

A study on photo-oxidation under high-NO_x conditions forming secondary organic aerosols from isoprene

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ABSTRACT

The oxidation of isoprene (2-methyl-1,3-butadiene) is known to play a central role in the photochemistry of the troposphere, but is generally not considered to lead to the formation of secondary organic aerosol (SOA), due to the relatively high volatility of known reaction products. However, in the chamber studies described here, we measure SOA production from isoprene photo-oxidation under high-NO_x conditions, at significantly lower isoprene concentrations than had been observed previously. Mass yields are low (0.9-3.0%), but because of large emissions, isoprene photo-oxidation may still contribute substantially to global SOA production. Results from photo-oxidation experiments of compounds structurally similar to isoprene (1,3-butadiene and 2- and 3-methyl-1-butene) suggest that SOA formation from isoprene oxidation proceeds from the further reaction of first-generation oxidation products (i.e., the oxidative attack of both double bonds). The gas-phase chemistry of such oxidation products is in general poorly characterized and warrants further study.

Key words: Photo-oxidation, isoprene, NO_x, Secondary organic aerosols.

INTRODUCTION

Isoprene (2-methyl-1,3-butadiene, C₅H₈) is the most abundant non-methane hydrocarbon emitted into the troposphere. Global emissions are estimated at 500 Tg/year [Guenther *et al.*, 1995], and concentrations of several ppb are routinely measured in deciduous forests. Because of its large concentrations and high reactivity with the hydroxyl radical (OH), isoprene can have a major impact on tropospheric photochemistry, and in particular regional ozone production, in both rural and urban environments [e.g., Trainer *et al.*, 1987; Biesenthal *et al.*, 1997]. The initial steps of the OH-isoprene reaction (under high-NO_x conditions) are generally well understood. While product yields vary somewhat among different laboratory studies, and structures of all products are not fully established, total carbon balance is close to 100% [Zhao *et al.*,

2004]. Fragmentation to C₄ compounds, most importantly methyl vinyl ketone and methacrolein, accounts for ~50-70% of the reacted isoprene; the remainder leads to multifunctional C₅ products, hydroxynitrates (4-14%), hydroxycarbonyls (15-19%), 3-methylfuran (<2-5%), and carbonyls (8%) [Tuazon and Atkinson 1990; Paulson *et al.*, 1992; Miyoshi *et al.*, 1994; Chen *et al.*, 1998; Sprengnether *et al.*, 2002; Zhao *et al.*, 2004; Baker *et al.* 2005]. Because of the relatively high volatility of these products, oxidation of isoprene is generally not considered to contribute significantly to the formation of secondary organic aerosol (SOA) in the troposphere. Indeed, chamber studies by Pandis *et al.* [1991] and Edney *et al.* [2005] found that the photo-oxidation of isoprene (at concentrations below a few hundred ppb) leads to insignificant SOA growth, suggesting that condensable compounds are not formed in sufficient concentrations to

partition into the aerosol phase. Recent work suggests isoprene may instead contribute to organic aerosol via routes other than the gas-phase formation of condensable oxidation products. Tetrols with the same carbon backbone as isoprene have recently been measured in ambient aerosols [Claeys *et al.*, 2004a] and are believed to be formed by the heterogeneous acidcatalyzed oxidation of isoprene in the presence of peroxides [Claeys *et al.*, 2004b]. Edney *et al.*, [2005] observed aerosol growth from isoprene photo-oxidation when SO₂ was added to the chamber, acidifying the aerosol seed; tetrols and related compounds accounted for 6% of aerosol mass. Heterogeneous reaction of isoprene under highly acidic conditions was also observed to lead to the formation of polymeric, humic-like substances [Limbeck *et al.*, 2003]. Uptake of volatile, water-soluble isoprene oxidation products (such as glycolaldehyde and hydroxyacetone [Matsunaga *et al.*, 2003]) may also contribute to aerosol growth, though laboratory studies on such a mechanism are scarce. Polymerization of methylglyoxal, a second-generation product, has been suggested to contribute to SOA growth [Kalberer *et al.*, 2004]; however, growth from methylglyoxal uptake was not observed in recent chamber experiments [Kroll *et al.*, 2005]. Finally, models [Ervens *et al.*, 2004; Lim *et al.*, 2005] predict that cloud processing of watersoluble isoprene oxidation products may also lead to the formation of low-volatility SOA components. Thus isoprene might contribute to the organic fraction of tropospheric aerosol via a number of pathways, though most are poorly understood or await experimental verification. To our knowledge, only the studies of Pandis *et al.* [1991] and Edney *et al.* [2005] have investigated whether SOA is formed directly from condensable isoprene photo-oxidation products. In the present work, we investigate the gas-phase oxidation of isoprene under different reaction conditions (at lower temperatures and with a different radical precursor), observing SOA formation at lower isoprene concentrations than have been observed previously. Aerosol yield is small compared to that of other SOA-forming reactions, but given the large source strength of isoprene, isoprene may still have an impact on SOA production on both the local and global scales. We

show that the SOA is likely formed from the oxidation of first-generation oxidation products, the chemistry of which is generally poorly understood.

MATERIAL AND METHODS

Experiments are carried out in 28 m³ Teflon chambers [Cocker *et al.*, 2001; Keywood *et al.*, 2004] at ~25-28°C and 40-50% relative humidity. Aqueous ammonium sulfate seed particles, providing surface area for the initial condensation of condensable products, are introduced into the chamber (at volume concentrations of 10-25 µm³/cm³) by atomization of a 0.03 M salt solution. A known concentration of isoprene is then introduced by sending air over a measured volume of the pure compound (Aldrich, 99.8%) and into the chamber. Nitrous acid (HONO) is used as the OH precursor. HONO is prepared by dropwise addition of 1% NaNO₂ into 10% H₂SO₄ and introduced by blowing dry air over the mixture and into the chamber; this also introduces NO_x as a side product. Reaction is initiated by irradiation of the chamber with blacklights centered at 354 nm, efficiently photolyzing HONO to OH and NO; only 10% of available lights are used to minimize temperature increases.

After ~3h of irradiation, the chamber temperature rises by 1-2°C, and relative humidity decreases correspondingly (RH never drops below 40%, the efflorescence point of ammonium sulfate). Isoprene decay is monitored using GC-FID, and commercial monitors (Horiba) are used to measure O₃ (by UV absorption) and NO_x (by conversion to NO by activated carbon, followed by NO+O₃ chemiluminescence). HONO is not measured directly but might be detected by the NO_x monitor as NO₂ (or NO); consideration of the rate of isoprene decay after reaction initiation suggests [HONO] is unlikely to be significantly greater than measured [NO₂].

Aerosol growth is monitored using two instruments, a differential mobility analyzer (DMA, for the measurement of aerosol volume) and an Aerodyne aerosol mass spectrometer (AMS, for the measurement of aerosol mass and composition [Jayne *et al.*, 2000]).

RESULTS AND DISCUSSION

Prior to irradiation, isoprene concentrations are stable and no organic growth is observed, indicating that heterogeneous reaction of isoprene (or reaction with HONO) does not contribute to aerosol growth. Once the lights are turned on, isoprene is observed to decay immediately, and is consumed within 120 minutes (at the highest concentration studied). Measured NO_x increases slightly from the photolysis of HONO, reaches a maximum after 25-35 minutes, and then decreases throughout the remainder of the experiment due to chain-termination (HO_x+NO_x) reactions. The evolution of concentrations during a typical experiment is shown in Figure 1.1.

Aerosol growth, measured by both the DMA and the AMS, is observed at all isoprene concentrations studied. Growth typically begins 20-30 minutes after reaction initiation, corresponding approximately to when NO approaches zero and the formation of O₃ begins. AMS spectra indicate the growth is indeed by condensation of organic matter, rather than by uptake of inorganic nitrate, water, etc. At the highest isoprene concentrations (e.g. 250 ppb), additional particle formation is even observed. By contrast, no growth is observed from the photooxidation of 500 ppb propene under similar conditions.

Experimental conditions and results are given in Table 1.1. All growth data reported are from DMA measurements; growth measurements from the AMS are in general agreement. SOA growth is corrected for loss to the walls by applying a size-dependent first-order loss coefficient [Keywood et al., 2004], with typical corrections of 1.37-1.5-5.0 μm³/cm³ over the course of a 3-h experiment. At the lowest concentrations studied (25 and 50 ppb), particle growth is of the same order as loss to the chamber walls, so further work is necessary to determine whether SOA growth occurs at concentrations typical for the troposphere (<10 ppb). Shown in Figure 1.2 is particle growth as a function of isoprene reacted; the nonlinear relationship is typical for SOA-forming reactions [Kroll and Seinfeld, 2005]. Comparison of DMA and AMS data indicates the organic aerosol has a density of ~1.4 g/cm³, leading to mass yields (ratios of organic aerosol formed to amount of hydrocarbon reacted) of 0.9-3.0%. There is no obvious dependence of aerosol growth on initial seed particle volume.

Our observation of aerosol growth from the photo-oxidation of isoprene, even at relatively low concentrations, is in contrast with the results of Pandis et al. [1991] and Edney et al. [2005]. Pandis et al. [2005] observed no growth at <120 ppb isoprene, and mass yields never exceeding 1.4% (0.8% carbon yield) at high (ppm) concentrations;

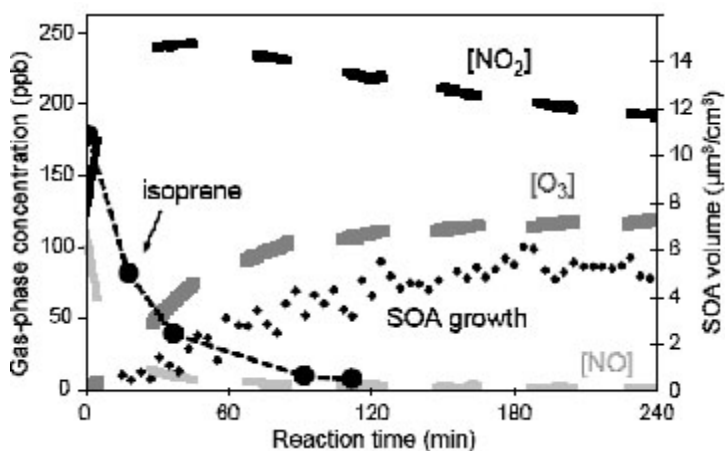


Fig. 1.1: A typical experiment (no. 6 in Table 1.1), showing [isoprene] (black circles), [O₃] (dark gray lines), [NO] (light gray lines), [NO₂] (black lines), and particle volume increase (black dots) as a function of reaction time. Gaps in the O₃ and NO_x data are a result of switching between chambers

Edney et al. [2005] observed even less growth (yield of 0.2% at 1.6 ppm isoprene reacted). Such differences likely arise from differing experimental conditions: for example, in our experiments RH and ammonium sulfate seed loadings are higher than those of the previous studies. Moreover, those experiments were carried out at temperatures of $\sim 30^{\circ}\text{C}$, about 10 degrees warmer than the present experiments. Such a temperature difference is expected to have a large effect on gas-particle partitioning. In addition, the oxidative conditions in those studies are different from those of the present experiments. In the studies by Pandis et al. [1991] and Edney et al. [2005], reaction was initiated by irradiation of NO_x /isoprene mixtures. The hydroxyl radical is formed from a number of secondary reactions, including ozone photolysis to form $\text{O}(^1\text{D})$, heterogeneous production of HONO , isoprene ozonolysis, and the $\text{O}(^3\text{P})$ +isoprene reaction [Paulson et al., 1992].

In the present investigation, OH is produced directly from the photolysis of HONO , and JNO_2 is a factor of 3-10 lower, leading to the lower ozone levels in our experiments. Based upon the measured ozone production and rate of isoprene decay in our experiments (Figure 1.1), the O_3 -isoprene reaction cannot account for more than a small fraction of the total isoprene reacted; it is likely to be more important in isoprene/ NO_x photo-oxidation experiments.

In addition, the NO concentrations reported in those experiments do not approach zero, in contrast to the present experiments. High concentrations (10's of ppb or more) of NO may have the effect of suppressing SOA growth [e.g., Johnson et al., 2005], which might explain the lack of observed growth in the previous studies. As noted above, condensable compounds partitioning into the aerosol phase are unlikely to be any of the known first-generation products of OH +isoprene, as they are all relatively volatile. It is possible that a minor, as yet unidentified, product (yield $\sim 2\%$) may be responsible for SOA production. However, the observed time lag between the decay of isoprene and particle growth (Figure 1.1) suggests SOA is instead formed by the further oxidation of first-generation oxidation products [Bowman et al., 1997]. The role of second-generation oxidation products in SOA formation is also suggested by measurements of aerosol growth from the photo-oxidation of compounds structurally similar to isoprene. No growth was observed from the photo-oxidation experiments of monoalkene C_5 analogs of isoprene (500 ppb of 2- and 3-methyl-1-butene). Such compounds are expected to undergo only one oxidation step under our reaction conditions: first-generation reaction products are expected to be unreactive towards NO_3 and O_3 , and to react with OH slowly (at a rate 10-100 times slower than if a second double bond were present). By contrast, photo-oxidation of the C_4 analog of isoprene, 1,3-

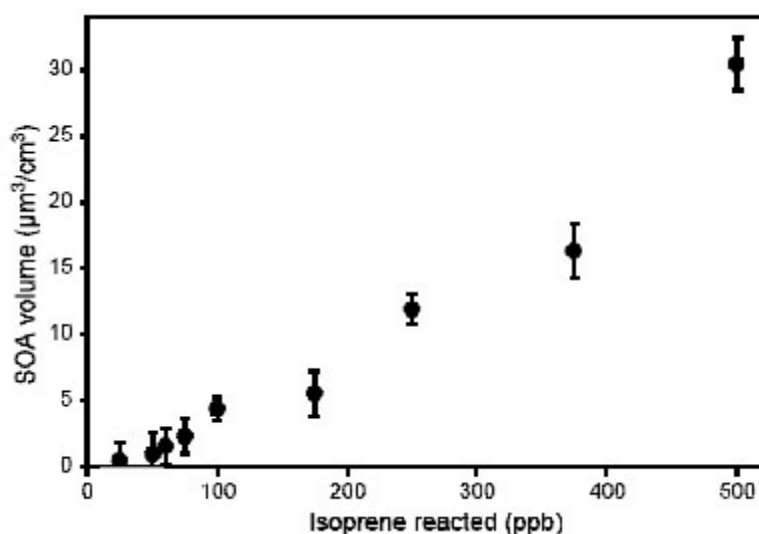


Fig. 1.2: Aerosol growth as a function of concentration of isoprene reacted

butadiene, was observed to lead to aerosol growth, though in lower yields (1.5% at 560 ppb). Thus the aerosol formation we observe is likely the result of oxidation of both double bonds of isoprene. This can lead to a complex array of reaction products, with up to four functional (hydroxy, carbonyl, carboxylic acid, or nitrate) groups; such tetrasubstituted compounds are likely to be of sufficiently low volatility to partition efficiently into the aerosol phase. Their formation route may be complex, due to the number of potential oxidation routes available to first-generation oxidation products.

While the loss of isoprene is dominated by reaction with OH, ozone and the nitrate radical (NO₃) are formed over the course of the experiment and so may react with OH isoprene oxidation products to form condensable compounds; photolysis of such products may also play a role. The importance of these different oxidation pathways and the product yields of each are for the most part poorly constrained, as the atmospheric fates of first-generation isoprene oxidation products (other than methacrolein and methyl vinyl ketone) have received little study. Measurements of rates and products of the gas-phase oxidation of these compounds would be very useful. In preliminary photo-oxidation experiments of isoprene oxidation

products, we observe no aerosol growth from methyl vinyl ketone (500 ppb) but do from methacrolein (2.2% yield at 100 ppb). Oxidation of 3-methylfuran was also observed to lead to SOA formation (3.5% yield at 100 ppb); the oxidation of other multifunctional products of OH+isoprene are also likely candidates for SOA formation. We note that from the AMS spectra we do not observe significant organic signal at high masses ($m/z > 130$), which might suggest that particle-phase oligomers, observed in other SOA-forming reactions [e.g., Kalberer *et al.*, 2004], are not major components of SOA produced from isoprene oxidation. However, it is possible that oligomers are formed but are not detected by the AMS, due to fragmentation and the relatively small total organic signal. Further study of the chemical composition of SOA and the effects of seed composition and loading on particle growth is required to understand the role of particle-phase reactions. The photo-oxidation of isoprene, even with small (<1%) SOA yields, may be an important contributor to global SOA production, given the large source strength of isoprene (~500 Tg/year); global production of SOA from other precursor VOC's is estimated at 12-70 Tg/year [Kanakidou *et al.*, 2005]. From the present results alone it is difficult to estimate global SOA production from isoprene oxidation, as these measurements are only at high concentrations of isoprene and NO_x. Very recent

Table 1: Experimental conditions and results

Exp. No	Isoprene (ppb)	Seed volume ($\mu\text{m}^3/\text{cm}^3$) ^a	[NO] ₀ (ppb)	[NO ₂] ₀ (ppb)	[NO _x] _{max} (ppb)	[NO ₃] _{max} (ppb)	T (°C) ^e	RH ^c	SOA Volume ($\mu\text{m}^3/\text{cm}^3$) ^a	SOA yield ^d
1	500	11.0±0.7	138	124	280	n.m ^e	20.3	43.9%	30.4±2.0	3.0%
2	250	10.0±0.6	85	147	242	70	20.1	42.4%	11.9±1.2	2.3%
3	100	14.8±0.6	85	136	240	4	19.9	47.3%	4.4±0.8	2.2%
4	50	17.4±1.0	100	98	213	10	20.8	46.6%	0.9±1.6	0.9%
5	25	12.2±0.9	87	102	202	25	20.9	41.1%	0.5±1.3	1.1%
6	175	17.1±1.3	107	120	240	119	20.2	44.2%	5.5±2.1	2.1%
7	375	25.6±0.9	107	120	239	213	20.5	49.5%	16.3±1.7	1.6%
8	75	17.4±0.8	75	165	255	32	21.9	48.1%	2.3±1.3	1.5%
9	30	13.2±0.7	83	139	249	24	21.2	43.1%	1.5±1.4	1.2%

Stated uncertainties (2 σ) are from noise in the DMA measurements. b May include contribution from HONO. c Averaged over the course of the experiment. d Assuming a density of 1.4 g/cm³. E Not measured. f Accurate initial values of NO_x were not obtained for this experiment but are expected to be similar to those of Expt. 6

results from our laboratory show that aerosol is formed from isoprene photo-oxidation initiated by H_2O_2 photolysis as well, indicating that isoprene may also serve as a source of SOA in low- NO_x (remote) regions, and that oxidation of isoprene by OH alone (with no O_3 or NO_3 present) leads to aerosol formation. In a forthcoming paper we will discuss the NO_x dependence of the aerosol yield, and the chemical composition of the SOA produced, in order to better understand the chemical mechanism of

aerosol growth by isoprene photo-oxidation.

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