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ABSTRACT. Chlorine atoms may be important in the marine boundary layer at mid-latitudes at dawn. The rate constants for chlorine atom reactions with organic compounds are typically about one or two orders of magnitude larger than the corresponding OH reactions. Given the high ozone-forming potential of alkenes, understanding their oxidation paths in coastal areas is important. Using the relative rate technique, the kinetics of the gas phase reactions of atomic chlorine with a series of alkenes, relative to heptane, have been investigated at (298 ± 3) K and 1 atmosphere in synthetic air and nitrogen. Using 3.97×10^{-10} cm³ molecule⁻¹ s⁻¹ as the rate constant for the reaction of chlorine atoms with *n*-heptane, the rate constants, *k* (in units of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) for the following alkenes were determined: propene (2.64 ± 0.21); isobutene (3.40 ± 0.28); 1-butene (3.38 ± 0.48); *cis*-2-butene (3.76 ± 0.84); *trans*-2-butene (3.31 ± 0.47); 2-methyl-1-butene (3.58 ± 0.40); 2-methyl-2-butene (3.95 ± 0.32); 3-methyl-1-butene (3.29 ± 0.36); 2-ethyl-1-butene (3.89 ± 0.41); 1-pentene (3.97 ± 0.36); 3-methyl-1-pentene (3.85 ± 0.35); and *cis*-4-methyl-2-pentene (4.11 ± 0.55). Cl atom reactions with alkenes mainly occurred through the addition to the double bond. From the known rate constant for alkyl hydrogen abstraction, the rate constant of chlorine atom addition to the double bond and that for the abstraction of the allylic hydrogen atoms can be calculated. The rate constant for the allylic hydrogen abstraction is showing to be surprisingly small. The atmospheric implications will be discussed.

1. INTRODUCTION

Chlorine atom precursors have been observed in the marine boundary layer and in the Arctic at polar sunrise [Keene *et al.*, 1993; Pszenny *et al.*, 1993; Impey *et al.*, 1997a; Impey *et al.*, 1997b; Spicer *et al.*, 1998; Impey *et al.*, 1999]. Although the mechanisms of their formation are not well understood, these chlorine species will photolyzed at sunrise to generate Cl atoms at concentrations estimated to be on the order of 10⁵ atoms cm⁻³ [Keene *et al.*, 1990; Keene *et al.*, 1993; Pszenny *et al.*, 1993; Keene, 1995; Wingenter *et al.*, 1996; Spicer *et al.*, 1998; Wingenter *et al.*, 1999a; Wingenter *et al.*, 1999b]. Since the rate constants for Cl atom reactions with organic compounds are fast, Cl atoms could be the most important oxidant in the

marine boundary layer at dawn when the OH concentration is small.

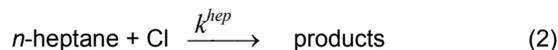
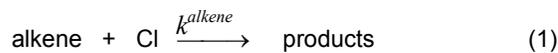
Cl atom reactions with alkanes have been studied by several research groups and the structure-reactivity relationships for these alkane reactions were established [Atkinson and Aschmann, 1985; Senkan and Quam, 1992; Aschmann and Atkinson, 1995; Atkinson, 1997; Tyndall *et al.*, 1997]. Although Cl-alkene reactions have higher ozone-forming potential than Cl-alkane reactions, Cl atom reactions with alkenes are not as thoroughly studied.

We report here relative rate studies of the reactions of chlorine atoms with a series of alkenes at 1 atm pressure and 298 K. The rate constants were used to establish structure-reactivity relationship for Cl-alkene reactions.

2. EXPERIMENTAL

Rate constants for the Cl-alkene reactions were measured using a relative rate technique. A mixture of the alkene and *n*-heptane, used as a reference compound, was introduced into a 50 L collapsible Teflon reaction chamber. Molecular chlorine was also added and then photolyzed using a set of blacklamps to generate chlorine atoms. With the lamps off, the reactant mixture was withdrawn into a sampling loop and injected onto the head of a GC column. The decays of reactants were followed with time using GC-FID (Hewlett Packard Model 5890 and Series II).

The alkene and *n*-heptane react simultaneously with chlorine atoms:



As described in detail elsewhere [Atkinson and Aschmann, 1985; Aschmann and Atkinson, 1995; Finlayson-Pitts and Pitts, 2000; Ezell *et al.*, 2002], the relative rate constant, $k^{\text{alkene}}/k^{\text{hep}}$, can be obtained using equation (I)

$$\ln\{[\text{alkene}]_0/[\text{alkene}]_t\} = (k^{\text{alkene}}/k^{\text{hep}}) \ln\{[\text{hep}]_0/[\text{hep}]_t\} \quad (I)$$

where $[\text{alkene}]_0$ and $[\text{hep}]_0$ are the initial concentrations of alkene and *n*-heptane, respectively, and $[\text{alkene}]_t$ and $[\text{hep}]_t$ are their concentrations at time *t*. The absolute rate constant was then calculated using this relative rate and the known rate constant of Cl-heptane reaction [Ezell *et al.*, 2002].

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Table 1. Rate Constants for the Reactions of Chlorine Atoms with Some Alkenes at 298 K and 1 Atm Pressure from This and Previous Studies^a

| Alkene | This Study ^b ($\pm 2s$) | Literature Values | Reference |
|--------------------------------|--------------------------------------|-----------------------------|---------------------------------|
| Propene | 2.64 \pm 0.21 | 2.7 \pm 0.09 ^c | Atkinson and Aschmann, 1985 |
| | | 3.1 \pm 0.1 ^c | Wallington <i>et al.</i> , 1988 |
| | | 2.5 \pm 0.4 | Kaiser and Wallington, 1996 |
| | | 2.3 \pm 0.3 | Stutz <i>et al.</i> , 1998 |
| | | 2.8 \pm 0.06 | Coquet and Ariya, 2000 |
| 1-butene | 3.38 \pm 0.48 | 2.2 \pm 0.3 | Stutz <i>et al.</i> , 1998] |
| | | 3.52 \pm 0.07 | Coquet and Ariya, 2000 |
| Isobutene | 3.40 \pm 0.28 | | |
| <i>trans</i> -2-butene | 3.31 \pm 0.47 | 3.4 \pm 0.7 ^d | Ullerstam <i>et al.</i> , 2001 |
| <i>cis</i> -2-butene | 3.76 \pm 0.84 | | |
| 2-methyl-2-butene | 3.95 \pm 0.32 | | |
| 3-methyl-1-butene | 3.29 \pm 0.36 | | |
| 2-methyl-1-butene | 3.58 \pm 0.40 | | |
| 2-ethyl-1-butene | 3.89 \pm 0.41 | | |
| 1-pentene | 3.97 \pm 0.36 | 4.93 \pm 0.08 | Coquet and Ariya, 2000 |
| <i>cis</i> -4-methyl-2-pentene | 4.11 \pm 0.55 | | |
| 3-methyl-1-pentene | 3.85 \pm 0.35 | | |

^a Units of rate constants are $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b The rate constant used for Cl + *n*-heptane is that measured in this study, $(3.97 \pm 0.27) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2s). The error cited includes the 7% error in the heptane/butane relative rate measurements but not the error in the absolute value for the *n*-heptane rate constant that is due to the uncertainty in the absolute rate constant for the *n*-butane reaction.

^c Corrected to a reference rate constant for Cl + *n*-butane of $2.18 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^d Corrected to a reference rate constant for Cl + C₃H₆ of $2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3. RESULTS AND DISCUSSION

The rate constants for the reactions of Cl atoms with alkenes are summarized in Table 1. As expected, all of the reactions are of the order of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, approaching the collision-controlled limit. Literature values are also summarized in Table 1.

Previous studies of the reactions of alkanes with chlorine atoms showed that the total rate constant can be expressed as the sum of the reactions of chlorine atoms with different alkyl groups in an alkane and structure-reactivity relationships have been developed for alkane reactions [Senkan and Quam, 1992; Atkinson, 1997; Tyndall *et al.*, 1997]. The reactions of chlorine atoms with alkenes proceed mainly by addition to the double bond, with smaller contributions from the abstractions of allylic hydrogen atoms and alkyl hydrogen atoms remote to the double bond. Thus, the overall rate constant for Cl-alkene reactions can be expressed as:

$$k^{\text{overall}} = k^{\text{alkyl}} + k^{\text{add}} + k^{\text{allyl}} \quad (\text{II})$$

We assumed that k^{alkyl} was the same as in the alkane reactions and was calculated using the result from the structure-reactivity relationships for alkane reactions.

The rate constant for addition to the double bond, k^{add} , may vary from alkene to alkene. We treat the addition paths separately for each alkene depending on the intermediate radicals formed. Table 2 shows the addition parameters used for the alkenes in this study. For example, $k^{\text{add}(2^{\circ},1^{\circ})}$ was used for addition leading to combination of a primary and a secondary radical in the case of 1-butene; $k^{\text{add}(2^{\circ},2^{\circ})}$ was used for addition leading to two equivalent secondary radicals in the case of *cis*- or *trans*-2-butene; etc.

Three different parameters, $k^{\text{allyl}(1^{\circ})}$, $k^{\text{allyl}(2^{\circ})}$ and $k^{\text{allyl}(3^{\circ})}$, were used for abstractions of allylic hydrogens depending on whether the allylic hydrogen is primary, secondary, or tertiary.

The overall rate constants for the 11 alkenes measured in this study were first calculated using equation (II), the literature values for k^{alkyl} and the initial values assumed for k^{allyl} and k^{add} . The difference between the measured and calculated values was then minimized by varying k^{allyl} and k^{add} to minimize the sum of the squares of these differences. Table 2 shows the best fit values obtained for k^{add} and k^{allyl} when using the rate constants for alkyl abstraction from Atkinson *et al.* [1997]. The use of values for alkyl abstraction from

Senkan and Quam [1992] and Tyndall *et al.* [1997] yield similar results for k^{add} and k^{allyl} [Ezell *et al.*, 2002].

The addition rate constant for alkenes with more than four carbons are, as expected, in the vicinity of $2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the high pressure limit for addition to propene. The contribution from allylic hydrogen abstraction is smaller than expected. This is probably due to the fact that the net abstraction may

proceed in part or all by addition-elimination as is the case for isoprene, for example [Ragains and Finlayson-Pitts, 1997]. Another possibility is that the C-H bond might be disturbed by interaction with the neighboring double bond to form a delocalized orbital. This results in favored Cl atom addition to the double bond and diminished reactivity toward abstraction [Ezell *et al.*, 2002].

Table 2. Best Fit Values

| Parameters for Applicable Alkenes | Rate Constants ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) |
|--|--|
| $k^{add(2^\circ,1^\circ)}$ for 1-butene, 1-pentene, 3-methyl-1-butene, 3-methyl-1-pentene | 2.60 |
| $k^{add(2^\circ,2^\circ)}$ for <i>cis</i> - and <i>trans</i> -2-butene, <i>cis</i> -4-methyl-2-pentene | 2.98 |
| $k^{add(3^\circ,1^\circ)}$ for isobutene, 2-methyl-1-butene, 2-ethyl-1-butene | 2.64 |
| $k^{add(3^\circ,2^\circ)}$ for 2-methyl-2-butene | 2.93 |
| $k^{allyl(1^\circ)}$ | 0.34 |
| $k^{allyl(2^\circ)}$ | 0.37 |
| $k^{allyl(3^\circ)}$ | 0.11 |

Table 3. Calculated Contributions for Addition and Abstraction for Reaction of Chlorine Atoms with Simple Alkenes and Comparison to Measured Rate Constants^a

| Alkene | k^{add} | k^{allyl} | $k^{alkyl\ b}$ | $k^{calculated}$ | $k^{measured}$ | % Difference $\frac{ k^{calculated} - k^{measured} }{k^{measured}}$ |
|--------------------|------------------|-------------|----------------|------------------|----------------|--|
| Propene | 2.3 ^c | 0.34 | | 2.64 | 2.64 | 0.0% |
| 1-butene | 2.60 | 0.37 | 0.28 | 3.25 | 3.38 | 3.8% |
| 1-pentene | 2.60 | 0.37 | 1.01 | 3.98 | 3.97 | 0.3% |
| 3-methyl-1-butene | 2.60 | 0.11 | 0.55 | 3.26 | 3.29 | 0.9% |
| 3-methyl-1-pentene | 2.60 | 0.11 | 1.29 | 4.00 | 3.85 | 3.9% |
| Isobutene | 2.64 | 2(0.34) | | 3.32 | 3.40 | 2.4% |
| 2-methyl-1-butene | 2.64 | 0.34 + 0.37 | 0.28 | 3.62 | 3.58 | 1.1% |
| 2-ethyl-1-butene | 2.64 | 2(0.37) | 0.55 | 3.93 | 3.89 | 1.0% |
| 2-methyl-2-butene | 2.93 | 3(0.34) | | 3.95 | 3.95 | 0.0% |
| 2-butene | 2.98 | 2(0.34) | | 3.66 | 3.54 | 3.4% |
| 4-methyl-2-pentene | 2.98 | 0.34 + 0.11 | 0.55 | 3.98 | 4.11 | 3.2% |

^a Units of rate constants are $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b The rate constants for alkyl abstraction, k^{alkyl} , are from Atkinson *et al.* [1997].

^c From Kaiser & Wallington [1996].

Table 3 summarizes the rate constants calculated using the values of k^{add} and k^{allyl} from Table 2 and the values of k^{alkyl} from Atkinson *et al.* [1997]. Similar results were obtained [Ezell *et al.*, 2002] when using the values of alkyl abstraction from Senkan and Quam [1992] and Tyndall *et al.* [1997]. The average difference between the measured and calculated rate constants is 2%.

4. ATMOSPHERIC IMPLICATIONS

The reactions of chlorine atoms with alkenes are all very fast. Using concentrations of $1 \times 10^5 \text{ cm}^{-3}$, typical of early morning hours for both Cl and OH, the lifetimes of these alkenes with respect to reaction with chlorine atoms is about an order of magnitude shorter than those with respect to reaction with OH. Therefore, the major loss process of the simple alkenes in the early morning will be due to their reactions with chlorine atoms, generated by the photolysis of photolyzable chlorine species.

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