Kinetics and Thermochemistry of the Reaction Cl + Cyclopropane ⇄ HCl + Cyclopropyl. Heat of Formation of the Cyclopropyl Radical

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Abstract: The bimolecular rate constant for the reaction of chlorine atoms with cyclopropane, $Cl + c\text{-}C_3H_6 \rightleftharpoons HCl + c\text{-}C_3H_5$ (1, −1), was measured at 298 K using the very low pressure reactor (VLPR). The rate constant was found to be $k_{1_{298}} = (1.21 \pm 0.05) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The equilibrium constant $K_1 = k_1/k_{-1}$ was observed at 298 K to be 0.91 ± 0.1. This gives a heat of formation of the cyclopropyl radical $\Delta H_f{}^\circ{}_{298}$ (cyclopropyl) = 66.9 ± 0.25 kcal mol^{-1} and a C-H bond dissociation energy of BDE ($c\text{-}C_3H_5\text{-}H$) = 106.3 ± 0.25 kcal mol^{-1}. This is the highest C-H bond energy for any saturated hydrocarbon. It is reconciled with a model for the cyclopropane ring which associates an excess strain energy of about 13 kcal with each π-bond center in the ring, external and internal. Such a strain model is also shown to explain the lack of olefinic conjugation between cyclopropane and external unsaturation.

Introduction

Direct measurements of the heats of formation of organic free radicals are very difficult.[1-3] Instead, values of $\Delta H_f{}^\circ$ are obtained from kinetic measurements buttressed with reasonable assumptions and the result is that they have an almost unavoidable uncertainty of about 1.5 kcal/mol. This situation has changed during the past year with the successful operation of the very low pressure reactor (VLPR),[4,5] which permits direct study of atom-molecule reactions for which the equilibrium constant is in the range 10^{-2} to 10^2. Both forward and reverse rate constants and the equilibrium constant for the elementary reaction are directly measured. We have recently employed the VLPR to measure $\Delta H_f{}^\circ(CH_3)$ using the equilibrium $Cl + CH_4 \rightleftharpoons HCl + CH_3$.[4,5] In the present study we report on the elementary reaction system

$$Cl + c\text{-}C_3H_6 \underset{-1}{\overset{1}{\rightleftharpoons}} HCl + c\text{-}\dot{C}_3H_5$$

at ambient temperatures.

The first quantitative measurements of step 1 were made by Knox and Nelson,[6] who reported

$$\log (k_1/\text{L/mol·s}) = 10.73 \pm 0.04 - 4.1/\theta$$

where $\theta = 2.303RT$ kcal/mol. Later studies have been made, using the technique of competitive reactions,[7,8] with results in good agreement. A few years ago we made some effort to study equilibria involving the cyclopropyl radical[9] employing the sensitized, radical-buffer technique with CH_3 and CF_3 radicals.[10,11] While we were able to observe I-atom abstraction by CH_3 and H atom abstraction by CF_3, we were unable to observe cyclopropyl radical products other than $c\text{-}C_3H_6$ in system 2 and small amounts of a dubious C_4 compound in system 3. From these studies, however, we were able to infer a surprisingly high C-H bond strength in $c\text{-}C_3H_6$ in excess of 105 kcal/mol.

$$CH_3 + c\text{-}C_3H_5I \overset{2}{\rightleftharpoons} CH_3I + c\text{-}C_3H_5$$

$$CF_3 + c\text{-}C_3H_6 \overset{3}{\rightleftharpoons} CF_3H + c\text{-}C_3H_5$$

Experimental Section

The VLPR apparatus used in this study was similar to those described elsewhere.[3,4] The reactor had about a 1-mm exit aperture, a volume of 69.2 cm^3, and a unimolecular, escape rate constant k_{eM} for species of molecular weight M given by $k_{eM}/s^{-1} = 0.236(T/M)^{1/2}$. $k_e = A\bar{c}/4V$ is taken from gas kinetic theory. A is the area of the exit aperture, V is the reactor volume, and $\bar{c}$ is the mean molecular velocity of species M. It was coated with a thin film of halocarbon wax to prevent atom recombination. The flow of reactant gas was measured and introduced into the reactor. All of the experiments were carried out at room temperature (~25 °C). A modulated molecular beam with a UTI Model 100C quadrupole mass spectrometer and phase-sensitive lock-in amplifier was used as a detector. The diagram of the flow tube and the quadrupole mass spectrometer is shown in Figure 1.

Chlorine atoms were produced by flowing a mixture of <1% Cl_2 in He through a microwave (Raytheon, 100 W) discharge tube, and leaked into the reactor through a pinhole (~100 μ). Some argon was added to the Cl_2 mixture to serve as an internal standard. The flow rate was very low (~2 mm/s) and the pinhole was located almost 6 cm from the end of the discharge region. The discharge tube was treated with H_3PO_4, and molecular chlorine was completely (100%) dissociated in the discharge tube. No measurable recombination took place inside of the reactor. The design of the apparatus, the low flow rate, the low Cl_2 concentration, and the short distance between discharge and leak were probably responsible for the total dissociation of Cl_2 that was observed. One can calculate that the average molecule or atom could diffusively traverse the discharge-pinhole region in about 0.1 s. During this time there would have been less than 1% homogeneous recombination to Cl_2. Our sensitivity to Cl_2 (molecular peaks at *m/e* 70, 72, 74) at 70 eV electron energy was about 10^9 molecules/cm^3 so that the absence of Cl_2 at the 1% of Cl atom level is well verified. On the other hand, about 10% of Cl_2 was converted to HCl in the discharge tube, possibly through reaction with H_3PO_4, and we had a constant background of about 10^{10} molecules HCl/cm^3 in the reactor in all experiments. This was constant in time, could be measured independently, and caused no problems in the data interpretation. (It was about 5% of the Cl_2 added.) In all of the experiments the condition $[c\text{-}C_3H_6 \gg Cl]$ was maintained. The products of the equilibrium reaction Cl + cyclopropane ⇄ HCl + cyclopropyl were the only ones detected.

Reactants were stored in 22-L bulbs and leaked into the reactor via a series of precision capillaries. Flow rates were measured by monitoring the pressure drop in a calibrated volume using a pressure transducer (Validyne Model CD 12). The pressure of cyclopropane inside of the reactor was varied from 0.02 to 0.32 μm (these values correspond to about 0.5×10^{12} to 10×10^{12} molecules/cm^3).

Argon (Air Products, >99.999%), helium (Matheson, UHP), chlorine (Matheson, 3% in helium), cyclopropane (Matheson, research grade), and hydrogen chloride (Matheson, research grade) were used.

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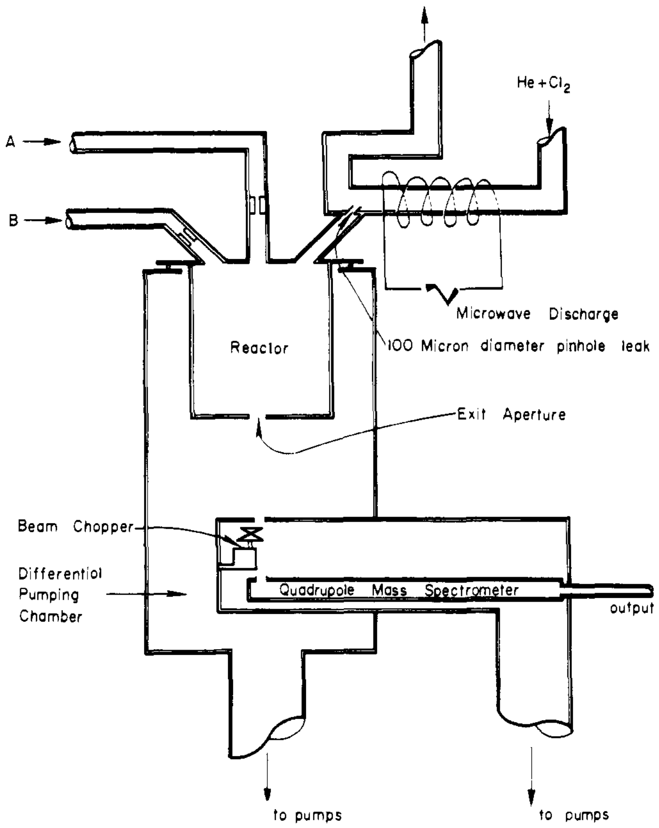


Figure 1. Diagram of flow tube and modulated beam quadrupole mass spectrometer.

Their purities were confirmed by comparison of their recorded mass spectra at 70 eV with those found in the literature.

Cyclopropyl radicals are thermodynamically unstable relative to the isomeric allyl radicals by about 27 kcal/mol and one might expect to see such an isomerization occurring. However, we found no evidence for such isomerization in our system nor is any expected on the time scale of our experiments (residence time ~1 s) because of the high (~35 kcal) estimated activation energy for the isomerization. The allyl radical could not have reacted with excess HCl in our reactor since its C–H bond energy is about 15 kcal weaker than that of the H–Cl bond.

Results

After a steady-state flow of Cl atoms was established, cyclopropane was introduced into the reactor, leading to the chemical reaction

$$\mathrm{Cl} + \text{cyclopropane} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{HCl} + \text{cyclopropyl} \qquad (1)$$

By using low electron energies of 18-22 eV in the ion source of our quadrupole mass spectrometer, we can measure Cl and cyclopropyl in the presence of larger amounts of HCl, Cl$_2$, and cyclopropane. Thus we can measure the steady-state concentrations of all the species present in the reactor. With small amounts of Cl and large amounts of cyclopropane (Δ), the chlorine concentration is given by

$$[\mathrm{Cl}] = \frac{F_{\mathrm{Cl}}}{k_{\mathrm{eCl}} + k_1(\Delta)} \qquad (2)$$

where F_{Cl} is the total specific entrance flux of Cl atoms into the reactor. k_{eCl} is the unimolecular rate constant for escape of Cl atoms from the reactor and is measured from a simple gas kinetic equation using the known exit aperture and reactor volume. In the absence of cyclopropane, $[\mathrm{Cl}]_0 = F_{\mathrm{Cl}}/k_{\mathrm{eCl}}$ and eq 2 can be arranged as

$$\frac{[\mathrm{Cl}]_0}{[\mathrm{Cl}]} = 1 + \frac{k_1}{k_{\mathrm{eCl}}}(\Delta) \qquad (3)$$

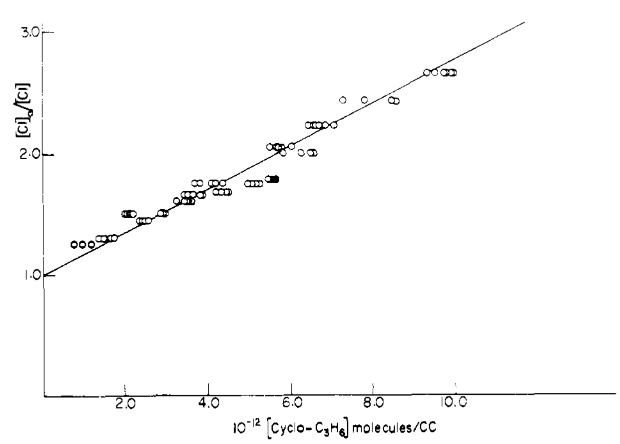


Figure 2. Plot of $[\mathrm{Cl}]_0/[\mathrm{Cl}]$ vs. [cyclopropane].

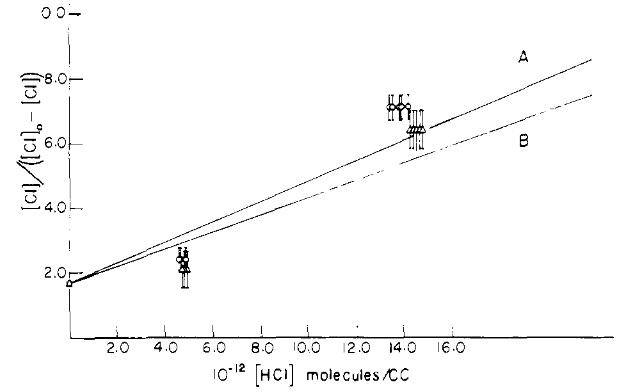


Figure 3. Plot of $[\mathrm{Cl}]/([\mathrm{Cl}]_0 - [\mathrm{Cl}])$ vs. [HCl] at different concentrations of cyclopropane: A (○), [cyclopropane] = 3.44×10^{12} molecules/cm^3; B (△), [cyclopropane] = 3.35×10^{12} molecules/cm^3.

If the back reaction makes negligible contributions to the kinetics, then a plot of $[\mathrm{Cl}]_0/[\mathrm{Cl}]$ (signal at the mass spectrometer) against [cyclopropane] should be a straight line of unit intercept and slope of k_1/k_{eCl} (Figure 2). From the independently measured $k_{\mathrm{eCl}} = 0.69\ \mathrm{s}^{-1}$ and this slope we obtain a value of

$$\begin{aligned} k_{1_{298}} &= (1.21 \pm 0.05) \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \\ &= 7.2 \times 10^7\ \mathrm{L\ mol^{-1}\ s^{-1}} \end{aligned}$$

in good agreement with the literature value of $(5.1 \pm 1.5) \times 10^7$ found in competitive chlorination studies.[7]

On adding HCl to the reaction mixture, we reverse the foregoing reaction and can actually obtain the original Cl signal. Thus the reaction is reversible. The steady-state concentration of cyclopropyl in the reactor may be obtained from the following equations for the steady-state flows for Cl atoms and cyclopropyl ($\dot{\Delta}$) radicals.

$$k_{\mathrm{eCl}}[\mathrm{Cl}]_0 = k_{\mathrm{eCl}}[\mathrm{Cl}] + k_1[\Delta][\mathrm{Cl}] - k_{-1}[\dot{\Delta}]\,[\mathrm{HCl}] \qquad (4)$$

$$k_1[\Delta][\mathrm{Cl}] - k_{-1}[\dot{\Delta}][\mathrm{HCl}] - k_{\mathrm{e}\dot{\Delta}}[\dot{\Delta}] = 0 \qquad (5)$$

which upon rearrangement give

$$\frac{[\mathrm{Cl}]}{[\mathrm{Cl}]_0 - [\mathrm{Cl}]} = \frac{k_{\mathrm{eCl}}}{k_1[\Delta]} + \frac{k_{-1}}{k_1}\left(\frac{k_{\mathrm{eCl}}}{k_{\mathrm{e}\dot{\Delta}}}\right)\left(\frac{[\mathrm{HCl}]}{[\Delta]}\right) \qquad (6)$$

At constant Δ, a plot of $[\mathrm{Cl}]/([\mathrm{Cl}]_0 - [\mathrm{Cl}])$ against [HCl] should be a straight line with intercept of $k_{\mathrm{eCl}}/k_1[\Delta]$ and a slope of $(k_{-1}/k_1)(k_{\mathrm{eCl}}/(\Delta)k_{\mathrm{e}\dot{\Delta}})$. Figure 3 shows the plot of $[\mathrm{Cl}]/([\mathrm{Cl}]_0 - [\mathrm{Cl}])$ vs. [HCl] at slightly different concentrations of cyclopropane. It can be seen that, in two different series of runs (A, B) done on different dates, reasonably reproducible results were obtained in each series.

Table I. Thermochemical Data at 298 K[12,13]
$Cl + cyclopropane \rightleftarrows HCl + cyclopropyl$

	Cl	cyclopropane	HCl	cyclopropyl
$\Delta H_f°_{(298)}$	29.0	12.7	−22.1	66.9[a]
$S°_{(298)}$	39.50	56.8	44.60	61.7 ± 0.5

$$\Delta H_1° = 3.1 \text{ kcal/mol}$$

$$\Delta S_1° = 10.0 \pm 0.7 \text{ cal/mol·K}$$

[a] Present work.

The intercept in this plot (Figure 3) corresponds to the starting point for the introduction of HCl and represents the consumption by Δ of about ⅓ of the original $(Cl)_0$ flow. It has the highest precision of the points measured. This is a direct result of the fact that each measured value for (Cl) is not better than about ±5%. In consequence the ratio of $[Cl]/([Cl]_0 - [Cl])$ has an intrinsic uncertainty of about ±28% near the value of 3. Much, if not all, of this scatter arises from the difficulty with present circuitry of maintaining a constant electron energy in the vicinity of 21 eV. In this region the ionization cross-section energy of Cl atoms is very sensitive to the precise electron energy and with our present system it was not always possible to return to the previous voltage setting with sufficient accuracy. Despite this, the value of $k_{1_{298}} = 0.91 \pm 0.1$ is reasonably well established.

Discussion

The entropies of all the species in eq 1 are known or can be estimated to within ±0.5 cal/mol·K.[12,13] This allows us to estimate the heat of formation of the cyclopropyl radical.

$$\Delta G_1° = -RT \ln K_1 = 0.056 \pm 0.14 \text{ kcal/mol}$$

This result, in conjunction with thermochemical data for reaction (Table I), leads to the heat of formation of the cyclopropyl radical.

$$\Delta G_1° = \Delta H_1° - T\Delta S_1°$$

$$\Delta H_1° = 3.1 \pm 0.25 \text{ kcal/mol}$$

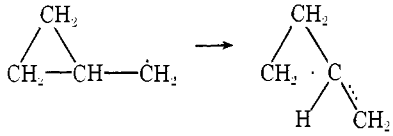
$$\Delta H_f° \text{ (cyclopropyl)} = 66.9 \pm 0.25 \text{ kcal/mol}$$

The C–H bond dissociation energy in Δ can be calculated:

$$\text{BDE}(\Delta\text{-H}) = 106.3 \pm 0.25 \text{ kcal/mol}$$

This C–H bond strength is higher than that in CH_4, which was reported as 105.1 ± 0.15 kcal/mol,[4] and at first sight seems surprisingly high. However, it is in line with other properties of the cyclopropane molecule which suggests that the electron density is more typical of an olefin than of a saturated compound. The ^{13}C–H coupling constant (161 Hz) in cyclopropane, for example, is very close to that in C_2H_4 (157 Hz) and very different from that in alkanes (126 ± 2 Hz).[14] The ionization potential of c-C_3H_6 at 10.09 eV[15] is also typically olefinic, being midway between that of C_3H_6 (9.73 eV) and C_2H_4 (10.5 eV) and much below the alkanes C_2H_6 (11.5 eV) and C_3H_8 (11.1 eV). Perhaps of closer interest are the strain energies in cyclopropene and methylenecyclopropane, which can be computed from the known heats of formation[12] as 53.7 and 41 kcal/mol, respectively. If we subtract from these the 27.6 kcal/mol of strain energy in cyclopropane[12] we obtain "excess" strain energies of 26.1 and 13.4 kcal/mol, respectively. If we naively attribute these values to the π bond centers attached to the cyclopropane ring (2 in cyclopropene and 1 in methylenecyclopropane) we arrive at 13 kcal/mol strain energy associated with a π bond center in a three-membered ring. If we now assume that the scission of the C–H bond in cyclopropane releases a π electron in the ring we can estimate a priori the bond strength as 95 kcal/mol (the normal C–H bond strength in an unstrained methylene group) plus 13 kcal/mol for the extra π bond strain for a total of 108 kcal/mol. We see that this value is in excellent agreement with the observed value of 106.3 kcal/mol and supports the very simple addition of strain energies.

This observed strain energy also makes understandable the absence of conjugative effect between cyclopropane rings and external unsaturation. Thus we have found that the cyclopropylmethyl radical shows no allylic stabilization[16] despite the olefinic type properties of cyclopropane. In order to conjugate the radical to the ring we would need to form a π bond center at the ring carbon atom which we may represent by the valence bond structure:



While this might gain about 12 kcal/mol of allylic stabilization by electron delocalization it would lose about 13 kcal/mol due to excess π bond strain for a net loss of about 1 kcal/mol.

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