SUPPORTING INFORMATION

Fenton Oxidation of Gaseous Isoprene on Aqueous Surfaces

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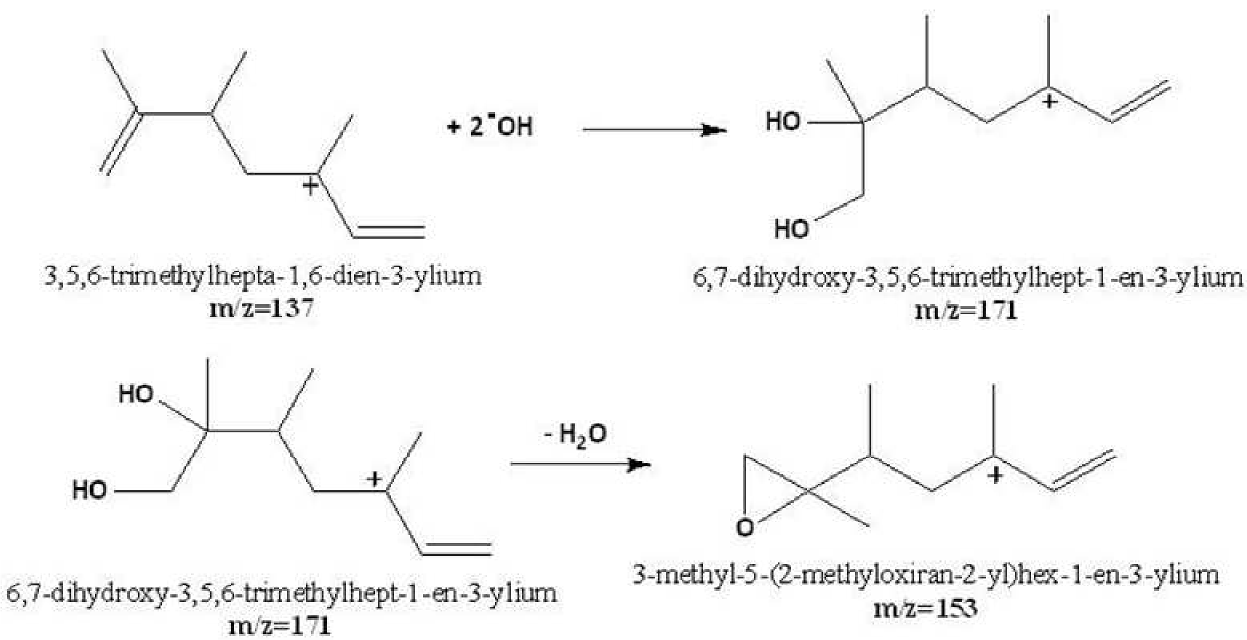
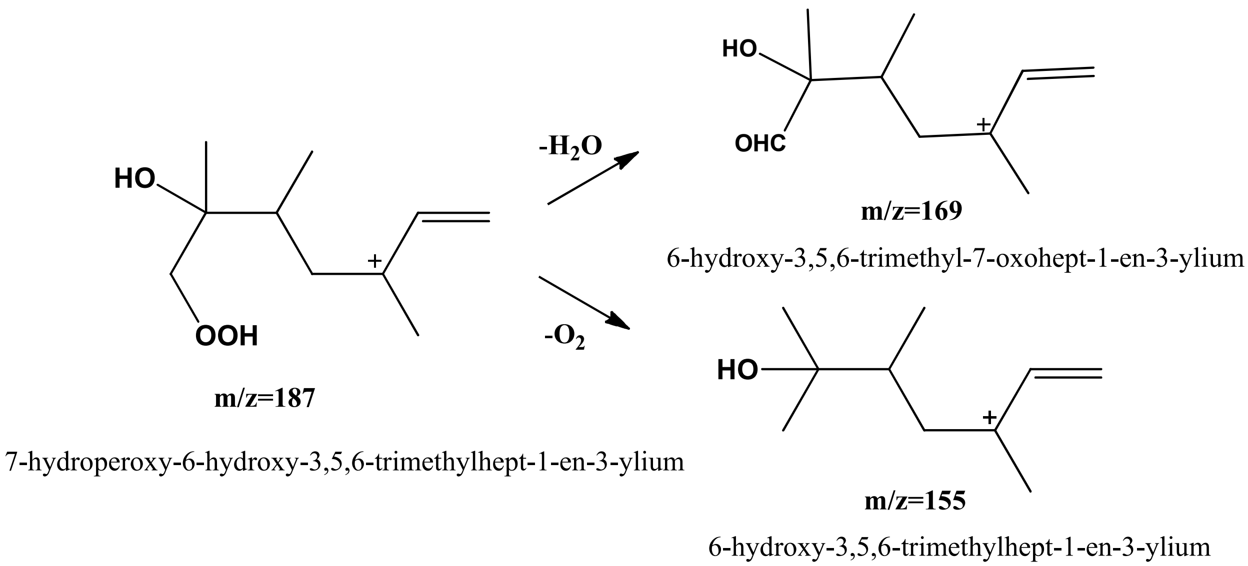
In all experiments $FeCl_2$ microjets at pH 2 were exposed to 202 ppmv of ISO(g) in N_2(g) mixtures for $\tau \sim 10$ μs . 1 ppbv = 2.6×10^{10} molecules cm^{-3} at 1 atm and 288 K experimental conditions. A value of [ISO(g)] $\sim 5 \times 10^{15}$ molecules cm^{-3} at the surface of the microjets 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 1.9×10^{-3} by the 8 L min^{-1} nebulizer N_2(g) gas flow. Similarly, A value of $[H_20_2(g)] \sim 4 \times 10^{14}$ 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).

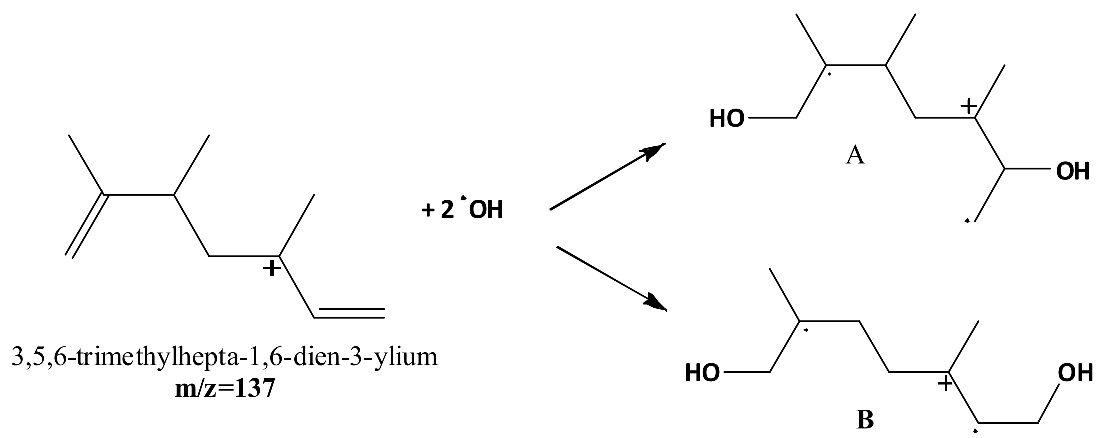


SCHEME S1:

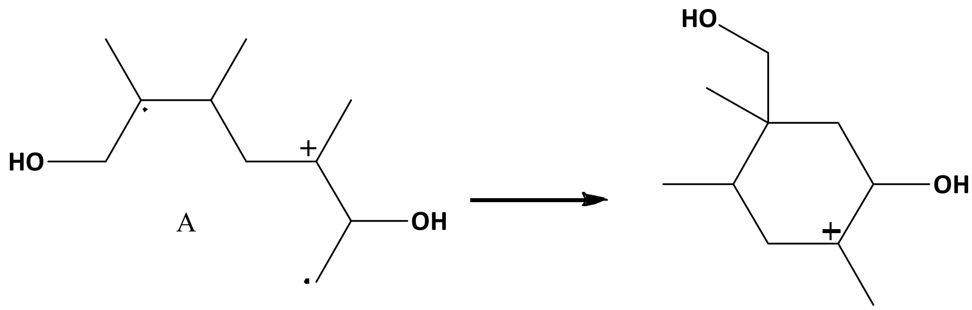


SCHEME S2:

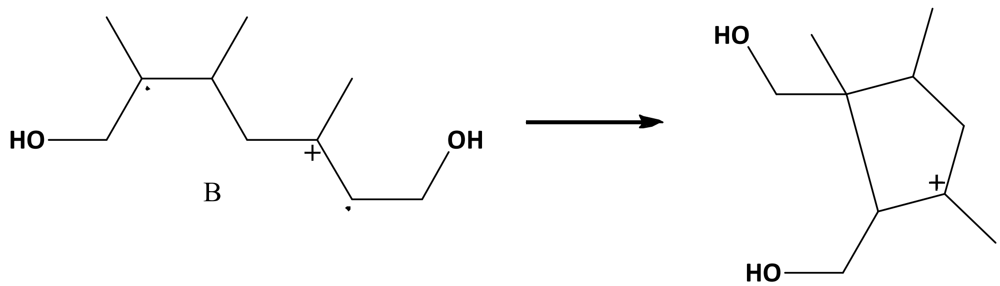
Scheme S1 and S2 display possible structures of some of the oxidized species observed in figure 5 (A, B, C and D). The addition of two ·OH radicals to $(ISO)_2H^+$ ($C_{10}H_{17}^+$, $m/z^+ = 137$) we get : $C_{10}H_{17}^+ + 2\ \cdot OH \rightarrow C_{10}H_{19}O_2^+$, $m/z^+ = 171$, and $C_{10}H_{19}O_2^+ - H_2O \rightarrow C_{10}H_{17}O^+$, $m/z^+ = 153$ (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: $C_{10}H_{19}O_3^+ - H_2O \rightarrow C_{10}H_{17}O_2^+$, $m/z^+ = 169$, and $C_{10}H_{19}O_3^+ - O_2 \rightarrow C_{10}H_{19}O^+$, $m/z^+ = 155$ (Scheme S2) respectively.



SCHEME S3:



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



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

SCHEME S4:

Similarly Scheme 3 represents other possible products that can be formed due to the OH radical addition to the double bonds of $(ISO)_2H^+$ (137^+). 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.