

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/229885381>

# Rate Coefficients for the Gas-Phase Reaction of Isoprene with NO<sub>3</sub> and NO<sub>2</sub>

ARTICLE *in* INTERNATIONAL JOURNAL OF CHEMICAL KINETICS · FEBRUARY 2005

Impact Factor: 1.52 · DOI: 10.1002/kin.20050

---

CITATIONS

9

---

READS

40

3 AUTHORS, INCLUDING:



Matthew S Johnson

University of Copenhagen

138 PUBLICATIONS 1,686 CITATIONS

SEE PROFILE



Sarka Langer

IVL Swedish Environmental Research Instit...

66 PUBLICATIONS 925 CITATIONS

SEE PROFILE

# Rate Coefficients for the Gas-Phase Reaction of Isoprene with NO<sub>3</sub> and NO<sub>2</sub>

JEANETTE R. STABEL,<sup>1</sup> MATTHEW S. JOHNSON,<sup>2</sup> SARKA LANGER<sup>3</sup>

<sup>1</sup>H. Lundbeck A/S, Department of Quality Chemical Production, Oddenvej 182, Lumsås, DK-4500 Nykøbing Sj., Denmark

<sup>2</sup>University of Copenhagen, Department of Chemistry, Universitetsparken 5, DK-2100 Copenhagen, Denmark

<sup>3</sup>SP Swedish National Testing and Research Institute, Department of Chemistry and Materials Technology, Brinellgatan 4, P.O. Box 857, SE-501 15 Borås, Sweden

Received 8 January 2004; accepted 13 August 2004

DOI 10.1002/kin.20050

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Rate coefficients for the gas-phase reaction of isoprene with nitrate radicals and with nitrogen dioxide were determined. A Teflon collapsible chamber with solid phase micro extraction (SPME) for sampling and gas chromatography with flame ionization detection (GC/FID) and a glass reactor with long-path FTIR spectroscopy were used to study the NO<sub>3</sub> radical reaction using the relative rate technique with *trans*-2-butene and 2-buten-1-ol (crotyl alcohol) as reference compounds. The rate coefficients obtained are  $k(\text{isoprene} + \text{NO}_3) = (5.3 \pm 0.2) \times 10^{-13}$  and  $k(\text{isoprene} + \text{NO}_3) = (7.3 \pm 0.9) \times 10^{-13}$  for the reference compounds *trans*-2-butene and 2-buten-1-ol, respectively.

The NO<sub>2</sub> reaction was studied using the glass reactor and FTIR spectroscopy under pseudo-first-order reaction conditions with both isoprene and NO<sub>2</sub> in excess over the other reactant. The obtained rate coefficient was  $k(\text{isoprene} + \text{NO}_2) = (1.15 \pm 0.08) \times 10^{-19}$ . The apparent rate coefficient for the isoprene and NO<sub>2</sub> reaction in air when NO<sub>2</sub> decay was followed was  $(1.5 \pm 0.2) \times 10^{-19}$ . The discrepancy is explained by the fast formation of peroxy nitrates. Nitro- and nitrito-substituted isoprene and isoprene-peroxynitrate were tentatively identified products from this reaction.

All experiments were conducted at room temperature and at atmospheric pressure in nitrogen or synthetic air. All rate coefficients are in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and the errors are three standard deviations from a linear least square analyses of the experimental data. © 2004 Wiley Periodicals, Inc. *Int J Chem Kinet* 37: 57–65, 2005

## INTRODUCTION

Isoprene (2-methyl-1,3-butadiene, CH<sub>2</sub>=C(CH<sub>3</sub>)-CH=CH<sub>2</sub>) is one of the most abundant non-methane hydrocarbons emitted into the troposphere with a global average production rate of about 500 Tg year<sup>-1</sup>

[1]. Isoprene is emitted from trees, shrubs, and grasses; about 50% of the emissions are from tropical trees. In addition, bacteria emit isoprene [2] and on a smaller scale, isoprene is emitted from the phytoplankton in the oceans [3]. Isoprene emission is stimulated by sunlight, and increases with light intensity and temperature [4]. Typical atmospheric concentrations of isoprene are in the range of ppt to several ppb [5]. Isoprene is also emitted by humans, probably as a

Correspondence to: Sarka Langer; e-mail: sarka.langer@sp.se.  
© 2004 Wiley Periodicals, Inc.

by-product in cholesterol biosynthesis. The amount of isoprene in the human breath is 12–580 ppb [6].

Isoprene plays an important role in ozone formation in the local and regional atmosphere, due to its high chemical reactivity and the generation of organic peroxy radicals [7]. The oxidation of isoprene is initiated by reactions with a variety of species (e.g. OH radicals, NO<sub>3</sub> radicals, O<sub>3</sub>). Since trees emit isoprene primarily during the day, the daytime reaction between isoprene and the hydroxyl radical (OH) should be the main degradation pathway, whereas at night isoprene will react with the NO<sub>3</sub> radical. The main reaction products from the reactions between isoprene and OH and O<sub>3</sub> are methacrolein, methyl vinyl ketone, and formaldehyde. The reaction products from the reaction between isoprene and NO<sub>3</sub> and in the presence of NO are methyl vinyl ketone, 2-methylfuran, and methacrolein [8].

While the rate coefficient for the isoprene and NO<sub>3</sub> reaction has been studied for almost 20 years [9–17], the reaction has received a great deal of attention during the past few years and the recent IUPAC evaluation is now available on the Web [18]. The experimental methods used include both the absolute and relative rate techniques. Although many scientists have studied the reaction by a variety of techniques, values of the rate coefficient differ from one another by up to a factor of 2. It is critical to have reliable rate coefficient data for modeling work, as isoprene is an abundant hydrocarbon, and uncertainty in its reaction rate coefficients introduces uncertainty in model results.

As mentioned, isoprene reacts rapidly with the OH radical during the day. Using a daytime OH concentration [1] of  $1.6 \times 10^6$  molecule cm<sup>-3</sup> and a rate constant of  $k_{\text{OH}} = 1.0 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [18], the lifetime  $\tau_{\text{isoprene-OH}}$  in atmosphere is 1.7 h. The reaction between isoprene and NO<sub>3</sub> is also rapid and takes place during the night. Using a concentration of NO<sub>3</sub> of  $2.5 \times 10^9$  molecule cm<sup>-3</sup> (~100 ppt average at night; the average during the day is 0.6 ppt) [1] and a rate coefficient of  $k_{\text{NO}_3} = 7.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [18], one obtains a lifetime ( $\tau_{\text{isoprene-NO}_3}$ ) in the atmosphere of 10 min. The reaction of isoprene with O<sub>3</sub> is much slower,  $k_{\text{O}_3} = 1.27 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [18], and the lifetime of isoprene calculated with an O<sub>3</sub> concentration between 20 and 45 ppb ( $5\text{--}11.2 \times 10^{11}$  molecule cm<sup>-3</sup>) [1] gives  $\tau_{\text{isoprene-O}_3}$  in the atmosphere of 20–44 h. Comparing  $\tau_{\text{isoprene-OH}}$  with  $\tau_{\text{isoprene-NO}_3}$  and  $\tau_{\text{isoprene-O}_3}$ , it is easy to see that the reaction with OH is the dominant loss mechanism for isoprene during the day, and that the reaction with NO<sub>3</sub> is the dominant process at night.

The reaction between isoprene and NO<sub>2</sub> is not important under ambient atmospheric conditions, but

should be taken into account when doing experiments in the laboratory, particularly for environmental chambers involving concentrations of NO<sub>2</sub> above ppm levels. The NO<sub>2</sub>–isoprene reaction has been studied [19–24] and apart from one study [20], the values are in the range of  $(1.03\text{--}1.8) \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. One study was performed using pseudo-first-order conditions [21]. Other workers report values based on one-point experiments, or do not specify the experimental conditions.

Less attention has been directed toward the products of the reaction between isoprene and NO<sub>2</sub>. The reaction steps leading to these products will probably be similar to those in the reaction between isoprene and NO<sub>3</sub>, methacrolein and methyl vinyl ketone. However, almost exclusively, the experimental setups used for studying this reaction only allow the nitrated products to be observed [21].

This work presents re-examinations of the rate coefficients for the reaction of isoprene with NO<sub>3</sub> radical, and the reaction of isoprene with NO<sub>2</sub> in a more systematic way. Motivation for the re-examination of the isoprene + NO<sub>3</sub> reaction was curiosity, as different results were obtained even in studies [9,12,16] using relative rate technique, the same reference compound (*trans*-2-butene), and the same analytical technique (gas chromatography) for quantification of the reacting organic compounds. We have employed solid phase micro extraction sampling technique for gas chromatographic analysis of the organic compounds, and also another reference compound. Furthermore, we have investigated the product formation in the reaction of isoprene and NO<sub>2</sub>, and have made a product assignment.

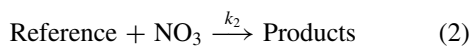
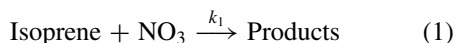
## EXPERIMENTAL SETUP AND PROCEDURES

### Isoprene + NO<sub>3</sub>

In the present study, the relative rate technique [25] was used to determine the rate coefficient for the gas-phase reaction of isoprene with NO<sub>3</sub>. The technique employs the fact that the compound in question is lost only due to a reaction with one species, i.e. a reaction with NO<sub>3</sub> radicals. An advantage of the relative rate technique is that only the ratio of the concentration of the test compound relative to the reference compound is required. The relative rate can be determined using any quantity proportional to the concentration, instead of the concentration itself.

The nitrate radical reacts with isoprene, with an unknown rate coefficient  $k_{\text{organic}}$ , and with the reference compounds, with known rate coefficients  $k_{\text{reference}}$ . The

following reaction pathways are considered:



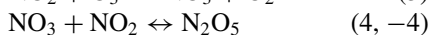
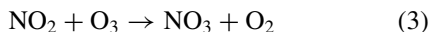
in addition, the ratio of the rate constants is given by

$$\frac{k_{\text{organic}}}{k_{\text{reference}}} = \frac{\ln([\text{Isoprene}]_0/[\text{Isoprene}]_t)}{\ln([\text{Reference}]_0/[\text{Reference}]_t)} \quad (\text{A})$$

where  $[\text{Isoprene}]_0$  and  $[\text{Reference}]_0$  denote the initial concentrations at time  $t = 0$ ;  $[\text{Isoprene}]_t$  and  $[\text{Reference}]_t$  are corresponding values at time  $t$ , respectively.

The rate coefficient is obtained from a linear regression, based on the least square fitting method, where  $\ln([\text{Isoprene}]_0/[\text{Isoprene}]_t)$  is plotted against  $\ln([\text{Reference}]_0/[\text{Reference}]_t)$ . The slope of the straight line gives the relative rate coefficient for the reaction  $k_{\text{rel}} = k_{\text{organic}}/k_{\text{reference}}$ . By combining the absolute rate coefficient  $k_{\text{rel}}$  with the literature value of  $k_{\text{reference}}$ , we obtain the value of the rate coefficient for reaction (1). In this work, we have used *trans*-2-butene and 2-buten-1-ol (crotyl alcohol) as reference compounds. We used the following values of  $k_{\text{organic}}$ :  $k(\text{trans-2-butene} + \text{NO}_3) = 3.90 \times 10^{-13}$  [26] and  $k(2\text{-buten-1-ol} + \text{NO}_3) = (4.1 \pm 0.4) \times 10^{-13}$  [27], in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The experimental techniques used in determining the relative rates are described in the following sections.

The thermal decomposition of N<sub>2</sub>O<sub>5</sub>, given in reaction (−4) was used as the source of NO<sub>3</sub> radicals. The gas phase N<sub>2</sub>O<sub>5</sub> was synthesized by reaction of excess O<sub>3</sub> with NO<sub>2</sub> according to reaction (3) followed by reaction (4) [28]. The N<sub>2</sub>O<sub>5</sub> was collected in a trap and stored at 195 K between runs.



## SPME/GC

The first set of experiments was carried out in a 100 L collapsible Teflon gas-sampling bag, and solid phase micro extraction (SPME) was used as the sampling technique. The following analysis was performed on a Finnigan 9001 gas chromatograph (GC) equipped with a flame ionization detector (FID) to quantify isoprene and the reference compound. The principles and main application areas of the SPME technique are described by Pawlizsyn [29,30].

The SPME needle was a Carboxen<sup>TM</sup>/polydimethylsiloxane (Supelco). A capillary gas chromatographic

column GS-Q 30 m 0.32 mm i.d. (J&W Scientific) was used for the GC analyses. The injector port and detector temperatures of the GC were set at 240°C and 280°C, respectively. The GC oven temperature was 130°C for 1 min, followed by an increase of 40°C min<sup>−1</sup> to 180°C, held for 9 min. The carrier gas was ultra high pure He.

The SPME sampling was accomplished by inserting the needle into the bag through a septum. The fiber was exposed to the reaction mixture for a predetermined time. The exposure time is important, since the adsorbed quantity times sampling time is not a linear function; the clean fiber adsorbs compounds at an initially constant rate, but after some time the rate drops as gas–solid equilibrium is reached (alternatively, as equilibria are reached). After sampling, the fiber was inserted into the heated GC-injector port, and the compounds were desorbed for the chromatographic analysis. This work was carried out in the linear region, and the sampling time was 2 min.

The experiments were conducted by first introducing the isoprene and the reference compound into the bag. Before introducing the N<sub>2</sub>O<sub>5</sub>, an initial test of the stability of the mixture was performed by at least three measurements. The standard deviation of the mean integrated area of the corresponding peaks was less than 2%.

Isoprene and a reference compound were introduced into the Teflon bag via a vacuum line equipped with a barometric dilution system, and by using a stream of bath gas (either pure N<sub>2</sub> or synthetic air). N<sub>2</sub>O<sub>5</sub> was introduced into the sample bag with a syringe through the septum on the bag. For all of the experiments N<sub>2</sub>O<sub>5</sub> was introduced several times in portions to the reaction bag. The initial concentration of the isoprene or the reference compound was typically  $(1.2\text{--}1.8) \times 10^{14}$  molecule cm<sup>−3</sup>.

A volume between 2 and 10 mL of N<sub>2</sub>O<sub>5</sub> in N<sub>2</sub>, corresponding to a concentration of  $(2.5\text{--}10) \times 10^{13}$  molecule cm<sup>−3</sup>, was then injected into the bag using a syringe. Filling and emptying the syringe and needle with gas phase N<sub>2</sub>O<sub>5</sub> preconditioned the inner surface of the syringe and needle. This was done to avoid loss by adsorption and hydrolysis of the N<sub>2</sub>O<sub>5</sub>. After introduction of N<sub>2</sub>O<sub>5</sub>, the bag was shaken vigorously to promote mixing of the compounds inside. Sampling was done by inserting the SPME fiber through the septum into the bag, and exposing the fibers to the reaction mixture for 2 min each time. After exposure, the fiber was retracted inside the protection needle, and the SPME was detached from the bag. Immediately after sampling, the SPME fiber was inserted into the heated GC injection port, followed by thermal desorption and chromatographic analysis. The amount of compound

was expressed as the integrated peak area.  $\text{N}_2\text{O}_5$  was added to the reaction chamber repeatedly to compensate for loss by the reactions with isoprene and the reference compound.

### FTIR Spectroscopy

The experimental setup has been described in detail previously [31] and only a brief description is given here. The reaction chamber is made of borosilicate glass and has a volume of 153 L. It is equipped with a White mirror system with a base optical path of 2 m. Fourier transform infrared spectroscopy (Nicolet Magna 560 spectrometer with an MCT detector cooled by liquid nitrogen) was used for the quantification of the isoprene and the reference compounds. An optical path length of 40 m and spectral resolution of  $1\text{ cm}^{-1}$  were used in all of the experiments. The desired amounts of the organic compounds were measured using standard manometric techniques with the same barometric dilution system as was used for the SPME/GC experiments. The reactants were introduced into the chamber experiments by a stream of bath gas (nitrogen or synthetic air) via a Teflon line with nozzles placed axially along the bottom of the reactor.  $\text{N}_2\text{O}_5$  was introduced into the reactor in several small portions of about  $2.5 \times 10^{13}\text{ molecule cm}^{-3}$ . The initial concentrations of the reactants were in the range of approximately  $(1.0\text{--}1.5) \times 10^{14}\text{ molecule cm}^{-3}$ .

The concentrations of the reacting compounds were determined using scaled subtraction of the reference spectra (at known concentrations) collected in the same way as the experimental spectra. The linearity between IR absorbance and concentrations of the studied compounds was confirmed in separate experiments.

### Isoprene + $\text{NO}_2$

The rate coefficient for the reaction of isoprene with  $\text{NO}_2$  was determined under pseudo-first-order conditions using FTIR spectroscopy. Two experimental approaches were used, first isoprene in excess over  $\text{NO}_2$  and second  $\text{NO}_2$  in excess over isoprene. The concentration of the excess compound was varied and from the decay of the minor compounds as the reaction proceeded, the rate coefficient was determined.

The natural logarithm ( $\ln$ ) of the minor compound concentration was plotted against the reaction time, and the pseudo-first-order rate coefficient,  $k'$ , was the slope of the straight line fitted to experimental data. In the next step, the values of  $k'$  were plotted against the corresponding concentration of the excess compound. The slope of the straight line fitted by the linear least square method was the second-order rate coefficient.

The initial concentration of the excess isoprene was  $(1\text{--}5) \times 10^{15}\text{ molecule cm}^{-3}$  and of the nitrogen dioxide  $(8.2\text{--}19) \times 10^{13}\text{ molecule cm}^{-3}$ . The initial concentration of excess nitrogen dioxide was  $(1\text{--}10) \times 10^{15}\text{ molecule cm}^{-3}$  and of isoprene was  $(9\text{--}12) \times 10^{13}\text{ molecule cm}^{-3}$ .

The following chemicals were used: 2-buten-1-ol ( $>97\%$ , Merck), *trans*-2-butene (99.0%, AGA Gas AB), and isoprene ( $>99\%$ , Merck). Synthetic air (20%  $\text{O}_2$  in 99.996%  $\text{N}_2$ , AGA Gas AB) and nitrogen plus (99.996%, AGA Gas AB) were employed as bath gases for the experiments, and helium (99.9995%, AGA Gas AB) was used as the GC carrier gas. For all liquid compounds, freeze–pump–thaw cycles were repeated several times to eliminate dissolved gases before use in the dilution system.

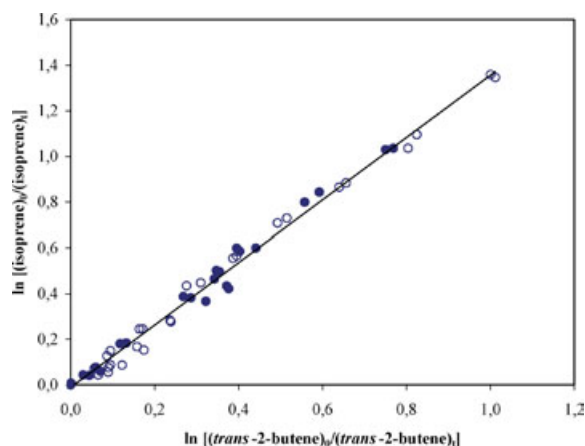
## RESULTS AND DISCUSSION

### Isoprene and $\text{NO}_3$

For determination of the rate coefficient of the isoprene and  $\text{NO}_3$  reaction, two reference compounds were used: *trans*-2-butene and 2-buten-1-ol (crotyl alcohol). For the experiments with *trans*-2-butene as the reference compound, only the GC setup was used, and in the experiments with 2-buten-1-ol, both the FTIR and GC setups were used. Experiments were conducted in either nitrogen or synthetic air as the bath gas, to check for any possible secondary reactions due to absence or presence of molecular oxygen in the reaction system. The motivation for using the gas chromatographic separation of *trans*-2-butene and isoprene was the difficulty encountered in resolving the FTIR spectra in terms of contributions from the individual compounds in the reactor.

Figure 1 presents a plot of data from the experiments with *trans*-2-butene as the reference compound. First, the data from the experiments in air and nitrogen were plotted separately. The slope of the straight line was  $1.38 \pm 0.095$  (air) and  $1.37 \pm 0.072$  (nitrogen), respectively. The statistical confidence interval used was  $3\sigma$  from the linear least square analysis for all experiments. We decided to plot all data in one diagram, and fit a straight line through the points. The resulting  $k_{\text{rel}} 1.367 \pm 0.055$  combined with the value of *trans*-2-butene +  $\text{NO}_3$  resulted in  $k_{\text{isoprene}} = (5.3 \pm 0.2) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ .

Figure 2 presents the data from the experiments with 2-buten-1-ol as the reference compound. The relative rate plot was constructed according to equation (A). The results of the experiments in  $\text{N}_2$  or air were indistinguishable for the individual setups. The slope of the straight line from the FTIR was  $1.72 \pm 0.24$  and from

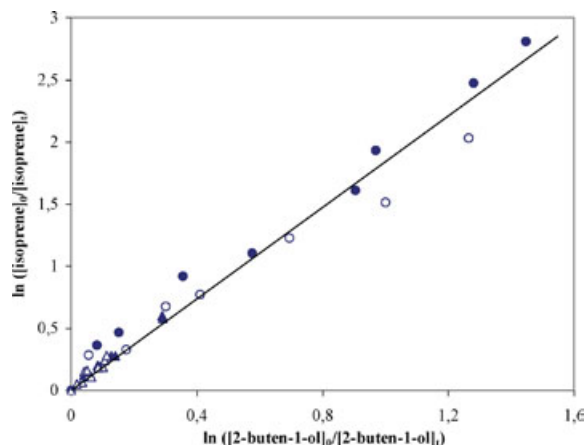


**Figure 1** Relative rate plot for the reaction of isoprene with NO<sub>3</sub> radical with *trans*-2-buten-1-ol as the reference compound using SPME/GC technique. Open circles: nitrogen as the bath gas; filled circles: air as the bath gas.

the GC runs was  $1.98 \pm 0.20$ . The statistical confidence interval used was  $3\sigma$  from the linear least square analysis for all experiments. No systematic differences in the results between the FTIR and GC methods could be observed. We therefore decided to use both sets of data for the calculation of the relative rate coefficient for the reaction. Fitting all the data gave a straight line with a slope of  $1.78 \pm 0.13$ . Combining the  $k_{\text{rel}}$  with the rate coefficient for the 2-buten-1-ol + NO<sub>3</sub> resulted in  $k_{\text{isoprene}} = (7.3 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The rate coefficient for the reaction between isoprene and NO<sub>3</sub> has been studied over the past 20 years

with varying results. In Table I, the values for the rate coefficients including descriptions of the experimental technique are summarized. The values differ from each other by up to a factor of 2. The recommended value [18] from a recent critical evaluation of rate constants for the reaction is  $7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Our results of  $5.3 \times 10^{-13}$  and  $7.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  fall in the lower end of the values found in the literature, and are close to the recommended value. The two values differ significantly from each other, depending on the reference compound used for the determination of the rate coefficient. Relative rate experiments with the two reference compounds from the present work were performed previously in a study of a series of structurally similar unsaturated alcohols [27]. Resulting rate coefficient ratio,  $k_{\text{rel}} = k(\text{NO}_3 + \text{2-buten-1-ol})/k(\text{NO}_3 + \text{trans-2-buten-1-ol})$ , has been determined to  $1.011 \pm 0.047$ . In this case, the value of  $k(\text{NO}_3 + \text{trans-2-buten-1-ol})$  of  $(4.06 \pm 0.33) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from an absolute rate determination [32] was used for the calculation of  $k(\text{NO}_3 + \text{2-buten-1-ol})$ . Using the recommended value of  $k(\text{NO}_3 + \text{trans-2-buten-1-ol})$  of  $3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  would have resulted in  $k(\text{NO}_3 + \text{2-buten-1-ol}) = (3.94 \pm 0.18) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The value for the rate coefficient for the reaction of isoprene and NO<sub>3</sub> from this work, using the recalculated value of  $k(\text{NO}_3 + \text{2-buten-1-ol})$ , will result in  $(7.0 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the same as the recommended value [18]. Unrecognized artifacts in sampling of isoprene and *trans*-2-buten-1-ol with the SPME technique, leading to the significantly lower value of the examined rate coefficient  $k(\text{NO}_3 + \text{isoprene})$  with *trans*-2-buten-1-ol as the reference compound, might be possible explanation of the two different values of the rate coefficient in this study.



**Figure 2** Relative rate plot for the reaction of isoprene with NO<sub>3</sub> radical with 2-buten-1-ol as the reference compound. Open circles: FTIR, nitrogen; filled circles: FTIR, air; open triangles: SPME/GC, nitrogen; filled triangles: SPME/GC, air. The line is fitted to all the points.

## Isoprene + NO<sub>2</sub>

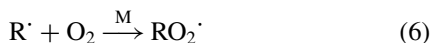
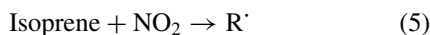
The reaction has been studied previously with varying results. Table II shows the values obtained for the rate coefficient for the reaction. In Fig. 3, we present an example of experimental data: the decay of isoprene in excess of nitrogen dioxide in air as a function of reaction time. Figure 4 shows a plot of the pseudo-first-order rate coefficient against the concentration of excess reactant. It should be noted that data for excess NO<sub>2</sub> in both air and nitrogen together with data for excess isoprene in nitrogen fall on the same straight line with a slope of  $(1.15 \pm 0.08) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The decay of NO<sub>2</sub> in excess of isoprene in air resulted in another straight line with the slope of  $(1.5 \pm 0.2) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The statistical confidence interval used was  $3\sigma$  from the linear least square analysis for all experiments.

**Table I** Rate Coefficients for the Reaction of Isoprene with NO<sub>3</sub> at Room Temperature Determined in This Work Together with Data from the Literature

$k_{\text{NO}_3} \times 10^{13}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Method	Reference Compound	Year [Reference]
5.94 ± 0.16	RR	<i>trans</i> -2-butene	1984 [9]
13 ± 1.2	FT-MS		1988 [10]
6.42 ± 0.78	FT-LIF		1989 [11]
12 ± 2	RR	<i>trans</i> -2-butene	1990 [12]
8.26 ± 0.6	FT-MS		1991 [13]
7.78 ± 0.6	FT-MS		1991 [14]
6.78	Extensive literature review		1991 [15]
10.7 ± 2.0	PR-UV		1993 [16]
6.86 ± 2.60	RR	<i>trans</i> -2-butene	1997 [17]
7.3 ± 0.2	FT-CIMS		2001 [18]
5.3 ± 0.2	RR	<i>trans</i> -2-butene	2003 [This work]
7.3 ± 0.9	RR	2-buten-1-ol	2003 [This work]

RR = relative rate; FT = flow tube; MS = mass spectroscopy; LIF = laser-induced fluorescence; PR = pulse radiolysis; UV = ultraviolet; CIMS = chemical ionization mass spectroscopy.

A possible reason for the discrepancy in the rate coefficients can be explained using the reaction schemes (5)–(7):



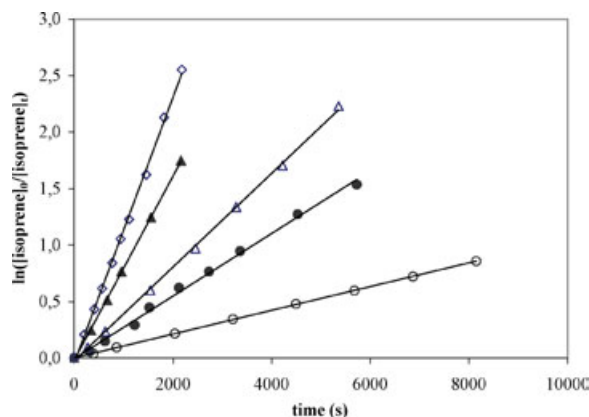
Reaction (5) was monitored in the experiments conducted with excess NO<sub>2</sub> both with and without O<sub>2</sub> present, allowing the reaction to be isolated. Changes in the NO<sub>2</sub> concentration (in experiments with excess NO<sub>2</sub> only) were not quantified; in any case they would have been within the limits of errors for the determination. When loss of NO<sub>2</sub> was followed in an excess of isoprene, two cases could be clearly distinguished. In the absence of molecular oxygen, the radical formed in

reaction (5) added another NO<sub>2</sub> molecule but at such a slow rate that it did not influence the rate of loss of NO<sub>2</sub>. In the presence of O<sub>2</sub>, the peroxyxynitrate was formed according to reactions (5)–(7). The rate coefficients for reactions (6) and (7) can be estimated to be  $\sim 2 \times 10^{-12}$  and  $\sim 4 \times 10^{-12}$ , respectively [33,34], in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; the reactions are fast enough to speed up the consumption of NO<sub>2</sub> leading to the larger apparent value of the rate coefficient for the reaction between isoprene and NO<sub>2</sub>. The loss of isoprene in excess NO<sub>2</sub> gives then the preferred rate coefficient.

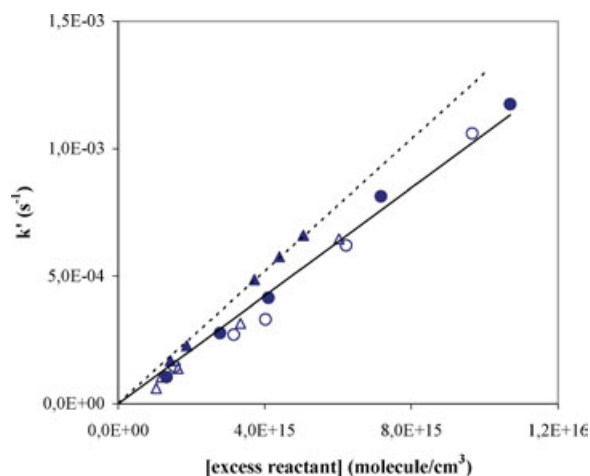
**Table II** Rate Coefficients for the Reaction of Isoprene with NO<sub>2</sub> at Room Temperature Determined in This Work Together with Data from the Literature

$k_{\text{NO}_2} \times 10^{19}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Technique	Year [Reference]
1.15 ± 0.07	Loss rate of NO <sub>2</sub>	1970 [19]
8.24	Not specified	1975 [20]
1.03 ± 0.03	GC pseudo-first-order	1984 [21]
1.63 ± 0.14	Loss rate of NO <sub>2</sub>	1985 [22]
1.79 ± 0.30	GC	1986 [23]
1.81 ± 0.20	GC	1992 [24]
1.15 ± 0.08	FTIR	2003 [This work]

GC = Gas chromatography; FTIR = Fourier transform infrared spectroscopy.



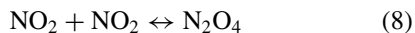
**Figure 3** An example of experimental data from the reaction of isoprene with excess NO<sub>2</sub> in air using FTIR spectroscopy. Pseudo-first-order plots for various concentrations of NO<sub>2</sub>. Open circles:  $1.32 \times 10^{15}$ ; filled circles:  $2.78 \times 10^{15}$ ; open triangles:  $4.10 \times 10^{15}$ ; filled triangles:  $7.17 \times 10^{15}$ ; and open diamonds:  $10.7 \times 10^{15}$  (all in molecule cm<sup>-3</sup>). The corresponding rate coefficients were  $1.05 \times 10^{-4}$ ,  $2.77 \times 10^{-4}$ ,  $4.15 \times 10^{-4}$ ,  $8.14 \times 10^{-4}$ , and  $11.8 \times 10^{-4}$ , respectively (all in s<sup>-1</sup>).



**Figure 4** Plot of pseudo-first-order rate coefficients versus concentration of the excess reactant. Open circles: excess NO<sub>2</sub>, nitrogen as the bath gas; filled circles: excess NO<sub>2</sub>, air as the bath gas; open triangles: excess isoprene, nitrogen as the bath gas; filled triangles: excess isoprene, air as the bath gas.

A stability test with respect to the concentration of isoprene was performed using the FTIR experimental setup; we were expecting a slow reaction rate meaning long reaction time for the reaction of isoprene with NO<sub>2</sub>. About  $1.4 \times 10^{14}$  molecule cm<sup>-3</sup> of isoprene was introduced into the chamber and its concentration was followed over the course of 21 h. The change in the concentration of isoprene was around 3%. As the longest experiment was about 4 h, the adsorption of isoprene onto the wall of the chamber did not influence the results.

One experiment examining the stoichiometry of the reaction was performed. Plotting the concentration change of NO<sub>2</sub> versus that of isoprene during the 22-h experiment gave a straight line with slope of 1.95. Thus the reaction stoichiometry is one molecule of isoprene reacting with two molecules of NO<sub>2</sub>. As shown in reaction scheme (8), NO<sub>2</sub> forms an equilibrium involving N<sub>2</sub>O<sub>4</sub>.



In order to check if the reacting species was the molecule N<sub>2</sub>O<sub>4</sub> instead of two NO<sub>2</sub>, we performed the following calculation: At the highest concentration of NO<sub>2</sub> ( $1.07 \times 10^{16}$  molecule cm<sup>-3</sup>) encountered, and using the well-known equilibrium constant [35]  $K_{\text{eq}} = 2.8 \times 10^{-19}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, the equilibrium concentration of N<sub>2</sub>O<sub>4</sub> will be  $3.2 \times 10^{13}$  molecule cm<sup>-3</sup>. This gives a contribution from N<sub>2</sub>O<sub>4</sub> of 0.003 to the total reaction of isoprene and NO<sub>2</sub>, assuming they react

at the same rate. The stoichiometric ratio  $R = \Delta[\text{NO}_2]/\Delta[\text{isoprene}]$  for the reaction in air, averaged over 1 h, was calculated to be 2.05 using the FACSIMILE modeling program [36], and the reaction mechanism is described by reactions (5)–(7).

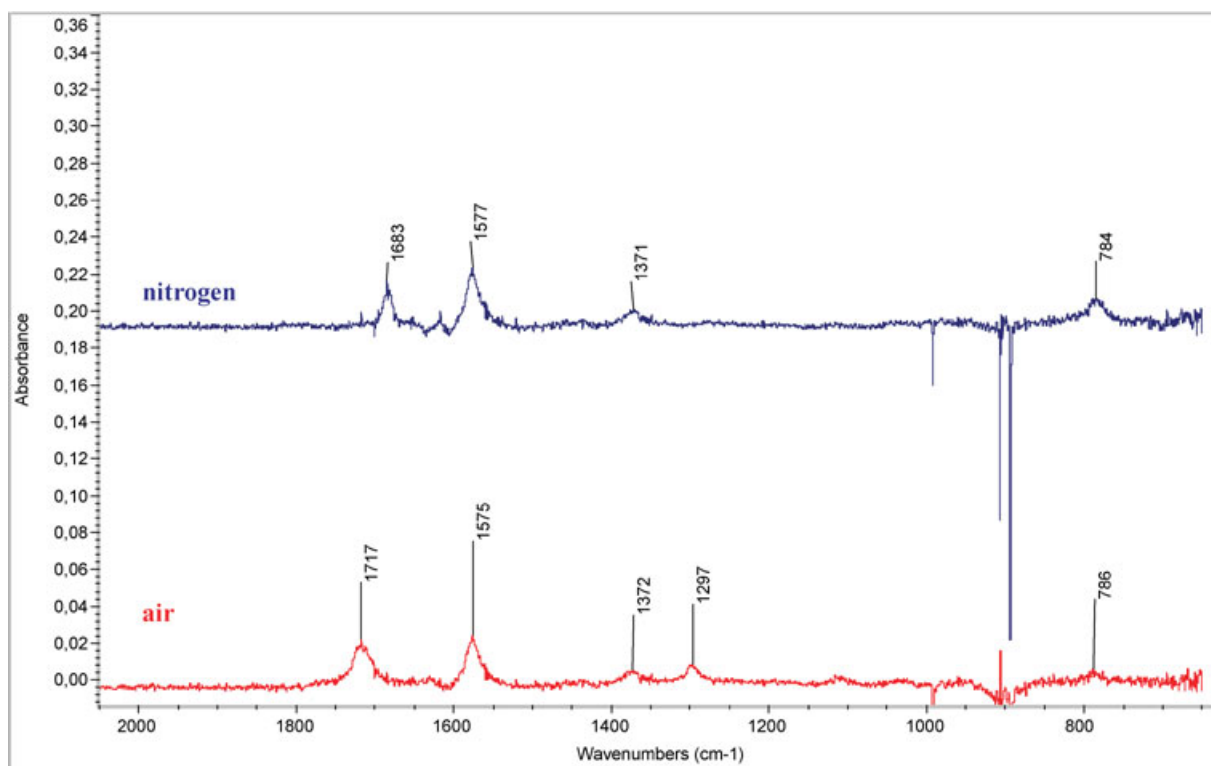
Nitrogen dioxide has one unpaired electron, and is considered a radical; however, it is not as potent an oxidant as NO<sub>3</sub>. The initial reaction between isoprene and NO<sub>2</sub> proceeds mainly as a radical addition to the isoprene molecule, meaning that NO<sub>2</sub> will add to one of the >C=C< double bonds, forming a NO<sub>2</sub>-isoprene adduct radical, R'. While there are four possible positions for the NO<sub>2</sub>, C1 is probably preferred. The mechanism for the addition of NO<sub>2</sub> to isoprene will be similar to the addition of NO<sub>3</sub> to isoprene, where approximately 83% will add at C1 and 15% to C4, while the C2 and C3 share the last 2% [8]. In the absence of molecular oxygen, the radical formed may add another NO<sub>2</sub> molecule to form a stable product. Under atmospheric conditions, the NO<sub>2</sub>-adduct will react with O<sub>2</sub>, leading to the formation of four β- and two δ-nitroalkyl peroxy radicals. The peroxy radicals can react further with NO<sub>2</sub>, engage in self-reactions or react with other peroxy radicals, or undergo isomerization or decomposition, giving various oxygenated or nitrated organic compounds. In absence of O<sub>2</sub>, the second NO<sub>2</sub> addition will lead to the formation of dinitro- or nitro-nitrito-compounds.

FTIR spectra of the products from the reaction between isoprene and NO<sub>2</sub> are presented in Fig. 5. The top spectrum shows the products from the reaction performed in nitrogen, and the bottom spectrum from the reaction in air. The peaks were assigned assuming that the IR absorptivity depends mainly on the nitrogen-containing groups and less on the organic part of the molecule. The assignment was made in accordance with the tetramethylethylene-NO<sub>2</sub> and similar reactions [37–39]. The peaks at 1575 cm<sup>-1</sup> and 1372 cm<sup>-1</sup> can be assigned to R-NO<sub>2</sub> in both spectra. The other three peaks found in the spectrum when air was the bath gas at 1717, 1297, and 786 cm<sup>-1</sup> can be assigned to R-OOONO<sub>2</sub>. The peaks at 1683 cm<sup>-1</sup> and 784 cm<sup>-1</sup> in the top spectrum were assigned to R-ONO.

## CONCLUSIONS

The rate coefficient for the isoprene-NO<sub>3</sub> reaction was determined using a new method for the determination of the organic compound concentration, namely solid phase micro extraction followed by gas chromatography for separation and detection. SPME/GC is a useful technique for measuring relative rate coefficients, and it offers an alternative to FTIR spectroscopy, e.g.





**Figure 5** FTIR spectra of the products from the reaction of isoprene and  $\text{NO}_2$ . Bottom: air as the bath gas, top: nitrogen the bath gas.

when reactants or products contain similar functional groups that cannot be resolved by FTIR. It is, however, more time consuming and experimentally demanding to perform the experiments with SPME/GC compared to FTIR for the relative rate determinations.

The rate coefficient for the reaction between isoprene and  $\text{NO}_3$  was determined using two different reference compounds, resulting in two different rate coefficients. The rate coefficient determined using 2-buten-1-ol as the reference was in good agreement with previous determinations. When using *trans*-2-butene as the reference compound, a slightly smaller rate coefficient was found. It is still within the limits of error of the recommended rate coefficient from the IUPAC evaluation [18].

The rate coefficient for the isoprene- $\text{NO}_2$  reaction has been determined quite accurately and with good confidence. The previous values of this rate coefficient are based on single point measurements or under conditions that were not strictly pseudo-first order. As mentioned in the Introduction, the reaction between isoprene and  $\text{NO}_2$  is not important under normal atmospheric conditions due its slow rate. However, when modeling the impact of isoprene on the environment, either the troposphere or indoor air should be taken into consideration.

Products from the reaction between isoprene and nitrogen dioxide were tentatively identified as nitro- and nitrito-substituted isoprene and isoprene-peroxynitrate.

## BIBLIOGRAPHY

1. Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; Wiley: New York, 1998.
2. Kuzma, J.; Nemecek-Marshall, M.; Pollock, W. H.; Fall, R. *Curr Microbiol* 1995, 30, 97–103.
3. Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J Geophys Res* 1995, 100, 8873–8892.
4. Skov, H.; Hjorth, J.; Lohse, C.; Jensen, N. R.; Restelli, G. *Atmos Environ* 1992, 26A, 2771–2783.
5. Kesselmeier, J.; Staudt, M. *J Atmos Chem* 1999, 33, 23–88.
6. Fenske, J. D.; Paulson, S. E. *J Air Waste Manage Assoc* 1999, 49, 594–598.
7. Chameides, W. L.; Lindsay, R. W.; Richardson, J.; Kiang, C. S. *Science* 1988, 241(4872), 1473–1475.

8. Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere. Theory, Experiments, and Applications*; Academic: San Diego, CA; 2000; Ch. 6 and references there-in.
9. Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts Jr., J. N. *Environ Sci Technol* 1984, 18, 370–375.
10. Benter, T.; Schindler, R. N. *Chem Phys Lett* 1988, 145, 67–70.
11. Dlugokencky, E. J.; Howard, C. J. *J Phys Chem* 1989, 93, 1091–1096.
12. Barnes, I.; Bastian, V.; Becker, K. H.; Tong, Z. *J Phys Chem* 1990, 94, 2413–2419.
13. Lancar, I. T.; Daele, V.; Le Bras, G.; Poulet, G. *J Chim Phys* 1991, 88, 1777–1792.
14. Wille, U.; Becker, E.; Schindler, R. N.; Lancar, I. T.; Poulet, G.; Le Bras, G. *J Atmos Chem* 1991, 13, 183–193.
15. Ellermann, T.; Nielsen, O. J.; Skov, H. *Chem Phys Lett* 1992, 200, 224–229.
16. Berndt, T.; Böge, O. *Int J Chem Kinet* 1997, 29, 755–765.
17. Suh, I.; Lei, W.; Zhang, R. *J Phys Chem A* 2001, 105, 6471–6478.
18. <http://www.iupac-kinetic.ch.cam.ac.uk/> Summary table of kinetic data: July 2004.
19. Glasston, W. A.; Tuesday, C. S. *Environ Sci Technol* 1970, 4, 752–757.
20. Gryaznov, V. A.; Rozlovskii, A. I. *Dokl Phys Chem* 1975, 220, 1099.
21. Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts Jr., J. N. *Int J Chem Kinet* 1984, 16, 697–706.
22. Gu, C.-L.; Rynard, C. M.; Hendry, D. G.; Mill, T. *Environ Sci Technol* 1985, 19, 151–155.
23. Ohta, T.; Nakagura, H.; Suzuki, S. *Int J Chem Kinet* 1986, 18, 1–7.
24. Paulson, S. E.; Flagan, R. C.; Seinfeld, J. H. *Int J Chem Kinet* 1992, 24, 79–101.
25. Atkinson, R.; Plum, C. N.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J Phys Chem* 1984, 88, 1210–1215 and 4446 (correction).
26. Atkinson, R. *J Phys Chem Ref Data* 1997, 26, 215–290.
27. Noda, J.; Nyman, G.; Langer, S. *J Phys Chem A* 2002, 106, 945–951.
28. Davidson, J. A.; Viggiano, A. A.; Howard, C. J.; Dotan, I.; Fehsenfeld, F. C.; Albritton, G. L.; Ferguson, E. E. *J Phys Chem* 1978, 68, 2805–2087.
29. Pawliszyn, J. *Solid Phase Microextraction: Theory and Practice*; Wiley-VCH: Weinheim, 1997.
30. Pawliszyn, J. (Ed.). *Applications of Solid Phase Microextraction*; Royal Society of Chemistry: London, 1999.
31. Svensson, R.; Ljungström, E.; Lindqvist, O. *Atmos Environ* 1987, 21, 1529–1539.
32. Rudich, Y.; Talukdar, R. K.; Fox, R. W.; Ravishankara, A. R. *J Phys Chem* 1996, 100, 5374–5381.
33. Nielsen, O. J.; Wallington, T. J. Formation of peroxy radicals in the gas phase; In *Peroxy Radicals*; Zeev Alfassi (Ed.); Wiley: New York, 1997.
34. Wallington, T. J.; Nielsen, O. J.; Sehested, J. Reactions of organic peroxyradicals in the gas phase; In *Peroxy Radicals*; Zeev Alfassi (Ed.); Wiley: New York, 1997.
35. Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Moortgat, G. K.; Ravishankara, A. R.; Kolb, C. E.; Molina, M.; Finlayson-Pitts, B. J. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation no. 14*, JPL Publication 02–25, 2003.
36. FACSIMILE, AEA Technology Plc., 1998.
37. Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P.; Hurley, M. D. *Int J Chem Kinet* 1986, 18, 1235–1247.
38. Skov, H. 2003. Personal communication.
39. Tuazon, E. C.; Atkinson, R. *Int J Chem Kinet* 1990, 22, 1221–1236.