Supplementary material

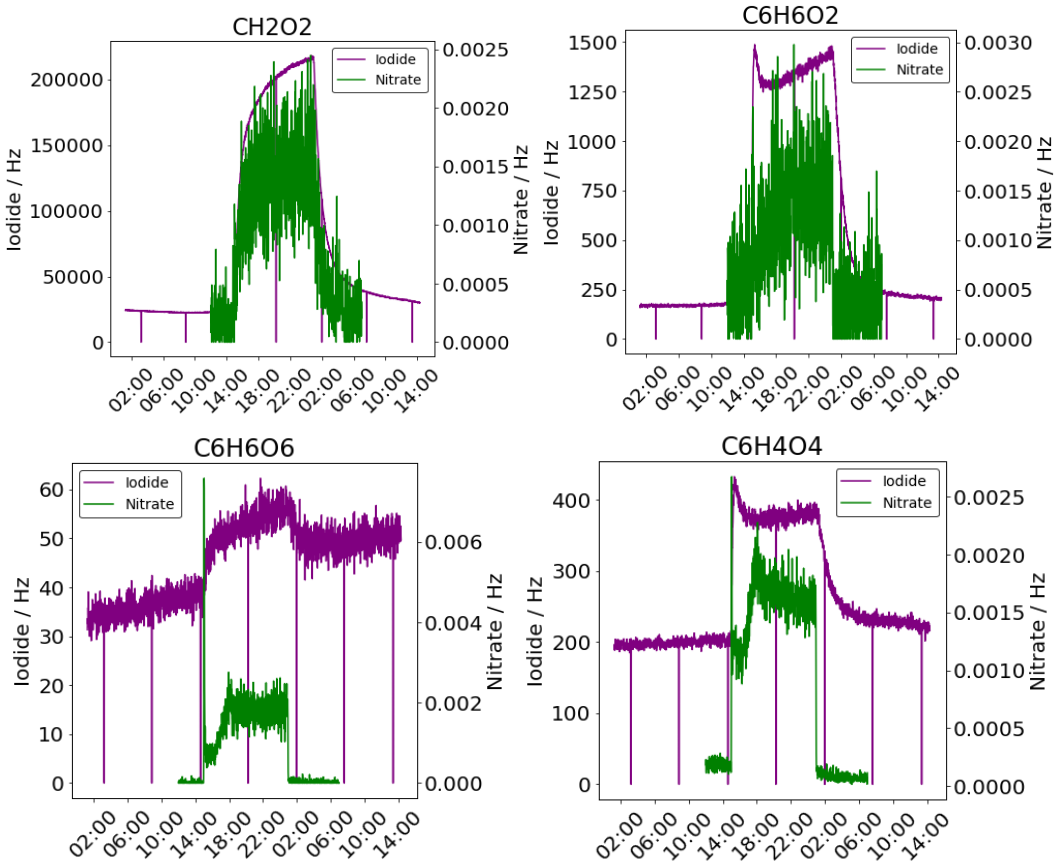

Fig S1. Example of time series profiles nitrate vs iodide for CH_2O_2 (formic acid), $C_6H_6O_2$ (phenol), highly oxidised product $C_6H_6O_6$ and ring retaining oxidation product C_6H_4O.

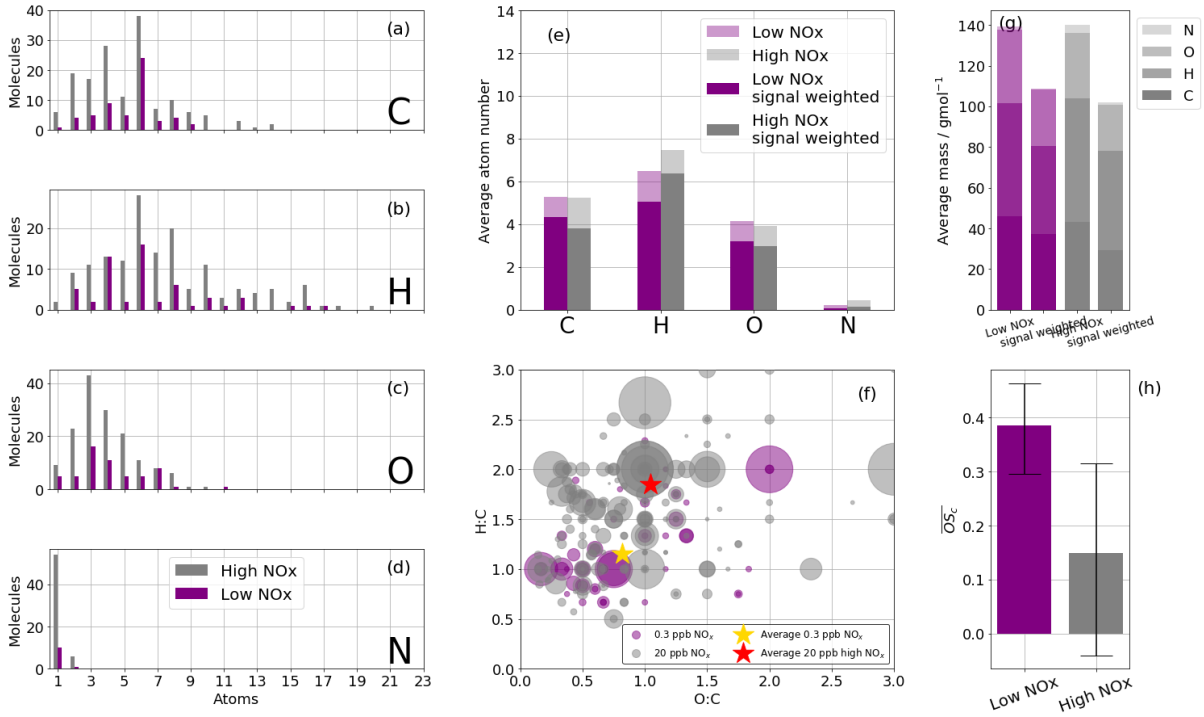

Fig S2. Summary of CHO + CHON and statistics of detected oxidation products with higher relative signal during high (20 ppb, grey) and low (0.3 ppb, purple) NO_x benzene oxidation with the iodide ionisation scheme. (a, b, c, d.) Frequency distributions of the atoms C, H, O and N for the detected oxidation products. (e.) The average number of atoms per detected oxidation product split into C, H, O and N atoms, also shown is signal weighted average atom number. (f.) Van Krevelen diagram (O:C vs H:C) sized by signal. (g.) The average mass of a detected oxidation product for high and low NO_x conditions, also shown signal weighted average masses. (h.) The mean, average carbon oxidation state (OS_c) of the detected oxidation products for high and low NO_x conditions. Limits represent minimum and maximum OS_C as a function of minimum and maximum OS_N, see section 2.3.

		High NOx							Low NOx		
Autoxidation step	Termination group	Benzene	Phenol	Catechol		Autoxidation step	Termination group	Benzene	Phenol	Catechol	Key
0	precursor	C6H6	C6H6O	C6H6O2		0	precursor	C6H6	C6H6O	C6H6O2	observed
0	R-OH	C6H8O2	C6H8O3	C6H8O4		0	R-OH	C6H8O2	C6H8O3	C6H8O4	observed as autox prod only
0	R-OOH	C6H8O3	C6H8O4	C6H8O5		0	R-OOH	C6H8O3	C6H8O4	C6H8O5	observed as 2nd gen autox prod only
0	R-ONO2	C6H7NO4	C6H7NO5	C6H7NO6		0	R-ONO2	C6H7NO4	C6H7NO5	C6H7NO6	
0	R-OONO2	C6H7NO5	C6H7NO6	C6H7NO7		0	R-OONO2	C6H7NO5	C6H7NO6	C6H7NO7	
0	R-NO2	C6H7NO3	C6H7NO4	C6H7NO5		0	R-NO2	C6H7NO3	C6H7NO4	C6H7NO5	
0	R=O	C6H8O2	C6H8O3	C6H8O4		0	R=O	C6H8O2	C6H8O3	C6H8O4	
1	R-OH	C6H8O4	C6H8O5	C6H8O6		1	R-OH	C6H8O4	C6H8O5	C6H8O6	
1	R-OOH	C6H8O5	C6H8O6	C6H8O7		1	R-OOH	C6H8O5	C6H8O6	C6H8O7	
1	R-ONO2	C6H7NO6	C6H7NO7	C6H7NO8		1	R-ONO2	C6H7NO6	C6H7NO7	C6H7NO8	
1	R-OONO2	C6H7NO7	C6H7NO8	C6H7NO9		1	R-OONO2	C6H7NO7	C6H7NO8	C6H7NO9	
1	R-NO2	C6H7NO5	C6H7NO6	C6H7NO7		1	R-NO2	C6H7NO5	C6H7NO6	C6H7NO7	
1	R=O	C6H8O4	C6H8O5	C6H8O6		1	R=O	C6H8O4	C6H8O5	C6H8O6	
2	R-OH	C6H8O6	C6H8O7	C6H8O8		2	R-OH	C6H8O6	C6H8O7	C6H8O8	
2	R-OOH	C6H8O7	C6H8O8	C6H8O9		2	R-OOH	C6H8O7	C6H8O8	C6H8O9	
2	R-ONO2	C6H7NO8	C6H7NO9	C6H7NO10		2	R-ONO2	C6H7NO8	C6H7NO9	C6H7NO10	
2	R-OONO2	C6H7NO9	C6H7NO10	C6H7NO11		2	R-OONO2	C6H7NO9	C6H7NO10	C6H7NO11	
2	R-NO2	C6H7NO7	C6H7NO8	C6H7NO9		2	R-NO2	C6H7NO7	C6H7NO8	C6H7NO9	
2	R=O	C6H8O6	C6H8O7	C6H8O8		2	R=O	C6H8O6	C6H8O7	C6H8O8	

Table S1. Theoretical formulae from termination of different generations of autoxidation. Highlighted indicate the formulae was observed as either an adduct or deprotonated peak in the mass spectrum. Green highlight indicates this formula is only producible from at least 1 autoxidation step. Orange highlight indicates this formula is only producible from 2 autoxidation steps. No highlighting indicates the species was not observed.

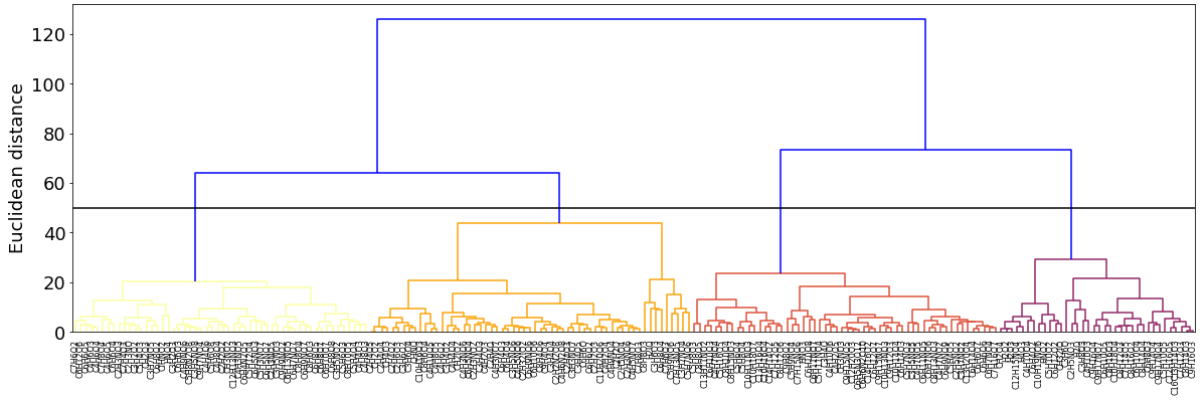

Figure S3. Hierarchical clustering dendrogram. Four clusters of the high NO_x condition benzene oxidation products are chosen as the solution.

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Low NOx				High NOx			
Ion	**Formula**	**Mw (g/mol)**	**Cluster**	**Ion**	**Formula**	**Mw (g/mol)**	**Cluster**
C2H4O2	C2H4O2	60.0211	2	C2H4O2	C2H4O2	60.0211	2
C2H4O3	C2H4O3	76.0160	2	C2H4O3	C2H4O3	76.0160	2
C2H4O4	C2H4O4	92.0110	2	C2H4O4	C2H4O4	92.0110	2
C3H4O3	C3H4O3	88.0160	2	C3H4O3	C3H4O3	88.0160	2
C3H4O4	C3H4O4	104.0110	2	C3H4O4	C3H4O4	104.0110	2
C3H4O5	C3H4O5	120.0059	2	C3H4O5	C3H4O5	120.0059	2
C4H4O3	C4H4O3	100.0160	1	C4H3NO5	C4H3NO5	145.0011	1
C4H4O4	C4H4O4	116.0110	2	C4H4O3	C4H4O3	100.0160	1
C4H5NO7	C4H5NO7	179.0066	2	C4H4O4	C4H4O4	116.0110	2
C4H6O4	C4H6O4	118.0266	1	C4H5NO7	C4H5NO7	179.0066	2
C4H6O5	C4H6O5	134.0215	1	C4H6O4	C4H6O4	118.0266	1
C5H6O3	C5H6O3	114.0317	1	C4H6O5	C4H6O5	134.0215	1
C6H5NO3	C6H5NO3	139.0269	1	C5H6O3	C5H6O3	114.0317	1
C6H6O	C6H6O	94.0419	2	C5H6O4	C5H6O4	130.0266	3
C6H6O2	C6H6O2	110.0368	2	C6H5N3O12	C6H5N3O12	310.9873	3
C6H6O3	C6H6O3	126.0317	1	C6H5NO3	C6H5NO3	139.0269	1
C6H6O4	C6H6O4	142.0266	1	C6H5NO4	C6H5NO4	155.0219	2
C6H6O5	C6H6O5	158.0215	1	C6H5NO7	C6H5NO7	203.0066	1
C6H8O5	C6H8O5	160.0372	1	C6H6N2O10	C6H6N2O10	266.0022	3
				C6H6O	C6H6O	94.0419	2
				C6H6O2	C6H6O2	110.0368	2
				C6H6O3	C6H6O3	126.0317	1
				C6H6O4	C6H6O4	142.0266	1
				C6H6O5	C6H6O5	158.0215	1
				C6H7NO7	C6H7NO7	205.0223	1
				C6H8O5	C6H8O5	160.0372	1

Table S2. List of MCM species from the low and high NO_x experiments and their respective clusters.