Direct Kinetics Study of the Product-Forming Channels of the Reaction of Isoprene-Derived Hydroxyperoxy Radicals with NO

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ABSTRACT: A direct kinetics study of the product-forming channels of the reaction of isoprene-derived hydroxyalkylperoxy radicals with NO has been performed at 100 Torr pressure and 298 K using the turbulent flow technique with high-pressure chemical ionization mass spectrometry for the detection of reactants and products. For comparative purposes, a similar study was also performed for the reaction of 1- and 2-butene-derived hydroxyalkylperoxy radicals with NO. The measured hydroxyalkylnitrate product channel branching ratios were determined to be 0.061, 0.068, and 0.070 for the 1-butene, 2-butene, and isoprene systems, respectively. The results are compared to previous measurements of the hydroxyalkylnitrate-branching ratios for these systems, and the atmospheric significance of the results is discussed. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 353–361, 2007

INTRODUCTION

The reactions involved in the oxidation of alkenes are known to be a major source of tropospheric ozone [1]. Atmospheric concentrations of alkenes are signif-

icantly impacted by both anthropogenic and biogenic emissions. Alkenes are important constituents of fuels and automobile exhaust [2,3] as well as other industrial and agricultural (biomass-burning) processes [4]. Biogenic sources of alkenes include emissions from vegetation, soils, and the oceans [5]. In rural areas, isoprene (2-methyl-1,3-butadiene), which is emitted by deciduous trees, is one of the most abundant nonmethane hydrocarbons (up to 1/3 of the total organic content of the atmosphere [1]). Because of the high-chemical reactivity of isoprene, it plays a large role in the production of
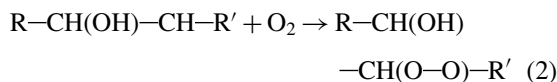
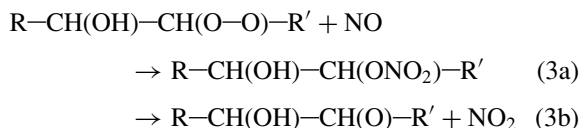ozone in rural locations and is responsible for nearly 100% of ozone formation in certain environments [1].

The atmospheric oxidation of alkenes is usually initiated by the addition of a hydroxy radical.

$$R-CH=CH-R' + OH \rightarrow R-CH(OH)-CH-R' \quad (1)$$

The two possible hydroxy adduct isomers—with OH adding to either the R or R′ side of the C=C double bond—are both commonly observed. For example, it is observed that OH preferentially adds to the terminal carbon of the C=C double bond in propene at about a 2:1 ratio as compared to OH addition at the central carbon [6]. However, in order to simplify and clarify the subsequent chemical steps in the oxidation of the alkenes, the notation used in the article will arbitrarily specify one isomer, with the implicit understanding that the other isomer is usually present and can undergo the same chemical transformations (since the final oxidation products are not the subject of this article, this notation simplification does not present any ambiguities). The OH adduct then reacts rapidly with O_2 to produce a β-hydroxyalkylperoxy (hereafter referred to as hydroxyperoxy) radical

$$R-CH(OH)-CH-R' + O_2 \rightarrow R-CH(OH)$$
$$-CH(O-O)-R' \quad (2)$$

Note that because of the presence of two nonequivalent double bonds and isomerization processes, there are six different hydroxyperoxy isomers for isoprene [7]. The hydroxyperoxy radical reacts with NO to form either a hydroxynitrate (reaction (3a)) or an alkoxy radical and NO_2 (reaction (3b))

$$R-CH(OH)-CH(O-O)-R' + NO$$
$$\rightarrow R-CH(OH)-CH(ONO_2)-R' \quad (3a)$$
$$\rightarrow R-CH(OH)-CH(O)-R' + NO_2 \quad (3b)$$

The formation of NO_2 in reaction (3b) leads to ozone production, whereas the formation of the hydroxynitrate in reaction (3a) terminates the oxidation cycle. The formation of hydroxynitrates via reaction (3a) can also affect the tropospheric ozone balance through the removal of NO_x. The hydroxynitrate product of reaction (3a) is relatively stable under tropospheric conditions and acts as an NO_x sink. Although the lifetimes of hydroxynitrates compounds in the presence of OH are on the order of only 1 day [8], they are significantly longer than the other products of alkene oxidation. A study by Chen et al. calculated that isoprene-derived hydroxynitrates alone accounted for up to 6.8% of summer NO_x removal in the eastern United States [9].

The stable products of the atmospheric oxidation of alkenes have been extensively studied [1], and there have been several measurements of the hydroxynitrate-branching ratios (k_{3a}/k_3) for reaction (3). As mentioned above, the hydroxynitrate-branching ratios are important kinetic parameters to determine, as the formation of hydroxynitrates represents a mechanistic roadblock to ozone production. In particular, a systematic study of hydroxynitrate formation from the C_2–C_6 alkenes by Shepson and coworkers found that, like the alkanes, the hydroxynitrate-branching ratio increases as the number of carbons in the alkene chain is increased [10]. However, they also found that the hydroxynitrate-branching ratios for the alkene oxidations were a factor of 2–3 lower than the branching ratios for the corresponding alkane oxidations. In particular, the hydroxynitrate-branching ratio has been extensively investigated for the oxidation of isoprene via product studies [7,9,11] and OH-cycling experiments [12]. The measured values of the hydroxynitrate-branching ratio obtained from these experiments range from 0.04 to 0.15. Field measurements of isoprene nitrates made in rural northern Michigan are more consistent with hydroxynitrate-branching ratio values on the low end of the laboratory measurement range cited above [13], whereas field measurements of alkyl nitrates made in rural northern California are consistent with much higher isoprene hydroxynitrate-branching ratios [14]. Sprengnether et al. point out that the current uncertainty in this value as it relates to the NO budget is equivalent to a 10% uncertainty in the total NO emissions in the eastern United States [7]. Therefore, it is of interest to perform new measurements of the hydroxynitrate-branching ratios for alkene-based hydroxyperoxy radical (for isoprene, in particular) + NO reactions.

This article describes the first direct simultaneous product study of both the hydroxynitrate- and NO_2-producing channels for the reaction of isoprene-derived hydroxyperoxy radicals with NO. These branching ratio measurements were conducted at 100 Torr and 298 K using a turbulent flow-chemical ionization mass spectrometry (TF-CIMS) kinetics apparatus. Similar branching ratio measurements were made for hydroxynitrate and NO_2 formation from the oxidation of the 1- and 2-butene systems.

EXPERIMENTAL

Turbulent Fast Flow Kinetics

A schematic of the experimental apparatus is given in Fig. 1 and is similar to that described by Miller et al. in
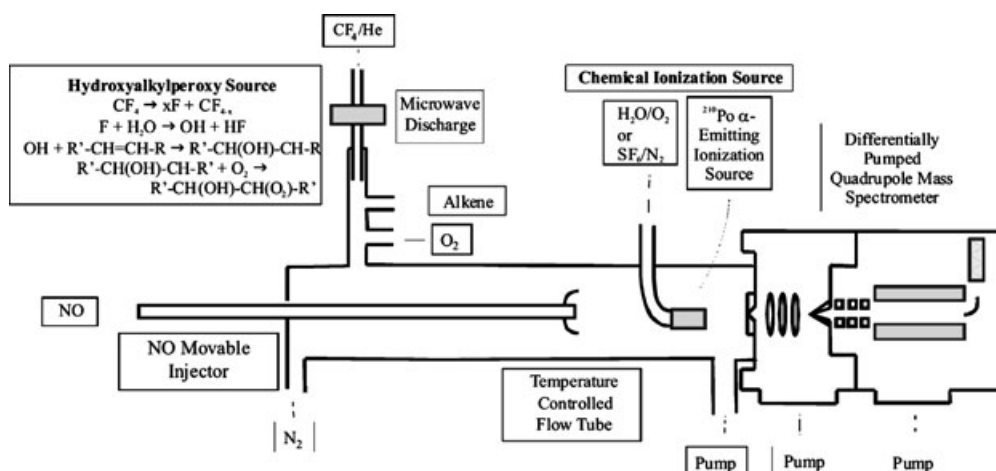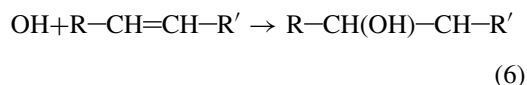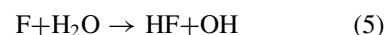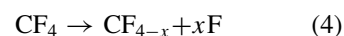
Figure 1   Experimental apparatus.

their study of the overall reaction rate of alkene-derived hydroxyperoxy radicals with NO [15]. The main flow tube was 100 cm in length and constructed with 2.2-cm-inner-diameter Pyrex tubing. A large flow of nitrogen carrier gas (30 STP L min^{-1}) was introduced at the rear of the flow tube to serve as the bulk flow gas. The reactants necessary for the production of the hydroxyperoxy radicals were also introduced at the rear of the flow tube through a 20-cm-long, 12.5-cm-inner-diameter sidearm. NO was introduced into the main flow tube through an encased moveable injector. The encasement was made of corrugated Teflon tubing and allowed the injector to be moved to various injector positions without breaking any vacuum seals. A fan-shaped Teflon device was placed at the end of the injector to enhance turbulent mixing. All gas flows were monitored with calibrated mass flow meters. A polonium-210 (^{210}Po) α-particle-emitting ionization source was placed between the flow tube and the entrance to the CIMS. The turbulent flow tube conditions were held to 100 ± 1 Torr and 298 ± 2 K, and velocities around 1100 cm s^{-1}. Both the radical source and the CIMS instrument operate optimally at this pressure, which is necessary to achieve the sensitivity required to carry out the desired measurements. Flow tube pressure and temperature were measured upstream of the ionization source. Pressure was measured using a 0–1000 Torr capacitance manometer. Temperature was determined using Cu-constantan thermocouples. Most of the flow tube gases were removed at the CIMS inlet using a 31 L s^{-1} roughing pump.

Preparation of Reactants

The hydroxyperoxy radical species were generated through the following reactions:

$$CF_4 \rightarrow CF_{4-x}+x\text{F} \qquad (4)$$

$$\text{F}+H_2O \rightarrow HF+OH \qquad (5)$$

$$OH+R-CH{=}CH-R' \rightarrow R-CH(OH)-CH-R' \qquad (6)$$

$$R-CH(OH)-CH-R'+O_2 \rightarrow$$
$$R-CH(OH)-CH(O_2)-R' \qquad (7)$$

The OH radicals were produced using the microwave discharge technique. A dilute mixture of He/CF$_4$ was passed through a microwave discharge, produced by a Beenakker cavity operating at 50 W, to create fluorine atoms (reaction (4)). The dilute mixture was obtained by combining a 5.0 STP L min^{-1} flow of ultra-high purity helium (99.999%) with a 1.0 STP mL min^{-1} flow of a 2% CF$_4$ (99.9%)/He mixture. The 5.0 STP L min^{-1} helium flow was first passed through a silica gel trap immersed in liquid nitrogen to remove any possibly impurities. The fluorine atoms were then injected into the flow tube sidearm and mixed with H$_2$O/He, produced by bubbling 10.0 mL min^{-1} He through a trap filled with H$_2$O at about 298 K. This generated OH radicals (reaction (5)). Hydroxyperoxy radicals were produced by adding excesses of the alkene and O$_2$ to the flow tube sidearm. The alkene reacted with OH to produce a hydroxy radical (reaction (6)), which then immediately reacted with O$_2$ to produce the hydroxyperoxy radical (reaction (7)). The order of reagent addition in the sidearm ensures that peroxy radical generation is complete before entering the main flow tube. This important point will be discussed more fully in the Results and Discussion section. An excess of NO was introduced to the main flow tube as a 1% NO/N$_2$ mixture through the moveable injector. The mixture was

first passed through a silica gel trap held between –20 and –30°C to remove any traces of NO_2 impurities. Negligible amounts of NO_2 impurities were observed using the CIMS technique.

Branching Ratio Measurements

In this study, the branching ratio for reaction (3) is defined as the ratio of the hydroxynitrate products to the sum of the hydroxynitrate and NO_2 products:

$$\frac{k_{3a}}{k_{3a} + k_{3b}} = \frac{[\text{hydroxynitrate}]_t}{[\text{hydroxynitrate}]_t + [NO_2]_t} \quad (8)$$

In many previous studies, the branching ratio is determined by measuring the proportion of hydroxynitrate produced to the amount of the alkene consumed

$$\frac{k_{3a}}{k_3} = \frac{[\text{hydroxynitrate}]_t}{[\text{alkene}]_{\text{consumed},t}} \quad (9)$$

If reactions (3a) and (3b) are the only product channels for reaction (3), and if there are no other reactions that consume the parent alkene in the specific photochemical system, equations (8) and (9) will yield identical values. However, if there are other reactions that consume the parent alkene, branching ratios calculated according to equation (9) will be erroneously low. This study is the first to directly measure the two known product channels and define the branching ratio according to equation (8).

Although a single measurement of the hydroxynitrate and NO_2 products under any specific experimental conditions will yield the branching ratio, data were collected over a variety of NO concentrations and reaction times to monitor and account for any possible secondary chemistry. As will be fully discussed in the Results and Discussion section, there are secondary sources of NO_2 that must be accounted for in order to calculate an accurate branching ratio for reaction (3). Individual measurements were done by sending a known concentration of NO through the moveable injector. At each injector position, the signals resulting from the NO_2 and hydroxynitrate products were monitored using the CIMS.

CIMS Detection

The chemical ionization reagent ions were produced using a commercial polonium-210 α-particle emitting ionization source consisting of a hollow cylindrical (69 by 12.7 mm) aluminum body with 10 mCi (3.7×10^8 disintegrations s^{-1}) of polonium-210 coated on the interior walls. The hydroxynitrate species were detected using a proton transfer chemical ionization scheme. The $H^+(H_2O)_n$ ions were produced by passing a large O_2 flow (7.0 STP L min^{-1}) through the ionization source with H_2O impurities being sufficiently abundant to produce an adequate amount of reagent ions. The $n = 4$ species usually accounts for more than 80% of the total ion signal, and thus the hydroxynitrate-$H^+(H_2O)_3$ species was the predominant species detected. For each parent alkene, there are at least two possible hydroxynitrate isomers (there are six possible isomers for isoprene) due to nonpreferential OH addition to either side of the double bond. Our detection method is not sensitive to the isomeric distribution of species, and thus our branching ratio measurements represent a weighted average for all isomers produced at the alkene-specific mass. A negative ion chemical ionization scheme was used to detect the NO_2 product. SF_6^- reagent ions were produced by combining a large flow of N_2 (7 STP L min^{-1}) with a 1.5 STP mL min^{-1} flow of 10% SF_6/N_2 and passing the mixture through the ionization source. The predominant species detected were NO_2^- and $H_2O \cdot NO_2^-$. Ions were detected with a quadrupole mass spectrometer housed in a two-stage differentially pumped vacuum chamber. Flow tube gases (neutrals and ions) were drawn into the front chamber through a charged 0.1-mm aperture. The front chamber was pumped by a 6-in. 2400 L s^{-1} diffusion pump. The ions were focused by three lenses constructed from 3.8-cm-inner-diameter and 4.8-cm-outer-diameter aluminum gaskets, and then entered the rear chamber through a skimmer cone with a charged 1.0-mm orifice. The skimmer cone was placed approximately 5 cm from the front aperture. The rear chamber was pumped by a 250 L s^{-1} turbomolecular pump. After the ions had passed through the skimmer cone, they were mass filtered and detected with a quadrupole mass spectrometer.

Absolute Concentration Determination

To determine the branching ratio as defined in equation, it is necessary to determine the absolute concentrations of hydroxynitrate and NO_2. Calibration curves were created to relate detector response to concentration by sending a known concentration of the product species into the flow reactor and measuring detector response. A 0.5% NO_2/N_2 mixture was added to the flow reactor via mass flow metering in order to construct the NO_2 response curves. Two hydroxynitrate standards, 1,2-hydroxynitratobutane and 2,3-hydroxynitratobutane (the hydroxynitrates formed in the oxidation of 1- and 2-butene, respectively), were synthesized according to the technique developed by Muthuramu et al. [16]. Attempts to synthesize hydroxynitrates arising from

isoprene oxidation via the same method did not succeed. Vapor pressures of the standards were measured directly using a low-pressure capacitance manometer. The vapor pressures of 1,2-hydroxynitratobutane and 2,3-hydroxynitratobutane were found to be 0.091 and 0.202 Torr, respectively, at 295 K, the ambient laboratory temperature. The hydroxynitrates were added to the flow reactor by sweeping helium through a trap containing the hydroxynitrate sample. The helium flow rate and hydroxynitrate vapor pressure were used to calculate the absolute concentrations of hydroxynitrate in the flow reactor. Hydroxynitrate response curves were constructed by measuring the CIMS response as a function of helium flow rate.

RESULTS AND DISCUSSION

Reaction Conditions

In order to minimize the amount of unwanted secondary chemistry, care was taken to ensure that radical-forming reactions in the sidearm were allowed to reach completion before entering the main flow tube. The following conditions were typically present in the sidearm: velocity $= 533$ cm s^{-1}, $[H_2O] = 1.4 \times 10^{15}$, [alkene] $= 6.0 \times 10^{13}$, and $[O_2] = 6.0 \times 10^{15}$ molecule cm^{-3}. Using the rate constant (all rate constant values taken from [17] unless otherwise noted) for the F + H$_2$O initial step in the peroxy radical synthesis (reaction (5), $k = 1.4 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}) and the H$_2$O concentration given above, the lifetime of F is calculated to be 0.05 ms. The distance between the H$_2$O addition port and the alkene/O$_2$ addition port is 4 cm, which corresponds to a time of 7.5 ms. The F + H$_2$O reaction is therefore complete before the alkene/O$_2$ components are added. Using the rate constant for the C$_3$H$_6$ + OH reaction ($k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) as an average value for the alkenes used in this study and the alkene concentration given above, the lifetime of OH is calculated to be 0.64 ms. The alkene-OH adduct is calculated to have a lifetime of 6.4 µs using the O$_2$ value given above and the rate constant for the C$_3$H$_6$(OH) + O$_2$ reaction ($k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) again as an average for all the alkene species. The distance between the alkene/O$_2$ addition port on the sidearm and the intersection of the sidearm with the main flow tube is 16 cm, which corresponds to a time of 30 ms. Therefore, the OH + alkene reaction goes to completion well before exiting the sidearm, and the subsequent alkene (OH) + O$_2$ reaction occurs nearly instantaneously.
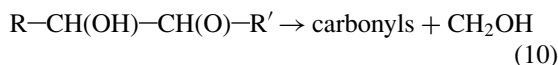
Absolute Concentration Determination Considerations

The CIMS response to both the 1- and 2-butene related hydroxynitrates (1,2-hydroxynitratobutane and 2,3-hydroxynitratobutane, respectively) was found to be identical within the uncertainties of the measurement. Because the proton transfer is expected to take place at the hydroxy position for these species, and most proton transfer reactions of this type are known to take place at the collision-limited rate [18], this result is not surprising. However, this aspect is important, as an authentic hydroxynitrate standard was not available for the isoprene system branching ratio measurements. It is expected that any isoprene-derived hydroxynitrate would have a similar collision-limited proton-transfer rate, and thus any similarly sized hydroxynitrate species should serve as a suitable calibration standard for isoprene-derived hydroxynitrates. 2,3-Hydroxynitratobutane was arbitrarily chosen as the standard that was used for determining the absolute concentration of isoprene-derived hydroxynitrates.

Branching Ratio Measurements and Secondary NO$_2$ Production

The branching ratio was determined by measuring the concentrations of the products of the reaction of the alkene-derived peroxy radicals with NO under a number of different conditions. During a run, the time that NO was allowed to react with the hydroxyperoxy radicals was varied between 20 (0-cm injector position) and 50 ms (30-cm injector position). Between four and seven different injector position data points were collected for each run. The CIMS was quickly (within 2 min) switched from positive to negative polarity to allow the hydroxynitrate and NO$_2$ production data, respectively, to be collected under nearly identical flow reactor conditions. Runs were also carried out at NO concentrations ranging between 1.5×10^{12} and 7×10^{12} molecules cm^{-3}. The typical absolute concentrations were around 2×10^{10} molecules cm^{-3} for the hydroxynitrates and around 3×10^{11} molecules cm^{-3} for NO$_2$. In order to calculate the branching ratio according to reaction (8), it is important that any other secondary sources of NO$_2$ be identified and excluded from the calculation. The hydroxyalkoxy radical produced in reaction (3b) is unstable and can undergo isomerization and dissociation reactions. For several alkenes (including isoprene), it is known that CH$_2$OH is a major product of the dissociation of hydroxyalkoxy
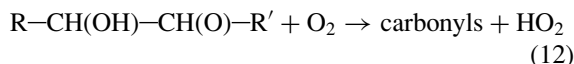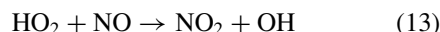
radicals [19].

$$R-CH(OH)-CH(O)-R' \rightarrow carbonyls + CH_2OH \quad (10)$$

CH_2OH can further react with O_2 to give formaldehyde and a hydroperoxyl radical

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (11)$$

The hydroxyalkoxy radical can also undergo reaction with O_2 to directly produce HO_2

$$R-CH(OH)-CH(O)-R' + O_2 \rightarrow carbonyls + HO_2 \quad (12)$$

For either hydroxyalkoxy fate, HO_2 is formed. HO_2 can then react with NO and regenerate OH and produce additional NO_2

$$HO_2 + NO \rightarrow NO_2 + OH \quad (13)$$

Thus, the NO_2 produced in reaction (13) is a secondary process that can impact the interpretation of the branching ratios as defined in equation (8). As there is no way to distinguish the secondary NO_2 products from the primary NO_2 produced by reaction (3b), the secondary NO_2 produced in reaction (13) leads to increased NO_2 concentrations and thus can make the apparent hydroxynitrate-branching ratio smaller than that dictated by reaction (3). However, the extent of secondary NO_2 production is quantifiable and the secondary NO_2 production was modeled and used to calculate the NO_2 production arising solely from reaction (3b). The reactions used in the kinetic modeling are given in Table I. An overall rate hydroxyperoxy + NO rate constant of 9.0×10^{-12} cm^3 molecule^{-1} s^{-1} was used for all three alkene systems, as determined by Miller et al. [15]. Initial concentrations of reactants were as follows: [alkene] = 8.0×10^{12}

molecules cm^{-3}, [O_2] = 8.0×10^{14} molecules cm^{-3}, [peroxy] = 1.0×10^{11} molecules cm^{-3}, and a range of NO initial concentrations from 2.5×10^{12} to 6×10^{12} molecules cm^{-3}. In order to separate primary and secondary NO_2 production, the model tagged the NO_2 produced in reaction (13), and this value was subtracted from the experimental NO_2 values for the purpose of calculating branching ratios according to equation (8).

The amount of secondary NO_2 formed was found to be independent of peroxy concentration and fairly weakly dependent on NO concentration and reaction time. This was expected, as the chemistry of the secondary NO_2 production is limited by the rate of the HO_2 + NO reaction, which has a rate constant similar to that of the hydroxyperoxy + NO reaction. However, the amount of secondary NO_2 produced was significant (about 30% of the total NO_2 observed).

Figure 2 shows a typical set of NO_2 (corrected for secondary chemistry as described above) and hydroxynitrate kinetic traces. The branching ratio is then calculated at each time according to equation (8). Figure 3 shows the dependence of the branching ratio for the data in Fig. 2 as a function of time. Figure 4 shows the dependence of the branching ratio on NO concentration. Since both Figs. 3 and 4 correctly show no branching ratio dependence on time nor NO concentration, the secondary chemistry appears to be have been appropriately accounted for.

Between 15 and 20 experiments like those depicted in Figs. 2 and 3 were performed for each of the three alkene systems, and average branching ratio values were determined. Both the corrected and uncorrected (to illustrate the importance of dealing with the secondary NO_2 chemistry) branching ratio values are given in Table II. The corrected branching ratios determined were 0.061, 0.068, and 0.070 for the 1-butene, 2-butene, and isoprene systems, respectively. These values are identical within the 95% confidence

Table I Kinetic Parameters Used in Modeling Secondary NO_2 Generation and Effect on Hydroxynitrate-Branching Ratios

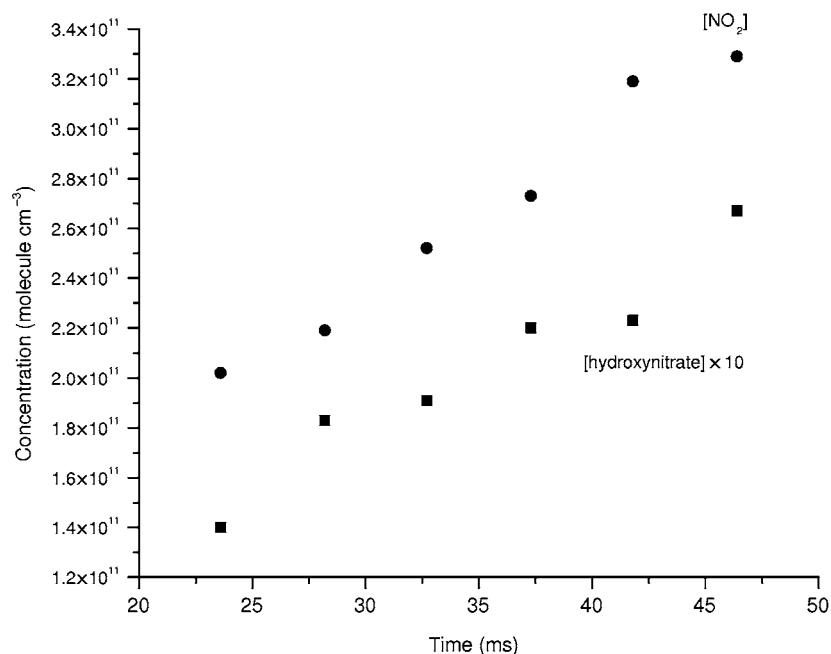| Reaction	k (cm^3 s^{-1} molecule^{-1})	Reference
Alkene + OH $\rightarrow$ R—CH(OH)—CH—R'	Varies	[17]
R—CH(OH)—CH—R' + O_2 $\rightarrow$ R—CH(OH)—CH(O_2)—R'	7.0×10^{-13}	[17]
R—CH(OH)—CH(O_2)—R' + NO $\rightarrow$ R—CH(OH)—CH(O)—R' + NO_2	8.4×10^{-12}	[15]
R—CH(OH)—CH(O_2)—R' + NO $\rightarrow$ R—CH(OH)—CH(ONO_2)—R'	0.6×10^{-13}	This work
R—CH(OH)—CH(O)—R' $\rightarrow$ aldehyde + CH_2OH	1.5×10^5 s^{-1} (first order)	[12]
CH_2OH + O_2 $\rightarrow$ HCHO + HO_2	9.6×10^{-12}	[17]
HO_2 + NO $\rightarrow$ NO_2 + OH	8.0×10^{-12}	[17]
OH + NO $\rightarrow$ HONO	1.7×10^{-12}	[17]
OH + NO_2 $\rightarrow$ HNO_3	3.4×10^{-12}	[17]
HO_2 + HO_2 $\rightarrow$ HOOH + O_2	2.1×10^{-12}	[17]

Figure 2   Production of NO_2 (corrected) and hydroxynitrate from isoprene oxidation system.

interval of each individual measurement. The statistical uncertainties in the branching ratios were largely driven by the day-to-day variations in the CIMS response to the hydroxynitrates and NO_2.

There are also possible systematic errors in the determination of the branching ratios due to the calibration and kinetics-modeling procedures. The main possible source of systematic error in the calibration procedure is the determination of the vapor pressures of the nitrate standards. We estimate that these values were measured to about 10% uncertainty. As described above, the kinetics modeling showed that the
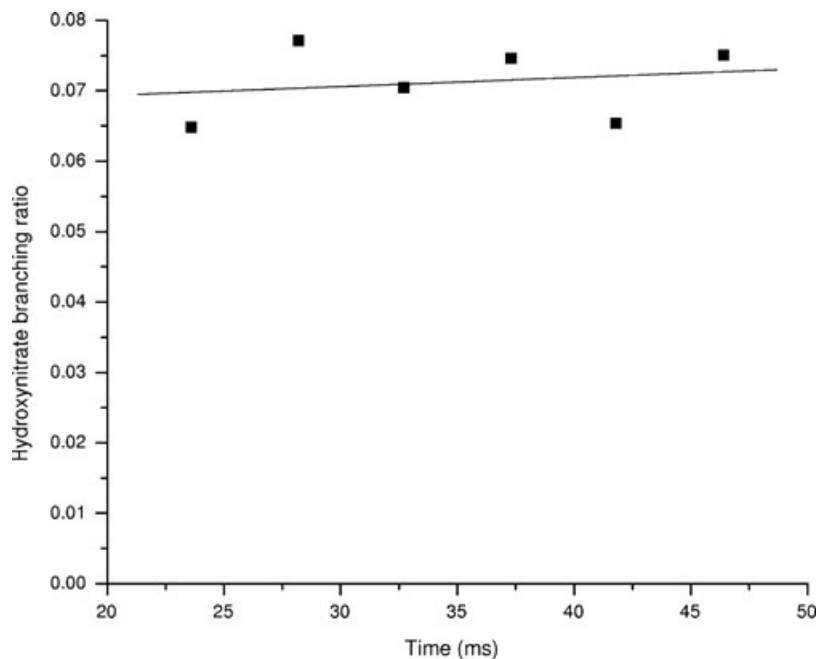

Figure 3   Time dependence of hydroxynitrate-branching ratios for the isoprene oxidation system from data in Fig. 2.
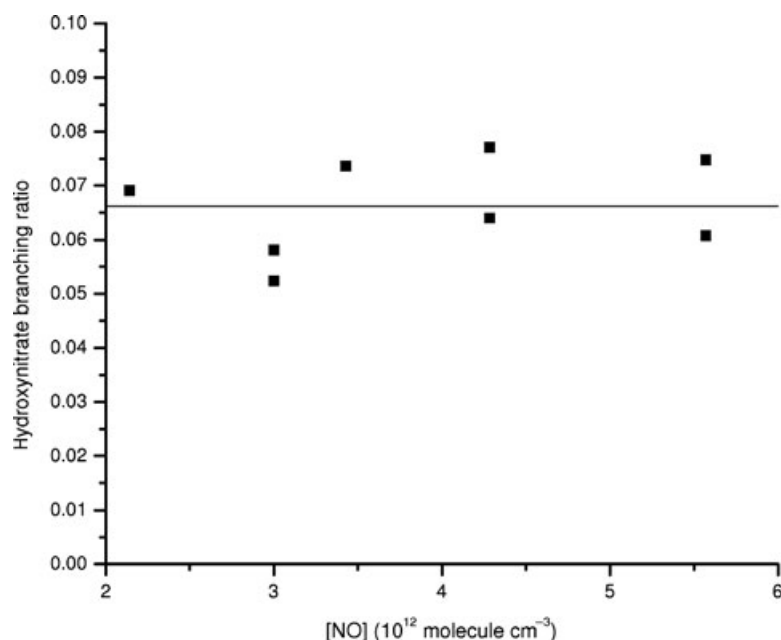
Figure 4   [NO] Dependence of hydroxynitrate-branching ratios for the isoprene oxidation system.

secondary production of NO_2 was almost totally controlled by the value of the $HO_2 + NO$ rate constant. The assumed value for the nitrate-branching ratio had very little effect on the kinetics modeling, as the fractional NO_2 contribution for different nitrate-branching ratios was quite similar. Therefore, the uncertainty introduced into the branching ratio measurements from the modeling procedure depends almost entirely on the uncertainty of the $HO_2 + NO$ rate constant, which has a recommended value of 15% [20]. Both the calibration and kinetics-modeling uncertainties propagate approximately linearly into the determined branching ratios. Therefore, we estimate the total measurement uncertainty to be on the order of 50%.

Comparison to Previous Measurements

The majority of previous branching ratio measurements were done at atmospheric pressure (760 Torr),

whereas experiments in this investigation were done at 100 Torr. Pressure dependence studies done by Atkinson et al. [21] on nitrates derived from *alkane* oxidation systems show a strong pressure dependence. Branching ratios for the *n*-pentane and *n*-heptane systems decreased with decreasing pressure at constant temperature, with 100 Torr branching ratios a factor of 3 smaller than measurements done at 760 Torr. Sprengnether et al. [7] have carried out the only pressure dependence study for hydroxynitrates produced from alkene oxidation. They measured branching ratios of the isoprene and 1,3-butadiene systems at 750 and 445 Torr. The hydroxynitrate-branching ratio measured for the isoprene system showed a possible pressure dependence of similar magnitude to the alkane systems, but the hydroxynitrate-branching ratio measured for the 1,3-butadiene was apparently unaffected by pressure. Using the alkane study as a guide, we might expect smaller branching ratios at lower pressures for the

Table II   Comparison of Hydroxynitrate-Branching Ratio Measurements (2σ Uncertainties Given)

Alkene	This Work, NO_2 Uncorrected (100 Torr)	This Work, NO_2 Corrected (100 Torr)	Previous Work (760 Torr, Unless Otherwise Noted)	Previous Work Method and Reference
1-Butene	0.043 ± 0.019	0.061 ± 0.027	0.025 ± 0.002	GC [10]
2-Butene	0.048 ± 0.016	0.068 ± 0.023	0.034 ± 0.005	GC [10]
			0.06	IR [21]
Isoprene	0.049 ± 0.022	0.070 ± 0.031	0.044 ± 0.008	GC [9]
			0.12 ± 0.06	IR [7]
			0.08 ± 0.06 (445 Torr)	
			0.08–0.13	IR [11]
			0.15 ± 0.10 (150 Torr)	OH cycling/LIF [12]

alkene systems as well, but the structural differences between the alkane- and alkene-derived products are significant enough to discourage an attempt to perform a simple extrapolation of the alkane dependence to the alkenes.

The results of this investigation are compared with previous results in Table I. As discussed above, while there is no straightforward method to extrapolate our 100 Torr results to 760 Torr pressure, it is a virtual certainty that the extrapolated 760 Torr values would be higher than the 100 Torr values. Therefore, the present values probably represent a lower limit to the hydroxynitrate-branching ratios at atmospheric pressure. These values are somewhat higher than the O'Brien et al. [10] work on the 1- and 2-butene systems and consistent with the Tuazon et al. [22] work for the 2-butene. For the isoprene system, our results are higher than the branching ratio measured by Chen et al. [9] and lower than those measured by Sprengnether et al. [7], Tuazon et al. [11], and Chuong and Stevens [12]. Once again, however, the probable pressure dependence of the hydroxynitrate-branching ratios indicates that our results are probably lower limits to the atmospheric pressure values.

Atmospheric Implications

As discussed above, the present branching ratio results, especially when extrapolated to atmospheric pressure, are more consistent with the set of larger branching ratio values that have been previously measured. The atmospheric implications of higher hydroxynitrate-branching ratios are that ozone production due to the oxidation of alkenes may be less efficient and that alkene-derived species may represent a larger NO_x sink than is currently represented in atmospheric models.

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