

## Kinetic Study of the OH-isoprene and O<sub>3</sub>-isoprene reaction in the atmosphere simulation chamber, SAPHIR

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[1] Kinetic studies conducted in the new atmosphere simulation chamber SAPHIR at the Research Center Jülich allow a thorough investigation of oxidation of isoprene induced by O<sub>3</sub> and the OH radical under atmospheric conditions. Rate coefficients for the O<sub>3</sub>-isoprene and OH-isoprene reaction are determined from measured concentration-time profiles. For the reaction of O<sub>3</sub> with isoprene the rate coefficient is determined to be  $(9.6 \pm 0.7) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 286 K. The rate coefficient for the reaction OH + isoprene is  $(10.0 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 294 K. The kinetic parameters determined in SAPHIR at atmospheric concentrations agree well with recent recommendations. **INDEX TERMS:** 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques. **Citation:** Karl, M., Th. Brauers, H.-P. Dorn, F. Holland, M. Komenda, D. Poppe, F. Rohrer, L. Rupp, A. Schaub, and A. Wahner (2004), Kinetic Study of the OH-isoprene and O<sub>3</sub>-isoprene reaction in the atmosphere simulation chamber, SAPHIR, *Geophys. Res. Lett.*, 31, L05117, doi:10.1029/2003GL019189.

### 1. Introduction

[2] Isoprene (2-methyl-1,3-butadiene) plays an important role for the chemistry of the lower troposphere and in particular of the continental boundary layer. An estimated global emission rate of approximately  $500 \text{ TgCyr}^{-1}$  [Guenther *et al.*, 1995] and its high reactivity towards OH radicals make isoprene the most important biogenically emitted volatile organic compound (VOC). Once emitted it reacts readily with the OH radical. The atmospheric lifetime of isoprene is 1–2 h during daytime [Atkinson, 2000]. Isoprene thus strongly contributes to regional ozone formation [Wiedinmyer *et al.*, 2001]. The atmospheric residence time of isoprene at night is primarily determined by the reaction with the nitrate radical NO<sub>3</sub> (50 min at 20 ppt NO<sub>3</sub>, [Atkinson, 2000]). Despite the longer lifetime (about 22 h at 40 ppb O<sub>3</sub>), the reaction of O<sub>3</sub> with isoprene is still important since it represents a source of OH radicals [Paulson and Orlando, 1996]. Numerous kinetic studies have been performed within the last two decades to elucidate the atmospheric oxidation of isoprene. Absolute rate constants for OH radical and O<sub>3</sub> reactions have been obtained in flow systems using excess reactant concentra-

tions. Irradiations of NO<sub>x</sub>-isoprene-air mixtures were performed in indoor and outdoor smog chambers [Carter and Atkinson, 1996]. These investigations aimed to derive the mechanism involved in photochemical ozone formation of isoprene using high NO<sub>x</sub> mixing ratios in the range of several ppm which is much larger than typical atmospheric abundances.

[3] Here we present for the first time simulation chamber studies of the initial steps of the degradation of isoprene (ISO) at tropospheric concentrations:



Additionally the behaviour of the reaction system was investigated using model simulations to make sure that the experiments were only sensitive to the respective reaction of interest. The current model for tropospheric degradation of isoprene from Geiger *et al.* [2003] incorporated into the regional atmospheric chemistry mechanism (RACM, [Stockwell *et al.*, 1997]) was used to identify the main reaction pathways.

### 2. The Atmosphere Simulation Chamber

[4] The Atmosphere Simulation Chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber) consists of double-walled Teflon FEP bag of cylindrical shape (length  $\approx 20 \text{ m}$ , diameter  $\approx 5 \text{ m}$ , effective volume  $V_c \approx 270 \text{ m}^3$ , surface/volume  $\approx 1 \text{ m}^{-1}$ ) that is held by a steel frame.

[5] Typically 80% of the outside actinic flux (290 nm–420 nm) is available inside the chamber. Technical details of the SAPHIR chamber are described by Rodriguez Bares [2003].

[6] The SAPHIR chamber is equipped with a comprehensive set of sensitive instruments including the measurements of radical concentrations (OH and HO<sub>2</sub>), concentrations of CO, hydrocarbons, aldehydes, nitrogen oxides, and ozone, along with the photolysis frequencies of atmospheric key processes, temperature, pressure, and humidity.

[7] OH radicals were measured by laser induced fluorescence (LIF), which utilizes the specific resonant fluorescence excitation of OH radicals at low pressure by short laser pulses at 308 nm. The accuracy of the LIF calibration is 10% [Holland *et al.*, 2003]. Isoprene is measured with an online system that combines adsorptive sampling with

**Table 1.** Measurements Used to Determine Rate Coefficients

Instrument	Comp.	Detection Limit	1 $\sigma$ -Precision	1 $\sigma$ -Accuracy
LIF	OH	$0.9 \times 10^6 \text{ cm}^{-3}$	15%	10%
GC-MS	ISO	5–10 ppt	3%	5–10 ppt
UV-Photom.	O <sub>3</sub>	2 ppb	1 ppb	2%

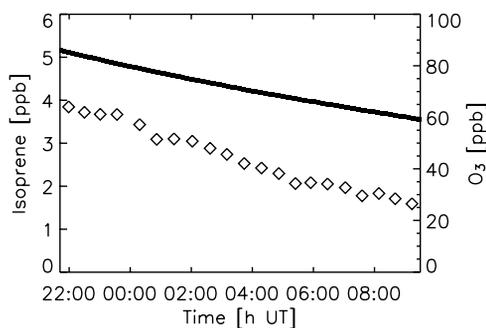
thermal desorption and GC-FID analysis [Komenda *et al.*, 2003]. Ozone is measured using an UV-photometer.

[8] Before experiments were started the chamber volume was flushed for 7 h with  $300 \text{ m}^3 \text{ h}^{-1}$  synthetic air (N<sub>2</sub>:O<sub>2</sub> = 80:20, purity = 99.99999% N<sub>2</sub> or O<sub>2</sub>) in order to purge all trace gases below the detection limits of the instruments (Table 1, NO<sub>2</sub> < 10 ppt, CO < 5 ppb, CH<sub>4</sub> < 15 ppb, HCHO < 50 ppt). After flushing the chamber the compounds of interest were injected. Complete mixing of the chamber air was obtained within 30 min in the dark and within 5–10 min in the sunlit chamber [Rodríguez Bares, 2003]. In the sunlit chamber the Teflon walls constitute a well determined source of nitrous acid (HONO) leading to the formation of OH radicals with a source strength ranging from  $3.4 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$  to  $3.4 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$  depending on the photolysis frequency of NO<sub>2</sub> and humidity (F. Rohrer, personal communication, 2003).

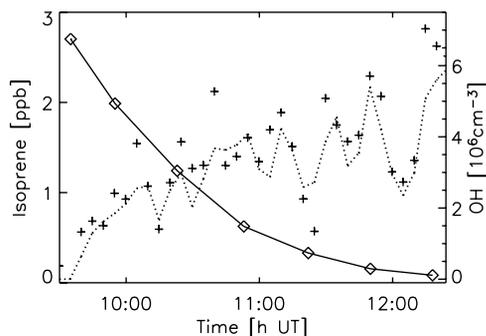
[9] The budget of isoprene in the chamber is influenced by the pressure loss in the chamber due to leakage and air consumption by the detecting instruments. This was compensated for by a flow of synthetic air (replenishment flow) leading to dilution of the reactants. The replenishment flow  $F_e$  ranged from 3 to  $7 \text{ m}^3 \text{ h}^{-1}$  during the experiments. Homogeneous distribution of the reactants in the effective chamber volume allows to describe the dilution of isoprene through the replenishment flow as a first order loss, determined by the rate constant  $k_3$  ( $k_3 = F_e/V_c$ ). Thus the budget for isoprene in chamber experiments can be expressed as:

$$-\frac{d[\text{ISO}]}{dt} = (k_1[\text{O}_3] + k_2[\text{OH}] + k_3)[\text{ISO}] \quad (3)$$

Therefore measurements of the time dependent concentrations of ozone, isoprene, OH and the replenishment flow during the experiment are sufficient to determine both  $k_1$  and  $k_2$ .



**Figure 1.** Time dependent mixing ratios of isoprene (diamonds) and O<sub>3</sub> (line, smoothed data) measured in the ozonolysis experiment. It was carried out in the dark chamber, with an initial gas mixture of 4.5 ppb isoprene, 90 ppb ozone, and 500 ppm CO in synthetic air. Monitoring started 30 min after injection.



**Figure 2.** Measurements of OH concentration by laser induced fluorescence (crosses, plotted as 10-min averages for the sake of clearness) and isoprene mixing ratio by GC-FID (diamonds) in the experiment to determine  $k_2$ . OH calculated from the model (dotted line) nicely reproduces the measured OH.

[10] An ozonolysis experiment in the dark chamber was accomplished to determine rate constant  $k_1$  of the O<sub>3</sub>-isoprene reaction (Figure 1). About 90 ppb O<sub>3</sub> and 4.5 ppb isoprene were injected into synthetic air in the dark chamber containing 500 ppm CO (see below). Since CO exhibits neither reactivity towards isoprene nor towards O<sub>3</sub> at the concentrations employed ( $k(\text{CO} + \text{O}_3) < 4.0 \times 10^{-25} \text{ cm}^3 \text{ s}^{-1}$ ), this deviation from atmospheric conditions is tolerable. The experiment lasted for nearly 11 h starting at 21:30 UT. The chamber air temperature was constant at 286 K. Levels of NO<sub>x</sub> remained below 50 ppt.

[11] The rate constant of the OH + isoprene reaction ( $k_2$ ) was investigated in the sunlit chamber where isoprene was removed primarily by the OH radical, and to a minor fraction by ozone and through dilution. The chamber experiment started at 09:35 UT with initial mixing ratios of 2.7 ppb for isoprene, 40 ppb for ozone, and 1 ppb for NO<sub>x</sub>. After exposing the chamber to sun light, isoprene was removed by the OH radicals produced from ozone photolysis and photolysis of HONO, emitted from the chamber walls. Isoprene mixing ratio reached the detection limit after 3 h. Concentrations of the OH radical peaked at  $8 \times 10^6 \text{ cm}^{-3}$  (Figure 2). The chamber air temperature during the experiment remained at 294 K.

### 3. Ozone-Isoprene Reaction

[12] Ozone initially adds to the >C=C< bond to form an energy-rich primary ozonide, which rapidly decomposes into two sets of carbonyls and biradicals. In the ozonolysis of isoprene OH radicals are generated with a yield of approximately 0.25 [Paulson *et al.*, 1999]. The presence of OH radicals in an ozonolysis experiment would lead to the fast reaction of OH with isoprene and thus would interfere with the determination of the rate coefficient of O<sub>3</sub> with isoprene. For this reason, an excess concentration of CO [Gutbrod *et al.*, 1997] is used in most kinetic studies to scavenge OH.

[13] Before conducting the ozonolysis experiment, rates of all reactions included in the model were calculated. Only three reaction rates (in  $10^6 \text{ cm}^{-3} \text{ s}^{-1}$ ) were found to constitute the reaction system: ISO + O<sub>3</sub> (1.2), CO + OH (1.1), and HO<sub>2</sub> + O<sub>3</sub> (0.8). All other reaction rates remained insignificant.

**Table 2.** Rate Coefficients of Isoprene With OH and O<sub>3</sub> Obtained in the Present Study

React.	$k(T_e)^a$	$k(T_e)$	$T_e \pm \sigma$ [K] <sup>d</sup>
O <sub>3</sub>	$(9.78 \pm 1.96) \times 10^{-18b}$	$(9.6 \pm 0.7) \times 10^{-18}$	$286 \pm 0.2$
OH	$(1.02 \pm 0.04) \times 10^{-10c}$	$(1.00 \pm 0.12) \times 10^{-10}$	$294 \pm 1.1$

Rate coefficients in molecular units [cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup>].

<sup>a</sup>Calculated using the Arrhenius expression recommended by *Atkinson* [1997]; units [cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup>].

<sup>b</sup> $k_1^I = (7.86 \pm 1.6) \times 10^{-15} \exp[(-1913 \text{ K} \pm 139 \text{ K})/T]$ .

<sup>c</sup> $k_2^I = (2.54 \pm 0.1) \times 10^{-11} \exp[(410 \text{ K} \pm 28 \text{ K})/T]$ .

<sup>d</sup>Mean experimental temperature and standard deviation.

icantly small. Average rates given as fraction of the total isoprene loss rate were calculated to be 78% for O<sub>3</sub>-isoprene reaction, 22% for isoprene dilution, 0.2% for OH-isoprene reaction, and 0.04% for the NO<sub>3</sub>-isoprene reaction. The O<sub>3</sub>-isoprene reaction was the dominant loss process while the influence of the OH-isoprene and the NO<sub>3</sub>-isoprene reaction was negligible.

[14] Formal integration of rate equation (3) leads to the time dependent concentration of ISO in the ozonolysis experiment:

$$[\text{ISO}] = [\text{ISO}]_0 \exp^{-\int (k_1[\text{O}_3] + k_3) dt} \quad (4)$$

The experimentally derived rate coefficient of reaction (1),  $k_1$  is related to the rate coefficient used in the model based on the currently valid recommendation in literature [*Atkinson*, 1997],  $k_1^I$ , by a scaling factor  $f_1$ ,

$$f_1 = \frac{k_1}{k_1^I} \quad (5)$$

thus equation (4) can be written as:

$$\ln[\text{ISO}]_t = \ln[\text{ISO}]_0 - f_1 \int_0^t k_1^I [\text{O}_3] dt - \int_0^t k_3 dt \quad (6)$$

The integrals in equation (6) were determined numerically from the measured data of O<sub>3</sub> and k<sub>3</sub>. A scaling factor of 0.98 was determined from the slope of a linear least-squares fit of the logarithmic isoprene concentration (Figure 3) corrected by  $\int_0^t k_3 dt$  versus the integral  $\int_0^t k_1^I [\text{O}_3] dt$  in equation (6). The rate coefficient for the O<sub>3</sub>-isoprene reaction was determined to be  $(9.6 \pm 0.7) \times 10^{-18}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup> at 286 K. The error limits given are within 2σ standard deviations derived from the least-squares fit. The obtained value is in good agreement with the recommended value of *Atkinson* [1997] (Table 2).

#### 4. OH-Isoprene Reaction

[15] There is generally good agreement among previously measured rate constants for the reaction of isoprene and OH, as recommended in the data compilation of tropospheric gas-phase chemistry of VOCs [*Atkinson*, 1997]. The negative activation energy of the isoprene OH-reaction is well established and similar to the ones observed in the OH addition to alkenes in general [e.g., *Siese et al.*, 1994; *Campuzano-Jost et al.*, 2000; *Gill and Hites*, 2002]. The measured rate constants under low pressure conditions agree well with those measured at high pressure [*Stevens et al.*, 1999]. Pressure dependence was only observed at temperatures above 343 K [*Chuang and Stevens*, 2000], and thus it is not relevant for

tropospheric chemistry. *Campuzano-Jost et al.* [2000] have reported a 15% lower rate coefficient under tropospheric conditions.

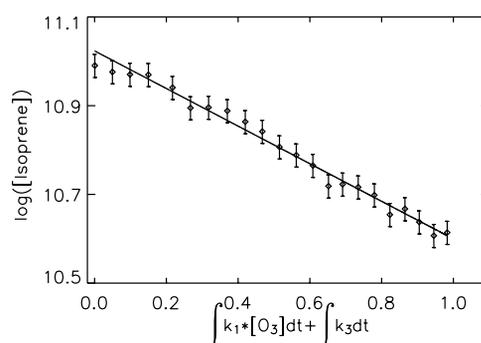
[16] Model calculations predicted the reaction with OH (reaction (2)) to be the dominant isoprene loss (over 96%) in the experiment. From the rate equation (3) the time dependent concentration of isoprene can be expressed as

$$\ln[\text{ISO}]_t = \ln[\text{ISO}]_0 - f_2 \int_0^t k_2^I [\text{OH}] dt - \int_0^t (k_1[\text{O}_3] + k_3) dt \quad (7)$$

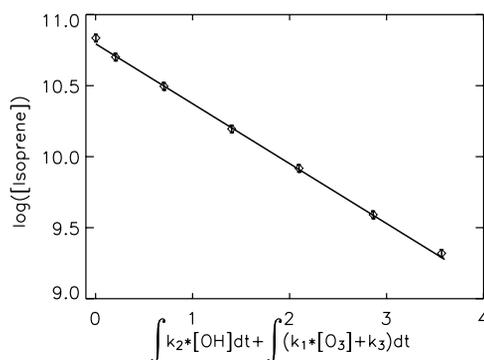
Using equation (7)  $k_2$  was calculated based on the measurements of isoprene, OH, ozone, and the replenishment flow. For the calculation of  $k_2$  the rate coefficient  $k_1^I$  of the O<sub>3</sub>-isoprene reaction scaled by  $f_1$  was used. Comparison of the  $k_2$  derived from equation (7) and the recommended temperature dependence with the value for  $k_2$  used in the model (i.e.,  $k_2^I$ ) according to equation (5) gives  $f_2 = 0.97$  (see (Figure 4)). Consequently, the determined rate coefficient  $k_2$  is in good agreement with the recommendation given by *Atkinson* [1997]. The experimentally determined value of  $k_2$  is  $(10.0 \pm 1.2) \times 10^{-11}$  cm<sup>3</sup>molecule<sup>-1</sup> s<sup>-1</sup> at 294 K. The attributed 2σ standard deviation is derived from the least-squares fit. The systematic error of  $k_2$  is estimated to be 10%.

#### 5. Conclusions

[17] The possibility to perform atmospheric simulation experiments using tropospheric concentrations of isoprene, ozone and the OH radical is a unique advantage of the SAPHIR chamber. Experiments were carried out in extremely clean synthetic air where all reactive trace gases and radicals are well below the detection limits of the measuring instruments. Using low reactant mixing ratios prevents the kinetic investigation from being disturbed by side reactions, which might become important at high reactant concentrations as applied in smog chamber studies.



**Figure 3.** Determination of  $k_1$  (ISO + O<sub>3</sub>) from measurements of isoprene, O<sub>3</sub> and replenishment flow ( $k_3$ ). Measurements of isoprene concentrations (log scale, base 10) are shown as diamonds with error bars representing the experimental 2σ standard deviations. The solid line is a linear least-squares fit to the isoprene concentration vs. the sum of the integrals  $\int k_1[\text{O}_3] dt$  and  $\int k_3 dt$ . Since the dilution rate of isoprene contributes significantly to the isoprene loss it is not possible to determine the scaling factor  $f_1$  from the slope of the solid line. Solving equation (6) using measured data of O<sub>3</sub> and k<sub>3</sub> gives  $f_1 = 0.98$ .



**Figure 4.** Determination of  $k_2$  (ISO + OH) from measurements of isoprene (diamonds) and OH: plot of logarithmic isoprene concentration vs. the combined integrals of  $k_2[\text{OH}]$  and  $(k_1[\text{O}_3] + k_3)$ . Error bars represent  $2\sigma$  standard deviations of the GC analysis. A scaling factor  $f_2 = 0.97$  is obtained from the linear least-squares fit (solid line). Relative contributions to the isoprene loss by ozonolysis and the replenishment flow were only 2% and 0.6%, respectively, therefore  $f_2$  can be directly determined from the slope of the regression line.

[18] Our experiments using tropospheric concentrations of the reactants confirm most of the kinetic studies which determined rate constants at much higher concentrations.

[19] From an ozonolysis experiment in SAPHIR we obtained a rate constant for the reaction between  $\text{O}_3$  and isoprene of  $(9.6 \pm 0.7) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 286 K which is only 2% lower than the recommended value of Atkinson [1997]. The rate constant for the reaction of OH with isoprene was determined to be  $(10.0 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 294 K. Taken into account the uncertainty attributed to our rate coefficient, it is not in agreement with the lower values published by Kleindienst *et al.* [1982] and Campuzano-Jost *et al.* [2000]. The value of the rate constant is not significantly different from the current recommendation of Atkinson [1997].

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