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Kinetics Investigation of OH Reaction with Isoprene at 240−340 K and 1−3 Torr Using the Relative Rate/Discharge Flow/Mass Spectrometry Technique

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The kinetics of the reaction of OH radical with isoprene has been investigated at a total pressure of 1−3 Torr over a temperature range of 240−340 K using the relative rate/discharge flow/mass spectrometry (RR/DF/MS) technique. The reaction of isoprene with OH was found to be independent of pressure over the pressure range of 1−3 Torr at 298 K, and the reaction had reached its high-pressure limit at 1 Torr. However, the rate constant of this reaction is found to positively depend on pressure at 1−3 Torr and 340 K. At 298 K, the rate constant of this reaction was determined to be $k_1 = (10.4 \pm 1.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is in good agreement with literature values. The Arrhenius expression for this reaction was determined to be $k_1 = (2.33 \pm 0.09) \times 10^{-11} \exp[(444 \pm 27)/T]$ cm^3 molecule^{-1} s^{-1} at 240−340 K. The atmospheric lifetime of isoprene was estimated to be 2.9 h based on the rate constant of isoprene + OH determined at 277 K in the present work.

Introduction

Isoprene is a major non-methane hydrocarbon that is primarily emitted to the atmosphere from natural sources such as vegetation and phytoplankton during daytime.[1−5] To a lesser extent, isoprene is released to the atmosphere due to anthropogenic activities such as ethylene production, wood pulping, oil fires, wood-burning stoves and fireplaces, biomass burning, tobacco smoking, and gasoline combustion.[6] Isoprene is considered a significant toxic substance and an atmospheric pollutant. It has been suggested to be an animal and human carcinogen and a neuro and respiratory toxin,[7] and it was included in the list of chemicals known to cause cancer or reproductive toxicity under the safe drinking water and toxic enforcement act.[8] During its atmospheric degradation, isoprene is oxidized producing major atmospheric pollution ingredients such as ozone, NO_x ($NO + NO_2$), peroxy acetyl nitrate (PAN), and carbonyl compounds.[3] Recent studies have also shown that isoprene can significantly contribute to the formation of secondary organic aerosols (SOAs) through photooxidation initiated by OH radicals.[9−11]

Isoprene is removed from the atmosphere mainly by reacting with atmospheric oxidants such as O_3, NO_3, Cl, and OH. The reaction of isoprene with the OH radicals is the dominant process by which isoprene is removed during daytime. It is known that the OH can add to one of the four positions on the skeleton chain of the isoprene, resulting in the formation of four possible hydroxylalkyl radicals,[4]

$$C_5H_8 + OH \rightarrow (OH)C_5H_8 \qquad (1)$$

This reaction has also been regarded as a major sink for hydroxyl radicals in troposphere, accounting for nearly 30% of the OH removal rate.[4]

Acquisition of the kinetic information as a function of both temperature and pressure is essential in understanding the isoprene chemistry for the purpose of both atmospheric application and fundamental insight. Numerous experimental kinetic studies have been carried out for reaction 1 using various techniques, including relative rate,[12−14] discharge flow combined with laser-induced fluorescence,[15] flash photolysis,[16] laser photolysis,[2] fast flow coupled with chemical ionization mass spectrometer,[17] and Laval nozzle expansion[18] techniques. Early kinetics investigations of reaction 1 at room temperature reported a k_1 value of (7.8−10.2) × 10^{-11} cm^3 molecule^{-1} s^{-1}. Kleindienst et al.[16] measured the absolute rate constant for reaction 1 at 50−200 Torr over a temperature range of 299−422 K using the absolute rate flash photolysis-resonance fluorescence technique. They reported a rate constant of $k_1 = (9.26 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature and an Arrhenius expression of $k_1 = 2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$ cm^3 molecule^{-1} s^{-1}. Zhang et al.[17] determined a rate constant of $k_1 = (10.1 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for reaction 1 using a turbulent flow reactor coupled to a chemical ionization mass spectrometer, while a $k_1 = (9.9 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was reported by McGivern et al.[2] using the pulse photolysis/laser-induced fluorescence detection of OH. Chuong and Stevens[3,4] examined the kinetics of reaction 1 using a discharge flow coupled with laser-induced fluorescence under both laminar and turbulent flow conditions and reported a rate constant of $k_1 = (11.0 \pm 0.4) \times 10^{-11}$ and $k_1 = (10.8 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K, respectively. Later, Gill and Hites, and Mcquaid et al.[12] measured the relative rate constant for reaction 1 using the technique of gas chromatography combined with mass spectrometer detection, and they reported a rate constant of $k_1 = (10.1 \pm 1.9) \times 10^{-11}$ and $(11.1 \pm 0.23) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, respectively. Gill and Hites also reported an Arrhenius expression of $k_1 = (2.56^{+0.35}_{-0.31}) \times 10^{-11} \exp[(408 \pm 42)/T]$ cm^3 molecule^{-1} s^{-1} at 298−363 K. Campuzano-Jost and co-workers[1] have recently measured the k_1 value to be $(8.47 \pm 0.59) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 297 K and a temperature expression of $k_1(250{-}340\ \mathrm{K}) = (8.63 \pm 0.42) \times 10^{-11} \exp[(348 \pm 136)(1/T - 1/298\ \mathrm{K})]$ cm^3 molecule^{-1} s^{-1}. More recently, Spangenberg

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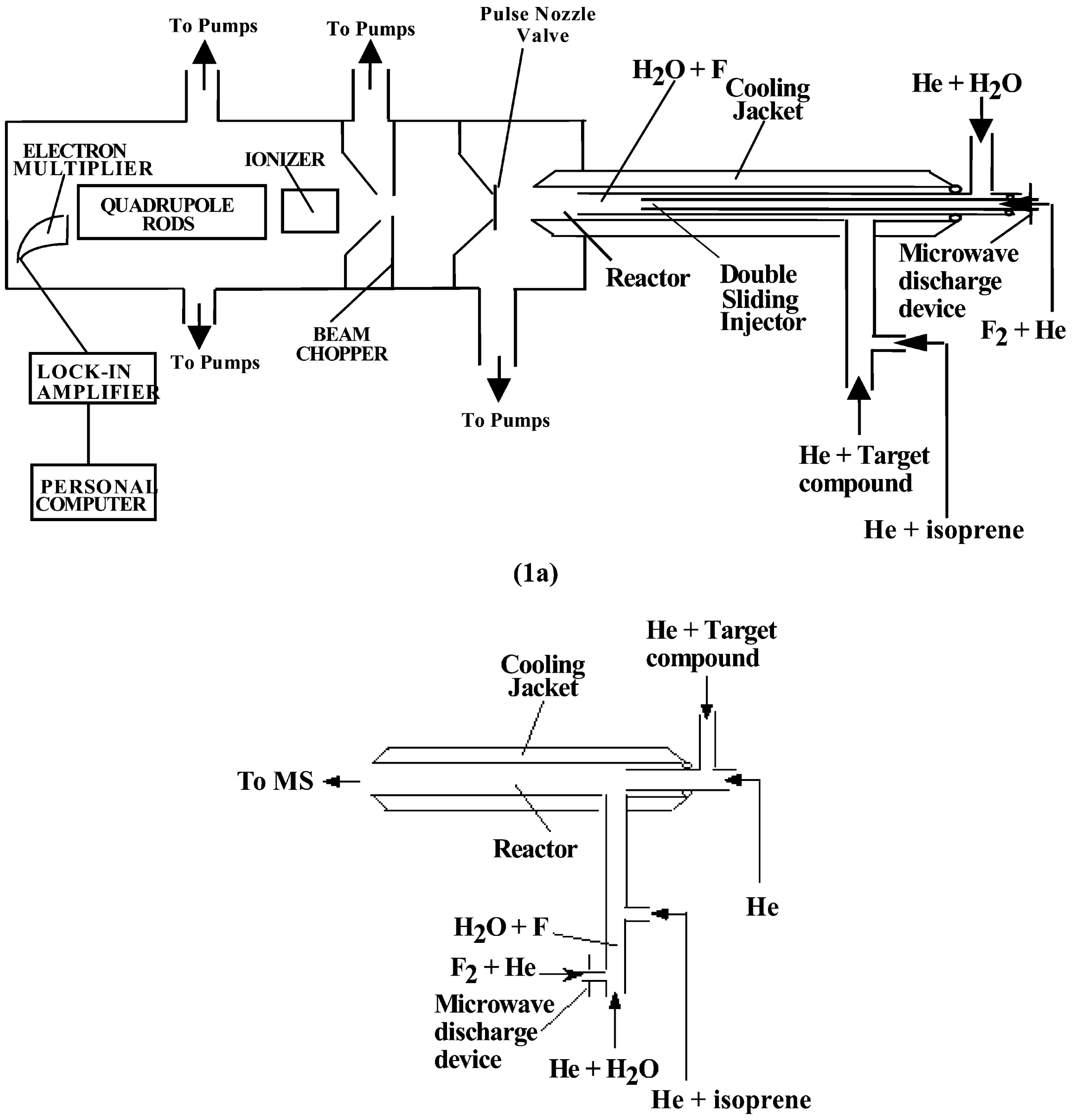

Figure 1. Experimental apparatus for RR/DF/MS kinetics study of isoprene + OH radical reaction at 240−320 K (1a) and for controlled experiments (1b). For all kinetic experiments, F atom is produced by microwave discharge of F_2 in the sliding injector. H_2O is added through the outer sliding injector as the OH precursor. Both isoprene and reference compounds are mixed and introduced into the reactor from the sidearm.

et al.[18] determined the rate constant for reaction 1 over the range of 58−293 K using the Laval nozzle expansion, and they reported a $k_1(293\ \text{K}) = (10.0 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and observed negative temperature dependence of the rate constant at some of the very low temperatures for this reaction.

Several investigations have been conducted on the pressure dependence of the rate coefficient for reaction 1.[1−4,16] Campuzano-Jost et al.[1,19] reported that the rate coefficient of reaction 1 was independent of pressure over 60−600 Torr, with $k_1(297\ \text{K}) = (8.47-8.56) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Choung and Stevens[3] observed that the high-pressure limit was reached at 2 Torr because their k_1 value was essentially independent of pressure at 2 Torr or higher. However, Park et al.[5] observed a slight increasing trend of the k_1 value at 2, 4, 6.1, and 8.1 Torr. McGivern et al.[2] also reported a significant decrease of the rate constant from $(9.5 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 10 Torr to $(8.5 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1 Torr, and the pressure of 1 Torr was reported to be within the fall-off region of the OH + isoprene system. The sporadic kinetic data at low temperatures and low pressures and the inconsistency of previous kinetic results from different groups for the reaction 1 warrant more kinetics studies to better help understand the role of isoprene in the atmosphere. In this Article, we will report our findings in the kinetics investigation for this reaction at 240−340 K and a total pressure of 1−3 Torr using the relative rate/discharge flow/mass spectrometry (RR/DF/MS) technique.

Experimental Section

A detailed description of the RR/DF/MS experimental apparatus for studying reactions of VOCs with radicals has been presented previously.[20−23] Figure 1 shows the RR/DF/MS apparatus used in the present study of reaction 1, with Figure 1a illustrating the arrangement for kinetics investigation and Figure 1b depicting the composition for controlled experiments. The flow reactor consisted of an 80 cm long Pyrex tube with an internal diameter of 5.08 cm. The internal surface of the reactor was covered with a poly(tetrafluoroethylene) (TFE) Teflon sheet (0.79 mm thick) to reduce both the OH radical wall loss and the contamination of the internal surface of the flow reactor due to deposition of the products from reactions. The flow tube was wrapped by a Pyrex jacket for variation of reactor temperature. A mechanical pump (Edwards E2M175) was used to maintain a steady-state gas flow in the flow tube. An electron impact mass spectrometer (Extrel MAX-1000) was housed in a vacuum chamber, which was two-stage differentially pumped by two 6-in. diffusion pumps with liquid nitrogen baffles, resulting in an ultimate vacuum of $<5 \times 10^{-10}$ Torr in the second stage. The carrier gas, helium, was introduced into the flow reactor through both a double-sliding injector and a sidearm inlet port located upstream of the reactor. Throughout the experiment, a total pressure of about 1−3 Torr was maintained in the flow reactor. Mean gas velocity in the flow tube was about 1200 cm s^{-1}. The interaction between OH radicals and the VOCs was confined to a contact distance of 30 cm, which corresponded to a reaction time of about 24 ms. A removable liquid nitrogen trap was placed downstream of the reactor to protect the vacuum pump from corrosive reactants and products.

Mass spectrometric detection of reactants and products was carried out by continuous sampling at the downstream end of the flow tube. A 200-Hz tuning fork chopper was used for beam modulation, and ion signals were sent to a lock-in amplifier (SR510) that was referenced to the chopper frequency. The amplified analog signal was converted to digital form using an analog to digital convertor (Analog Devices RTI/815) and recorded on a microcomputer. In the present study, an electron impact energy of 40 eV was used to minimize fragmentation of the reactants without significantly compromising the ionization efficiency. Parent ions of isoprene, ethanethiol, and dimethyl disulfide were monitored at $m/z = 68$, 62, and 94, respectively. Essentially no fragment daughter ions were observed at $m/z = 68$ from dimethyl disulfide, nor at $m/z = 62$ from isoprene. This suggested that there was very little overlapping in our mass spectroscopic detection of both target and reference compounds, and the decay of these reactants was monitored separately without any interference from other species. Under normal operational conditions, the detection limit of gas samples was on the order of 10^9−10^{10} molecules cm^{-3} depending on the individual species detected.

The OH radicals were generated by reacting F atoms with H_2O inside a double sliding injector, which consisted of two concentric Pyrex tubes with an inside diameter of 7 and 12.7 mm, respectively. The internal surface of the inner Pyrex tube was coated with halocarbon wax (series 1500, Halocarbon Products Corp.) to reduce the loss of atomic fluorine due to reacting with SiO_2. The H_2O vapor was carried by 100 sccm (standard cube centimeter per minute) of helium to the double-sliding injector, and the fluorine atoms were generated by microwave discharge (Opthos Instruments, Inc. model MPG-4) of 5% F_2 carried by 1500 sccm of helium,

$$F + H_2O \rightarrow OH + HF \qquad k_2 = 1.4 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ {}^{24} \quad (2)$$

Isoprene and a reference compound (either dimethyl disulfide or ethanethiol) were carried by 100−200 sccm of helium and introduced to the reactor from the sidearm inlet port. Prior to entering the reactor, the target and reference compounds were mixed to ensure that they shared the same reaction time with the OH radicals.

The VOCs were quantified by calibrating the mass spectral signal using known concentrations of the VOCs. This was accomplished either by introducing the known amount of a VOC sample into the reactor or by quantitative conversion of the species through chemical reactions. In particular, the initial concentration of the OH radicals was taken to be the same as the atomic fluorine concentration, which was determined by measuring the $[F_2]$ difference between "switch on" and "switch off" of the microwave discharge device while F_2 was passed through the discharge cavity,[22,23] $[F] = 2 \times \Delta[F_2] = 2 \times ([F_2]_{\text{switch off}} - [F_2]_{\text{switch on}})$. It was found that 90−98% of the F_2 dissociated under 50 W of microwave discharge power, with dissociation efficiency inversely proportional to the amount of F_2. Excessive amount of water ($\sim 7 \times 10^{14}$ molecule cm^{-3}) was introduced into the double sliding injector to ensure complete titration of the fluorine atoms in the present work; thus the variation of the OH radical concentration was achieved by altering the amount of F_2 ($(0-2) \times 10^{13}$ molecule cm^{-3}) passing through the cavity. The possible loss of F atoms in our discharge tube was checked by rearranging the experimental setup such that the travel time of the F atoms can be varied before reacting with water. A direct reaction of F atoms with isoprene was used for the checking purpose. It was found that essentially the same amount of isoprene was consumed by the F atom at 0.1−2.5 ms, suggesting that there was little loss of F atom in the inner sliding injector under our experimental conditions. The stoichiometric consumption of the VOCs by the OH radicals was then used to determine the concentration of the VOCs in the flow reactor. The intensity of the mass spectral signal was found to be always linearly proportional to the amount of organic samples in the reactor.

The temperature of the reactor was controlled and varied at 240−340 K using a temperature bath circulator (Neslab ULT-80). Either methanol or water was pumped through the Pyrex jacket for a reactor temperature below or above 298 K, respectively. At each temperature, experiments were performed two to four times on different days under the same experimental conditions to check the consistency of the experimental results. For kinetics study as a function of pressure, the total pressure of the rector was regulated at 1−3 Torr by adjusting the throttle valve at the downstream of the vacuum line.

On the basis of kinetics formulation of the RR/DF/MS technique,[20] rate constant determination for reaction 1 was achieved by observing the decay of both isoprene and a reference compound in the presence of OH radicals. Assuming that both compounds only reacted with the OH radicals:

$$C_5H_8 + OH \rightarrow (OH)C_5H_8 \qquad (1)$$

$$\text{reference} + OH \rightarrow \text{products} \qquad (3)$$

it can be shown that

$$\ln \frac{[\text{isoprene}]_{t,0}}{[\text{isoprene}]_{t,[OH]}} = \frac{k_1}{k_3} \ln \frac{[\text{reference}]_{t,0}}{[\text{reference}]_{t,[OH]}} \qquad (I)$$

where $[\text{isoprene}]_{t,0}$ and $[\text{reference}]_{t,0}$ represent the concentration of isoprene and reference compounds in the absence of OH radicals at time t, $[\text{isoprene}]_{t,[OH]}$ and $[\text{reference}]_{t,[OH]}$ stand for the concentrations of isoprene and the reference compound in the presence of OH radicals at time t, and k_1 and k_3 are the rate constants for reactions 1 and 3, respectively. A straight line with a slope equal to k_1/k_3 was generated from the plot of $\ln([\text{isoprene}]_{t,0}/[\text{isoprene}]_{t,[OH]})$ versus $\ln([\text{reference}]_{t,0}/[\text{reference}]_{t,[OH]})$. The k_1 was then calculated from the known value of k_3. If the temperature dependence of k_3 was known, repeating the above exercise at different temperatures allowed the determination of k_1 as a function of temperature. Finally, k_1 was measured as a function of pressure by repeating the experiment at different

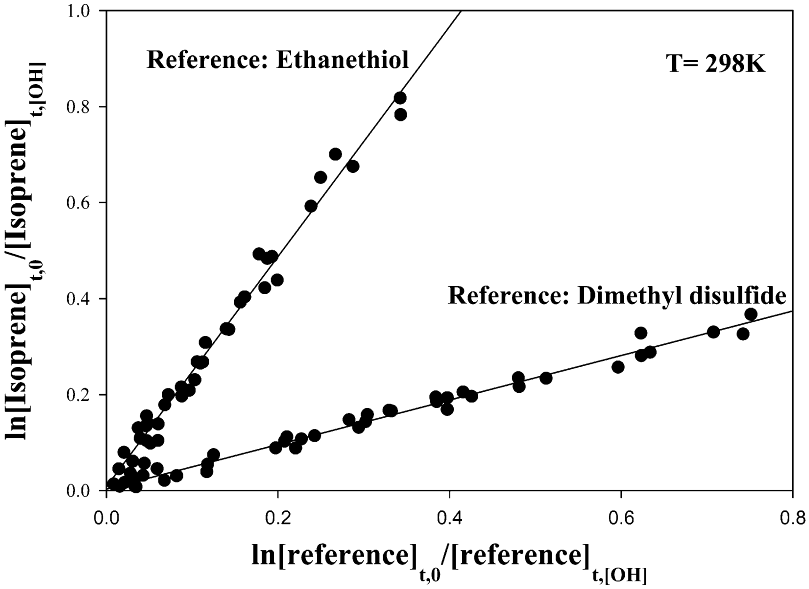

Figure 2. Typical kinetic data acquired with the RR/DF/MS technique for the reaction of isoprene with OH radicals at 240−340 K and a fixed reaction time of 24 ms using dimethyl disulfide and ethanethiol as reference compounds. The experiments are carried out at a total pressure of 1.0−1.1 Torr. Initial concentrations were (1.3−4.0) × 10^{13}, (5.7−1.1) × 10^{12}, and (1.2−3.0) × 10^{13} molecules cm^{-3} for isoprene, dimethyl disulfide, and ethanethiol, respectively. The OH concentration was varied in a range of (0−4.0) × 10^{13} molecules cm^{-3}.

TABLE 1: Rate Constant of OH + Isoprene at Room Temperature

T (K)	reference compound[a]	slope[b]	$k_1 \times (10^{11})$[c]	P_{total} (Torr)	technique[d]	reference
298	dimethyl disulfide	0.464 ± 0.010(42)	9.8 ± 0.8	1.0−1.1	RR/DF/MS	this work
298	ethanethiol	2.398 ± 0.043(44)	11.1 ± 1.6	1.0−1.1	RR/DF/MS	this work
299	na	na	9.26 ± 1.5	200	FP/RF	16
298	2-methyl propene	1.962 ± 0.096	10.1 ± 1.9	760	GC/MS	12
298	(*E*)-2-butene	1.74 ± 0.14	11.1 ± 0.23	760	GC/FID	12
295 ± 1	1,3-butadiene	1.51 ± 0.08	10.0	735	GC/MS	13
297 ± 2	1,3-butadiene	1.48 ± 0.04	10.1 ± 0.3	760	GC/FID	27
297	propylene	na	10.1 ± 0.2	758	GC/FID	14
298	na	na	10.2 ± 0.9	112.7	FF/CIMS	17
295	na	na	9.6 ± 0.5	20	LP/LIF	2
300	na	na	11.0 ± 0.4	2	DF/LIF	3
300	na	na	10.8 ± 0.5	150	DF/LIF	4
298	na	na	11.0 ± 0.5	2	DF/LIF	15
293	na	na	10.0 ± 1.5	na	LNE/LIF	18
300	ethene	na	7.4	757	GC/FID	28
297	na	na	8.47 ± 0.59	200	PLP/LIF	1
294	na	na	10.1 ± 0.29	2	LP/LIF	5

[a] The rate constant of the hydroxyl radical reaction with dimethyl disulfide and ethanethiol was calculated from Arrhenius equations previously published.[25,26] [b] The error bar was taken as 2σ. The number in parentheses represents number of data points collected at the corresponding temperature. [c] cm^3 molecule^{-1} s^{-1}. [d] RR/DF/MS, relative rate/discharge flow/mass spectrometer; GC/MS, gas chromatography/mass spectrometer; GC/FID, gas chromatography/flame ionization detection; FP/RF, flash photolysis/resonance fluorescence; FF/CIMS, fast flow/chemical ionization mass spectrometry; DF/LIF, discharge flow/laser-induced fluorescence; LP/LIF, laser photolysis/laser-induced fluorescence; LNE/LIF, Laval nozzle expansion/laser-induced fluorescence; PLP/LIF, pulsed photolysis-pulsed/laser-induced fluorescence.

pressures provided that the pressure dependence of k_3 was known. It was desirable that the k_3 value was independent of pressure to simplify the investigation. In the present work, the rate constant of k_3 was assumed to be pressure independent based on previous reports of little variation of rate constant for reactions of OH radicals with dimethyl disulfide at 50−200 Torr and ethanethiol at 30−100 Torr.[25,26]

Helium (>99.999%) was obtained from the Oxygen Service Co. F_2 (5% in ultra-high purity He) was obtained from Spectra Gases, Inc. The following reactants were purchased from Acros Organics: ethanethiol (>99%) and dimethyl disulfide (99%). The isoprene (99%) was purchased from Aldrich Chemical Co., Inc. All samples were used as received. Distilled water was used as the OH precursor.

Results and Discussion

(A) Temperature Dependence of k_1. In the present work, it was observed that dimethyl disulfide and ethanethiol reacted with F_2 molecules, causing a decay of these compounds. To reduce the contribution of these reactions to our rate constant determination of reaction 1, the microwave discharge was kept "on" to minimize the direct contact between reference compounds and F_2 during the kinetic data collection.

Figure 2 shows typical decay of isoprene versus the decay of dimethyl disulfide and ethanethiol at 298 K, respectively. It can be seen that the decay of both isoprene and the reference compounds follows the relationship given by eq I. For a total of 42 and 44 data points at 298 K, linear least-square fit of the experimental data yielded a rate constant ratio of

TABLE 2: Reaction Scheme Used in Chemical Model Simulation

reaction[a]	k (cm^3 molecule^{-1} s^{-1})	reference
$F + H_2O \rightarrow HF + OH$	1.4×10^{-11}	24
$OH + OH \rightarrow H_2O + O$	1.9×10^{-12}	24
OH + wall → product	10[b]	estimate[d]
$O + OH \rightarrow O_2 + H$	3.3×10^{-11}	24
H + wall → product	10[b]	estimate[d]
$H + OH + M \rightarrow H_2O + M$	2.3×10^{-31} [c]	36
$O + F_2 \rightarrow FO + F$	1.0×10^{-16}	37
$FO + OH \rightarrow O_2 + HF$	1.3×10^{-12}	estimate[e]
$H + F_2 \rightarrow HF + F$	1.38×10^{-12}	38
$OH + C_5H_8 \rightarrow$ products	1.04×10^{-10}	39
$OH + (CH_3S)_2 \rightarrow$ products	2.11×10^{-10} [f]	25
$O + C_5H_8 \rightarrow$ products	3.50×10^{-11}	40
$O + (CH_3S)_2 \rightarrow$ products	1.5×10^{-10} [g]	42
$H + C_5H_8 \rightarrow$ products	8.34×10^{-12} [h]	44
$H + (CH_3S)_2 \rightarrow$ products	8.0×10^{-12} [i]	45

[a] Initial concentrations are: $[F]_0 = 4.4 \times 10^{13}$, $[H_2O]_0 = 7.1 \times 10^{14}$, $[F_2]_0 = 2.0 \times 10^{12}$, $[C_5H_8]_0 = 3.99 \times 10^{13}$, $[(CH_3S)_2]_0 = 1.08 \times 10^{13}$, and $[C_2H_5SH]_0 = 3.03 \times 10^{13}$ molecule cm^{-3}, respectively. The initial concentrations of all other species are set to zero. [b] The unit is s^{-1} for the wall-loss process. [c] The unit is cm^6 molecule^{-2} s^{-1}. [d] Estimate based on OH wall loss. [e] Estimate based on k(ClO + OH). [f] When ethanethiol was used as a reference, $k = 4.64 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for ethanethiol + OH at 298 K.[26] [g] $k = 2.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for ethanethiol + O at 298 K.[41] [h] $k = 8.34 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is estimated for isoprene + H at 298 K based on $k(C_4H_6 + H)$. [i] $k = 2.41 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for ethanethiol + H at 298 K.[43]

$k_1/k_{3,\text{dimethyl disulfide}} = 0.464 \pm 0.010$ and $k_1/k_{3,\text{ethanethiol}} = 2.398 \pm 0.043$, respectively. The rate constant for the reaction of OH radicals with dimethyl disulfide and ethanethiol at 298 K was determined to be $k_{3,\text{dimethyl disulfide}} = (2.11 \pm 0.11) \times 10^{-10}$ and $k_{3,\text{ethanethiol}} = (4.64 \pm 0.62) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.[25,26] The rate constant for reaction 1 was then determined to be $k_1 = (9.78 \pm 0.82) \times 10^{-11}$ and $k_1 = (11.1 \pm 1.64) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K using dimethyl disulfide and ethanethiol as the reference compound, respectively. The quoted error bars were taken as 2σ for this work, which took into account the scatter of data, the uncertainty of the reference rate constant, and the uncertainty of the experimental parameters such as pressure, temperature, and flow rates. Note that the larger error bar of the rate constant did not result from the uncertainty of the slope, but from the uncertainty of reference rate constants. An average of $k_1 = (10.4 \pm 1.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was derived for the reaction of OH with isoprene at 298 K. It should be pointed out that the $k_{3,\text{dimethyl disulfide}}$ and the $k_{3,\text{ethanethiol}}$ values used above were calculated from the corresponding Arrhenius expressions of refs 25 and 26. Our k_1(298 K) values would be $(9.18 \pm 0.86) \times 10^{-11}$ and $(10.3 \pm 0.79) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} if the original values of $k_{3,\text{dimethyl disulfide}} = (1.98 \pm 0.18) \times 10^{-10}$ and $k_{3,\text{ethanethiol}} = (4.31 \pm 0.32) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (the weighted average) measured in these references were used, leading to an average of $k_1 = (9.74 \pm 1.17) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Thus, the average k_1 value at 298 K derived using reference constants from the Arrhenius expressions is about 7% higher than that derived using the original reference rate constants. This work chose to use the reference rate constants calculated from Arrhenius expressions for the determination of the rate constant of reaction 1 so that the trend of temperature dependence can be followed. Table 1 summarizes our rate constant along with available literature values for reaction 1 at room temperature. Within the experimental uncertainty, our k_1(298 K) value is in very good agreement with most previous investigations reporting a k_1 value of $(9.26-11.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperature for this reaction,[2−5,12−18,27,28] but is ∼15% higher than the most recent value of $k_1(297\text{ K}) = (8.47 \pm 0.59) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} reported by Campuzano et al.[1] using the pulse laser photolysis-pulsed/laser-induced fluorescence technique.

The cause of difference between Campuzano et al.[1] and the present work in the k_1 value is unclear. We are aware of the assumption on which the relative rate technique was based.[22,23] The assumption is that both the target and the reference molecules are consumed only by the OH radicals. One potential error source of the relative rate technique could come from secondary reactions that affect the concentration of either target or reference compound. To address this issue, control experiments were carried out in the present work. The control experiments were designed to see if the decay of both target and reference compounds was affected by secondary reactions involved in our chemical system. In a particular experiment, it was to examine if the primary product, OHC_5H_8, from reaction 1 reacted with the reference compounds that would contribute to the decay of the reference compounds. Similarly, it was also imperative to know if CH_3SSCH_2 or C_2H_5S radicals from reaction 3 further reacted with isoprene, contributing to the decay of this reactant. The experimental setup for the control experiments is shown in Figure 1b, in which the OH radicals reacted with a reference compound (or a target compound) while traveling through the sidearm.[22,23] The primary products then entered the reactor to interact with isoprene (or a reference compound). This arrangement facilitated monitoring the effects on the decay of the reference compound (or isoprene) due to the direct contacts between the OHC_5H_8 adduct and the reference compound (or between the isoprene molecules and the CH_3SSCH_2 or C_2H_5S radicals). It was found that the products from OH + dimethyl disulfide or ethanethiol had little effect on the isoprene mass spectral signal intensity (<1.4%). Likewise, the products from the OH + isoprene reaction had little effects on the dimethyl disulfide or ethanethiol mass spectral signal intensity (<2.2%). This indicated that the decay of both target and reference compounds was not significantly affected by the primary products of the reactions of OH + reference compound and OH + target compound, respectively.

Another factor that could affect the accuracy of the rate constant measured using the relative rate technique is the accuracy of the reference rate constant. An erroneous reference rate constant would result in an inaccurate target rate constant. The kinetics for the reactions of OH with CH_3SSCH_3 and C_2H_5SH was investigated by several groups using different

TABLE 3: Arrhenius Expression of OH + Isoprene

T (K)	P_{total} (Torr)	k_1 (cm^3 molecule^{-1} s^{-1})	technique[a]	reference
240−340	1.0−1.1	$(2.33 \pm 0.09) \times 10^{-11} \exp[(444 \pm 27)/T]$	RR/DF/MS	this work
298−363	760	$(2.56 \pm 0.35) \times 10^{-11} \exp[(408 \pm 42)/T]$	GC/MS	12
299−422	200	$2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$	FP/RF	16
251−342	200	$(8.63 \pm 0.42) \times 10^{-11} \exp[(348 \pm 136)((1/T) - (1/298\text{ K}))]$	PLP/LIF	1

[a] RR/DF/MS, relative rate/discharge flow/mass spectrometer; GC/MS, gas chromatograph/mass spectrometer; FP/RF, flash photolysis/resonance fluorescence; PLP/LIF, pulsed photolysis-pulsed/laser-induced fluorescence.

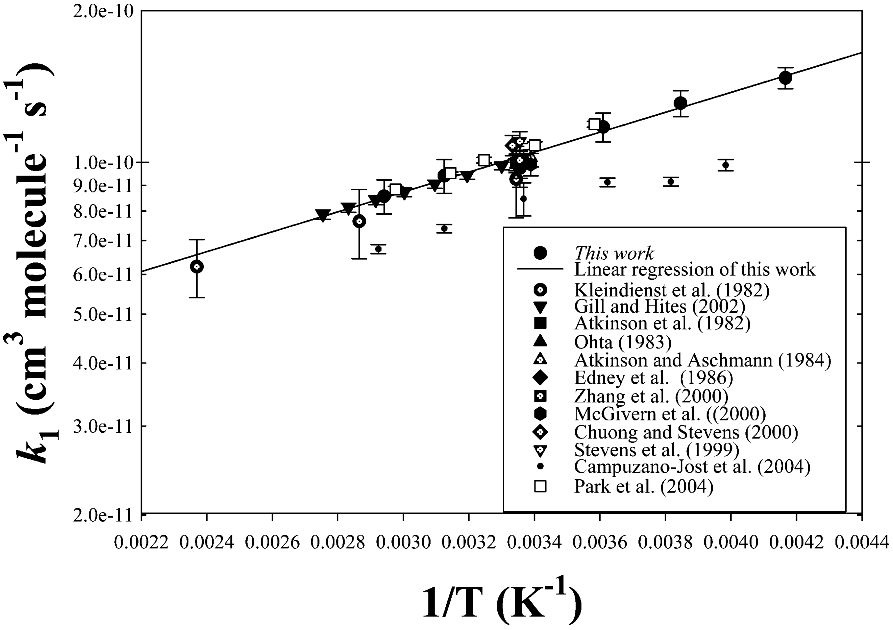

Figure 3. Arrhenius plot for the reaction of isoprene + OH at 240−340 K along with available experimental data in literature.

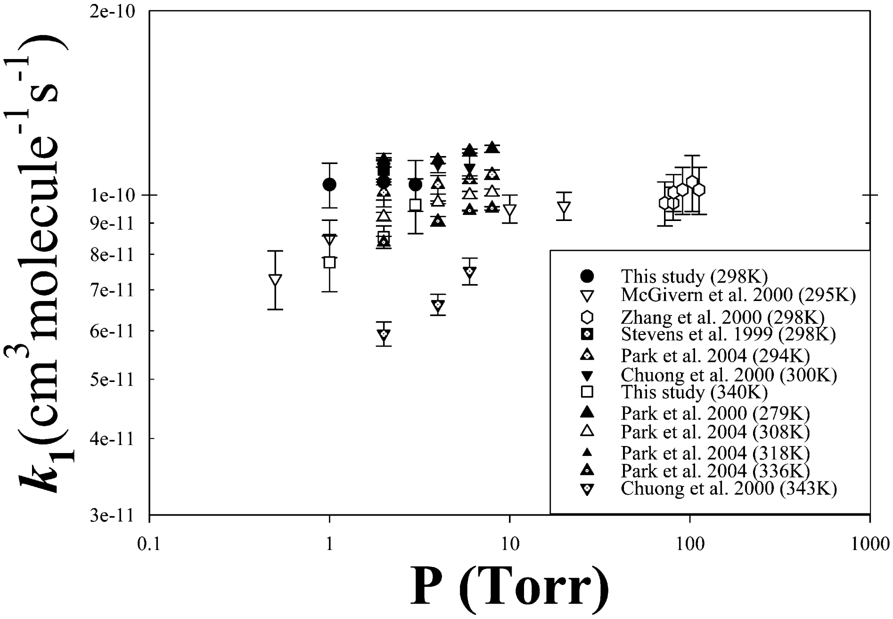

Figure 4. Pressure-dependent plot for the reaction of isoprene with OH at 1−3 Torr and 298−340 K along with available experimental data in the literature.

techniques, and the results were in good agreement within the estimated error limits.[28−33] The fact that the k_1 values derived in the present study using two different references agreed with each other indicated an overall consistency of our kinetic measurements. Hence, we believe that our average k_1 value should be accurate provided that the previous kinetics studies of OH + CH_3SSCH_3 and C_2H_5SH were accurate. We chose to use the rate constants of Wine et al.[25,26] in the present kinetics study of reaction 1 for two reasons. First, these rate constants provide a k_1 that is in good agreement with the literature k_1 value when they are used as reference rate constant in the present work. Second, this group performed temperature-dependent study of the kinetics at a temperature range representative of troposphere, which allowed the temperature-dependent investigation for reaction 1 in the present work.

The effect of atomic oxygen and atomic hydrogen produced from secondary reaction, in our chemical system, on the decay of target and reference compounds is also a concern in this study. In the present work, the effect of O and H atom on our kinetic results was evaluated by chemical simulation including a group of chemical reactions given in Table 2. The evaluation was carried out by numerically solving these differential kinetic equations in our chemical system, and the concentration of chemical species of interest was calculated as a function of time using the the Runge−Kutta method,[34] with initial concentrations of 4.0 × 10^{13} and (1.1−3.0) × 10^{13} molecule cm^3 for the isoprene and reference compounds and an initial concentration of 4.0 × 10^{13} molecule cm^3 for the OH radical, respectively. Our simulation calculation results indicated that the secondary reactions involving both oxygen and hydrogen atoms contributed to less than 2% of the decay of isoprene and reference compounds when 70% of these reactants were consumed in the reactor. Because reactant consumption was controlled within 50% during our kinetic data collection, the effects of the secondary reactions on the kinetics results should be less than 2% in the present study.

TABLE 4: Rate Constant of OH + Isoprene as a Function of Pressure at 294−343 K

P_{total} (Torr)	T (K)	reference compound[a]	slope[b]	$k_1 \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	technique[c]	reference
1.0	298	dimethyl disulfide	0.463 ± 0.020(42)	9.78 ± 0.82	RR/DF/MS	this work
2.0		dimethyl disulfide	0.469 ± 0.030(43)	9.91 ± 0.96	RR/DF/MS	this work
3.0		dimethyl disulfide	0.467 ± 0.024(41)	9.86 ± 0.87	RR/DF/MS	this work
1.0		ethanethiol	2.397 ± 0.086(44)	11.1 ± 1.64	RR/DF/MS	this work
2.0		ethanethiol	2.402 ± 0.134(26)	11.1 ± 1.71	RR/DF/MS	this work
3.0		ethanethiol	2.344 ± 0.158(20)	10.9 ± 1.72	RR/DF/MS	this work
1.0	340	dimethyl disulfide	0.420 ± 0.018(57)	7.56 ± 0.65	RR/DF/MS	this work
2.0		dimethyl disulfide	0.473 ± 0.012(14)	8.51 ± 0.67	RR/DF/MS	this work
3.0		dimethyl disulfide	0.534 ± 0.022(20)	9.61 ± 0.82	RR/DF/MS	this work
0.5	295	na	na	7.3 ± 0.8	LP/LIF	2
1.0		na	na	8.5 ± 0.6	LP/LIF	2
10		na	na	9.5 ± 0.5	LP/LIF	2
20		na	na	9.6 ± 0.5	LP/LIF	2
72.7	298	na	na	9.7 ± 0.8	FF/CIMS	17
80.8		na	na	9.7 ± 0.6	FF/CIMS	17
81.3		na	na	10.1 ± 0.7	FF/CIMS	17
91.2		na	na	10.2 ± 0.9	FF/CIMS	17
103.1		na	na	10.5 ± 1.1	FF/CIMS	17
112.7		na	na	10.2 ± 0.9	FF/CIMS	17
2.0	294	na	na	10.1 ± 0.29	LP/LIF	5
4.0		na	na	10.4 ± 0.36	LP/LIF	5
6.0		na	na	10.6 ± 0.15	LP/LIF	5
8.0		na	na	10.8 ± 0.19	LP/LIF	5
2.0	308	na	na	9.22 ± 0.15	LP/LIF	5
4.0		na	na	9.73 ± 0.05	LP/LIF	5
6.0		na	na	10.0 ± 0.13	LP/LIF	5
8.0		na	na	10.1 ± 0.13	LP/LIF	5
2.0	318	na	na	8.37 ± 0.19	LP/LIF	5
4.0		na	na	9.06 ± 0.16	LP/LIF	5
6.0		na	na	9.43 ± 0.02	LP/LIF	5
8.0		na	na	9.51 ± 0.06	LP/LIF	5
2.0	336	na	na	7.53 ± 0.29	LP/LIF	5
4.0		na	na	8.10 ± 0.10	LP/LIF	5
6.0		na	na	8.54 ± 0.06	LP/LIF	5
8.0		na	na	8.83 ± 0.13	LP/LIF	5
2.0	300	na	na	10.99 ± 0.38	DF/LIF	3
4.0		na	na	11.22 ± 0.34	DF/LIF	3
6.0		na	na	11.10 ± 0.48	DF/LIF	3
2.0	321	na	na	7.88 ± 0.50	DF/LIF	3
4.0		na	na	8.96 ± 0.30	DF/LIF	3
6.0		na	na	9.02 ± 0.34	DF/LIF	3
2.0	343	na	na	5.93 ± 0.27	DF/LIF	3
4.0		na	na	6.62 ± 0.26	DF/LIF	3
6.0		na	na	7.51 ± 0.38	DF/LIF	3

[a] The rate constant of the hydroxyl radical reaction with dimethyl disulfide and ethanethiol was calculated from Arrhenius equations previously published.[25,26] [b] The error bar was taken as 2σ. The number in parentheses represents number of data points collected at the corresponding temperature. [c] RR/DF/MS, relative rate/discharge flow/mass spectrometry; FF/CIMS, fast flow/chemical ionization mass spectrometry; DF/LIF, discharge flow/laser-induced fluorescence; LP/LIF, laser photolysis/laser-induced fluorescence.

The rate constant of reaction 1 was also determined at 240, 260, 277, 320, and 340 K, and the results are given in Table 3 and summarized in Figure 3. Previous studies reported that the rate constant of reaction 1 decreased with increase of temperature.[1,12,16] Our kinetics results confirmed the negative temperature dependence of the reaction 1 at 240−340 K. An Arrhenius expression was then derived from our kinetic data to be $k_1 = (2.33 \pm 0.09) \times 10^{-11} \exp[(444 \pm 27)/T]$ cm^3 molecule^{-1} s^{-1} at 240−340 K. This result is in good agreement with the Arrhenius expression of $k_1 = (2.56^{+0.35}_{-0.31}) \times 10^{-11} \exp[(408 \pm 42)/T]$ cm^3 molecule^{-1} s^{-1} reported by Gill and Hites[12] at 298−363 K, and of $k_1 = 2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$ cm^3 molecule^{-1} s^{-1} reported by Kleindienst et al.[16] at 299−422 K. However, as compared to the temperature-dependent kinetic results reported by Campuzano-Jost et al.,[1] our k_1 values are systematically higher in the similar temperature domain. Nevertheless, all temperature-dependent measurements revealed the same trend for the kinetic behavior as a function of temperature for reaction 1, confirming that the reaction is an addition process with formation of the OH−isoprene adducts.

(B) Pressure Dependence of k_1. Pressure dependence of the k_1 value was investigated at a total pressure of 1−3 Torr at 298 and 340 K, and the results are presented in Table 4 and Figure 4. At 298 K and 1, 2, and 3 Torr, $k_1/k_{3,\text{dimethyl disulfide}} = 0.463 \pm 0.020$, 0.469 ± 0.030, 0.467 ± 0.024, and $k_1/k_{3,\text{ethanethiol}} = 2.397 \pm 0.086$, 2.402 ± 0.134, 2.344 ± 0.158, respectively, and rate constants for the reaction of OH radicals with isoprene were determined to be $(9.78 \pm 0.82) \times 10^{-11}$, $(9.91 \pm 0.96) \times 10^{-11}$, and $(9.86 \pm 0.87) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} using dimethyl disulfide as the reference compound, and $(11.1 \pm 1.64) \times 10^{-11}$, $(11.1 \pm 1.71) \times 10^{-11}$, $(10.9 \pm 1.72) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} using ethanethiol as the reference compound, respectively. The averages of these values are $(10.4 \pm 1.9) \times 10^{-11}$, $(10.5 \pm 1.9) \times 10^{-11}$, and $(10.4 \pm 1.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 1, 2, and 3 Torr, respectively. At 340 K, the k_1/k_3 ratio was determined to be 0.420 ± 0.018, 0.473 ± 0.012, and 0.534 ± 0.022 at 1, 2, and 3 Torr, and the corresponding k_1 value was determined to be $(7.56 \pm 0.65) \times 10^{-11}$, $(8.51 \pm 0.67) \times 10^{-11}$, and $(9.61 \pm 0.82) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively, using dimethyl disulfide as the reference compound. We were unable to determine the pressure dependence of k_1 at 340 K using ethanethiol as the reference compound due to the fact that the product of OH + ethanethiol deposited on the reactor wall and contributed to the decay of the reactants at this temperature. Our results suggest that reaction of OH radicals with isoprene is essentially independent of pressure over 1−3 Torr at 298 K. This observation is consistent with the Chuong and Stevens'[3] conclusion of k_1 being independent of pressure at 2−6 Torr at room temperature, but is in contrast to Park et al.'s[5] recent observation of a slight increase of the rate coefficient going from 2 to 8 Torr. Our kinetic results of the pressure dependent investigation also suggest that reaction 1 has reached its high-pressure limit at 1 Torr at 298 K, which is in contrast to the observation of McGiven et al.,[2] suggesting that the pressure of 1 Torr is within the fall-off region. Our finding of increasing k_1 from 1 to 3 Torr at 340 K suggests that the reaction of isoprene with OH radicals is positively dependent on pressure in this pressure range, and 1−3 Torr is within the fall-off region for this reaction at 340 K. This pressure dependence trend is consistent with that reported by Chuong and Steven[3] at 343 K and by Park et al.[5] at 336 K, respectively. However, our absolute k_1 values at 340 K are systematically higher than those reported by both groups. Further investigation is needed to resolve the differences between these pressure-dependent studies.

(C) Atmospheric Lifetime of Isoprene Due to OH Radicals. While there are several oxidants that can initiate the oxidation of isoprene in the troposphere, hydroxyl radicals are considered dominant for the removal of isoprene in the atmosphere.[4] The atmospheric lifetime of isoprene is then estimated using the following equation:

$$\tau_{\mathrm{isoprene}} \approx \frac{1}{k_{\mathrm{isoprene+OH}}[\mathrm{OH}]} \qquad \text{(II)}$$

where τ_{isoprene} is the atmospheric lifetime of the isoprene due to its reaction with the OH radicals, $k_{\mathrm{isoprene+OH}}$ is the rate constant of the reaction of isoprene with OH radicals at a typical tropospheric temperature of 277 K, and [OH] is the atmospheric concentration of the hydroxyl radicals. The average tropospheric hydroxyl concentration has previously been found to be $(8.1 \pm 0.9) \times 10^5$ molecules cm^{-3}.[35] Using the $k_{\mathrm{isoprene+OH}}$ (277 K) value determined in the present work, an upper limit of atmospheric lifetime for isoprene is estimated to be 2.9 h. The actual atmospheric lifetime of isoprene is expected to be shorter because isoprene may also react with other oxidants such as ozone and atomic chlorine during the daytime, and NO_3 radicals during nighttime.

Conclusion

The kinetics of the reaction of OH radical with isoprene has been investigated in the temperature range of 240−340 K and 1−3 Torr using the relative rate/discharge flow/mass spectrometry (RR/DF/MS) method. At 298 K, the rate constant for this reaction was determined to be $k_1 = (10.4 \pm 1.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is in good agreement with most literature values. The Arrhenius expression for this reaction was determined to be $k_1 = (2.33 \pm 0.09) \times 10^{-11} \exp[(444 \pm 27)/T]$ cm^3 molecule^{-1} s^{-1} at 240−340 K, which is consistent with two previous studies[12,16] at 298−422 K, but systematically higher than that reported by Campuzano-Jost et al.[1] The reaction of isoprene with OH was found to be independent of pressure over the pressure range of 1−3 Torr at 298 K, and the reaction has reached its high-pressure limit at 1 Torr. This finding is in good agreement with the observation of Chuong and Stevens,[3] but in contrast with the observation of McGivern et al.[2] and Park et al.[5] At 340 K, the rate constant of reaction 1 was found to positively depend on pressure over 1−3 Torr. However, our absolute k_1 values at 340 K were systematically higher than those reported by Chuong and Stevens[3] and Park et al.[5] Finally, the atmospheric lifetime of isoprene was estimated to be 2.9 h based on the rate constant of isoprene + OH determined at 277 K in the present work.

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