

Overall Rate Constant Measurements of the Reaction of Hydroxy- and Chloroalkylperoxy Radicals Derived from Methacrolein and Methyl Vinyl Ketone with Nitric Oxide

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The overall rate constants of the reactions of NO with hydroxy- and chloroalkylperoxy radicals, derived from the OH- and Cl-initiated oxidation of methacrolein and methyl vinyl ketone, respectively, were directly determined for the first time using the turbulent-flow technique and pseudo-first-order kinetics conditions with high-pressure chemical ionization mass spectrometry for the direct detection of peroxy radical reactants. The individual 100 Torr, 298 K hydroxyalkylperoxy + NO rate constants for the methacrolein $[(0.93 \pm 0.12) (2\sigma) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ and methyl vinyl ketone $[(0.84 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ systems were found to be identical within the 95% confidence interval associated with each separate measurement, as were the chloroalkylperoxy + NO rate constants for both methacrolein $[(1.17 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ and methyl vinyl ketone $[(1.14 \pm 0.14) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$. However, the difference in the rate constants between the hydroxyperoxy + NO and chloroalkylperoxy + NO systems was found to be statistically significant, with the chloroalkylperoxy + NO rate constants about 30% higher than the corresponding hydroxyalkylperoxy + NO rate constants. This substituent effect was rationalized via a frontier molecular orbital model approach.

Introduction

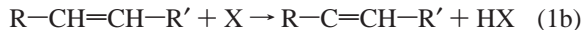
Isoprene (2-methyl-1,3-butadiene) is the dominant non-methane hydrocarbon present in the atmosphere. Isoprene is biogenic in origin (it is emitted by a number of plant species), and its global source strength is larger than that of the anthropogenic nonmethane hydrocarbons. Because of its high chemical reactivity, isoprene plays a significant role in the production of ozone in rural locations and is responsible for nearly 100% of tropospheric ozone formation in certain environments.¹ Methacrolein (2-methyl-2-propenal) and methyl vinyl ketone (3-buten-2-one) are two of isoprene's major oxidation products, and these compounds are also known to be highly reactive and to lead to additional ozone production in regions where isoprene oxidation chemistry is dominant.

The oxidation of alkenes such as methacrolein and methyl vinyl ketone in the troposphere is usually initiated by reaction with OH radical.² However, there are several atmospheric situations in which Cl radicals are suspected to play an important role in hydrocarbon oxidation. For example, in marine areas, the concentrations of Cl radicals (produced by heterogeneous chemistry occurring on sea-salt aerosols³) are believed to be significant, and Cl radicals might be a major hydrocarbon oxidant in these locations. In addition, the ozone-producing impact of Cl radical chemistry initiated by photolysis of Cl₂ emitted from industrial sources has been explored in Houston, TX.^{4–6}

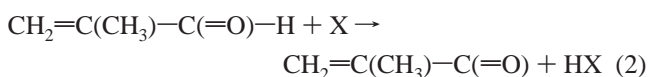
The oxidation mechanism for both the OH- and Cl-initiated oxidation of methacrolein and methyl vinyl ketone can be generalized by invoking a generic oxidant X in the writing of the oxidation sequence. For both the OH- and Cl- initiated oxidation of alkenes, the reaction is known to proceed primarily through an addition mechanism²



A measurable, but small, abstraction pathway has also been observed for the reaction of Cl radicals with alkenes⁷

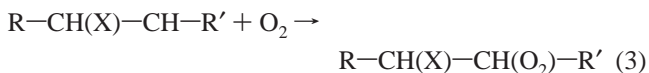


More importantly, the aldehydic proton in methacrolein is also the target of oxidative attack via an abstraction mechanism



For the dominant addition mechanism (reaction 1a), there are two possible oxidant adduct isomers, with the oxidant radical adding to either the R or the R' side of the C=C double bond. Although the oxidant radical is most likely to add to the least-substituted carbon (to create a more stable highly substituted radical center at the other carbon), the existence of both isomers has been indirectly observed in the Cl-initiated oxidation products of 1-butene.⁸ However, to simplify and clarify the subsequent chemical steps in the oxidation of 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. (Because the final oxidation products are not the main subject of this article, this simplification in notation does not present any ambiguities.)

In the next step in the oxidation, the oxidant adduct rapidly reacts with O₂ to form a β-hydroxy- or chloroalkylperoxy radical



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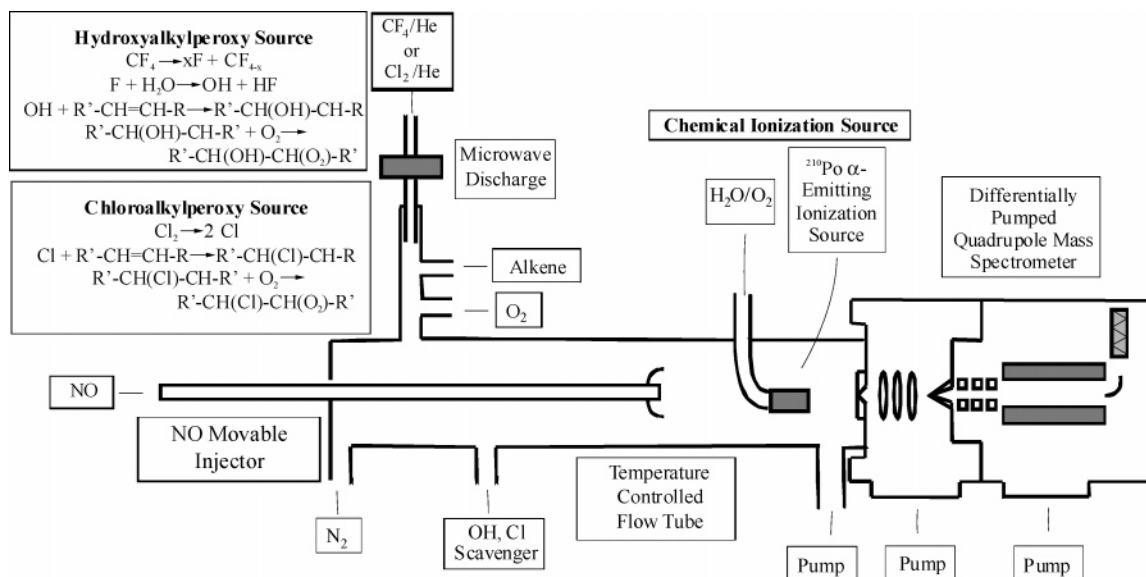
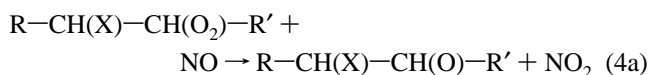


Figure 1. Experimental apparatus.

which, except under remote tropospheric conditions, generally reacts with nitric oxide



The formation of NO₂ in reaction 4a leads to ozone production, whereas the formation of the nitrate species in reaction 4b terminates the oxidation cycle.

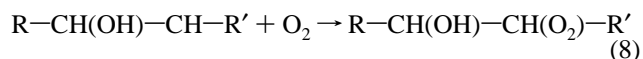
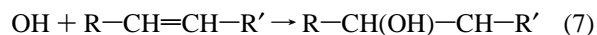
Whereas reaction 1 has been previously studied by direct kinetic methods for OH + methacrolein,^{9–11} OH + methyl vinyl ketone,^{9–11} Cl + methacrolein,^{8,12,13} and Cl + methyl vinyl ketone,^{8,12,14} neither reaction 3 nor reaction 4 has been directly investigated for any of these systems. Although rate constants have generally not been measured for reaction 3, this step is likely very fast in the atmosphere (owing to the high atmospheric concentrations of O₂) and is not expected to affect the overall oxidation rate. Chuong and Stevens have used indirect OH cyclic methods to estimate the rate constant for reaction 4 for the OH-initiated oxidation of methacrolein and methyl vinyl ketone.⁹ Although the rate constant values were determined with relatively high uncertainty owing to the indirect methodology, the actual values determined were surprisingly large, suggesting that the ozone-producing capabilities of methacrolein and methyl vinyl ketone might be more efficient than previously thought. In any case, more certain rate constant values for reaction 4 are needed to allow for an accurate understanding of the kinetics of the complete oxidative pathways for methacrolein and methyl vinyl ketone.

This article describes an investigation of the kinetics of the reaction of hydroxy- and chloroalkylperoxy radicals with NO derived from methacrolein and methyl vinyl ketone (reaction 4). 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 peroxy radicals. The results are interpreted with the aid of a semiempirical model for the kinetics of the reaction of NO with both hydroxyalkylperoxy and chloroalkylperoxy radicals.¹⁵

Experimental Methods

Turbulent Fast Flow Kinetics. The experimental apparatus, a schematic of which is presented in Figure 1, is similar to that used in our previous study of the reactions of hydroxyalkylperoxy and chloroalkylperoxy radicals (derived from the OH- and Cl-initiated oxidation, respectively, of alkenes) with NO.^{16,17} The flow tube was constructed with 2.2-cm-i.d. Pyrex tubing and was 100 cm in total length. A large flow of nitrogen carrier gas (approximately 30 STP L min⁻¹) was injected at the rear of the flow tube. The gases necessary to generate the hydroxy- or chloroalkylperoxy 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 enclosed movable injector. The enclosure (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 to enhance turbulent mixing. The polonium-210 α-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⁻¹ 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. The kinetics measurements were carried out at 100 ± 1 Torr and 298 ± 2 K.

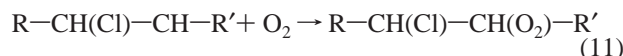
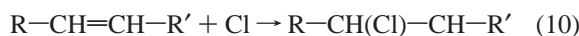
Preparation of Reactants. The hydroxyperoxy radical species were generated through the following reactions



The OH radicals were produced using the microwave discharge technique. A dilute He/CF₄ mixture was passed through a microwave discharge, produced by a Beenakker cavity operating at 50 W to create fluorine atoms (reaction 5). 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% CF₄ (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 possible impurities. The fluorine atoms were then injected into the flow-tube side arm and mixed with H₂O/He, produced by bubbling 10.0 mL min⁻¹ He through a trap filled with H₂O at about 298 K, to produce OH radicals (reaction 6). Hydroxylperoxy radicals were produced by adding excesses of either methacrolein or methyl vinyl ketone and O₂ to the flow-tube side arm. Either methacrolein or methyl vinyl ketone reacted with OH to produce a hydroxy adduct (reaction 7), which then immediately reacted with O₂ to produce the hydroxylperoxy radical (reaction 8). The order of reagent addition in the side arm ensured that peroxy radical generation was complete before the mixture entered the main flow tube.

Cl radicals were also produced using the microwave discharge technique. The chloroalkylperoxy species were generated using the following reactions



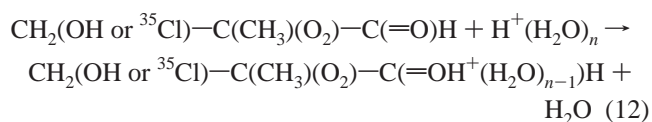
A dilute mixture of He/Cl₂ was obtained by combining a 5.0 STP L min⁻¹ flow of helium (99.999%), which had passed through a silica gel trap immersed in liquid nitrogen, with a 1.0 STP mL min⁻¹ flow of a 1% Cl₂ (99.5%)/He mixture. Chlorine atoms were then produced by passing the He/Cl₂ mixture through a microwave discharge produced by a Beenaker cavity operating at 50 W (reaction 9). As in the hydroxyalkylperoxy generation method described above, chloroalkylperoxy radicals were produced when excesses of either methacrolein or methyl vinyl ketone and O₂ were added to the Cl already present in the side arm (reactions 10 and 11).

Overall Rate Constant Determination. To ensure pseudo-first-order kinetics conditions (with NO as the excess reactant), it was necessary to estimate the typical concentrations of hydroxy- and chloroalkylperoxy radicals. An upper limit to the concentration of hydroxyalkylperoxy radicals was estimated by determining the absolute OH concentrations produced in the radical source. This was accomplished via the reaction of OH radicals with excess NO₂ to produce HNO₃, followed by calibration of the HNO₃ signal. Absolute HNO₃ concentrations were determined by calibration of the HNO₃ mass spectrometer signal using a bubbler containing 60% HNO₃ solution by weight, immersed in an ice-water bath. The vapor pressure of HNO₃ for this solution at 273 K is 0.20 Torr.¹⁸ An upper limit to the concentration of chloroalkylperoxy radicals was estimated by determining the absolute Cl concentrations produced in the radical source. This was accomplished via the reaction of Cl radicals with excess propane to produce HCl, followed by calibration of the HCl signal. Absolute HCl concentrations were determined by calibration of the HCl CIMS signal using a bubbler containing a 20% HCl solution immersed in an ice-water bath.¹⁹ The vapor pressure of HCl at 273 K is 0.038 Torr.¹⁸

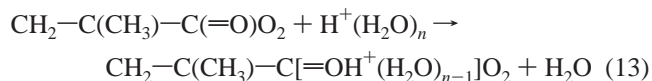
For the overall rate determinations for the reactions of hydroxy- and chloroalkylperoxy with NO, an excess of NO was added to the flow tube as a 0.5% mixture in N₂ through the movable injector. To ensure the absence of NO₂ impurities, NO was passed through a silica gel trap held at -40 °C. Negligible NO₂ concentrations were observed via CIMS methods.

To prevent potential regeneration of OH or Cl in the system from secondary chemistry (and subsequent hydroxy- or chloroalkylperoxy radical regeneration, which could compromise the pseudo-first-order kinetics conditions), a scavenger species was introduced downstream of the hydroxy- or chloroalkylperoxy radical injection point, but upstream of all possible NO injector positions. In these experiments, the scavenger was 2-butene (C₄H₈, 56 amu), which has a lower mass than the parent hydrocarbons [methacrolein and methyl vinyl ketone (C₄H₆O, 70 amu)] of the hydroxy- and chloroalkylperoxy radicals under investigation.

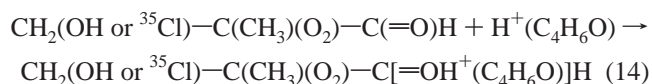
Chemical Ionization Mass Spectrometric Detection. A positive-ion chemical ionization scheme [with H⁺(H₂O)_n as the reagent ion] was used to detect the dominant isotope of the hydroxy- or chloroalkylperoxy radicals with a quadrupole mass spectrometer. The dominant reaction is shown below specifically for the addition mechanism products for methacrolein, but is easily generalized to methyl vinyl ketone as well



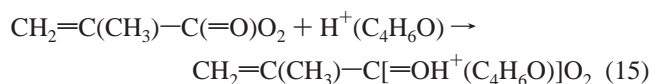
Peroxy radicals resulting from the abstraction oxidation pathway for methacrolein were also detected via this method



It was also noted that secondary chemical ionization was occurring because of the presence of protonated methacrolein or methyl vinyl ketone in the system (again shown for methacrolein specifically, but easily generalized to methyl vinyl ketone)



Again, peroxy radicals resulting from the abstraction oxidation pathway for methacrolein were also detected via this method



Although chemical ionization pathways 14 and 15 were found to be minor compared to pathways 12 and 13, as discussed below, they were useful in assessing the quantitative branching into the addition (reaction 1a) and abstraction (reaction 2) channels for the oxidation of methacrolein.

It is important to note that, for both methacrolein and methyl vinyl ketone, two hydroxy- or chloroalkylperoxy isomers are possible, but our mass spectrometric detection method (reaction 12 was used for the rate constant measurements) is not sensitive to the isomeric distribution of species. Therefore, our kinetics measurements represent a weighted average for the reaction with NO of all hydroxy- or chloroalkylperoxy species (of a specific mass) present. H⁺(H₂O)_n (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 O₂ flow (8 STP L min⁻¹) through the polonium-210 α-emitting ionization source (with H₂O impurities being sufficiently abundant to produce

adequate quantities of reagent ions). The commercial ionization source consisted of a hollow cylindrical (69 × 12.7 mm) aluminum body with 10 mCi (3.7 × 10⁸ disintegrations s⁻¹) 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-i.d., 4.8-cm-o.d. aluminum gaskets. The front chamber was pumped with a 6-in. 2400 L s⁻¹ diffusion pump. The gases entered the rear chamber through a skimmer cone with a charged 1.0-mm orifice that was placed approximately 5 cm from the front aperture. The rear chamber was pumped with a 250 L s⁻¹ turbomolecular pump. Once the ions had passed through the skimmer cone, they were mass filtered and detected with a quadrupole mass spectrometer.

Semiempirical Rate Constant Calculation Methods. Rate constants were predicted using the semiempirical method of King and Thompson.¹⁵ Gaussian 03 calculations²⁰ on various hydroxy- and chloroalkylperoxy isomers were carried out at the ROB3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) level to determine the ground-state geometries and energies of the singly occupied molecular orbital for each species. The NO rate constants were then determined using the expression

$$k = e^c e^{-mE_{\text{SOMO}}} \quad (16)$$

where c and m are empirically derived terms ($c = -28.150$ and $m = 0.698$ eV) and E_{SOMO} is the energy of the singly occupied molecular orbital for the particular hydroxy- or chloroalkylperoxy isomer.

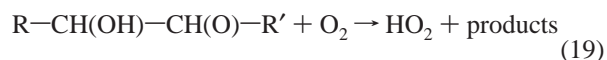
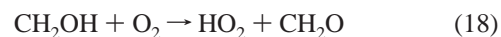
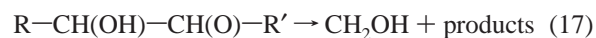
Results and Discussion

Estimate of Branching into Addition and Abstraction Channels. Because the molecular masses of peroxy radicals produced from addition (reaction 1a) and abstraction (reaction 2) for methacrolein differ by 18 and 36 amu (multiples of the molecular mass of H₂O), respectively, for OH- and Cl-initiated oxidation, the chemical ionization reactions shown in reactions 12 and 13 cannot be used to definitively separate these specific peroxy radicals. In particular, although the dominant CH₂(OH or ³⁵Cl)-C(CH₃)(O₂)-C[=OH⁺(H₂O)₃]H (similarly for methyl vinyl ketone) ions are unambiguously related to the neutral addition channel products, the CH₂=C(CH₃)-C[=OH⁺(H₂O)₃]-O₂ ion resulting from the neutral methacrolein abstraction channel product has the same mass as the ions resulting from the neutral methacrolein addition channel products: CH₂(OH)-C(CH₃)(O₂)-C[=OH⁺(H₂O)₂]H or CH₂(³⁵Cl)-C(CH₃)(O₂)-C[=OH⁺(H₂O)]H. However, the chemical ionization schemes shown in reactions 14 and 15 can be used to definitively quantify the abstraction and addition branching (because no H₂O molecules are present in the detected ions to interfere with the interpretation). As the proton transfer is expected to occur at the carbonyl oxygen for all relevant species, chemical ionization sensitivity is expected to be similar for all species, as these reactions are thought to occur at the collision-limited rate.²¹ For the OH-initiated oxidation, a value of 25% ± 10% (where the error limit is based on the barely acceptable detection limit for the abstraction channel peroxy radical) for the abstraction channel was determined based on the relative ion signals of CH₂=C(CH₃)-C[=OH⁺(C₄H₆O)]O₂ (abstraction) and CH₂(OH)-C(O₂)(CH₃)-C[=OH⁺(C₄H₆O)]-H (addition). For the Cl-initiated oxidation, a value of 14% ± 10% for the abstraction

channel was similarly determined via a comparison of the same relative ion signals. Previously, Orlando et al. estimated that the OH-initiated oxidation for methacrolein occurs 45% of the time via an abstraction pathway at 1 atm and 298 K.²² Similarly, the Cl-initiated oxidation was previously found to occur 11% of the time via an abstraction pathway at 1 atm and 298 K.⁸ Compared to these previous studies, the present 100 Torr, 298 K abstraction channel percentage is lower for the OH-initiated system, but is in good agreement for the Cl-initiated system. It is possible that the lower abstraction channel branching ratio for OH-initiated system obtained here is the result of a pressure-dependent effect.

Pseudo-First-Order Kinetics Conditions. Unfortunately, the amount of ion signal resulting from chemical ionization pathways 14 and 15 was not sufficient for kinetics measurements. Therefore, specific studies of the peroxy + NO rate constants for the abstraction channel for methacrolein were not possible. Thus, all of the kinetics measurements were specific for the addition pathway only, i.e., hydroxy- and chloroalkylperoxy + NO reactions.

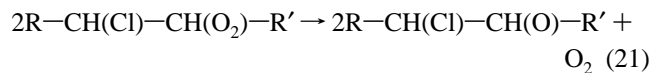
In our previous study of the reaction of hydroxyalkylperoxy radicals with NO,¹⁶ pseudo-first-order conditions were achieved only through the scavenging of OH radicals produced in the main flow tube as a result of secondary reactions involving the R-CH(OH)-CH(O)-R' product of the main reaction



In the previous experiments, the OH produced in reaction 20 could then react with the excess alkene and O₂ present in the flow tube and regenerate hydroxyalkylperoxy radicals, thereby invalidating the desired pseudo-first-order conditions for the loss of the hydroxyalkylperoxy radicals occurring as a result of reaction with NO. The OH produced via reactions 17–20 was scavenged by adding an excess of a second alkene (2-butene, which has a different molecular mass than either methacrolein or methyl vinyl ketone) to the main flow. Because the detection scheme in these types of experiments is mass-specific, the hydroxyalkylperoxy radicals generated as a result of the presence of the scavenger alkene did not interfere with the measurements. The need for this scavenging procedure was confirmed by the observation of 2-butene-derived peroxy radicals. For conditions similar to those of the previous experiments, it was determined that pseudo-first-order conditions are ensured (i.e., effective pseudo-first-order rate constants within 5% of the value calculated if there were no OH regeneration chemistry) as long as $k_{\text{OH+scavenger}}[\text{scavenger}]/k_{\text{OH+alkene}}[\text{alkene}] \geq 5$.¹⁶

To our knowledge, no comprehensive mechanism has been proposed for the Cl-initiated oxidation of alkenes in the presence of NO. Therefore, it is not clear whether Cl regeneration might similarly interfere with measurements of the pseudo-first-order decay of chloroalkylperoxy radicals in the presence of excess NO. However, Orlando et al. investigated the products of the Cl-initiated oxidation of several alkenes in the absence of NO and proposed mechanisms that explain the observed products.⁸ Because one of the product channels of the self-reaction of chloroalkylperoxy radicals (a dominant reaction in the absence

of NO) leads to one of the major products of the chloroalkylperoxy + NO reaction (reaction 4a)



the proposed mechanisms for the NO-free cases can be used to predict some of the products expected in the presence of NO. For the cases of 1- and 2-butene and 1,3-butadiene, Orlando et al. did not propose mechanisms that lead to the regeneration of Cl radicals. However, for the isoprene case, they did propose a mechanism in which the subsequent reactions of a chloroalkoxy radical with O_2 and then with another peroxy species could lead to the regeneration of Cl. Because of the possibility of Cl regeneration, all kinetics studies were performed with alkene scavenger concentrations calculated so that the ratio $k_{Cl+scavenger}/k_{Cl+alkene}$ [scavenger]/[alkene] was equal to or greater than 5 to ensure efficient scavenging. However, no chloroalkylperoxy radicals derived from 2-butene were observed.

Overall Rate Constant Determination. Bimolecular rate constants were obtained via the usual pseudo-first-order approximation method, using NO as the excess reagent. Based on the titration and calibration methods described above, an upper limit of approximately 1×10^{11} molecule cm^{-3} for the initial hydroxyalkylperoxy radical concentrations was calculated, and an upper limit of approximately 2×10^{11} molecule cm^{-3} for the initial chloroalkylperoxy radical concentrations was calculated. Therefore, to ensure pseudo-first-order conditions, NO concentrations were kept at concentrations at least 10 times higher than these values. Because peroxy self-reaction rate constants are typically on the order of 10^{-12} cm^3 molecule $^{-1}$ s^{-1} , pseudo-first-order loss rates of hydroxy- and chloroalkylperoxy radicals due to self-reaction should be negligible in our system (<1 s^{-1} , as compared to pseudo-first-order loss rates due to reaction with NO of 15–50 s^{-1}). Typical chloroalkylperoxy decay curves (for the specific case of the chloroalkylperoxy radicals derived from methacrolein) as a function of injector distance are shown in Figure 2 for the NO kinetics measurements. The first-order rate constants obtained by fitting the chloroalkylperoxy decay curves were plotted against the NO concentration ([NO]) to determine the bimolecular rate constant, as shown in Figure 3. The approach for determining bimolecular rate constants assumes that deviations from the plug-flow approximation (molecular velocities equal to the bulk flow velocity) are negligible. Under ideal flow conditions similar to those present in our turbulent-flow tube (Reynold's number ≈ 2200 , flow velocity ≈ 1200 cm s^{-1}), Seeley et al. estimated that these deviations result in apparent rate constants that are at most 8% below the actual values.²³ Because the actual flow conditions deviate somewhat from the idealized situation modeled by Seeley et al. and because 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 was 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 to obtain accurate results using turbulent-flow conditions.²⁴ The other likely systematic errors in the determination of rate constants occur in the measurements of gas flows, temperatures, detector signals, and pressures. Considering such sources of error, it is estimated that rate constants can be determined with an accuracy of $\pm 30\%$ (2σ).

Measurements similar to those depicted in Figures 2 and 3 for the methacrolein-derived chloroalkylperoxy + NO reaction

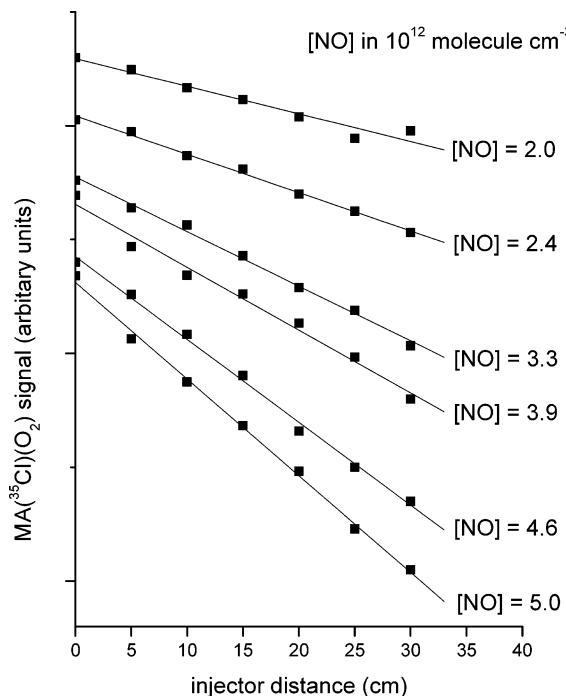


Figure 2. Pseudo-first-order decay curves for the methacrolein-derived chloroalkylperoxy + NO reaction at 100 Torr and 298 K carried out at a velocity of 1200 cm s^{-1} .

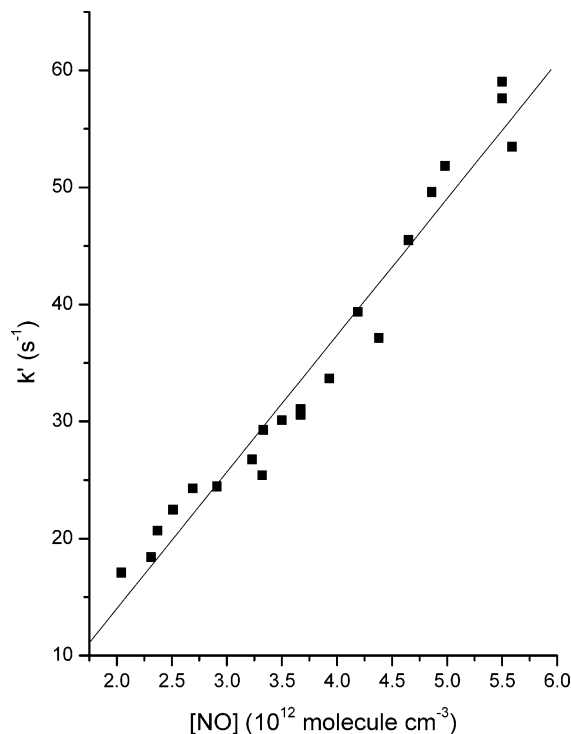


Figure 3. Determination of the overall bimolecular rate constant for the methacrolein-derived chloroalkylperoxy + NO reaction (which includes some data from Figure 2).

were performed for the methacrolein-derived hydroxyalkylperoxy + NO and the methyl vinyl ketone-derived hydroxy- and chloroalkylperoxy + NO reactions. Approximately 20 pseudo-first-order decay curves were used to determine the rate constant for each alkene system. See Table 1 for the experimentally measured rate constants and 2σ statistical uncertainties. The individual 100 Torr, 298 K hydroxyalkylperoxy + NO rate constants for the methacrolein and methyl vinyl ketone systems were found to be identical within the 95% confidence interval

TABLE 1: Experimental Results for the Reaction of NO with Hydroxy- and Chloroalkylperoxy Radicals Derived from Methacrolein and Methyl Vinyl Ketone

| alkene | $k \pm 2\sigma$ (10^{-11} cm ³ molecule ⁻¹ s ⁻¹) | |
|---------------------|---------------------------------------------------------------------------------------|--------------|
| | OH-initiated | Cl-initiated |
| methacrolein | 0.93 ± 0.12 | 1.17 ± 0.11 |
| methyl vinyl ketone | 0.84 ± 0.10 | 1.14 ± 0.14 |

associated with each separate measurement, as were the chloroalkylperoxy + NO rate constants for both methacrolein and methyl vinyl ketone. However, the difference in the rate constants between the hydroxy- and chloroalkylperoxy + NO systems were found to be statistically significant, with the chloroalkylperoxy + NO rate constants being about 30% higher than the corresponding hydroxyalkylperoxy + NO rate constants. In our earlier studies of these rate constants for peroxy radicals derived from OH- and Cl-initiated oxidation of non-functional monoalkenes, we found that all of the rate constants were statistically identical,^{16,17} with values statistically identical to the present results for the hydroxyalkylperoxy + NO rate constants.

To the best of our knowledge, these are first rate constant values to be directly determined for these reactions. However, Chuong and Stevens used OH-cycling techniques to indirectly estimate the overall peroxy + NO rate constant for the OH-initiated oxidation of methacrolein and methyl vinyl ketone.⁹ In this method, there is no way to distinguish between the addition and abstraction pathways for methacrolein, as the peroxy + NO rate constants are extracted from the effect of NO on the OH decay curves. A value of $(2.0 \pm 1.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ was determined for the overall peroxy + NO rate constants for both the methacrolein and methyl vinyl ketone systems. Although the present values are within the stated error limits of this previous study, the much more precisely determined rate constants in the present study indicate a smaller rate constant value of about 0.9×10^{-11} cm³ molecule⁻¹ s⁻¹. Chuong and Stevens pointed out that several studies of NO reaction rate constants for peroxy radicals of the type R-C(=O)O₂ have reported values near 2×10^{-11} cm³ molecule⁻¹ s⁻¹.⁹ However, radicals of this type are produced only by the abstraction mechanism for methacrolein (estimated to be 25% of the total oxidation pathway in this study) and not at all for methyl vinyl ketone. Rather, the dominant peroxy radical species are expected to be the same as for the oxidation of a generic (nonfunctional) alkene. For nonfunctional alkenes, the NO reaction rate constants have been found to about 0.9×10^{-11} cm³ molecule⁻¹ s⁻¹.¹⁶ Therefore, the present rate constant values are consistent with the notion that the peroxy + NO step of the OH-initiated oxidation of methacrolein and methyl vinyl ketone is kinetically similar to that for nonfunctional alkenes. However, for the Cl-initiated cases, the peroxy + NO step is about 30% faster than that determined for nonfunctional alkenes.

Semiempirical Calculations of Isomer-Specific Rate Constants. It is of interest to consider why the chloroalkylperoxy radicals derived from the carbonyl-containing methacrolein and methyl vinyl ketone alkenes react faster with NO, whereas no such difference is observed for NO reactions with hydroxyalkylperoxy radicals derived from any alkene. To address this issue, the semiempirical model of King and Thompson (henceforth referred to as the KT model)¹⁵ was used to calculate isomer-specific rate constants for the reaction of NO with hydroxy- and chloroalkylperoxy radicals derived from methacrolein and methyl vinyl ketone. Similar calculations have previously been performed for the same reactions for peroxy radicals derived from nonfunctional alkenes.¹⁷ The KT model

TABLE 2: Semiempirical Model Results for NO Reaction with Hydroxy- and Chloro- Alkylperoxy Radical Isomers Derived from Methacrolein and Methyl Vinyl Ketone

| isomer | $-E_{\text{SOMO}}^a$ (eV) | k (10^{-11} cm ³ molecule ⁻¹ s ⁻¹) |
|-----------------------|------------------------------|------------------------------------------------------------------------------|
| Methacrolein | | |
| 2-OH 3-O ₂ | -4.042 525 | 1.00 |
| 3-OH 2-O ₂ | -3.976 129 | 0.96 |
| 2-Cl 3-O ₂ | -4.029 464 | 0.99 |
| 3-Cl 2-O ₂ | -4.186 746 | 1.11 |
| Methyl Vinyl Ketone | | |
| 3-OH 4-O ₂ | -3.943 748 | 0.93 |
| 4-OH 3-O ₂ | -4.003 885 | 0.97 |
| 3-Cl 4-O ₂ | -4.043 341 | 1.00 |
| 4-Cl 3-O ₂ | -4.224 297 | 1.14 |

^a ROB3LYP/6-311+G(2d,p).

is based on the expectation from frontier molecular orbital theory that the rate constants for the reaction of a specific molecule (in this case, NO) with a class of compounds (in this case, alkylperoxy radicals) are correlated to the energies of the frontier orbitals of the specific compounds (in this case, the singly occupied molecular orbitals of the alkylperoxy radicals). The KT model was derived by fitting experimentally observed alkylperoxy radical + NO rate constant data (which exist mostly for monofunctional peroxy radicals derived from saturated hydrocarbons) to eq 16 as a function of ab initio values for the energy of the singly occupied molecular orbital (E_{SOMO}) of the appropriate alkylperoxy radical. With the empirical parameters (c and m) derived from the fitting process for a specific method of calculating the energy of the frontier molecular orbitals [ROB3LYP/6-311+G(2d,p)], the KT model can then be used to predict alkylperoxy radical + NO rate constants for any system. When the errors in c and m from the global fit are considered, the calculated *absolute* rate constants have significant uncertainties (about a factor of 2). However, the *relative* relationship between rate constants for a related class of peroxy radicals is more accurately reproduced. For example, the KT model accurately reproduces the order of the increasing values of the experimental NO reaction rate constants for the following systems: CH₃O₂, CH₂BrO₂, CH₂ClO₂, and CH₃C(=O)O₂.¹⁵

In their work, King and Thompson showed that, for difunctional peroxy radicals (such as hydroxy- and chloroalkylperoxy radicals), the NO rate constants are predicted to increase with the increasingly electron-withdrawing nature of the non-peroxy functional group.¹⁵ In particular, they used the KT model to predict NO rate constants for alkylperoxy radicals derived from OH-, Cl-, and NO₃-initiated oxidation of ethene and 1,3-butadiene, among other compounds. In general, the NO rate constants increased as the functional group was varied from OH to Cl to NO₃ (in order of increasing electron-withdrawing ability), as expected, but the effect for ethene was relatively modest, with the calculated rate constants varying by only 7%. Therefore, for hydroxy- and chloroalkylperoxy radicals derived from methacrolein and methyl vinyl ketone, the presence of a carbonyl group (with its own electron-withdrawing ability) might be expected to result in higher NO rate constants compared to peroxy radicals derived from nonfunctional alkenes.

The results of these calculations for the reactions of NO with hydroxy- and chloroalkylperoxy radicals are reported in Table 2. For methacrolein, the 3-OH or -Cl, 2-O₂ isomer is expected to be dominant because the 3-OH or -Cl adduct species has the radical localized on a tertiary carbon, which is more favorable than the 2-OH or -Cl adduct, which has the radical localized on a secondary carbon. For methyl vinyl ketone, the 4-OH or -Cl, 3-O₂ isomer is expected to be dominant because the 4-OH

or -Cl adduct has the radical localized on a secondary carbon, which is more favorable than the 3-OH or -Cl adduct, which has the radical localized on a primary carbon. For the hydroxyalkylperoxy + NO calculated rate constants, there is very little dependence on the isomeric form, and the calculated rate constant values are similar to those calculated for the NO reaction with hydroxyalkylperoxy radicals derived from nonfunctional alkenes. However, there is a more significant isomer-dependent difference for the chloroalkylperoxy + NO rate constants in the present case, with the dominant isomer predicted to have larger NO rate constants. Previous computational studies of the reaction of NO with chloroalkylperoxy radicals derived from nonfunctional alkenes also indicated a larger isomer dependence, but the dominant isomers in those cases were calculated to have smaller rate constants.¹⁷ The KT model predicts that, for the dominant isomer, the chloroalkylperoxy + NO rate constants should be 16% and 18% higher than the corresponding hydroxyalkylperoxy + NO rate constants for the methacrolein and methyl vinyl ketone systems, respectively. This result is in fair agreement with the approximately 30% difference determined experimentally. Therefore, the KT model apparently indicates that the Cl and carbonyl substituents have a synergistic effect in lowering the energies of the frontier molecular orbitals of the chloroalkylperoxy radicals and thus explains the larger calculated (and experimental) NO reaction rate constants in those cases.

Conclusions

The overall rate constants for the reactions of NO with hydroxy- and chloroalkylperoxy radicals, derived from OH- and Cl-initiated oxidation, respectively, of methacrolein and methyl vinyl ketone, were directly determined for the first time using the turbulent-flow technique and pseudo-first-order kinetics conditions with high-pressure chemical ionization mass spectrometry for the direct detection of peroxy radical reactants. The individual 100 Torr, 298 K hydroxyalkylperoxy + NO rate constants for the methacrolein and methyl vinyl ketone systems were found to be identical within the 95% confidence interval associated with each separate measurement, as were the chloroalkylperoxy + NO rate constants for both methacrolein and methyl vinyl ketone. However, the difference in the rate constants between the hydroxy- and chloroalkylperoxy + NO systems was found to be statistically significant, with the chloroalkylperoxy + NO rate constants being about 30% higher than the corresponding hydroxyalkylperoxy + NO rate constants. Whereas the present results for the NO reaction rate constants for hydroxyalkylperoxy radicals derived from methacrolein and methyl vinyl ketone are generally consistent with the simplification that many atmospheric models employ, i.e., that all RO₂ + NO reactions are modeled using the same rate constant value ($\sim 0.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the present results for the NO reaction rate constants for chloroalkylperoxy radicals are 30% higher. These results are qualitatively supported by the computational King–Thompson model, which predicts higher peroxy + NO rate constants in the case of the pairing of the Cl and carbonyl electron-withdrawing substituents.¹⁵ The higher NO rate constants for Cl-initiated oxidation imply that more efficient tropospheric ozone production will occur via methacrolein and methyl vinyl ketone oxidation for atmospheric conditions in which Cl-initiated oxidation is competitive with OH initiation. Interestingly, our previous study on peroxy + NO rate constants for the Cl-initiated oxidation of isoprene itself

revealed larger rate constants (also by about 30%) than the “standard” peroxy + NO rate of $0.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁷ Therefore, isoprene more efficiently leads to tropospheric ozone production under conditions of Cl-initiated oxidation because of the fact that, in both the primary (isoprene itself) and secondary (methacrolein and methyl vinyl ketone) oxidation sequences, the peroxy + NO reaction occurs more quickly than in the OH-initiated case.

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References and Notes

- (1) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: New York, 2000.
- (2) Finlayson-Pitts, B. J.; Pitts, J. N. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, CA, 2000.
- (3) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Platridge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* **1998**, *394*, 353.
- (4) Tanaka, P. L.; Oldfield, S.; Neece, J. D.; Mullins, C. B.; Allen, D. T. *Environ. Sci. Technol.* **2000**, *34*, 4470.
- (5) Tanaka, P. L.; Riemer, D. D.; Chang, S.; Yarwood, G. M.-B. E. C.; Apel, E. C.; Orlando, J. J.; Silva, P. J.; Jimenez, J. L.; Canagaratna, M. R.; Neece, J. D.; Mullins, C. B.; Allen, D. T. *Atmos. Environ.* **2003**, *37*, 1393.
- (6) Tanaka, P. L.; Allen, D. T.; McDonald-Buller, E. C.; Chang, S.; Kimura, Y.; Mullins, C. B.; Yarwood, G.; Neece, J. D. *J. Geophys. Res.* **2003**, *108*, ACH 6-1.
- (7) Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5813.
- (8) Orlando, J. J.; Tyndall, G. S.; Apel, E. C.; Riemer, D. D.; Paulson, S. E. *Int. J. Chem. Kinet.* **2003**, *35*, 334.
- (9) Chuong, B.; Stevens, P. S. *Int. J. Chem. Kinet.* **2004**, *36*, 12.
- (10) Kleindienst, T. E.; Harris, G. W.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1982**, *16*, 844.
- (11) Gierczak, T.; Burkholder, J. B.; Talukdar, R. K.; Mellouki, A.; Barone, S. B.; Ravishankara, A. R. *J. Photochem. Photobiol. A: Chem.* **1997**, *110*, 1.
- (12) Canosa-Mas, C. E.; Cotter, E. S. N.; Duffy, J.; Thompson, K. C.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3075.
- (13) Wang, W.; Ezell, M. J.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1824.
- (14) Finlayson-Pitts, B. J.; Keoshian, C. J.; Buehler, B.; Ezell, A. A. *Int. J. Chem. Kinet.* **1999**, *31*, 491.
- (15) King, M. D.; Thompson, K. C. *Atmos. Environ.* **2003**, *37*, 4517.
- (16) Miller, A. M.; Yeung, L. Y.; Kiep, A. C.; Elrod, M. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3402.
- (17) Patchen, A. K.; Pennino, M. J.; Elrod, M. J. *J. Phys. Chem. A* **2005**, *109*, 5865.
- (18) Fritz, J. J.; Fuget, C. R. *Chem. Eng. Data Ser.* **1956**, *1*, 10.
- (19) Lipson, J. B.; Elrod, M. J.; Beiderhase, T. W.; Molina, L. T.; Molina, M. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2665.
- (20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2004.
- (21) Zhao, J.; Zhang, R. *Atmos. Environ.* **2004**, *38*, 2177.
- (22) Orlando, J. J.; Tyndall, G. S.; Paulson, S. E. *Geophys. Res. Lett.* **1999**, *26*, 2191.
- (23) Seeley, J. V.; Jayne, J. T.; Molina, M. J. *Int. J. Chem. Kinet.* **1993**, *25*, 571.
- (24) Chuong, B.; Stevens, P. S. *J. Geophys. Res.* **2002**, *107*, ACH2-1.