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Infrared frequency-modulation measurements of absolute rate coefficients for Cl + HD → HCl(DCl) + D(H) between 295 and 700 K

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Abstract

Absolute rate coefficients and HCl branching fractions for the Cl + HD reaction have been measured. The rate coefficient for Cl + HD is fit well by $k_1 = (1.28 \pm 0.18) \times 10^{-16} \, T^{1.67} \, e^{-(1646 \pm 60)/T}$ cm^3 molecule^{-1} s^{-1}, approximately 30% smaller than the mean of literature rate coefficients for Cl + H$_2$ and D$_2$. The branching fraction into the HCl channel is 0.67 ± 0.09 at 295 K and decreases at higher temperature. The present results agree well with literature measurements of relative rates, confirming different isotope effects in thermal conditions than in molecular beam measurements. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The reaction of chlorine atom with hydrogen is a prototypical three-atom reactive system. This reaction and its isotopic variant Cl + D$_2$ have been extensively studied both experimentally [1] and theoretically [2]. However, the reaction of Cl with the mixed isotope species HD,

$$Cl + HD \overset{k_1}{\to} \text{products} \qquad (1)$$

has been less thoroughly investigated. The mixed isotope reaction provides a further check on the accuracy of the theoretical understanding of the reaction and allows a measurement of the intramolecular kinetic isotope effect k_{1a}/k_{1b}:

$$
\begin{aligned}
Cl + HD \quad &\overset{k_{1a}}{\to} \quad HCl + D \\
&\overset{k_{1b}}{\to} \quad DCl + H
\end{aligned}
\qquad (2)
$$
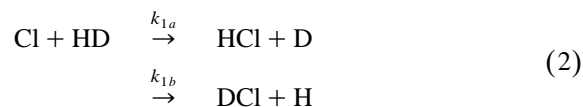
Persky and Klein measured relative rates for Cl + H$_2$, Cl + D$_2$, and Cl + HD between 235 and 340 K in 1966 [3], but until now there has been no absolute measurement of the Cl + HD rate coefficient. In addition, the intramolecular kinetic isotope effect has been measured [4,5]. An additional impetus for investigating the reaction of the mixed isotope is the recent activity on understanding the dynamics of these systems. The dynamics of the Cl + HD reaction have been studied by Bersohn and coworkers [5], and more recently by Liu in a crossed molecular

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beam experiment [6]. Interestingly, molecular beam measurements of intramolecular kinetic isotope effect tend to differ with thermal kinetic measurements.

Reactions of radical species with HD provide an important test for theoretical understanding of simple reactions since the primary and secondary kinetic isotope effects can be separated in the mixed isotope species. Rate coefficients and intramolecular kinetic isotope effects of several radical + HD abstraction reactions have been measured. The reaction of OH + HD has recently been investigated by Ravishankara and coworkers, who observed that the rate coefficient for OH + HD was identical to the mean of the rate coefficients for OH + H_2 and OH + D_2 over the temperature range 230–420 K [7]. They also found that the intramolecular kinetic isotope effect was well described by assuming the reaction with HD to be the simple sum of independent H- and D-atom abstractions, i.e., the ratio of the production of H_2O to the production of HDO in the OH + HD reaction was the same as the ratio of rate coefficients for OH + H_2 and OH + D_2. The abstraction reaction of O(^{3}P) with HD was measured by Presser and Gordon using flash photolysis resonance fluorescence methods [8]. In this case the reaction with HD was again found to match the arithmetic mean of the rate coefficients for H_2 and D_2. Subsequent measurements of the OH/OD branching fractions using a discharge-flow apparatus found intramolecular kinetic isotope effects in disagreement with the sum of independent abstractions, with the disagreement increasing at higher temperatures [9]. Most recently the reactions of CN with H_2, D_2 and HD were measured using infrared (IR) absorption techniques by Mac-Donald and co-workers, and compared to transition state theory calculations on an ab initio potential energy surface [10,11]. In most of these reactions, the thermal rate coefficient for X + HD is very near the mean of the rate coefficients for X + H_2 and X + D_2, suggesting that the leaving atom plays little role in the reactivity.

The dynamics of the reactions of HD with atoms and small radicals reflect effects of reagent rotation and vibration on the course of the reaction. The reaction of F atoms with isotopic hydrogen species has become a benchmark reaction [12]. The Liu group has recently undertaken crossed molecular

beam measurements of several radical + HD reactions [6,13–15]. There are systematic differences between thermal kinetic measurements and predicted rate coefficients based on cross-sections in molecular beam scattering experiments. Measurements of the reactive cross-section as a function of energy for S(^{1}D) + H_2, D_2, and HD show a trend which is contrary to kinetic intuition, with $\sigma_{HD} > \sigma_{D_2} > \sigma_{H_2}$ [6]. In contrast, kinetic experiments on reactions of a number of radicals with hydrogen isotopomers show reaction rate coefficients for HD which are near the mean of those for H_2 and D_2. Differing intramolecular kinetic isotope effects are also expected depending on whether an insertion or an abstraction mechanism dominates [16]. Abstractions from HD under thermal conditions prefer to remove an H atom, i.e., X + HD → HX + D, displaying a normal kinetic isotope effect. Reactions which proceed by an insertion mechanism to form a transient complex show an inverse kinetic isotope effect under thermal conditions. In a molecular beam, this situation is reversed [6].

The discrepancy between molecular beam measurements and thermal kinetic measurements of the intramolecular kinetic isotope effect is thought to be partially a consequence of HD rotation. This phenomenon can occur because of the differing rotational populations in the thermal and molecular beam experiments. It has been proposed, in connection with the F + HD reaction, that a kinematic preference for D-end attack operates at low J_{HD} because the center of charge in the molecule is moved away from the center of mass [17]. This effect is removed by HD rotation, with the preference for H atom abstraction dramatically increasing with increasing J_{HD}.

The reaction of Cl + HD is an excellent target for further investigations of such effects. Dynamical information on the Cl + hydrogen reaction is becoming available from exquisite molecular beam scattering experiments [2,18]. Beam experiments performed in the Liu group found HD to be far less reactive than H_2, and only slightly more reactive than D_2 [19], in contrast to the thermal relative rate measurements of Persky and Klein between 235 and 340 K [3]. The H_2Cl system has been the object of recent theoretical attention; a new potential energy surface is now available, and quantum-mechanical calcula-

tions of rate coefficients and kinetic isotope effects have been reported [20,21]. The effects of vibration and rotation on the reaction have been calculated by several groups. Aoiz and Bañares found that the scattering of Cl with HD to form HCl and D is vibrationally adiabatic, with HD $(v = 0)$ producing predominantly $v = 0$ and $v = 1$ producing mainly $v = 1$ [22]. Song and Gislason have investigated rotational and vibrational effects in the Cl + H_2 and Cl + HD reactions, confirming the orientational effect favoring DCl production at low J and high kinetic energy [23].

In the present study absolute measurements of the rate coefficient for Cl reacting with HD are presented. The yield of HCl in the reaction is measured, which allows the intramolecular kinetic isotope effect to be estimated. The present results can be combined with the established literature values for the reaction with H_2 and D_2 to extract kinetic isotope effects. The absolute measurements are in relatively good agreement with the relative measurements of Persky and Klein, showing $k_{HD}/k_{D_2} > k_{H_2}/k_{HD}$ below 400 K, although there is a slight discrepancy as to the temperature dependence of k_{H_2}/k_{HD}. Theoretical predictions for the kinetic isotope effects are at larger variance with the experimental values, suggesting that additional consideration of possible rotational effects may be necessary to correctly predict the thermal rate coefficients for Cl + HD.

2. Experiment

The kinetics of the Cl + HD reaction have been investigated using the technique of laser photolysis/continuous-wave (cw) IR frequency-modulation (FM) spectroscopy. The apparatus used is similar to that previously reported [24–26]. Chlorine atoms are produced by photolysis of CF_2Cl_2 or CCl_4 at 193 nm, and the progress of the reaction is followed in time by frequency modulation spectroscopy using a cw IR probe laser tuned to the $R(2)$ line of the fundamental vibrational transition in the $H^{35}Cl$ product, which provides sufficient signal-to-noise at all temperatures of the present study. Signal averaging is used to improve signal-to-noise ratios.

The cw probe beam is passed through the reactor multiple times using a cell based on the Herriott design [27]. A Herriott cell uses off-axis paths in a spherical resonator. By propagating the pump beam along the resonator axis, the pump–probe overlap is confined to the center of the cell, where the temperature is well-controlled $(\pm 3$ K). The multipass cell is described in detail in a previous publication [27]. In addition, two-tone frequency modulation (FM) is employed in the present experiments to reduce the contributions of laser amplitude noise and thermal lensing noise [26,28].

The reactor is a stainless-steel vessel approximately 1 m in length. The central 60 cm is enclosed by three resistive heaters under individual microprocessor control using temperature feedback from three separate thermocouples placed along the length of the reactor. Pure CF_2Cl_2 (99.7%) is used as the photolyte in all experiments except the measurement at 700 K, where CCl_4 (neat) was also used. The concentration of photolyte in these experiments is typically 2×10^{14} cm^{-3}, and the initial Cl atom concentration is 2–3 $\times 10^{12}$ cm^{-3}. The reaction of H atoms with CF_2Cl_2 and with CCl_4 should be quite slow, in analogy with the H + CF_3Cl reaction, which has an activation energy of nearly 9 kcal mol^{-1} and a rate coefficient of 4×10^{-14} cm^3 molecule^{-1} s^{-1} at 676 K [29]. Secondary formation of HCl by reactions of H atoms with the photolyte would appear as a bi-exponential time behavior of the HCl signal. No bi-exponential behavior was observed in these experiments.

Ar (99.9999%) serves as the buffer gas in the experiments reported here. The gases (CF_2Cl_2, Ar, and HD) are flowed through the cell at a rate sufficient to replenish the cell between laser shots, but remain essentially static on the timescale of the kinetics. The individual gas flows are controlled by separate calibrated mass flow controllers, and the pressure in the reactor is actively controlled by a butterfly valve which changes the pumping speed to maintain the desired pressure for a given flow.

The reaction of Cl with HD is slightly endothermic [30], and the contribution of vibrationally excited HCl product (which requires ~ 9 kcal mol^{-1} of energy) is expected to be negligible. Comparison of HCl absorption traces using Ar with those using CO_2 as a buffer (which relaxes HCl $(v = 1)$ effi-

ciently) [31] showed no evidence of vibrational excitation at the highest temperatures in this study (700 K).

The IR light is produced by difference-frequency generation (DFG) in $LiNbO_3$, using the output of a ring dye laser and a single-frequency Ar^+ laser. The dye laser beam passes through a phase modulator, which is driven at two closely spaced radio frequencies (RF), 499 ± 0.9 MHz. The RF power applied to the resonant phase modulator (2–3 W) is sufficient to generate a peak phase shift of approximately 1 radian; the power is adjusted to produce the highest FM signal. The periodic phase shift on the dye laser beam is carried onto the generated IR beam, and is equivalent to adding sidebands spaced 498.1 and 499.9 MHz from the central carrier. Differential absorption of the sidebands relative to the carrier generates a signal at the frequency corresponding to the sideband spacing and at the beat frequency between them, 1.8 MHz. The signal at the intermodulation frequency of 1.8 MHz is demodulated and the resulting DC signal is digitized, averaged over several hundred photolysis laser shots, and stored. This technique has been described more fully in other publications [26,32].

The time profiles for the production of HCl from the Cl atom + HD reaction are well described by simple exponential behavior. Because of the small rate coefficient for the reaction, the pseudo-first order rate coefficients are relatively low at the pressures of HD used in these experiments, especially at the lowest temperatures. This is shown in Fig. 1, where a typical absorption trace at room temperature is shown. Fitting such a trace requires consideration of the decay of the HCl concentration, which is principally due to radial diffusion under the conditions of these experiments. Although radial diffusion is not expected to be strictly first order, the deviation of the HCl decay from a single exponential is negligible. The kinetic equations used to describe the experiment are therefore simple:

$$\frac{d}{dt}[Cl] = -k_1[HD][Cl] - k_x[Cl],$$

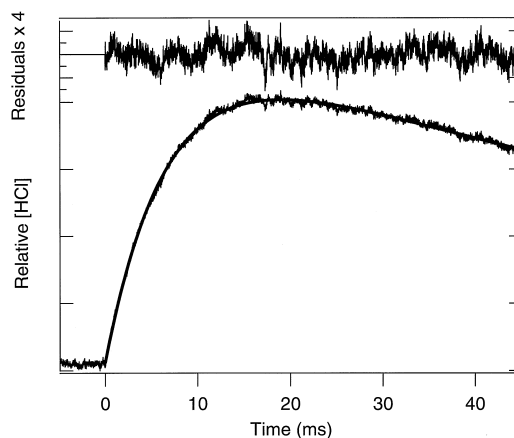$$\frac{d}{dt}[HCl] = k_{1a}[HD][Cl] - k_y[HCl], \qquad (3)$$

Fig. 1. A typical time-resolved FM measurement of HCl production in the Cl + HD reaction, taken at 293 K with an HD concentration of 1.03×10^{15} molecule cm^{-3}.

where $k_1 \equiv k_{1a} + k_{1b}$, and k_x represents all Cl loss processes other than reaction with HD, including contributions from Cl reactions with contaminants in the photolyte or the buffer and diffusion of Cl from the reaction region. The rate coefficient k_y similarly represents the removal of HCl (principally by diffusion). The HCl time profile is then given by

$$[HCl]_t = \frac{[Cl]_0 k_{1a}[HD]}{k_1[HD] + k_x - k_y}$$

$$\times \left(e^{-k_y t} - e^{-(k_1[HD] + k_x)t} \right). \qquad (4)$$

The time traces are therefore fit to the difference of two exponentials, where the rise time is related to the production rate of HCl, since in these experiments $k_1[HD] > k_y$. A plot of this time constant versus the HD concentration gives a straight line whose slope is k_1 and whose intercept reflects the losses of Cl atoms that do not depend on the HD concentration. Such a plot is shown in Fig. 2 for the reaction of Cl + HD at 500 K.

The measurements of the HCl yield, $\phi_{HCl} \equiv k_{1a}/k_1$ ($= [HCl]_\infty / [Cl]_0$ when competing reactions can be ignored), is performed by comparison with the Cl + propane or Cl + ethane reaction, where $\phi_{HCl} = 1$. A measurement is made of the time profile of HCl formation from the reaction of Cl with HD. Immediately thereafter, ethane or propane is substituted for the HD, keeping the other conditions identical. The amplitude of the FM signal is directly
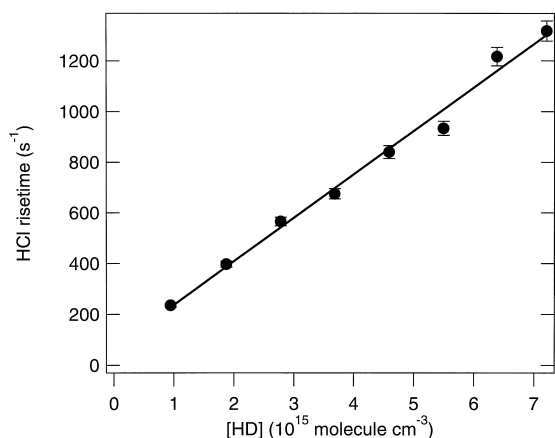
Fig. 2. A plot of the pseudo-first order rate coefficients versus HD concentration, taken at 500 K. The second-order rate coefficient is the slope of such a plot. The intercept of ~ 65 s^{-1} reflects all other loss mechanisms for Cl atoms, including diffusion and reaction with photolyte and buffer gas impurities.

Table 1
Rate coefficients and HCl yields for the reaction of Cl with HD[a]

Temperature (K)	k_{Cl+HD} (cm^3 molecule^{-1} s^{-1})	ϕ_{HCl}
293	$(6.4 \pm 0.6) \times 10^{-15}$	0.67 ± 0.09
350	$(2.1 \pm 0.2) \times 10^{-14}$	0.63 ± 0.09
400	$(4.5 \pm 0.4) \times 10^{-14}$	
450	$(9.3 \pm 0.9) \times 10^{-14}$	0.5 ± 0.1
500	$(1.59 \pm 0.14) \times 10^{-13}$	0.56 ± 0.08
550	$(2.3 \pm 0.2) \times 10^{-13}$	0.5 ± 0.1
705	$(6.9 \pm 0.7) \times 10^{-13}$	

[a]Error bars represent $\pm 2\sigma$ and include estimates of systematic errors.

proportional to the absorption strength, so the size of the observed HCl signal is proportional to the HCl produced. The traces are fitted, and the ratio of the amplitude with HD to that with the alkane reactant gives the HCl yield. Consideration of Eq. (4) shows that the contributions of competing reactions and the removal rate of the product must be taken into account in comparing amplitudes of product time traces [7]. Ideally, yield measurements would be made at relatively high values of [HD], so that the amplitude $[Cl]_0 k_{1a}[HD]/(k_1[HD] + k_x - k_y) \approx [Cl]_0 k_{1a}[HD]/k_1[HD]$. However, since the rate coefficient for Cl reacting with HD is so small, this condition is only obtained at impractically high HD concentrations. Therefore, in the present work the HCl yields are corrected using the model of Eq. (4). For most of the present measurements, the corrections to the yield for competing reactions and HCl removal are much smaller than other sources of error, chiefly frequency and amplitude instability of the Ar$^+$ laser and power fluctuations of the excimer laser.

3. Results

The measured rate coefficients for the reaction of Cl atoms with HD are given in Table 1 and dis-

played in Fig. 3. The rate coefficients for Cl + H$_2$ and Cl + D$_2$, taken from the evaluation of Kumaran et al. [1], are also shown for reference. In several other abstraction reactions with HD, e.g., OH and O(^{1}D), the thermal rate coefficient has been seen to be very close to the average of the rate coefficients with H$_2$ and with D$_2$. This would imply that the departing atom has little effect on the abstraction rate constant. In Fig. 3, the average of the evaluated rate coefficients for Cl + H$_2$ and Cl + D$_2$ is shown as

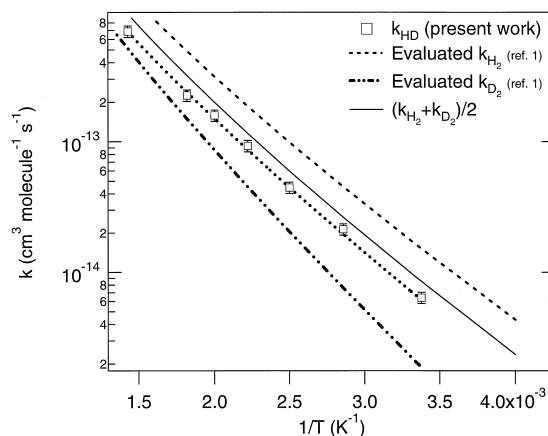

Fig. 3. Rate coefficients for the reactions of Cl atom with hydrogen molecule isotopomers. The dashed line is the rate coefficient for Cl + H$_2$, and the dot–dashed line that for Cl + D$_2$, both taken from the evaluation of Ref. [1]. The mean of the evaluated Cl + H$_2$ and Cl + D$_2$ rate coefficients is shown as the thin solid line. The present measurements of the Cl + HD rate coefficient, shown as the individual points with $\pm 2\sigma$ error bars, fall significantly below the mean of the Cl + H$_2$ and Cl + D$_2$ rate coefficients. The fitted temperature dependence of the Cl + HD reaction, $k_1 = (1.28 \pm 0.18) \times 10^{-16} T^{1.67} \exp[-(1646 \pm 60)/T]$ cm^3 molecule^{-1} s^{-1}, is shown as the dotted line.
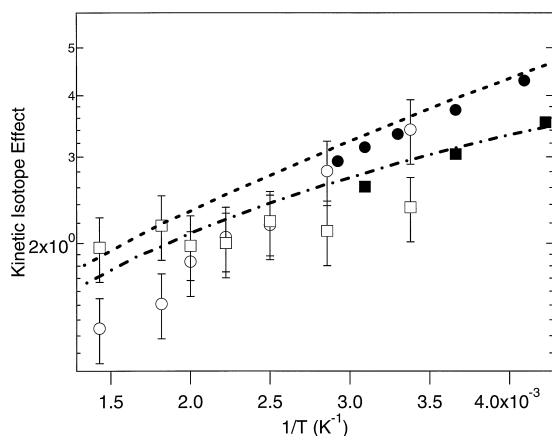
Fig. 4. Kinetic isotope effects for the Cl+hydrogen system. Circles represent k_{HD}/k_{D_2}, and squares represent k_{H_2}/k_{HD}. The open data points ($\bigcirc$, $\square$) are the present measurements, combined with the evaluated H_2 and D_2 rate coefficients from Ref. [1]. The filled data points ($\bullet$, $\blacksquare$) are kinetic isotope effect measurements from Ref. [3]. Calculated kinetic isotope effects from Ref. [20] are also shown as the dashed line (k_{H_2}/k_{HD}) and the dot–dashed line (k_{HD}/k_{D_2}).

the thin solid line. The present results are significantly smaller than the average of the H_2 and D_2 rate coefficients, indicating a secondary kinetic isotope effect of the leaving atom on the rate coefficient.

The rate coefficients for Cl + HD can be fitted nearly to within the experimental error estimates (maximum deviation of 20%) by a simple Arrhenius function $k_1 = 1.8 \times 10^{-11}\,e^{-2370/T}$ cm^3 molecule^{-1} s^{-1}. However, significant curvature is seen in an Arrhenius plot of the corresponding Cl + H_2 and Cl + D_2 reactions, with fitted temperature exponents of 1.72 and 1.62, respectively, and a similar curvature would be expected in Cl + HD. A slightly improved fit (reduction in χ^2 of a factor of 3) is given by fixing a $T^{1.67}$ dependence to the pre-exponential factor for Cl + HD, yielding the expression $k_1 = (1.28 \pm 0.18) \times 10^{-16}\,T^{1.67}\,e^{-(1646 \pm 60)/T}$ cm^3 molecule^{-1} s^{-1}, where the error bars reflect the precision ($\pm 2\sigma$) of the fit. The temperature exponent is chosen as the average of the exponents in the evaluated H_2 and D_2 rate coefficients [1], and is fixed to reduce parameter correlation.

While no previous absolute measurements exist for the rate coefficient of Cl with HD, the kinetic

isotope effects for Cl reacting with the various isotopomers of hydrogen have been measured by Persky and Klein [3]. Fig. 4 shows the results of Persky and Klein along with the kinetic isotope effects calculated from the present rate coefficient measurements combined with the recommended values for Cl + H_2 and Cl + D_2 from Ref. [1]. The agreement with the earlier determinations is reasonable, but there appears to be a larger discrepancy with the H_2/HD isotope effect than with the HD/D_2 determination. The kinetic isotope effects decrease with increasing temperature, and an Arrhenius fit to the calculated isotope effects yields $k_{H_2}/k_{HD} = (1.75 \pm 0.24)e^{-(80 \pm 30)/T}$, and $k_{HD}/k_{D_2} = (0.66 \pm 0.09)e^{-(490 \pm 60)/T}$. As can be seen in Fig. 4, the slope of the Arrhenius plot for k_{H_2}/k_{HD} is significantly smaller than that from the lower temperature results of Ref. [3], but the agreement is better for k_{HD}/k_{D_2}.

The intramolecular kinetic isotope effect of the Cl + HD reaction has also previously been measured [4]. In the present work the relative yields of HCl, ϕ_{HCl}, have been measured at several temperatures. This quantity is straightforwardly related to the kinetic isotope effect, $\eta_{intra} \equiv k_{1a}/k_{1b} \equiv \phi_{HCl}/(1 - \phi_{HCl})$. The present results for ϕ_{HCl} are displayed in Fig. 5 along with HCl yields calculated from available literature measurements of the thermal intra-
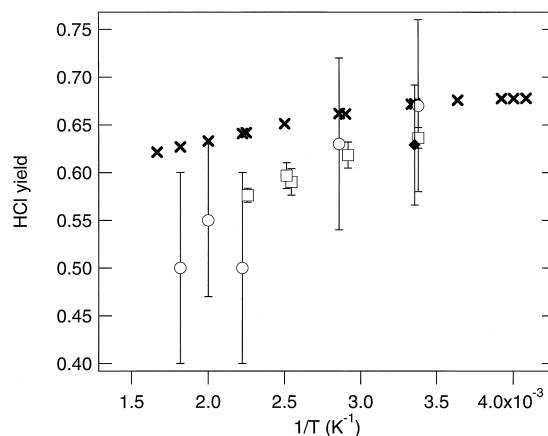

Fig. 5. HCl yield in the reaction of Cl with HD, $\phi_{HCl} \equiv k_{la}/k_1$. The present measurements are shown as the open circles ($\bigcirc$). The measurements of Bar Yaakov et al. [4] are shown as open squares ($\square$) and the results of Xing et al. [5] as diamonds ($\blacklozenge$). HCl yields from the ab initio calculations of Ref. [20] are denoted by an $\times$.

molecular kinetic isotope effect. The error estimates are $\pm 2\sigma$ and are based on several (3–5) measurements at each temperature and include a consideration of possible systematic errors. While the precision in the present system is inferior to the relative rate studies of Bar Yaakov et al. [4], the present HCl yields are in reasonable agreement with their measurements as well as those of Bersohn and co-workers [5].

4. Discussion

The absolute measurements of the rate coefficients for the reaction of Cl + HD are in reasonably good agreement with those predicted from relative rate measurements. The kinetic isotope effect for HD versus D_2 from the absolute measurements agrees both in magnitude and temperature dependence with the determinations of Persky and Klein. The ratio of absolute determinations for H_2 versus HD has a slightly shallower temperature dependence than the Persky and Klein result, while the magnitude of the effect near room temperature is in good agreement. This slight disagreement between the Persky and Klein results and the absolute measurements also appears in the kinetic isotope effect k_{H_2}/k_{D_2}, which links the two HD isotope effects [1]. The Persky and Klein value is also slightly higher than that of Miller and Gordon [33], and shows a steeper dependence on temperature.

A new potential energy surface has recently become available for the H_2Cl system, and rate coefficients and kinetic isotope effects have been calculated using a canonical variational transition state theory method [20]. A comparison of the results of the present experiments with the predictions of the theoretical calculations shows reasonable agreement as to the general magnitude of the kinetic isotope effects, but significant discrepancies remain. The calculations predict a kinetic isotope effect k_{H_2}/k_{HD} larger than k_{HD}/k_{D_2}, whereas the experimental data show that the opposite is the case up to 400 K. The semi-classical variational transition state theory method is known to overestimate the barriers for high bend states [20], and perhaps some rotational effect may underlie the discrepancy between theory and experiment. Recent experimental examinations

of initial rotational state dependence in the Cl + H_2 reaction address this directly [19]. Quantum mechanical calculations have recently been performed for the Cl + H_2 system [20,34], and more detailed calculations of Cl + HD may also be desirable. At higher temperatures the kinetic isotope effects become comparable, and at the highest temperatures of the present study, the absolute rate data suggest k_{H_2}/k_{HD} slightly greater than k_{HD}/k_{D_2}. The error bars on the ratio of the absolute rate coefficients reflect the present experimental uncertainties and the stated precision of the evaluation of the Cl + H_2 and Cl + D_2 rate coefficients in Ref. [1]. Further experimental investigations, including relative rate measurements at higher temperatures, would help confirm the temperature dependence of the kinetic isotope effects.

Molecular beam measurements of the excitation function have shown $\sigma_{H_2}/\sigma_{HD} \gg \sigma_{HD}/\sigma_{D_2}$, with the reactive cross-section for Cl + HD similar to that for Cl + D_2, and much below Cl + H_2 [19]. Molecular beam scattering experiments also show a much higher branching for the DCl product than thermal energy experiments. The effect of the mass asymmetry on the reactions of HD is well known, and in a number of systems, including Cl + HD, calculations show that the D-atom is preferentially abstracted at low rotational energy, especially at the higher collision energies of molecular beam experiments [23]. Such a picture is broadly consistent with the differences in both intramolecular and kinetic isotope effects in the Cl + HD reaction. Whereas the thermal kinetic isotope effect favors the hydrogen abstraction by nearly a factor of two, abstraction of a deuterium atom dominates the beam reaction by a factor of three [6]. The cross-section for the beam reaction of HD may be relatively reduced because of the higher contribution of D-end collisions whose only reactive pathway is the presumably less favorable D-atom transfer.

The present results for the Cl + HD reaction highlight some discrepancies of the most sophisticated calculations with experimental kinetics measurements. The reaction of Cl with hydrogen has gained the status of a prototypical reaction because of the extensive theoretical and experimental work which exists on its dynamics and kinetics [2]. Nonetheless, a consensus on this reaction has not yet been attained. The present absolute rate coefficient measure-

ments for the Cl + HD reaction may aid in further theoretical refinements or in a possible reinvestigation of the potential energy surface.

Acknowledgements

References

[1] S.S. Kumaran, K.P. Lim, J.V. Michael, J. Chem. Phys. 101 (1994) 9487.

[2] M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia, E.H. van Kleef, G.G. Volpi, F.J. Aoiz, L. Bañares, D.W. Schwenke, T.C. Allison, S.L. Mielke, D.G. Truhlar, Science 273 (1996) 1519.

[3] A. Persky, F.S. Klein, J. Chem. Phys. 44 (1966) 3617.

[4] Y. Bar Yaakov, A. Persky, F.S. Klein, J. Chem. Phys. 59 (1973) 2415.

[5] G. Xing, X. Huang, R. Bersohn, K. Tsukiyama, B. Katz, J. Chem. Phys. 102 (1995) 3169.

[6] S.-H. Lee, K.-P. Liu, Chem. Phys. Lett. 290 (1998) 323.

[7] R.K. Talukdar, T. Gierczak, L. Goldfarb, Y. Rudich, B.S. Madhava Rao, A.R. Ravishankara, J. Phys. Chem. 100 (1996) 3037.

[8] N. Presser, R.J. Gordon, J. Chem. Phys. 82 (1985) 1291.

[9] D.C. Robie, S. Arepalli, N. Presser, T. Kitsopoulos, R.J. Gordon, J. Chem. Phys. 92 (1990) 7382.

[10] G. He, I. Tokue, L.B. Harding, R.G. Macdonald, J. Phys. Chem. A 102 (1998) 7653.

[11] G. He, I. Tokue, R.G. Macdonald, J. Phys. Chem. A 102 (1998) 4585.

[12] D.E. Manolopoulos, J. Chem. Soc. Faraday Trans. 93 (1997) 673.

[13] D.C. Che, K.-P. Liu, J. Chem. Phys. 103 (1995) 5164.

[14] Y.-T. Hsu, K.-P. Liu, J. Chem. Phys. 107 (1997) 1664.

[15] Y.-T. Hsu, J.-H. Wang, K.-P. Liu, J. Chem. Phys. 107 (1997) 2351.

[16] K. Tsukiyama, B. Katz, R. Bersohn, J. Chem. Phys. 83 (1985) 2889.

[17] G.W. Johnston, H. Kornweitz, I. Schechter, A. Persky, B. Katz, R. Bersohn, R.D. Levine, J. Chem. Phys. 94 (1990) 2749.

[18] M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, G.G. Volpi, J. Chem. Soc. Faraday Trans. 91 (1995) 575.

[19] K.-P. Liu, personal communication, 1999.

[20] T.C. Allison, G.C. Lynch, D.G. Truhlar, M.S. Gordon, J. Phys. Chem. 100 (1996) 13575.

[21] S.L. Mielke, T.C. Allison, D.G. Truhlar, D.W. Schwenke, J. Phys. Chem. 100 (1996) 13588.

[22] F.J. Aoiz, L. Bañares, Chem. Phys. Lett. 247 (1995) 232.

[23] J.-B. Song, E.A. Gislason, Chem. Phys. 237 (1998) 159.

[24] J.S. Pilgrim, C.A. Taatjes, J. Phys. Chem. A 101 (1997) 4172.

[25] J.S. Pilgrim, C.A. Taatjes, J. Phys. Chem. A 101 (1997) 8741.

[26] J.T. Farrell, C.A. Taatjes, J. Phys. Chem. A 102 (1998) 4846.

[27] J.S. Pilgrim, R.T. Jennings, C.A. Taatjes, Rev. Sci. Instrum. 68 (1997) 1875.

[28] D.E. Cooper, R.E. Warren, J. Opt. Soc. Am. B 4 (1987) 470.

[29] J.N. Bradley, D.A. Whytock, T.A. Zaleski, J. Chem. Soc. Faraday Trans. 1 (72) (1976) 2284.

[30] J. Berkowitz, G.B. Ellison, D. Gutman, J. Phys. Chem. 98 (1994) 2744.

[31] S.R. Leone, J. Phys. Chem. Ref. Data 11 (1982) 953.

[32] P.E. Powers, C.A. Taatjes, T.J. Kulp, Appl. Opt. 35 (1996) 4735.

[33] J.C. Miller, R.J. Gordon, J. Chem. Phys. 79 (1983) 1252.

[34] H.B. Wang, W.H. Thompson, W.H. Miller, J. Chem. Phys. 107 (1997) 7194.