Kinetics and Thermochemistry of the Reaction C_2D_6 + Cl $\rightleftharpoons$ C_2D_5 + DCl. The Heat of Formation of the C_2D_5 and C_2H_5 Radicals
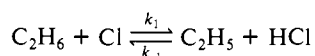
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Abstract: The bimolecular rate constant for the title reaction has been measured with the very low pressure reactor technique (VLPR) at 295 K. The rate constant at room temperature (295 K) was found to be $k_1 = (8.30 \pm 0.7) \times 10^{-12}$ cm^3/(molecule·s). The value of K_1, i.e., equilibrium constant at room temperature, was found to be $(4.70 \pm 0.3) \times 10^2$. From third law calculations at 295 K $\Delta H_f°(C_2D_5) = (24.30 \pm 0.4)$ kcal/mol and DH°(C_2D_5–D) = 102.8 ± 0.4 kcal/mol. With use of known zero-point energy differences DH°(C_2H_5–H) can be calculated from this as 100.4 kcal/mol and $\Delta H_f°(C_2H_5) = 28.3$ kcal/mol in excellent agreement with recent data.

The gas-phase reactions of hydrocarbons (RH) with chlorine atoms have been of interest to kineticists for many years. The recent inquiry into the possible role that naturally occurring or man-made chlorine containing compounds might play in determining the chemistry of earth's atmosphere has resulted in an upsurge of interest in chlorine atom gas-phase reactions.[1] This has led to the renewal effort in the determination of accurate thermochemical properties and kinetic behavior of such systems. Heats of formation of radicals are of fundamental importance to our understanding of bonding and of chemical reactions. Nevertheless, the values of some of these simplest quantities are controversial and incomplete. In particular, values of 25.8 and 28.9 kcal/mol have recently been quoted[2-6] for the heat of formation of ethyl radical, $\Delta H_f°(C_2H_5)$.

Pilling et al.[7] studied the system H + $C_2H_4 \rightleftharpoons C_2H_5$ using excimer laser flash photolysis/resonance fluorescence over the temperature range 775–825 K at 200 Torr and found $\Delta H_f°(C_2H_5)$ to be 28.36 ± 0.4 kcal/mol. From a study of pyrolysis of C_2H_6 at 902 K Pacey and Wimalasena[8] deduced $\Delta H_f°(C_2H_5) = 28.44 \pm 0.3$ kcal/mol. Cao and Back[9] reviewed the general evidence for an upward revision of $\Delta H_f°(C_2H_5)$ and made a detailed analysis of the available rate data for the reaction $C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$. Despite the considerable scatter in the data these authors found an overwhelming support for the higher heat of formation but were unable to recommend a precise figure. In an earlier incomplete study in this laboratory[10] a value for the heat of formation of ethyl radical $\Delta H_f°(C_2H_5)$ has been found to be 28.62 ± 0.4 kcal/mol with the VLPR technique. The system under consideration was

$$C_2H_6 + Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_5 + HCl$$

Using the VLPR technique we found that the value of $k_1 = (5.0 \pm 0.5) \times 10^{11}$ cm^3/(molecule s) and K_1(353 K) = (3.0 ± 0.6) × 10^3.

The study of the chlorine/ethane (C_2H_6) system for the determination of equilibrium constant K_1 is complicated by the fact that the back reaction is very slow compared to the forward reaction and its accurate determination is less reliable as we have to add 10^3 times more HCl than Cl atoms, which makes difficult an accurate measurement of Cl. Because of the discrepancy in the values of $\Delta H_f°(C_2H_5)$ and DH°(C_2H_5–H) in the literature it is of great interest to know these values with great accuracy. Therefore in the present article we have extended our study to the deuterated ethane/chlorine system using VLPR. We hope that this study will provide accurate values of $\Delta H_f°(C_2D_5)$ and DH°(C_2D_5–D) which then can be used to estimate $\Delta H_f°(C_2H_5)$ and DH°(C_2H_5–H) from zero point energy considerations.

VLPR is a versatile tool for the quantitative study of fast elementary reactions in the gas phase near room temperature. The Knudsen conditions for molecular flow in the reactor cell, the chemical treatment of walls, and rapid discharge favor the elimination of most side reactions. These are further checked by direct sampling with mass spectrometry. The discharge or cell escape rate is the physical process serving to fix the steady-state concentrations of reactants in the reactor cell.[13] When the equilibrium constant is measured, even with poor accuracy, let us say ±20%, the Gibbs free energy change at 295 K is then known to ±0.12 kcal/mol. Since the entropy change is usually known or estimable to within ±0.6 cal/(mol K), $\Delta H°$ for the reaction can be obtained from the thermodynamic relation

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K_1$$

with an expected accuracy of about 0.2 kcal at 300 K.

Since $\Delta H_f°$ are usually available for all other species we can obtain $\Delta H_f°$ of the radical from $\Delta H_1°$ for any reaction from a van't Hoff plot (ln K_1 vs 1/T) over a suitable temperature range. Generally because of the limitations on the temperature range, third-law calculations are more accurate.

Experimental Section

The theory of the Very Low Pressure Reactor (VLPR) has been discussed in detail.[11,13] Briefly, halogen atoms produced in a microwave discharge are allowed to react for a known length of time in a Teflon-coated cell with some molecule of interest, RH, at total pressure of less than 5 mTorr. In the well-stirred reactor flow system comprising VLPR, reactants and products exit the reaction vessel in a divergent molecular beam that is collimated into a quadrupole mass spectrometer chamber. The molecular beam is modulated by a tuning fork chopper and the mass spectrometer signal is passed through a lock-in amplifier and displayed on a chart recorder for analysis.

The VLPR system used in the present investigation has been described in a report[11] published earlier from this laboratory. It differs from previous systems in having three differentially pumped chambers instead of two. This gives us a better collimated molecular beam, lower background, and improved sensitivity.[13] Other improvements include a

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quickly adjustable orifice size 2, 3, or 5 mm at the outlet of the reactor cell allowing us to change the residence time of the reacting species in the cell and thus permitting us to measure a wider range of rate constants, all without breaking vacuum.

A 0.94% chlorine/helium mixture was prepared with Matheson research purity Cl_2 and ultrahigh-purity helium. This mixture was prepared in a 3 L Pyrex bulb by admitting Cl_2 and performing 2 free-pump–thaw cycles to remove any noncondensable. Helium was purified by passing through a molecular sieve at 77 K to remove any hydrocarbon impurities. Deuteriated ethane and DCl were Matheson research grade (99.99%) and were subjected to 2 freeze–thaw cycles before use. Purities were checked with mass spectrometry.

Flow rates of the gases were determined by following the pressure drop (measured on a Validyne DP 15-30 S/N 56005 ± 1 psi transducer) in a known volume (~500 cm³) as the gases flowed across a 100-cm capillary with ID of 0.020, 0.035, or 0.065 cm. During the experiment the flows were maintained constant by adding gas to the buffer volume by means of a needle valve.

The reactor cell was mounted on a stainless steel flange containing the adjustable orifice. The orifice was machined out of Teflon to prevent wall recombination, and the interior of the cell (v = 238.3 cm³) was coated with FEP Teflon which also effectively inhibited wall recombination. The Knudsen reactor used was characterized by a directly measured escape rate constant k_{em}. The value of k_{em} depends on the orifice size, temperature (K), and molecular weight M of existing species. For the 3-mm orifice, $k_{em} = 0.569(T/m)^{1/2}$ and for the 5-mm orifice $k_{em} = 1.052(T/M)^{1/2}$.

Chlorine atoms were generated by flowing a 0.94% Cl_2/He mixture through a quartz tube coated with phosphoric acid and enclosed in a 2.45 GHz microwave cavity operating at 50 W. The chlorine atoms were admitted to the reaction cell through a 2-cm tapered capillary having approximate diameters 0.3 and 1 mm at the two ends. The completeness of dissociation was checked by mass spectrometry with the peaks (m/e) at 70, 72, and 74 for Cl_2 and 35 and 37 for Cl. Peaks at 36 and 39 were used to follow DCl.

The temperature of the reaction cell was held constant by circulating a thermostated liquid (water or ethanol) through the outer jacket surrounding the cell   The temperature was monitored with a copper–constantan thermocouple.

Molecules that exit the aperture of the reaction cell effuse through collimated apertures before each of three differentially pumped chambers thus creating a molecular beam. This beam was chopped at 200 Hz before entering the ionization chamber of the mass spectrometer and the AC component was detected with a lock-in analyzer (Ithaco Dynatrac 3). The quadrupole mass spectrometer is a Balzers Model QMG 511 with a cross beam analyzer made specially for beam work. The choice of the electron energy of the ionizer is critical because the appearance of Cl^+ (m/e 35) from DCl (m/e 37) fragmentation would interfere with the chlorine signal from Cl atoms. Under our experimental conditions the fragmentation was less than 1% at 25 eV. Therefore, all analyses for forward rate constant measurements were carried out at 25 eV. For reverse reaction studies 20 eV was used as in the latter case the DCl/Cl was very high and 1% fragmentation could cause appreciable error. At 20 eV the fragmentation of DCl is 0.3% and appropriate corrections were made to the 35 mass signal.

The maximum flow rate of the reactants was limited to about 2 × 10¹⁷ molecules/s (which corresponds to a pressure of about 10 mTorr inside the reaction cell) in order to satisfy the Knudsen conditions.

The VLPR system used in the present investigation had been tested earlier[11] by measuring the rate constant of a well-characterized reaction, Cl + CH_4. Before starting earlier work on the vinyl radical we had obtained a rate constant for the reaction between chlorine and methane of 1.0 × 10⁻¹³ cm³/molecule s) which is in excellent agreement with a NASA panel for data evaluation[12] and earlier work from this laboratory.[13]

For the determination of k_1, we added ethane to a steady flow of chlorine atoms. We monitored the peaks at 35 and 37 at different C_2D_6 concentrations. The value of k_1 was also measured monitoring the decrease in ethane (C_2D_6) concentration on adding different amounts of chlorine atoms. It was decided to monitor a fragmentation peak (m/e = 34) of C_2D_6 rather than the parent peak m/e = 36 as the latter has considerable interference due to the presence of HCl in the system. (This arises in the discharge, probably from wall reactions.) The ionization voltage was kept high (75 eV) so that the contribution to our m/e = 34 signal from the C_2D_5 radical is minimal. It was observed that at this ionization voltage C_2D_5 is completely dissociated. With these concentrations the instrument was calibrated for the measurement of C_2D_6 concentration with m/e = 34 signal (Figure 1).

We checked the mass balances of Cl + DCl and verified that they were constant to within our experimental precision (±5%) in all runs.
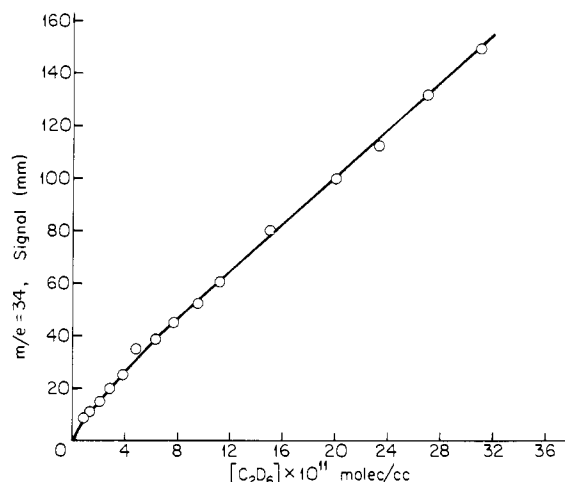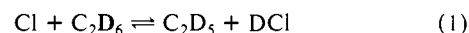

Figure 1. Calibration curve for the quadrupole mass analyzer to measure $[C_2D_6]$ using m/e = 34 signal of fragment.
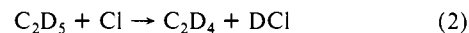
Our sensitivity to Cl_2 was significantly less than 10¹⁰ molecules/cm³ so that $[Cl_2]/[Cl]$ was established at well under 1%.

Results and Discussion

The reaction under study is

$$Cl + C_2D_6 \rightleftharpoons C_2D_5 + DCl \qquad (1)$$

with a possible secondary reaction

$$C_2D_5 + Cl \rightarrow C_2D_4 + DCl \qquad (2)$$

Reaction 2 probably goes via a recombination step yielding an energized $(C_2D_5Cl)^*$ which further decomposes to C_2D_4 and deuterium chloride at VLPR conditions. The first step, recombination of deuteriated ethyl radical and chlorine atom, is rate determining. Since VLPR is a well-stirred flow reactor in which complete mixing occurs in times short compared to the residence time, exact steady-state analysis of similar systems,[14] including the fact that the flow in must be equal to flow out, shows that

$$\frac{[Cl]_0}{[Cl]} - 1 = \frac{k_1[RD]}{k_{eCl}} \left\{ \frac{k_{eR} + 2k_2[Cl]}{k_{eR} + k_2[Cl] + k_{-1}[DCl]} \right\} \qquad (3)$$

When no DCl is added the term k_{-1} [DCl] in the denominator of eq 3 is very small and can be neglected. Therefore

$$\frac{[Cl]_0}{[Cl]} = 1 + \frac{k_1[RD]}{k_{eCl}} \left\{ \frac{k_{eR} + 2k_2[Cl]}{k_{eR} + k_2[Cl]} \right\} \qquad (4)$$

Where [RD] is the deuteriated ethane concentration, R is the deuteriated ethyl radical, k_{eM} represents the escape rate constant for mass M, and $[Cl]_0$ is the initial chlorine atom concentration in the system.

Under our experimental conditions, no C_2D_5Cl or C_4D_{10} were observed. Monitoring of C_2D_4 (m/e = 32) was not reliable because of some interference from O_2, and also from fragmentation of C_2D_6 and/or C_2D_5. Therefore, the value of k_2 was estimated (k_2 = 1.2 × 10⁻¹¹ cm³/(molecule s)) from the modified Gorin model[15a] for

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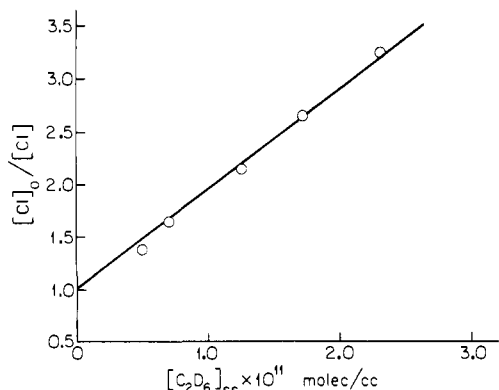(21) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

Figure 2. Plot of $[Cl]_0/[Cl]$ vs $[C_2D_6]_{ss}$ (i.e., steady-state concentration) at 295 K, $[Cl]_0 = 1.5 \times 10^{12}$ molecules/cm^3.

the recombination of ethyl radicals and chlorine atoms. The direct metathesis of ethyl radical with Cl is estimated to be much slower.[15b] Equation 4 can be written as

$$\frac{[Cl]_0}{[Cl]} = 1 + \frac{k_1[RD]}{k_{eCl}}A \qquad (5)$$

Where $A = (k_{eR} + 2k_2[Cl])/(k_{eR} + k_2[Cl])$ and is restricted to values between 1 and 2.

Normally, these reactions are studied under pseudo-first-order conditions where the hydrocarbon concentrations are much higher than $[Cl]_0$ so that the consumption of hydrocarbon by Cl is much smaller than $[RH]_0$. In this system, because of the large rate constant, even a small amount of $[C_2D_6]$ addition causes a large decrease in $[Cl]_0$ signal. In order to determine k_1, we monitored $[Cl]_0/[Cl]$ and the steady-state concentration of deuteriated ethane in the system. To do this the system was calibrated for deuteriated ethane fragment ($m/e = 34$) as shown in Figure 1. A plot of $[Cl]_0/[Cl]$ vs $[C_2D_6]$ gave a straight line (Figure 2) with a slope corresponding to $k_1(A/k_{eCl})$. Note that the origin is a well-measured point. As the steady-state concentration of chlorine in the system is not constant (in the range $0.7-2.0 \times 10^{12}$ molecules/cm^3), the value of A varies between 1.8 and 1.9. An average value of 1.85 ± 0.1 for A and 1.75 s^{-1} for k_{eR} was used for the determination of k_1. The average value of k_1 at 293 K from five such measurements is

$$k_1(293 \text{ K}) = (9.0 \pm 0.6) \times 10^{-12} \text{ cm}^3/(\text{molecule s})$$

Another method for the determination of k_1 is to monitor the decrease in C_2D_6 concentration on varying the chlorine concentration in the system. Using the steady-state conditions

$$\frac{[RD]_0}{[RD]} - 1 = \frac{k_1[Cl]}{k_{eRD}} \left\{ \frac{k_2[Cl] + k_{eR}}{k_2[Cl] + k_{eR} + k_{-1}[DCl]} \right\} \qquad (6)$$

When no DCl is added, the term $k_{-1}[DCl]$ in the denominator of eq 6 is very small and can be neglected. Therefore,

$$\frac{[RD]_0}{[RD]} - 1 = \frac{k_1[Cl]}{k_{eRD}} \qquad (7)$$

A plot of $[C_2D_6]_0/[C_2D_6]$ vs $[Cl]$ gave a straight line (Figure 3) with a slope and intercept corresponding to $k_1/k_{eC_2D_6}$ and 1, respectively. The value of k_1 determined from the slope is

$$\langle k_1 \rangle = (7.5 \pm 1.0) \times 10^{-12} \text{ cm}^3/(\text{molecule s})$$

This value of k_1 is independent of the value of k_2 that we were required to estimate in order to obtain k_1 from measurements of the decline in (Cl) as C_2D_6 was added. We are thus inclined to take an error weighted average of the two different methods, giving

$$k_1 = (8.5 \pm 0.6) \times 10^{-12} \text{ cm}^3/(\text{molecule s})$$

To bring the two measurements into agreement we would have to increase our estimated value of k_2 by a factor of about 3, which seems too high relative to other recombination rate constants.
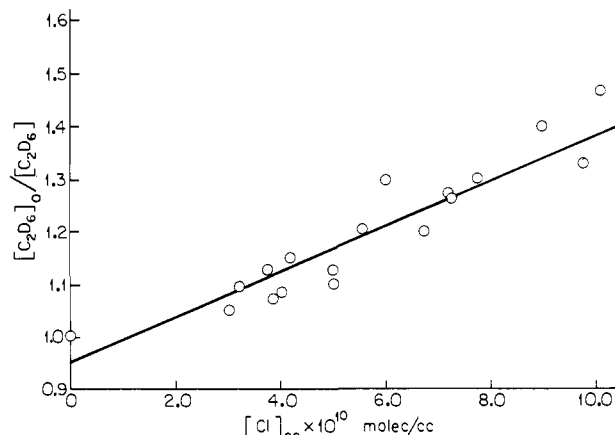

Figure 3. Plot of $[C_2D_6]_0/[C_2D_6]$ vs $[Cl]_{ss}$ (i.e., steady-state concentration) at 295 K, $[C_2D_6]_0 = 1.13 \times 10^{12}$ molecules/cm^3.
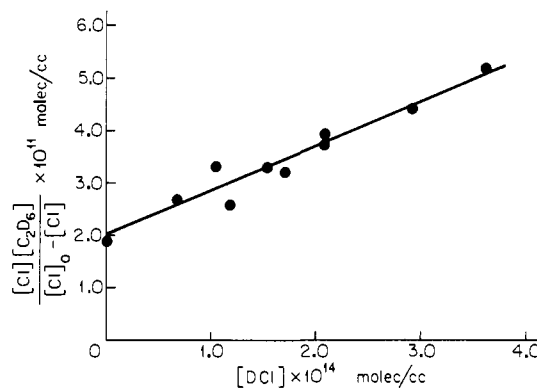

Figure 4. Plot of $[C_2D_6][Cl]/([Cl]_0 - [Cl])$ vs $[DCl]$, $[C_2D_6]_0 = 1.90 \times 10^{11}$ and 1.30×10^{11} molecules/cm^3, $[Cl]_0 = 2.0 \times 10^{11}$ and 1.3×10^{11} molecules/cm^3.

The data in Figure 3 are a combination of two different experiments in which $[C_2D_6]_0$ ranges from 1.13×10^{12} to 3.04×10^{12} molecules/cm^3, and $[Cl]_0$ ranges between 1.5×10^{11} and 1.35×10^{12} molecules/cm^3. The values of k_1 determined by two different methods described above are in reasonable agreement with each other.

To study the back reaction, DCl was added to a constant flow of Cl/He and C_2D_6. The increase in Cl signal ($m/e = 35$) was monitored at different amounts of DCl added. Rearranging eq 3, we have

$$\frac{[Cl][RD]}{[Cl]_0 - [Cl]} = \frac{k_{eCl}}{k_1} + \frac{k_{eCl}[DCl]}{K_1 k_{eR}} \frac{1 - k_2[Cl]/k_{-1}[DCl]}{1 + 2k_2[Cl]/k_{eR}} \qquad (8)$$

or

$$\frac{[Cl][RD]}{[Cl]_0 - [Cl]} = \frac{k_{eCl}}{k_1} + \frac{k_{eCl}[DCl]}{K_1 k_{eR}} B$$

where

$$B = \frac{1 - k_2[Cl]/k_{-1}[DCl]}{1 + 2k_2[Cl]/k_{eR}}$$

The value of B, which varies between 0.38 and 0.42, was calculated at different values of $[Cl]$ and $[DCl]$ in the system. An average value of 0.4 for B was used for the determination of equilibrium constant (K_1). A plot of $[Cl][RH]/([Cl]_0 - [Cl])$ vs $[DCl]$ at 295 K gave a straight line (Figure 4) with a slope of intercept corresponding to $k_{eCl}(B/K_1 k_{eR})$ and k_{eCl}/k_1, respectively. The data for this plot are given in Table I (a and b). From the slope and intercept (Figure 4)

$$K_1 = 470 \pm 40$$

$$k_1 = (8.50 \pm 1.0) \times 10^{-12} \text{ cm}^3/(\text{molecule s})$$

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Table I. Data for Equilibrium Constant (K_1) Studies at 295 K

no.	$[DCl]^a$	$10^{11}[Cl]^a$	$10^{11}[C_2D_6]^a$	$10^{11}([C_2D_6][Cl]/\{[Cl]_0 - [Cl]\})^a$
	$[Cl]_0 = 2.0 \times 10^{11}$ molecules/cm^3; $[C_2D_6]_0 = 1.90 \times 10^{11}$ molecules/cm^3			
1	0.0	1.30	1.0	1.85
2	1.21×10^{14}	1.40	1.10	2.56
3	1.71×10^{14}	1.46	1.20	3.24
4	2.10×10^{14}	1.52	1.25	3.75
5	2.90×10^{14}	1.55	1.28	4.40
6	3.64×10^{14}	1.60	1.30	5.2
	$[Cl]_0 = 1.0 \times 10^{11}$ molecules/cm^3; $[C_2D_6]_0 = 1.30 \times 10^{11}$ molecules/cm^3			
7	6.88×10^{13}	0.73	1.0	2.70
8	1.07×10^{14}	0.76	1.05	3.32
9	1.55×10^{14}	0.76	1.05	3.32
10	2.11×10^{14}	0.78	1.10	3.90

^{a} Molecules/cm^3.

Table II. Thermochemical Data Used from Literature in the Present Investigation^e

	C_2D_6	Cl	DCl	HCl	C_2H_5	C_2D_5	C_2H_6
$\Delta H_f^{\circ}{}_{(295)}$	-26.45^b	28.9	-22.3	-22.1	28.3^a	24.3 ± 0.4^a	-20.0^d
S°	58.4^b	39.5	46.0	44.6	59.2^c	62.6^b	54.9

^{a} Our value from the present study. ^{b} A. Burcat, report (ref 22). ^{c} Reference 16. ^{d} Padley, etc.. ^{e} All values not explicitly labeled are taken from JANAF Tables.

hence $k_{-1} = (1.8 \pm 0.2) \times 10^{-14}$ cm^3/(molecule s). The value of k_1 obtained from the intercept (Figure 4) is in close agreement with that obtained from Figures 2 and 3.

From our measurements of equilibrium constant at 295 K, $\Delta G_1 = -3.60 \pm 0.1$ kcal/mol. From thermochemical data given in Table II, $\Delta S^{\circ}(295\text{ K}) = (10.7 \pm 0.6)$ eu which gives $\Delta H^{\circ}{}_1 = -0.45 \pm 0.2$ kcal/mol. This gives the heat of formation of deuteriated ethyl radical $\Delta H_f^{\circ}{}_{(295)}(C_2D_5) = (24.30 \pm 0.4)$ kcal/mol and $DH^{\circ}(C_2D_5 - D) = 102.8 \pm 0.4$ kcal/mol.

From this experimentally determined thermochemical data obtained for the reaction $C_2D_6 + Cl \rightleftharpoons C_2D_5 + DCl$ further information on a parallel system $C_2H_6 + Cl \rightleftharpoons C_2H_5 + HCl$ can be estimated from the known zero point energy difference of 2.4 kcal/mol between the two systems,[22]

$$C_2D_5-D \rightleftharpoons C_2D_5 + D \qquad (9)$$

and
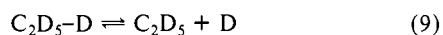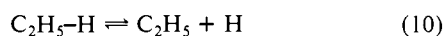
$$C_2H_5-H \rightleftharpoons C_2H_5 + H \qquad (10)$$

Therefore

$$DH^{\circ}(C_2H_5-H) = 102.8 - 2.4 = 100.4 \text{ kcal/mol}$$

and

$$\Delta H_f^{\circ}(C_2H_5) = DH(C_2H_5-H) - \Delta H_f^{\circ}(H) + \Delta H_f^{\circ}(C_2H_6)$$

using the thermochemical data in Table II.

$$\Delta H_f^{\circ}(C_2H_5) = 28.3 \text{ kcal/mol}$$

This gives the heat of reaction and equilibrium constant for the reaction

$$C_2H_6 + Cl \rightleftharpoons C_2H_5 + HCl \qquad (11)$$
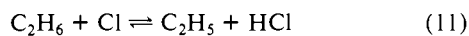
to be $\Delta H^{\circ}{}_{(295)} = -2.4$ kcal/mol and $K_{1(295)} = 8.80 \times 10^3$, respectively.

The thermochemical data derived for the C_2H_6 system are in good agreement with our previous studies[10] and are particularly important as the direct measurements of the equilibrium constant (K_1) are less reliable due to very slow back reaction ($\sim5.0 \times 10^{-15}$ cm^3/(molecule s)). The rate constant ratio k_H/k_D for H/D ab-

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Table III. Heats of Formation ($\Delta H_f^{\circ}{}_{(295)}(C_2H_5)$) Values for Ethyl Radical and $\Delta H_f^{\circ}{}_{(295)}$ Determined with VLPR

ref	$\Delta H_f^{\circ}{}_{(295)}(C_2H_5)$	technique
7	28.36 ± 0.4	laser flash photolysis resonance fluorescence
4	25.9 ± 1.0	halogenation studies
19	26.6 ± 1.0	EtI + HI kinetics (recalculated in ref 19)
18	28.0	radical buffer technique
8	28.44 ± 0.3	pyrolysis of C_2H_6
10	28.6 ± 0.4	VLPR
3	28.5 ± 0.5	decomposition of alkanes
	28.3 ± 0.4	VLPR (this study)
		this study

$$\Delta H_f^{\circ}{}_{(295)}(C_2D_5) = 24.3 \pm 0.4$$

straction by Cl atoms from C_2H_6[10] and C_2D_6 is 5.8.

This is in excellent agreement with a critical review of recently measured values,[12] log $k_1 = 10.7 - 0.2/\theta$. If we use the same bent, tight transition state to describe the Cl + C_2D_6 reaction we can estimate a difference in zero point energies of about 0.9 kcal for the two reactions. At room temperature this would amount to a factor of 5 favoring the H-atom reaction. This is in good agreement with the experimental ratio of about 6 if we assume that the A-factors for the two reactions are about the same. Since the zero point energy difference is very sensitive to the high frequencies in the transition state which have very little effect on the estimated rate constant, the isotope effects are not a good check on the transition state.

A measurement of the relative rates of Cl + C_2D_6 and Cl + H_2 has given an activation energy of 1.3 kcal for the former[20] based on $E_{act}(Cl + H_2) = 3.8$ kcal. The absolute rate of Cl + C_2D_6 from this ratio is 10×10^{-12} cm^3/(molecule s) in good agreement with our measured value at 295 K.

There have been numerous studies on the heat of formation of C_2H_5 radical and the C–H bond strength in C_2H_6, but no data exist for $\Delta H_f^{\circ}(C_2D_5)$ and $DH^{\circ}(C_2D_5-D)$. Wing Tsang[3] analyzed the data on alkane decomposition, obtained from different techniques, and found that heats of formation of ethyl, isopropyl, and *tert*-butyl radicals should be higher by 10–20 kJ than the numbers from previously accepted values. He suggested that the value of $\Delta H_f^{\circ}(C_2H_5)$ should be 28.5 ± 0.5 kcal/mol.

This is in good agreement with the studies of Pacey and Wimalasena[8] mentioned earlier as well as the more recent studies of Brouard et al.[7] In both of these studies entropies and heat capacities of the ethyl radical had to be calculated from spectroscopic measurements.[16] From VLPR studies[10] we found that $\Delta H_f^{\circ}(C_2H_5)$ is 28.6 ± 0.4 kcal/mol. A comparison of $\Delta H_f^{\circ}(C_2H_5)$ values from literature along with our value for the heat of formation of deuteriated ethyl radical ($\Delta H_f^{\circ}(C_2D_5)$) is given in Table III.

The quoted confidence limits were calculated from the uncertainties in the value of k_1 and K_1. The only source of error in the determination of k_1 is the measurement of the steady-state concentration of ethane which is not more than 10%. Similarly, the possible error in K_1 comes from the measurement of steady-state concentration of ethane and from the calculated value of k_2. Relatively large errors of even as much as 20% in the value of K_1 at 300 K alter the heats of formation of C_2H_5 (or C_2D_5) and the bond strengths by only 0.2 kcal/mol.

Iodination studies on hydrocarbons in the author's laboratories and by colleagues[19,21] have been used to provide what had been assumed to be accurate data on bond dissociation energies for hydrocarbons. Recent studies, however, have provided values for CH_3, C_2H_5, i-C_3H_7, and t-butyl which are from 1 to 2 kcal/mol higher than these. Numerous suggestions have been put forward to account for these differences including the one that the back reactions of R + HI have increasingly negative activation energies as R goes from CH_3 to *tert*-butyl. A much simpler explanation is that the experimental uncertainty in the activation energy for the forward reaction, I + RH → HI + R, is of the order of 1.0 to 1.5 kcal/mol. E_a has ranged from 24 to 34 kcal/mol and a 1.0 to 1.5 kcal/mol error is in the range of 3–4%. The fact that

it is systematically lower may arise from the possibility that there is a small contribution from wall reactions. At the 10% level these would be difficult to detect. In addition, in many of the studies it was assumed that the back reaction had an activation energy of 1 ± 1 kcal/mol. It now seems much more likely that these

are actually in the range 0 to 0.5 kcal/mol.[19]

Gas-Phase Reactions of Si+(2P) with Hydrogen Cyanide, Acetonitrile, Cyanogen, and Cyanoacetylene: Comparisons with Reactions of C+(2P)

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Abstract: Reactions of ground-state Si+(2P) ions have been investigated with the cyanide molecules HCN, CH_3CN, C_2N_2, and HC_3N at 296 ± 2 K with the selected-ion flow tube (SIFT) technique. All four cyanides were observed to form adduct ions with Si+ in one reaction channel, but otherwise the nature and degree of reactivity were found to be strongly dependent on the nature of the substituent. Si–N bond formation in the bimolecular products prevailed with HCN and C_2N_2, while Si–C bond formation was predominant with CH_3CN and HC_3N. These primary reactions as well as several observed secondary reactions are discussed as sources for neutral molecules such as CNSi, SiCH, SiC_2, and other, more complex, silicon-bearing molecules in partially ionized interstellar gas clouds. Results of quantum chemical calculations performed at the MP4SDTQ/6-31G**//6-31G** level are presented which provide insight into the possible structure of the adduct ion between Si+ and HCN. The reactivities observed with Si+ are compared with those available for the analogous reactions of C+ proceeding under similar conditions of temperature and pressure. The reactions with Si+ are uniformly slower and less efficient than the corresponding reactions of C+, and the competition with adduct formation is not apparent for the reactions of C+. These differences in reactivity are rationalized in terms of perceived differences in the potential energy profiles.

The growing interest in fundamental aspects of the chemical bonding of atoms to silicon,[1] and the importance of silicon-bearing compounds in the chemistry of interstellar gas clouds,[2,3] recently has prompted us to conduct systematic investigations of ion chemistry initiated by atomic silicon ions in their ground electronic state in the gas phase. We have established previously that the chemistry initiated by atomic silicon ions reacting with molecules containing hydroxyl groups can lead to molecules containing silicon–oxygen double bonds.[4] Also, we have found that reactions of atomic silicon ions with ammonia and methylamines can lead to the formation of molecules such as SiNH, $SiNCH_3$, and H_2SiNH in which silicon is doubly bonded with nitrogen.[5,6] Here we monitor the response of atomic silicon ions to molecules containing the triply bonded C≡N substituent in an attempt to identify further routes to Si–N bond formation and to explore the competition with Si–C bond formation. The kinetics and product distributions are investigated for reactions of Si+(2P) with hydrogen cyanide, acetonitrile, cyanoacetylene, and cyanogen. These particular cyanides were chosen as substrates, in part because of their importance in the chemistry of interstellar gas clouds.[2,3]

A second incentive for this investigation was provided by the availability of experimental results for the gas-phase reactions of the four cyanides selected for study with atomic carbon ions in their ground electronic state. These results presented a unique

opportunity to compare the reactivities of the group IV atomic ions Si+(2P) and C+(2P). The comparison is possible without complications due to charge transfer. The relatively low electron recombination energies of these two atomic ions, 8.151 eV for Si+ and 11.260 eV for C+, ensures that thermal collisions with the cyanides do not lead to charge transfer (due to endothermicity) while still permitting chemical bond formation channels. Differences in the chemical reactivities of these two atomic ions are expected from the substantial difference in their enthalpy of formation, 136 kcal mol^{-1} at 298 K, and should be manifested in the nature of these bond formation channels and their relative efficiencies. Differences also may be expected to appear in the overall reaction efficiencies.

Experimental Section

All measurements were performed with the selected-ion flow tube (SIFT) apparatus which has been described in detail elsewhere.[7,8] Atomic silicon ions were derived from a 2–3% mixture of tetramethylsilane in deuterium by electron impact at 50–100 eV. The deuterium was added to scavenge the metastable Si+(4P) ions in the source with the following reaction:[4]

$$Si^+(^4P) + D_2 \rightarrow DSi^+ + D \qquad (1)$$
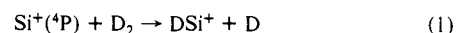
The isotope of Si+ at $m/e = 28$ was selected and introduced into helium buffer gas at 0.35 Torr or 1.15×10^{16} He atoms cm^{-3}. Neutral reagents were added downstream. Primary and secondary ions were monitored as a function of the added neutral reagent. Rate constants and product distributions were derived from these observations in the usual manner.[7,9] No attempt was made to investigate the pressure dependence of rate

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