9.36E-03
267.1658	2870.33	15	22	0	4	-6.13	OC(OC1=C(O)C(O) =CC=C1C)CCCCC=CC [c]	4.59E-12 (N)	9.90E-01

[a] (A.U.) [b] The difference between the measured and proposed compound exact mass. [c] Est. VP = Estimated vapor pressure. Estimation Method in parenthesis: E = EVAPORATION method, and N = Nannoolal method.[c] Smiles in table is that of the structure predicted to form. Vapor pressure method could not estimate the vapor pressure of this structure so a very similar structure was used instead (OC(C(O)=CC=C1C)=C1OCC(O)CCCC=CC).

Table S8: DART-MS data from high-NO toluene oxidation (experiment 14).

m/z (+) (Da)	Intensity [a]	C	H	N	O	Δ [b] (mDa)	Smiles	Est. VP (atm) [c]	Abundance (R_f)
61.026497	5540.57	2	4	0	2	2.46	CC(O)=O	4.49E-03 (E)	7.02E-10
69.067377	1410.70	5	8	0	0	3.05	C=CC=CC	6.49E-01 (E)	1.24E-12
76.035796	3623.11	2	5	1	2	4.06	OCC(N)=O	5.43E-08 (N)	3.80E-05
80.048339	1641.73	5	5	1	0	1.69	C1=CC=CC=N1	3.46E-02 (N)	2.71E-11
83.082762	1684.25	6	10	0	0	3.31	C=CCCC=C	2.12E-01 (E)	4.52E-12
85.025484	2836.08	4	4	0	2	3.47	O=CC=CC=O	3.42E-03 (E)	4.72E-10
87.007038	2179.84	3	2	0	3	1.18	O=CC(C=O)=O	7.03E-02 (E)	1.77E-11
87.039802	6440.08	4	6	0	2	4.80	O=CCCC=O	6.19E-03 (E)	5.93E-10
90.013837	2080.44	2	3	1	3	5.28	C=CON(=O)=O	7.95E-02 (E)	1.49E-11
90.047162	1148.22	3	7	1	2	8.34	OC(C)C(N)=O	2.13E-07 (N)	3.07E-06
94.06261	7800.17	6	7	1	0	3.06	N1C=CC=CC=C1	2.04E-02 (N)	2.18E-10

Table S8: DART-MS data from high-NO toluene oxidation (experiment 14).

m/z (+) (Da)	Intensity [a]	C	H	N	O	Δ [b] (mDa)	Smiles	Est. VP (atm) [c]	Abundance (R_f)
95.053048	1261.49	6	6	0	1	-3.36	OC1=CC=CC=C1	1.44E-03 (N)	4.98E-10
95.081585	1364.08	7	10	0	0	4.49	CC1C=CCC=C1	6.93E-02 (E)	1.12E-11
97.026419	6227.32	5	4	0	2	2.53	O=CC1=CC=CO1	2.96E-03 (N)	1.20E-09
97.061018	4637.55	6	8	0	1	4.32	CC(C=CC=C)=O	8.87E-03 (E)	2.98E-10
98.06128	1349.16	5	7	1	1	-0.69	NC(C=CC=C)=O	1.44E-06 (N)	5.35E-07
99.043366	11466.81	5	6	0	2	1.24	O=C(C)C=CC=O	1.12E-03 (E)	5.84E-09
99.089977	2449.13	6	10	0	1	-8.99	CC(C=CCC)=O	8.87E-03 (E)	1.57E-10
100.042055	2453.04	4	5	1	2	-2.20	O=CC=CC(N)=O	2.02E-07 (N)	6.91E-06
100.071332	1379.97	5	9	1	1	4.91	NC(C=CCC)=O	2.52E-06 (N)	3.12E-07
101.022218	2932.23	4	4	0	3	1.65	O=CC=CC(O)=O	2.01E-05 (E)	8.30E-08
101.051638	1499.95	5	8	0	2	8.62	O=C(C)CCC=O	2.02E-03 (E)	4.22E-10
102.054463	1439.00	4	7	1	2	1.54	NCC=CC(O)=O	2.92E-05 (N)	2.81E-08
102.089947	2487.60	5	11	1	1	1.94	NC(CCCC)=O	3.50E-06 (N)	4.05E-07
103.03847	1574.86	4	6	0	3	1.05	CC(C(C=O)O)=O	2.00E-03 (E)	4.48E-10
104.033168	2667.65	3	5	1	3	1.60	CC=CON(=O)=O	2.60E-02 (E)	5.85E-11
105.014648	2141.85	3	4	0	4	4.14	O=C(O)C(CO)=O	2.22E-06 (E)	5.49E-07
109.096678	3357.59	8	12	0	0	5.05	C=CC=CC=CCC	2.27E-02 (E)	8.44E-11
110.058713	1424.19	6	7	1	1	1.88	OC1=CC=CN=C1C	1.53E-03 (N)	5.29E-10
111.043476	4684.00	6	6	0	2	1.13	O=CC1=CC=C(O1)C	1.25E-03 (N)	2.13E-09
112.038821	2037.51	5	5	1	2	1.03	OC1=CC(O)=CN=C1	5.32E-05 (N)	2.18E-08
113.026161	2657.15	5	4	0	3	-2.29	O=C1C(C)=CC(O1)=O	7.03E-04 (E)	2.15E-09
113.05728	3740.34	6	8	0	2	2.97	O=CCCC=CC=O	4.92E-04 (E)	4.33E-09
114.055338	2438.47	5	7	1	2	0.17	C=C(C=CC(O)=O)N	1.45E-05 (N)	9.56E-08
115.038947	7677.84	5	6	0	3	0.57	O=C(C)C=CC(O)=O	6.57E-06 (E)	6.65E-07
116.033084	1330.37	4	5	1	3	1.68	C=CC=CON(=O)=O	8.50E-03 (E)	8.92E-11
116.064614	1348.08	5	9	1	2	6.54	CC(N)C=CC(O)=O	1.87E-05 (N)	4.12E-08
117.050497	2483.76	5	8	0	3	4.67	O=C(C)CCC(O)=O	1.00E-05 (E)	1.41E-07
118.046909	1887.46	4	7	1	3	3.51	CCC=CON(=O)=O	8.50E-03 (E)	1.27E-10
123.046863	1686.79	7	6	0	2	-2.26	CC1=CC(C=CC1=O)=O	8.12E-06 (E)	1.18E-07
125.06148	1442.25	7	8	0	2	-1.23	CC1=CC=CC(O)=C1O	6.77E-06 (N)	1.21E-07
126.051919	2178.90	6	7	1	2	3.58	OC1=CN=C(C)C(O)=C1	1.36E-05 (N)	9.10E-08
127.039667	4187.31	6	6	0	3	-0.15	O=C(C)C=CC(C=O)=O	1.64E-04 (E)	1.46E-08
127.112254	3174.50	8	14	0	1	0.04	O=CCCCCC=CC	1.45E-03 (E)	1.25E-09
128.03127	2068.51	5	5	1	3	3.50	O=N(C1=CC=C(C)O1)=O	1.93E-03 (N)	6.09E-10
129.053327	3905.59	6	8	0	3	1.84	O=C(C=CC(O)C=O)C	6.36E-05 (E)	3.50E-08

Table S8: DART-MS data from high-NO toluene oxidation (experiment 14).

m/z (+) (Da)	Intensity [a]	C	H	N	O	Δ [b] (mDa)	Smiles	Est. VP (atm) [c]	Abundance (R_f)
130.052743	1472.64	5	7	1	3	-2.32	O=N(OC=CC=CC)=O	2.78E-03 (E)	3.02E-10
131.035911	1919.85	5	6	0	4	-1.48	OC(C(O)=C(C=O)C)=O	1.09E-07 (E)	1.00E-05
131.062715	1156.33	6	10	0	3	8.10	O=C(C)CCC(C=O)O	4.99E-05 (E)	1.32E-08
133.047111	1311.02	5	8	0	4	2.97	OC(C(C(C)C=O)O)=O	1.22E-01 (E)	6.13E-12
138.049261	2335.43	7	7	1	2	6.24	CC1=C(N(=O)=O)C=CC=C1	2.18E-04 (N)	6.12E-09
139.034538	2994.57	7	6	0	3	4.98	CC1=CC(C=C(O)C1=O)=O	5.26E-07 (E)	3.24E-06
140.030245	2170.62	6	5	1	3	4.52	OC1=CC=CC=C1N(=O)=O	8.71E-05 (N)	1.42E-08
141.050361	5078.50	7	8	0	3	4.81	CC1=CC=C(O)C(O)=C1O	5.97E-08 (N)	4.85E-05
142.046271	3022.13	6	7	1	3	4.15	C=CC=CC(ON(=O)=O)=C	9.08E-04 (E)	1.90E-09
143.031682	2933.82	6	6	0	4	2.75	O=C(C)C=CC(C(O)=O)=O	5.77E-07 (E)	2.90E-06
145.047972	2291.30	6	8	0	4	2.11	O=C(C=CC(O)C(O)=O)C	3.56E-08 (E)	3.66E-05
152.068107	1146.80	8	9	1	2	3.05	NC(C=CC=CC=CC=O)=O	4.05E-09 (N)	1.61E-04
154.045164	2966.87	7	7	1	3	5.25	OC1=C(N(=O)=O)C=CC=C1C	1.77E-05 (N)	9.55E-08
155.034837	3800.38	7	6	0	4	-0.40	CC1=CC(C(O)=C(O)C1=O)=O	8.26E-09 (E)	2.62E-04
156.06424	1417.63	7	9	1	3	1.83	CC=CC=CC=CON(=O)=O	2.97E-04 (E)	2.72E-09
157.045695	5036.75	7	8	0	4	4.39	CC1=CC(O)=C(O)C(O)=C1O	3.28E-10 (N)	8.74E-03
158.044945	1517.74	6	7	1	4	0.39	O=N(OC=CC(CC=C)=O)=O	3.80E-05 (E)	2.27E-08
159.062128	1321.64	7	10	0	4	3.61	CC(C=CC(C(O)C=O)O)=O	3.41E-07 (E)	2.21E-06
161.046849	1846.47	6	8	0	5	-1.85	O=C(CO)C=CC(C(O)=O)O	1.79E-10 (E)	5.89E-03
170.046401	1573.59	7	7	1	4	-1.07	OC1=C(O)C(N(=O)=O) =CC=C1C	2.01E-07 (N)	4.46E-06
173.044149	1855.62	7	8	0	5	0.85	CC1=C(O)C(O) =C(C(O)=C1O)O	1.12E-12 (N)	9.44E-01
174.069813	1324.07	7	11	1	4	6.82	O=N(OC=CCCCCC=O)=O	1.90E-05 (E)	3.98E-08
175.059781	1319.16	7	10	0	5	0.87	O=C(C)C=CC(O)C(O) C(O)=O	1.33E-10 (E)	5.64E-03
177.157199	1399.51	9	20	0	3	-8.13	CCCCC(O)C(O)CCCO	2.29E-09 (E)	3.49E-04
178.069959	2175.62	6	11	1	5	1.59	O=N(OCCCCCC(O)=O)=O	2.20E-07 (E)	5.63E-06
223.064145	2037.80	11	10	0	5	-3.50	O=C(O)C=CC=CC=CC =CC(C(O)=O)=O	3.35E-11 (E)	3.46E-02

[a] (A.U.) [b] The difference between the measured and proposed compound exact mass. [b] Est. VP = Estimated vapor pressure. Estimation Method in parenthesis: E = EVAPORATION method, and N = Nannoolal method.

Other studies have reported structural isomers of the compounds listed in Table S6, S7, and S8 in the gas-phase and particle-phase from toluene SOA (Jang and Kamens, 2001; Sato et al., 2007). As here, peaks for $C_7H_8O_4$ and $C_7H_8O_5$ had the largest

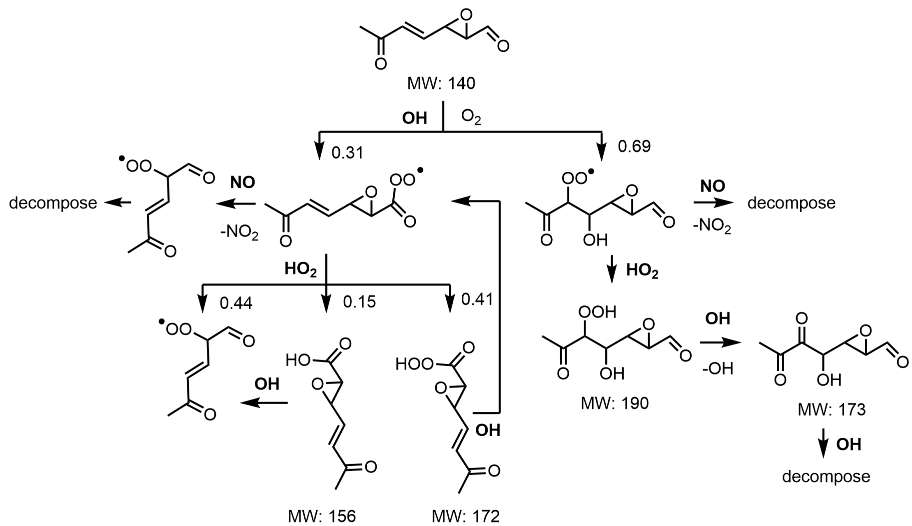


Figure S6. Epoxide pathway oxidation mechanism under both low- and high-NO conditions as recommended by MCM v3.3.1

intensity in the particle-phase measurements in the study by Sato et al. (2007), but it should be noted that only 1% of the SOA constituents were quantified in that study. Both of these studies suggest that the compounds are ring-opening products not produced from the cresol pathway. Given the new evidence from the CF_3O^- CIMS in this study, it is clear that these compounds are produced from the cresol pathway.

Products detected in the particle-phase by the DART-MS under *o*-cresol high NO conditions are shown in Figure S7. An oligomer product, $C_{15}H_{22}O_4$, is detected as one of the dominant products in *o*-cresol oxidation under high-NO conditions (Figure S7). It is possible this product forms from oligomerization of trihydroxy toluene and $C_8H_{14}O$ to form a hemiacetal.

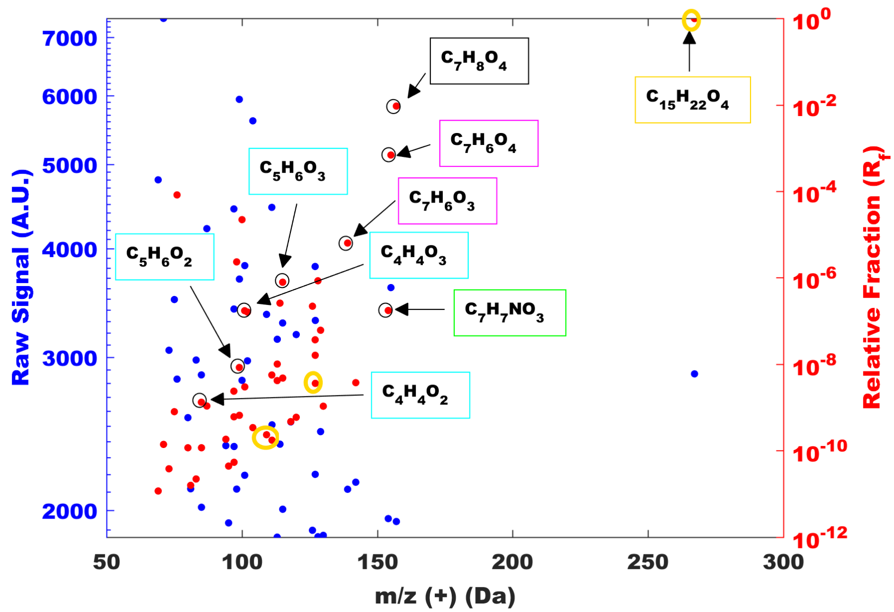


Figure S7. Products detected by DART-MS in the particle phase during oxidation of *o*-cresol under high NO conditions (experiment 15) with boxes identifying the following types of compounds: polyols (black), methyl benzoquinone type compounds (magenta), decomposition products from the bicyclic intermediate pathway (cyan), products with more than 7 carbons (gold), and nitro compounds (green).

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