Rate Constants and Kinetic Isotope Effects in the Reactions of Atomic Chlorine with *n*-Butane and Simple Alkenes at Room Temperature

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Rate constants for the reactions of chlorine atoms with *n*-butane and simple alkenes, as well as most of their deuterated analogs, were studied at room temperature using two independent techniques. Using a fast flow discharge system (FFDS), the decay of chlorine atoms in 1 Torr He was followed using resonance fluorescence at 135 nm. In relative rate (RR) studies the decay of the organic was followed, relative to a reference compound, using GC-FID when they both reacted with chlorine atoms. These RR measurements were performed at 1 Torr in N_2 and at 1 atm in both N_2 and air. The results of the FFDS and RR studies at 1 Torr were generally in excellent agreement with each other and, where available, with literature data. Discrepancies appear to exist at 1 atm for isoprene, where the addition portion of the rate constant measured in this laboratory is 40% higher than a value for k_∞ reported recently by Bedjanian et al.[40] Our rate constant for 1,3-butadiene is 25% smaller than that of Bierbach et al.[39] Rate constants measured in these studies which have not been previously reported in the literature are as follows (in units of cm^3 molecule^{-1} s^{-1}, with the errors being the statistical 2σ errors): C_3D_6 $(4.1 \pm 0.8) \times 10^{-11}$ in 1 Torr He, $(4.3 \pm 1.0) \times 10^{-11}$ in 1 Torr N_2, and $(2.3 \pm 0.3) \times 10^{-10}$ in 1 atm N_2 or air; 1-C_4H_8 $(1.0 \pm 0.1) \times 10^{-10}$ in 1 Torr He, $(1.2 \pm 0.2) \times 10^{-10}$ in 1 Torr N_2, and $(2.2 \pm 0.3) \times 10^{-10}$ at 1 atm N_2 or air; 1-C_4D_8 $(1.0 \pm 0.2) \times 10^{-10}$ in 1 Torr He, $(1.2 \pm 0.2) \times 10^{-10}$ in 1 Torr N_2, and $(2.0 \pm 0.4) \times 10^{-10}$ in 1 atm N_2 or air; *n*-C_4D_{10} $(1.6 \pm 0.1) \times 10^{-10}$ averaged over all pressures and carrier gases. Deuteration results in a normal kinetic isotope effect (KIE) for direct hydrogen abstraction, but an inverse kinetic isotope effect for addition to the double bond. The KIE (k^H/k^D) for *n*-butane was measured to be 1.4 ± 0.2. For ethene, an inverse KIE was measured, 0.74 ± 0.06 at 1 atm in N_2 or air compared to an average of 0.35 at 1 Torr in N_2 or He reported in earlier studies.[29] The KIEs for the larger alkenes were unity within experimental error. For propene at 1 Torr, the inverse KIE for addition is largely counterbalanced by a normal KIE for abstraction of an allylic hydrogen. For the larger alkenes, this result is consistent with expectations because addition is close to the high-pressure limit even at 1 Torr and abstraction is expected to play a minor role in the overall reaction. The atmospheric implications of these measurements are discussed.

Introduction

It is a pleasure to contribute to this special issue in honor of Professor Benson's 80th birthday. Professor Benson's seminal work in the fields of kinetics and thermodynamics has provided key insights into many reaction systems in laboratories throughout the world in the past and continues to do so today. His books have educated several generations of kineticists, photochemists, and atmospheric chemists and are "must haves" on the bookshelves of colleagues and students in these fields. The work presented here is in an area in which Professor Benson and his group have played a major role, that of chlorine atom reactions with hydrocarbons. As will be evident in the following, his insights into chlorine atom chemistry have greatly aided in understanding the reactions with a variety of organics, and we look forward to continuing to benefit from his scientific insights and collegiality for many years to come.

While chlorine atoms are known to play an important role in the stratosphere,[1] their importance in the troposphere is controversial.[2−4] The most likely source of tropospheric Cl atoms is the photolysis of species generated by reactions of sea salt aerosols or other salt-covered surfaces. For example, the reaction of N_2O_5 on a salt surface forms gaseous $ClNO_2$,[5,6] which photolyzes to Cl and NO_2. Recently, the production of Cl_2 from the reaction of ozone with wet sea salt aerosols in the presence of ultraviolet light was observed in this laboratory.[7] Concentrations of up to 150 ppt Cl_2 (and perhaps other photolyzable chlorine-containing compounds such as HOCl as well) have been measured[8,9] in the marine boundary layer and in the Arctic.[10] Photolysis of these species is expected to result in peak concentrations of chlorine atoms as high as 10^5 atoms cm^{-3} in the marine boundary layer at dawn.

The main fates of Cl atoms in the troposphere are their reactions with organics or with ozone:[11−13]

$$Cl + RH \rightarrow products \tag{1}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{2}$$

Even small chlorine atom concentrations can play a role in the destruction of organics in the marine boundary layer since the rate constants for chlorine atom reactions with species such as alkanes and dimethyl sulfide are much larger than those for other atmospheric oxidants such as OH.[11−13]

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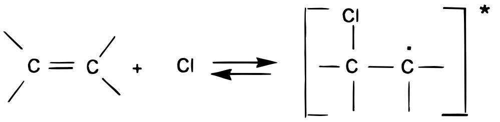
The kinetics and mechanisms of the reactions of alkanes with chlorine atoms, which proceed by direct abstraction to produce HCl, have been studied in the past (see refs 11 and 13 for recent reviews). There have also been a number of studies of simple alkenes, including ethene,[14−31] propene,[19,20,32−37] isoprene,[38−42] 1,3-butadiene[38,39,41,42] and the butenes.[41] These reactions are pressure dependent. For example, Wallington et al.[21] and Kaiser and Wallington[26] observed that the rate constant for Cl + C_2H_4 increases by more than 3 orders of magnitude from 0.3 to 3000 Torr. Over the same pressure range, the rate constant for the propene reaction increases only by a factor of 5,[35] and that for isoprene by less than 2.[39−42] This difference is consistent with addition of chlorine atoms to the double bond:



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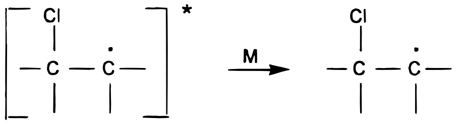

(4)

Larger alkenes have greater numbers of degrees of freedom over which the energy in the excited adduct can be distributed and, hence, reach their high-pressure limit at lower total pressures.

Abstraction may also occur when a weakly bound allylic hydrogen atom is present, as in propene and isoprene:

$$CH_3CH{=}CH_2 + Cl \rightarrow \dot{C}H_2CH{=}CH_2 + HCl \qquad (5)$$

Interestingly, the rate constant for net abstraction in the propene reaction increased by 50% as the total pressure decreased from 100 to 10 Torr.[35] This was attributed to direct abstraction combined with a contribution at lower pressures from an addition−elimination process, reaction 6a:

$$C_3H_6 + Cl \rightarrow (C_3H_6Cl)^* \rightarrow C_3H_5 + HCl \qquad (6a)$$

$$\xrightarrow{M} C_3H_6Cl \qquad (6b)$$

The contribution of an addition−elimination pathway was confirmed by recent studies of the temperature dependence of the rate constants and the observation of vibrationally excited HCl as a product.[36] Ragains and Finlayson−Pitts[38] reached a similar conclusion for the isoprene reaction based on an unusual pressure dependence of the rate constants for the reactions of Cl with isoprene and isoprene-d_8.

Rate constants may decrease (a *normal* kinetic isotope effect, KIE) or increase (an *inverse* KIE) upon deuteration of a reactant organic, depending on the reaction mechanism.[43] Normal KIEs originate in larger zero-point energy differences in the reactants compared to the transition state, increasing the activation energy and hence slowing the reaction. Normal KIEs can be either primary, where the mechanism directly involves the isotopes, or secondary, in which they are not directly involved. On the other hand, addition reactions generally exhibit an inverse KIE. As discussed in more detail below, this is due to the increased lifetime of the excited adduct with respect to decomposition back to reactants (reaction −3), which increases the relative importance of stabilization in reaction 4. For reactants such as propene, where both direct abstraction and addition occur, both effects are expected to be operable.

Here we present measurements of rate constants of chlorine atoms with a series of small alkenes: ethene, propene, 1-butene, *trans*-2-butene, isobutene, 1,3-butadiene, isoprene, and most of the corresponding fully deuterated analogs. Effects of deuteration and total pressure on the rate constants provide insights into the reaction mechanisms. We show that the rate constants and KIE for chlorine atom reactions with simple alkenes are consistent with a combination of addition to the double bond and, where allylic hydrogen atoms are present, with a contribution from abstraction and addition−elimination reactions.

Experimental Section

Two different methods were used: (1) a fast flow discharge system at 1 Torr in He and (2) a relative rate technique at 1 Torr (in N_2) and at 1 atm total pressure (in N_2 or air).

Fast Flow Discharge Studies. The fast flow discharge system (FFDS)[44] consisted of a water-jacketed Pyrex flow tube 25 mm in diameter and ~1 m in length, which was coated with halocarbon wax (Halocarbon Products, Series 1500) to minimize wall reactions. The temperature was held at 20 °C. A flow of He carrier gas (320 μmol s^{-1}) was maintained by a rotary pump (Leybold TRIVAC D25B) and a mass flow controller (MKS 1259C). The pressure was measured as 1.05 ± 0.01 Torr using a capacitance manometer (MKS 690A, 1000 Torr). The linear flow speed was $v = 1114 \pm 25$ cm s^{-1}.

Chlorine atoms were formed via the fast reaction F + HCl → HF + Cl ($k = 1.1 \times 10^{-11}$ cm^{-3}),[45] where the fluorine atoms were produced by a microwave discharge of 1% F_2 in He. Excess HCl was added downstream of the discharge to react all F atoms, forming Cl atoms prior to addition of the organic. Dilute mixtures of the alkenes in He, whose concentrations were measured to a typical uncertainty of <2% by following the pressure drop with time in a known volume, were added via a movable, halocarbon wax-coated injector.

The chlorine atom concentration was followed by resonance fluorescence (RF) at 135 nm. A mixture of 1% Cl_2 in He at 0.6 Torr was flowed through a discharge lamp with a MgF_2 window mounted perpendicular to the flow tube. The RF signal was isolated and detected perpendicular to the flow tube and lamp using a vacuum monochromator (Minuteman 302VM), a solar blind photomultiplier (EMR 541G09-17), and a photon counter (Princeton Applied Research Corp. 1140) and digitized using an A/D converter (Keithley DAS-802).

Higher Cl concentrations, in the range $(3-7) \times 10^{11}$ atoms cm^{-3}, than used in the kinetics runs were determined by titration with ClNO. The signal was proportional to [Cl] in this range within experimental error. Extrapolation to lower concentrations indicates that a signal of 2000 counts s^{-1} corresponds to a concentration of 1×10^{10} atoms cm^{-3} typically used in the kinetics experiments. The signal was typically integrated for 50 s to improve the signal-to-noise ratio. With typical backgrounds of 100−200 counts s^{-1}, the detection limit for a S/N of 2 was 7×10^7 Cl atoms cm^{-3}.

The background signal had two components: stray light, which was measured by turning the F_2 discharge off, and a small oxygen atom fluorescence signal due to O_2 impurities in the F_2/He gas mixture. The oxygen atom signal was determined by adding an excess of an organic at long reaction times to preferentially remove Cl atoms. For example, *n*-butane at 2×10^{12} molecules cm^{-3} reduces [Cl] by 4 orders of magnitude but leaves [O] essentially unchanged.[46] For the alkenes, where some oxygen atom reaction also occurs, the measured background signal was corrected based on the calculated loss of oxygen atoms. For example, using a rate constant[47] for the O

+ isobutene reaction of 1.69×10^{-11} cm^3 molecule^{-1} s^{-1}, addition of 1.6×10^{12} molecules cm^{-3} of isobutene at a reaction time of 20 ms reduced [O] to 58% of its initial value, while decreasing [Cl] by more than 99%. The uncertainty in the background due to the correction for oxygen atom fluorescence is ~10%.

Rate constants were determined from the decrease in the chlorine fluorescence signal with increasing distance between the detector and movable injector. Reaction times were typically changed in 10 steps from 6 to 30 ms or 6 to 16 ms for fast reactions. The decay of chlorine atoms in the presence of a great excess of the organic is described by eq I:

$$\ln\frac{I}{I_0} = \ln\frac{[\mathrm{Cl}]}{[\mathrm{Cl}]_0} = -(k_1[\mathrm{organic}] + \Delta k_\mathrm{w})t = -k't \qquad \text{(I)}$$

$[\mathrm{Cl}]$ and $[\mathrm{Cl}]_0$ are the chlorine atom concentrations at time t and at time $t = 0$, measured in the absence of the organic, and k_2 is the rate constant of interest. Δk_w is the change in the rate constant for wall loss (k_w) of Cl upon addition of the organic, which was zero within experimental error. In some early runs, a small loss of Cl (<7%) on the injector was observed. Comparison of corrected rate constants from such runs to those without such losses showed no significant differences.

Relative Rate Method. Relative rates were measured with an apparatus similar to the one described by Ragains and Finlayson-Pitts.[38] The rate constant was determined by following the simultaneous loss of the alkene and a reference compound during their reactions with chlorine atoms. For experiments at 1 Torr, a 6.5 L Pyrex bulb surrounded by seven Sylvania 350 blacklight lamps (20W F20T12/350BL) was used. The organics, Cl_2, and a bath gas (N_2 or air) were directly expanded into the bulb, and the pressure was measured (Datametrics model 600). For experiments at atmospheric pressure, a 50 L collapsible Teflon reaction chamber faced a bank of seven blacklights. The chamber was filled by flushing the premixed organics and Cl_2 from a 645 cm^3 transfer bulb with N_2 or air and monitoring the flow with a calibrated rotameter (Omega Engineering Inc. model FL4213-V).

Typical concentrations in the experiments at 1 Torr were in the range $(1.4-18) \times 10^{14}$ molecules cm^{-3} each for the alkenes and reference compounds and $(1.7-14) \times 10^{14}$ molecules cm^{-3} for Cl_2. In the atmospheric pressure experiments, the alkene and reference compounds were each in the range $(7.4-23) \times 10^{14}$ molecules cm^{-3} and Cl_2 was in the range $(1.5-3.0) \times 10^{15}$ molecules cm^{-3}. Absolute concentrations and ratios of reactants were varied to test for possible systematic errors. No dark reactions of the hydrocarbons with Cl_2 were observed over the range of reactant concentrations used here.

The decay of the hydrocarbons upon photolysis of Cl_2 was measured by injecting gas samples from the reactors into a GC (Hewlett Packard 5890) using a six-port gas sampling valve (Valco Instruments Co. Inc.). The GC was equipped with a flame ionization detector and a 30 m GS-Q column (0.32 mm I.D., J & W Scientific) operated isothermally at 60 °C or a 30 m or 60 m Cyclodex B column (0.25 mm ID, J & W Scientific) usually operated at 15 °C.

Relative rate constants were determined by following the change in the ratio of the organic of interest to that of the reference compound as a function of reaction time:

$$\ln\left(\frac{[\mathrm{organic}]_0}{[\mathrm{organic}]_t}\right) = \frac{k_\mathrm{org}}{k_\mathrm{ref}} \ln\left(\frac{[\mathrm{reference}]_0}{[\mathrm{reference}]_t}\right) \qquad \text{(II)}$$

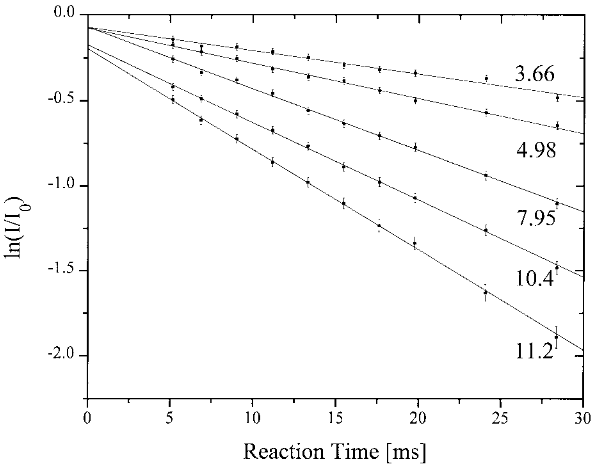

Figure 1. Typical first-order decay of the chlorine atom resonance fluorescence signal at 135 nm for the reaction with propene (in units of 10^{11} molecules cm^{-3}). The errors bars are the 2σ errors in $\ln(I/I_0)$ and reaction times.

Here $[\ ]_0$ and $[\ ]_t$ denote the initial concentrations and those after various reaction times, t, respectively.

Materials. Ethylene (Research Grade 99.98%), 1-butene (99%), *n*-butane (Research Grade 99%+), and isobutene (99%) were supplied by Matheson Gas Products; propene (Research Grade 99%+), 1,3-butadiene (Research Grade 99%+), and isoprene (Research Grade 99%) were supplied by Aldrich; and *trans*-2-butene (Research Grade, 99%+) was supplied by M. G. Industries. The deuterated reactants 1-butene-d_8 (98%+), *n*-butane-d_8 (98%+), propene-d_6 (98%+), isoprene-d_8 (98%+), ethylene-d_4 (98%+), and 1,3-butadiene-d_6 (98%+) were supplied by Cambridge Isotopes. All deuterated gases were analyzed for isotopic purity by MS. A 5% impurity of C_2D_3H was found in C_2D_4 and 12% C_3D_5H in the C_3D_6. The other gases were fully deuterated within our detection limits. Helium and N_2 (both ultrahigh purity, 99.999%) were supplied by Liquid Carbonic. HCl, Cl_2, 1% Cl_2 in He (UHP), and 1% F_2 in He (UHP) were from Matheson. All organics except ethylene and ethylene-d_4 were subjected to several freeze/pump/thaw cycles at 78 K before use.

The presence of organic impurities does not interfere in RR studies as long as they do not overlap the peaks of the compound of interest or the reference. However, impurities can contribute to errors in the absolute rate constant measurements using FFDS. Potential errors are greatest for the alkenes having the smallest rate constants. In the case of C_2H_4 and C_2D_4, GC analysis showed methane as the only other hydrocarbon detectable by FID, at 0.6% and 0.1% levels. Since the rate constant[11-13] for the Cl + CH_4 reaction is $(1.0 \pm 0.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, CH_4 contributes <0.2% to the loss of atomic chlorine in the FFDS. For C_3H_6, if there were a 1% impurity present which reacted at essentially the collision-controlled rate (e.g., $k = 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), the error in the abolute rate constant measurement would be ~10%. The major impurity in C_3D_6 was C_3D_5H (~12%). The contribution of this impurity to the measured rate constant is less than our experimental error. For the higher alkenes for which the rate constants are all larger than 1×10^{-10} cm^3 molecule^{-1} s^{-1}, the error due to a 1% impurity is <5%.

Results

A. Fast Flow Discharge Studies. Figure 1 shows the expected linear decay in $\ln(I/I_0)$ with reaction time for typical propene runs. The nonzero intercept may be due to a small

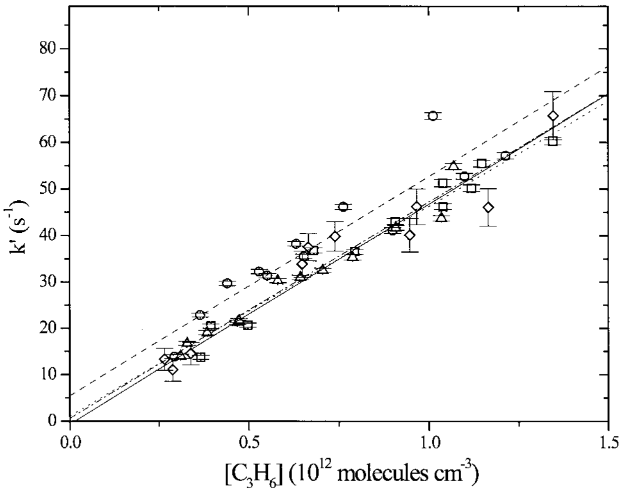

Figure 2. Pseudo-first-order rate constant (k') for the reaction of chlorine atoms with propene. The four symbols represent data sets measured on four different days with different Cl atom concentrations and different propene/He mixtures. The lines are the best fit lines for these four runs, showing excellent reproducibility in the derived rate constant despite poorer precision in the measured individual pseudo-first-order rate constants.

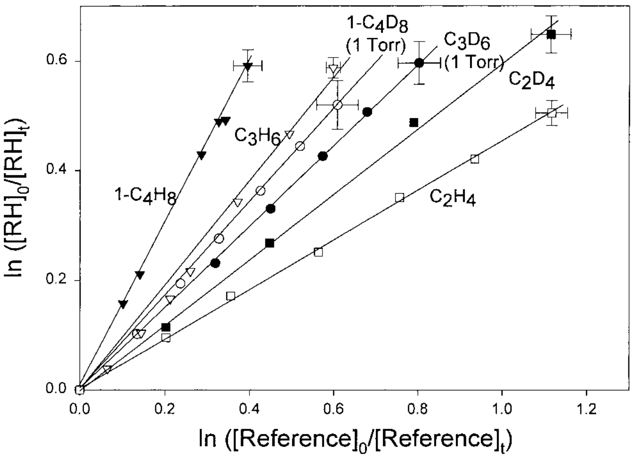

Figure 3. Typical relative rate data for Cl reactions at room temperature: (□) C_2H_4 in 1 atm N_2; (■) C_2D_4 in 1 atm N_2; (▽) C_3H_6 in 1 atm air, all using *n*-butane as the reference compound; (●) C_3D_6 at 1 Torr in N_2 using ethane as the reference; (○) 1-C_4D_8 at 1 Torr in N_2 using propane as the reference; (▼) 1-C_4H_8 at 1 atm in N_2 using propane as the reference compound.

region of incomplete mixing around the point of injection of the organic. Errors in $\ln(I/I_0)$ were calculated using the errors in the integrated signals I and I_0, the background signals, and, where appropriate, the injector loss correction. The errors in $\ln(I/I_0)$ are typically 3−10%. Errors in the flow speed and hence the reaction time t are ~2%. The pseudo-first-order rate constant k' was, in all cases, calculated using a linear least-squares fit, weighted with the errors in both $\ln(I/I_0)$ and reaction time.[48,49] Corrections[50,51] for axial diffusion (usually <4%) were applied to k' (but not for radial diffusion, which was insignificant).

Typically, 8−15 measurements of I versus t were carried out in one run using different alkene concentrations. This set of experiments was repeated two to four times on different days with different Cl concentrations and new alkene mixtures. Figure 2 shows the results of such measurements for propene. The second-order rate constant of interest (k_1) was determined using a weighted linear least-squares fit to data such as those in Figure 2, assuming that errors in the alkene concentrations were negligible. The intercept on the vertical axis was always zero within the 2σ error limits, indicating there was no significant change in the chlorine atom wall loss upon addition of the organic.

A typical uncertainty of 10−20% (2σ) was observed for rate constants measured in different runs. The isoprene measurements had higher uncertainty (33%) due to its lower vapor pressure and apparently higher tendency to wall loss and reactions. Experiments with lower vapor pressure compounds such as α-pinene, p-cymene, and nonane were unsuccessful since they gave rate constants that increased with the chlorine atom concentration and were sometimes higher than the collision-controlled limit, suggesting interference by wall reactions.

Table 1 summarizes the FFDS rate constants as well as the kinetic isotope effect (KIE = k^H/k^D) for each pair where the deuterated analog was also studied.

B. Relative Rate Studies. Figure 3 shows typical plots using eq II for some runs at 1 Torr and 1 atm total pressure, respectively. As expected, the plots are linear with zero intercepts. The slopes of such data sets were calculated using a linear least-squares fit which takes into account errors in the individual measurements of both organics.[52]

Table 2 summarizes the relative rate constants as well as the absolute rate constants derived from these for a total pressure of 1 Torr in N_2. Table 3 summarizes the data at atmospheric pressure in N_2 or air. There was no significant difference in the rate constants measured at 1 atm in air compared to N_2,

TABLE 1: Rate Constants for the Reaction of Chlorine Atoms with Alkenes and Deuterated Alkenes at 1 Torr Total Pressure and 20 ± 0.5 °C in He Determined Using a Fast Flow Discharge System

reactant	number of runs	k ($\pm 2\sigma$)^b (cm^3 molecule^{-1} s^{-1})	kinetic isotope effect k^H/k^D	major contribution to KIE
C_2H_4^{a}	4	$(3.3 \pm 0.6) \times 10^{-13}$	0.33 ± 0.09	addition
C_2D_4^{a}	2	$(1.0 \pm 0.2) \times 10^{-12}$		
C_3H_6	4	$(4.6 \pm 0.3) \times 10^{-11}$	1.1 ± 0.2	addition plus abstraction
C_3D_6	3	$(4.1 \pm 0.8) \times 10^{-11}$		
1-C_4H_8	3	$(1.0 \pm 0.1) \times 10^{-10}$	1.0 ± 0.2	addition dominates
1-C_4D_8	2	$(1.0 \pm 0.2) \times 10^{-10}$		
trans-2-C_4H_8	3	$(1.8 \pm 0.2) \times 10^{-10}$	n.d.^{c}	
isobutene	3	$(1.5 \pm 0.1) \times 10^{-10}$	n.d.^{c}	
1,3-butadiene	4	$(2.5 \pm 0.4) \times 10^{-10}$	0.98 ± 0.24	addition
1,3-butadiene-d_6	3	$(2.5 \pm 0.4) \times 10^{-10}$		
isoprene	4	$(3.7 \pm 1.0) \times 10^{-10}$	1.1 ± 0.4	addition dominates
isoprene-d_8	2	$(3.3 \pm 0.8) \times 10^{-10}$		

[a] Reported in ref 29. [b] Weighted average of individual runs using $w_i = 1/\sigma_i^2$. The errors cited are the maximum of the standard deviation of the individual runs or the error calculated with $\sigma^2 = (1/\sum w_i)$ where w_i are the weights of the individual runs. [c] n.d. = not determined

TABLE 2: Relative Rate Constants, the Derived Absolute Values, and the Kinetic Isotope Effects at Room Temperature for the Reactions of Chlorine Atoms with Some Alkenes[a] at 1 Torr Total Pressure in N_2

compound	reference compound	no. of runs	k/k^{ref} $(\pm 2\sigma)^b$	k $(\pm 2\sigma)^c$ (cm^3 molecule^{-1} s^{-1})	kinetic isotope effect k^H/k^D
C_3H_6	C_2H_6	3	0.82 ± 0.16	$(4.7 \pm 1.1) \times 10^{-11\ d}$	1.1 ± 0.3
C_3D_6	C_2H_6	3	0.75 ± 0.16	$(4.3 \pm 1.0) \times 10^{-11\ d}$	
1-C_4H_8	C_3H_8	3	0.85 ± 0.13	$(1.2 \pm 0.2) \times 10^{-10\ e}$	0.96 ± 0.18
1-C_4D_8	C_3H_8	3	0.89 ± 0.10	$(1.2 \pm 0.2) \times 10^{-10\ e}$	

[a] Relative rate measurements[29,31] of the KIE for C_2H_4 and C_2D_4 at 1 Torr in N_2 give 0.37 ± 0.10, in agreement with the FFDS results in Table 1. However, the large error bars on the individual runs and the possibility of a systematic error preclude their use for absolute rate constant determinations. [b] Standard deviation calculated as $\sigma^2 = (1/\sum w_i)$ where w_i are the weights of the individual runs.[49] [c] Includes 2σ error in relative rate constant measurements and 10% uncertainty in rate constant for reference organic. [d] Using $k(Cl + C_2H_6) = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, with a 10% uncertainty.[12] [e] Using $k(Cl + C_3H_8) = 1.37 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} with a 10% uncertainty.[11,13]

TABLE 3: Relative Rate Constants and the Corresponding Absolute Values at Room Temperature for the Reactions of Chlorine Atoms with Some Alkenes and Their Fully Deuterated Analogs at 1 atm Total Pressure in N_2 or Air, and the Kinetic Isotope Effects

compound	reference compound	carrier gas[a]	k/k^{ref} $(\pm 2\sigma)^b$	$(k/k^{ref})_{av}$ $(\pm 2\sigma)^c$	k $(\pm 2\sigma)$ (units of 10^{-10} cm^3 molecule^{-1} s^{-1})	kinetic isotope effect k^H/k^D
C_2H_4	n-C_4H_{10}	N_2 (3)	0.46 ± 0.03	0.45 ± 0.02	0.99 ± 0.11^d	0.74 ± 0.06
		air (2)	0.44 ± 0.04			
C_2D_4	n-C_4H_{10}	N_2 (2)	0.61 ± 0.05	0.61 ± 0.04	1.3 ± 0.2^d	
		air (2)	0.61 ± 0.05			
C_3H_6	n-C_4H_{10}	N_2 (3)	1.1 ± 0.1	1.1 ± 0.1	2.3 ± 0.3^d	0.99 ± 0.09
		air (2)	1.0 ± 0.1			
C_3D_6	n-C_4H_{10}	N_2 (3)	1.0 ± 0.1	1.1 ± 0.1	2.3 ± 0.3^d	
		air (2)	1.1 ± 0.1			
1-C_4H_8	C_3H_8	N_2 (3)	1.5 ± 0.1	1.6 ± 0.1	2.2 ± 0.3^e	1.1 ± 0.2
		air (3)	1.8 ± 0.1			
1-C_4D_8	C_3H_8	N_2 (3)	1.5 ± 0.4	1.5 ± 0.3	2.0 ± 0.4^e	
		air (2)	1.5 ± 0.4			
1,3-butadiene[f]	n-C_4H_{10}	(8)[g]		2.0 ± 0.1	4.2 ± 0.4	1.1 ± 0.1
1,3-butadiene-d_6[f]	n-C_4H_{10}	(10)[g]		1.9 ± 0.1	3.9 ± 0.4	
isoprene[f]	n-C_4H_{10}	(23)[g]		2.2 ± 0.2	4.6 ± 0.5	1.2 ± 0.2
isoprene-d_8[f]	n-C_4H_{10}	(9)[g]		1.8 ± 0.2	3.8 ± 0.6	

[a] Number of runs shown in parentheses. [b] Using $\sigma^2 = (1/\sum w_i)$.[49] [c] Weighted average of all runs in N_2 and in air taken together as one data set with $\sigma^2 = (1/\sum w_i)$.[49] [d] Using $k(Cl + n\text{-}C_4H_{10}) = 2.18 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and taking into account both the statistical error in the relative rate and a 10% error in the Cl + n-C_4H_{10} rate constant.[11,13] [e] Using $k(Cl + C_3H_8) = 1.37 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and taking into account both the statistical error in the relative rate and a 10% error in the Cl + C_3H_8 rate constant.[11,13] [f] Reported in ref 38. [g] Total number of runs; most runs carried out in air but two runs in N_2 in each case showed no significant difference.

showing that interference from secondary OH chemistry was not significant.

C. FFDS and RR Studies of n-C_4H_{10} and n-C_4D_{10}. As an additional test for unrecognized systematic errors, the reactions of n-C_4H_{10}, whose rate constant with chlorine atoms is well-known (see refs 11 and 13 for reviews), were also carried out. To elucidate the kinetic isotope effect for the abstraction of secondary hydrogen atoms, the reaction of its fully deuterated isomer, n-C_4D_{10} (for which literature data do not appear to be available), was also studied. The data in Table 4 summarize the rate constants at 1 Torr and 1 atm in both the FFDS and RR studies.

Discussion

A. Reaction of Chlorine Atoms with n-C_4H_{10} and n-C_4D_{10}. The rate constants for the reaction of chlorine atoms with n-C_4H_{10} using the two different approaches, FFDS and RR, at 1 Torr are in good agreement. No pressure dependence is observed from 1 Torr to 1 atm, as expected for a simple hydrogen abstraction. The value of $(2.3 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is in excellent agreement with the recommended value[11,13] of 2.18×10^{-10} cm^3 molecule^{-1} s^{-1} based on past studies and with a more recent value of $(2.15 \pm 0.15) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} reported by Tyndall et al.[53]

The kinetic isotope effect is defined as KIE = k^{C4H10}/k^{C4D10}. It is relatively small for n-butane, 1.4 ± 0.2. For comparison, several groups have reported a KIE for ethane of 2.4−3.1.[54−57]

TABLE 4: Rate Constants for the Reaction of Chlorine Atoms with n-C_4H_{10} and n-C_4D_{10} at Room Temperature

compound	technique[a]	total pressure	k $(\pm 2\sigma)$ (10^{-10} cm^3 molecule^{-1} s^{-1})	k^{av} $(\pm 2\sigma)$ (10^{-10} cm^3 molecule^{-1} s^{-1})
n-C_4H_{10}	FFDS (4)	1.05 Torr	2.0 ± 0.4	2.3 ± 0.2
	RR (5)[b]	1.05 Torr	2.4 ± 0.3^d	
	RR(12)[c]	1 atm	2.3 ± 0.3^d	
n-C_4D_{10}	FFDS (3)	1.05 Torr	1.5 ± 0.3	1.6 ± 0.1
	RR (6)[e]	1.05 Torr	1.6 ± 0.2^d	
	RR (5)[f]	1 atm	1.5 ± 0.2^d	

[a] FFDS = fast flow discharge system in He carrier gas; RR = relative rate technique in N_2 or air as indicated. Number of runs shown in parentheses. [b] Two runs in N_2 as the carrier gas, three in air. [c] Five runs in N_2, seven in air. [d] Measured relative to ethane using $k(Cl + C_2H_6) = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; error includes that in our measurement from $\sigma^2 = (1/\sum w_i)$, where $w_i = 1/\sigma^2$ for each run, and a 10% error in $k(Cl + C_2H_6)$.[12] [e] Three runs in N_2, three in air. [f] Two runs in N_2, three in air.

The rate constants for reactions of chlorine atoms with alkanes have been parametrized as the sum of abstraction of primary, secondary, and tertiary hydrogen atoms, respectively, either with[13] or without[53] different neighboring group effects. For n-C_4H_{10}, Tyndall et al.[53] report that the contribution from the two methyl groups is (29 ± 2)% of the overall reaction. Using our value for the total rate constant of $(2.3 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, the contribution due to the two end methyl groups must be $(0.66 \pm 0.07) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and

TABLE 5: Room-Temperature Rate Constant for the Reaction of Chlorine Atoms with Ethene at Total Pressures of 1 Torr and 1 atm

k (cm^3 $molecule^{-1}$ s^{-1})	T (K)	total pressure/carrier gas	reference
$(1.17 \pm 0.03) \times 10^{-10}$	296	1 atm (air)	Atkinson and Aschmann[19] [a]
$(1.17 \pm 0.07) \times 10^{-10}$	295	1 atm (air)	Wallington et al.[20]
$(0.95 \pm 0.06) \times 10^{-10}$	295	740 Torr (air)	Wallington et al.[21]
$(1.00^{+0.47}{}_{-0.12}) \times 10^{-10}$	295	1 atm (air)	Kaiser and Wallington[26]
$(1.08 \pm 0.03) \times 10^{-10}$	298	1 atm (N_2)	Kaiser and Wallington[30] [b]
$(0.99 \pm 0.11) \times 10^{-10}$	298	1 atm (air, N_2)	this work
$(4.97 \pm 0.2) \times 10^{-13}$	297	1 Torr (N_2)	Kaiser and Wallington[30] [b]
$(3.0 \pm 0.3) \times 10^{-13}$	297	1 Torr (He)	Kaiser and Wallington[30] [b]
$(3.3 \pm 0.4) \times 10^{-13}$	298	1 Torr (He)	Le Bras et al.[28]
$(3.3 \pm 0.6) \times 10^{-13}$	298	1 Torr (He)	this work

[a] Corrected to a rate constant for Cl + *n*-butane of 2.18×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[13] [b] Using values for $k_0 = 1.65 \times 10^{-29}$ cm^6 $molecule^{-2}$ s^{-1} in N_2, $k_0 = 1.0 \times 10^{-29}$ cm^6 $molecule^{-2}$ s^{-1} in He, and $k_\infty = 3.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.[30]

that due to the two methylene groups is $(1.6 \pm 0.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

If it is assumed that deuteration of the methyl groups results in a reduced rate constant by a factor of 2.89 ± 0.08 as reported by Dobis et al.[57] for the ethane reaction, then the contribution of these methyl groups to the rate constant for the n-C_4D_{10} reaction must be $(0.66 \times 10^{-10}/2.89)$, or $(0.23 \pm 0.02) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Using $k(Cl + n\text{-}C_4D_{10}) = (1.6 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (Table 4), the contribution of the ($-CD_2CD_2-$) group must be $(1.4 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Thus the KIE for abstraction of the secondary hydrogen atoms in *n*-butane is $1.6/1.4 = 1.2 \pm 0.2$.

Kinetic isotope effects for abstraction originate primarily in zero-point energy (E_0) differences. As discussed by Melander and Saunders,[58] the most important factor for hydrogen isotope effects such as that measured for the chlorine atom reaction with *n*-butane is the energy term

$$\frac{k_H}{k_D} \propto \exp\left\{-\frac{1}{2}\left[\sum_{i}^{3N^{\ddagger}-7}(u^{\ddagger}_{i,H} - u^{\ddagger}_{i,D}) - \sum_{i}^{3N-6}(u_{i,H} - u_{i,D})\right]\right\} \qquad \text{(III)}$$

In eq III, $u_i = h\nu_i/kT$, where ν_i are the vibrational frequencies and k is the Boltzmann constant. The first term represents the transition-state energy differences between the H and D isomers, while the second term represents the differences in the reactant ground states, and $N^{\ddagger}$ and N are the number of atoms in the transition state and ground state, respectively.

The simplest case is that of a dissociating C$-$H(D) bond. Consider a molecule that has a stretching mode at ∼3000 cm^{-1} for C$-$H and at 2200 cm^{-1} for C$-$D (which becomes the reaction coordinate) and a number of bending modes. If the bending modes do not change in the transition state, the terms corresponding to these modes in eq III cancel out, leaving only the term corresponding to the stretching mode in the reactant uncancelled. Then k^H/k^D is determined by $\exp[1/2\{hc(3000)/kT - hc(2200)/kT\}] = 7$.

For abstraction of secondary hydrogen atoms from n-C_4H_{10}, the experiments reported here show the KIE is quite small, suggesting that contributions from vibrational modes (e.g., bending) other than the stretching mode may play a role in the reaction and hence contribute to the difference in terms in eq III.

B. Reactions with Alkenes. As expected for a reaction that proceeds mainly by addition, the rate constants increase with the size of the reactants at 1 Torr total pressure (Tables 1 and 2). The increase is due to greater numbers of vibrational degrees of freedom over which the excess energy in the adduct can be spread. The rate constants also increase with total pressure, with that for ethene increasing by more than 2 orders of magnitude from 1 Torr to 1 atm. On the other hand, the rate constants at 1 Torr for the C_4 and larger alkenes are within a factor of approximately 2 of their values at 1 atm (Tables 1−3). The results for specific alkenes are discussed in the following.

Ethene. There have been a number of previous studies of the reaction of chlorine atoms with ethene.[14−31] Table 5 summarizes the kinetics studies carried out under conditions closest in pressure and temperature to those reported here.

As discussed in detail elsewhere,[29,43] the observed increase in the rate constant upon deuteration of ethene, i.e., an *inverse* kinetic isotope effect, is consistent with the known pressure dependence[26,30] of the $Cl + C_2H_4$ reaction and the increase in the density of vibrational states in the C_2D_4Cl adduct. At 1 Torr, the reaction is in the low-pressure limit, and even at 1 atm, the high-pressure limit has not been reached. Deuteration increases the lifetime of the excited adduct with respect to decomposition (reaction −3) back to reactants, so that collisional stabilization (reaction 4) becomes relatively more important.

This effect can be shown to be quantitatively consistent with our measured KIE for the ethene reaction. Thus, the effective bimolecular rate constant can be calculated in the falloff region from eq IV:[12,59−61]

$$k = \frac{k_0[M]}{1 + \dfrac{k_0[M]}{k_\infty}} F_{cent}^{\{1+[\log(k_0[M]/k_\infty)]^2\}^{-1}} \qquad \text{(IV)}$$

Using a low pressure limiting rate constant for the $Cl + C_2H_4$ reaction of $k_0 = (1.65 \pm 0.05) \times 10^{-29}$ cm^6 $molecule^{-2}$ s^{-1} in N_2 for $F_{cent} = 0.6$ and $k_\infty = (3.2 \pm 0.15) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature,[30] the rate constant at 1 atm is calculated to be $(1.08 \pm 0.03) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. This is in excellent agreement with the value of $(0.99 \pm 0.11) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} measured here (Table 5).

Deuteration increases k_0 by a factor that can be calculated using unimolecular rate theory. The ratio of the limiting low-pressure rate constants for unimolecular decomposition is given[59−61] by eq V:

$$\frac{k_0(C_2D_4)}{k_0(C_2H_4)} = \frac{\left[\dfrac{\rho_{vib}(E_0)}{Q_{vib}}\right]_{C_2D_4}}{\left[\dfrac{\rho_{vib}(E_0)}{Q_{vib}}\right]_{C_2H_4}} \frac{[F_E F_{ROT} F_{ROT-INT}]_{C2D4}}{[F_E F_{ROT} F_{ROT-INT}]_{C2H4}} \qquad \text{(V)}$$

This also provides the ratio of the low-pressure addition rate constants, $k_0(Cl + C_2H_4)/k_0(Cl + C_2D_4)$, for the exothermic chlorine atom reactions, where the excess energy in the adduct is derived from the reaction exothermicity.[62] In eq V, ρ_{vib} is

TABLE 6: Some Literature Values for the Room Temperature Rate Constant for the Reaction of Chlorine Atoms with Propene, Isoprene, and 1,3-Butadiene at Total Pressures of 1 Torr and 1 atm

organic	k (cm^3 molecule^{-1} s^{-1})	T (K)	total pressure/carrier gas	reference
propene	$(2.70 \pm 0.09) \times 10^{-10\,a}$	296	1 atm (air)	Atkinson and Aschmann[19]
	$(3.12 \pm 0.13) \times 10^{-10\,a}$	295	1 atm (air)	Wallington et al.[20]
	$(2.5 \pm 0.5) \times 10^{-10\,b}$	298	1 atm (N_2)	Kaiser and Wallington[35]
	$(2.3 \pm 0.3) \times 10^{-10}$	298	1 atm (air, N_2)	this work
	$(4.7 \pm 0.3) \times 10^{-11\,b}$	298	1 Torr (N_2)	Kaiser and Wallington[35]
	$(6.0 \pm 0.8) \times 10^{-11}$	298	0.48−0.94 Torr (He)	Le Bras et al.[28]
	$(4.6 \pm 0.3) \times 10^{-11}$	298	1 Torr (He)	this work
	$(4.7 \pm 1.1) \times 10^{-11}$	298	1 Torr (N_2)	this work
isoprene	$(4.6 \pm 0.5) \times 10^{-10}$	298	1 atm (air, N_2)	Ragains and Finlayson-Pitts[38]
	5.5×10^{-10}	298	1 atm (air)	Bierbach et al.[39]
	$(5.5 \pm 0.4) \times 10^{-10}$	298	1 atm (N_2)	Barnes et al.[41]
	$(2.8 \pm 0.7) \times 10^{-10}$	298	k_∞	Bedjanian et al.[40]
	$(3.46 \pm 0.40) \times 10^{-10}$	298	0.58 Torr (air)	Ragains and Finlayson-Pitts[38]
	$(3.6 \pm 0.5) \times 10^{-10}$	298	0.25-3 Torr (He)	Bedjanian et al.[40]
	$(3.61 \pm 0.10) \times 10^{-10}$	298	15-60 Torr (He)	Notario et al.[42]
	$(3.7 \pm 1.0) \times 10^{-10}$	293	1 Torr (He)	this work
1,3-butadiene	$(4.2 \pm 0.4) \times 10^{-10}$	298	1 atm (air, N_2)	Ragains and Finlayson-Pitts[38]
	5.6×10^{-10}	298	1 atm (air)	Bierbach et al.[39]
	$(5.6 \pm 0.4) \times 10^{-10}$	298	1 atm (N_2)	Barnes et al.[41]
	$(3.48 \pm 0.10) \times 10^{-10}$	298	15-60 Torr (He)	Notario et al.[42]
	$(2.5 \pm 0.4) \times 10^{-10}$	293	1 Torr (He)	this work

[a] Corrected to a rate constant for Cl + *n*-butane of 2.18×10^{-10} cm^3 molecule^{-1} s^{-1}.[11,13] [b] Calculated using $F_{cent} = 0.6$, $k_0 = (4.0 \pm 0.4) \times 10^{-28}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = (2.7 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and including the contribution from direct abstraction and addition-elimination (the latter only at 1 Torr).[35]

the harmonic oscillator density of states at the threshold dissociation energy, Q_{vib} is the vibrational partition function, F_E reflects the density of states energy dependence, F_{ROT} takes into account the rotational state dependence of the threshold energy and vibrational density of states, and $F_{ROT-INT}$ corrects for internal rotations in the molecule. The energy in the excited adduct can be calculated from the reaction enthalpy, where the heat of formation of the adduct can be derived using the group additivity approach described in detail by Benson.[62]

Using a value of 0.33 ± 0.09 for the kinetic isotope effect[29] at 1 Torr (Table 1), k_0 for C_2D_4 is calculated to be $(1.65 \times 10^{-29}/0.33) = (5.0 \pm 1.4) \times 10^{-29}$ cm^6 molecule^{-2} s^{-1}. The high-pressure limiting rate constant for the C_2D_4 reaction should be the same as for C_2H_4. Using these values of k_0 and k_∞, the rate constant for Cl + C_2D_4 at 1 atm is calculated to be $(1.7 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, within experimental error of our measured value of $(1.3 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The ratio of rate constants for Cl + C_2H_4 to that for Cl + C_2D_4 based on the recent values of k_0 and k_∞ is therefore calculated to be 0.62 ± 0.18. (This only changes by 5% if $F_{cent} = 0.4$ and the corresponding derived values[30] for k_0 and k_∞ are used.) This is in good agreement with the measured KIE at 1 atm of 0.74 ± 0.06 (Table 3).

Propene. There have been relatively few studies of the propene reaction.[19,20,32−37] The results reported here are compared in Table 6 to those carried out under similar conditions. They are generally in good agreement with previous studies of this reaction. Only one of the earliest studies[20] of the reaction at 1 atm is outside the error bars of our measurements, and the 1 Torr value of Le Bras et al.[28] in He is ∼30% larger than our FFDS value.

The reaction of Cl with propene involves a combination of addition, direct abstraction of an allylic hydrogen, and an addition−elimination. Kaiser and Wallington[35] report a net rate constant for HCl production at total pressures below 10 Torr of $(3.7 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. About 60% (2.3×10^{-11}) of this is attributed to direct abstraction, and the remainder (1.4×10^{-11}) to the addition−elimination path, which is quenched at higher pressures (see reactions 6a,b above). Table 7 summarizes these contributions as well as addition to the overall Cl + C_3H_6 rate constant at 298 K at 1 Torr and 1 atm.

The rate constant for the Cl + C_3D_6 reaction, which has not been reported previously, is expected to change from that for C_3H_6 due to two counterbalancing factors. First, the low-pressure limiting rate constant for addition (k_0) should increase with deuteration due to the increased lifetime of the excited adduct, as has been observed in the C_2H_4 reaction.[29] On the other hand, the rate constant for direct abstraction should decrease due to zero-point energy effects.

The effect of deuteration on the low-pressure limiting rate constant (k_0) can be estimated using eq V. Using group additivity rules described by Benson,[62] the heat of formation of the adduct was calculated to be +10.9 kcal mol^{-1}, giving a reaction exothermicity for addition of Cl to the terminal position of the double bond, and hence the amount of energy in the excited adduct, of 22.9 kcal mol^{-1}. The ratio ρ_{vib}/Q_{vib} was estimated using calculated vibrational frequencies for the adducts,[63] the Whitten-Rabinovitch approximation,[43,64] and the F factors as described by Troe.[61] This approach predicts a KIE for k_0(Cl + C_3H_6)/k_0 (Cl + C_3D_6) of 0.22.

The effect of deuteration on direct abstraction can be estimated using the value 2.89 ± 0.08, as measured by Dobis et al.[57] for ethane. Assuming there is no KIE for the addition−elimination path, the net rate constant for the C_3D_6 reaction at 1 Torr is calculated to be $(5.6 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Table 7), in reasonable agreement with our values of $(4.3 \pm 1.0) \times 10^{-11}$ and $(4.1 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} in N_2 and He, respectively. The predicted KIE is 0.84 ± 0.10, in agreement with our value of 1.1 ± 0.2 from the FFDS studies (Table 1) and 1.1 ± 0.3 from the RR studies (Table 2).

The assumption that the KIE for direct abstraction from the methyl group in propene is the same as that in ethane may not be strictly valid since the methyl hydrogens in propene are allylic. In addition, it is not known whether the KIE will be unity for the addition−elimination path, although this is the case for the Cl + C_2H_5 reaction, which proceeds by recombination-elimination.[57] Further evidence for this is found in the results presented here; if the addition−elimination path had an inverse

TABLE 7: Calculated Contributions to the Overall Rate Constant for the Cl + $C_3H_6(C_3D_6)$ Reactions at Room Temperature from Addition, Direct Abstraction and Addition−Elimination

total pressure	process	contribution to rate constant for C_3H_6 (cm^3 molecule^{-1} s^{-1})[a]	contribution to rate constant for C_3D_6 (cm^3 molecule^{-1} s^{-1})
1 Torr	addition	$(1.0 \pm 0.1) \times 10^{-11}$	$(3.4 \pm 0.3) \times 10^{-11}$ [b]
	direct abstraction	$(2.3 \pm 0.3) \times 10^{-11}$	$(0.8 \pm 0.1) \times 10^{-11}$ [c]
	addition-elimination	$(1.4 \pm 0.4) \times 10^{-11}$	$(1.4 \pm 0.4) \times 10^{-11}$ [d]
	overall rate constant:	$(4.7 \pm 0.3) \times 10^{-11}$	$(5.6 \pm 0.5) \times 10^{-11}$
1 atm	addition	$(2.3 \pm 0.3) \times 10^{-10}$	$(2.5 \pm 0.4) \times 10^{-10}$ [b]
	direct abstraction	$(2.3 \pm 0.3) \times 10^{-11}$	$(0.8 \pm 0.1) \times 10^{-11}$ [c]
	addition-elimination	0	0
	overall rate constant:	$(2.5 \pm 0.3) \times 10^{-10}$	$(2.6 \pm 0.4) \times 10^{-10}$

[a] Calculated using the low- and high-pressure limiting rate constants of Kaiser and Wallington[35] of $k_0 = (4.0 \pm 0.4) \times 10^{-28}$ cm^6 molecule^{-2} s^{-1} and $k_\infty = (2.7 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for $F_{cent} = 0.6$ and their estimates for the contributions from direct abstraction and addition−elimination. [b] Calculated using $k_0(Cl + C_3D_6) = 4.5k_0(Cl + C_3H_6)$ as described in the text and no change in k_∞. [c] Assuming a direct KIE of 2.89 as measured for ethane by Dobis et al.,[57] i.e., $k_{abst} = (2.3 \times 10^{-11})/2.89$. [d] Assuming KIE = 1.

KIE of 0.3 as calculated for the addition path at 1 Torr, an overall rate constant of $(0.9 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} would be predicted, a factor of 2 greater than that measured here.

Our measured rate constant at 1 atm pressure, $(2.3 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, is close to the reported[35] high-pressure limiting rate constant $k_\infty = 2.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and to a rate constant of $(5 \pm 3.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} measured recently[37] at 1000−4000 Torr in $CClF_3$. Thus, the addition process dominates (Table 7), and as a result, a KIE of 0.96 ± 0.19 is expected, in agreement with our observations. It is also in agreement with a KIE of unity measured recently at high pressures.[37]

C_4 and C_5 Alkenes. Table 6 also compares reported rate constants for the isoprene and 1,3-butadiene reactions with those measured here and in earlier studies in this laboratory.[38] Our rate constants at 1 atm for 1,3-butadiene and isoprene are about 20−25% smaller than those of Bierbach et al.[39] and unpublished results of Barnes et al.[41] Our rate constant for 1,3-butadiene at 1 Torr in He is significantly smaller than that of Notario et al.[42] in the 15−60 Torr region, over which they report the rate constant does not change. Our atmospheric pressure rate constant for the 1-butene reaction, $(2.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, is significantly smaller than the value of 4.0×10^{-10} cm^3 molecule^{-1} s^{-1} of Barnes et al.[41] The reason for these discrepancies is not clear.

Although our low-pressure rate constant for isoprene is in excellent agreement with the recent work of Bedjanian et al.[40] and Notario et al.,[42] there are some discrepancies between the results of those studies and the measurements from this laboratory. In contrast to our earlier work,[38] Bedjanian et al.[40] and Notario et al.[42] observe no pressure dependence of the isoprene reaction over the pressure range from 0.25 to 60 Torr and hence conclude that the reaction is in the high-pressure limit at these pressures. Bedjanian et al.[40] derive a high-pressure limiting rate constant $k_\infty = (2.8 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This is significantly smaller than the overall rate constant of $(4.6 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} measured at 1 atm in earlier studies in this laboratory.[38] Taking into account that 15% of the reaction at 1 atm is due to abstraction, our earlier studies suggest that $k_\infty \geq (3.9 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, 40% larger than the Bedjanian et al.[40] value.

C. Comparison to OH Reactions. Since the hydroxyl radical reactions with simple alkenes proceed by a similar electrophilic addition mechanism, one might expect the rate constants for the reactions of chlorine atoms to be related to those of the corresponding OH reactions. Figure 4 shows a plot of the rate constants for the chlorine atom reactions with ethene through isoprene versus the corresponding rate constants for OH reactions at 1 atm total pressure. As expected, there is an approximately linear relationship. The falloff at the higher rate constants is likely due to the chlorine atom reactions approaching the collision-controlled limit.

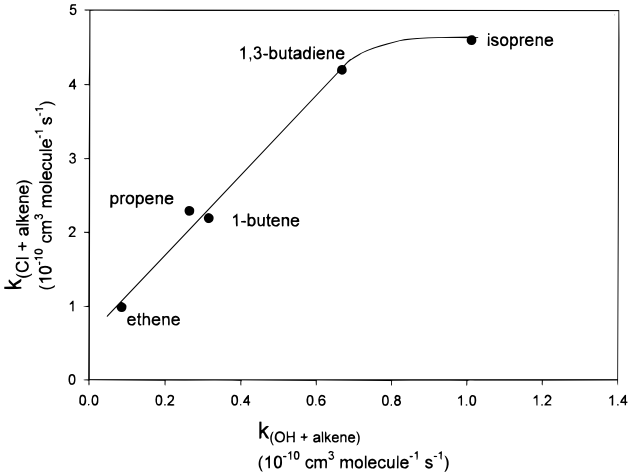

Figure 4. Relationship between Cl and OH rate constants for their reactions with simple alkenes at 1 atm total pressure.

Kinetic isotope effects have also been investigated by other laboratories in the reaction of OH with ethene and propene. In the low-pressure regime, an inverse KIE of 3 has been reported for the OH reaction with C_2H_4,[65] essentially the same as that measured in this laboratory for the chlorine atom reaction. At 1 atm total pressure and 343−563 K, the KIE for the OH reactions with C_2H_4/C_2D_4 is unity.[66] Similarly, the ratio at room temperature and 700 Torr has been reported to be 0.97 ± 0.06.[67] This is not surprising since the OH + C_2H_4 reaction at 1 atm is close to its high-pressure limit, whereas the Cl + C_2H_4 rate constant at 1 atm is still a factor of 3 smaller than the high-pressure limiting value. A KIE of unity has also been reported for the OH + C_3H_6 reaction at 293 K and total pressures of 200−400 Torr in He.[68]

D. Atmospheric Implications. Emission of alkenes occurs both from anthropogenic activities[69] and from marine phytoplankton.[70,71] At 1 atm pressure, all of the alkene reactions are very fast, $\geq 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The chlorine atom concentration is expected to peak at dawn, much earlier than OH or O_3. The peak chlorine atom concentration has been predicted[8,9] to be $\sim 1 \times 10^5$ atoms cm^{-3}, about an order of magnitude smaller than the simultaneous OH concentration.[8,72] The calculated lifetimes ($\tau = 1/k[X]$ where X = Cl, OH, or O_3) of C_2H_4 with respect to chlorine atoms at a concentration of 1×10^5 atoms cm^{-3}, OH at 1×10^6 radicals cm^{-3}, and O_3 at 40 ppb are 28, 33, and 178 h, respectively. (Nitrate radicals photolyze rapidly at dawn and hence do not compete.) In short, chlorine atom chemistry is expected to play a significant role in the reactions of alkenes at dawn both in the marine boundary layer and in coastal regions.

Conclusions

The kinetics of the reaction of chlorine atoms with n-C_4H_{10}, n-C_4D_{10}, and a series of simple C_2-C_5 alkenes have been measured at room temperature. Rate constants measured here are generally in good agreement with available literature values. The exceptions are isoprene, where an earlier value[38] from this laboratory for the addition process at 1 atm is 40% larger than the high-pressure limiting rate constant reported recently by Bedjanian et al.,[40] and 1-butene, where the value reported here at 1 atm is about half that of Barnes et al.[41]

The butane reaction proceeds by direct abstraction of a hydrogen atom. A normal kinetic isotope effect, KIE $= k^H/k^D$, of 1.4 ± 0.2 for this reaction arises from zero-point energy effects. For the alkenes, however, there are three potential reaction pathways that contribute to the overall reaction mechanism: addition to the double bond, direct abstraction of a hydrogen atom, and an addition−elimination process which also forms HCl. Deuteration has two effects on these pathways. The low-pressure limiting rate constant for addition to the double bond increases, an *inverse* KIE, by increasing the lifetime of the excited adduct with respect to decomposition back to reactants. This effect dominates in the ethene reaction, where the rate constant for C_2D_4 is a factor of three greater than that for C_2H_4 at 1 Torr and 35% greater at 1 atm. The second effect of deuteration is a slowing of direct abstraction due to zero point energy effects. In the propene reaction at low pressures, this partially counteracts the inverse KIE for the addition process, leading to no significant difference between the C_3H_6 and C_3D_6 rate constants.

Even at 1 Torr, the C_4 and C_5 alkenes are sufficiently close to their high-pressure limits that a significant KIE is not expected for addition. If direct abstraction is a minor pathway, no significant effects of deuteration on the overall rate constants are anticipated. This is in agreement with our measurements, where the KIEs are all within experimental error of unity for these compounds.

On the basis of the rate constants at 1 atm, the reaction of alkenes with chlorine atoms is expected to play a role in the tropospheric chemistry at dawn in the marine boundary layer and in coastal regions.

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