Infrared Absorption Probing of the Cl + C_2H_4 Reaction: Direct Measurement of Arrhenius Parameters for Hydrogen Abstraction

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The laser photolysis/infrared long path absorption technique has been used to study the reaction of Cl atoms with C_2H_4. The time-resolved population of HCl produced in the reaction is monitored by continuous infrared absorption after pulsed photolytic generation of Cl atoms. At room temperature, the reaction proceeds principally through addition to form a chloroethyl radical, and the HCl production at 10 Torr is almost exclusively via secondary reactions. Above 500 K the abstraction channel dominates the HCl production, allowing direct extraction of Arrhenius parameters for the hydrogen abstraction. The abstraction rates are extracted by correcting the total rate by the HCl yield, which is determined by comparison with the Cl + C_3H_8 reaction. The abstraction reaction is well-described between 500 and 800 K by the simple Arrhenius expression $k(T) = (6.2 \pm 1.4) \times 10^{-11} e^{-(3400\pm450)/T}$ cm^3 molecule^{-1} s^{-1} (2σ). The activation energy determined in the present work would yield a heat of formation of the vinyl radical of $\Delta H^\circ_{f,298}(C_2H_3) = 71.3 \pm 1.3$ kcal mol^{-1} when combined with an extrapolation of published 298−495 K measurements of the HCl + C_2H_3 activation energy. A third-law analysis at 500 K yields $\Delta H^\circ_{f,298}(C_2H_3) = 71.6 \pm 0.3$ kcal mol^{-1}.

Introduction

Knowledge of Cl reaction rates with hydrocarbons at elevated temperatures is necessary for modeling the formation of chlorinated species in waste incineration and in combustion of chlorine-containing fuel contaminants.[1] The abstraction of hydrogen by chlorine atoms is the initiation step in chlorination chain reactions and is thought to be responsible for Cl action in promotion of sooting and polycyclic aromatic hydrocarbon (PAH) production.[2,3] The reaction of chlorine atoms with ethylene is a prototype for halogen reactions with alkenes. Chlorine atom reactions with alkenes are characterized by a competition between abstraction to form HCl and an alkenyl radical and addition to form a haloalkyl radical, e.g., for Cl + ethylene:

$$\mathrm{Cl} + \mathrm{C_2H_4} \xrightarrow{k_1} \mathrm{C_2H_3} + \mathrm{HCl} \tag{1}$$

$$\mathrm{Cl} + \mathrm{C_2H_4}\ (+\mathrm{M}) \xrightarrow{k_2([\mathrm{M}])} \mathrm{C_2H_4Cl}\ (+\mathrm{M}) \tag{2}$$

Characterization of the abstraction channel in these reactions is of additional interest because of the relationship to the heats of formation of important radical species.[4] The reaction of Cl with ethylene is notable in this respect, since hydrogen abstraction produces the vinyl radical.

The vinyl radical is an important species in hydrocarbon combustion, and its heat of formation is a critical quantity for accurate modeling of combustion processes. Previous determinations of $\Delta H^\circ_{f,298}(C_2H_3)$ have largely fallen into two groups. Kinetics determinations, many based on the measurements of Cl + C_2H_4 rate coefficients by Benson and co-workers,[5−7] have produced values for the heat of formation of the vinyl radical between 64 and 67 kcal mol^{-1}. However, spectroscopic measurements of the C−H bond energy in ethylene yield heats of formation nearer 72 kcal mol^{-1}.[4,8] A step toward bridging this long-standing discrepancy was made in the past year by Kaiser and Wallington, who studied the Cl + C_2H_4 reaction as a function of pressure.[9] Using determinations of product yields, they were able to make an estimate of the abstraction rate. Their results produce heats of formation that agree with the spectroscopic determinations to within their experimental error. In addition, recent work by Knyazev and Slagle on the unimolecular decomposition of C_2H_3 yields $\Delta H^\circ_{f,298}(C_2H_3)$ of 71.4 ± 1.6 kcal mol^{-1}.[10] In this work we describe experiments to measure the rate coefficient for the abstraction channel of Cl + C_2H_4 at high temperatures, where the contributions of the addition reaction can be minimized.

The present investigations use the technique of laser photolysis/infrared long-path absorption (LP/IRLPA) to measure reaction rate coefficients for Cl + ethylene as a function of temperature. At temperatures below 500 K, the reaction is dominated by addition (2) to form a chloroethyl radical, and the production of HCl is principally via secondary reactions such as the reaction of chloroethyl with Cl,

$$\mathrm{Cl} + \mathrm{C_2H_4Cl} \xrightarrow{k_3} \mathrm{HCl} + \mathrm{C_2H_3Cl} \tag{3}$$

However, at higher temperatures the addition reaction is less important, and the abstraction reaction (1) can be studied directly. The determination of the forward reaction temperature dependence in this study allows a direct measurement of the activation energy of the reaction. Using an extrapolation of lower temperature results for the HCl + C_2H_3 reaction,[11] the present measurements offer additional experimental evidence for a value of $\Delta H^\circ_{f,298}(C_2H_3) \sim 71.6$ kcal mol^{-1}. While a more precise determination of the vinyl radical heat of formation may be possible when rate data for the reverse reaction becomes available at a higher temperature range, the discrepancy between kinetic and spectroscopic determinations of $\Delta H^\circ_{f,298}(C_2H_3)$ appears to have been removed.

Experiment

Apparatus. In the present work the technique of laser photolysis/continuous-wave infrared long path absorption, LP/

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CWIRLPA,[12−15] is used to obtain absolute reaction rates for the reaction Cl + ethylene. Chlorine atoms are generated by excimer laser photolysis of CF_2Cl_2 or CCl_4 using the 193 nm ArF line, and the progress of the reaction is monitored via time-resolved absorption of a CW infrared (IR) laser by the HCl reaction product. The reaction takes place in a stainless steel slow flow reactor about 1 m long and 5 cm in diameter. The linear flow velocities in these experiments are kept high enough to provide a fresh reaction mixture every 1−2 photolysis laser shots while remaining essentially static on the time scale of the kinetics. At the temperatures (292−800 K) and pressures (5−10 Torr) in these experiments, this constrained the excimer laser repetition rate to ≤2 Hz. Ar buffer gas, the photolytic precursor, and the ethylene reactant enter the reactor through separate calibrated mass flow controllers. The ethylene reactant ((0.5−3) × 10^{15} molecules cm^{-3}) is present in great excess over the Cl atoms (∼5 × 10^{12} molecules cm^{-3}), maintaining pseudo-first-order kinetic conditions. The bulk of the gas flow is Ar buffer gas, which ensures rapid thermal equilibration of the photolytically produced Cl atoms at the pressures used in these experiments.

Tunable infrared laser light is produced by difference frequency mixing (DFM). The outputs of a single-frequency argon ion laser at 514.5 nm and single-frequency ring dye laser (Rhodamine 6G dye) are combined in a temperature-tuned $LiNbO_3$ crystal.[16] About 6 μW of tunable IR around 3.3 μm is produced from 500 mW Ar^+ and 600 mW dye laser input power. The relative HCl concentration is measured by the absorption on the R(2) line of the $H^{35}Cl$ fundamental vibrational transition. The infrared laser is tuned to this transition by monitoring the absorption through an HCl reference cell. The IR probe laser beam is split into reference and signal beams of approximately equal intensity. The reference beam passes through a polarizer and onto an InSb detector, and the signal beam traverses the flow cell and is imaged onto another InSb detector. Adjustment of the IR polarizer before the reference cell is used to balance the incident power on the two detectors. The output of the reference detector is subtracted from that of the signal detector in a differential amplifier, digitized in a digital oscilloscope, and transferred to a microcomputer for storage and analysis.

The detection sensitivity of the infrared absorption technique is enhanced by employing a modified Herriott-type multipass cell.[17−19] The Herriott design uses off-axis paths in a spherical resonator, the mirrors of which form the windows of the reactor cell in our apparatus. The excimer beam is telescoped and apertured to a diameter of 20 mm and sent through the uncoated center section of the spherical mirrors, along the resonator axis. This optical arrangement effectively confines the region of pump−probe overlap to the center of the cell, where the temperature profile is flat and controllable. The temperature in the overlap region is maintained to within ±3 K by three microprocessor-controlled heaters with individual thermocouple feedback. In the present optical arrangement the probe beam makes 41 passes through the cell, giving almost 16 m of path length in the temperature-controlled region with a negligible contribution from the cooler areas near the cell ends.

Kinetic Analysis. The experimental signal consists of a time-resolved absorption trace which is proportional to the time-varying concentration of the HCl reaction product. Since the Cl + C_2H_4 reaction is endothermic and the Boltzmann fraction of HCl(v=1) is less than 1% at the temperatures of these experiments, no correction is necessary for production of HCl in the vibrationally excited state. For a pure abstraction reaction (1) the rate of HCl production is identical to the Cl disappearance rate. The time behavior of the Cl and HCl concentration is then given by the simple expressions

$$[\mathrm{Cl}]_t = [\mathrm{Cl}]_0 e^{-k_1[\mathrm{C_2H_4}]t} \qquad (4a)$$

$$[\mathrm{HCl}]_t = [\mathrm{Cl}]_0(1 - e^{-k_1[\mathrm{C_2H_4}]t}) \qquad (4b)$$

For a competition between addition and abstraction, reactions 1 and 2, the functional form of the kinetics equations is similar. However, the apparent rate constant will now be the sum of the rates for the two reactions, one of which (k_2) will depend on the total pressure. In the present experiments, especially at higher temperatures, redissociation of the chloroethyl radical may contribute to the kinetics.[20,21] The initially formed adduct should correspond to the 2-chloroethyl radical, CH_2CH_2Cl, whose decomposition by C−Cl bond fission has been estimated by Barat and Bozzelli as 3.9 × 10^{13} exp[−10919/T] s^{-1}, or more than 12 000 s^{-1} at 500 K.[20] The thermal decomposition of the more stable 1-chloroethyl radical CH_3CHCl is negligible under the conditions of the present study.[22] Since a sizable barrier exists to the 1,2-hydrogen shift that effects the isomerization between the two radicals, production of the 1-chloroethyl radical from Cl + C_2H_4 would presumably have to proceed by tunneling in the present experiments. Additionally, reactions of the chloroethyl adduct may compete with stabilization and redissociation. In general, the kinetics scheme for the competition between addition and abstraction should take all of these possible processes into account:

$$\mathrm{Cl + C_2H_4} \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} \mathrm{CH_2CH_2Cl^{\#}} \underset{k_{-s}([M])}{\overset{k_s([M])}{\rightleftarrows}} \mathrm{CH_2CH_2Cl}$$

$$\xrightarrow{k_r} \text{products}$$

$$\mathrm{Cl + C_2H_4} \xrightarrow{k_1} \mathrm{CH_2CH + HCl} \qquad (5)$$

Here the rate coefficient k_r is an effective total rate coefficient for the removal of the (excited) CH_2CH_2Cl adduct. If we use a Lindemann mechanism to split the phenomenological addition rate coefficient into constituent steps, as above, the resulting [Cl] and [HCl] time behavior will be biexponential, with time constants which are relatively complicated functions of the individual rate coefficients. However, at higher temperatures where thermal decomposition of the 2-chloroethyl radical to Cl + C_2H_4 is rapid,[20,21] a steady-state approximation can be made for [CH_2CH_2Cl]. In this case the time behavior is once again single-exponential

$$[\mathrm{Cl}]_t = [\mathrm{Cl}]_0 e^{-(k_1+k_2')[\mathrm{C_2H_4}]t} \qquad (6a)$$

$$[\mathrm{HCl}]_t = \frac{k_1[\mathrm{Cl}]_0}{k_1 + k_2'}(1 - e^{-(k_1+k_2')[\mathrm{C_2H_4}]t}) \qquad (6b)$$

where the composite rate coefficient $k_2' = k_a k_r/(k_{-a} + k_r)$, which may depend on total pressure, can now be viewed as an effective rate coefficient for all reactions of Cl atoms which produce no HCl, including addition followed by either tunneling or removal of the chloroethyl by subsequent reaction.

Expression 6b is used to fit the HCl time profiles in these experiments. The sum of rate coefficients, $k_1 + k_2'$, is extracted from the slope of a plot of the observed pseudo-first-order rate coefficients vs C_2H_4 concentration in the customary way. It should be noted that while the observed time behavior in these experiments is exponential, the HCl yield is not unity. Since HCl is a primary product of the abstraction reaction, where abstraction is significant the time behavior of the HCl production

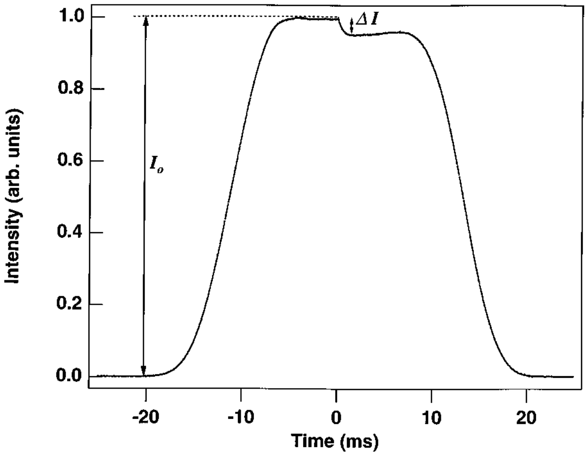

Figure 1. Schematic depiction of the method used for determination of the HCl yield. A sample data trace is shown for Cl + C_3H_8, using a chopped probe beam for clarity. The excimer is fired synchronously with the chopper so that the laser pulse ($t = 0$) arrives while the probe beam is unblocked. The $[HCl]_\infty$ absorption is calculated as the ratio of the final transient absorption (after correcting for diffusion), ΔI, to the transmitted intensity before the pump laser fires, I_0, which can be seen in the figure as the difference between the probe-on and probe-off levels of the chopped signal. Transient absorptions of $\leq$5% are typically used in these determinations.

reflects the total Cl atom removal rate. The abstraction rate coefficient k_1 is always obtained by multiplying the total rate coefficient by the HCl yield; from eq 6b, $\phi_{HCl} \equiv [HCl]_\infty/[Cl]_0 = k_1/(k_1 + k_2')$.

At lower temperatures, where addition dominates over abstraction, secondary reactions are the principal source of HCl, and the time behavior is nonexponential. One possible source of secondary HCl is the reaction of the chloroethyl radical with excess chlorine atoms, reaction 3. The differential equations for the kinetics of HCl formation via secondary reactions are nonlinear and have no analytical solution. Numerical integration is used to model the HCl production by secondary reactions.

Measurement of HCl Yield. The yield of HCl in the reaction, $\phi_{HCl} = [HCl]_\infty/[Cl]_0$, can be ascertained by comparison of the HCl signals from Cl + C_3H_8 ($\phi_{HCl} = 1$) under identical photolysis conditions. This is accomplished by flowing the two reactants through separate calibrated flow controllers and alternately measuring traces (100 shot average) with C_3H_8 and C_2H_4 as reactant, keeping the photolyte concentration constant. Figure 1 schematically depicts a typical measurement of the HCl yield, for $T = 550$ K and a total pressure of 5 Torr. The change in transmitted intensity after photolysis, ΔI, is compared for the two species, taking into account the difference in the initial total transmitted IR intensity, I_0, because of the differing absorbance of propane and ethylene at the probe wavelength. Several (4–8) measurements are made for each temperature and pressure.

Results

Since the present experiments probe a product of the Cl + C_2H_4 reaction, the time behavior of the absorption traces will be sensitive to the details of the reaction scheme. Time-resolved absorption traces taken at 292 and 600 K are shown in Figures 2 and 3. The two traces show a clear qualitative difference. At room temperature the addition channel is dominant,[23] and the HCl time behavior is a convolution of addition, adduct redissociation, and secondary radical–radical reaction rates. However, as the temperature increases, the abstraction reaction becomes important and the addition rate is reduced, so that above 550 K the production of HCl is largely governed by the abstraction rate. The relative importance of the abstraction rate can be ascertained by measuring the HCl yield of the reaction. For $T = 800$ K, where the addition reaction is essentially absent, $\phi_{HCl} = 1$. As the temperature decreases the HCl yield drops, and at 292 K ϕ_{HCl} has fallen to $\leq$0.1.

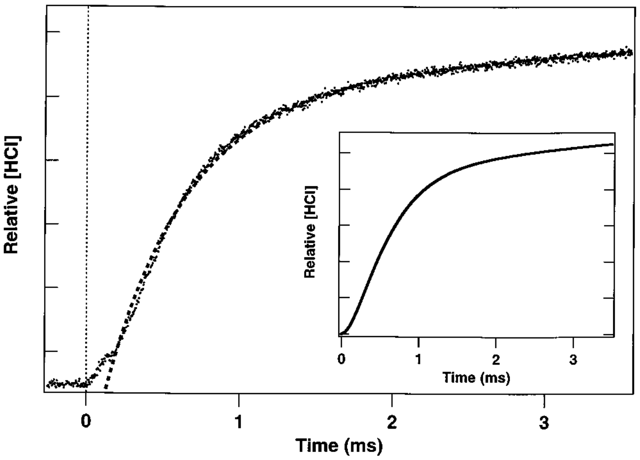

Figure 2. Time trace showing evolution of the HCl reaction product at 292 K and 10 Torr, demonstrating nonexponential behavior due to the Cl + C_2H_4 association reaction and HCl formation by secondary reactions. The dashed line is the best-fit biexponential, which would be the functional form if the HCl were produced by a competition between abstraction and addition. The time behavior of the HCl concentration suggests that the secondary reaction, perhaps the radical–radical reaction between Cl and C_2H_4Cl, is fast. The inset shows a numerical integration of kinetic equations for production of HCl by secondary reactions of Cl with the chloroethyl adduct.

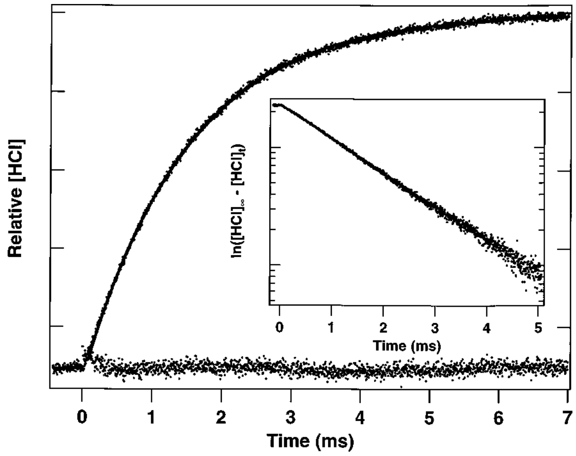

Figure 3. Plot of the time-resolved [HCl] from the Cl + C_2H_4 reaction at 600 K and 10 Torr total pressure, corrected for diffusion. The residuals to a simple exponential fit (×2) are shown below. The inset shows a logarithmic plot of $[HCl]_\infty - [HCl]_t$, demonstrating simple exponential behavior under these conditions.

An exponential fit is unable to describe the observed HCl time traces at temperatures below 500 K as a result of complications due to the addition channel. Reliable extraction of the abstraction rate coefficient depends on the ability to distinguish and eliminate the contributions of secondary reactions in the HCl time profile. Figure 2 shows the HCl time profile from Cl + C_2H_4 at 292 K and 10 Torr. If the Cl + ethylene reaction were described by two competitive reactive routes, addition and abstraction, including the possibility of redissociation of the C_2H_4Cl adduct to reactants, the evolution of the HCl reaction product would be biexponential. The data appear biexponential, but the sigmoidal behavior evident at short time indicates an induction period for the formation of HCl.

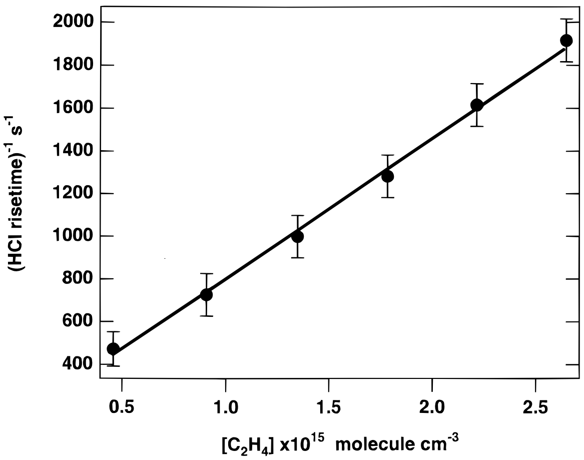

Figure 4. Typical plot of the extracted pseudo-first-order rate coefficient, ([HCl] rise time)$^{-1}$, vs [C_2H_4] for Cl reacting with ethylene at 700 K and 10 Torr. The second-order rate coefficient is given by the slope. The error limits represent ± 2σ and include statistical and estimated systematic contributions.

This observation is clearly inconsistent with a simple competition between addition and abstraction and implies a secondary reaction mechanism for HCl production, for example, via reaction 3.

Since abstraction reactions for Cl + hydrocarbons have preexponential factors of (1−2) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} per H atom (*vide infra*), and since reaction 3 is an exothermic radical−radical reaction, a rate coefficient $k_3 \sim 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} may not be unreasonable. The rate coefficient for the similar abstraction reaction of Cl + ethyl radicals has been reported to be between 1.2 × 10^{-11} and 3 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[24−26] Direct numerical integration of kinetic equations including reaction 3 confirms that the time behavior and the HCl yields from this mechanism are consistent with the observed data. The inset in Figure 2 shows the output of an integration of the differential equations for the kinetic system of reactions 2 and 3, with no contribution from direct abstraction, reaction 1. Because of the dependence of fitted rate coefficients on the poorly characterized initial Cl concentration in this system, a quantitative measurement of rate coefficients from the low-temperature HCl measurements is impractical. The data near room temperature are characteristic of HCl production by a secondary radical−radical reaction and suggest an extremely small abstraction rate at 292 K.

At higher temperature, as shown by the 600 K absorption trace in Figure 3, the HCl production shows simple exponential behavior, indicating a significant contribution from direct abstraction. The kinetics of the reaction at these temperatures are adequately described by eqs 6a and 6b. The second-order rate coefficients for the sum of the abstraction reaction and the addition reaction are measured directly for temperatures between 500 and 800 K by fitting a simple exponential to the absorption traces, after correcting for diffusion, and plotting the first-order rate constants as a function of ethylene concentration. A sample plot of ([HCl] rise time)$^{-1}$ vs [C_2H_4] is shown in Figure 4 for the Cl + C_2H_4 reaction at 700 K and 10 Torr. Whereas at room temperature the observed HCl time behavior shows a marked qualitative dependence on pressure down to a few Torr, above 500 K the measured rate coefficients at 5 and 10 Torr total pressure agree to within experimental error.

The possible contribution of secondary reactions of chloroethyl + Cl to the HCl time profile must still be considered. If the abstraction rate is significant, the time behavior can be exponential even in the presence of secondary reactions. A neglected contribution of reaction 3 would both increase the HCl production rate and artificially inflate the HCl yield, giving a measured k_1 greater than the true abstraction rate for $\phi_{HCl} < 1$. The measured activation energy would therefore be smaller than the true value. However, while the rate coefficient of the radical−radical reaction (3) could be large, the much larger concentration of C_2H_4 than C_2H_4Cl in the reaction mixture ensures that the Cl + C_2H_4 abstraction reaction (1) dominates HCl production at elevated temperatures for even modest values of k_1. In addition, the contribution of secondary reactions is further reduced by decreasing the initial Cl atom concentration. Data taken using CCl_4 and CF_2Cl_2, with estimated $[Cl]_0$ varying over a factor of 3, give identical Arrhenius parameters. No dependence of the rate coefficient or HCl yield on initial Cl atom concentration, to within ±10% experimental uncertainties, is observed above 500 K under the conditions of these experiments, confirming a negligible contribution from secondary reactions above 500 K.

The rate coefficients for the abstraction reaction are extracted by correcting the data for the measured HCl yields. The abstraction rate coefficient is given by the product of the yield and the observed rate coefficient, i.e., $k_1 = \phi_{HCl}(k_1 + k_2')$. The resulting rate coefficients are given in Table 1, and an Arrhenius plot is shown in Figure 5. The temperature dependence of the rate coefficient over this temperature range is well-described by a simple Arrhenius expression,

$$k_1(T) = (6.2 \pm 1.4) \times 10^{-11} e^{-3400 \pm 450/T} \tag{7}$$

where error values are ±2σ and indicate the precision of the fit.

Discussion

Rate Coefficient Determinations. Several previous measurements of the Cl + C_2H_4 reaction have been reported. The first measurements of the abstraction rate were carried out by Benson and co-workers.[5−7] They employed the very low-pressure reactor (VLPR) technique to study the abstraction reaction from 202 to 343 K. The reported room temperature (298 K) abstraction rate coefficient of (5.0 ± 0.2) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} is several orders of magnitude faster than that obtained by extrapolating our Arrhenius expression and is approximately the value measured at 700 K in the present work. Wallington and co-workers have recently performed an extensive investigation of this reaction system[9,23] which indicates that the abstraction reaction is considerably slower than reported by Benson. Wallington et al. measured the pressure dependence of the overall reaction rate coefficient between 0.2 and 3000 Torr and used a fit to the falloff curve and measurements of relative product concentrations to establish the rate for abstraction between 300 and 383 K. The abstraction rate coefficient reported by Kaiser and Wallington at their highest temperature, 383 K, is (1.16 ± 0.60) × 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, which is in good agreement with an extrapolation of the present Arrhenius fit.

Arrhenius parameters for the abstraction reaction have been previously measured by Dobis and Benson and by Kaiser and Wallington. The preexponential factor determined in the work of Dobis and Benson is 1.15 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, which is about 1.5 times larger than the present determination.[5] They obtained an activation energy of 3.2 kcal mol^{-1} (E_a/R = 1610 K), which is nearly 4 kcal mol^{-1} smaller than the present work. Kaiser and Wallington also measured the temperature dependence of the abstraction channel from 300 to 383 K.[9] The preexponential factor for the abstraction channel reported in that

TABLE 1: Measured Rate Coefficients for Cl + C_2H_4

	$k_1 + k_2'$ [a]		ϕ_{HCl} [b]		k_1 [a]	
T (K)	5 Torr	10 Torr	5 Torr	10 Torr	5 Torr	10 Torr
500	1.6 ± 0.2	1.6 ± 0.1	0.37 ± 0.05	0.38 ± 0.04	0.58 ± 0.10	0.67 ± 0.08
	1.9 ± 0.3				0.73 ± 0.15	
550	2.9 ± 0.4	2.0 ± 0.6	0.47 ± 0.06	0.51 ± 0.07	1.3 ± 0.2	1.0 ± 0.3
	4.3 ± 1.5				2.0 ± 0.7	
600	3.2 ± 1.0	2.9 ± 0.3	0.55 ± 0.05	0.49 ± 0.07	1.8 ± 0.5	1.4 ± 0.3
650	4.8 ± 0.8	4.3 ± 0.5	0.66 ± 0.06	0.64 ± 0.10	3.2 ± 0.6	2.7 ± 0.5
700	7.6 ± 1.8	5.4 ± 0.7	0.69 ± 0.05	0.77 ± 0.05	5.3 ± 1.3	4.1 ± 0.6
	6.5 ± 0.6	6.6 ± 1.0			4.5 ± 0.5	5.1 ± 0.6
750	7.0 ± 1.6	7.5 ± 2.6	0.85 ± 0.10	0.85 ± 0.09	6.0 ± 1.5	6 ± 2
800	11 ± 2	8.7 ± 2.4	0.98 ± 0.05	1.04 ± 0.06	11 ± 2	9 ± 3

[a] Units of 10^{-13} cm^3 molecule^{-1} s^{-1}; error bars are $\pm 2\sigma$ precision only. [b] $[HCl]_\infty/[Cl]_0$ determined by comparison with Cl + C_3H_8 (see text); error bars are $\pm 2\sigma$ and are based on statistical errors from repeated measurements and estimates of systematic errors.

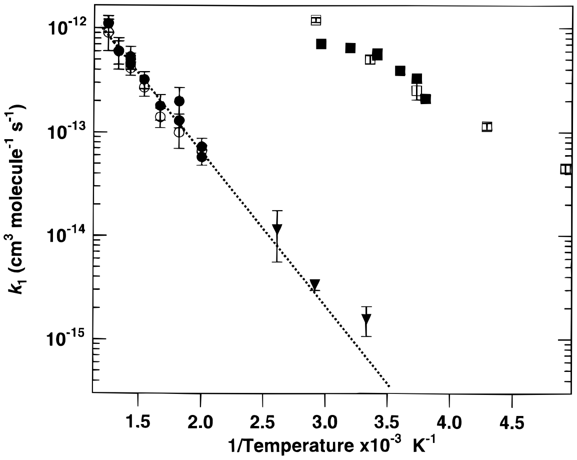

Figure 5. An Arrhenius plot of the abstraction rate data in Table 1. The data follow simple Arrhenius behavior between 500 and 800 K. The Arrhenius expression obtained for this temperature range is $k_1(T) = (6.2 \pm 1.4) \times 10^{-11} e^{-(3400 \pm 450)/T}$ cm^3 molecule^{-1} s^{-1}, given as the dashed line in the figure. The circles are the rate coefficients determined in the present work; solid circles represent data taken at 5 Torr total pressure, and open circles represent data taken at 10 Torr total pressure. Previous measurements of the temperature dependence of the abstraction rate coefficient are also given: triangles, Kaiser and Wallington (ref 9); open squares, Dobis and Benson (ref 6); solid squares, Parmar and Benson (ref 7).

work, $1.2^{+8}_{-0.9} \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, is considerably lower than the value determined in these experiments. Their activation energy of 5.43 ± 1.4 kcal mol^{-1} is about 1.5 kcal mol^{-1} smaller than the present value although the error bars of the respective determinations overlap. However, Kaiser and Wallington argued that a larger preexponential factor of approximately 6×10^{-11} cm^3 molecule^{-1} s^{-1} was warranted, based on comparison with other H atom abstraction reactions by Cl. Using this value, they arrive at an activation energy of 7.1 kcal mol^{-1}, which is in excellent agreement with the value determined at higher temperatures in the present work. The preexponential factor for H abstraction from hydrocarbons by Cl is typically $(1-2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} per H atom. For example, the abstraction reactions of Cl with ethane, propane, and *n*-butane have preexponential factors of 8.6×10^{-11}, 1.38×10^{-10}, and 1.8×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively.[15,27] The value for the preexponential measured in the present work is consistent with the values obtained in other Cl reactions with hydrocarbons.

Interestingly, where the abstraction reaction dominates the HCl production, i.e., above 500 K, the observed rate coefficients and the HCl yields are identical to within experimental error at 5 and 10 Torr total pressure. This observation is consistent with the proposed instability of the 2-chloroethyl radical at these temperatures.[20] The addition reaction is near the low-pressure limit under these circumstances, so if simple addition were responsible for the nonunity HCl yield, it might be expected that the phenomenological rate coefficient k_2' in eqs 6a and 6b would be linear in the total pressure. If the initially formed 2-chloroethyl radical is thermally unstable, another process besides collisional stabilization is necessary to remove the Cl atoms from the reaction mixture at higher temperatures. The similarity between the 5 and 10 Torr measurements may suggest that production of the more stable 1-chloroethyl radical, presumably by tunneling, contributes to Cl atom removal at these temperatures. The value of k_2' in these experiments is $(1-2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} between 500 and 700 K. The high-pressure limiting rate coefficient for the addition reaction has been estimated by Kaiser and Wallington, based on an extensive study of the pressure dependence of the Cl + C_2H_4 reaction, as $k_{2,\infty} = k_a = 3.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This indicates that, for approximately 3×10^{-4} of the collisions which form an excited C_2H_4Cl adduct, the adduct is removed either by subsequent reaction or by stabilization. Whether tunneling through the significant barrier (perhaps ~15 kcal mol^{-1} above the entrance channel)[20,22] to form CH_3CHCl is sufficient to remove ~10^{-4} of the Cl + C_2H_4 collisions is unclear. Other reactions of the excited chloroethyl radical could also produce a similar result. Since the aim of this work is to characterize the abstraction reaction, the nature of the non-HCl-producing channels is not investigated in these experiments. Statements about the mechanism of these channels must therefore remain somewhat speculative.

Heat of Formation of C_2H_3. One central motivation for the study of the abstraction reaction (1) is to determine the heat of formation of the vinyl radical. A long-standing discrepancy exists between kinetics-based measurements of $\Delta H°_{f,298}(C_2H_3) = 66.9 \pm 0.3$ kcal mol^{-1}, relying in part on the results of Benson and co-workers,[5-7] and photoelectron spectroscopic measurements of C_2H_3−H bond strengths by Ervin et al.,[8] which suggest $\Delta H°_{f,298} = 71.6 \pm 0.8$ kcal mol^{-1}. A step toward bridging this disagreement has been made by the work of Kaiser and Wallington, who were able to perform both second- and third-law determinations of the heat of formation. They reported $\Delta H°_{f,298}(C_2H_3) = 70.6 \pm 0.4$ kcal mol^{-1} using a third-law determination and $\Delta H°_{f,298}(C_2H_3) = 69.6 \pm 1.6$ kcal mol^{-1} by a second-law method,[9] based on their activation energy of 5.43 kcal mol^{-1} and the reverse-rate measurements of Russell et al.[11] While abstraction reactions of Cl with hydrocarbons typically show some non-Arrhenius behavior, the current measurements of the activation energy for the reaction at the higher temperatures clearly suggest closer agreement with the recent measurements of Kaiser and Wallington than with previous determinations.

Studies of the reverse reaction in a temperature range overlapping the present data would allow an independent assessment of the vinyl radical heat of formation. However, we can use an extrapolation of the lower temperature measurements of Russell et al. to estimate a value for the heat of formation of the vinyl radical based on the present direct measurements of the abstraction rate. Using their measurements of the reverse activation energy, 0.67 ± 0.27 kcal mol^{-1}, and the activation energy of 6.8 ± 0.9 kcal mol^{-1} measured in the present work, we arrive at an estimate for the heat of reaction, ΔH_{615}, of 7.5 ± 1.2 kcal mol^{-1}. We use the midpoint of the $1/T$ span of the present measurements as the temperature of the determination, since there is no overlap of the measurements. Taking the known heats of formation of C_2H_4, Cl, and HCl, and using published heat capacity data to correct to 298 K,[9,11,28] this yields a $\Delta H^{\circ}_{f,298}(C_2H_3) = 71.3 \pm 1.3$ kcal mol^{-1}.

Additionally, we can use the present measurement of the abstraction rate at 500 K in combination with the rate coefficient measured by Russell et al. at 495 K to perform a third-law estimation of the heat of formation of the vinyl radical. Russell et al. report a rate coefficient of $(1.34 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction of HCl + C_2H_3 at 495 K. The present determination of the abstraction rate coefficient is $(6.7 \pm 0.8) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 500 K. The equilibrium constant at 498 ± 3 K is thus $K = k_1/k_{-1} = 0.05 \pm 0.01$. Using published values for entropies and heat capacities,[9,11,28] we arrive at a $\Delta S_{498} = 9.37$ cal mol^{-1} K^{-1} and a ΔH_{498} of 7.63 kcal mol^{-1}. Once again correcting to 298 K, this yields a $\Delta H^{\circ}_{f,298}(C_2H_3) = 71.6 \pm 0.3$ kcal mol^{-1}. Both the third- and second-law determinations are in excellent agreement with the bond energy measurements of Ervin et al.[8]

The present measurements therefore provide additional experimental evidence for the "high" value for the heat of formation of the vinyl radical. The second-law determination given here has relied on an extrapolation of lower temperature data for the reaction HCl + C_2H_3. Additional studies of the reverse reaction at higher temperatures would provide a more solid foundation for a second-law determination of $\Delta H^{\circ}_{f,298}(C_2H_3)$ using the present measurements. Nevertheless, the value calculated in this way is in excellent agreement with a third-law determination using data for forward and reverse reactions near 498 K. Given the emerging consensus of recent chemical kinetic measurements of $\Delta H^{\circ}_{f,298}(C_2H_3)$,[9,10] it appears that the long-standing discrepancy between kinetic and spectroscopic determinations of this quantity has been removed.

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