Overall Rate Constant Measurements of the Reaction of Chloroalkylperoxy Radicals with Nitric Oxide

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The overall rate constants of the NO reaction with chloroalkylperoxy radicals derived from the Cl-initiated oxidation of several atmospherically abundant alkenes—ethene, propene, 1-butene, 2-butene, 2-methylpropene, 1,3-butadiene, and isoprene (2-methyl-1,3-butadiene)—were determined for the first time via the turbulent flow technique and pseudo-first-order kinetics conditions with high-pressure chemical ionization mass spectrometry for the direct detection of chloroalkylperoxy radical reactants. The individual 100 Torr, 298 K rate constants for each monoalkene system were found to be identical within the 95% confidence interval associated with each separate measurement, whereas the corresponding rate constants for 1,3-butadiene and isoprene were both ∼20% higher than the monoalkene mean value. Our previous study of the reaction of hydroxylalkylperoxy radicals (derived from the OH-initiated oxidation of alkenes) with NO yielded identical rate constants for all of the alkenes under study, with a rate constant value within the statistical uncertainty of the value determined here for the NO reaction of chloroalkylperoxy radicals derived from monoalkenes. Thus, the reaction of NO with chloroalkylperoxy radicals derived from dialkenes is found to be significantly faster than the NO reaction with either chloroalkylperoxy radicals derived from monoalkenes or hydroxyalkylperoxy radicals derived from either mono- or dialkenes.

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 significantly 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] The direct role of anthropogenically produced alkenes in tropospheric ozone production was illustrated by a recent field study in which it was revealed that alkenes emitted by the petrochemical industry in Houston, Texas, are largely responsible for that city's severe ozone pollution problem.[5] Biogenic sources of alkenes include emissions from vegetation, soils, and the oceans.[6] 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 one-third 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 the tropospheric ozone formation in certain environments.[1]

The oxidation of alkenes in the troposphere is usually initiated by reaction with an OH radical.[7] 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 aerosols[8]) are believed to be significant, and Cl radicals may be a major hydrocarbon oxidant in these locations. In addition, the unusual hydrocarbon oxidation-driven surface ozone depletion chemistry observed in the Arctic springtime is believed to largely be the result of the reactions of Cl radicals that have been formed from sea-salt aerosol processing.[9,10] Finally, the ozone-producing impact of Cl radical chemistry initiated by photolysis of Cl_2 emitted from industrial sources has been explored in Houston, Texas.[11−13]

As in the OH-initiated oxidation of alkenes, the reaction of Cl with alkenes is known to proceed primarily through an addition mechanism:[7]

$$R{-}CH{=}CH{-}R' + Cl \rightarrow R{-}CH(Cl){-}CH{-}R' \quad (1a)$$

However, unlike the OH-initiated case, a minor but measurable abstraction pathway has been observed for the reaction of Cl radicals with alkenes:[14]

$$R{-}CH{=}CH{-}R' + Cl \rightarrow R{-}C{=}CH{-}R' + HCl \quad (1b)$$

For the dominant addition mechanism, there are two possible chloro adduct isomers, with the Cl radical adding to either the R or R′ side of the C═C double bond. Although the Cl radical tends 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.[15] However, 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 (because the final oxidation products are not the subject of this article, this notation simplification does not present any ambiguities).

In the next step of the Cl-initiated oxidation of alkenes, the Cl adduct rapidly reacts with O_2 to form a β-chloroalkylperoxy radical,

$$R{-}CH(Cl){-}CH{-}R' + O_2 \rightarrow R{-}CH(Cl){-}CH(O_2){-}R' \quad (2)$$

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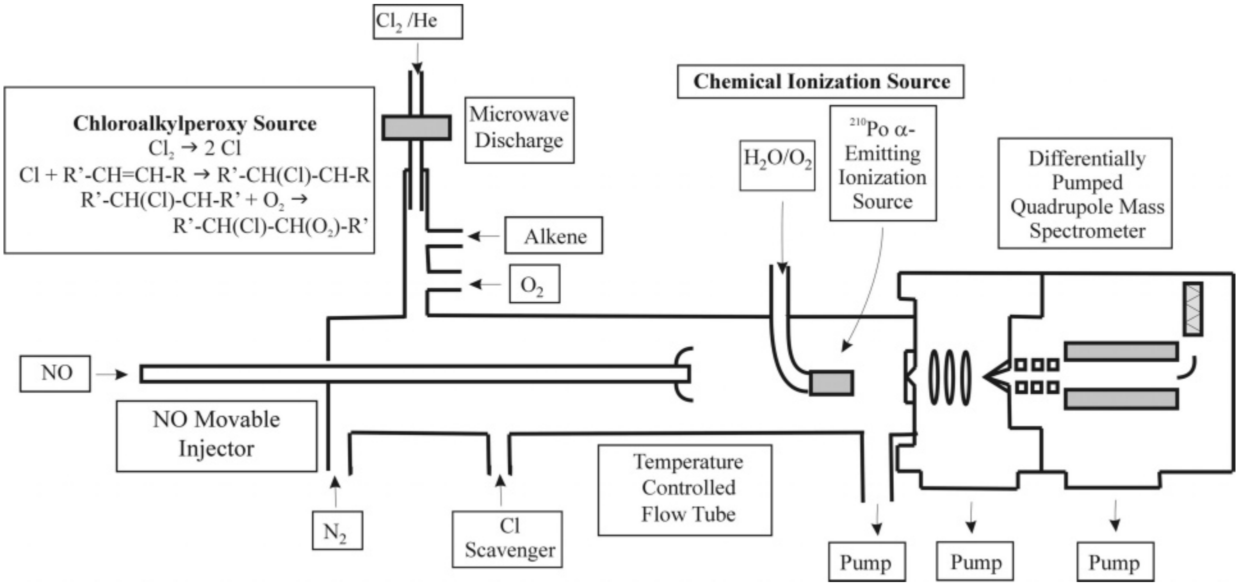

Figure 1. Experimental apparatus.

which, with the exception of remote tropospheric conditions, is generally followed by a reaction with nitric oxide:

$$\mathrm{R{-}CH(Cl){-}CH(O_2){-}R' + NO} \rightarrow \mathrm{R{-}CH(Cl){-}CH(O){-}R' + NO_2} \tag{3a}$$

$$\rightarrow \mathrm{R{-}CH(Cl){-}CH(ONO_2){-}R'} \tag{3b}$$

The formation of NO_2 in reaction 3a leads to ozone production, whereas the formation of the chloronitrate species in reaction 3b terminates the oxidation cycle.

Although reaction 1 has been studied fairly thoroughly by direct kinetic methods for a number of alkenes,[16] reaction 2 has been directly measured for the ethene system only,[17] and reaction 3 has not yet been directly investigated for any alkene system. Stutz et al. have shown that for the small alkenes, the rate constant of reaction 1 is approximately six times greater than that for the analogous OH reactions, indicating that the first step in the Cl-initiated oxidation of alkenes is significantly faster than the same step in the OH-initiated case.[16] Although rate constants have generally not been measured for reaction 2, it is likely that this step is very fast in the atmosphere (because of the high atmospheric concentrations of O_2) and is not expected to affect the overall alkene oxidation rate. However, the lack of rate constants for reaction 3 precludes an accurate understanding of the kinetics of the complete Cl-initiated oxidative pathway for alkenes.

This article describes an investigation of the kinetics of the reaction of several alkene-derived chloroalkylperoxy radicals with NO (reaction 3). The measurements were conducted at 100 Torr and 298 K under pseudo-first-order kinetics conditions via a turbulent flow (TF) tube coupled to a high-pressure chemical ionization mass spectrometer (CIMS), which allowed for direct detection of the chloroalkylperoxy radicals. The NO reaction kinetics of chloroalkylperoxy radicals obtained from the Cl-initiated oxidation of ethene, propene, 1-butene, 2-butene, 2-methylpropene, 1,3-butadiene, and isoprene were investigated in this work. These parent alkenes were chosen to allow for a systematic investigation of the possible structural and electronic effects that varying alkene functionality has 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[1]). The results are compared to previous kinetics measurements of the reaction of alkene-derived hydroxyalkylperoxy radicals with NO[18] as well as to a semiempirical model for the kinetics of the reaction of NO with both hydroxyalkylperoxy and chloroalkylperoxy radicals.[19]

Experimental Methods

Turbulent Fast Flow Kinetics. A schematic of the experimental apparatus is presented in Figure 1 and is similar to that which was used in our previous study of the reaction of hydroxylalkylperoxy radicals (derived from the OH-initiated oxidation of alkenes) with NO.[18] The flow tube was constructed with 2.2-cm i.d. Pyrex tubing and was 100 cm long. A large flow of nitrogen carrier gas [~30 standard temperature and pressure (STP) L min^{-1}] was injected at the rear of the flow tube. The gases that were necessary to generate the chloroalkylperoxy radicals were introduced though 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 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^{-1} roughing pump. All gas flows were monitored with calibrated mass flow meters. We measured the flow tube pressure upstream in relation to the ionization source using a 0−1000-Torr capacitance manometer. We determined the temperature in the flow tube using Cu−constantan thermocouples.

Overall Rate Constant Determination. The chloroalkylperoxy species were generated via the following reactions:

$$\mathrm{Cl_2} \rightarrow \mathrm{Cl + Cl} \tag{4}$$

$$\mathrm{R{-}CH{=}CH{-}R' + Cl} \rightarrow \mathrm{R{-}CH(Cl){-}CH{-}R'} \tag{1a}$$

$$\mathrm{R{-}CH(Cl){-}CH{-}R' + O_2} \rightarrow \mathrm{R{-}CH(Cl){-}CH(O_2){-}R'} \tag{2}$$

The kinetics measurements were carried out at 100 ± 1 Torr and 298 ± 2 K. We obtained a dilute mixture of He/Cl_2 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% Cl_2 (99.5%)/He mixture. We then produced chlorine atoms by passing the He/Cl_2 mixture through a microwave discharge produced by a Beenakker cavity operating at 50 W. To make the chloroalkylperoxy radicals, excesses of both the alkene (CP grade; typically $\sim 5.0 \times 10^{12}$ molecule cm^{-3}) and the O_2 (99.995%; typically $\sim 4.0 \times 10^{15}$ molecule cm^{-3}) were then added to the Cl already present in the sidearm (reactions 1a and 2).

To ensure pseudo-first-order kinetics conditions (with NO as the excess reactant), it is necessary to estimate the typical concentration of chloroalkylperoxy radicals. 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. We determined the absolute HCl concentrations by calibrating the HCl CIMS signal using a bubbler containing a 20% HCl solution immersed in an ice water bath.[20] The vapor pressure of HCl under these conditions was 0.038 Torr.[21]

For the overall rate determination for the chloroalkylperoxy + NO reaction, an excess of NO was added to the flow tube as a 0.5% mixture in N_2 through the movable injector. To ensure the absence of NO_2 impurities, NO was passed through a silica gel trap held at −40 °C. Negligible NO_2 concentrations were observed via CIMS methods.

To prevent the potential regeneration of Cl in the system from secondary chemistry (and subsequent chloroalkylperoxy radical regeneration, which could compromise the pseudo-first-order kinetics conditions), a scavenger species was introduced downstream from the chloroalkylperoxy radical injection point, but upstream in relation to all possible NO injector positions. In these experiments, the scavenger was an alkene with a molecular mass that was different from that of the parent alkene of the chloroalkylperoxy radical under investigation. For comparison, experiments in which no Cl-scavenger was added to the system were also performed.

CIMS Detection. A positive ion chemical ionization scheme (with $H^+(H_2O)_n$ as the reagent ion) was used to detect the dominant isotope (containing ^{35}Cl) of the chloroalkylperoxy radicals with a quadrupole mass spectrometer:

$$\begin{aligned} &R{-}CH(^{35}Cl){-}CH(O_2){-}R' + H^+(H_2O)_n \rightarrow \\ &\qquad R{-}CH(^{35}Cl){-}CH[O_2H^+(H_2O)_{n-1}]{-}R' + H_2O \quad (5) \end{aligned}$$

A similar proton-transfer reaction method was used in our previous studies of the kinetics of peroxy radicals derived from small alkanes[22−25] and alkenes.[18] It is important to note that, for each parent alkene, there are at least two chloroalkylperoxy isomers possible (two for the monoalkenes, three for 1,3-butadiene, and six 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 of the chloroalkylperoxy species (of a specific mass) present with NO. We produced $H^+(H_2O)_n$ (the $n = 4$ species usually accounted for more than 80% of the total ion signal) in the ion source by passing a large O_2 flow (8 STP L min^{-1}) through the polonium-210 alpha-emitting ionization source (with H_2O 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 (3.7×10^8 dps) 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., 48-cm o.d. aluminum gaskets. The front chamber was pumped by 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 by a 250-L s^{-1} turbomolecular pump. Once the ions 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 via the semiempirical method of King and Thompson.[19] Gaussian 98 calculations[26] 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. We then determined the NO rate constants using the expression

$$k = e^{c} \times e^{-mE_{\mathrm{SOMO}}} \qquad (6)$$

in which 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

Pseudo-First-Order Kinetics Conditions. In our previous study of the reaction of hydroxylalkylperoxy radicals with NO,[18] 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:

$$R{-}CH(OH){-}CH(O){-}R' \rightarrow CH_2OH + \text{products} \qquad (7)$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \qquad (8)$$

$$R{-}CH(OH){-}CH(O){-}R' + O_2 \rightarrow HO_2 + \text{products} \qquad (9)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (10)$$

In the previous experiments, the OH produced in reaction 10 could then react with the excess alkene and O_2 present in the flow tube to regenerate hydroxyalkylperoxy radicals and thus invalidate the desired pseudo-first-order conditions for the loss of the hydroxyalkylperoxy radicals due to the reaction with NO. The OH produced via reactions 7−10 was scavenged by adding an excess of a second alkene (with a different molecular mass) to the main flow. Because the detection scheme in these types of experiments is mass specific, the hydroxyalkylperoxy radicals generated due to the presence of the scavenger alkene did not interfere with the measurements. For the 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 the ratio of $k_{\mathrm{OH+scavenger}}[\mathrm{scavenger}]/k_{\mathrm{OH+alkene}}[\mathrm{alkene}] \geq 5$.[18]

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. have investigated the products of the Cl-initiated oxidation of several alkenes in the absence of NO and have proposed mechanisms that explain the observed products.[15] 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 3a),

$$2\ \mathrm{R{-}CH(Cl){-}CH(O_2){-}R'} \rightarrow 2\ \mathrm{R{-}CH(Cl){-}CH(O){-}R'} + \mathrm{O_2} \quad (11)$$

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, they did propose a mechanism for isoprene in which the subsequent reactions of a chloroalkoxy radical with O_2 followed by a reaction 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 $k_{\mathrm{Cl+scavenger}}$[scavenger]/$k_{\mathrm{Cl+alkene}}$[alkene] was equal to or greater than five to ensure efficient scavenging. Kinetics studies were also performed in the absence of a scavenger.

The ethene system was the only system in which the rate constants that were determined in the absence of a scavenger were different from those determined in experiments in which an appropriate scavenger was used. In fact, the effect was so pronounced in the case of ethene that in the absence of a scavenger (isoprene) it was clear that the decay of the ethene-derived chloroalkylperoxy species was non-pseudo-first-order. Therefore, with the exception of ethene, the scavenger studies seem to indicate that no Cl-regeneration is observed under our experimental conditions for the alkene systems studied. As stated above, a mechanistic framework to predict the fate of the products of reaction 3 does not exist, but this general result is consistent with the mechanism for small alkenes suggested by Orlando et al., which does not predict the regeneration of Cl radicals from chloroalkoxy radicals.[15] It is interesting that the sole exception to this general result was found in the smallest system under study (ethene). Previous studies of the Br-initiated oxidation of alkenes have shown that Br radical addition to alkenes is reversible,[27,28] indicating that halogen atoms can be labile in these systems. The loss of Cl radicals from the chloroalkoxy product resulting from the NO reaction with the chloroperoxy species derived from ethene is one possible explanation for the observed Cl radical regeneration in the ethene system.

Overall Rate Constant Determination. Bimolecular rate constants were obtained via the usual pseudo-first-order approximation method, with NO serving as the excess reagent. On the basis of the HCl production and calibration method for determining Cl radical concentrations, an upper limit of ~2 × 10^{11} molecule $\mathrm{cm^{-3}}$ was calculated for the initial chloroalkylperoxy radical concentrations. Therefore, to ensure pseudo-first-order conditions, NO concentrations were kept at levels that were at least 10 times higher than this value. Because peroxy self-reaction rate constants are typically on the order of 10^{-12} $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, the pseudo-first-order loss rates of chloroalkylperoxy radicals due to self-reaction should be negligible in our system ($<1\ \mathrm{s^{-1}}$, whereas the pseudo-first-order loss rates due to reaction with NO are 15 to 50 $\mathrm{s^{-1}}$). Typical chloroalkylperoxy decay curves (for the specific case of the chloroalkylperoxy radicals derived from 2-methylpropene) as a function of injector distance are shown in Figure 2 for the NO kinetics measurements. The first-order rate constants obtained from fitting the chloroalkylperoxy decay curves were plotted against [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 are equal to the bulk flow velocity) are negligible. Under ideal flow conditions similar to

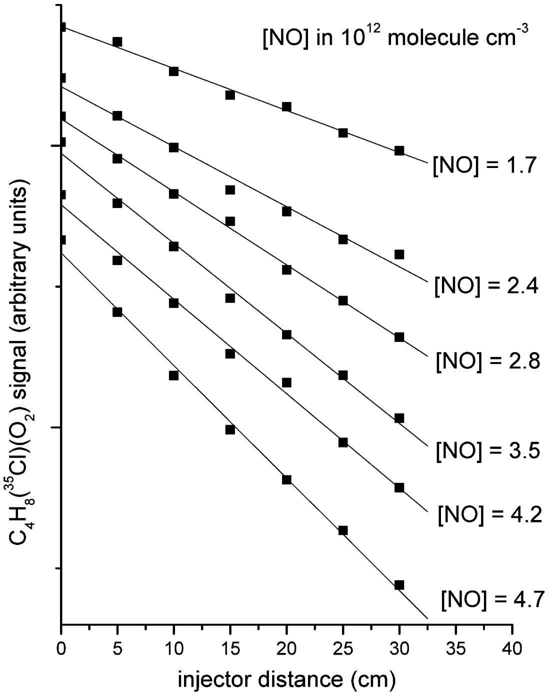

Figure 2. Pseudo-first-order decay curves for the 2-methylpropene-derived chloroalkylperoxy + NO reaction at 100 Torr and 298 K, carried out at a velocity of 1210 cm $\mathrm{s^{-1}}$.

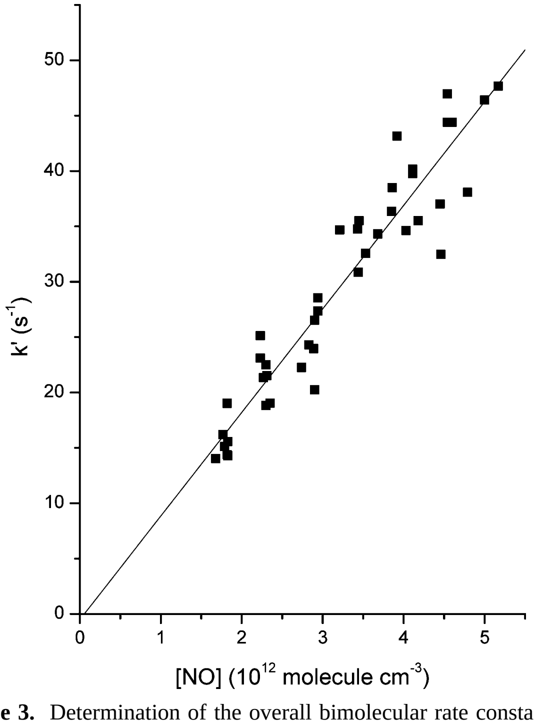

Figure 3. Determination of the overall bimolecular rate constant for the 2-methylpropene-derived chloroalkylperoxy + NO reaction (which includes some data from Figure 2).

TABLE 1: Comparison of Overall Rate Constants for the NO Reaction with Peroxy Radicals Derived from the OH- and Cl-Inititated Oxidation of Selected Alkenes

	k (10^{-12} cm^3 molecule^{-1} s^{-1})[a]	
alkene	OH-initiated (ref 18)	Cl-initiated (this work)
ethene	8.7 ± 1.2	9.7 ± 1.2
propene	9.5 ± 1.2	10.2 ± 1.2
1-butene	9.6 ± 1.2	9.6 ± 1.0
2-butene	9.3 ± 1.4	9.8 ± 1.2
2-methylpropene	9.6 ± 1.2	9.4 ± 1.0
1,3-butadiene	8.83 ± 0.83	11.8 ± 1.0
isoprene	8.8 ± 1.2	11.5 ± 1.1
monoalkene composite	9.1 ± 0.6	9.8 ± 0.5
dialkene composite	9.0 ± 0.8	11.6 ± 0.7
alkene composite	9.1 ± 0.5	

[a] Statistical 2σ uncertainty cited.

those present in our TF 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.[29] Because the actual flow conditions deviate somewhat from the idealized situation modeled by Seeley et al. and because, to date, no systematic errors have been apparent in the systems that have been studied 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 to obtain accurate results under TF conditions.[30] The other likely systematic errors in the determination of rate constants occur in the measurements of gas flows, temperature, detector signal, and pressure. When such sources of error are considered, it is estimated that rate constants can be determined with an accuracy of ±30% (2σ).

Measurements similar to those depicted in Figures 2 and 3 for the 2-methylpropene-derived chloroalkylperoxy + NO reaction were performed for ethene, propene, 1-butene, 2-butene, 1,3-butadiene, and isoprene. Approximately 30 pseudo-first-order decay curves were used to determine the rate constant for each alkene system (see Table 1 for a complete list of the experimentally measured rate constants and 2σ statistical uncertainties). To the best of our knowledge, these are the first rate constant values to be directly determined for the reaction of chloroalkylperoxy radicals with NO. The individual 100 Torr, 298 K rate constants for each monoalkene system were found to be identical within the 95% confidence interval associated with each separate measurement. In Figure 4, all of the present data for the kinetics measurements of the reaction of monoalkene-derived chloroalkylperoxy radicals with NO are used to derive a "composite" overall rate constant of 9.8 ± 0.5 × 10^{-12} cm^3 molecule^{-1} s^{-1}. The individual 100 Torr, 298 K rate constants for each dialkene system were found to be identical within the 95% confidence interval associated with each of the measurements for the 1,3-butadiene and isoprene systems but were statistically larger than the composite value for the monoalkenes. Additionally, in Figure 4, all of the present data for the kinetics measurements of the reaction of dialkene-derived chloroalkylperoxy radicals with NO are used to derive a composite overall rate constant of 11.6 ± 0.7 × 10^{-12} cm^3 molecule^{-1} s^{-1}. The rate constants previously determined for the reaction of NO with alkene-derived hydroxyalkylperoxy radicals[18] are also given in Table 1. Interestingly, in the OH-initiated case, there was no difference in the measured rate constants for hydroxyalkylperoxy radicals derived from monoalkenes or dialkenes (i.e., the monoalkene and dialkene composite rate constants are statistically identical). In addition, although the composite NO rate constant for the chloroalkylperoxy radicals derived from monoalkenes is slightly higher (9.8 ± 0.5 × 10^{-12} cm^3 molecule^{-1} s^{-1}) than the composite value for the hydroxylalkylperoxy radicals derived from both mono- and dialkenes (9.1 ± 0.5 × 10^{-12} cm^3 molecule^{-1} s^{-1}), the two composite values are indistinguishable within the 95% confidence interval.

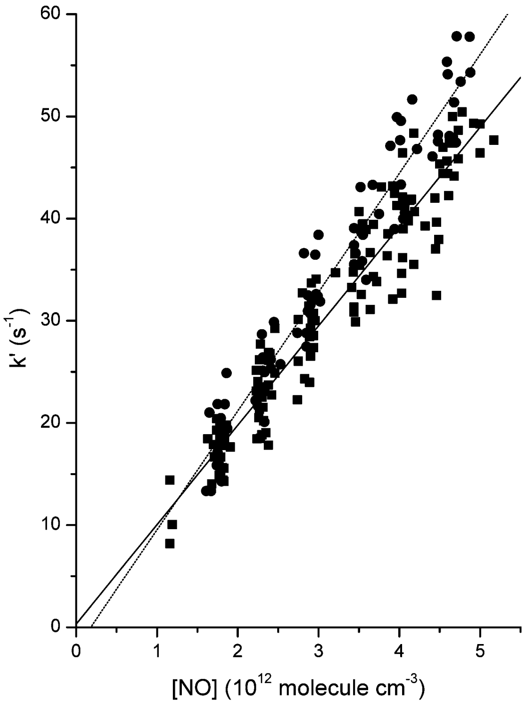

Figure 4. Determination of the composite overall bimolecular rate constants for the monoalkene-derived and dialkene-derived Chloroalkylperoxy + NO reactions (■ = monoalkenes, ● = dialkenes).

Semiempirical Calculations of Isomer-Specific Rate Constants. It is of interest to consider why the chloroalkylperoxy radicals derived from the dialkenes 1,3-butadiene and isoprene react faster with NO, whereas no such difference is observed for NO reactions with hydroxylalkylperoxy radicals. To address this issue, the semiempirical model of King and Thompson (henceforth referred to as the KT model)[19] was used to calculate isomer-specific rate constants for the reaction of NO with hydroxyl- and chloroalkylperoxy radicals. The KT model 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 energy of the frontier orbitals of the specific compounds (in this case, the single occupied molecular orbitals of the alkylperoxy radicals). The KT model was derived by the fitting of experimentally observed alkylperoxy radical + NO rate constant data (which exists mostly for monofunctional peroxy radicals derived from saturated hydrocarbons) to eq 6 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, the KT model can be used to predict alkyperoxy radical + NO rate constants for any system. The reported uncertainties in c and m can be used to determine an estimated uncertainty in the calculated rate constant (which does not include uncertainties in E_{SOMO}, which are also probably significant). When the reported errors of 0.481 and 0.105 eV for c and m, respectively, are propagated for an average E_{SOMO} value of 4.00 eV, an estimated error of 2×10^{-14} cm^3 molecule^{-1} s^{-1} is calculated. This value is undoubtedly unrealistically low because of the neglect of errors in E_{SOMO}. However, the agreement between experimental and calculated values for the limited data set available is quite good (within 1%, or an uncertainty of $\sim 10 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for the typical rate constant values calculated for the systems under study). In any case, the subsequent discussion will focus on relatively large calculated differences in rate constant values (15−60%).

In their work, King and Thompson showed that for difunctional peroxy radicals (such as hydroxyl- and chloroalkyperoxy radicals), the NO rate constants are predicted to increase with the increasingly electron-withdrawing nature of the non-peroxy functional group.[19] In particular, they used the KT model to predict NO rate constants for alkylperoxy radicals derived from the OH-, Cl-, and NO_3-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 NO_3 (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%. Interestingly, for the 1,3-butadiene system, King and Thompson found that the rate constants varied more significantly between the 1-OH, -Cl, or -NO_3, 2-O_2 and 1-OH, -Cl, or -NO_3, 4-O_2 alkylperoxy isomers (∼15%) and that the electron-withdrawing effect was more pronounced for the 1,4 isomer (an ∼20% higher rate constant for NO_3 functionality as compared to OH functionality).

To explore the possibility that specific isomers could have significantly different rate constants and significantly different dependencies on the electron-withdrawing nature of the non-peroxy functional group, we performed similar calculations using the KT model for the NO rate constants for all alkylperoxy radicals derived from the Cl- and OH-initiated oxidation of the seven alkenes under study in this work. The results of these calculations for the NO reaction with hydroxyalkylperoxy radicals and with chloroalkylperoxy radicals are shown in Tables 2and 3,respectively. For the alkylperoxy radicals derived from monoalkenes, the NO rate constants for the isomers with the peroxy group at an external position are consistently larger by ∼5% for both the hydroxy and the chloro cases. More importantly, the KT model predicts that the NO rate constants for alkylperoxy radicals derived from monoalkenes (whether they are formed from Cl- or OH-initiated chemistry) are expected to be indistinguishable from each other at the level of the present experimental uncertainty (the calculated values vary by less than 10%, which is on the order of the present experimental 2σ uncertainty). This calculated result is in accordance with the previous results for the NO rate constants for hydroxyalkylperoxy radicals[18] as well as the present results for the NO rate constants for chloroalkylperoxy radicals derived from monoalkenes.

TABLE 2: Semiempirical Model Results for the NO Reaction with Hydroxyalkylperoxy Radical Isomers

isomer	$-E_{\mathrm{SOMO}}$ [ROB3LYP/6-311+G(2d,p)// B3LYP/6-31G(d,p)] (eV)	k (10^{-12} cm^3 molecule^{-1} s^{-1})
ethene		
1-OH, 2-O_2	4.06804	10.18
propene		
1-OH, 2-O_2	3.95860	9.43
2-OH, 1-O_2	4.05226	10.07
1-butene		
1-OH, 2-O_2	3.92736	9.23
2-OH, 1-O_2	4.03920	9.98
2-butene		
2-OH, 3-O_2	3.98102	9.58
2-methylpropene		
1-OH, 2-O_2	3.89552	9.03
2-OH, 1-O_2	4.03890	9.98
1,3-butadiene		
1-OH, 2-O_2	4.04310	10.01
2-OH, 1-O_2	4.11158	10.50
1-OH, 4-O_2	3.81634	8.54
isoprene		
1-OH, 2-O_2	3.96540	9.48
2-OH, 1-O_2	4.08320	10.29
3-OH, 4-O_2	4.09443	10.37
4-OH, 3-O_2	4.02967	9.91
1-OH, 4-O_2	3.72981	8.04
4-OH, 1-O_2	3.76219	8.22

TABLE 3: Semiempirical Model Results for the NO Reaction with Chloroalkylperoxy Radical Isomers

isomer	$-E_{\mathrm{SOMO}}$ [ROB3LYP/6-311+G(2d,p)// B3LYP/6-31G(d,p)] (eV)	k (10^{-12} cm^3 molecule^{-1} s^{-1})
ethene		
1-Cl, 2-O_2	4.07457	10.23
propene		
1-Cl, 2-O_2	3.93938	9.31
2-Cl, 1-O_2	4.05525	10.09
1-butene		
1-Cl, 2-O_2	3.96028	9.44
2-Cl, 1-O_2	3.99920	9.70
2-butene		
2-Cl, 3-O_2	3.94477	9.34
2-methylpropene		
1-Cl, 2-O_2	3.90390	9.08
2-Cl, 1-O_2	3.97797	9.56
1,3-butadiene		
1-Cl, 2-O_2	3.95050	9.38
2-Cl, 1-O_2	4.21525	11.28
1-Cl, 4-O_2	3.89062	9.00
isoprene		
1-Cl, 2-O_2	3.89000	8.99
2-Cl, 1-O_2	3.96460	9.47
3-Cl, 4-O_2	4.28165	11.82
4-Cl, 3-O_2	3.63729	7.54
1-Cl, 4-O_2	3.72137	7.99
4-Cl, 1-O_2	3.89060	8.99

On the other hand, the calculated NO rate constants predicted for alkylperoxy radicals derived from the dialkenes 1,3-butadiene and isoprene show a much more interesting dependence on the specific functional group and isomeric form. In particular, the NO rate constants for the chloroalkylperoxy radicals derived from 1,3-butadiene and isoprene show a much larger range of values depending on the specific isomer. More specifically, the KT model predicts that the 3-Cl, 4-O_2 alkylperoxy radical derived from isoprene will have an NO rate constant that is 57% larger than the 4-Cl, 3-O_2 alkylperoxy radical, with the values for the other four isomers falling between these values. Therefore, one possible explanation for the present experimental result of the NO rate constants for chloroalkylperoxy radicals derived from 1,3-butadiene and isoprene being significantly larger is that the dominant isomers for these systems are more reactive with NO than the dominant isomers for the monoalkene systems and all hydroxyalkylperoxy systems. In other words, the experimentally larger NO rate constant for the chloroalkyperoxy radicals derived from isoprene could be explained if the 3-Cl, 4-O_2 isomer were a dominant one. However, this is not what would be expected from simple radical stabilization considerations: the 4-Cl, 3-O_2 isomer would be expected to be more abundant because the 4-Cl adduct precursor resulting from the initial reaction of Cl with isoprene would be expected to be more stable as a result of the radical being centered on a secondary carbon; thus the 4-Cl adduct would be expected to have a longer lifetime than the 3-Cl adduct and would therefore be expected to go on to preferentially produce (via reaction with O_2) the 4-Cl, 3-O_2 isomer. The canonical variational transition state theory calculations of Lei et al. bear out this simple expectation: the 4-Cl, 3-O_2 isomer is predicted to make up 30% of the total chloroalkylperoxy radicals derived from the Cl-initiated oxidation of isoprene, whereas the 3-Cl, 4-O_2 isomer is only predicted to make up 8% of the total.[31] Indeed, if the 4-Cl, 3-O_2 isomer is dominant, the KT model predicts that the NO rate constant for the chloroalkylperoxy reaction should be lower than that for the hydroxyalkylperoxy reaction. Of course, the KT model is a crude method that basically attempts to model how transition state energies might depend on the identity of the alkyl group. Isomer-specific rate constants are also likely to depend on the nature of the transition state (e.g., tight or loose), which is not even approximately represented in the KT model. However, the KT model suggests the possibility that the larger NO rate constants experimentally determined in the present work for chloroalkylperoxy radicals derived from dialkenes might be due to isomer-specific effects that are more enhanced for the chloroalkylperoxy radicals than for the analogous hydroxyalkylperoxy radicals.

Conclusions

The overall rate constants of the NO reaction with chloroalkylperoxy radicals derived from the Cl-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 for the first time via the TF technique and pseudo-first-order kinetics conditions with high-pressure CIMS for the direct detection of chloroalkylperoxy radical reactants. The individual 100 Torr, 298 K rate constants for each monoalkene system were found to be identical within the 95% confidence interval associated with each separate measurement, whereas the corresponding rate constants for 1,3-butadiene and isoprene were both ~20% higher than the monoalkene mean value. The rate constant values are statistically indistinguishable from the NO rate constants determined previously in our lab for hydroxyalkylperoxy radicals derived from the same set of mono- and dialkenes.[18] To investigate the increased NO reactivity of the chloroalkylperoxy radicals derived from the dialkenes 1,3-butadiene and isoprene, isomer-specific semi-empirical calculations were carried out using the model of King and Thompson.[19] Although the predicted rate constants and the expected isomeric distribution of species do not appear to explain the present experimental results, the calculations indicate that the isomer-specific rate constants for the NO reaction of chloroalkylperoxy radicals derived from 1,3-butadiene and isoprene vary significantly more than those for the hydroxyalkylperoxy species.

The present results for the NO rate constants for chloroalkylperoxy radicals derived from monoalkenes support the simplification that many atmospheric models employ: all $RO_2 + NO$ reactions are modeled via the same rate constant value ($\sim 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). However, the faster NO rate constant determined in the present work for chloroalkylperoxy radicals derived from isoprene suggests more efficient tropospheric ozone production by isoprene for atmospheric conditions in which Cl-initated oxidation is competitive with OH-initiation.

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