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# Kinetics of reactions of chlorine atoms with a series of alkenes at 1 atm and 298 K: structure and reactivity

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Chlorine atoms are important oxidants at dawn in the marine boundary layer where a variety of organics are also present, including alkenes. Using the relative rate technique, the kinetics of the gas phase reactions of atomic chlorine with a series of alkenes, relative to *n*-heptane as a reference, have been investigated at (298 ± 3) K and 1 atmosphere in either synthetic air or nitrogen. The rate constant for *n*-heptane, relative to *n*-butane whose rate constant was taken to be  $2.18 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , was also measured and found to be  $(3.97 \pm 0.27) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (2s). Based on this value for the *n*-heptane reaction, the following absolute values for the rate constants, *k* (in units of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the chlorine atom reactions were determined: propene,  $2.64 \pm 0.21$ ; isobutene,  $3.40 \pm 0.28$ ; 1-butene,  $3.38 \pm 0.48$ ; *cis*-2-butene,  $3.76 \pm 0.84$ ; *trans*-2-butene,  $3.31 \pm 0.47$ ; 2-methyl-1-butene,  $3.58 \pm 0.40$ ; 2-methyl-2-butene,  $3.95 \pm 0.32$ ; 3-methyl-1-butene,  $3.29 \pm 0.36$ ; 2-ethyl-1-butene,  $3.89 \pm 0.41$ ; 1-pentene,  $3.97 \pm 0.36$ ; 3-methyl-1-pentene,  $3.85 \pm 0.35$ ; and *cis*-4-methyl-2-pentene,  $4.11 \pm 0.55$  (±2s). The errors reflect those in our relative rate measurements but do not include the 10% error in the absolute value of the *n*-butane rate constant upon which these rate constants are ultimately based. A structure–reactivity scheme is presented that assumes that rate constants for addition of chlorine atoms to the double bond, as well as that for abstraction of an allylic hydrogen atom, depend upon the degree of alkyl substitution at the double bond and allylic carbons. The surprising result is that the allylic hydrogen atoms react less rapidly with chlorine atoms than the analogous alkyl hydrogens in alkanes. The atmospheric implications for loss of alkenes in the marine boundary layer are discussed.

## Introduction

Organic compounds released into the atmosphere react with oxidants, such as OH, O<sub>3</sub>, NO<sub>3</sub> and in coastal areas, chlorine atoms, leading to the formation of O<sub>3</sub>. While the OH radical is generally considered to be the major daytime oxidant, chlorine atoms may be important in the marine boundary layer at mid-latitudes at dawn.<sup>1–18</sup> Although average chlorine atom concentrations throughout the global troposphere<sup>19,20</sup> are calculated to be small,  $<10^3 \text{ atoms cm}^{-3}$ , their concentrations for a brief period at dawn in the marine boundary layer are estimated to be significantly larger, as high as  $10^5 \text{ atoms cm}^{-3}$  or more.<sup>4–8,12,14,15</sup> Since 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, even these relatively small chlorine atom concentrations can compete with the OH radicals in determining the fate of organics in the early morning.

Rate constants for the reaction of chlorine atoms with a variety of alkanes have been measured.<sup>21</sup> These reactions proceed by simple hydrogen abstraction, and structure–reactivity relationships<sup>21–25</sup> have been developed that can be used to predict the rate constant for the reaction of alkanes with chlorine atoms. These relationships are based on the premise that the total rate constant can be expressed as the sum of abstraction of hydrogen atoms from primary RCH<sub>3</sub> groups ( $k^{1^\circ}$ ), from secondary R<sub>2</sub>CH<sub>2</sub> groups ( $k^{2^\circ}$ ) and from tertiary R<sub>3</sub>CH groups ( $k^{3^\circ}$ ). These group rate constants are adjusted to take into account neighboring group effects; these close neighbor effects are represented by *F*(*X*) for the single group attached to a primary CH<sub>3</sub>, *F*(*X*) and *F*(*Y*) for the two groups attached to

a secondary CH<sub>2</sub> and *F*(*X*), *F*(*Y*) and *F*(*Z*) for the three groups attached to a tertiary CH group. The overall rate constant is given by eqn. (1):

$$k^{\text{alkyl}} = \sum [k^{\text{alkyl}(1^\circ)} F(X) + k^{\text{alkyl}(2^\circ)} F(X)F(Y) + k^{\text{alkyl}(3^\circ)} F(X)F(Y)F(Z)] \quad (1)$$

Table 1 summarizes some of the values proposed for the group rate constants and the neighboring *F* factors.

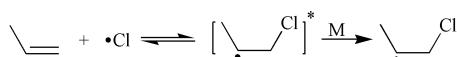
**Table 1** Some group rate constants and the neighboring group factors for the reaction of chlorine atoms with alkanes at 298 K

Group	<i>k</i> ( $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	<i>F</i>	Reference
Primary (RCH <sub>3</sub> )	3.5	1.00	Atkinson <sup>21</sup>
	2.91 <sup>a</sup>	1.00	Tyndall <i>et al.</i> <sup>25</sup>
	3.0	1.00	Senkan and Quam <sup>23</sup>
Secondary (R <sub>2</sub> CH <sub>2</sub> )	9.3	0.79	Atkinson <sup>21</sup>
	9.14	0.80	Tyndall <i>et al.</i> <sup>25</sup>
	5.5	1.02	Senkan and Quam <sup>23</sup>
Tertiary (R <sub>3</sub> CH)	6.8	0.79	Atkinson <sup>21</sup>
	6.53	0.80	Tyndall <i>et al.</i> <sup>25</sup>
	3.5	1.33	Senkan and Quam <sup>23</sup>
(R <sub>4</sub> C)		0.79	Atkinson <sup>21</sup>
		0.80	Tyndall <i>et al.</i> <sup>25</sup>
		0.91	Senkan and Quam <sup>23</sup>

<sup>a</sup> Fit obtained assuming all *F* factors that can influence a primary methyl group are 1.0.

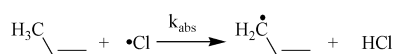
While the kinetics and mechanisms of reaction of chlorine atoms with alkanes are reasonably well understood, those for reaction with alkenes are not as thoroughly studied. Given the higher ozone-forming potential<sup>17</sup> of alkenes compared to alkanes, for example, understanding their oxidation paths in coastal areas is important.

The kinetics of the chlorine atom reactions under various conditions of temperature and pressure with simple alkenes such as ethene, propene, 1-butene, *trans*-2-butene, and 1-pentene<sup>17,21,22,26–49</sup> and with some dienes<sup>50–60</sup> have been reported. The reaction proceeds primarily by reversible addition to the double bond; at sufficiently high pressures, the chlorine–alkene adduct is stabilized as a chlorinated alkyl radical, for example in the case of propene:

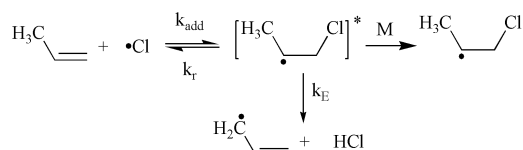


The abstraction of a hydrogen atom from side-chains, particularly of the weaker allylic hydrogen, also occurs through two different mechanisms: direct abstraction, and addition–elimination.<sup>41,51</sup>

Direct abstraction:



Addition–elimination:



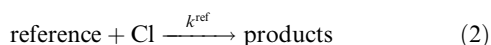
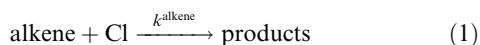
The products of the addition–elimination reaction are identical to those for direct abstraction.

The goal of the present study was to measure the room temperature rate constants for the reactions of chlorine atoms with a series of alkenes of different structures at 1 atm pressure and 298 K. These data are useful for assessing the importance of this reaction for alkene oxidation in coastal marine areas, and for probing structure reactivity relationships for these reactions.

## Experimental

Rate constants were measured at room temperature (298 ± 3) K and 1 atm in air or N<sub>2</sub> using a relative rate technique. A mixture of the alkene and a reference compound, where the rate constant for reaction with Cl atoms is known, was introduced into a 50 L collapsible Teflon reaction chamber. Chlorine atoms were generated by photolysis of molecular chlorine. A GC-FID was used to follow the loss of both alkene and the reference compound as their reactions with Cl atoms proceed.

The alkene and the reference compound react simultaneously with chlorine atoms:



As described in detail elsewhere,<sup>17,22,24</sup> the simultaneous decay of the alkene and the reference compound from their initial concentrations at time  $t = 0$ , [alkene]<sub>0</sub> and [ref]<sub>0</sub>, to [alkene]<sub>*t*</sub> and [ref]<sub>*t*</sub> at time  $t$  is given by eqn. (II):

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

Thus, a plot of  $\{\ln[\text{alkene}]_0/[\text{alkene}]_t\}$  vs.  $\{\ln[\text{ref}]_0/[\text{ref}]_t\}$  should be linear through the origin with a slope equal to the ratio of rate constants  $k^{\text{alkene}}/k^{\text{ref}}$ . The data were analyzed

taking into account errors in both the alkene and reference compound as described in detail elsewhere.<sup>61</sup> We report the errors as two standard deviations, defined as  $s = \{\sum_i(x_i - x_{\text{av}})^2/(N - 1)\}^{1/2}$  where  $x_i$  and  $x_{\text{av}}$  are the individual and average values of the rate constant ratios respectively, and  $N$  is the total number of measurements made of that ratio. We use  $s$ , the standard deviation for a sample population, because of the limited number of measurements; this measure of the precision of the data is larger than  $\sigma$ , the standard deviation of the entire population.

*n*-Heptane was used as the reference compound since its rate constant<sup>21</sup> for reaction with atomic chlorine is similar in magnitude to those for the alkene reactions and it simplified the chromatography, having a longer retention time than any of the alkenes. Measurements of the relative rate of the atomic chlorine reaction with *n*-heptane using *n*-butane as a reference were performed in order to provide a consistent set of rate constants traceable to the *n*-butane absolute rate constant that is well established.<sup>21</sup>

Concentrations used in these experiments were in the range of (0.3–14) × 10<sup>14</sup> molecules cm<sup>-3</sup> (1–57 ppm) for the alkenes, (0.3–14) × 10<sup>14</sup> molecules cm<sup>-3</sup> (1–57 ppm) for *n*-heptane, and (0.3–17) × 10<sup>14</sup> molecules cm<sup>-3</sup> (1–69 ppm) for Cl<sub>2</sub>. Molecular chlorine was added to generate chlorine atoms and was photolyzed using a set of blacklamps (Sylvania 350, 20 W, F20T12/350BL) surrounding the reaction chambers. These lamps provide radiation in the 300–450 nm range with a maximum intensity at ~360 nm, providing a good overlap with the Cl<sub>2</sub> absorption spectrum. Photolysis was carried out in increments such that ~5–8% of the organics reacted during each photolysis period. The lamps were turned off to stop the reaction during sampling. Six incremental photolysis periods were typically used, giving total losses of the organics of approximately 30–50%.

The reactant mixture was withdrawn from the collapsible chambers by pumping slowly through the sampling loop of a gas-sampling valve (Valco Instruments or Carle Gas). The sampling loop pressure was then allowed to equilibrate to 1 atm with the reaction chamber prior to injection onto the column. The reactants were followed with time using GC-FID (Hewlett Packard Model 5890 and Series II). Two different GC columns were used, an SPB-1 column (Supelco, 60 m × 0.53 mm) and a GS-Q column (J&W Scientific, 30 m × 0.32 mm).

The mixture was first sampled in the dark to test for potential losses of the alkene or reference compound by a dark reaction with Cl<sub>2</sub>, as has been observed at higher reactant concentrations in earlier studies of the isoprene reaction.<sup>51</sup> No dark reactions were observed for the alkenes reported here. However, a dark reaction was observed for 2,3-dimethyl-2-butene, even at concentrations down to ~0.5 ppm, and hence studies of this compound could not be carried out. These dark runs were also used to obtain an estimate of the precision associated with the measurements for use in the error analysis;<sup>61</sup> one standard deviation of these replicate measurements was typically less than 5%. Experiments were also carried out with the individual alkene or *n*-heptane alone with Cl<sub>2</sub> under photolysis to ensure that the reactions did not produce species with the same retention times as the reactant peaks.

Simple averages of the runs in each diluent gas were used to obtain rate constant ratios in air and nitrogen. No significant differences were observed between the results using N<sub>2</sub> or air. The overall rate constant was calculated as a simple average of all of the runs in N<sub>2</sub> and air.

**Chemicals.** The chemicals used were as follows: *n*-heptane (EM Science, 99.67%); propene (Aldrich, 99+%); 1-butene (Matheson, CP Grade); isobutene (Matheson, CP Grade); *trans*-2-butene (Matheson, CP Grade); *cis*-2-butene

(Matheson, CP Grade); 2-methyl-2-butene (Aldrich, 99+%); 3-methyl-1-butene (Aldrich, 95%); 2-methyl-1-butene (Aldrich, 96%); 2-ethyl-1-butene (Aldrich, 98%); 3-methyl-1-pentene (Aldrich, 99%); *cis*-4-methyl-2-pentene (Aldrich, 95%); *n*-butane (Matheson, Research Grade, 99.99%); N<sub>2</sub> (Oxygen Service Company, Ultrahigh Purity, 99.999%); air (Oxygen Service Company, Ultrahigh Purity). The gases were used as received. Liquid organics were subjected to several freeze-pump-thaw cycles prior to vaporization and storage in a 5 L bulb for use.

## Results and discussion

### Measurement of rate constant for the reference compound, *n*-heptane

There have been two previous measurements of the rate constant for the reaction of chlorine atoms with *n*-heptane, both relative to *n*-butane. Hooshiyar and Niki<sup>62</sup> reported a value relative to *n*-butane of  $1.88 \pm 0.03$ , while Aschmann and Atkinson<sup>24</sup> measured a ratio of  $1.73 \pm 0.06$ . The recommended<sup>21</sup> absolute rate constant,  $3.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is an average of these two studies. The rate constant for the reaction of chlorine atoms with *n*-heptane measured in the present studies,  $(3.97 \pm 0.27) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is in excellent agreement with the average of these previous studies. (The error represents two standard deviations of the relative rate constants and does not include an estimated 10% error in the absolute rate constant for *n*-butane). Our measured rate constant for *n*-heptane was then used to calculate the absolute rate constants for the series of alkenes.

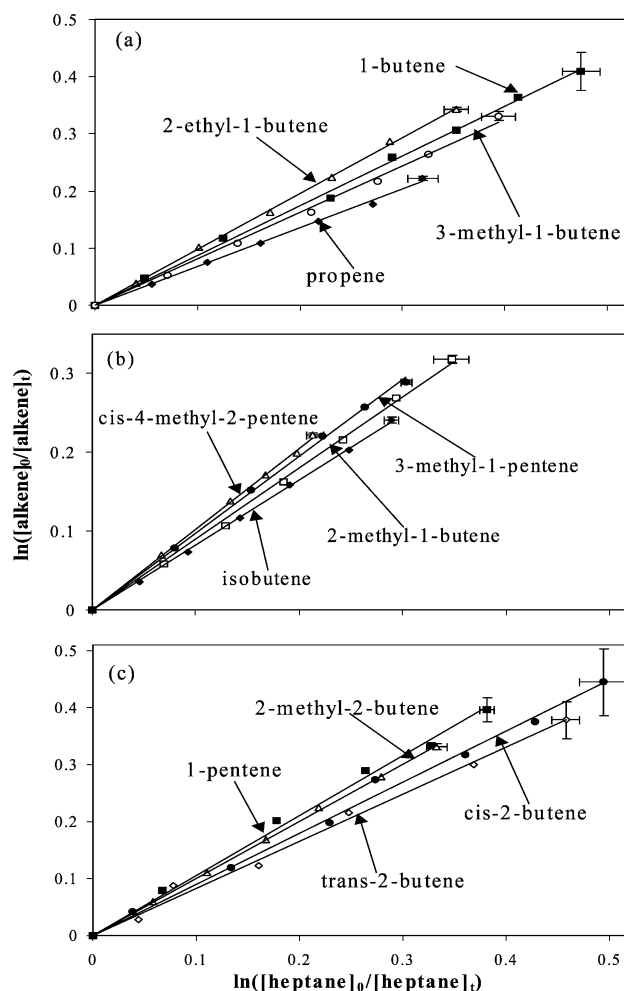
### Rate constants for the alkene reactions

Fig. 1 shows typical data for the reactions of chlorine atoms with the alkenes relative to *n*-heptane. The rate constants are summarized in Table 2, which also gives previously measured values in the few cases where they are available. As expected, all of the reactions are fast, approaching the collision-controlled limit.

Our rate constants for propene and *trans*-2-butene are in excellent agreement with previous measurements when the latter are adjusted to the same absolute rate constants for the reference compounds used in those studies.<sup>22,34,41,45,48,49</sup> For 1-butene, our value of  $(3.38 \pm 0.48) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is in excellent agreement with that reported by Coquet and Ariya,<sup>48</sup> but not with the previous study of Stutz *et al.*, conducted in this laboratory.<sup>45</sup> The reason for the latter discrepancy is not clear, particularly since the rate constants measured for other compounds in that study agree with the present values. However, the rate constant for the 1-butene reaction is expected to be at least as large as that for the propene reaction and hence the value reported in the present studies is preferred. Our rate constant for 1-pentene  $(3.97 \pm 0.36) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is 18% lower than that reported by Coquet and Ariya,<sup>48</sup> but is still within experimental error of their value when the error in the rate constant for their reference compound is included.

There do not appear to be previous measurements of the rate constant for the reaction of Cl atoms with *cis*-2-butene. Our studies show that the rate constant for *cis*-2-butene is slightly (14%) larger than that for the *trans*-isomer (although the error bars for the two rate constants overlap). However, because additional data for a series of *cis/trans* pairs are not available to characterize the differences quantitatively, we have used an average value for the rate constant for the 2-butene isomers in the structure–reactivity scheme discussed below.

**Structure–reactivity relationships.** As discussed above, a structure–reactivity relationship expressed in eqn. (I) for the



**Fig. 1** Typical kinetics plots for loss of the alkenes and *n*-heptane (reference compound) according to eqn. (II). The 2 $\sigma$  errors, calculated as described elsewhere,<sup>61</sup> are shown for representative data points.

reaction of atomic chlorine with alkanes has been developed. We use experimental results for propene to suggest how this relationship may be extended to the larger alkenes by considering the overall rate constants as the sum of those for different reaction sites in the molecule.

Propene reacts with atomic chlorine mainly by addition, with a smaller contribution from what appears as abstraction of an allylic hydrogen atom.<sup>41</sup> The addition rate constant at 1 atm pressure and 298 K, is  $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , based on the high- and low-pressure limiting rate constants measured by Kaiser and Wallington,<sup>41</sup>  $k_0 = 4.0 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $k_\infty = 2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Given that the total rate constant measured in this study at 1 atm is  $2.64 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Table 2), the contribution due to allylic abstraction must be only  $0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . As seen from Table 1, this is about the same as the contribution expected from abstraction of a methyl hydrogen atom of propane based on eqn. (I). Rate constants for abstraction often correlate with the bond energy of the bond being broken.<sup>63</sup> Since the bond-dissociation energy of the allyl H–CH<sub>2</sub>CH=CH<sub>2</sub> bond is so much smaller than that for the H–*n*C<sub>3</sub>H<sub>7</sub> (87 vs. 101 kcal mol<sup>-1</sup>), this result is surprising and supports the suggestion that a different mechanism than direct abstraction of allylic hydrogen atoms by chlorine may be important. Moreover, this small value indicates that allylic abstraction should be treated separately in any structure–reactivity scheme.

We therefore propose a structure–reactivity approach for atomic chlorine reactions with alkenes by considering the

**Table 2** Relative rate measurements for the reactions of chlorine atoms with some alkenes at 298 K and 1 atm pressure, the corresponding absolute values, and previous literature measurements

Alkene	Diluent gas (No. of runs)	$\frac{k^{\text{alkene}}}{k^{\text{ref}}}$ ( $\pm 2s$ ) <sup>a</sup>	Overall $\frac{k^{\text{alkene}}}{k^{\text{ref}}}$ ( $\pm 2s$ ) <sup>b</sup>	Absolute rate constant ( $\pm 2s$ ) ( $10^{-10} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$ ) <sup>c</sup>	Literature values ( $10^{-10} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$ )	Reference
Propene	N <sub>2</sub> (4)	0.664 $\pm$ 0.037	0.664 $\pm$ 0.027	2.64 $\pm$ 0.21	2.7 $\pm$ 0.09 <sup>d</sup>	22
	Air (3)	0.665 $\pm$ 0.010			3.1 $\pm$ 0.1 <sup>d</sup>	34
1-Butene	N <sub>2</sub> (8)	0.862 $\pm$ 0.022	0.853 $\pm$ 0.106	3.38 $\pm$ 0.48	2.5 $\pm$ 0.4	41
	Air (6)	0.840 $\pm$ 0.165			2.3 $\pm$ 0.3	45
Isobutene	N <sub>2</sub> (3)	0.870 $\pm$ 0.011	0.855 $\pm$ 0.038	3.40 $\pm$ 0.28	2.8 $\pm$ 0.06	48
	Air (3)	0.840 $\pm$ 0.030			2.2 $\pm$ 0.3	45
<i>trans</i> -2-Butene	N <sub>2</sub> (6)	0.823 $\pm$ 0.110	0.834 $\pm$ 0.102	3.31 $\pm$ 0.47	3.4 $\pm$ 0.7 <sup>e</sup>	49
	Air (2)	0.867 $\pm$ 0.029				
<i>cis</i> -2-Butene	N <sub>2</sub> (5)	1.02 $\pm$ 0.18	0.946 $\pm$ 0.203	3.76 $\pm$ 0.84		
	Air (5)	0.875 $\pm$ 0.092				
2-Methyl-2-butene	N <sub>2</sub> (3)	1.01 $\pm$ 0.02	0.996 $\pm$ 0.041	3.95 $\pm$ 0.32		
	Air (3)	0.981 $\pm$ 0.035				
3-Methyl-1-butene	N <sub>2</sub> (2)	0.811 $\pm$ 0.085	0.829 $\pm$ 0.071	3.29 $\pm$ 0.36		
	Air (2)	0.847 $\pm$ 0.053				
2-Methyl-1-butene	N <sub>2</sub> (3)	0.917 $\pm$ 0.094	0.903 $\pm$ 0.080	3.58 $\pm$ 0.40		
	Air (3)	0.889 $\pm$ 0.071				
2-Ethyl-1-butene	N <sub>2</sub> (3)	0.987 $\pm$ 0.119	0.979 $\pm$ 0.078	3.89 $\pm$ 0.41		
	Air (3)	0.970 $\pm$ 0.016				
1-Pentene	N <sub>2</sub> (4)	0.994 $\pm$ 0.026	1.000 $\pm$ 0.059	3.97 $\pm$ 0.36	4.93 $\pm$ 0.08	48
	Air (3)	1.008 $\pm$ 0.093				
<i>cis</i> -4-Methyl-2-pentene	N <sub>2</sub> (3)	1.042 $\pm$ 0.131	1.035 $\pm$ 0.119	4.11 $\pm$ 0.55		
	Air (3)	1.028 $\pm$ 0.132				
3-Methyl-1-pentene	N <sub>2</sub> (3)	0.976 $\pm$ 0.067	0.970 $\pm$ 0.058	3.85 $\pm$ 0.35		
	Air (3)	0.963 $\pm$ 0.059				

<sup>a</sup> As described in the text, this is the simple average of the runs in either N<sub>2</sub> or in air. <sup>b</sup> Simple average of all runs (N<sub>2</sub> and air). <sup>c</sup> The rate constant used for Cl + *n*-heptane is that measured in these studies,  $(3.97 \pm 0.27) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (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. <sup>d</sup> Corrected to a reference rate constant for Cl + *n*-butane of  $2.18 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>e</sup> Corrected to a reference rate constant for Cl + C<sub>3</sub>H<sub>6</sub> of  $2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

overall rate constant as the sum of three contributions: (1) hydrogen abstraction from alkyl groups remote from the double bond; (2) addition to the double bond, and (3) abstraction of allylic hydrogen atoms:

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

We first discuss each of these contributions separately and then apply a minimization technique to our measured rate constants to obtain the optimal values for  $k^{\text{add}}$  and  $k^{\text{allyl}}$ .

**Abstraction of alkyl hydrogen.** We assume the first term in eqn. (III), direct abstraction of a non-allylic hydrogen, may be calculated using eqn. (I). This seems reasonable since such hydrogen atoms are at least two carbons removed from the double bond and hence their reactivity should not be strongly influenced by the  $\pi$  bond. Because numerical values for  $k^{\text{alkyl}(1^\circ)}$ ,  $k^{\text{alkyl}(2^\circ)}$ ,  $k^{\text{alkyl}(3^\circ)}$  and  $F(X)$ ,  $F(Y)$ , and  $F(Z)$  for alkanes reported by various researchers vary substantially (Table 1), this contribution was calculated separately using each of the different sets of values for alkyl hydrogen abstraction shown in Table 1.

**Addition to the double bond.** The addition path for the Cl-propene reaction at a total pressure of 1 atm is close to, but not quite at, the high pressure limit of  $2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>41</sup> For the Cl atom reactions with larger alkenes ( $\geq C_4$ ), it is assumed the reactions at 1 atm pressure are at the

high pressure limit and the addition rate should be approximately  $2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, this value may vary from alkene to alkene, depending on the intermediate radicals formed. For example, the addition of atomic chlorine to propene produces either a secondary [ClCH<sub>2</sub>C $\cdot$ (H)-CH<sub>3</sub>] or a primary radical adduct [-CH<sub>2</sub>CHClCH<sub>3</sub>], but not with equal probability. Thus, the rate constant for addition of chlorine atoms to the double bond,  $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1 atm, represents a combination of addition leading to a primary radical,  $k^{\text{add}(1^\circ)}$  and addition leading to a secondary radical,  $k^{\text{add}(2^\circ)}$ . Addition of atomic chlorine to the other alkenes measured here would result in further possibilities: two equivalent secondary radicals in the case of *cis*- or *trans*-2-butene; tertiary and primary radicals in the case of isobutene; *etc.*

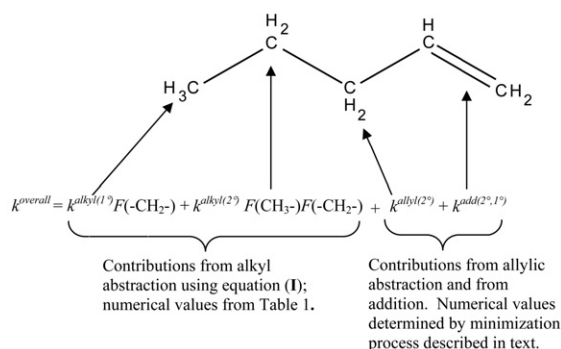
The following scheme considers possible addition rate constants and compounds to which they would apply:

*Addition leading to either a secondary or a primary radical.*  $k^{\text{add}(2^\circ, 1^\circ)}$  used for 1-butene, 1-pentene, 3-methyl-1-butene, and 3-methyl-1-pentene.

*Addition leading to two secondary radicals.*  $k^{\text{add}(2^\circ, 2^\circ)}$  used to describe *cis*- and *trans*-2-butene and *cis*-4-methyl-2-pentene.

*Addition leading to either a tertiary or a primary radical.*  $k^{\text{add}(3^\circ, 1^\circ)}$  used for isobutene, 2-methyl-1-butene, and 2-ethyl-1-butene.

*Addition leading to either a tertiary or a secondary radical.*  $k^{\text{add}(3^\circ, 2^\circ)}$  used for 2-methyl-2-butene.



**Fig. 2** Breakdown of overall rate constant for chlorine atom reaction with 1-pentene as an illustration of our structure–reactivity approach.

In our reactivity scheme, we treat each of these addition paths separately.

**Abstraction of allylic hydrogen.** The contribution from abstraction of allylic hydrogen,  $k^{\text{allyl}}$ , is complicated by the fact that both direct abstraction and addition–elimination are possible.<sup>41,51</sup> However, in either case it is expected to depend on whether the allylic hydrogen is primary, secondary, or tertiary. To take this into account,  $k^{\text{allyl}}$ , the contribution to the overall rate constant for net allylic hydrogen abstraction, was allowed three possible values,  $k^{\text{allyl}(1^\circ)}$ ,  $k^{\text{allyl}(2^\circ)}$ , and  $k^{\text{allyl}(3^\circ)}$ . For example,  $k^{\text{allyl}(2^\circ)}$  would represent the contribution of abstraction of one of the secondary allylic hydrogen atoms in 1-butene or 1-pentene. For 2-ethyl-1-butene, with two secondary allylic carbon atoms,  $2 \cdot k^{\text{allyl}(2^\circ)}$  would represent the analogous contribution and for 4-methyl-2-pentene, with a primary allylic carbon on one side of the double bond and a tertiary allylic carbon on the other, the contribution would be  $k^{\text{allyl}(1^\circ)} + k^{\text{allyl}(3^\circ)}$ .

**Application of structure–reactivity scheme.** Fig. 2 illustrates this approach using 1-pentene as an example. The overall rate constant,  $k^{\text{overall}}$ , is comprised of contributions from direct hydrogen abstraction from the terminal ethyl group, abstraction (either direct or through addition–elimination) of an allylic hydrogen atom, and finally, addition to the double bond which can form either a secondary or a primary radical depending on the addition site. We assume that the terminal ethyl group is sufficiently far removed from the double bond that it can be treated as if part of an alkane and that the parameters shown in Table 1 can be applied. For example, using the parameters of Atkinson,<sup>21</sup>

$$\begin{aligned}
 k^{\text{alkyl}} &= k^{\text{alkyl}(1^\circ)} F(-\text{CH}_2-) + k^{\text{alkyl}(2^\circ)} F(\text{CH}_3-) F(-\text{CH}_2-) \\
 &= (0.35 \times 0.79) + (0.93 \times 1.0 \times 0.79) \\
 &= 1.0 \text{ (in units of } 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}.
 \end{aligned}$$

The rate constants for abstraction of an allylic hydrogen and for addition to the double bond are then the unknowns and

must together comprise a rate constant equal to the difference between the total measured rate constant and the contribution  $k^{\text{alkyl}}$ , *i.e.*  $(3.97 - 1.0) \times 10^{-10} = 2.97 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The approach used to obtain best fit values for  $k^{\text{allyl}}$  and  $k^{\text{add}}$  from our data set for the alkenes was to take one set of values at a time from Table 1 for  $k^{\text{alkyl}}$  and the associated neighboring group factors. Initial values for  $k^{\text{allyl}}$  and  $k^{\text{add}}$  were assumed and the overall rate constant calculated for the entire set of alkenes. The difference between the measured and calculated values was then minimized by varying  $k^{\text{allyl}}$  and  $k^{\text{add}}$  using a generalized reduced gradient (GRG2) nonlinear optimization code that minimizes the sum of the squares of these differences. This procedure gave optimized values for  $k^{\text{allyl}}$  and  $k^{\text{add}}$  based on the 11 alkenes for which rate constants were measured in this study. The starting point for the minimization routine for addition was  $k^{\text{add}(2^\circ, 1^\circ)}$ ,  $k^{\text{add}(3^\circ, 1^\circ)}$ ,  $k^{\text{add}(2^\circ, 2^\circ)}$  or  $k^{\text{add}(3^\circ, 2^\circ)} = 2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and for allylic abstraction, the values of  $k^{\text{allyl}(1^\circ)}$ ,  $k^{\text{allyl}(2^\circ)}$ , and  $k^{\text{allyl}(3^\circ)}$  were initially set to  $0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

However, while these values were assumed initially, it is noteworthy that when there were no constraints placed on any of the fitting parameters (*i.e.*, no initial values were assumed), the *same set* of parameters were obtained from the minimization algorithm. This indicates that a global, rather than a local minimum was located by this fitting procedure. The values obtained using this minimization algorithm resulted in an average percent difference between  $k^{\text{calculated}}$  and  $k^{\text{measured}}$  of 2% regardless of which of the three sets of parameters from Table 1 were used.

**Best fit values of  $k^{\text{add}}$  and  $k^{\text{allyl}}$ .** Table 3 summarizes the best fit values obtained for  $k^{\text{add}}$  and  $k^{\text{allyl}}$  using this approach. There were some differences in the set of best-fit parameters found when the different values of alkyl abstraction parameters from Table 1 were used in the optimization procedure. The values for alkyl hydrogen abstraction recommended by Atkinson<sup>21</sup> or Tyndall *et al.*<sup>25</sup> gave the same set of best-fit parameters for addition, and similar contributions for abstraction of a 1° or 2° allylic hydrogen atom. The main difference was found in the contribution from a tertiary allylic hydrogen where the calculated contributions differed by a factor of about two. The best-fit parameters for addition and allylic abstraction using the parameters of Senkan and Quam<sup>23</sup> are not quite as consistent with those of Atkinson and Tyndall and coworkers, and predict that tertiary allylic hydrogen atoms are not abstracted by chlorine atoms.

In all cases, the best fit parameters of addition for ( $\geq$ C4), 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 propene. As noted above, atomic chlorine may add to either of the doubly bonded carbon atoms, but it is found experimentally that electrophilic radicals add most easily to the least substituted carbon and produce the most substituted radical intermediates. Regardless of the particular set of abstraction rate constants from Table 1

**Table 3** Best-fit parameters calculated using different values for alkyl abstraction from Table 1<sup>a</sup>

Best-fit parameters and applicable alkenes	Atkinson <sup>21</sup>	Tyndall <i>et al.</i> <sup>25</sup>	Senkan and Quam <sup>23</sup>
$k^{\text{add}(2^\circ, 1^\circ)}$ for 1-butene, 1-pentene, 3-methyl-1-butene, 3-methyl-1-pentene	2.60	2.60	2.54
$k^{\text{add}(2^\circ, 2^\circ)}$ for <i>cis</i> - and <i>trans</i> -2-butene, <i>cis</i> -4-methyl-2-pentene	2.98	2.98	2.79
$k^{\text{add}(3^\circ, 1^\circ)}$ for isobutene, 2-methyl-1-butene, 2-ethyl-1-butene	2.64	2.64	2.44
$k^{\text{add}(3^\circ, 2^\circ)}$ for 2-methyl-2-butene	2.93	2.93	2.68
$k^{\text{allyl}(1^\circ)}$	0.34	0.34	0.42
$k^{\text{allyl}(2^\circ)}$	0.37	0.41	0.45
$k^{\text{allyl}(3^\circ)}$	0.11	0.20	0.00
Ratio <i>per hydrogen</i> for allylic abstraction 1° : 2° : 3°	1 : 2 : 1	1 : 2 : 2	1 : 2 : 0

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

that are used, the best-fit parameters for addition show some trends:  $k^{\text{add}}(3^\circ, 2^\circ) \cong k^{\text{add}}(2^\circ, 2^\circ)$ ,  $k^{\text{add}}(3^\circ, 2^\circ) > k^{\text{add}}(3^\circ, 1^\circ)$ , and  $k^{\text{add}}(2^\circ, 2^\circ) > k^{\text{add}}(2^\circ, 1^\circ)$ .



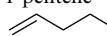

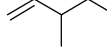




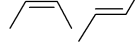

Table 4 summarizes the rate constants calculated using the best fit values of  $k^{\text{add}}$  and  $k^{\text{allyl}}$  for each of the values of  $k^{\text{alkyl}}$  shown in Table 1. Also shown are the measured rate constants and the percent difference between the measured and calculated rate constants. The maximum difference is only 4%, and the average difference is 2%.

The most surprising result is that the contribution of allylic hydrogen abstraction to the overall rate constant is small, regardless whether the hydrogen is primary, secondary or tertiary. For example, the contribution for  $2^\circ$  hydrogen abstraction

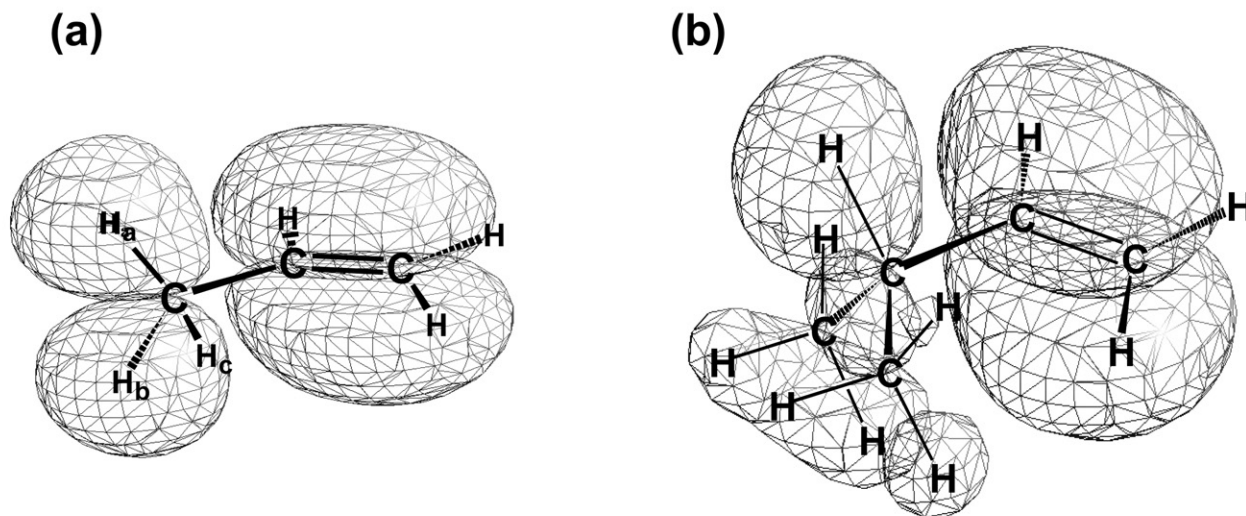
from *n*-butane using eqn. (1) and the data in Table 1 is about  $0.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  per  $-\text{CH}_2-$  group. However, the contribution from allylic hydrogen abstraction in 1-butene is only  $0.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the  $-\text{CH}_2-$  group. The effect is even more dramatic for tertiary hydrogens. For example, for isopentane, the rate constant for abstraction of the tertiary hydrogen atom is about  $0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  compared to a range of  $(0.0-0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained for abstraction of the tertiary allylic hydrogen in 3-methyl-1-butene (Table 4).

Our optimization procedure gives a ratio of 2 : 1 for abstraction *per hydrogen* of secondary vs. primary allylic hydrogen atoms (Table 3), regardless of which set of parameters from

**Table 4** Calculated contributions for addition and abstraction for reaction of chlorine atoms with simple alkenes and comparison to measured rate constants<sup>a</sup>

Alkene	Source <sup>b</sup> of parameters for $k^{\text{alkyl}}$	$k^{\text{add}}$	$k^{\text{allyl}}$	$k^{\text{alkyl}}$	$k^{\text{calculated } c}$	$k^{\text{measured}}$	Absolute % difference
	Atkinson	2.3	0.34		2.64		0.0%
	Tyndall <i>et al.</i>	2.3	0.34		2.64	2.64	0.0%
	Senkan and Quam	2.3	0.42		2.72		3.0%
	Atkinson	2.60	0.37	0.28	3.25		3.8%
	Tyndall <i>et al.</i>	2.60	0.41	0.23	3.24	3.38	4.1%
	Senkan and Quam	2.54	0.45	0.31	3.30		2.4%
	Atkinson	2.60	0.37	1.01	3.98		0.3%
	Tyndall <i>et al.</i>	2.60	0.41	0.96	3.97	3.97	0.0%
	Senkan and Quam	2.54	0.45	0.87	3.86		2.8%
	Atkinson	2.60	0.11	0.55	3.26		0.9%
	Tyndall <i>et al.</i>	2.60	0.20	0.47	3.27	3.29	0.6%
	Senkan and Quam	2.54	0.00	0.80	3.34		1.5%
	Atkinson	2.60	0.11	1.29	4.00		3.9%
	Tyndall <i>et al.</i>	2.60	0.20	1.20	4.00	3.85	3.9%
	Senkan and Quam	2.54	0.00	1.44	3.98		3.4%
	Atkinson	2.64	2(0.34)		3.32		2.4%
	Tyndall <i>et al.</i>	2.64	2(0.34)		3.32	3.40	2.4%
	Senkan and Quam	2.44	2(0.42)		3.28		3.5%
	Atkinson	2.64	0.34 + 0.37	0.28	3.63		1.4%
	Tyndall <i>et al.</i>	2.64	0.34 + 0.41	0.23	3.62	3.58	1.1%
	Senkan and Quam	2.44	0.42 + 0.45	0.31	3.62		1.1%
	Atkinson	2.64	2(0.37)	0.55	3.93		1.0%
	Tyndall <i>et al.</i>	2.64	2(0.41)	0.47	3.93	3.89	1.0%
	Senkan and Quam	2.44	2(0.45)	0.61	3.95		1.5%
	Atkinson	2.93	3(0.34)		3.95		0.0%
	Tyndall <i>et al.</i>	2.93	3(0.34)		3.95	3.95	0.0%
	Senkan and Quam	2.68	3(0.42)		3.94		0.3%
	Atkinson	2.98	2(0.34)		3.66		3.4%
	Tyndall <i>et al.</i>	2.98	2(0.34)		3.66	3.54	3.4%
	Senkan and Quam	2.79	2(0.42)		3.63		2.5%
	Atkinson	2.98	0.34 + 0.11	0.55	3.98		3.2%
	Tyndall <i>et al.</i>	2.98	0.34 + 0.20	0.47	3.99	4.11	2.9%
	Senkan and Quam	2.79	0.42	0.80	4.01		2.4%
Average % Difference $\frac{ k^{\text{calculated}} - k^{\text{measured}} }{k^{\text{measured}}}$	Atkinson						1.8%
	Tyndall <i>et al.</i>						1.8%
	Senkan and Quam						2.2%

<sup>a</sup> Units of rate constants are  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>b</sup> Atkinson is ref. 21; Tyndall *et al.* is ref. 25; Senkan and Quam is ref. 23. <sup>c</sup>  $k^{\text{calculated}} = k^{\text{overall}}$  from eqn. (III).



**Fig. 3** The  $\pi$ -HOMO orbitals for (a) propene and (b) 3-methyl-1-butene. The orbitals and geometry shown were obtained by semi-empirical calculations using the AM1 approximate Hamiltonian. Calculations using the PM3 approximate Hamiltonian gave similar results.

Table 1 for alkyl hydrogen abstraction is used. However, the ratio for abstraction of a tertiary allylic hydrogen atom to that of a primary allylic hydrogen ranges from 0 to 2 : 1, depending on the set of values taken for  $k^{\text{alkyl}}$ . In no case does the abstraction of a tertiary allylic hydrogen atom exceed that of a secondary allylic hydrogen. This is in contrast to the situation for abstraction of hydrogen from simple alkanes, where the ratios *per hydrogen* for abstraction of tertiary, secondary and primary hydrogen atoms are  $\sim 6 : 4 : 1$  (see Table 1).

In short, the rate constants for abstraction of allylic hydrogen atoms by atomic chlorine are smaller than expected in an absolute sense, and in addition, the differences between primary, secondary and tertiary allylic hydrogen abstraction are not as large as for abstraction from simple alkanes.

The relatively small rate constants for allylic hydrogen abstraction may be due in part to increased steric hindrance around the allylic carbon, impeding the approach of chlorine atoms toward allylic hydrogen. This may be particularly important if most or all of what appears to be abstraction actually proceeds by addition–elimination as is the case for isoprene, for example.<sup>51</sup> Energy minimization, using the PM3 approximate Hamiltonian applied to several of the alkenes studied here, shows that the closest approach between chlorine at a terminal carbon and the allylic hydrogen, a configuration required for the formation of a 5-membered ring during addition–elimination, is 2.7 Å. Small amounts of steric hindrance to rotation into the appropriate configuration for formation of the 5-membered ring could therefore have a significant effect.

Another possibility is that the allylic C–H bond interacts strongly with the C=C double bond. Frontier orbital theory indicates that singly occupied  $p$  orbital of the chlorine atom, an electrophilic radical, may interact with either the LUMO or HOMO  $\pi$ -orbitals of the alkene, but more favorably with the latter.<sup>64,65</sup> However, as seen in Fig. 3, semi-empirical calculations (using either AM1 or PM3 approximate Hamiltonians) reveal significant orbital density from the HOMO of the alkene as far out as the allylic hydrogen atoms for propene and 3-methyl-1-butene. It can be seen that two of the allylic hydrogens of propene, designated  $H_a$  and  $H_b$ , and the only allylic hydrogen of 3-methyl-1-butene are spatially “buried” in a portion of the delocalized  $\pi$ -orbitals. Instead of abstracting a hydrogen atom, a chlorine atom approaching these allylic hydrogens may be shunted into the chlorine addition channel, resulting in diminished reactivity toward abstraction in general, and abstraction of tertiary allylic hydrogen in particular.

#### Atmospheric implications

These reactions are all sufficiently fast that the reaction with chlorine atoms will be an important removal process in coastal urban areas at dawn when a pulse of chlorine atoms is generated from the photolysis of species such as  $\text{Cl}_2$ . Table 5 summarizes the lifetimes of these alkenes with respect to reaction with Cl and OH, both at concentrations of  $1 \times 10^5 \text{ cm}^{-3}$  as might be typical of early morning hours. It is seen that the lifetimes of these alkenes with respect to reaction with chlorine atoms is about an order of magnitude shorter than

**Table 5** Lifetimes of alkenes with respect to reaction with Cl atoms and OH radicals

Alkene	$k(\text{Cl})^a$ ( $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Lifetime with respect to Cl <sup>b</sup> (hours)	$k(\text{OH})^c$ ( $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Lifetime with respect to OH <sup>b</sup> (hours)
Propene	2.6	11	2.6	107
Isobutene	3.4	8.2	5.1	54
<i>trans</i> -2-Butene	3.3	8.4	6.4	43
<i>cis</i> -2-Butene	3.8	7.3	5.6	50
2-Methyl-2-butene	4.0	6.9	8.7	32
1-Butene	3.4	8.2	3.1	90
2-Methyl-1-butene	3.6	7.7	6.1	46
3-Methyl-1-butene	3.3	8.4	3.2	87
2-Ethyl-1-butene	3.9	7.1		

<sup>a</sup> Rate constants from this work. <sup>b</sup> Assuming  $[\text{Cl}] = [\text{OH}] = 1 \times 10^5 \text{ cm}^{-3}$  characteristic of early morning coastal regions. <sup>c</sup> From Atkinson.<sup>21</sup>



those with respect to reaction with OH. Thus, for some period of time in the early morning when chlorine atoms are being generated by the reaction of photolyzable chlorine compounds, they will dominate in the loss of the simple alkenes.

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