

The Reaction Rate Coefficient for the Clustering of He to Li⁺ at Low Centre of Mass Energies

R. A. Cassidy^{A,B} and M. T. Elford^A

^A Ion Diffusion Unit, Research School of Physical Sciences, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601.

^B Present address: Department of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033.

Abstract

A drift tube-mass spectrometer employing Bradbury-Nielsen grids and the method of Takebe *et al.* (1982) has been used to determine the reaction rate coefficient for the primary clustering reaction of He to Li⁺ at 80 K at mean centre of mass energies from 10 to 15 meV. The influence of mass discrimination in experiments where reactions are studied by ion sampling of both parent and product ions is discussed.

1. Introduction

Although ion-molecule clustering reactions have been studied extensively (see e.g. McDaniel *et al.* 1970) the simplest reactions of this type, the clustering of alkali ions to inert gas atoms, have received only limited attention. In the particular case of Li⁺ ions clustering with helium atoms there appears to be no previous study, possibly because the Li⁺.He cluster ion has such a low binding energy (≈ 70 meV) that it is thermally dissociated by collisions at room temperature. Any measurement of the reaction rate coefficient k therefore requires the use of low temperatures.

In the present study of the reaction



k was measured using the 'tsureko' method of Takebe *et al.* (1982). This method is based on a simple analysis of time-of flight spectra obtained when parent and product ion species are present and is particularly useful in the measurement of very small values of k . The method does not require ions to be sampled from the drift tube, but in the present work checks were made using a quadrupole mass spectrometer and ion sampling to determine the identities of the ions present.

Information on ion-atom clustering has been obtained in previous studies (Colonna-Romano and Keller 1976) by sampling both parent and product ions from a drift tube. Part of the present work was therefore devoted to the study of the effect of mass discrimination in experiments of this kind (Section 5).

2. Apparatus

The arrival-time spectra were obtained using a Bradbury–Nielsen time-of-flight system shown schematically in Fig. 1. Three drift lengths S1–S2 (≈ 9 cm), S2–S3 (≈ 3 cm) and S1–S3 (≈ 12 cm) could be used. Details of the Bradbury–Nielsen method have been given by Elford (1972), while the construction and operation of the drift tube–mass spectrometer (DTMS) has been described by Cassidy and Elford (1985; present issue p. 587).

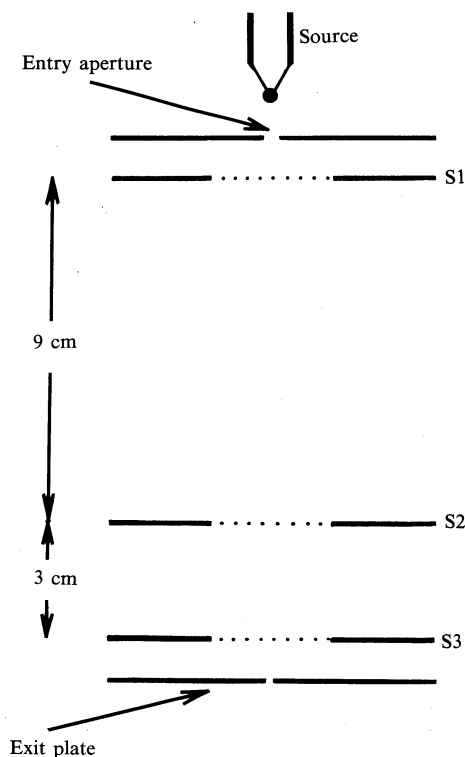


Fig. 1. Schematic layout of the apparatus where S1, S2 and S3 are Bradbury–Nielsen shutter grids.

The lithium ions were produced by thermionic emission from a bead of lithium aluminosilicate glass which was heated by a tungsten coil. In the measurement of an arrival-time spectrum the ion current was usually measured at the exit plate. A small fraction of the ions passed through a knife edged sampling aperture (0.2 mm in diameter) centrally located in the exit plate and were focussed into a quadrupole mass spectrometer. The measurement of an arrival-time spectrum was computer controlled using an IMSAI 8080 microcomputer.

The temperature of the gas in the drift region was measured by two calibrated copper–constantan thermocouples, one attached to the electrode immediately before S1 and one to the electrode after S3. No data were taken if the difference between the two temperatures exceeded 0.5 K.

3. Method

The 'peak area' or 'tsureko' method of Takebe and coworkers relies on the extraction of an isolated arrival-time spectrum for the parent ion species from the composite

spectra for both parent and cluster ions obtained in a conventional drift tube. The presence of a clustering reaction distorts the peaks in the arrival-time spectrum from gaussians centred at shutter signal frequencies corresponding to the parent ion drift velocity. The form of the spectra depends on the drift length, the gas number density N , the value of E/N and the reaction rate coefficient. Under the conditions of interest here only clustering is significant, i.e. dissociation of clusters can be ignored.

The solution of the rate equation describing the depletion of the parent ion species is

$$[\text{Li}^+]_t^p = [\text{Li}^+]_0^p \exp(-k N^2 t), \quad (2)$$

where $[\]_t$ indicates the number density of ions at time t and the superscript p indicates parent ions which have not reacted. If the reaction time t is replaced by d/v_{dr} (where d is the length over which the reaction occurs and v_{dr} the ionic drift velocity), equation (2) can be rewritten as

$$k = \frac{d}{N^2 v_{\text{dr}}} \ln \left(\frac{[\text{Li}^+]_0^p}{[\text{Li}^+]_t^p} \right). \quad (3)$$

The observed spectra can be grouped into three distinct classes depending on the operating conditions:

- (a) where there is significant clustering before the first operating shutter of the drift space and negligible clustering in the drift space;
- (b) where there is negligible clustering before the first operating shutter and significant clustering in the drift space; and
- (c) where there is significant clustering both before the first shutter and in the drift space.

When there is significant clustering before the first operating shutter of the drift region and negligible clustering in the drift space (class a), the peaks due to the Li^+ and $\text{Li}^+ \cdot \text{He}$ ions are undistorted gaussians and the observed arrival-time spectrum is the sum of the two peak systems (see Fig. 2a). This arises in the present apparatus when the 3 cm drift length is used. In this case there is a distance of 10 cm between the source electrode and the first operating shutter S2. The ratio of the area under the $\text{Li}^+ \cdot \text{He}$ peak to the sum of the areas under the $\text{Li}^+ \cdot \text{He}$ and Li^+ peaks is a function of E/N and N . Small contributions from $\text{Li}^+ \cdot 2\text{He}$ and $\text{Li}^+ \cdot 3\text{He}$ may also be present.

Under conditions where clustering is negligible in the approach region before the first shutter but significant in the drift space, the large gaussian peaks due to Li^+ ions have a 'reactant foot' arising from ions which have clustered between the two shutters (Fig. 2b). These spectra occurred when the drift lengths S1-S2 and S1-S3 were used. The area under this foot depends on k and hence is a function of E/N and N . The reactant foot has its maximum height at a frequency corresponding to the passage of clusters which are formed at the first shutter and do not dissociate in the drift region. The slope in the reactant tail is due to the fact that the maximum number of $\text{Li}^+ \cdot \text{He}$ ions is formed where the Li^+ number density is greatest, i.e. at the first shutter. If the reaction rate coefficient for the dissociation of clusters is negligible, the slope of the reactant foot depends on the rate $\alpha = k N^2$.

Spectra of both classes (a) and (b) were analysed to determine the reaction rate for the primary clustering of He to Li^+ ions. Spectra of class (c) are a composite of the other two and were not used in the present analysis.

The ions giving rise to specific peaks in the arrival-time spectra were identified initially by the variation of their abundance on the gas number density and E/N , and their identity confirmed by the use of the mass spectrometer. The clustering reaction is a three body reaction and hence the area of the cluster peaks increases as N^2 , while the peak height decreases as E/N increases due to the decrease in reaction time and reaction rate. The ion species observed using the mass spectrometer were Li^+ , the major product ion $\text{Li}^+ \cdot \text{He}$ together with low levels of $\text{Li}^+ \cdot 2\text{He}$. Higher order clusters were not seen in the mass spectra due to their low abundance and possible dissociation in the analyser region.

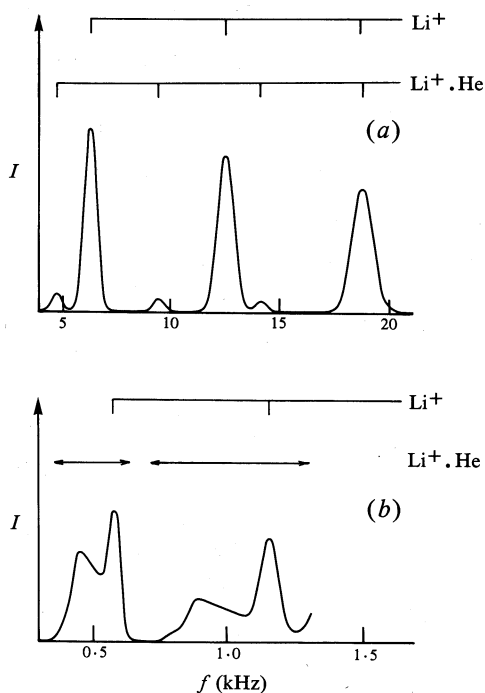


Fig. 2. Examples of arrival-time spectra demonstrating (a) significant clustering before the first shutter of the drift region and negligible clustering between the shutters, and (b) negligible clustering before the first shutter and significant clustering between the shutters.

Before analysis the arrival-time spectra of both classes (a) and (b), recorded as a function of shutter frequency, were transformed to give spectra of current against drift time. The method of analysis is based on the use of equation (3). The ratio of the total ion number density $[\text{Li}^+]_t + [\text{Li}^+ \cdot \text{He}]_t$ to the number density $[\text{Li}^+]_i^0$ of Li^+ ions which had not reacted is assumed to be equal to the ratio of the total area under the composite peak to the area under the non-reacting parent ion peak, i.e. the ratio of the total number of ions (assumed conserved) to the number of Li^+ ions *which have not reacted*. Implicit in the use of this expression is the assumption that no clusters are formed before the ions pass the entrance aperture of the drift tube, i.e. the reaction drift length is well defined.

For spectra of class (a) the determination of this ratio is not difficult; the areas of the Li^+ and $\text{Li}^+ \cdot \text{He}$ peaks can be determined independently and the sum of the total area under the two peaks is divided by the area of the parent ion peak.

When analysing spectra of class (b) it is more difficult to isolate the contribution of those ions which do not react. The ratio required is that of the total peak area to the area of the isolated non-reacting ion gaussian (see Fig. 3).

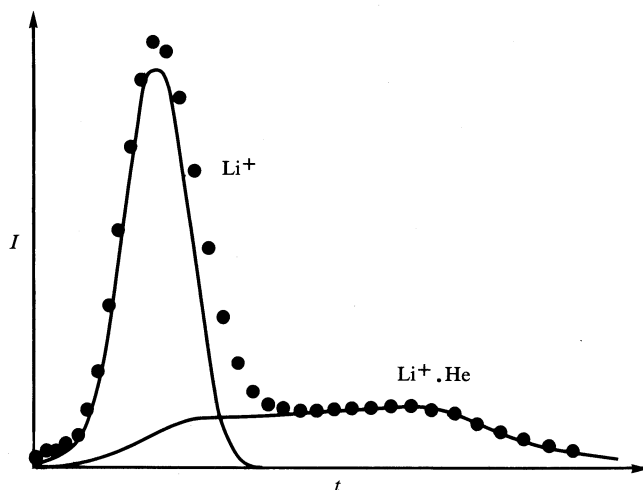


Fig. 3. An arrival-time spectrum measured under conditions where there was negligible clustering before the first shutter of the drift region and significant clustering between the shutters. The contributions to the arrival-time spectrum (experimental points) from Li^+ ions and $\text{Li}^+ \cdot \text{He}$ ions are indicated.

A number of assumptions are made when using this method to determine reaction rate coefficients:

- (a) all ions are collected at the end plate of the drift tube;
- (b) the transmission of ions by the shutters is independent of ion mass;
- (c) no cluster ions pass through the entry aperture; and
- (d) the effects of diffusion can be ignored.

These assumptions were shown to be valid in the following ways:

(a) Calculations of the radial diffusion of the ions over the drift lengths, pressures and E/N values used showed that a negligible fraction of the ions could reach the internal diameter of the guard ring system. Furthermore, the results were not dependent on the drift section used.

(b) The transmission characteristics of the shutters were tested by measuring the 'cut-off' curves, i.e. the fraction of the ion current transmitted as a function of the potential difference between adjacent wires of the shutter. These curves were obtained for both Li^+ and K^+ and no significant difference was found. It was therefore assumed that there would be no significant difference between the transmission of

Li^+ and Li^+He ions. The measured reaction rate coefficients were found to be independent of the amplitude of the shutter signals.

(c) This assumption was checked by varying the electric field strength between the filament and the entry aperture. By making the transit time for Li^+ ions sufficiently small, the number of Li^+He ions at the entry aperture can be made negligible.

(d) The independence of the measured rate coefficient with variation in pressure indicates that diffusion is not a significant source of error.

Although, for simplicity, the preceding discussion assumed that the reaction rate for the dissociation of the primary ion cluster was negligible, this assumption is not implicit in the method. We are only interested in the ratio of the number density for non-reacting ions to the total ion number density. Once an ion has reacted in the drift region, it is of no concern whether it undergoes further reactions (such as dissociation or further clustering), since all such product ions are included in the measurement of the total ion current. Any reacting ion travels some distance as a slow-moving cluster ion and is thus removed from the peak arising from the drift of non-reacting Li^+ ions.

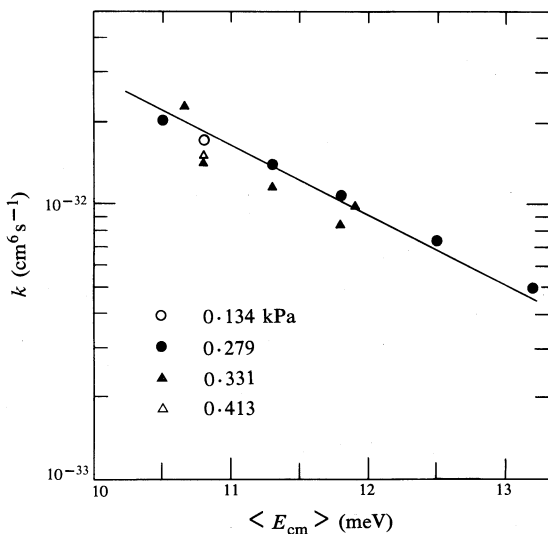


Fig. 4. Reaction rate coefficient k for the primary clustering of He to Li^+ for the four pressures indicated. The solid line is a fit to all the raw data using a linear least-squares fit.

4. Results

The present results for the reaction rate coefficient k for the primary clustering of He to Li^+ are given in Fig. 4. The mean energies $\langle E_{\text{cm}} \rangle$ (in the c.m. frame) were calculated using the Wannier expression. The results were taken at four pressures from 0.134 to 0.413 kPa and include measurements using drift distances of 3, 9 and 12 cm and different peaks in the arrival-time spectra. The solid line is a fit to all the raw data using a linear least-squares fit and is therefore weighted towards the results of the pressure at which most of the data were taken (0.279 kPa).

At a c.m. energy of 15.4 meV, the upper limit to the reaction rate coefficient k is estimated to be $2.5 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$. This value was obtained at a pressure of 0.133 kPa and an E/N value of 9 Td ($\equiv 9 \times 10^{-17} \text{ V cm}^2$) and, under these conditions, the cluster contribution to the arrival-time spectrum is small. Small uncertainties in the determination of the area of the cluster ion contribution can therefore give large relative errors in the value of k .

The errors in the determination of the reaction rate coefficient arise from two main sources. First, there are the errors arising from the determination of experimental parameters; these are at most 1.5% and are small compared with the other errors. (The maximum error due to the temperature determination is estimated to be <1.0% and for the pressure <0.12%.) The error associated with the determination of the ion drift velocity is estimated to be 0.2%.

The major contribution to the total uncertainty is in estimation of $\ln\{[\text{Li}^+]_0^p/[\text{Li}^+]_t^p\}$ at the end of the drift region. This error increases as the size of the cluster ion peak decreases and hence increases with decreasing reaction rate. For the data shown in Fig. 3, this error is estimated to be 25%, increasing to 50% for $k = 3 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$.

The presence of a significant level of contaminants (e.g. N_2 , CO_2) which could cluster to the Li^+ ions can invalidate the determination of reaction rate coefficients by this method. The mass analysis facility of the apparatus enabled the ion species in the drift region to be monitored and the presence of contaminant ion species to be detected. No data were taken when the mass scans indicated a significant level of such contaminant ions.

The reaction rate for dissociation of the primary cluster is small under conditions of interest in this work. A significant level of dissociation would distort cluster ion peaks in the arrival-time spectra from a gaussian, making them asymmetrical. Significant distortion was not observed.

5. Mass Discrimination Effects

Mass discrimination effects in the sampling, analysis and detection of ions from drift tubes have been studied in a number of investigations (for a review, see Helm *et al.* 1980). The discrimination may occur in the transmission of the ions through the exit hole of the drift tube, in the passage of the ions through the ion lens and in the mass spectrometer itself. Furthermore, errors may be introduced into the determination of the relative abundances of various ion species due to the presence of association and dissociation reactions in the transition region.

Mass discrimination effects are not important in the method used here since the ions are sampled and mass analysed only to identify the ion species present. They may, however, be a source of serious error in experiments which measure the relative abundance of different species by extraction of ions from a drift tube and subsequent mass analysis.

During the present work, mass discrimination effects in the transmission of ions and reactions in the analysis region were observed by comparing details of the arrival-time spectra measured at the exit plate with mass analysed arrival-time spectra. In agreement with the results of Milloy and Elford (1975), it was shown that the sampling and analysis region discriminated in favour of the more massive cluster ions, the current corresponding to the Li^+ ions being attenuated.

Evidence for the presence of reactions in the sampling region was also obtained. When the mass of the $\text{Li}^+ \cdot \text{He}$ cluster was selected by the quadrupole mass spectrometer, the mass selected arrival-time spectra displayed peaks at frequencies corresponding to the drift velocities of both species; that is, a fraction of the ions which traversed the drift region as Li^+ ions clustered in the sampling region. However, when the mass spectrometer was tuned to transmit Li^+ ions, a single pure peak system at the frequencies corresponding to the passage of Li^+ ions was observed. Thus, under these particular experimental conditions, there was negligible dissociation of clusters in the sampling region.

The presence of such mass discrimination effects and the possibility of reactions in the sampling regions of a DTMS have serious ramifications for any method for determining reaction rates which relies on the determination of the relative abundance of the parent and product ion species after sampling. For such a method to be accurate the magnitude of the mass discrimination effects and the rates of reactions in the sampling region must be known.

6. Discussion

The first recorded mention of the $\text{Li}^+ \cdot \text{He}$ cluster ion appears to be by Munson and Hoselitz (1939). They did not observe the cluster ion directly but inferred its presence from low temperature mobility measurements. The only other known observation of the $\text{Li}^+ \cdot \text{He}$ cluster was reported by Keller and Niles (1971) and more fully by Colonna-Romano and Keller (1976). Using a DTMS of variable length (7.5 to 44 cm) at 319 K, a pressure of 0.13 kPa, an E/N value of 18 Td and a current ratio method, these workers determined the equilibrium constant K_E to be of the order of 10^{-22} cm^3 at a mean ion energy of 50 meV. Because of the problems of mass discrimination and reactions in the sampling region, which were discussed in Section 5, their value of K_E must be regarded with caution.

Several measurements of reaction rate coefficients have been made for Li^+ ions clustering with other inert gas atoms, although all were made at room temperature and are for c.m. energies of ≈ 50 meV. The present values indicate that for Li^+ clustering with He atoms at room temperature, the reaction rate coefficient at ≈ 50 meV will be $< 5 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$. This may be compared with values of $1.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ (for Ar), $2.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ (for Kr) and $4 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ (for Xe) obtained by Takebe *et al.* (1982).

The technique for the determination of reaction rate coefficients used in this work is particularly suitable for use with a conventional drift tube. The primary advantage is its simplicity; unlike methods involving drift tube models the technique does not require sophisticated computing methods and the mobilities can be determined independently of the reaction rates. The mobilities of the Li^+ and $\text{Li}^+ \cdot \text{He}$ ions in helium will be published separately (Cassidy and Elford 1985). This technique can also compete with methods involving ion sampling and fitting to current transients as it is not affected by serious mass discrimination effects.

Although the method does not rely on the presence of mass analysis facilities, the use of a mass spectrometer in the present work enabled the identities of the ion species to be checked. No such direct check has been possible in previous studies using this method.

The method is generally limited to cases where only a single forward reaction channel and single back reaction channel are present. In the presence of a second reaction,

the method can merely provide an upper limit to the reaction rate coefficient, unless the contributions of the various ion species can be clearly identified. Furthermore, if more than one reaction channel yielding a given ion species is available, the method can do no more than give information on the sum of the rates.

The technique also relies on the drift velocities of the ion species being significantly different. If the drift velocities are too similar, the contribution of the product ions to the arrival-time spectra cannot be separated with sufficient accuracy from that of the parent ions. Cases in which heavy gases are used and where there is a large difference between the reduced masses of the parent and cluster ions (and hence their mobilities) are therefore more favourable.

7. Conclusion

The reaction rate for the clustering of Li^+ ions to helium has been measured at low c.m. energies using the 'tsureko' method of Takebe *et al.* (1982). The present study demonstrates why $\text{Li}^+\cdot\text{He}$ ions are not normally observed at room temperature and provides data for testing theories of ternary association reactions.

Acknowledgments

We wish to thank K. B. Roberts and J. Gascoigne for their technical assistance and G. N. Haddad for advice on the data acquisition system. The comments of Dr R. W. Crompton and Dr S. J. Buckman on this paper are also appreciated.

References

- Cassidy, R. A., and Elford, M. T. (1985). *Aust. J. Phys.* **38**, 587.
- Colonna-Romano, L. M., and Keller, G. E. (1976). *J. Chem. Phys.* **64**, 2684.
- Elford, M. T. (1972). In 'Case Studies in Atomic Collision Physics' (Eds E. W. McDaniel and M. R. C. McDowell), Vol. 2, Ch. 2 (North-Holland: Amsterdam).
- Helm, H., Märk, T. D., and Lindinger, W. (1980). *Pure Appl. Chem.* **52**, 1739.
- Keller, G. E., and Niles, F. E. (1971). *Chem. Phys. Lett.* **10**, 526.
- McDaniel, E. W., Čermák, V., Dalgarno, A., Ferguson, E. E., and Friedman, L. (1970). 'Ion-Molecule Reactions' (Wiley-Interscience: New York).
- Milloy, H. B., and Elford, M. T. (1975). *Int. J. Mass Spectrom. Ion Phys.* **18**, 21.
- Munson, R. J., and Hoselitz, K. (1939). *Proc. R. Soc. London A* **172**, 43.
- Takebe, M., Satoh, Y., Iinuma, K., and Seto, K. (1982). *J. Chem. Phys.* **76**, 5283.

