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Atmospheric oxidation of isoprene and 1,3-butadiene: influence of aerosol acidity and relative humidity on secondary organic aerosol

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Abstract

The effects of acidic seed aerosols on the formation of secondary organic aerosol (SOA) have been examined in a number of previous studies, several of which have observed strong linear correlations between the aerosol acidity (measured as nmol H^+ per m^3 air sample volume) and the percent change of secondary organic carbon (SOC). The measurements have used several precursor compounds representative of different classes of biogenic hydrocarbons including isoprene, monoterpenes, and sesquiterpenes. To date, isoprene has displayed the most pronounced increase in SOC, although few measurements have been conducted with anthropogenic hydrocarbons. In the present study, we examine several aspects of the effect of aerosol acidity on the secondary organic carbon formation from the photooxidation of 1,3-butadiene, as well as extending the previous analysis of isoprene.

The photooxidation products measured in the absence and presence of acidic sulfate aerosols were generated either through photochemical oxidation of SO_2 or by nebulizing mixtures of ammonium sulfate and sulfuric acid into a 14.5 m^3 smog chamber system. The results showed that, like isoprene and β-caryophyllene, 1,3-butadiene SOC yields linearly correlate with increasing acidic sulfate aerosol. The observed acid sensitivity of 0.11 %SOC increase per nmol m^{-3} increase in H^+ was approximately a factor of three less than that measured for isoprene. The results also showed that the aerosol yield decreased with increasing humidity for both isoprene and 1,3-butadiene, although to different degrees. Increasing the absolute humidity from 2 to 12 $g\,m^{-3}$ reduced the 1,3-butadiene yield by 45 % and the isoprene yield by 85 %.

1 Introduction

The role of aerosol acidity to increase formation of secondary organic aerosol (SOA) in the atmosphere continues to be a topic of considerable debate. Field studies at ground level have indicated that increases in ambient secondary organic carbon (SOC) due to ambient acidity are likely subtle. Zhang et al. (2007) examined increases of SOA species in the Pittsburgh area under acidic conditions, found at most a 25 % increase in ambient SOA from the Pittsburgh area that could be attributed to acid catalyzed effects. In another study from the SEARCH network, Tanner et al. (2009) report low apparent impacts to aerosol acidity at the rural sites at Yorkville, GA and Centreville, AL, where biogenic hydrocarbons and anthropogenic oxidants from nearby urban centers might be expected to produce relatively high levels of aerosol acidity in the presence of the oxidation products of biogenic hydrocarbons.

Most laboratory studies aimed at addressing the impact of aerosol acidity on SOA concentrations have focused on isoprene. Emissions of isoprene (C_5H_8) from vegetation constitute the greatest worldwide source of nonmethane hydrocarbons (Guenther et al., 1995). SOC formation from isoprene has been shown to increase in the presence of sulfate acidity in smog chamber experiments (Edney et al., 2005; Surratt et al., 2007), with a variety of organosulfate compounds detected in the aerosol phase (Surratt et al., 2008, 2010).

The effect of acidity to produce organosulfates has been studied mainly for aerosols with strong biogenic inputs. Surratt et al. (2007) initially showed that sulfate esters were formed in the aerosol products from photooxidations of isoprene and α-pinene in the presence of acidic seed aerosol. These products were then compared to those found in ambient aerosol collected at ground sites in the Southeast US (i.e., the SEARCH network) and found to be similar to the laboratory aerosol (Jaoui et al., 2008). Additional studies (Froyd et al., 2010) showed that products of isoprene oxidation could render a single organosulfate compound (IEPOX-sulfate), which comprised up to 3 % of the organic aerosol mass under some conditions in the free troposphere.

On a broader basis, laboratory studies have readily shown that acidic sulfate aerosol produces increased organic aerosol yields from the products of biogenic and anthropogenic oxidation systems (e.g., Jang et al., 2002). Since the initial studies, efforts have been undertaken to quantify the magnitude of the aerosol acidity effect. Surratt et al. (2007) investigated the effect of sulfate acidity on photooxidation products from the isoprene/NO_x system. They found that secondary organic carbon increases linearly with aerosol acidity, $[H^+]_{air}$, an acidity measure that gives its air concentration (nmol m^{-3}) rather than an aerosol pH. Offenberg et al. (2009) extended this same analysis to examine the acidity effects on monoterpenes (α-pinene) and sesquiterpenes (β-caryophyllene). For α-pinene aerosol products, the effect of acidity was found to be independent of organic carbon mass present and was a factor of eight lower than the effect for isoprene. The β-caryophyllene aerosol products, by contrast, showed an effect similar to that for isoprene and a factor of five higher than that for α-pinene. Analysis by Chan et al. (2011) confirmed the presence of organosulfate compounds in β-caryophyllene SOA formed under these conditions. Zhang et al. (2012) performed acidity experiments for 2-methyl-3-buten-2-ol (MBO), a compound structurally related to isoprene. MBO was shown to be less influenced by acidity than isoprene or β-caryophyllene, but more affected than α-pinene. However, this comparison is complicated by the fact that the MBO experiments were conducted under dry conditions using the photolysis of hydrogen peroxide to generate OH radicals; in contrast, Surratt et al. (2007) and Offenberg et al. (2009) relied upon NO_x photochemistry conducted at 30 % RH to generate their data.

Concentrations of the isoprene SOA tracer products, 2-methylthreitol and 2-methylerythritol, have also been found to rise with increased aerosol sulfate acidity. These results suggested that particle phase reactions could contribute to the increased isoprene aerosol yields and compound concentrations. Mechanisms for C_5 and C_{10} organosulfate formation in the atmosphere have been proposed (Surratt et al., 2008). Subsequent studies by Paulot et al. (2009) gave strong evidence that the atmospheric formation of isoprene sulfates under conditions of low nitrogen oxides involved a stable gas-phase C_5-hydroperoxide epoxide. Once uptake of the epoxide into acidified aerosol occurs, inorganic sulfate nucleophiles were able to convert the epoxide to organosulfates, and hydrolysis led to the formation of the 2-methyl tetrols, depending on the competitive rates of different nucleophiles in the aerosol. However, a recent study by Lin et al. (2013) reports measurements made in Chapel Hill, NC, an area impacted by anthropogenic oxidant emissions, that show epoxide formation also occurs through NO_x channel reactions. In these reactions, methylacryloylperoxy nitrate (MPAN), an intermediate stable product from isoprene oxidation, reacts with OH radicals leading to methyl acrylic epoxide (MAE).

While considerable effort has been expended studying acidic effects of biogenic precursors, far less effort has been made to examine such effects on hydrocarbons having an anthropogenic origin. An interesting anthropogenic compound for consideration is 1,3-butadiene (C_4H_6). The main source for this compound is from automotive exhaust emissions, although additional sources from cigarette smoke, evaporative emissions of gasoline, and from biomass combustion have been reported (Anttinen-Klemetti et al., 2006; Dollard et al., 2001; Eatough et al., 1990; Hurst, 2007; Pankow et al., 2004; Penn and Snyder, 1996; Sorsa et al., 1996; Thornton-Manning et al., 1997; Ye et al., 1998). It has been classified as a hazardous compound in the 1990 Clean Air Act Amendments (US EPA, 1996), a carcinogenic and toxic pollutant, and a genotoxic chemical in humans and other mammals (Acquavella, 1996; US EPA, 2002). With respect to aerosol formation, 1,3-butadiene is also of interest as a structural analog for isoprene. SOA formation from 1,3-butadiene has been examined in a number of recent studies (Angove at al., 2006; Sato, 2008; Sato et al., 2011; Jaoui et al., 2014), although with only limited consideration of the effects of aerosol acidity.

The main focus of the present study is to explore some additional aspects of the role of acidic sulfate aerosol of the formation of SOA from isoprene and 1,3-butadiene. For isoprene, we examine the increase of SOA using acidic sulfate derived from the photooxidation of SO_2 to see if the results are consistent with those using nebulized acidic sulfate seed aerosol. In addition, we have measured the extent to which the isoprene analog – 1,3-butadiene – also shows an increase in SOA formation in the presence of acidic aerosol. The results are then compared to biogenic compounds previously studied to determine the relative magnitudes of the effect. In addition, this study attempts to extend the analysis over a broader range of humidities in an effort to assess the impact of aerosol water content on acidic influenced SOA formation. In the previous studies by Surratt et al. (2007) and Offenberg et al. (2009), all measurements were conducted at a single humidity level (30 % RH), while Zhang et al. (2012) examined only dry conditions. Extending these studies to a wider range of hydrocarbons and across a more realistic range of humidities should provide data of greater atmospheric relevance and contribute to further development of acidity-influenced SOA chemistry in air quality models.

2 Experimental

Secondary organic aerosol was generated in a 14.5 m^3 fixed-volume, Teflon-coated reaction chamber. The chamber used a combination of UV-fluorescent bulbs that provided radiation from 300–400 nm with a distribution similar to that of solar radiation to the extent that can be achieved with UV bulbs (Kleindienst et al., 2006). The reaction chamber was operated as a continuous stirred tank reactor having a residence time of 4 h, to produce a constant, steady-state aerosol distribution which could be repeatedly sampled at different seed aerosol acidities.

To supply isoprene and 1,3-butadiene, high concentration gas mixtures were produced in high-pressure cylinders diluted with nitrogen (N_2). Tank concentrations were approximately 2000 ppm for isoprene and 4500 ppm for 1,3-butadiene. The hydrocarbons, NO, and SO_2 (when used) were added through flow controllers into the inlet manifold, where they were diluted and mixed prior to introduction into the chamber. Inorganic aerosol was added to the chamber by nebulizing dilute aqueous solutions of ammonium sulfate and/or sulfuric acid (TSI, Model 9302, Shoreville, MN), with total sulfate concentration of the combined solution held constant in order to maintain stable inorganic concentrations in the chamber. The seed aerosol stream then passed through a ^{85}Kr neutralizer (TSI, Model 3077, Shoreville, MN) and equilibrated to the computer-controlled relative humidity designated for a particular experiment. To change the acidity of the seed aerosol, the ratio of the ammonium sulfate and sulfuric acid solutions was changed to produce a constant aerosol sulfate concentration (typically $\sim 30\,\mu g\,m^{-3}$) across the range of acidities used.

Concentrations of isoprene and 1,3-butadiene in the inlet manifold and chamber were measured using a gas chromatograph with flame ionization detection (Hewlett–Packard, Model 5890 GC). NO and total NO_Y were measured with a ThermoElectron (Model 8840, Thermo Environmental, Inc., Franklin, MA) oxides of nitrogen chemiluminescence analyzer. Temperature and relative humidity were measured with an Omega Digital Thermo-Hydrometer (Model RH411, Omega Engineering, Inc., Stamford, CT).

Aerosol samples were collected on 47 mm Teflo membrane filters (Pall Corporation, Ann Arbor, MI) for determination of the aerosol hydrogen ion concentration per unit volume of air sampled, or $[H^+]_{air}$, expressed as nmol $H^+\,m^{-3}$. Aerosol produced in the chamber was collected at a rate 10 to 20 $L\,min^{-1}$ over a period of approximately 4 h. Filters were extracted by sonication for 30 min using 10 mL of distilled, deionized water in a 50 mL polypropylene vial. Once the extract cooled to room temperature, the pH of each extract was measured with a temperature-compensated Oakton 300 series pH/conductivity meter (OAKTON Instruments, Vernon Hills, IL). The $[H^+]_{air}$ was calculated by dividing the measured aqueous concentration of hydrogen ions by the volume of air collected, as described by Surratt et al. (2007). While this method provides a simple, easily repeatable measure of bulk acidity, it does not fully capture the actual acidity of individual aerosol particles, which is more likely to be of physical significance in these chemical systems. Nevertheless, in the absence of a true aerosol pH measurement, the $[H^+]_{air}$ approach appears to provide a useful surrogate measure under sufficiently constrained experimental conditions.

Measurements of particulate organic carbon were performed with an on-line thermal optical transmittance carbon analyzer using a parallel plate, carbon strip denuder (Sunset Laboratories, Tigard, OR; Birch and Cary, 1997) prior to aerosol collection on the quartz filter within the instrument. Other details of operation for the carbon analyzer on the photochemical reaction chamber are described elsewhere (Offenberg et al., 2007).

The duty cycle for this measurement was 0.75 h (i.e., 0.5 h sampling and 0.25 h analysis times, respectively). All particulate carbon concentrations measured during the interval of aerosol acidity filter collections were averaged for comparison with the integrated measurements of aerosol acidity.

Four different sets of experiments were performed, each involving multiple stages: (1) an isoprene/NO experiment in which different concentrations of SO_2 were used to generate varied levels of aerosol acidity, (2) a 1,3-butadiene/NO experiment in which different nebulizer solutions were used to generate varied levels of aerosol acidity, (3) a pair of isoprene/NO experiments, one using a low concentration ammonium sulfate seed and the other using an acidic inorganic component, in which the inorganic compositions were held constant while the humidity levels were varied, and (4) a comparable pair of 1,3-butadiene/NO experiments in which humidity levels were systematically varied.

In the isoprene/NO experiment (ER370), the initial mixture of isoprene, NO, and SO_2 was irradiated in the chamber until the reaction mixture reached a steady-state concentration. For each of the three successive stages, the SO_2 concentration was progressively reduced and the reaction mixture was allowed to equilibrate. In the final stage, SO_2 was turned off to generate a “base case” aerosol from the isoprene/NO_x reaction alone. In all cases, filter measurements were conducted only after the steady-state condition was achieved.

For the 1,3-butadiene/NO experiment (ER444), an ammonium sulfate solution was used to generate approximately 30 $\mu g\,m^{-3}$ of inorganic aerosol to provide a base case. In subsequent stages, the seed aerosol was made progressively more acidic by reducing the proportion of ammonium sulfate and adding increasing fractions of sulfuric acid to the solution. This approach offers two main advantages over the SO_2 oxidation method described above. First, it provides a consistent level of inorganic aerosol at all stages; in contrast, the SO_2 oxidation produces variable inorganic concentrations, and effectively no inorganic content in the base case without SO_2 addition. Second, the addition of the seed aerosol should have a negligible effect on the gas-phase radical chemistry, which may otherwise be affected by the conversion of SO_2 to sulfuric acid.

For the humidity studies, each hydrocarbon was examined with two different experiments. First, each hydrocarbon/NO system was tested at multiple humidity levels using only a low concentration (1 $\mu g\,m^{-3}$) ammonium sulfate seed aerosol (ER666 for 1,3-butadiene; ER667 for isoprene). This provided a base case for exploring the changes in SOC formation and aerosol yield in the absence of significant aerosol acidity. Relative humidities were varied between roughly 10 and 60 %, which corresponded to absolute humidities of approximately 2 to 14 $g\,m^{-3}$. For isoprene, this base case experiment was then repeated in the presence of a moderately acidic sulfate aerosol, which was held constant across the full range of humidities examined (ER662). For 1,3-butadiene, a more acidic inorganic aerosol, generated using a solution incorporating a higher fraction of sulfuric acid solution to ammonium sulfate solution, was employed (ER444).

3 Results and discussion

The experiments presented here support previous studies suggesting that acidic aerosol can lead to increased SOA formation from the photooxidation of isoprene under laboratory conditions. Changing the source of the acidity from nebulized inorganic aerosol to a more atmospherically relevant photochemical conversion of SO_2 into acidic sulfate aerosol produced only a minor change in the resulting percent increase in SOC per unit increase in $[H^+]_{air}$. In addition, 1,3-butadiene, a chemically similar compound released from primarily anthropogenic sources, was also demonstrated to produce higher concentrations of SOA under acidic conditions. However, the percent change in SOC observed for 1,3-butadiene was significantly lower than that seen for isoprene (0.11 % per nmol m^{-3} vs. 0.31 %) despite the structural similarities between the two hydrocarbons. The additional methyl side group in isoprene (and isoprene oxidation products) may influence reactions with an acidic sulfate nucleophile. The humidity experiments further suggest that humidity, and likely aerosol liquid water content, can have a substantial effect on SOA formation from isoprene and 1,3-butadiene. Increasing humidity produces a notable reduction in SOC formation in both the isoprene and 1,3- butadiene photochemical systems. However, this reduction is more pronounced in both systems in the presence of acidic inorganic aerosols, and was most pronounced for the isoprene/NO system. In the isoprene/NO photochemical systems examined in this study, SOC enhancement due to the presence of acidic inorganic aerosol was observed to be negligible at absolute humidity levels above approximately 11 g H_2O m^{-3}. This lower SOC enhancement at elevated humidities may explain, in part, the difficulties in detecting increased SOA formation under acidic conditions in field studies of ambient air masses. This work suggests that a more detailed understanding of the role of humidity and of aerosol liquid water content is likely required in order to accurately predict the impact of acidity-influenced oxidation chemistry on overall SOA yields. While the data presented here may suggest that enhanced SOA formation via acid influenced pathways is more constrained than previous studies may have suggested, it does still appear to represent a viable pathway for additional SOA formation from a number of precursor hydrocarbons, which may need to be incorporated into air quality models in order to accurately estimate secondary PM concentrations in certain locations.

3.1 Isoprene acidity variation

Data for the isoprene/SO_2 acidity experiment are provided in Table 1. For this experiment, the initial isoprene concentration was 8.4 ppmC, the initial NO was 0.37 ppm, and the relative humidity was 30 % (6.5 g m^{-3} absolute humidity, on average). SO_2 ranged from near background to 0.23 ppm. Residual SO_2 might have contributed to the background $[H^+]_{air}$ of 54 nmol m^{-3}, although this value is more likely due to aerosol-phase organic products of isoprene oxidation, particularly organic acids. However, in terms of the relative changes of percent OC increase, this background value is of little consequence. Generating the acidity with SO_2 allows the $[H^+]_{air}$ to achieve values in excess of 1500 nmol m^{-3}, a value much greater than can be reliably maintained using nebulized solutions. However, unlike nebulized aerosol, the concentrations of inorganic sulfate in the product aerosol vary at each stage of the experiment, as shown in Table 1.

With no added SO_2 (stage ER370-9), the organic carbon from the isoprene reaction resulted in 5.3 µg C m^{-3} of SOC formed (corrected for chamber losses). Percent increases over this base case value ranged from 62 to 459 % at the highest acidity level (1524 nmol m^{-3}). Figure 1 provides a plot of the percent change in OC against the aerosol acidity. As seen in the figure, the relative increase in organic carbon correlated well with increasing acidity with an R^2 of 0.985. The negative intercept resulted from the small amount of acidity measured under the condition without SO_2, and the slope indicates a 0.31 %SOC increase per nmol m^{-3} of increased $[H^+]_{air}$.

Despite employing different mechanisms for generating the acidic aerosol, the agreement in the data between this study and Surratt et al. (2007) is excellent. The %SOC increase appears to be quite consistent (0.31 SO_2 photooxidation vs. 0.32 via nebulization), suggesting both pathways lead to comparable acid enhancements. The results also suggest that variations in the inorganic aerosol loading do not strongly impact the observed %SOC increase, at least under the range of conditions considered, which is consistent with the results previously reported by Offenberg et al. (2009) for α-pinene/NO acidity experiments conducted at different SOC concentrations.

Attempting to expand the SO_2 experiment to incorporate additional humidity conditions revealed a further challenge for the use of SO_2 vs. nebulization of sulfate aerosols in these acidity experiments. Changes to the chamber humidification also resulted in changes in the amount of SO_2 converted to aerosol-phase acidic sulfate, with higher humidity resulting in lower aerosol sulfate concentrations. Nebulized sulfate aerosols, in contrast, appear to retain stable aerosol sulfate concentrations and $[H^+]_{air}$ levels under variable humidity conditions. This limitation could potentially be overcome through the use of a direct measure of acidity in aerosol particles. However, given the inherent limitations of the $[H^+]_{air}$ measurement, the nebulization approach provides a cleaner evaluation of the effects of humidity on SOC formation. For this reason, the remainder of the experiments presented will focus on nebulized inorganic sulfate for the generation of aerosol acidity.

3.2 1,3-butadiene acidity variation

Data for the 1,3-butadiene acidity experiment are provided in Table 2. For these experiments, the initial 1,3-butadiene and NO concentrations were 6.8 ppmC and 0.34 ppm, respectively. The first acidity condition once the reaction started was the base case of pure ammonium sulfate, which rendered a $[H^+]_{air}$ of 48 nmol m^{-3}. The next condition used a nebulizer solution of nominally one-third sulfuric acid and two-thirds ammonium sulfate to give an $[H^+]_{air}$ of 259 nmol m^{-3}; the third case was a nominal one-third ammonium sulfate and two-thirds sulfuric acid giving an $[H^+]_{air}$ of 666 nmol m^{-3}; and the last case used sulfuric acid solution only for an $[H^+]_{air}$ of 963 nmol m^{-3}. The 1,3-butadiene consumed by reaction ranged from 4.9 to 5.2 ppmC and averaged 5.03 ppmC.

Organic carbon concentrations increased with increasing acidity at the fixed relative humidity of 30 % from the base case of 22.6 to 44.7 µg C m^{-3} at the highest acidity condition. SOC concentrations and percent increases from the base case (ammonium sulfate) for the four stages are given in Table 2. The %SOC increases monotonically with sulfate acidity up to nearly a 100 % increase at the highest acidity condition. The yield determined as $[\mathrm{SOC}]/\Delta[\text{1,3-butadiene}_{\mathrm{carbon}}]$ was calculated for each condition and found to increase from 0.009 at the lowest acidity condition to 0.019 at the highest. Since ΔHC remained nearly constant over the entire experiment, the increase in yield was essentially equivalent to the increase in SOC, that is, a factor of two.

Figure 2 provides a plot of the percent change in organic carbon vs. the $[H^+]_{air}$ for 1,3-butadiene SOA at 30 % RH. As seen in the figure, the relative increase in organic carbon correlated well with increasing acidity with an R^2 of 0.967. The negative intercept resulted from the small amount of acidity measured in the base case with the ammonium sulfate nebulizer solution. The plot shows an increase of 0.112 %SOC for each nmol m^{-3} increase in $[H^+]_{air}$.

Figure 2 also compares the results from the 1,3-butadiene system with similar acidity measurements from this laboratory. Superimposed on the sulfate acidity effect from 1,3-butadiene SOA products are measurements made for three biogenic hydrocarbons previously studied: isoprene (Surratt et al., 2007), α-pinene, and β-caryophyllene (Offenberg et al., 2009). In those studies, SOA formation from isoprene, β-caryophyllene, and α-pinene was found to correlate with aerosol acidity as linear relationships with different slopes. From the present work, the 1,3-butadiene case also follows the same trend with a slope larger than that of α-pinene and smaller than that of β-caryophyllene. In all five of these studies, a relative humidity of 30 % was used.

Table 3 further summarizes all the data from these $[H^+]_{air}$ variation experiments. $[H^+]_{air}$ and absolute OC concentrations are given as ranges for the individual studies. For most of the experiments, Fig. 2 shows the relationship between the percent change in SOC concentration compared to the "neutral" base case. All data from experiments with isoprene, α-pinene, and β-caryophyllene are from prior studies in this laboratory (Surratt et al., 2007; Offenberg et al., 2009) and use a chamber relative humidity of 30 %. Table 3 also includes data for the MBO experiment described by Zhang et al. (2012) where SOA was produced under conditions of low NO_x with the aerosol generated through $RO_2 + HO_2$ and $RO_2 + RO_2$ reactions. Unlike the other experiments presented in Table 3, the MBO experiment was conducted under dry conditions (less than 3 % RH).

Overall, the sulfate acidity effect follows the order (from greatest to least effect): isoprene; β-caryophyllene; MBO; 1,3-butadiene; and α-pinene. However, the exact placement of MBO in this range is somewhat questionable given the dramatic differences in experimental conditions used in that study (low NO_x chemistry and dry conditions) compared to the others. In comparing the relative sensitivity of isoprene and 1,3-butadiene to sulfate acidity, there is about a factor of three difference in the %SOC response to increasing $[H^+]_{air}$ despite the general structural similarity of the compounds. This could represent a substituent effect which influences the sensitivity of the gas-phase precursors to reaction by the acidic sulfate nucleophile.

3.3 Isoprene humidity variation

Table 4 provides the initial conditions for the two isoprene/NO experiments designed to examine changes in SOC formation and yield resulting from changes in humidity. In the base case experiment (ER667), the reaction was conducted in the presence of only a low concentration ($\sim 1\,\mu g\,m^{-3}$) of inorganic aerosol produced through the nebulization of a $10\,mg\,L^{-1}$ ammonium sulfate solution. The relative humidity was then changed in stages from 9 to 49 % in ∼ 10 % increments. At each stage, the chamber was allowed to equilibrate before a complete set of $[H^+]_{air}$, SOC, and ΔHC measurements were made. Measured $[H^+]_{air}$ values averaged $54\,nmol\,m^{-3}$ over the course of the experiment, a level consistent with previous non-acidified isoprene/NO systems (both Surratt et al., 2007 and ER370 reported above). In addition, a comparable experiment (ER662) was conducted using a moderately acidic inorganic aerosol generated via nebulization of a mixed ammonium sulfate and sulfuric acid solution. In this experiment, duplicate measurements were made at steady-state relative humidity levels of 8, 28, 44, and 18 %. In this experiment, the measured $[H^+]_{air}$ values averaged $275\,nmol\,m^{-3}$. Based upon previous isoprene acidity experiments, this modest level of sulfate acidity would be expected to produce an increase in SOC of approximately 50–75 % at a relative humidity of 30 %.

Figure 3 provides a plot of the measured SOC levels as a function of humidity for these two isoprene systems. Due to temperature differences between these experiments (and the 1,3-butadiene experiments described below), measures of chamber relative humidity have been converted into absolute humidity ($g\,H_2O\,m^{-3}$) to provide a common basis for all four experiments. It is unclear whether relative humidity or absolute humidity is of greater physical significance in the systems under consideration. A direct measure of aerosol liquid water content would likely be a more appropriate metric than either relative or absolute humidity for this study. However, no method for the analysis of aerosol liquid water content was available for these experiments.

For the base case experiment, the SOC values range from a high of 13.3 $\mu g C m^{-3}$ at the lowest humidity level (2.6 $g H_2O m^{-3}$) to just over 3 $\mu g C m^{-3}$ at the higher humidities (10.4 to 13.1 $g m^{-3}$). For the acidified experiment, SOC declined from above 30 $\mu g C m^{-3}$ at the lowest humidity level (2.2 $g m^{-3}$) to around 4 $\mu g C m^{-3}$ under the highest humidity condition (11.3 $g m^{-3}$). Although the absolute humidities considered in the two experiments do not correspond precisely, the percent increase in SOC for the acidic experiment vs. the base case ranges from approximately 140 % at the lowest humidity levels, to approximately 65–75 % in the mid-range (where these experiments best overlap with the previous SOC vs. $[H^+]_{air}$ studies), to virtually no statistical difference between SOC levels above approximately 11 $g H_2O m^{-3}$. Figure 4 provides SOC yield curves for these two isoprene/NO scenarios. As in the experiments described in the previous sections, the humidity changes performed here had a minimal impact on the measured ΔHC. As a result, the isoprene/NO yield plots follow essentially the same pattern as that seen for SOC formation in Fig. 3.

These results suggest that humidity can have a profound effect on the acid-derived enhancement of SOC formation from isoprene. Although the range of conditions explored is limited (only a single bulk acidity level; only a partial range of relative humidities; and only a comparatively narrow temperature range, by atmospheric standards), the data imply that under some circumstances, high humidity (or perhaps high aerosol water content) can essentially suppress enhanced SOC formation from isoprene photochemistry. These results also reinforce the fundamental weakness of the $[H^+]_{air}$ measurement as a surrogate for acidity levels in actual aerosol particles. Although the bulk acidic potential of the systems, as measured by $[H^+]_{air}$, does not change significantly over the range of humidities considered, the resulting changes in the SOC concentrations suggest that the pH in aerosol particles may be changing significantly due to variations in aerosol liquid water content, solution ionic strength, or other factors not effectively captured by the $[H^+]_{air}$ measurement.

3.4 1,3-butadiene humidity variation

Conditions for the two 1,3-butadiene/NO experiments for examining changes due to humidity variations are presented in Table 4. As described above, the base case experiment (ER666) was conducted in the presence of ~ 1 $\mu g\,m^{-3}$ of ammonium sulfate aerosol. The relative humidity was then changed in stages from 10 to 60 % in increments of roughly 10 % each. This was compared with an additional experiment (ER444) employing an acidic inorganic aerosol nebulized from solution, with measurements made at steady-state relative humidity levels of 31, 50, 10, and 62 %. The nebulizer solutions used in ER444 used higher levels of sulfuric acid relative to ammonium sulfate that the isoprene experiment described above (ER662). This produced a more acidic inorganic aerosol, with measured $[H^+]_{air}$ values of 718 $nmol\,m^{-3}$ on average observed for the 1,3-butadiene acidic aerosol experiment.

Figure 5 provides a plot of the measured SOC levels as a function of humidity for these two 1,3-butadiene systems. For the base case experiment, the SOC values range from a high of 45.1 $\mu g\,C\,m^{-3}$ at the lowest humidity level (2.5 $g\,H_2O\,m^{-3}$) to 24.7 $\mu g\,C\,m^{-3}$ at the higher humidity (13.6 $g\,m^{-3}$). For the acidified experiment, SOC declined from 60.3 $\mu g\,C\,m^{-3}$ at the lowest humidity level (1.9 $g\,m^{-3}$) to 31.1 $\mu g\,C\,m^{-3}$ under the highest humidity (12.3 $g\,m^{-3}$). The range in SOC enhancement from the base case to the acidified case is far lower than that observed in the isoprene system, ranging from approximately 35 % at low humidity to 25 % at high humidity. These enhancements are somewhat lower than would be expected for this level of acidity based on the data presented in Fig. 2. SOC yield curves, provided in Fig. 4, follow this same trend, as the ΔHC shows only minimal variation with humidity.

These results are markedly different from those seen for isoprene/NO, both in terms of the level of SOC enhancement under the acidic condition and the extent to which the SOC enhancement declines with increasing humidification. It is not clear what factors are driving this difference in behavior. Part of the difference likely derives from structural differences between the two molecules, as was described above with respect to the SOC vs. $[H^+]_{air}$ studies. Additionally, the higher level of $[H^+]_{air}$ used for the 1,3-butadiene experiment may be partially offsetting the impact of increasing humidity, as more aerosol liquid water would be needed to reduce actual particle acidity under these conditions. Other factors, such as the relative hygroscopicity of isoprene and 1,3-butadiene SOA, may also be contributing. Further experimentation is needed to attempt to better understand which aspects of these aerosol systems are physically significant for activation or deactivation of these acid-influenced reaction pathways, in order to determine if these pathways are ultimately important to SOA formation in the ambient atmosphere.

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Table 1. Isoprene SOA as a function of sulfate acidity from the photooxidation of SO_2.

Stage	Initial SO_2 (ppb)	SO_4^{-2} ($\mu g\,C\,m^{-3}$)	$[H^+]_{air}$ ($nmol\,m^{-3}$)	OC ($\mu g\,C\,m^{-3}$)	OC Increase (%)	SOC Yield
ER370-9	11[a]	0	54	5.3	0.0	0.002
ER370-8	55	8.7	324	8.6	62	0.003
ER370-7	88	15.3	457	10.9	105	0.004
ER370-4	136	31.1	912	16.8	214	0.006
ER370-1	231	59.2	1524	29.8	459	0.011

[a] Measurement subject to possible HC interference. No SO_2 was added in stage ER370-9.

Table 2. Conditions and OC data for 1,3-butadiene photooxidation with the nebulized inorganic aerosol. For each stage, the initial 1,3-butadiene was 6.8 ppmC; initial NO was 0.34 ppm; and relative humidity was 30 % (6.1 g m^{-3} absolute humidity).

Stage	$[H^+]_{air}$ (nmol m^{-3})	OC (µg C m^{-3})	OC % Increase	ΔHC (ppmC)	SOC Yield
ER444-1	48	22.6	0.0	5.0	0.009
ER444-2	259	28.3	25	5.0	0.012
ER444-3	666	41.6	84	5.2	0.016
ER444-4	963	44.7	98	4.9	0.019

Table 3. Summary of the normalized yields for sulfate acidity effect for precursor hydrocarbons studied to date. SOA formed in the presence of NO_x at 30 % RH, except where indicated.

SOA precursor	$[H^+]_{air}$ ($nmol\,m^{-3}$)	[OC] ($\mu g\,C\,m^{-3}$)	Normalized OC Change[a]	Reference
1,3-Butadiene	48–963	22.6–44.7	0.11	(this work)
Isoprene[b]	54–1524	5.3–29.8	0.31	(this work)
Isoprene	32–517	12.2–31.1	0.32	Surratt et al. (2007)
α-pinene (low OC)	68–1229	8.0–11.6	0.044	Offenberg et al. (2009)
α-pinene (high OC)	153–1014	40.5–55.3	0.039	Offenberg et al. (2009)
β-caryophyllene	112–1147	10.0–34.0	0.22	Offenberg et al. (2009)
2-Methyl-3-butene-2-ol (MBO)[c]	125–1590	6.5–21.9	0.14	Zhang et al. (2012)

[a] %SOC change per $[H^+]_{air}$;
[b] acidity generated from SO_2 photooxidation;
[c] experiment conducted in the absence of NO_x under dry conditions.

Table 4. Reaction conditions for humidity variation experiments.

Exp	Hydrocarbon	Inorganic	HC (ppmC)	NO_x (ppm)	Humidity ($g\,m^{-3}$)
ER667	Isoprene	Low Conc $(NH_4)_2SO_4$	8.2	0.35	2.6–13.1
ER662	Isoprene	1/2 $(NH_4)_2SO_4$, 1/2 H_2SO_4	7.0	0.29	2.2–11.3
ER666	1,3-Butadiene	Low Conc $(NH_4)_2SO_4$	7.1	0.42	2.5–13.6
ER444	1,3-Butadiene	1/3 $(NH_4)_2SO_4$, 2/3 H_2SO_4	6.9	0.34	1.9–12.3

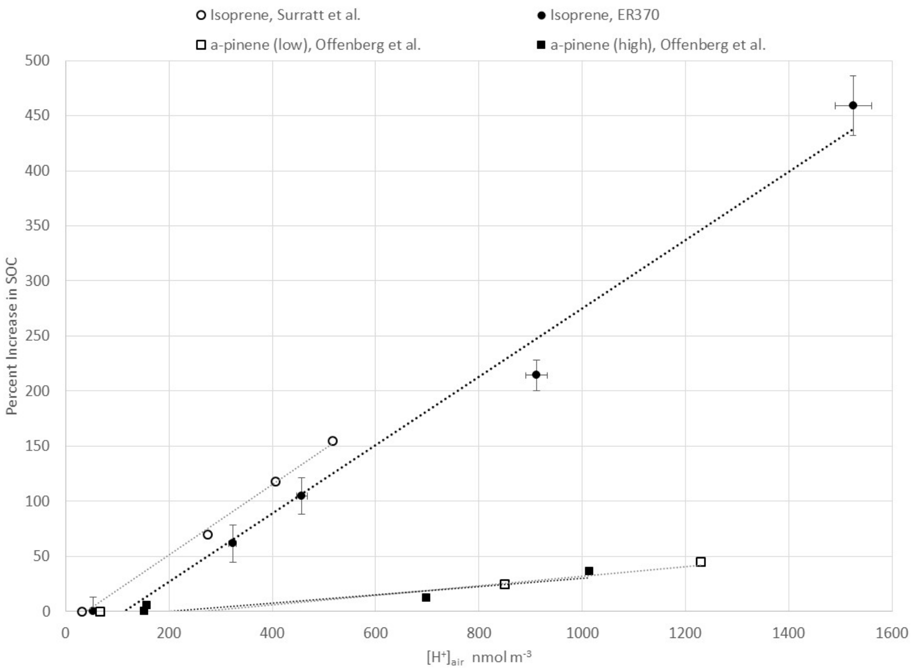

Figure 1. A comparison of the sulfate acidity effect for isoprene SOA. For Surratt et al. (2007) (open circles), the acidity was derived from nebulized sulfate aerosol. In the present study (closed circles), the acidity was derived from the photooxidation of SO_2.

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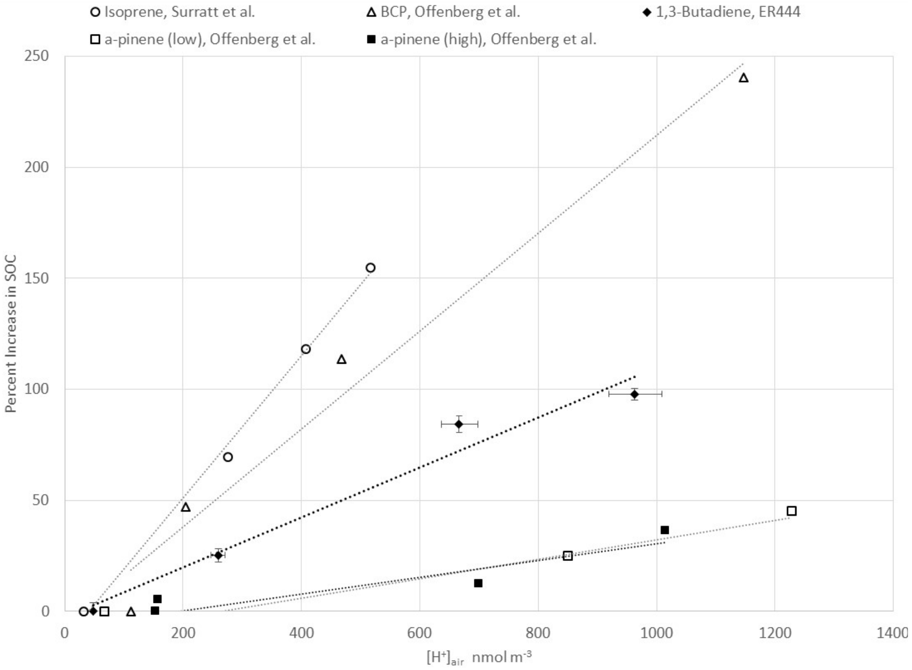

Figure 2. Aerosol acidity effect for 1,3-butadiene/NO, relative to previously published data (Surratt et al., 2007; Offenberg et al., 2009). All experiments were conducted with nebulized sulfate aerosol at 30 % RH.

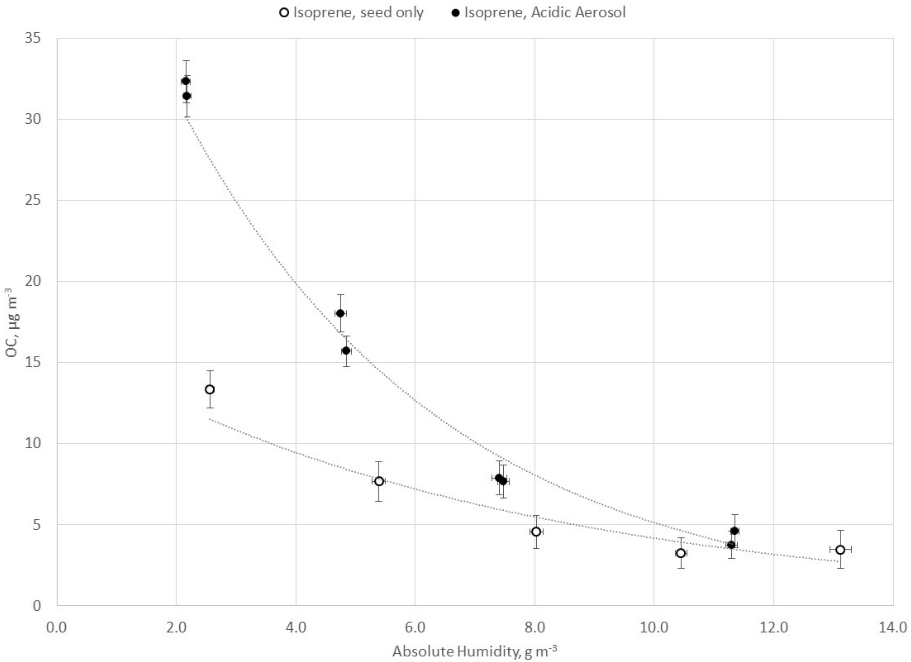

Figure 3. A comparison of the effects of humidity variation on isoprene/NO SOC formation. In ER667 (open circles), only a low concentration ammonium sulfate seed aerosol was present. In ER662 (closed circles), a moderately acidic sulfate aerosol was generated via nebulization.

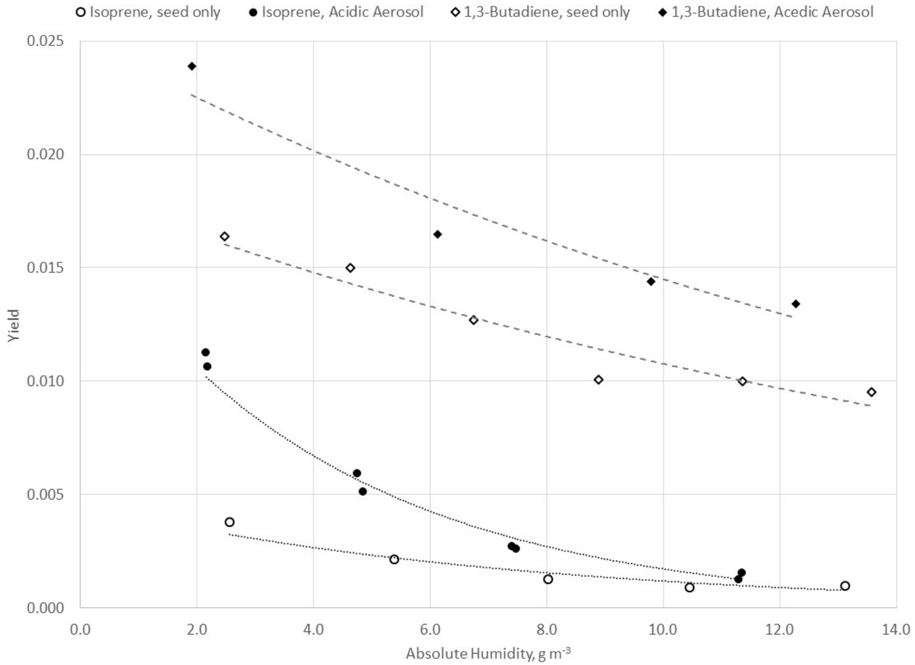

Figure 4. SOC yields for isoprene/NO and 1,3-butadiene/NO as a function of absolute humidity. In ER667 (isoprene, open circles) and ER666 (1,3-butadiene, open diamonds), only a low concentration ammonium sulfate seed aerosol was present. In ER662 (isoprene, closed circles) and ER444 (1,3-butadiene, closed diamonds), an acidic sulfate aerosol was present.

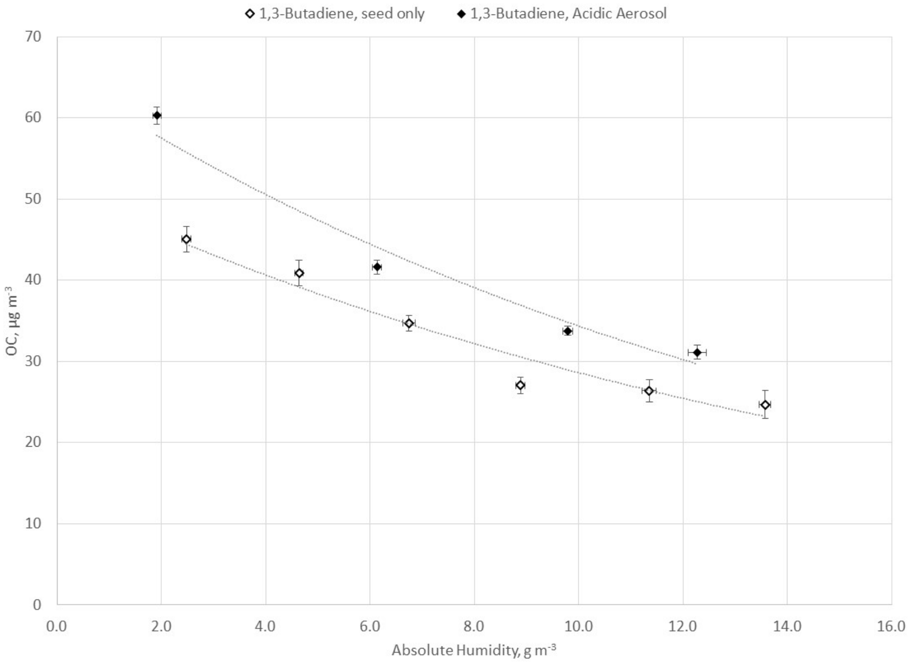

Figure 5. A comparison of the effects of humidity variation on isoprene/NO SOC formation. In ER666 (open diamonds), only a low concentration ammonium sulfate seed aerosol was present. In ER444 (closed diamonds), an acidic sulfate aerosol was generated via nebulization.