SUPPORTING INFORMATION

Fenton Oxidation of Gaseous Isoprene on Aqueous Surfaces

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In all experiments FeCl$_2$ microjets at pH 2 were exposed to 202 ppmv of ISO(g) in N$_2$(g) mixtures for $\tau \sim 10$ μs. 1 ppbv = $2.6 \times 10^{10}$ molecules cm$^{-3}$ at 1 atm and 288 K experimental conditions. A value of [ISO(g)] $\sim 5 \times 10^{15}$ molecules cm$^{-3}$ at the surface of the microjets was calculated by assuming that the 15 cm$^3$ min$^{-1}$ N$_2$(g) carrier flow was saturated with ISO vapor at 288 K (http://www.sigmaaldrich.com/catalog/product/aldrich/464953?lang=en&region=US), prior to entering the spraying chamber, where it was diluted by a factor of $1.9 \times 10^{-3}$ by the 8 L min$^{-1}$ nebulizer N$_2$(g) gas flow. Similarly, A value of [H$_2$O$_2$(g)] $\sim 4 \times 10^{14}$ molecules cm$^{-3}$ was calculated from the composition of the vapor in equilibrium with 50 wt. % in water 303 K (http://www.h2o2.com/technical-library/physical-chemical-properties/physical-properties/default.aspx?pid=25&name=Vapor-Pressures).

**Scheme S1:**
Scheme S1 and S2 display possible structures of some of the oxidized species observed in figure 5 (A, B, C and D). The addition of two $\cdot$OH radicals to (ISO)$_2$H$^+$ ($C_{10}H_{17}^+$, m/z$^+ = 137$) we get: $C_{10}H_{17}^+$ + 2 $\cdot$OH $\rightarrow$ $C_{10}H_{19}O_2^+$, m/z$^+ = 171$, and $C_{10}H_{19}O_2^+$ - H$_2$O $\rightarrow$ $C_{10}H_{17}O^+$, m/z$^+ = 153$ (Scheme S1). Alternatively, $C_{10}H_{17}^+$ + $\cdot$OH + $\cdot$OOH $\rightarrow$ $C_{10}H_{19}O_3^+$, m/z$^+ = 187$, whose fragmentations lead to: $C_{10}H_{19}O_3^+$ - H$_2$O $\rightarrow$ $C_{10}H_{17}O_2^+$, m/z$^+$ = 169, and $C_{10}H_{19}O_3^+$ - O$_2$ $\rightarrow$ $C_{10}H_{19}O^+$, m/z$^+$ = 155 (Scheme S2) respectively.

Scheme S3:

3,5,6-trimethylhepta-1,6-dien-3-ylium

$\cdot$OH

$\cdot$ OH

$\cdot$OH

6-hydroxy-3,5,6-trimethyl-7-oxohept-1-en-3-ylium

$\cdot$O

$\cdot$O

6-hydroperoxy-6-hydroxy-3,5,6-trimethylhept-1-en-3-ylium

$\cdot$O

$\cdot$O

6-hydroxy-3,5,6-trimethylhept-1-en-3-ylium

7-hydroperoxy-6-hydroxy-3,5,6-trimethylhept-1-en-3-ylium
Similarly Scheme 3 represents other possible products that can be formed due to the OH radical addition to the double bonds of (ISO)$_2$H$^+$ (137$^\ddagger$). The formed radical species A and B readily can undergo ring closure and form a stable 6 member cyclohexane ring and a cyclopentane ring as shown in Scheme S4.

**Scheme S4:**

2-hydroxy-4-(hydroxymethyl)-1,4,5-trimethylcyclohexan-1-ylium

2,3-bis(hydroxymethyl)-1,3,4-trimethylcyclopentan-1-ylium