Does Isoprene Gas Oligomerize on Acidic Water Microdroplets in the Atmosphere?

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INTRODUCTION

Isoprene (2-methyl 1,3-butadiene) is a volatile gas (at 298 K and 1 atm) and corresponds to 10% of the entire carbon fixed in photosynthesis1. The approximate global emission of isoprene is 10^{13} g/yr and it linked to global warming and formation of secondary organic aerosols in the atmosphere via reactions with hydroxyl radicals.2 It has been pointed out, however, that the atmospheric models for the consumption of isoprene do not match the in-canopy chemistry models for its emission.3 In fact, the atmospheric models overestimate the consumption of isoprene during night, when there are not enough (photo-generated) hydroxyl radicals available in atmosphere. Based on their analysis using a electrospray ionization mass spectrometer (ESIMS), Colusii and co-workers4 proposed that gaseous isoprene might be protonated and oligomerized into less volatile compounds at the acidic interface of water droplets and air. If true, this mechanism addresses a major standing problem in atmospheric chemistry and pushes the case of green chemistry via electrospray ionization.4 Herein, we revisit ESIMS experiments along with high-resolution NMR to investigate this problem.

MATERIALS AND METHODS

EXPERIMENTAL RESULTS (ELECTROSPRAY IONIZATION)

Figure 1 – Experimental Methodology for Liquid-Liquid Reactions: 20% (v/v) isoprene in pH-corrected water was set for continuous shaking via a vortexer for 6 hours and the organic phase was analyzed by mass spectrometry and NMR.

Figure 2 – Positive-ion mode mass spectra of the organic phase analyzed at ESIMS; pH 1 aqueous phase. (Max. Intensity: 6,000 a.u.)

Figure 3 – (A) Positive ion mode mass spectra of the organic phase measured at ESIMS; (B) Influence of temperature in the abundance of acetone [M+H]^+ and [2M+H]^+; analyzed at ESIMS. (Max. Intensity: 94,000 a.u.; a.u. = arbitrary units

INSIGHTS

1. The low intensities of ESIMS signals (below 6,000 a.u.) after isoprene was in contact with water, compared to signals for pure isoprene (intensity 110,000 a.u.), contradict the claim of superacidity of the air-water interface at pH < 3.7. As a test case, ESIMS of pure acetone showed presence of clusters (because C-C bond formation between acetone molecules is unlikely due to the fact that we see [2M+H]^+ and not [2M]^+). This fact is further corroborated by effects of temperature on mass spectra, i.e. heavier species are less stable at higher temperatures, suggesting that even the oligomers observed in the case of isoprene were clusters without C-C bond formation (Figure 3).

2. Positive-ion mode mass spectra of isoprene before and after shaking with acidic water were identical, but after ESIMS new peaks (smaller fragments) appeared due to ESI reactions. We consider capillary voltage, rapid evaporation and extreme curvatures of nanodroplets.

3. We conclude that there is no oligomerization of isoprene during mechanical agitation of pH-1-water-isoprene mixtures. Therefore, the isoprene-water (or oil-water) interface does not behave as the air-water interface, previously reported.2 These observations limit the scope of ‘on-water’ chemical reactions as a low-energy, green chemistry route for chemical syntheses.

References: