Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary: A SIFT-MS study of positive and negative ion chemistry of the *ortho*-, *meta*- and *para*- Isomers of cymene, cresol, and ethylphenol

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1 Summary of Reactions

A summary of the reactions discussed in the main manuscript are given below, along with the *m/z* values of the product ion, for each reaction (given in brackets after the reaction). Note that the molecular masses of the analyte ions are: cymene (RMM 134 g mol^{-1}), cresol (RMM 108 g mol^{-1}) and ethylphenol (RMM 122 g mol^{-1}).

1.1 H_3O^+ Reactions

$$H_3O^+ + C_{10}H_{14} \rightarrow C_{10}H_{15}^+ + H_2O \text{ (1a): } (m/z\ 135)$$
$$\rightarrow C_7H_9^+ + C_3H_7OH \text{ (1b): } (m/z\ 93)$$

$$H_3O^+ + C_7H_8O \rightarrow C_7H_8OH^+ + H_2O \text{ (2): } (m/z\ 109)$$

$$H_3O^+ + C_8H_{10}O \rightarrow C_8H_{10}OH^+ + H_2O \text{ (3): } (m/z\ 123)$$

1.2 NO^+ Reactions

$$NO^+ + C_{10}H_{14} \rightarrow C_{10}H_{14}^{+\bullet} + NO^\bullet \text{ (4): } (m/z\ 134)$$

$$NO^+ + C_7H_8O \rightarrow C_7H_8O^{+\bullet} + NO^\bullet \text{ (5): } (m/z\ 108)$$

$$NO^+ + C_8H_{10}O \rightarrow C_8H_{10}O^{+\bullet} + NO^\bullet \text{ (6): } (m/z\ 122)$$

1.3 $O_2^{+\bullet}$ Reactions

$$O_2^{+\bullet} + C_{10}H_{14} \rightarrow C_{10}H_{14}^{+\bullet} + O_2 \text{ (7a): } (m/z\ 134)$$
$$\rightarrow C_9H_{11}^+ + CH_3^\bullet + O_2 \text{ (7b): } (m/z\ 119)$$

$$O_2^{+\bullet} + C_7H_8O \rightarrow C_7H_8O^{+\bullet} + O_2 \text{ (8a): } (m/z\ 108)$$
$$\rightarrow C_7H_7O^+ + H^\bullet + O_2 \text{ (8b): } (m/z\ 107)$$

$$O_2^{+\bullet} + C_8H_{10}O \rightarrow C_8H_{10}O^{+\bullet} + O_2 \text{ (9a): } (m/z \text{ 122})$$

$$\rightarrow C_7H_7O^+ + CH_3^\bullet + O_2 \text{ (9b): } (m/z \text{ 107})$$

1.4 $O^{-\bullet}$ Reactions

$$O^{-\bullet} + C_{10}H_{14} \rightarrow C_{10}H_{13}^- + OH^\bullet \text{ (10): } (m/z \text{ 133})$$

$$O^{-\bullet} + C_7H_8O \rightarrow C_6H_5O_2^- + CH_3^\bullet \text{ (11a): } (m/z \text{ 109})$$

$$\rightarrow C_7H_7O^- + OH^\bullet \text{ (11b): } (m/z \text{ 107})$$

$$\rightarrow C_7H_6O^{-\bullet} + H_2O \text{ (11c): } (m/z \text{ 106})$$

$$O^{-\bullet} + C_8H_{10}O \rightarrow C_8H_9O^- + OH^\bullet \text{ (12a): } (m/z \text{ 121})$$

$$\rightarrow C_8H_7O^- + (H_2O + H^\bullet) \text{ (12b): } (m/z \text{ 119})$$

1.5 OH^- Reactions

$$OH^- + C_{10}H_{14} \rightarrow C_{10}H_{13}^- + H_2O \text{ (13a): } (m/z \text{ 133})$$

$$\rightarrow C_8H_7O^- + C_2H_6 + H_2 \text{ (13b): } (m/z \text{ 119})$$

$$OH^- + C_7H_8O \rightarrow C_7H_7O^- + H_2O \text{ (14a): } (m/z \text{ 107})$$

$$\rightarrow C_6H_5O^- + CH_3OH \text{ (14b): } (m/z \text{ 93})$$

$$OH^- + C_8H_{10}O \rightarrow C_8H_9O^- + H_2O \text{ (15): } (m/z \text{ 121})$$

1.6 $O_2^{-\bullet}$ Reactions

$$O_2^{-\bullet} + C_7H_8O \rightarrow C_7H_8O.O_2^{-\bullet} \text{ (16a): } (m/z \text{ 140})$$

$$\rightarrow C_7H_7O^- + HO_2^\bullet \text{ (16b): } (m/z \text{ 107})$$

$$O_2^{-\bullet} + C_8H_{10}O \rightarrow C_8H_{10}O.O_2^{-\bullet} \text{ (17a): } (m/z \text{ 154})$$

$$\rightarrow C_8H_9O^- + HO_2^\bullet \text{ (17b): } (m/z \text{ 121})$$

1.7 NO_2^- and NO_3^- Reactions

$$NO_2^- + C_7H_8O \rightarrow C_7H_8O.NO_2^- \text{ (18): } (m/z \text{ 154})$$

$$NO_2^- + C_8H_{10}O \rightarrow C_8H_{10}O.NO_2^- \ (19): (m/z\ 168)$$

$$NO_3^- + C_7H_8O \rightarrow C_7H_8O.NO_3^- \ (20): (m/z\ 170)$$

2 Ion-Source switching evolution

For each SIM scan conducted, only the last 20 data points (out of the 50 taken) were taken into consideration, due to the time in which it takes the instrument to stabilise the ion-source conditions. An example of this is given in Fig. S1.

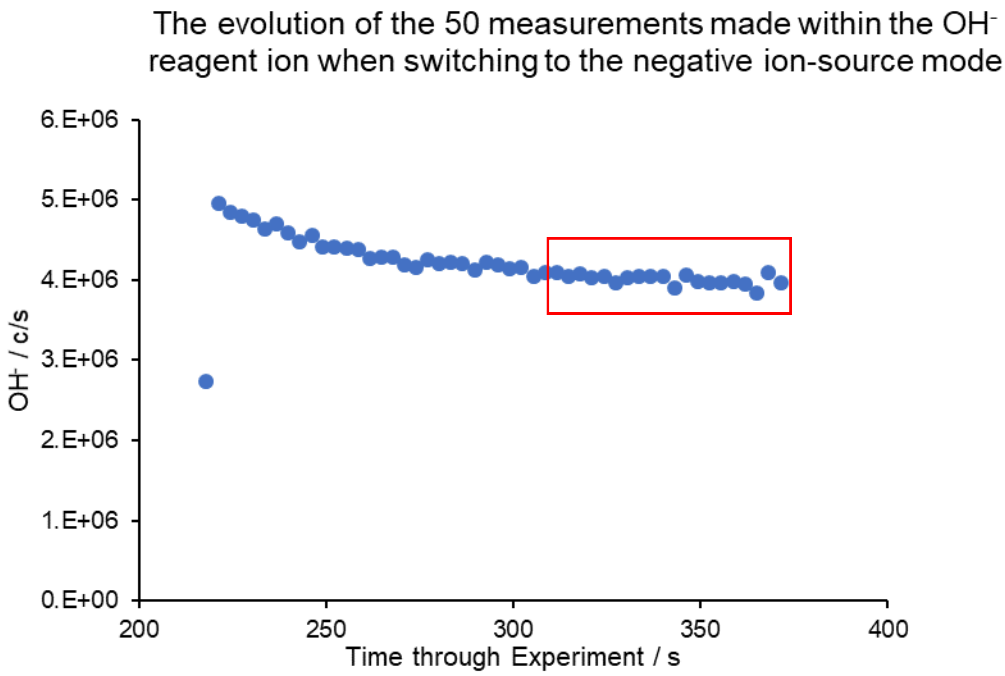

Figure. S1. Example raw data showing the evolution of the OH^- reagent ion (*m/z* 17), just after switching from the positive ion-source mode, to the first negative ion source mode (shown). Only the last 20 data points (out of 50) were taken (red box), as this is when the ion-source mode had stabilised after switching. This time period is shown by a red box in the figure above.

3 Impurity reagent ions in the Voice200infinity

To critically assess the plausibility of the presence of minor product ions and their associated pathways, it is essential to analyse the efficiency of the quadrupole mass filter of the SIFT-MS Voice200infinity instrument and the associated percentages of impurity ions for the target reagent generation species. The calculated relative percentages of target analyte species are shown below in Table S1 and have been calculated incorporating the hydrates of the reagent ion species.

Table S1. The relative percentages of impurity ions within the SIFT-MS instrument used in this study for the generation of each of the eight reagent ions. The percentages of each ion for a specific selection of reagent ion are shown in each row.

		Main and Impurity Ions / %								
		H_3O^+	NO^+	$O_2^{+\bullet}$	$O^{-\bullet}$	OH^-	$O_2^{-\bullet}$	NO_2^-	NO_3^-	Σ
Intended Precursor Ion	H_3O^+	99.85%	0.01%	0.14%	-	-	-	-	-	100.00%
	NO^+	0.03%	99.78%	0.19%	-	-	-	-	-	100.00%
	$O_2^{+\bullet}$	0.20%	0.05%	99.75%	-	-	-	-	-	100.00%
	$O^{-\bullet}$	-	-	-	99.33%	0.54%	0.13%	0.00%	0.00%	100.00%
	OH^-	-	-	-	3.08%	96.27%	0.64%	0.00%	0.01%	100.00%
	$O_2^{-\bullet}$	-	-	-	0.86%	0.01%	99.13%	0.00%	0.00%	100.00%
	NO_2^-	-	-	-	2.52%	0.01%	0.01%	97.46%	0.00%	100.00%
	NO_3^-	-	-	-	0.45%	0.00%	0.23%	7.15%	92.17%	100.00%