

UC Irvine

UC Irvine Previously Published Works

Title

A study of the reaction $\text{Li} + \text{HCl}$ by the technique of time-resolved laser-induced fluorescence spectroscopy of $\text{Li}(2^2P_{1/2} - 2^2S_{1/2})$, $\lambda = 670.7 \text{ nm}$ between 700 and 1000 K

Permalink

<https://escholarship.org/uc/item/4163p35p>

Journal

The Journal of Chemical Physics, 87(8)

ISSN

0021-9606

Authors

Plane, John MC
Saltzman, Eric S

Publication Date

1987-10-15

DOI

10.1063/1.452871

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

A study of the reaction $\text{Li} + \text{HCl}$ by the technique of time-resolved laser-induced fluorescence spectroscopy of Li ($2^2P_J - 2^2S_{1/2}$, $\lambda = 670.7$ nm) between 700 and 1000 K

John M. C. Plane and Eric S. Saltzman

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149-1098

(Received 16 June 1987; accepted 9 July 1987)

A kinetic study is presented of the reaction between lithium atoms and hydrogen chloride over the temperature range 700–1000 K. Li atoms are produced in an excess of HCl and He bath gas by pulsed photolysis of LiCl vapor. The concentration of the metal atoms is then monitored in real time by the technique of laser-induced fluorescence of Li atoms at $\lambda = 670.7$ nm using a pulsed nitrogen-pumped dye laser and box-car integration of the fluorescence signal. Absolute second-order rate constants for this reaction have been measured at $T = 700, 750, 800,$ and 900 K. At $T = 1000$ K the reverse reaction is sufficiently fast that equilibrium is rapidly established on the time scale of the experiment. A fit of the data between 700 and 900 K to the Arrhenius form, with 2σ errors calculated from the absolute errors in the rate constants, yields $k(T) = (3.8 \pm 1.1) \times 10^{-10} \exp[-(883 \pm 218)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result is interpreted through a modified form of collision theory which is constrained to take account of the conservation of total angular momentum during the reaction. Thereby we obtain an estimate for the reaction energy threshold, $E_0 = 8.2 \pm 1.4 \text{ kJ mol}^{-1}$ (where the error arises from uncertainty in the exothermicity of the reaction), in very good agreement with a crossed molecular beam study of the title reaction, and substantially lower than estimates of E_0 from both semiempirical and *ab initio* calculations of the potential energy surface.

INTRODUCTION

The reactions between the alkali metals and the hydrogen halides have played a central role in the development of reaction dynamics since the 1930's, when they were first studied by the diffusion flame technique.¹ Generally characterized by large reaction cross sections, this class of reactions was a primary candidate for pioneering the molecular beam technique: the first chemical reaction to be studied in crossed molecular beams was the $\text{K} + \text{HBr}$ system, investigated in 1955 by Taylor and Datz,² and many other reactions between the alkali atoms and hydrogen halides have been studied subsequently by this method.³

Recently, Marshall and Husain⁴ have employed the technique of flash photolysis and time-resolved resonance absorption spectroscopy to determine absolute rate constants for the reactions $\text{Na} + \text{HCl}$, HBr over a range of temperature.⁴ Such measurements complement studies in molecular beams by providing direct measurements of activation energies and collision factors which, by making the assumption of a Maxwell-Boltzmann distribution of reactant energies, can in suitable cases yield information about the reaction energy barriers and reaction cross sections.⁵ In addition, absolute rate measurements at high temperature provide the kinetic information which is required to elucidate the complex chemistry of both alkali metals and halogenated species in flames.⁶

This body of experimental work has prompted a number of theoretical investigations into the nature of the potential energy surfaces governing these reactions. Shapiro and Zeiri⁷ have generated semiempirical potential energy surfaces using the diatomics-in-molecules approach for most of the alkali atom + hydrogen halide combinations. In the case

of the title reaction, they found a collinear transition state located in the entrance channel at a height 47.2 kJ mol^{-1} above the asymptote of the reactants. This indicates roughly a threshold energy for reaction of $E_0 = 29 \text{ kJ mol}^{-1}$ (not including the zero point energy of the transition state nor quantum tunneling effects through the early barrier). This study was followed by an accurate quantum calculation of the potential energy surface for $\text{Li} + \text{HCl}$ by Garcia *et al.*,⁸ which found by contrast a bent transition state ($\text{Li}-\text{Cl}-\text{H}$ angle = 53°) halfway along the minimum energy path, but agreed with the calculated height of the transition state from the previous study.⁷

In this paper we report a study of the reaction



in which absolute second-order rate constants $k_1(T)$ are determined over a range in temperature. To the best of our knowledge, this is the first such study. However, the reaction dynamics of this reaction have been investigated in detail by Becker *et al.*⁹ using the crossed molecular beam technique. The motivation in the present study for carrying out a detailed measurement of $k_1(T)$ as a function of T , and hence deriving accurate Arrhenius parameters, is twofold. First, $k_1(T)$ can then be extrapolated with some confidence to temperatures which are inaccessible to direct experimental techniques; in particular, this reaction is important for describing and modeling the chemistry of lithium and chlorinated compounds in flames at temperatures above 1500 K.⁶

The second reason for studying reaction (1) is because of its interesting reaction dynamics, consisting of the exchange of a heavy particle between two lighter ones. The exchange is asymmetric and the reaction is characterized by

a dramatic reduction in the reduced mass of the system as the light hydrogen atom departs. The maximum impact parameter describing collisions between Li and HCl can thus be limited by the requirement of the conservation of total angular momentum during the reaction.¹⁰ The study of Becker *et al.*⁹ in fact demonstrated this to be the case at high collision energies (38.5 kJ mol^{-1}). That study⁹ also concluded that the energy barrier to reaction, E_0 , had an upper limit of about 8.4 kJ mol^{-1} . This is considerably less than the estimates from theoretical calculations discussed above.^{7,8} Furthermore, the semiempirical potential energy surface of Shapiro and Zeiri⁷ predicts that the barrier is exclusively in the entrance channel. This implies an attractive energy release resulting in some vibrational excitation in the nascent LiCl, as indeed was observed in trajectory calculations on that semiempirical surface.¹¹ However, the molecular beam study of Becker *et al.*⁹ concluded that very little of the exothermicity of the reaction ($37.5 \pm 13 \text{ kJ mol}^{-1}$)¹³ is partitioned into product vibration, and so the barrier is most probably in the exit channel, in better agreement with the more recent *ab initio* study.⁸

In the present work we interpret the experimental rate constants in terms of a modified form of simple collision theory which is constrained by the conservation of total angular momentum during the reaction.¹⁰ Thereby we derive an estimate for E_0 and the reaction cross section as a function of the average partitioning of the energy released during the reaction into product rotation.

EXPERIMENTAL

Reaction (1) has been investigated by the technique of time-resolved laser-induced fluorescence spectroscopy of Li atoms at 670.7 nm [$\text{Li}(2^2P_J) - \text{Li}(2^2S_{1/2})$], following the pulsed photolysis of LiCl vapor in an excess of HCl and He bath gas. This new experimental arrangement is described in detail elsewhere¹⁴ and only a brief description is given here.

The stainless steel reactor used in this study consists of a central cylindrical reaction chamber, at the intersection of two sets of arms which cross orthogonally. One set of opposite arms is the optical coupling for the nitrogen-pumped dye laser (Laser Science Inc., model VSL-337; laser dye DCM, maximum output $15 \mu\text{J}$) which is used to probe the Li atoms formed by photolyzing LiCl in the central chamber. The other set of arms comprises the optical coupling for the photolyzing flash lamp (EG&G, model FX193U) to the central chamber, through a pair of suprasil lenses, and the exit for the gases from the central chamber to the pump. A sample of LiCl is placed in a tantalum boat in the sidearm coupling the flash lamp to the reactor. This sidearm is independently heated and the resulting LiCl vapor is entrained in a flow of He which carries it into the central chamber. The central chamber is enclosed in a furnace which can heat it to over 1200 K; the temperature of the gases flowing through it are monitored by a Chromel-Alumel thermocouple that is permanently inserted into the chamber slightly below the volume intersected by the laser and flash lamp beams.

The laser-induced fluorescence signal is monitored orthogonally to both the flash lamp and laser beams by a pho-

tomultiplier tube (Thorn EMI Gencom Inc., Model 9816QB) after passing through an interference filter centered at 670 nm (Oriel Corporation, FWHM = 10 nm) to exclude scattered light from the flash lamp. The PMT is cooled to below 25°C by a flow of chilled air, and is coupled to the central chamber by a vertical sidearm above the chamber. This sidearm and the pair of arms providing the entrance and exit coupling for the dye laser beam each feature an input for a gas flow which enters the sidearm and then flows into the central chamber. These flows sweep the cooled end windows on the three sidearms clear of salt vapor from the central chamber. The flows consist of a three-way split of a main flow of HCl/He from the gas-handling line into the reactor. The ratio of HCl to He in this flow is varied by mixing a flow of a stock mixture of HCl/He with one of pure He to give a combined flow of 50 sccm. The flow of LiCl/He from the heated sidearm is kept constant at 30 sccm. The central chamber thus provides a mixing vessel for the flows of LiCl/He and HCl/He. The total pressure in the reactor is controlled by a needle valve on the exit line to the pump. It was established from previous work with a similar reactor¹⁵ that the residence time in the central chamber, about 5 s, was sufficient to ensure good mixing of the flows at a total pressure of 50 Torr and total mass flow rate of 80 sccm (MKS Mass Flow Controllers, model 247B).

Mixtures of HCl/He were made up and stored on an all-glass vacuum line. Fresh mixtures no more than 2 h old were used to limit the loss of HCl into the glass or grease, though no loss effect was observed to affect the kinetics during the duration of a set of experiments which took about 2 h to complete. This is in accord with previous experience we have had with HCl/He mixtures stored in glass.¹⁵ By contrast, a substantial loss of HCl from the flow of HCl/He through the stainless steel gas flow lines and the reactor was observed. This flow contained up to 30 mTorr HCl in 50 Torr He. In the course of the kinetic experiments it became apparent that up to half of the HCl could be absorbed and lost from the flow if a passivating procedure of the walls was not adopted. It was therefore critical for the stainless steel sections of the system to be thoroughly passivated before kinetic experiments could be carried out. The passivating procedure that was followed was to fill the reactor, heated to the temperature at which the experiment was to be conducted, and the flow lines with a few Torr of HCl for about 1 h. The system was then pumped out for a further hour, after which the degassing rate of HCl was small and decreasing only very slowly with time. Thus, with a constant flushing time of the gas flows through the system, a residual pressure of HCl in the reactor of about 5 mTorr was estimated to be present (see below). This background level of HCl remained constant over the 2 h duration of a set of experiments at a particular temperature, and was a reproducible effect over several days of kinetic experiments.

The experimental system is controlled by a pulse/delay generator (Stanford Research Systems, SRS DG535). In each triggering sequence, the PMT is first gated for $60 \mu\text{s}$ to reduce its gain while the flash lamp is fired. The flash lamp and the box-car averager (Stanford Research Systems, Model SR250) are triggered simultaneously $14 \mu\text{s}$ after the PMT

is gated. The probe laser is triggered by the box car to coincide with the opening of the integrator gate as it is scanned to monitor the LIF signal at increasing time intervals after the flash lamp fires. Data collection was normally initiated 105 μ s after the flash lamp was fired. Each scan is divided into 200 bins, and the scans were generally repeated once and averaged to improve the signal-to-noise ratio. The averaged decays were then transferred to a microcomputer for a curve-fitting analysis and storage.

Materials

Helium 99.9999% ("Matheson Purity") was used without further purification. LiCl, 99% (Aldrich, anhydrous) was kept sealed under dry air in the dark before use, and then refluxed in the reactor sidearm at 700 K for several hours prior to kinetic experiments, to remove traces of Cl_2 . HCl, 99.0% (Matheson, Technical Grade), was refluxed from 155 K (ethanol slush) to 77 K (liquid nitrogen) repeatedly before use.

RESULTS

Figure 1 illustrates examples of the decay of the LIF signal at $\lambda = 670.7$ nm [$\text{Li}(2^2P_J) \rightarrow \text{Li}(2^2S_{1/2})$], generated

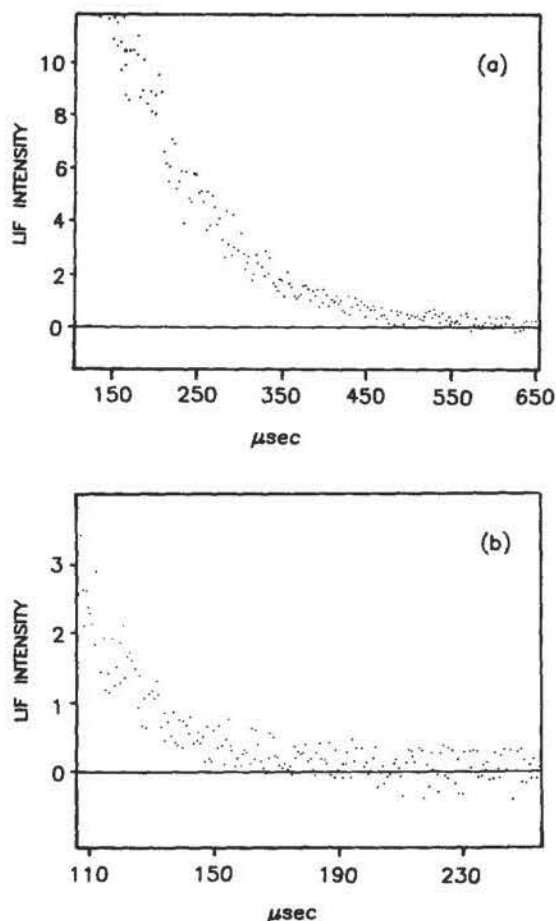
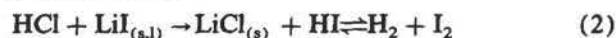


FIG. 1. (a) Time-resolved decay of the LIF signal from Li atoms at $\lambda = 670.7$ nm [$\text{Li}(2^2P_J) \rightarrow \text{Li}(2^2S_{1/2})$] following pulsed photolysis of LiCl vapor in HCl and He; $[\text{HCl}] = 3.7 \times 10^{13}$ molecule cm^{-3} , $[\text{He}] = 6.4 \times 10^{17}$ atoms cm^{-3} , $T = 750$ K. (b) Same as in (a), with $[\text{HCl}] = 2.6 \times 10^{14}$ molecule cm^{-3} , $[\text{He}] = 6.4 \times 10^{17}$ atoms cm^{-3} , $T = 750$ K.

by the pulsed photolysis of LiCl in the presence of He and HCl at 750 K; Fig. 1(a): $[\text{HCl}]_{\text{add}} = 3.7 \times 10^{13}$ molecule cm^{-3} , Fig. 1(b): $[\text{HCl}]_{\text{add}} = 2.6 \times 10^{14}$ molecule cm^{-3} , where $[\text{HCl}]_{\text{add}}$ indicates the concentration of HCl added to the reactor in the mixture of flows, as opposed to the residual level of HCl, termed $[\text{HCl}]_{\text{res}}$, remaining from the passivating procedure (see above).

Experiments were carried out at temperatures of 700–1000 K. The lower temperature limit is defined by the constraint of generating a sufficient concentration of LiCl vapor in the reaction vessel; at $T = 700$ K, $p_{\text{LiCl}} = 2.8 \times 10^{12}$ molecule cm^{-3} in equilibrium above the solid.^{13,16} Given a likely fraction of LiCl photolyzed by the flash lamp of less than 1%,¹⁷ and a further loss of Li atoms due to reaction (1) during the 105 μ s between the flash-lamp firing and the start of the box-car scan, decays such as that shown in Fig. 1(b) can be used to estimate the lower limit for detection of Li atoms with this system is about 10^8 atoms cm^{-3} . In order to increase the concentration of LiCl vapor in the reactor, the sidearm containing the boat of LiCl was heated to about 850 K ($p_{\text{LiCl}} = 2.6 \times 10^{14}$ molecules cm^{-3} ^{13,16}), although much of the LiCl vapor entrained will condense on the cooler walls of the central chamber.¹⁴ Previously¹⁴ we have used LiI as a photolytic precursor to work at temperatures below 700 K, since it is both more volatile¹⁶ and has a much greater photolysis cross section in the near ultraviolet.¹⁷ However, the exchange reaction



is thermodynamically allowed in the temperature range of interest,¹⁶ and the presence of even trace quantities of I_2 , which reacts very rapidly with alkali metals,¹⁸ would be a serious problem. When working at or above $T = 900$ K in the central chamber, the temperature of the LiCl source was kept at 850 K in order to limit the concentration of LiCl flowing into the chamber. Otherwise, for example, at $T = 1000$ K, $p_{\text{LiCl}} = 6 \times 10^{15}$ molecule cm^{-3} ,^{13,16} and the concentration of Li atoms formed in the flash would have been comparable to the HCl concentration. The energy flash was also kept under 1 J to limit LiCl photolysis when working above 800 K. Thus, over the temperature range studied, the concentration of HCl was always well in excess of the concentration of Li resulting from the pulsed photolysis of LiCl vapor, and the decay of Li atoms should be pseudo-first-order. However, above $T = 900$ K, the decays become distinctly non-exponential, as is shown in Fig. 2 at $T = 1000$ K where $[\text{HCl}]_{\text{add}} = 1.1 \times 10^{14}$ molecules cm^{-3} . The initial rapid decay is consistent with the removal of Li by reaction (1), followed by a small fraction of Li atoms remaining which are then lost through diffusion out of the volume probed by the dye laser. We believe this is evidence (see below) for reaction (1) proceeding until equilibrium is reached with the reverse reaction,



This effect limits the maximum temperature at which reaction (1) can be studied using the present technique to $T < 950$ K.

We have shown previously¹⁴ that exponential decays of

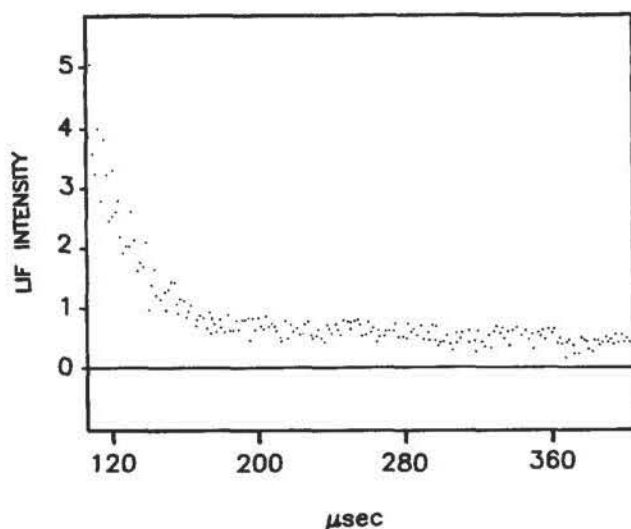


FIG. 2. Time-resolved decay of the LIF signal from Li atoms at $\lambda = 670.7$ nm [$\text{Li}(2^2P_{1/2})\text{-Li}(2^2S_{1/2})$] following pulsed photolysis of HCl vapor in HCl and He; $[\text{HCl}] = 1.1 \times 10^{14}$ molecule cm^{-3} , $[\text{He}] = 4.8 \times 10^{17}$ atoms cm^{-3} , $T = 1000$ K.

the signal-to-noise quality in Fig. 1 can be fitted satisfactorily to the form $A \exp(-k't)$, where k' is given by

$$k' = (k_{\text{diff}} + k_1[\text{HCl}]_{\text{res}}) + k_1[\text{HCl}]_{\text{add}}. \quad (3)$$

The term k_{diff} describes diffusion of the Li atoms out of the

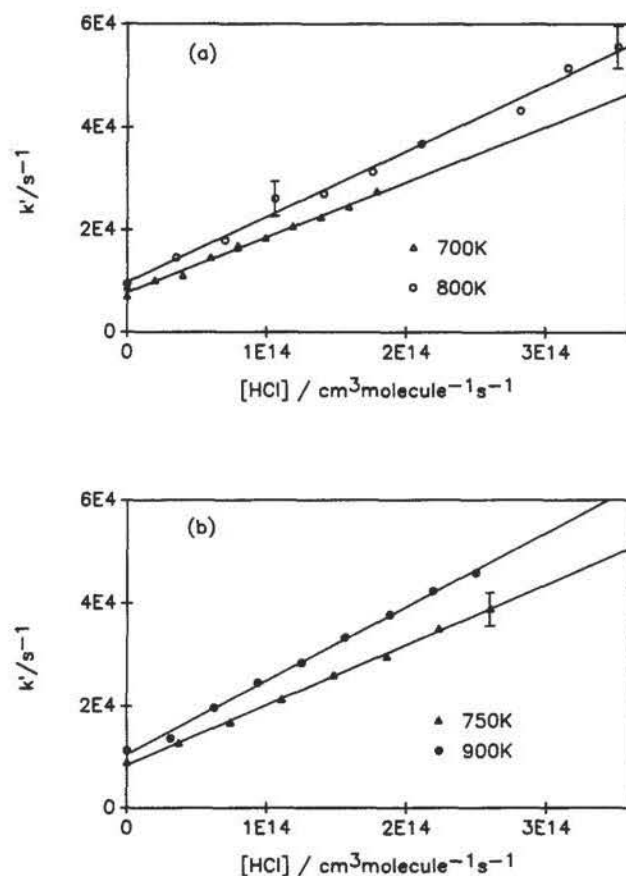


FIG. 3. (a) Plots of the pseudo-first-order rate coefficient (k') against $[\text{HCl}]$ added (see the text) for $T = 700$ and 800 K. Solid lines are linear least-squares fits to the data. Error bars indicate precision of determination of k' . (b) Same as in (a), for $T = 750$ and 900 K.

TABLE I. Experimental determinations of k_1 (Li + HCl) as a function of T (2σ errors from linear regression fits to the data in Fig. 3).

| k_1 (10^{-10} cm^3 molecule $^{-1}$ s $^{-1}$) | T/K |
|---|--------------|
| 1.08 ± 0.06 | 700 |
| 1.17 ± 0.07 | 750 |
| 1.27 ± 0.09 | 800 |
| 1.43 ± 0.07 | 900 |

volume defined by the intersection of the beams from the flash lamp and laser.

When studying the dependence of k' on $[\text{HCl}]_{\text{add}}$, the total pressure in the reactor and the mass flow rate are kept constant so that the terms k_{diff} and $k_1 \cdot [\text{HCl}]_{\text{res}}$ should comprise the intercept of a plot of k' against $[\text{HCl}]_{\text{add}}$. Such plots are illustrated in Fig. 3, for the temperatures 700, 750, 800, and 900 K. k' exhibits a clear linear dependence on $[\text{HCl}]_{\text{add}}$. The slopes of these plots thus yield k_1 as a function of temperature, listed in Table I with 2σ errors from a linear regression fit to each plot.

The intercepts of the plots in Fig. 2 increase slightly with temperature. We have previously¹⁴ measured and analyzed the term k_{diff} in this experimental arrangement; at a total He pressure of 50 Torr it increases from 2280 s $^{-1}$ at $T = 700$ K to 3500 s $^{-1}$ at 900 K. Taking values of k_1 from Table I, $[\text{HCl}]_{\text{res}}$ remains constant and equal to 5×10^{13} molecules cm^{-3} over the temperature range 700–900 K. This result probably indicates that most of the HCl that is absorbed during the passivating procedure is in the cold section of the reactor and the stainless steel flow lines.

Figure 4 is a standard Arrhenius plot of the data contained in Table I. A linear regression fit yields

$$k_1(T) = (3.8 \pm 1.1) \times 10^{-10} \exp[-(883 \pm 218)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (4)$$

The errors are 2σ , calculated from the absolute errors in Table I and depicted in Fig. 4.

The form of the decay in Fig. 2 can now be analyzed

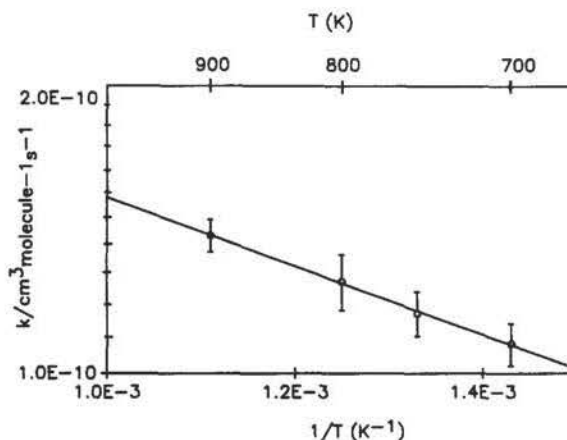


FIG. 4. Standard Arrhenius plot [$\ln k_1(T)$ vs $1/T$] over the temperature range 700–900 K. Error bars depict 2σ errors from the least-squares fits to the data in Fig. 3. The solid line is a regression curve through the experimental data.

further. From expression (4), $k_1(T = 1000 \text{ K}) = 1.58 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. From Eq. (2), assuming $[\text{HCl}]_{\text{res}} = 5 \times 10^{13} \text{ molecule cm}^{-3}$ and a value for $k_{\text{diff}} = 4180 \text{ s}^{-1}$,¹⁴ $k' = 29\,930 \text{ s}^{-1}$ which is in good agreement with an approximate curve fitting to the initial portion of the decay in Fig. 2. Extrapolating back to $t = 0$ in Fig. 2, indicates that the ratio $[\text{Li}]_{t=0}/[\text{Li}]_{\text{eq}} = \sim 100$, where $[\text{Li}]_{\text{eq}}$ is the lithium concentration remaining after $180 \mu\text{s}$ when reaction (1) reaches equilibrium. The equilibrium constant $K_1 (= k_1/k_{-1})$ is equal to 391 at $T = 1000 \text{ K}$.¹⁶ If we assume that $[\text{Li}]_{t=0} = [\text{H}]_{\text{eq}}$, and $[\text{HCl}] = [\text{HCl}]_{\text{res}} + [\text{HCl}]_{\text{add}}$, then

$$K_1 = \frac{[\text{Li}]_{t=0} \cdot [\text{LiCl}]}{[\text{Li}]_{\text{eq}} \cdot [\text{HCl}]} \quad (5)$$

and from Eq. (5), $[\text{LiCl}] = 6.3 \times 10^{14} \text{ molecule cm}^{-3}$. This concentration is only a factor of 2 greater than the equilibrium concentration of the source of LiCl vapor in the sidearm heated to about 850 K .^{13,16} This rough calculation is therefore consistent with the decay of Li atoms due to reaction (1) being limited above 900 K by a rapid approach to equilibrium.

DISCUSSION

There have been no previous determinations of the absolute rate coefficients for reaction (1). The Arrhenius expression (4) is in good agreement with an estimate of $k_1(T)$ for flame modelling by Jensen and Jones,⁶ which was obtained by extrapolating from information on the analogous reactions of Na and K. Extrapolating from Eq. (4) to flame temperatures yields $k_1(T = 2000 \text{ K}) = (2.4 \pm 1.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The combustion of chlorine-containing compounds generates Cl and ClO radicals which are rapidly converted to HCl through reactions with the flame radicals H and OH as well as flame gases such as H_2 and the combustion product H_2O .⁶ The above result for k_1 implies that when Li is seeded into a flame containing chlorinated species the HCl reservoir will be rapidly depleted, and Cl atoms may then be regenerated through the thermal dissociation of LiCl.

As a starting point in relating the reaction dynamics to $k_1(T)$, we consider simple collision theory¹² where the reaction cross section σ_R^{SCT} is related to the energy threshold E_0 by

$$\sigma_R^{\text{SCT}} = \pi D^2 (1 - E_0/E_T), \quad (6)$$

E_T is the collision energy and D is the "hard-sphere" diameter of the reactants.¹² This crude notion of D can be better stated in the present case in terms of long-range attractive forces defining a maximum impact parameter. The major component of the long-range attractive force between these reactants is dispersive⁹ and the van der Waal's constant C_6 can be estimated from the Slater-Kirkwood formula,^{9,19}

$$C_6 = 3/2 \alpha_{\text{Li}} \cdot \alpha_{\text{HCl}} / [(\alpha_{\text{Li}}/p_{\text{Li}})^{1/2} + (\alpha_{\text{HCl}}/p_{\text{HCl}})^{1/2}], \quad (7)$$

where α_{Li} and α_{HCl} are the polarizabilities of Li^{20} and HCl^{21} and $p_{\text{Li}} (= 1)$ and $p_{\text{HCl}} (= 8)$ are the number of outer-shell electrons in each of the reactants: $C_6 = 1.7 \times 10^7 \text{ J mol}^{-1} \text{ \AA}^6$.

Considering collisions occurring with an impact energy $E_T = 10 \text{ kJ mol}^{-1}$, which is the average impact energy over the temperature range in this study, the maximum impact parameter b_{max} permitted by the orbiting criterion on this spherically attractive surface is given by¹²

$$b_{\text{max}}^2 = (3/2)^{2/3} (3C_6/E_T)^{1/3} \quad (8)$$

yielding $b_{\text{max}} = 4.74 \text{ \AA}$. Since b_{max} varies as $E_T^{1/3}$, it is approximately constant over a large range of impact energies and is set equal to D in Eq. (6).

A factor which may limit the reaction cross section is the constraint imposed by the requirement of conservation of total angular momentum during the reaction. Gonzalez Urëna *et al.*²² have discussed this effect in detail. In the case of reaction (1), the reduced mass of the products is so small compared with that of the reactants, μ , because of the departing light H atom, that almost all of the orbital angular momentum possessed by the reactants will be conserved as rotational angular momentum in the nascent LiCl.⁹ Thus, the maximum impact parameter is defined by

$$b_{\text{max}} \cdot (2E_T \cdot \mu)^{1/2} \sim (2I'E'_R)^{1/2}, \quad (9)$$

where I' is the moment of inertia of LiCl; E'_R is the rotational energy of the LiCl product, given by

$$E'_R = (E_T + Q) \cdot \beta, \quad (10)$$

where Q is the exothermicity of the reaction and β is the fraction of total energy available to the products that is partitioned into rotation. The molecular beam study of Becker *et al.*⁹ showed that an average of 70% of the total energy available to the products in reaction (1) appears as product translational energy, and this percentage remains constant over a very wide range of collision energies. This study⁹ also concluded that very little vibrational excitation of the nascent LiCl occurred, so that β can be set equal to 0.3. The reaction cross section defined by conservation of angular momentum, σ_R^{CAM} , averaged over the degree to which energy is partitioned into rotation, is then given by

$$\sigma_R^{\text{CAM}} = \pi b_{\text{max}}^2 = \pi(I'\beta/\mu)(1 + Q/E_T). \quad (11)$$

(This is a special case of the general situation discussed by Gonzales Urëna *et al.*²²) Inspection of Eq. (6) indicates that σ_R^{SCT} increases with E_T to an asymptotic value πD^2 , whereas Eq. (11) indicates that σ_R^{CAM} decreases to an asymptotic value of $\pi I'\beta/\mu$. In the present case, σ_R^{SCT} and σ_R^{CAM} become equal and the reaction cross section reaches a maximum at an energy E_{max} defined by

$$E_{\text{max}} = (QI'\beta + D^2 E_0 \mu) / (\mu D^2 - I') \quad (12)$$

so that the reaction cross section, averaged over rotational energy partitioning in the products, is

$$\begin{aligned} \bar{\sigma}_R &= \sigma_R^{\text{SCT}} \quad (E_T < E_{\text{max}}), \\ &= \sigma_R^{\text{CAM}} \quad (E_T > E_{\text{max}}). \end{aligned} \quad (13)$$

Finally, an expression for the thermal rate constant can be obtained:

$$k(T) = \int_0^\infty (1/\pi\mu)^{1/2} (2/RT)^{3/2} \cdot \bar{\sigma}_R \cdot E_T \cdot \exp(-E_T/RT) dE_T \quad (14)$$

$$\begin{aligned}
 &\text{giving } k_1(T)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
 &= 4.24 \times 10^{-11} \cdot T^{1/2} \cdot \exp(-E_0/RT) \\
 &\quad + \exp(-E_{\max}/RT) \cdot (5.1 \times 10^{-12} \cdot E_0 \cdot T^{-1/2} \\
 &\quad + 1.04 \times 10^{-8} \cdot T^{-1/2} - 4.82 \times 10^{-12} \cdot E_{\max} \cdot T^{-1/2} \\
 &\quad - 4.01 \times 10^{-11} \cdot T^{1/2}) \quad (15)
 \end{aligned}$$

(E_0 and E_{\max} in J mol^{-1}). The first term in Eq. (15) is the result from simple collision theory, which is then modified by the second term to take account of conservation of angular momentum. The only adjustable parameter in fitting Eq. (15) to the measured $k_1(T)$ from the present work is the threshold energy, E_0 , since E_{\max} is defined in terms of E_0 by Eq. (12). Such a fitting procedure to determine E_0 is therefore unambiguous, within the context of this description of the reaction dynamics. A χ -squared goodness-of-fit procedure yields a value for $E_0 = 8.2 \pm 1.4 \text{ kJ mol}^{-1}$ and $E_{\max} = 10.9 \pm 2.3 \text{ kJ mol}^{-1}$. The statistical fitting errors are very small and the assigned errors above arise from the large uncertainty in $Q = 37.5 \pm 13 \text{ kJ mol}^{-1}$.¹³ The quality of the fit is extremely good and is indistinguishable from the best Arrhenius fit plotted in Fig. 4, over the experimental temperature range. Equation (15) can be used to extrapolate to experimentally inaccessible temperatures: $k_1(T = 300 \text{ K}) = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_1(T = 2000 \text{ K}) = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results are 10% lower than obtained using the Arrhenius expression (4).

Becker *et al.*⁹ estimated an upper limit to E_0 of about 8.4 kJ mol^{-1} from their crossed molecular beam study, in excellent agreement with the present estimate. However, as already noted, the estimate of the height of the transition state of 47.2 kJ mol^{-1} from the potential energy surfaces of Shapiro and Zeiri⁷ and Garcia *et al.*⁸ is clearly not in agreement with either experimental study. Classically, no reaction should occur at these low collision energies, and tunneling through the barrier does not reduce the threshold energy significantly.¹¹ Recently, Lagana *et al.*²³ have reported a promising new study of this problem employing trajectory calculations on their *ab initio* surface.⁸ Finally, it should be noted that a similar overestimation of the height of the transition state⁷ compared with an experimental determination of the threshold energy was observed in the case of $\text{Na} + \text{HCl}$.⁴

The reaction cross section can be estimated from Eq. (13) at the average impact energy in the present work ($E_T = 10 \text{ kJ mol}^{-1}$), as $\bar{\sigma}_R = 12.4 \text{ \AA}^2$. This is of course an averaged cross section for an average of 30% partitioning of the product energy into rotation, and may be compared with the result of Becker *et al.*⁹ who estimated $\sigma_R = 27 \text{ \AA}^2$ as the

maximum cross section observed for collisions with $E_T = 12.1 \text{ kJ mol}^{-1}$; this corresponded to particular collisions where more than 50% of the available energy was partitioned into product rotation,⁹ so that the two studies are consistent.

There is thus good agreement between the present work and the molecular beam study of Becker *et al.*⁹ It is clear that further work is required on the nature of the potential energy surface, in particular performing dynamical calculations to bring the theoretical estimate for the threshold energy for this reaction into better agreement with experiment.

ACKNOWLEDGMENTS

This work was supported by generous funds from the University of Miami, and under Grant No. ATM-8616338 from the National Science Foundation.

- ¹M. Polanyi, *Atomic Reactions* (Williams and Norgate, London 1932); C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.* **31**, 1392 (1935).
- ²E. H. Taylor and S. Datz, *J. Chem. Phys.* **23**, 1711 (1955).
- ³D. R. Herschbach, *Adv. Chem. Phys.* **10**, 319 (1966); J. L. Kinsey in *MTP International Review of Science*, edited by J. C. Polanyi (Butterworths, London, 1972), Vol. 9, p.173.
- ⁴P. Marshall and D. Husain, *Chem. Phys. Processes Combust.* (1985), paper 32; P. Marshall, Ph.D. Thesis, University of Cambridge, 1985.
- ⁵M. Eliason and J. O. Hirschfelder, *J. Chem. Phys.* **30**, 1426 (1959).
- ⁶D. E. Jensen and G. A. Jones, *Combust. Flame* **32**, 1 (1978).
- ⁷M. Shapiro and Y. Zeiri, *J. Chem. Phys.* **70**, 5264 (1979).
- ⁸E. Garcia, A. Lagana, and A. Palmieri, *Chem. Phys. Lett.* **127**, 73 (1986).
- ⁹C. H. Becker, P. Casavecchia, P. W. Tiedemann, J. J. Valentini, and Y. T. Lee, *J. Chem. Phys.* **73**, 2833 (1980).
- ¹⁰A. Gonzalez Urëna, *Adv. Chem. Phys.* **66**, 213 (1987).
- ¹¹L. Ciccarelli, E. Garcia, and A. Lagana, *Chem. Phys. Lett.* **120**, 75 (1985).
- ¹²I. W. M. Smith, in *Kinetics and Dynamics of Elementary Gas Reactions* (Butterworths, London, 1980).
- ¹³*Handbook of Physics and Chemistry*, 65th ed., edited by R. C. Weast (Chemical Rubber, Boca Raton, 1985).
- ¹⁴J. M. C. Plane, *J. Phys. Chem.* (in press).
- ¹⁵D. Husain, J. M. C. Plane, and N. K. H. Slater, *J. Chem. Soc. Faraday Trans. 77*, 1949 (1981); D. Husain, J. M. C. Plane, and C. C. Xiang, *ibid.* **80**, 713 (1984).
- ¹⁶*JANAF Thermochemical Tables*, 3rd ed., edited by M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Sververud (U.S. G.P.O., Washington, D.C., 1985).
- ¹⁷D. C. Brodhead, P. Davidovits, and S. A. Edelstein, *J. Chem. Phys.* **51**, 3601 (1969).
- ¹⁸J. Maya and P. Davidovits, *J. Chem. Phys.* **61**, 1082 (1974).
- ¹⁹J. C. Slater and J. G. Kirkwood *Phys. Rev.* **37**, 682 (1931).
- ²⁰G. E. Chamberlain and J. C. Zorn, *Phys. Rev.* **129**, 677 (1963).
- ²¹J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- ²²A. Gonzalez Urëna, V. J. Herrero, and F. J. Aoiz, *Chem. Phys.* **44**, 81 (1979).
- ²³A. Lagana, E. Garcia, J. M. Alvarino, and P. Palmieri, Paper E5, Proceedings of the 9th International Symposium on Gas Kinetics, Bordeaux, France, 1986.