

# Overall rate constant measurements of the reactions of alkene-derived hydroxyalkylperoxy radicals with nitric oxide

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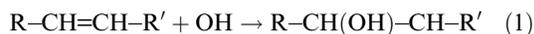
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The overall rate constants of the NO reaction with hydroxyalkylperoxy radicals derived from the OH-initiated oxidation of several atmospherically abundant alkenes—ethene, propene, 1-butene, 2-butene, 2-methyl propene, 1,3-butadiene, and isoprene (2-methyl-1,3-butadiene)—were determined using the turbulent flow technique and pseudo first-order kinetic conditions with high pressure chemical ionization mass spectrometry for the direct detection of hydroxyalkylperoxy radical reactants. The individual 100 Torr, 298 K rate constants for each alkene system were found to be identical within the 95% confidence interval associated with each separate measurement. The average overall rate constant for the reaction of all alkene-derived hydroxyalkylperoxy radicals with NO was determined to be  $9.1 \pm 0.5 (2\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Previous studies of this reaction for the ethene, 2-methyl propene and isoprene systems reported varying rate constant values that ranged from a factor of two lower to a factor of two higher than the present result. However, the invariant nature and value of the present rate constant determination closely parallels the results obtained in the measurement of rate constants for the reactions of several alkane-derived peroxy radicals with NO.

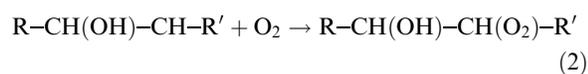
## Introduction

The reactions involved in the oxidation of alkenes are known to be a major source of tropospheric ozone.<sup>1</sup> Atmospheric concentrations of alkenes are significantly impacted by both anthropogenic and biogenic emissions. Alkenes are important constituents of fuels and automobile exhaust,<sup>2,3</sup> as well as other industrial and agricultural (biomass burning) processes.<sup>4</sup> Biogenic sources of alkenes include emissions from vegetation, soils and the oceans.<sup>5</sup> In rural areas, isoprene (2-methyl-1,3-butadiene), which is emitted by deciduous trees, is one of the most abundant non-methane hydrocarbons (up to 1/3 of the total organic content of the atmosphere<sup>1</sup>). Due to 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.<sup>1</sup>

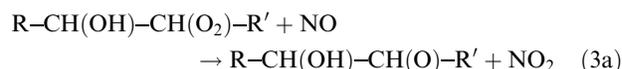
The oxidation of alkenes in the troposphere is usually initiated by reaction with OH radicals, which is known to proceed primarily through an addition mechanism:



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.<sup>6</sup> However, in order to simplify and clarify the subsequent chemical steps in the oxidation of the alkenes, the notation used in this 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 rapidly reacts with O<sub>2</sub> to form a  $\beta$ -hydroxyalkylperoxy radical,



which is generally followed by reaction with nitric oxide:



The formation of NO<sub>2</sub> in reaction (3a) leads to ozone production, while the formation of the hydroxynitrate in reaction (3b) terminates the oxidation cycle.

Despite the importance of alkenes to ozone formation in both urban and rural locations, the oxidation processes of alkenes have received less detailed scrutiny than the corresponding processes for the alkane family. There have been a large number of experiments (mostly using the environmental chamber technique) in which the end products of the OH-initiated oxidation of alkenes in the presence of NO have been explored. Observations of carbonyl and hydroxynitrate products have been interpreted as indicators of the importance of the hydroxyalkylperoxy + NO reaction in the overall oxidation sequence. The recent monograph by Calvert *et al.* provides an excellent review of these studies.<sup>1</sup> There have also been several direct studies of the formation and/or self-reaction kinetics of hydroxyalkylperoxy radicals derived from the small alkenes<sup>7-10</sup> and some studies of hydroxyalkylperoxy radical formation from the oxidation of isoprene.<sup>11-14</sup> To our knowledge, however, there have been only two direct measurements of the reaction kinetics of an alkene-derived hydroxyalkylperoxy radical with NO: 2-methyl propene ( $k_3 = 4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>7</sup> and isoprene ( $k_3 = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>15</sup> There have also been two indirect measurements of the hydroxyalkylperoxy + NO reaction for the important isoprene system: Stevens and co-workers<sup>12,16</sup> and North and co-workers<sup>17</sup> used indirect OH-cycling measurements to estimate the rate constant for reaction (3) and derived values of 11 and  $25 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. There is only one other alkene for which there is even an indirect estimate of the rate constant for reaction (3). Becker *et al.* used indirect OH-cycling

measurements to estimate the rate constant for reaction (3) for ethene-derived hydroxyalkylperoxy radicals and arrived at a value of  $9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

In contrast to the alkene situation, there have been numerous direct kinetics studies of the overall rate constant for the reaction of *alkane*-based peroxy radicals with NO. Based on these studies, Howard and co-workers concluded that for the C<sub>1</sub>–C<sub>5</sub> unsubstituted alkanes, an overall peroxy + NO rate constant of about  $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K is observed, regardless of the length or branching of the alkyl chain.<sup>19</sup> However, it is not clear from the limited rate constant values available thus far for the reaction of *alkene*-based hydroxyalkylperoxy radicals with NO (which, as described above, range in value from 4.9 to  $25 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) that the alkenes possess a similarly unvarying rate constant value. Therefore, it is important to perform direct measurements of the atmospherically relevant alkene-derived hydroxyalkylperoxy radicals with NO in order to better define the role of alkenes in tropospheric ozone formation.

In this article an investigation of the kinetics of the reaction of several alkene-derived hydroxyalkylperoxy radicals with NO is described. The measurements were conducted at 100 Torr and 298 K under pseudo first-order kinetics conditions using a turbulent flow (TF) tube coupled to a high pressure chemical ionization mass spectrometer (CIMS), which allowed for direct detection of the hydroxyalkylperoxy radicals. The NO reaction kinetics of hydroxyalkylperoxy radicals obtained from the OH-initiated oxidation of ethene, propene, 1-butene, 2-butene, 2-methyl propene, 1,3-butadiene, and isoprene were investigated in this work. These parent alkenes were chosen to allow a systematic investigation of the possible structural and electronic effects of varying alkene functionality on the rate constant. In addition, these species include the most atmospherically relevant alkenes (as a group, the seven alkenes listed above represent 77% of the total alkene concentration typically observed in Los Angeles<sup>1</sup>). The results are compared to previous kinetics measurements of the reaction of alkene-derived hydroxyalkylperoxy radicals with NO as well as to kinetics results for the reaction of alkane-derived peroxy radicals with NO.

## Experimental

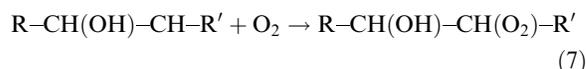
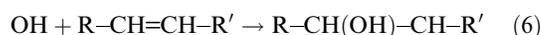
### Turbulent fast flow kinetics

A schematic of the experimental apparatus is presented in Fig. 1 and is similar to that used in our previous study of C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> + NO.<sup>20</sup> The flow tube was constructed with 2.2 cm id Pyrex tubing and was 100 cm in total length. A large flow of nitrogen carrier gas (approximately 30 STP L min<sup>-1</sup>) was

injected at the rear of the flow tube. The gases necessary to generate the hydroxyalkylperoxy radicals were introduced through a 20 cm long 12.5 mm diameter sidearm located at the rear of the tube. NO was added *via* an encased movable injector. The encasement (made from corrugated Teflon tubing) was used so that the injector could be moved to various injector positions without breaking any vacuum seals. A fan-shaped Teflon device was placed at the end of the injector in order to enhance turbulent mixing. The polonium-210  $\alpha$ -emitting ionization source was placed between the temperature regulated flow tube and the inlet to the CIMS. Most of the flow tube gases were removed at the CIMS inlet by a 31 L s<sup>-1</sup> roughing pump. All gas flows were monitored with calibrated mass flow meters. The flow tube pressure was measured upstream of the ionization source using a 0–1000 Torr capacitance manometer. The temperature in the flow tube was determined using Cu-constantan thermocouples.

### Overall rate constant determination

The hydroxyalkylperoxy species were generated using the following reactions:



The kinetics measurements were carried out at  $100 \pm 1$  Torr and  $298 \pm 2$  K. A dilute mixture of He/CF<sub>4</sub> was obtained by combining a 5.0 STP L min<sup>-1</sup> flow of helium (99.999%), which had passed through a silica gel trap immersed in liquid nitrogen, with a 1.0–1.5 STP mL min<sup>-1</sup> flow of a 2% CF<sub>4</sub> (99.9%) / He mixture. Fluorine atoms were then produced by passing the He/CF<sub>4</sub> mixture through a microwave discharge produced by a Beenakker cavity operating at 50 W. To make OH, the fluorine atoms were injected into the sidearm and mixed with H<sub>2</sub>O/He (produced by bubbling about 1.0 STP mL min<sup>-1</sup> He through a trap filled with H<sub>2</sub>O at ~298 K) (reaction (5)). To make the hydroxyalkylperoxy radicals, excesses of both the alkene (CP grade; typically about  $1.0 \times 10^{13}$  molecule cm<sup>-3</sup>) and O<sub>2</sub> (99.995%; typically about  $6.0 \times 10^{15}$  molecule cm<sup>-3</sup>) were then added to the OH already present in the side arm (reactions (6) and (7)). The order of the reagent addition ensures that the hydroxyalkylperoxy radical-forming reactions are complete before entering the main flow tube. This important point will be discussed more fully in the Results and discussion section.

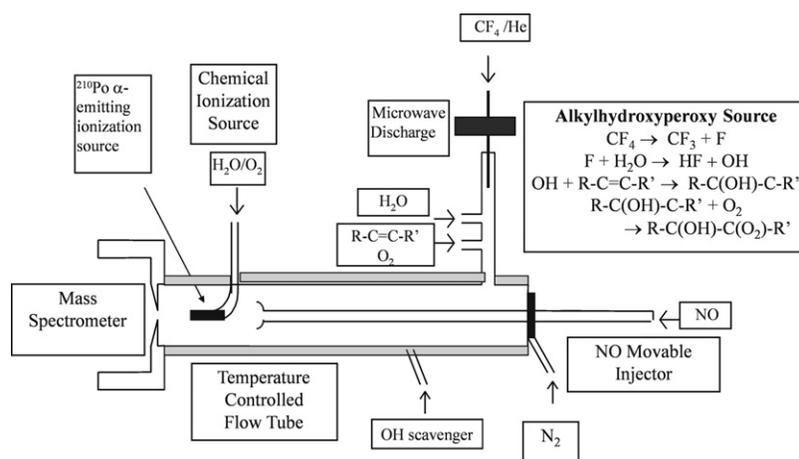


Fig. 1 Experimental apparatus.

In order to ensure pseudo first-order kinetics conditions (with NO as the excess reactant) and to allow accurate modeling of the hydroxyalkylperoxy radical chemistry, it is necessary to estimate the typical concentration of hydroxyalkylperoxy radicals. An upper limit to the concentration of hydroxyalkylperoxy radicals was estimated by determining the absolute OH concentrations in the absence of the alkene using the titration of OH with NO<sub>2</sub>



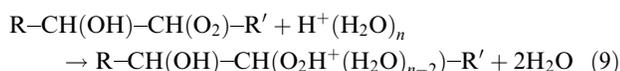
( $k_8 = 3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 100 Torr)<sup>21</sup> and calibration of the HNO<sub>3</sub> mass spectrometer signal using bubbler containing 60% HNO<sub>3</sub> solution by weight, immersed in an ice-water bath. The vapor pressure of HNO<sub>3</sub> for this solution at 273 K is 0.20 Torr.<sup>22</sup>

For the overall rate determination for the hydroxyalkylperoxy + NO reaction, an excess of NO was added to the flow tube as a 0.5% mixture in N<sub>2</sub> through the movable injector. To ensure the absence of NO<sub>2</sub> impurities, NO was passed through a silica gel trap held at -40 C. Negligible NO<sub>2</sub> concentrations were observed *via* CIMS methods.

To prevent regeneration of OH in the system (and subsequent hydroxyalkylperoxy radical regeneration, which could compromise the pseudo first-order kinetics conditions), a scavenger species was introduced downstream of the hydroxyalkylperoxy radical injection point, but upstream of all possible NO injector positions. In these experiments, the scavenger was an alkene of a different molecular mass than the parent alkene of the hydroxyalkylperoxy radical under investigation. The details of the OH scavenger conditions (*i.e.*, the appropriate relative scavenger/parent alkene concentration ratio) are discussed fully in the Results and discussion section.

### Chemical ionization mass spectrometric detection

A positive ion chemical ionization scheme (with H<sup>+</sup>(H<sub>2</sub>O)<sub>*n*</sub> as the reagent ion) was used to detect the hydroxyalkylperoxy radicals with a quadrupole mass spectrometer:



A similar proton transfer reaction method was used in our previous studies of the kinetics of peroxy radicals derived from small alkanes.<sup>20,23-25</sup> It is important to note that for each parent alkene, there are at least 2 possible hydroxyalkylperoxy isomers possible (there are six possible for isoprene), but that our mass spectrometric detection method is not sensitive to the isomeric distribution of species. Therefore, our kinetics measurements represent a weighted average for the reaction of all hydroxyalkylperoxy species (of a specific mass) present with NO. H<sup>+</sup>(H<sub>2</sub>O)<sub>*n*</sub> (with the *n* = 4 species usually accounting for more than 80% of the total ion signal) was produced in the ion source by passing a large O<sub>2</sub> flow (8 STP L min<sup>-1</sup>) through the polonium-210  $\alpha$ -emitting ionization source (with H<sub>2</sub>O impurities being sufficiently abundant to produce adequate quantities of reagent ions). The commercial ionization source consisted of a hollow cylindrical (69 by 12.7 mm) aluminium body with 10 mCi ( $3.7 \times 10^8$  disintegrations s<sup>-1</sup>) of polonium-210 coated on the interior walls. 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 ions were focused by three lenses constructed from 3.8 cm id, 48 cm od aluminium gaskets. The front chamber was pumped by a 6 in 2400 L s<sup>-1</sup> diffusion pump. The gases entered the rear chamber through a skimmer cone with a charged 1.0 mm orifice which was placed approximately 5 cm from the front aperture. The rear chamber was pumped by a 250 L s<sup>-1</sup> turbomolecular pump. Once the

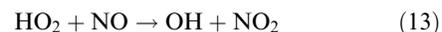
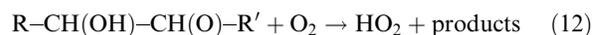
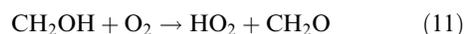
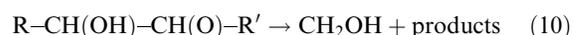
ions passed through the skimmer cone, they were mass filtered and detected with a quadrupole mass spectrometer.

## Results and discussion

### Pseudo first-order kinetics conditions

In order to perform experiments under pseudo first-order conditions, care was taken to ensure that the hydroxyalkylperoxy-forming reactions were completed in the flow tube sidearm before the radical synthesis components entered the main flow tube. The following conditions were typically present in the sidearm: velocity = 700 cm s<sup>-1</sup>, [H<sub>2</sub>O] =  $1.3 \times 10^{14}$ , [alkene] =  $1.0 \times 10^{13}$ , and [O<sub>2</sub>] =  $6.0 \times 10^{15}$  molecule cm<sup>-3</sup>. Using the rate constant for the F + H<sub>2</sub>O initial step in the hydroxyalkylperoxy radical synthesis (reaction (5);  $k_5 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , ref. 21)) and the H<sub>2</sub>O concentration given above, the lifetime of F is 0.55 ms. The distance between the H<sub>2</sub>O addition port and the alkene/O<sub>2</sub> addition port is 4 cm, which corresponds to a time of 5.7 ms. Therefore, the F + H<sub>2</sub>O reaction is complete before the alkene/O<sub>2</sub> components are added. In order to estimate the time scale of the second step in the reaction sequence, the rate constant for OH + alkene (reaction (6)) was modeled using the value for C<sub>3</sub>H<sub>6</sub>:  $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , ref. 1. Using this value for the rate constant and the alkene concentration given above, the lifetime of OH is calculated to be 3.6 ms. The time scale of the third and final reaction of the hydroxyalkylperoxy radical synthesis (reaction (7)) was modeled by using the rate constant value for the C<sub>3</sub>H<sub>6</sub>(OH) + O<sub>2</sub> reaction:  $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , ref. 10. Using this rate constant value and O<sub>2</sub> concentration cited above, the OH adduct is calculated to have a lifetime of only 0.0064 ms. The distance between the alkene/O<sub>2</sub> 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 23 ms. Therefore, the OH + alkene reaction goes to completion well before exiting the sidearm, after which the alkene(OH) + O<sub>2</sub> reaction occurs virtually instantaneously. In summary, it is clear that under our conditions, the hydroxyalkylperoxy forming reactions are complete by the time the radical synthesis components enter the main flow tube and encounter NO.

As mentioned in the Experimental section, pseudo first-order conditions are achieved only through the scavenging of OH radicals produced in the main flow tube as a result of reactions involving the R-CH(OH)-CH(O)-R' species produced in reaction (3a):



The OH produced in reaction (13) can then react with the excess alkene present in the flow tube and regenerate hydroxyalkylperoxy radicals *via* reactions (1) and (2), and thus invalidate the desired pseudo first-order conditions for the loss of the hydroxyalkylperoxy radicals occurring due to reaction (3). The OH produced *via* reactions (10)–(13) is scavenged by adding an excess of a second alkene (with a different molecular mass) to the main flow. Since our detection scheme is mass specific, the hydroxyalkylperoxy radicals generated due to the presence of the scavenger alkene do not interfere with our measurements. The most difficult system with respect to this potential problem is isoprene, because it possesses the largest alkene + OH rate constant ( $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; the other alkenes range from <0.1 (ethene) to  $0.66 (1,3\text{-butadiene}) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , ref. 1). Therefore, kinetic modeling was performed to investigate the conditions necessary to sufficiently scavenge OH to recover pseudo

first-order conditions for studying the reaction of isoprene-derived hydroxyalkylperoxy radicals with NO. The reactions used in the modeling are given in Table 1, with the inclusion of the 1-butene + OH reaction as the scavenger reaction (which was the scavenger used in all of the studies, except for the C<sub>4</sub>H<sub>8</sub> systems). The concentrations used in the kinetic modeling (which are representative of the typical experimental conditions) were as follows: [C<sub>5</sub>H<sub>8</sub>] = 1.8 × 10<sup>12</sup>, [O<sub>2</sub>] = 1.0 × 10<sup>15</sup>, [C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub>] = 1.0 × 10<sup>11</sup> and [NO] = 3.0 × 10<sup>12</sup> molecule cm<sup>-3</sup>. The C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub> concentration is estimated from the OH concentration determined in the titration procedure described in the Experimental section. The hydroxyalkylperoxy radical decays were typically measured between the absolute reaction times of 20 ms and 50 ms (relative to the flow entrance to the high vacuum chamber of the mass spectrometer). If the OH regeneration chemistry is removed from the model, the C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub> concentrations are calculated to decay 54% in a rigorous pseudo first-order manner under these conditions. With the OH regeneration chemistry included in the modeling, the C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub> concentrations are calculated to decay only 27% under the same conditions, and show non-pseudo first-order behavior. Therefore, it is clear that this secondary chemistry completely invalidates the pseudo first-order approximation for C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub> decay under the typical experimental conditions. However, if 3.1 × 10<sup>13</sup> molecule cm<sup>-3</sup> of 1-C<sub>4</sub>H<sub>8</sub> is added to the kinetic model, pseudo first-order conditions are recovered as C<sub>5</sub>H<sub>8</sub>(OH)O<sub>2</sub> concentrations are calculated to decay 50% over the same reaction times and conditions, which is nearly the same value that was calculated above for the case of no OH regeneration chemistry. Based on these results, it was determined that pseudo first-order conditions are insured (*i.e.*, effective pseudo first-order rate constants within 5% of the value calculated if there were no OH regeneration chemistry) as long as the ratio of  $k_{\text{OH}+\text{scavenger}}[\text{scavenger}]/k_{\text{OH}+\text{alkene}}[\text{alkene}] \geq 5$  (as is the case for the specific conditions discussed here). Therefore, all kinetics studies were performed with alkene scavenger concentrations calculated according to this rate ratio expression.

### Overall rate constant determination

Bimolecular rate constants were obtained *via* the usual pseudo first-order approximation method, using NO as the excess

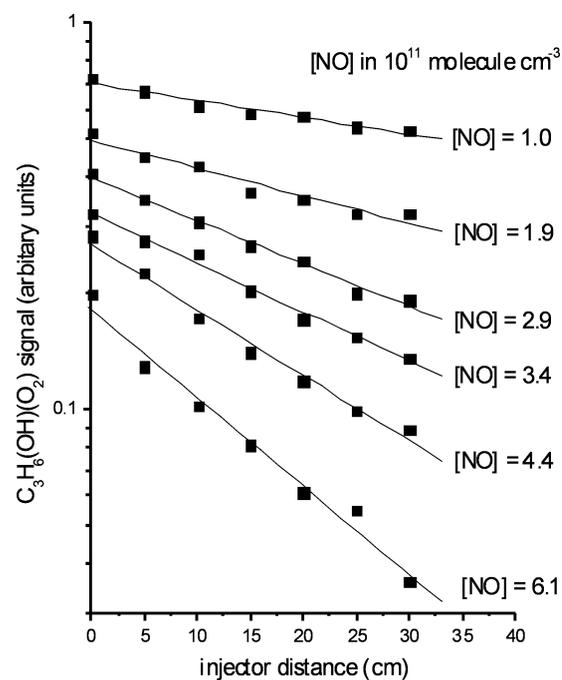
**Table 1** Kinetic parameters used in modeling hydroxyalkylperoxy regeneration and scavenger effect for isoprene system

Reaction	$k/\text{cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$	Reference
C <sub>5</sub> H <sub>8</sub> + OH → C <sub>5</sub> H <sub>8</sub> (OH)	1.0 × 10 <sup>-10</sup>	1
C <sub>5</sub> H <sub>8</sub> (OH) + O <sub>2</sub> → C <sub>5</sub> H <sub>8</sub> (OH)(O <sub>2</sub> )	7.0 × 10 <sup>-13</sup>	14
C <sub>5</sub> H <sub>8</sub> (OH)(O <sub>2</sub> ) + NO → C <sub>5</sub> H <sub>8</sub> (OH)(O) + NO <sub>2</sub>	7.9 × 10 <sup>-12</sup>	<sup>a</sup>
C <sub>5</sub> H <sub>8</sub> (OH)(O <sub>2</sub> ) + NO → C <sub>5</sub> H <sub>8</sub> (OH)(ONO <sub>2</sub> )	8.8 × 10 <sup>-13</sup>	<sup>a</sup>
C <sub>5</sub> H <sub>8</sub> (OH)(O) → CH <sub>2</sub> OH + products (1st order)	1.5 × 10 <sup>5</sup> s <sup>-1</sup>	12
CH <sub>2</sub> OH + O <sub>2</sub> → HO <sub>2</sub> + CH <sub>2</sub> O	9.6 × 10 <sup>-12</sup>	26
HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	8.0 × 10 <sup>-12</sup>	27
OH + NO → HONO	1.7 × 10 <sup>-12</sup> @ 100 Torr	21
OH + NO <sub>2</sub> → HNO <sub>3</sub>	3.4 × 10 <sup>-12</sup> @ 100 Torr	21
1-C <sub>4</sub> H <sub>8</sub> + OH → 1-C <sub>4</sub> H <sub>8</sub> (OH)	3.1 × 10 <sup>-11</sup>	1

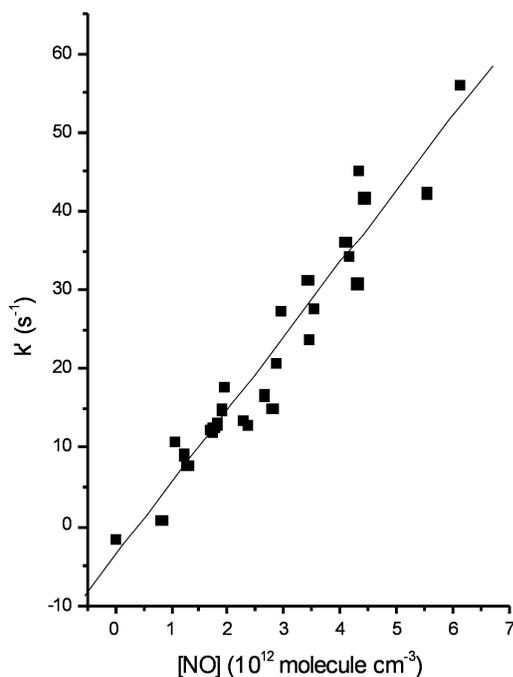
<sup>a</sup> The rate constants are calculated from the overall value determined in this work (8.8 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and a nitrate branching ratio of 0.10, which is a rough average of the range of values previously determined (0.04–0.15).<sup>12,28–30</sup>

reagent. Typical hydroxyalkylperoxy decay curves (for the specific case of the hydroxyalkylperoxy radicals derived from propene) as a function of injector distance are shown in Fig. 2 for the NO kinetics measurements. The first-order rate constants obtained from fitting the hydroxyalkylperoxy decay curves were plotted against [NO] in order to determine the bimolecular rate constant, as shown in Fig. 3. The small negative *y*-intercept evident in this figure is indicative of some hydroxyalkylperoxy radical loss on the injector, which is greatest at the shortest injector distances. The approach for determining bimolecular rate constants assumes that deviations from the plug flow approximation (molecular velocities are equal to the bulk flow velocity) are negligible. Under ideal flow conditions similar to those present in our turbulent flow tube (Reynold's Number > 2000), Seeley *et al.* estimated that these deviations result in apparent rate constants which are at most 8% below the actual values.<sup>31</sup> Because the actual flow conditions deviate somewhat from the idealized situation modeled by Seeley *et al.* and the fact that no systematic errors have been apparent in the systems that have been studied to date with the present flow configuration, no correction to the plug flow approximation is applied here. However, it is worth noting that other workers, using different flow system configurations, have found the need to apply small corrections to the plug flow approximation in order to obtain accurate results using turbulent flow conditions.<sup>12</sup> As discussed above, errors in the apparent rate constants due to deviations from pseudo first-order behavior resulting from OH regeneration are expected to be negligible under our conditions. The other likely systematic errors in the determination of rate constants are likely to occur in the measurements of gas flows, temperature, detector signal, and pressure. Considering such sources of error, it is estimated that rate constants can be determined with an accuracy of ±30% (2σ).

Measurements similar to those depicted in Figs. 2 and 3 for the propene-derived hydroxyalkylperoxy + NO reaction were performed for ethene, 1-butene, 2-butene, 2-methyl propene, 1,3-butadiene, and isoprene. See Table 2 for a complete list of the experimentally measured rate constants and 2σ statistical uncertainties. The individual 100 Torr, 298 K rate constants for each alkene system were found to be identical within



**Fig. 2** Pseudo first-order decay curves for the propene-derived hydroxyalkylperoxy + NO reaction at 100 Torr and 298 K carried out at a velocity of 1050 cm s<sup>-1</sup>.



**Fig. 3** Determination of overall bimolecular rate constant for the propene-derived hydroxyalkylperoxy + NO reaction (which includes some data from Fig. 2).

the 95% confidence interval associated with each separate measurement. In Fig. 4, all of the present data for the kinetics measurements of the reaction of alkene-derived hydroxyalkylperoxy radicals with NO are used to derive a “composite” overall rate constant of  $9.1 \pm 0.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

As noted in the Introduction, there have been previous studies of the alkene-derived hydroxyalkylperoxy + NO rate constant for ethene,<sup>18</sup> 2-methyl propene<sup>7</sup> and isoprene.<sup>12,15,17</sup> In Table 2 and in Fig. 5, the values determined in the present study are compared with these previous results. Our results are consistent with the previous results for ethene<sup>18</sup> and the work by Zhang *et al.*<sup>15</sup> and Stevens and coworkers<sup>12</sup> on isoprene, but are not consistent with the previous results for 2-methyl propene<sup>7</sup> and the work by North and coworkers on isoprene.<sup>17</sup>

The present results are likely to be more reliable than the previous results obtained for the reaction of alkene-derived hydroxyalkylperoxy radicals with NO because the hydroxyalkylperoxy radicals were directly detected and pseudo first-order kinetics conditions were used in this work. In particular, the direct detection of hydroxyalkylperoxy radicals and the isolation of the title reaction by using pseudo first-order kinetics

conditions obviates the need for modeling calculations to extract the rate constant (as is the case for all but one of the previous measurements). It is difficult to directly compare the uncertainties in the present work to those in the previous measurements because of the different methods by which uncertainty was determined (in some cases, it is not clear how the uncertainty was determined). However, it is likely that the more direct method of measurement of the rate constant in the present work is responsible for lower statistical uncertainties as compared to those in most of the previous experiments. For example, the previous result of Zhang *et al.*<sup>15</sup> for the isoprene system was obtained using similar direct CIMS detection of the hydroxyalkylperoxy radicals, but the rate constant was extracted through modeling calculations. Although that work and the present work both used similar direct detection methods, the use of pseudo first-order methods in the present work is responsible for the higher precision of the alkene-derived hydroxyalkylperoxy + NO rate constant reported here. It should be noted that the previous work on the 2-methyl propene system was also performed using direct UV detection of hydroxyalkylperoxy radicals and pseudo first-order conditions and a similar uncertainty to the present work is cited. While it is not possible to definitively determine the reasons for the discrepancy in the two experiments, it is well known that selective UV detection of peroxy radicals is difficult due to overlapping absorption profiles for the different peroxy radicals,<sup>32</sup> while the selective detection of peroxy radicals by CIMS is less prone to such interferences. In any case, the present body of results provides strong evidence that the rate constant for the reaction of alkene-derived hydroxyalkylperoxy radicals with NO is invariant with respect to the parent alkenes studied in this work (a conclusion made possible by the much lower rate constant uncertainties determined in the present work) and that this result is consistent with similar observations for the reaction of alkane-derived peroxy radicals with NO.

## Conclusions

The overall rate constants of the NO reaction with hydroxyalkylperoxy radicals derived from the OH-initiated oxidation of several atmospherically abundant alkenes—ethene, propene, 1-butene, 2-butene, 2-methyl propene, 1,3-butadiene, and isoprene (2-methyl-1,3-butadiene)—were determined using the turbulent flow technique and pseudo first-order kinetics conditions with high pressure chemical ionization mass spectrometry for the direct detection of hydroxyalkylperoxy radical reactants. The individual 100 Torr, 298 K rate constants for each alkene system were found to be identical within the 95% confidence interval associated with each separate

**Table 2** Comparison of present and previous determinations of the overall rate constants for the reaction of alkene-derived hydroxyalkylperoxy radicals with NO

Alkene	This work $k/10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1} \text{ }^a$	Previous work		
		$k/10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$	Method	Reference
Ethene	$8.7 \pm 1.2$	$9 \pm 4$	OH-cycling	18
Propene	$9.5 \pm 1.2$			
1-Butene	$9.6 \pm 1.2$			
2-Butene	$9.3 \pm 1.4$			
2-Methylpropene	$9.6 \pm 1.2$	$4.9 \pm 0.9$	Direct UV detection	7
1,3-Butadiene	$8.83 \pm 0.83$			
Isoprene	$8.8 \pm 1.2$	$25 \pm 5$	OH-cycling	17
		$11 \pm 8$	OH-cycling	12
		$9 \pm 3$	Direct CIMS detection	15
Composite	$9.1 \pm 0.5$			

<sup>a</sup> Statistical  $2\sigma$  uncertainty cited.

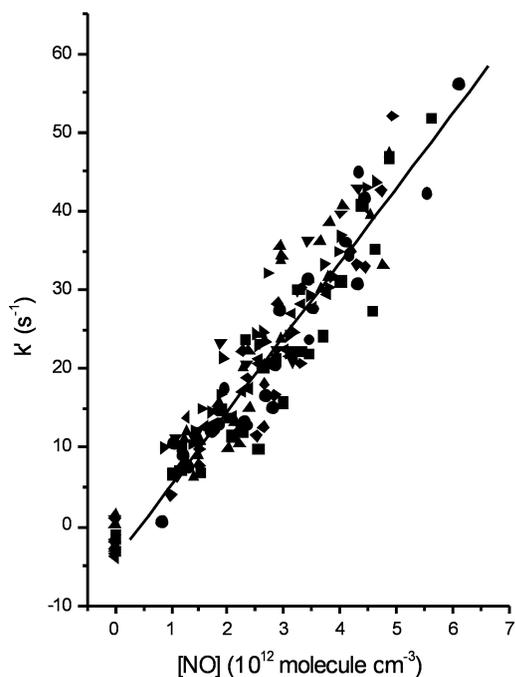


Fig. 4 Determination of the composite overall bimolecular rate constant for the alkene-derived hydroxyalkylperoxy + NO reaction (■, ethene, ●, propene, ▲, 1-butene, ▼, 2-butene, ◆, 2-methyl propene, ◄, 1,3-butadiene, ►, isoprene).

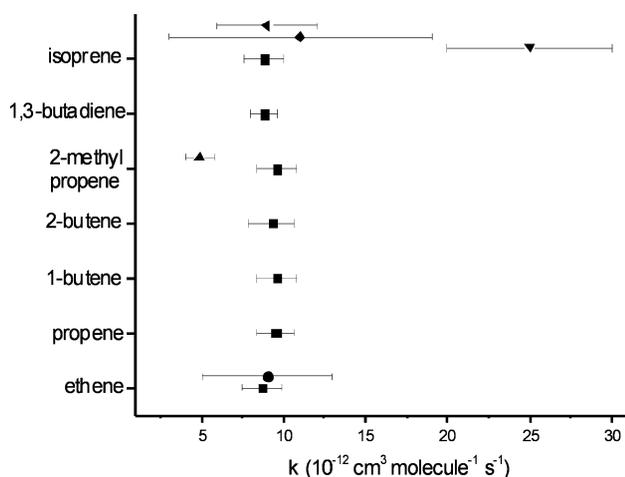


Fig. 5 Comparison of present (statistical  $2\sigma$  uncertainty indicated) and previous determinations of the overall bimolecular rate constant for the alkene-derived hydroxyalkylperoxy + NO reaction (■, this work, ●, ref. 18, ▲, ref. 7, ▼, ref. 17, ◆, ref. 12, ◄, ref. 15).

measurement, and a composite value of  $9.1 \pm 0.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was derived. The observed invariance as a function of the parent alkene and the actual value of the rate constant are very similar to previous findings for the kinetics of reactions of alkane-derived peroxy radicals with NO. The present result is consistent with some previous measurements of alkene-derived hydroxyalkylperoxy radicals with NO, but not with others. Since the parent alkenes investigated in this work often comprise the majority of alkenes observed in the atmosphere (these seven compounds typically account for 77% of the total alkene concentration in Los Angeles<sup>1</sup>), it is recommended that a value of  $9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  be adopted for atmospheric modeling purposes for all alkene-derived hydroxyalkylperoxy radical + NO reactions.

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