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Chemical Dynamics of the Reaction between Chlorine Atoms and Deuterated Cyclohexane

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Abstract: The dynamics of the reaction Cl + cyclohexane-d_{12} (c-C_6D_{12}) → DCl + C_6D_{11} have been investigated by using time-resolved diode laser absorption spectroscopy to probe the reaction product DCl. The chlorine atoms have been generated by the UV photolysis of S_2Cl_2 and NOCl. Nascent DCl produced in the reaction is rotationally cold (below room temperature) and translationally hot. As the collision energy increases, the DCl product translational energy increases dramatically, the rotational energy increases slightly, and the vibrational energy remains essentially the same. Most of the initial translational collision energy appears as translational energy of the reaction products, and this observation can be simply explained as being a result of the heavy–light–heavy atom reaction kinematics. An extremely simple "spectator" model, where C_6D_{11} is the spectator, fits this experimental result very well. The cold DCl rotational state distribution may be an indication that Cl atoms abstract D atoms with a collinear C--D--Cl recoil geometry. Quasi-classical trajectory calculations using an empirical three-body model LEPS surface (C_6D_{11} is considered as a structureless particle) successfully predict a number of the experimental results.

1. Introduction

The gas-phase reaction of chlorine atoms with organic species is an important loss process for chlorine atoms in the Earth's stratosphere.[1] The main channel for chlorine (Cl) atom reaction with saturated hydrocarbons (RH) is known to be the abstraction process

$$\mathrm{Cl}\ (^2P_J) + \mathrm{RH} \rightarrow \mathrm{HCl} + \mathrm{R} \qquad (1)$$

where R is an alkyl radical. Recognition of the importance of these chlorine atom reactions has led to a number of kinetic studies;[2] however, despite this growing kinetic data base for Cl atom reactions with organic compounds, no state to state reaction dynamic information is yet available for these processes. A few theoretical calculations have been performed for Cl atoms reacting with the simplest hydrocarbon CH_4;[3,4] however, the potential energy surface has not been tested due to lack of experimental data. In this paper, we describe an experimental study of the Cl atom abstraction reaction with deuterated cyclohexane (C_6D_{12}). The quantum state and recoil velocity distributions of $D^{35}Cl$ have been measured to provide insight into the dynamics of this reaction. Chlorine atoms are generated by photodissociation of a precursor to initiate the reaction. The reaction product $D^{35}Cl$ is then probed by time-resolved infrared absorption spectroscopy with the use of a high-resolution (~0.0003-cm^{-1}) tuneable diode laser.[5] The reaction and probe sequence can be described by the equations

$$\mathrm{NOCl} + h\nu\ (193\ \mathrm{nm}) \rightarrow \mathrm{NO} + \mathrm{Cl}^\dagger \text{ or}$$
$$\mathrm{S_2Cl_2} + h\nu\ (248\ \mathrm{nm}) \rightarrow \mathrm{S_2Cl} + \mathrm{Cl}^\dagger \text{ (hot Cl production)} \qquad (2)$$

$$\mathrm{Cl}^\dagger + \mathrm{C_6D_{12}} \rightarrow \mathrm{C_6D_{11}} + \mathrm{DCl}(v,J,V) \text{ (reaction)} \qquad (3)$$

$$\mathrm{D^{35}Cl}(v,J,V) + h\nu\ (\sim 4.9\ \mu\mathrm{m}) \rightarrow \mathrm{D^{35}Cl}(v+1,J\pm 1,V) \text{ (diode laser probe)} \qquad (4)$$

where v, J, and V are the $D^{35}Cl$ vibrational quantum number, rotational quantum number, and translational velocity, respectively, and $Cl^\dagger$ is a hot (high-velocity) chlorine atom. The resolution of the diode laser is sufficient to determine the rovibrational and translational state distribution of DCl very precisely. This probe technique provides substantially improved spectral resolution compared to infrared fluorescence measurements,[6] allows ground states to be observed, and has excellent response time.

The role of reactant translational energy has been an important subject in gas-phase bimolecular reactions for many years; however, no attempt has been made so far to investigate changes in product quantum state distributions for hydrocarbon/Cl atom reactions by varying the translational energy of the chlorine atom. In the present experiments, chlorine atoms having different translational energy are produced by photodissociation of two Cl atom precursors, S_2Cl_2 and NOCl. The measurement of DCl product state distributions as a function of collision energy can thus be determined and provides a detailed picture of the reaction mechanism.

2. Experimental Section

The diode laser absorption technique has been described in detail previously,[7,8] and only a brief description is given here. A pulse from a photolysis laser initiates the reaction by producing chlorine atoms. The photolysis laser is a Lambda Physik EMG 201 excimer laser. The DCl reaction products were monitored by a Laser Photonics continuous wave diode laser operating at a wavelength of ~4.9 μm. The photolysis laser and probe laser were copropagated through a 2-m sample cell. The infrared absorption changes in a particular rovibrational line were monitored with an InSb detector (response time ~700 ns), amplified, averaged on a LeCroy 9400 digital oscilloscope, and stored in an IBM PC-AT computer. Signals obtained when the diode laser was slightly detuned from a particular DCl transition were averaged and subtracted from the on-resonance signal in order to eliminate contributions to the transient signals from thermal lens effects. Such corrections were typically less than 10%. Chlorine atoms were produced by photodissociation of NOCl at 193 nm and S_2Cl_2 at 248 nm. These molecules are chosen to maximize the number of chlorine atoms produced. The absorption coefficient (ϵ) of NOCl at 193 nm is ~20 000 L/mol·cm,[9] and that of S_2Cl_2 at 248 nm is ~4400 L/mol·cm.[10] In order to measure the nascent DCl state

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(1) Rowland, F. S.; Molina, M. J. *Rev. Geophys. Space. Phys.* **1975**, *13*, 1.

(2) Kondratiev, V. N. *Rate Constants of Gas Phase Reactions Reference Book*; Fristrom, R. M., Ed.; NBS: Washington, DC, 1972 (and references therein). *Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling, Evaluation Number 6*; NASA: Washington, DC, 1983 (and references therein). Davis, D. D.; Braun, W.; Bass, A. M. *Int. J. Chem. Kinet.* **1970**, *2*, 101. Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1985**, *17*, 33. Wallington, T. J.; Skewes, L. M.; Siegl, W. O.; Wu, C. H.; Japar, S. M. *Int. J. Chem. Kinet.* **1988**, *20*, 867. Tschuikow-Roux, E.; Niedzielski, J.; Faraji, F. *Can. J. Chem.* **1985**, *63*, 1093. Manning, R. G.; Kurylo, M. J. *J. Phys. Chem.* **1977**, *81*, 291. Lewis, R. S.; Sander, S. P.; Wagner, S.; Watson, R. T. *J. Phys. Chem.* **1980**, *84*, 2009.

(3) Truong, T. N.; Truhlar, D. G.; Baldridge, K. K.; Gordon, M. S.; Steckler, R. *J. Chem. Phys.* **1989**, *90*, 7137.

(4) Wiberg, K. B.; Motell, E. L. *Tetrahedron* **1963**, *19*, 2009.

(5) Hossenlopp, J. M.; Hershberger, J. F.; Flynn, G. W. *J. Phys. Chem.* **1990**, *94*, 1346.

(6) Agrawalla, B. S.; Setser, D. W. *J. Phys. Chem.* **1986**, *90*, 2450.

(7) Khan, F. A.; Kreutz, T. G.; Flynn, G. W.; Weston, R. E., Jr. *J. Chem. Phys.* **1990**, *92*, 4856.

(8) Hershberger, J. F.; Hewitt, S. A.; Flynn, G. W. *J. Chem. Phys.* **1987**, *87*, 1894.

(9) Illies, A. J.; Takacs, G. A. *J. Photochem.* **1976/77**, *6*, 35.

0002-7863/92/1514-58$03.00/0

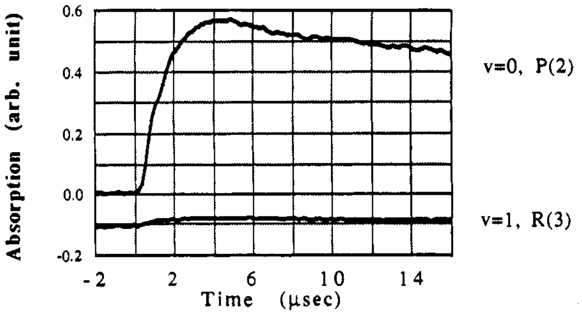

Figure 1. Transient absorption signals corresponding to rovibrational excitation of DCl produced in the reaction Cl + cyclohexane-d_{12}, obtained in a mixture containing 15 mTorr of S_2Cl_2 and 15 mTorr of cyclohexane-d_{12}. 20 laser shots were averaged. The excimer laser which photolyzes the S_2Cl_2 fires at $t = 0$. In the upper trace the diode laser probes the P(2), $v = 0 \rightarrow 1$ DCl transition while in the lower trace it probes R(3), $v = 1 \rightarrow 2$.

distribution, the total pressure of reactants was maintained below 30 mTorr. A 1:5 mixture of NOCl and cyclohexane-d_{12} and a 1:1 mixture of S_2Cl_2 and cyclohexane-d_{12} were used. The reactants were mixed just before the cell and flowed continuously through the cell. No significant DCl buildup between laser pulses was observed when the excimer laser repetition rate was below 0.05 Hz. All experimental measurements were made with excimer laser repetition rates of either 0.05 or 0.1 Hz. The reaction rate constant at room temperature has been measured at ~1-Torr total pressure in a 1:200 mixture of NOCl and Ne with the partial pressure of cyclohexane-d_{12} in the range 20–80 mTorr.

For the line width measurements, the diode laser frequency was locked to an infrared fringe of a Laser Photonics Confocal Etalon (Model SP 5945) using a 1-kHz modulation frequency. The modulation amplitude was roughly the width of a fringe, 0.002 cm^{-1}, and precise diode laser frequency control was accomplished by computer-controlled rotation of a scanner plate internal to the etalon. Transient absorption signals were obtained while the etalon fringe was over the absorption line of interest. The excimer laser was fired at the center of the modulation cycle in order to sample only a single diode laser frequency for a given etalon fringe position.

Cyclohexane-d_{12} (Aldrich, 99.5% d) was purified by several freeze–pump–thaw cycles at 0 °C. NOCl (99.2% minimum purity) purchased from Matheson was further purified by several freeze–pump–thaw cycles in an ethanol–dry ice bath (-72 °C). S_2Cl_2 (Aldrich, 98%) was pumped on at ~40 °C until a steady vapor pressure was obtained.

3. Results

(a) Rotational, Vibrational, and Translational Energy Distribution of DCl from Cl Atom Reaction with Cyclohexane-d_{12}. Typical time-resolved signals observed while monitoring DCl $v = 0 \rightarrow v = 1$ P(2) and $v = 1 \rightarrow v = 2$ R(3) transition lines are shown in Figure 1. The IR diode laser light absorbed in the $v \rightarrow v + 1$ transition is proportional to the population difference between v and $v + 1$ levels[11]

$$N(v,J) - N(v+1,J\pm1) \propto (\Delta I/I_0)/[X_J R^2 \nu] \qquad (5)$$

where ΔI is the change in the amount of IR light transmitted following the reaction, I_0 is the total IR intensity at frequency ν, X_J is the Honl–London factor given by $(J + 1)/(2J + 1)$ for R branch lines and $J/(2J + 1)$ for P branch lines, and R is the transition matrix element. In the present experiments, the upper state population has been determined to be negligible compared to the lower state populations. Thus, the observed transient absorption signals reflect the temporal behavior of the population in the lower rovibrational level only. The nascent population of rovibrational states was obtained by measuring the absorption signal amplitude at 800 ns after the excimer laser pulse.

A Boltzmann plot of the nascent rotational state distribution of DCl(v=0) from the reaction of deuterated cyclohexane with Cl atoms produced by photolysis of S_2Cl_2 is shown in Figure 2a. The best fit to a Boltzmann distribution gives a temperature of T_R = 135 K, and an average of several experimental runs provides T_R = 156 ± 35 K for the v = 0 state and T_R = 145 ± 45 K for the v = 1 state. The signal from the v = 2 state is negligible compared to those of v = 0 and v = 1. The reaction of Cl atoms produced by photolysis of NOCl generates DCl(v=0) whose average rotational temperature is 200 ± 50 K. Figure 2b shows a Boltzmann plot of the DCl(v=0) rotational state distribution produced by reaction with Cl atoms from NOCl.

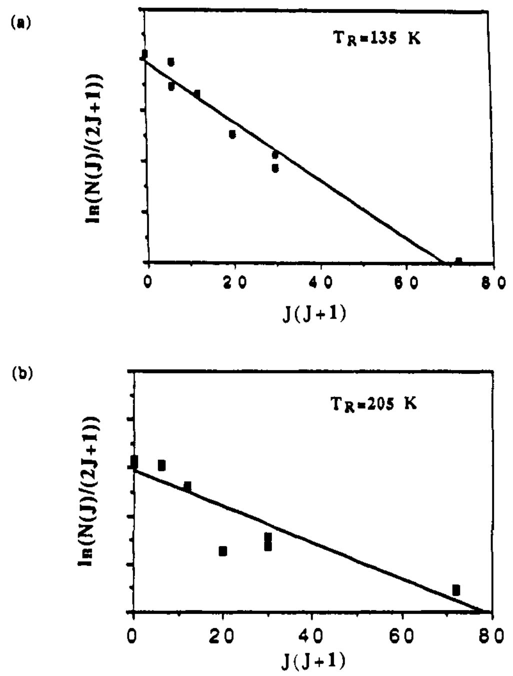

Figure 2. (a) Boltzmann plot of the nascent rotational distribution of DCl(v=0) produced by reaction of Cl (from S_2Cl_2 photolysis at 248 nm) + cyclohexane-d_{12}. The line is a best fit to a rotational temperature of 135 K. (b) Boltzmann plot of the nascent rotational distribution of DCl(v=0) produced by reaction of Cl (from NOCl photolysis at 193 nm) + cyclohexane-d_{12}. The line is a best fit to a rotational temperature of 205 K. N_J is the experimentally determined number of molecules produced in a given rotational state by the reaction.

Since the DCl rotational temperatures for the v = 0 and v = 1 states are the same for the reaction of Cl atoms produced by S_2Cl_2 photolysis, the relative vibrational populations of these two levels have been determined by measuring relative absorption amplitudes for the same rotational levels in the v = 0 and v = 1 states. Of the DCl 95% is formed in the vibrational ground state, and the vibrational temperature was found to be 1000 ± 300 K which corresponds to an average vibrational energy of 0.3 ± 0.1 kcal/mol above the DCl zero-point level. For the reaction of Cl atoms produced by NOCl photolysis, assuming that the rotational temperature in the v = 1 state is the same as that in the v = 0 state, the measurement of the relative absorption amplitude for the same rotational levels in the v = 0 and v = 1 states yields the vibrational temperature 1000 ± 300 K.

The Doppler profiles of the $v = 0 \rightarrow v = 1$, P(2) DCl absorption line produced by reaction of Cl atoms from S_2Cl_2 and NOCl photolysis are shown in Figure 3, parts a and b, respectively. For the reaction of Cl atoms produced by S_2Cl_2 photolysis, the fit of the Doppler absorption line profile to a Gaussian is excellent and the full width at half-maximum (fwhm) averaged over many experimental runs is 0.0088 ± 0.0010 cm^{-1}, which corresponds to a translational temperature of 1300 ± 300 K. Doppler profiles for different rotational states of the same vibrational level have the same line width within experimental error. For the reaction of Cl atoms from NOCl, the fwhm of the Doppler profile has been measured to be 0.015 ± 0.001 cm^{-1} for the $v = 0 \rightarrow v = 1$ P(2) absorption line and 0.013 ± 0.001 cm^{-1} for the $v = 1 \rightarrow v = 2$ R(2) absorption line. Thus, the average translational temperature for the v = 0 state is 3800 ± 500 K while that for v = 1 is 2900 ± 400 K. Table I lists the rotational, vibrational, and translational

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(10) Chasovnikov, S. A.; Chichinin, A. I.; Krasnoperov, L. N. *Chem. Phys.* **1987**, *116*, 91.

(11) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1950; Vol. 1.

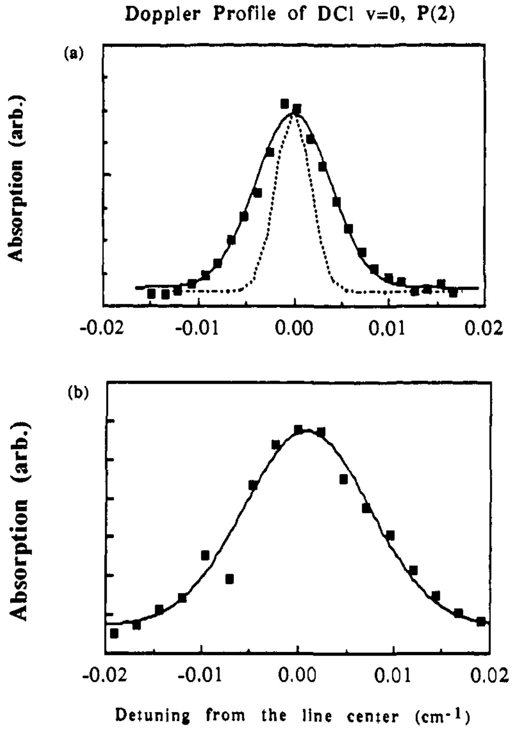

Figure 3. (a) Nascent Doppler profile line shapes of the DCl(v=0) P(2) line from the reaction of Cl (from S_2Cl_2 photolysis at 248 nm) + cyclohexane-d_{12}. The solid line is a best fit to a Gaussian line shape. The fitted fwhm is 0.0092 cm^{-1}, which corresponds to a translational temperature of 1430 K. The room-temperature line shape whose fwhm is 0.0042 cm^{-1} (300 K) is shown for comparison as a dotted line. (b) Nascent Doppler profile line shapes of the DCl(v=0) P(2) line from the reaction of Cl (from NOCl photolysis at 193 nm) + cyclohexane-d_{12}. The solid line is a best fit to a Gaussian line shape. The fitted fwhm is 0.015 cm^{-1}, which corresponds to a translational temperature of 3800 K.

Table I. Experimental Values of Translational, Rotational, and Vibrational Temperatures of Product DCl for the Reaction of Cl + Cyclohexane-d_{12}

Cl precursor	$h\nu$ (nm)	vibrational state of DCl	$T_T{}^a$ (K)	$T_R{}^b$ (K)	$T_V{}^c$ (K)
S_2Cl_2	248	$v = 0$	1300 ± 300	156 ± 35	
		$v = 1$		145 ± 45	1000 ± 300
NOCl	193	$v = 0$	3800 ± 500	200 ± 50	
		$v = 1$	2900 ± 400		1000 ± 300

[a] The translational temperature of DCl. [b] The rotational temperature of DCl. [c] The vibrational temperature of DCl.

temperatures of the DCl produced, obtained using different Cl atom precursors.

The translational energy of the Cl atoms produced from photodissociation of NOCl at 193 nm was measured to be 19.3 kcal/mol (0.8 eV) by Haas et al.[12] The translational energy of the Cl atoms produced from photodissociation of S_2Cl_2 at 248 nm has been recently measured in our laboratory to be 7 ± 1 kcal/mol (0.30 ± 0.06 eV) by direct probing of the Cl atom Doppler profile with a high-resolution diode laser.[13] The collisional energy in the Cl/C_6D_{12} center of mass frame (E_{COL}) is calculated to be 5.3 ± 0.7 kcal/mol for the reaction of Cl atoms produced from S_2Cl_2 at 248 nm and 14.3 ± 2 kcal/mol for the reaction of Cl atoms from NOCl at 193 nm. Table II lists the amount of energy appearing in various degrees of freedom of the reaction products. As the collision energy is increased, the translational energy of the reaction products increases dramatically, but the DCl rotational energy increases only slightly while the DCl vibrational energy remains approximately the same. Note that the total translational energy of the reaction products can be estimated from the translational energy of DCl using linear momentum conservation arguments. The internal energy of the cyclohexyl radicals is then obtained by subtracting the internal energy of the DCl and the translational energy of the two reaction products from the average available energy calculated as described in the Discussion. The fraction of available energy partitioned into reaction product states is also listed in Table II.

(b) Rate Constant Measurement for the Reaction Cl + Cyclohexane-d_{12} at Room Temperature. Under the conditions that the concentration of cyclohexane-d_{12} is large compared to the concentration of photolytically produced Cl atoms, the rate of the reaction Cl + cyclohexane-d_{12} will be pseudo-first-order in cyclohexane concentration. The time-dependent absorption signals for the DCl(v=0→v=1) P(3) and DCl(v=0→v=1) P(5) transitions have been measured as a function of cyclohexane-d_{12} concentration using NOCl as the Cl atom precursor in a large excess of Ne. The absence of any dependence of the signal rise times on Cl atom precursor concentration demonstrates the pseudo-first-order behavior of this reaction system. From the rate of rise of the absorption signals, corrected for diffusion, the reaction rate constant has been found to be $(1.3 \pm 0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

4. Discussion

The rate constant for the Cl atom reaction with cyclohexane-d_{12}, $(1.3 \pm 0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, obtained from these measurements is slightly smaller than the average value of ~2.3 $\times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} reported for the Cl atom reaction with cyclohexane.[2] This is consistent with the expected deuterium isotope effect for the Cl atom abstraction reaction with hydrocarbons. The energy barrier for Cl atom reaction with deuterated cyclohexane has not yet been measured, but the barrier for reaction with cyclopentane has been reported to be ~0.5 kcal/mol (the rate constant is 2×10^{-10} cm^3 $molecule^{-1}$ s^{-1}).[2] This, coupled with the kinetic rate constant for the Cl plus cyclohexane-d_{12} reactions, suggests that an energy barrier ≤1 kcal/mol can be assumed for the Cl atom reaction with cyclohexane-d_{12}. The collision energy of the Cl atoms photodissociated from NOCl and from S_2Cl_2 is thus easily large enough to overcome the reaction energy barrier.

Normally the available energy (E_{AVAL}) for a thermal reaction can be written[14]

$$E_{AVAL} = -\Delta H^\circ_0 + E_a + E_{th} \tag{6}$$

where $-\Delta H^\circ_0$ is the enthalpy change for the reaction at 0 K, E_a is the activation energy, and E_{th} is the thermal energy of reactants. In the present case, since the Cl atom has very high velocity, the available energy can be written to a good approximation as

$$E_{AVAL} = -\Delta H^\circ_0 + E_{COL} + E_{int} \tag{7}$$

E_{COL} is the center of mass translational energy for the $Cl-C_6D_{12}$ collision (E_{COL} = 5.3 kcal/mol for Cl atoms from S_2Cl_2 and 14.3 kcal/mol for Cl atoms from NOCl), and E_{int} is the rotational and vibrational energy of C_6D_{12}. We estimate $E_a \leq 1$ kcal/mol as noted above. This low value for E_a is consistent with the large rate for the reaction of Cl with C_6H_{12}. Since $E_a \ll E_{COL}$, the reaction rate is not expected to vary much for collisions within E_a of E_{AVAL}. Thus, the mean energy for species which actually go on to products will be near E_{AVAL} as defined by eq 7. This is in contrast to a thermal reaction where the reaction rate does vary significantly around E_{AVAL} because $E_{AVAL} \sim E_a$, and the mean energy for species which actually go on to products will be near E_{AVAL} as defined by eq 6. E_{COL} can be calculated from the measured translational energy of Cl plus a small correction for the thermal motion of C_6D_{12}. The rotational plus vibrational energy of cyclohexane is given by

$$E_{int} = \tfrac{3}{2}RT + \sum_i h\nu_i/[\exp(h\nu_i/kT) - 1] \tag{8}$$

where the ν_i are the 48 vibrational frequencies for C_6D_{12}.[15] The

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(12) Haas, B.-M.; Felder, P.; Huber, J. R. *Chem. Phys. Lett.* **1991**, *180*, 293.

(13) Park, J.; Lee, Y.; Flynn, G. W. Submitted for publication.

(14) Pilling, M. J.; Smith, I. W. M. *Modern Gas Kinetics: Theory, Experiment, and Application*; Blackwell Scientific: Boston, 1987.

Table II. Energy Partitioning (kcal/mol) for the Reaction of Cl + Cyclohexane-d_{12} at Different Collision Energies

E_{COL}[a]	E_{AVAL}[b]	E_T[c]	E_R[d] of DCl	E_V[e] of DCl	E_{INT}[f]
5.3 ± 0.7	16.1 ± 2	5.9 ± 1.2	0.3 ± 0.07	0.3 ± 0.07	9.6 ± 2
		(0.37 ± 0.08)[g]	(0.02)	(0.02)	(0.60 ± 0.12)
14.3 ± 2	25.1 ± 3	15.0 ± 2	0.4 ± 0.1	0.3 ± 0.07	9.4 ± 2
		(0.60 ± 0.08)	(0.02)	(0.01)	(0.37 ± 0.06)

[a] The relative translational energy in the center-of-mass frame. [b] The available energy for the reaction, $E_{AVAL} = -\Delta H^\circ_0 + E_{in}(C_6D_{12}) + E_{COL}$ (see text for the definition). [c] Total translational energy of both reaction products, DCl and cyclohexyl radical, in the laboratory frame. [d] The rotational energy of DCl. [e] The vibrational energy of DCl above the zero-point level. [f] The sum of the vibrational and the rotational energy of cyclohexyl radical derived by subtracting the internal energy of DCl and the relative translational energy of both DCl and cyclohexyl radical from E_{AVAL}. [g] The quantities in parentheses are the fractions of available energy (E_{AVAL}) observed in a given degree of freedom.

enthalpy change for the reaction at 0 K can be estimated as follows. ΔH°_{298} for the reaction of Cl + C_6H_{12} is obtained from ΔH_f° for reactants and products[16] and the correction to 0 K made by using ΔC_p, the difference in the heat capacity for reactants and products. To obtain ΔH°_0 for the deuterated species (for which ΔH_f° is generally not available), we correct the hydrogenated value of ΔH°_0 for the differences in zero-point energies for HCl and DCl and for the difference in the zero-point energies of the three vibrations lost in converting C_6D_{12} to C_6D_{11}. The values thus obtained are $\Delta H^\circ_0 = -7.96 \pm 2$ kcal/mol and $E_{int} = 2.8 \pm 0.1$ kcal/mol. E_{COL} is given in Table II for Cl atoms from the photodissociation of S_2Cl_2 and NOCl. Although the corrections necessary to obtain ΔH°_0 for the deuterated species from ΔH°_{298} for the hydrogenated species can only be made approximately, most of these corrections are quite small compared to ΔH°_{298}. In fact, we expect the major uncertainty in ΔH°_0 to be due to $\Delta H_f^\circ(C_6H_{11})$, which is only known to an accuracy ±1 kcal mol. Note that since ΔH°_0 is derived ultimately from measured ΔH_f° values, it includes the reorganization energy for converting the nuclear structure of C_6D_{12} to that of C_6D_{11} under thermal conditions. This point is considered further below. In addition, ΔH°_0 derived in this way represents an average for abstracting either an equatorial or an axial D atom.

There are several interesting features of the present study which are notable. First, much of the initial translational energy (E_{COL}) of the reactants appears as translational energy of the products. This feature becomes especially transparent when results for different initial translational energies are considered. Thus, if the translational collision energy of Cl + C_6D_{12} is increased from 5.3 to 14.3 kcal/mol, almost all of this energy increase appears as product translation (see Table II). This effect is largely a result of the kinematics for a reaction system in which a heavy atom abstracts a light atom attached to another heavy atom or radical (heavy–light–heavy). Here, Cl (MW35) attacks D (MW2) attached to C_6D_{11}(MW 94). Such systems are characterized by a small skew angle β, where in the present case

$$\cos^2\beta = m_{Cl}m_{C_6D_{11}}/m_{DCl}m_{C_6D_{12}} = 0.93 \qquad (9)$$

or $\beta = 15.3°$. For systems with small β, conservation of linear momentum on going from reactants to products largely dictates that only a small change in total translational energy can occur. Indeed, a simple "spectator model", which assumes that the velocity of C_6D_{11} is the same as the velocity of C_6D_{12} in the center of mass frame, predicts[17]

$$E_T^{fin}(\mathrm{COM}) = (\cos^2\beta)E_T^{ini}(\mathrm{COM}) \qquad (10)$$

where the indicated translational energies are evaluated in the center of mass frame. Experimentally, we find $E_T^{fin}(\mathrm{COM})/E_T^{ini}(\mathrm{COM}) = 0.63 \pm 0.2$. This corresponds to a center of mass velocity ratio for C_6D_{11} compared to C_6D_{12} of

$$w(C_6D_{12})/w(C_6D_{11}) = 1.22 \pm 0.20 \qquad (11)$$

which is very close to the spectator limit. The spectator model should work well here since hydrogen abstraction reactions are generally direct processes. The observation that translational energy of reactants is converted to translational energy of products for heavy–light–heavy reaction systems has been confirmed in a number of theoretical[18] and experimental investigations of atom/diatom reactions. One such example is the reaction of Cl atoms with HI and DI.[19,20] Polanyi and co-workers studied the reaction dynamics of Cl + HI, Cl + DI, and Cl + HBr. The collision energy was varied from 1.6 to 12 kcal/mol. Enhanced collision energy was found to give rise to a small decrease in product vibrational excitation, a small increase in product rotational excitation, and a large increase in product translational energy. A highly repulsive LEPS potential surface was employed to explain these effects of collision energy on the energy distribution among the reaction products. The change of the energy partitioning as a function of collision energy is very similar in the Cl atom/DI reaction and the Cl atom/cyclohexane-d_{12} reaction.

The second notable feature of the Cl + C_6D_{12} reaction observed here is the low internal energy of the DCl products, particularly the cold rotational distribution. While the lack of conversion of reactant translational energy to product rotation or vibration can be understood in terms of the kinematics of heavy–light–heavy reactions, there remains some 8 ± 2 kcal/mol of energy available to products from the reaction exoergicity and another 2.8 ± 0.1 kcal/mol from the thermal internal energy of C_6D_{12}. It is reasonable to expect that much of the thermal energy of C_6D_{12} will carry over to internal energy of C_6D_{11}, but the reaction exoergicity of 8 ± 2 kcal/mol is certainly available for distribution to internal states of the products. There seem to be three possible explanations for the cold DCl rotational distributions. First, the reorganization energy required to go from C_6D_{11}–D to C_6D_{11} + D (essentially a change in the zero-point energy of the 45 vibrational modes common to C_6D_{12} and C_6D_{11}) may be large and unavailable to the DCl product. If the abstraction is rapid compared to reorganization of the C_6D_{11} backbone structure to its equilibrium configuration, the reorganization energy would not be available to the DCl product. This has the effect of reducing E_{AVAL} since ΔH°_0 as computed above includes the reorganization energy. Second, although most of the reactant kinetic energy (E_{COL}) must appear as product kinetic energy, the remaining $-\Delta H^\circ_0 + E_{th}$ energy might be statistically distributed among the 45 C_6D_{11} and 1 DCl vibrational modes and the rotational degrees of freedom of the products. The large number of vibrations in C_6D_{11} would then soak up much of the available 10.8 ± 2 kcal/mol. Such a result seems unlikely for a direct abstraction reaction. Finally, the observation of a cold DCl rotational distribution may represent a bias toward collinear C–D–Cl recoil. This would require that the barrier for collinear reaction be low but rise steeply for geometries other than collinear. Though not in and of itself surprising, since a number of three-atom heavy–light–heavy Cl atom reactions exhibit this property,[21-23] such a picture needs to be reconciled with the low activation energy and large reaction rate observed for the thermal Cl + C_6D_{12} reaction. One way in which

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(15) Wieberg, K. B.; Shrake, A. *Spectrochim. Acta* **1971**, *27A*, 1139.

(16) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(17) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University: Oxford, 1987.

(18) Baer, M. *J. Chem. Phys.* **1975**, *62*, 4545.

(19) Maylotte, D. H.; Polanyi, J. C.; Woodall, K. B. *J. Chem. Phys.* **1972**, *57*, 1547.

(20) Parr, C. A.; Polanyi, J. C.; Wong, W. H. *J. Chem. Phys.* **1973**, *58*, 5.

(21) Kornweitz, H.; Persky, A. *Chem. Phys.* **1989**, *132*, 153.

(22) Mayne, H. R. *J. Chem. Phys.* **1980**, *73*, 217.

(23) Tan, K. G.; Laidler, K. J.; Wright, J. S. *J. Chem. Phys.* **1977**, *67*, 5883.

to obtain highly restricted collinear reaction geometries and yet have a low reaction barrier has been suggested by theoretical studies of "alignment" or "orientation" effects in the reaction of Cl + HCl.[21-23] Essentially, in this reaction system the light H atom can move to meet the incoming Cl reagent head on, thereby lowering the barrier to reaction. In the Cl + HCl system such an alignment occurs through a rotation of the HCl. For the Cl + C_6D_{12} system, the vibrational motion of the D atoms is both rapid and of large amplitude, and such orientation effects could be brought about by the zero-point vibrational motion of the D atoms. For the CD_2 bending motion of frequency, $\nu = 1100\ \mathrm{cm}^{-1}$, the time scale over which the D atoms move is $1/(3.3 \times 10^{13}\ \mathrm{s}) \sim 0.03$ ps. Hyperthermal Cl atoms of velocity 10^5 cm/s ($E \sim 5$ kcal/mol) move only $r \sim 10^5 \times 3 \times 10^{-14}\ \mathrm{cm} = 10^{-9}\ \mathrm{cm} = 0.3$ Å on this time scale. The zero-point fluctuations in the CD_2 bending angle are also relative large because of the light mass of the D atoms. Thus, as the Cl atom approaches C_6D_{12}, the large amplitude, rapid vibrational motion of the roughly six visible D atoms increases the opportunity for collinear C–D–Cl alignment at some point in the Cl trajectory. The vibrational motion of the D atoms on C_6D_{12} could play a similar role to the rotational motion of HCl (for the Cl + HCl system) in producing an alignment or orientation effect. Rotational motion of C_6D_{12} can also contribute to this effect, but the heavy mass of cyclohexane produces a relatively long rotational period for this molecule (less than one-thousandth of the vibrational period).

The abstraction reactions of O(^{3}P) with several hydrocarbons such as neopentane, cyclohexane, and isobutane have been studied by Luntz and co-workers.[24] Cold rotational state distributions were found for the OH products although translational energy recoil could not be measured. The observed OH vibrational state distribution is strongly dependent on the type of C–H bonds involved in the reaction. The reactions of F atoms with cycloalkanes (cyclanes), investigated by Setser and co-workers[25] and Parker,[26] release ~50% of the available energy as vibrational energy of HF. An estimate of the nascent rotational energy distribution for these systems suggests that ~7% of the available energy was partitioned into HF rotational energy.[25] Thus, both O(^{3}P) and F atom/hydrocarbon systems show relatively cold rotational distributions for the diatomic reaction product. Quasi-classical trajectory calculations using a London–Eyring–Polanyi–Sato (LEPS) semiempirical potential surface on a three-body model were carried out in order to interpret the experimental results for both O(^{3}P) and F atom reactions. The trajectory calculations for the reaction of O(^{3}P) predict most aspects of the experiment correctly and suggest a collinear geometry on a repulsive potential surface. Setser's trajectory calculations[25] for the F atom reactions using several empirical potential surfaces can reproduce the observed high vibrational excitation but show a significant portion of complex trajectories indicating the presence of some indirect reaction pathways.

Many features of the present results for the Cl(^{2}P) atom reactions with deuterated cyclohexane (cold rotational distributions and relatively low vibrational excitation) are similar to those for the reaction of O(^{3}P) atoms with cyclohexane.[24] In a manner similar to that employed for the O(^{3}P) + C_6H_{12} reaction, an empirical LEPS potential surface was constructed for the Cl + C_6D_{12} reaction, and quasi-classical trajectory calculations have been performed using this surface to evaluate the reactive cross section. The parameters used to define the surface for the reaction are given in Table III. S_1 was chosen to be the same as that used for the O(^{3}P) + C_6H_{12} reaction.[24] The adjustable parameters S_2 and S_3 were chosen to fit the classical trajectory calculations to two aspects of the experimental results. These were the DCl rotational state distribution and the DCl vibrational state distribution for the reaction at a collision energy of 5.3 kcal/mol. The rotational excitation depends mostly on the S_3 parameter.

Table III. Parameters Used To Construct a Model LEPS Surface for the Cl + $C_6D_{12} \rightarrow$ DCl + C_6D_{11} Reaction

i	species (i)	D_i[a] (eV)	β_i[a] (Å)	r_i[a] (Å)	S_i
1	C_6D_{11}–D[b]	4.25	1.83	1.09	0.24
2	DCl	4.48[c]	1.9046[c]	1.27[c]	0.37[d]
3	C_6D_{11}–Cl	3.40[c]	2.7086[c]	1.76[c]	−0.59[d]

[a] Morse potential parameters: D_i is the bond dissociation energy, $\beta_i = \pi c \nu (2\mu/D_i)^{1/2}$ where ν is the frequency (cm^{-1}) of the hypothetical classical oscillator and r_i = the equilibrium bond distance. [b] D_i, β_i, r_i, and the constant S_i of C_6D_{12} (i.e., S_1) have been obtained from ref 24. [c] D_i, β_i, and r_i of DCl and C_6D_{11}Cl have been calculated from known thermodynamic data and vibrational frequencies.[11,32] [d] S_i of DCl and C_6D_{11}Cl (i.e., S_2 and S_3) have been chosen to fit the observed vibrational and rotational excitation at a collision energy of 5.3 kcal/mol.

Table IV. Calculated Average Energies (kcal/mol) of Product DCl Produced in the Reaction Cl + $C_6D_{12} \rightarrow$ DCl + C_6D_{11} Using the LEPS Potential Surface with Parameters Given in Table III

E_{COL}[a]	E_{AVAL}	no. of trajectories	E_{R}[b]	E_{V}[b]	E_{T}[c]
5.3	16.1	7500	0.29 ± 0.08	6.7 ± 0.8	9.1 ± 1
14.3	25.1	5500	1.6 ± 0.2	6.3 ± 0.2	17.2 ± 2

[a] E_{COL} is the relative Cl/C_6D_{12} center-of-mass translational energy. [b] E_{R} is the rotational energy and E_{V} is the vibrational energy of product DCl. [c] E_{T} is the translational energy of the reaction products DCl and C_6D_{11}; $E_{\mathrm{T}} = E_{\mathrm{AVAL}} - E_{\mathrm{R}} - E_{\mathrm{V}}$.

Decreasing S_3 yields lower rotational excitation, and a value of $S_3 = -0.59$ fits the observed $v = 0$ rotational state distribution well. The vibrational state distribution is sensitive to S_2, and a value of $S_2 = 0.37$ was chosen to fit the vibrational excitation at 5.3 kcal/mol collision energy; however, no reasonable value of S_2 gives a good fit to the vibrational energy data as noted below.

Scattering calculations on this model potential surface were performed using Muckerman's classical trajectory program (CLASTR).[27] Trajectories were initiated at a Cl–DR internuclear separation (b_{max}) of 3 Å and with the DR quasi-diatomic molecule in the $v = 0$ and $J = 3$ level. Using the S_1 value for the O(^{3}P) + C_6H_{12} reaction and adjusting S_2 and S_3 to give the best fit to the DCl vibrational and rotational distributions for a collision energy of 5.3 kcal/mol yields a number of interesting results. Table IV lists the results calculated with these parameters for partitioning of energy into the rotational, vibrational, and translational degrees of freedom of the reaction products. First, increasing the initial translational energy from 5.3 to 14.3 kcal/mol leads to a substantial increase in the translational energy of the products as observed experimentally. This result reflects the kinematic limitations in converting the translational energy of the reactants to translational energy of the products as discussed earlier. Second, at 5.3 kcal/mol the best fit S_2 and S_3 values predict vibrational energy in the DCl product which is much too large compared to the experiments. Nevertheless, the vibrational energy of DCl does not increase on going from a collision energy of 5.3 to 14.3 kcal/mol as observed experimentally. The failure of the simple three-body model to predict quantitatively the DCl vibrational distribution is not surprising since the true Cl + C_6D_{12} reaction system has a very large number of vibrational degrees of freedom which are not well represented by this model. Third, the observed DCl rotational distribution fits the three-body model predictions at a collision energy of 5.3 kcal/mol; however, the experimentally observed rotational energy of DCl increases only slightly (~30%) going from a collision energy of 5.3 to 14.3 kcal/mol in contrast to the model calculations which show a larger increase (~500%) in DCl rotational energy. Last, the reaction cross section predicted by the three-body model calculations for the thermal reaction is much smaller than observed experimentally. This last observation is consistent with the difficulty discussed above in reconciling the observed cold DCl rotational distributions with the large observed reaction cross section and may signal the

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(24) Andresen, P.; Luntz, A. C. *J. Chem. Phys.* **1980**, *72*, 5842. Luntz, A. C.; Andresen, P. *J. Chem. Phys.* **1980**, *72*, 5851.

(25) Kim, K. C.; Setser, D. W. *J. Phys. Chem.* **1973**, *77*, 2493. Johnston, R. L.; Kim, K. C.; Setser, D. W. *J. Phys. Chem.* **1973**, *77*, 2499.

(26) Parker, J. H. *Int. J. Chem. Kinet.* **1975**, *7*, 433.

(27) Faist, M. B.; Muckerman, J. T.; Schubert, F. E. *J. Chem. Phys.* **1978**, *69*, 4087.

importance of alignment effects as noted above. While the three-body model is informative, considerable caution must be exercised in applying such a simple picture to a complex reaction involving a large number of atoms.

Given the observation above that C_6D_{11} acts almost like a spectator, at least with respect to translational energy, it is reasonable to treat C_6D_{11} as a structureless particle. Under this assumption, the vibrational state distribution of DCl from the reaction of deuterated cyclohexane with Cl atoms produced by photolysis of S_2Cl_2 can be compared with an expected three-body model prior, statistical distribution by using a surprisal analysis.[17] Using the prior distribution $P^\circ(v) \propto (E_{\rm AVAL} - E_v)^{3/2}$, a plot of $\ln [P(v)/P^\circ(v)]$ versus $f_v = E_v/E_{\rm AVAL}$ provides a slope of $\lambda_v = 3.5 \pm 1.0$. Thus, the experimental vibrational state distribution is colder than the prior distribution. The rotational state distribution can also be compared with a prior distribution by plotting $\ln [P(v,J)/P^\circ(v,J)]$ as a function of $g_R = E_R/E_{\rm AVAL}$. The prior distribution is $P^\circ(v,J) \propto (2J + 1)(E_{\rm AVAL} - E_v - E_R)^{1/2}$. The slope of a plot of $\ln [P(v,J)/P^\circ(v,J)$ is 41 ± 8, indicating that the experimental rotational state distribution is much *colder* than the statistical distribution.

The ground state of the Cl atom is split into two states, $^2P_{3/2}$ and $^2P_{1/2}$, due to spin–orbit coupling. The excited state $^2P_{1/2}$ is 882 cm^{-1} above the ground state $^2P_{3/2}$. The photodissociation of S_2Cl_2 at 248 nm produces a mixture of 78% ground-state Cl atoms and 22% excited Cl (Cl*) atoms.[13,28] The Cl* to Cl ratio has not been measured for the photodissociation of NOCl at 193 nm. The reactivity of excited- and ground-state fluorine atoms has been frequently discussed.[29-31] Hepburn et al. examined the reaction of fluorine atoms with HBr to produce HF and Br.[29] When the ratio of excited F (F*) atoms to ground-state F atoms was increased by heating, the ratio of excited Br (Br*) atoms to ground-state Br atoms was not changed. These workers concluded that Br* atoms are not produced directly from the reaction of F* atoms but rather by a potential surface jump. Bersohn and co-workers have investigated the reaction of F and F* atoms with I_2, HI, and ICN.[31] The production of I* atoms was not found in any of these reactions. Simple crystal field theory, which was used to estimate the potential energy for these processes, showed that the reaction channel to produce I* atoms from F* atoms has an energy barrier. Therefore, all these experiments show that F* atoms are less reactive than F atoms. Similar arguments would suggest that Cl* atoms are less reactive than Cl. The reactivity of Cl and Cl* for the reactions with NOCl and ICl has been investigated, and the rate constants for Cl* are much slower than those for Cl atoms.[10,13] Therefore, in the present study the reaction products must be formed mainly from the reaction of C_6D_{12} with ground-state Cl atoms, and the presence of $Cl(^2P_{1/2})$ atoms, known to be formed to a small extent in the photodissociation of S_2Cl_2,[13,28] should not have any significant effect on the interpretation of the present experiments.

5. Conclusions

Time-resolved diode laser absorption spectroscopy has been used to probe the nascent rotational and vibrational state distribution and the translational recoil of DCl formed from the reaction Cl + C_6D_{12}. Rotationally cold and translationally hot DCl are produced from the reaction. As the translational energy of the Cl atoms is increased, the rotational energy of DCl produced in the reaction is slightly increased and the vibrational energy of DCl produced in the reaction remains about the same; however, the translational energy of the reaction products is significantly enhanced. An extremely simple "spectator" model predicts the product translational energy recoils very well. This suggests that the light D atom is transferred directly from a spectator (C_6D_{11}) to the heavy Cl atoms. The cold DCl rotational energy may be an indication that Cl atoms abstract D atoms from C_6D_{12} with a collinear C- -D- -Cl recoil configuration. Quasi-classical trajectory calculations for this reaction have also been performed using an empirical LEPS surface constructed for a triatomic system, Cl—D—R(=C_6D_{11}), where the C_6D_{11} was treated as a structureless particle. This model calculation predicts many features of the experiments correctly, suggesting a direct abstraction mechanism with a collinear C- -D- -Cl recoil geometry.

The rate constant for this reaction at room temperature has been measured to be $\sim 1.3 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, which is slightly smaller than the rate for the light isotope reaction, Cl + C_6H_{12}, as expected.

The present experimental results may be applicable in a general way to the abstraction of light H or D atoms from hydrocarbons by Cl atoms. It will be quite interesting to see if a variety of such Cl reactions with different hydrocarbon precursors exhibit similarly cold HCl or DCl rotational profiles and if these profiles can be correlated with reaction exoergicity.

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Registry No. Cl, 22537-15-1; DCl, 7698-05-7; D_2, 7782-39-0; cyclohexane-d_{12}, 1735-17-7.

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(28) Tiemann, E.; Kanamori, H.; Hirota, E. *Annual Review*: Institute for Molecular Science: Okazaki, Japan, 1988; Vol. 37.

(29) Hepburn, J. W.; Liu, K.; Macdonald, R. G.; Northrup, F. J.; Polanyi, J. C. *J. Chem. Phys.* **1981**, *75*, 3353.

(30) Bergmann, K.; Leone, S. R.; Moore, C. B. *J. Chem. Phys.* **1975**, *63*, 4161.

(31) Das, P.; Venkitachalam, T.; Bersohn, R. *J. Chem. Phys.* **1984**, *80*, 4859.

(32) Kozima, K.; Sakashita, K. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 796.