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A selected ion flow tube investigation of the gas phase chemistry of Li^+

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Abstract

Lithium ion attachment is assessed in this study as a possible means of chemical ionization in the selected ion flow tube-mass spectrometric (SIFT-MS) technique. Measurements using a selected ion flow tube (SIFT) operating at room temperature are reported for lithium ion association reactions with 21 neutral reagents. The reagents ranged from small molecules such as CH_4 and CO, for which the association rate coefficients were very small, to larger organic molecules such as C_6H_6 and C_5H_5N, for which the association rates approached the collision rate coefficient. The bond dissociation energy (BDE) of the $(Li–X)^+$ bond was an important factor in deciding whether or not lithium ion association might be used in SIFT-MS. The attached molecule, X, in the LiX^+ molecular ion is switched out by H_2O for those species having BDEs $<137\,\mathrm{kJ\,mol^{-1}}$. For reactants having BDEs $\geq 137\,\mathrm{kJ\,mol^{-1}}$, some switching out by water occurred in $Li(X)_n{}^+$ resulting in $Li^+{\cdot}(H_2O)_n$ terminal ions. For those reagents having BDEs $\gg 137\,\mathrm{kJ\,mol^{-1}}$, mixed $LiX_m{}^+(H_2O)_n$ clusters were observed.

Keywords: Lithium ions; Association reactions; SIFT-MS; Gas phase ion chemistry; Bond dissociation energy

1. Introduction

Selected ion flow tube-mass spectrometry (SIFT-MS) is an analytical technique that is based on flow tube methodology and known kinetics. The technique utilizes known flow tube parameters and existing ion-molecule kinetics to provide quantitative analysis of volatile compounds in gas mixtures in real time [1]. It is similar to proton transfer mass spectrometry [2] except that it offers greater specificity from multiple reagent ions that effect chemical ionization of the analyte. The larger the range of reagent ions that is available to SIFT-MS, the greater chance there is for identification of a particular analyte. Because the volatile compounds for analysis are almost always in mixtures with air, the reagent ions chosen must not react with the major components of air. These reagent ions are usually H_3O^+, $O_2{}^+$ and NO^+ although other reagent ions have been used for specific applications [3]. Fujii, in a number of studies using a quite different technique, has explored the use of lithium ions, Li^+, as a means of identifying radicals and molecules from their attachment reactions in the gas phase [4–6]. Fujii reported that lithium ions attach to a wide range of radicals and molecules and noted that in favorable cases Li^+ attachment could be used to detect analytes down to a few pg s^{-1} [4].

In order to appraise the potential use of lithium ions as possible reagent ions in SIFT-MS, we examined what was known of their reaction chemistry. The most extensive study was carried out in the early days of ion-molecule chemistry using a flowing afterglow and was motivated by an interest in aeronomy. Spears and Ferguson conducted a study of Li^+ reactions with nineteen reagents of relevance to atmospheric chemistry [7]. They observed that most reactions exhibited pressure-dependent rate coefficients, as expected for association reactions which are viewed as occurring via the mechanism:

$$Li^+ + X \leftrightarrow (Li^+{\cdot}X)^* \tag{1}$$

$$(Li^+{\cdot}X)^* + M \rightarrow Li^+{\cdot}X + M \tag{2}$$

The overall reaction is written as

$$Li^+ + X + M \rightarrow Li^+{\cdot}X + M \tag{3}$$

(M is any molecule which can remove energy in a collision).

Spears and Ferguson varied the flow tube pressure between 0.1 and 2.2 Torr. Most of the reactions they reported exhibited termolecular rate coefficients in the range 10^{-30} to $10^{-28}\,\mathrm{cm^6\,s^{-1}}$. Some reactions may also have had a bimolecular association component indicated by a non-zero intersection with

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the origin in plots of the rate coefficient against bath gas pressure. Woodin and Beauchamp [8] also measured some reactions of Li^+ with carbonyl compounds (ketones and aldehydes) at much lower pressures than used in the flow tube measurements using ion cyclotron resonance (ICR) spectroscopy. They observed bimolecular association and inferred that radiative association of Li^+ with the carbonyl compounds to form the $(Li{\cdot}X)^*$ adduct occurred. Bimolecular rate coefficients were observed in their reactions with rate coefficients ranging from 2.2×10^{-10} ($X = (CH_3)_2CO$) to $1.37 \times 10^{-9}\,cm^3\,s^{-1}$ ($X = (C_2H_5)_2CO$). At higher pressures in the ICR cell ($>10^{-5}$ Torr) the onset of collisional stabilization was observed. Viggiano et al. also examined several reactions of Li^+-neutral clusters with a number of atmospheric reagents [9].

The objective of the present investigation was to examine the kinetics of Li^+ ions with a number of different neutral reagents and then to appraise the potential for the addition of Li^+ to the armory of reagent ions available to the SIFT-MS technique.

2. Experimental

The reactions examined in this work were all studied using the selected ion flow tube instrument that has been described previously [10]. The principal modification to this equipment was in the method of ion generation. The flowing afterglow ion source of the earlier studies was removed for the current investigation and replaced by a heated iridium filament. The filament was coated with either a paste of β-eucryptite [11] (a mineral found naturally and having a composition $Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$) made from a slurry of β-eucryptite in amyl acetate or with a paste of Li_2O in amyl acetate. Lithium ions were generated by thermionic emission and focused via an Einzel lens array, into a quadrupole mass filter for mass selection. The filament lifetime typically ranged between 1 and 10 h. A typical mass spectrum of all ions generated from a heated filament coated with β-eucryptite is shown in Fig. 1. Lithium has two isotopes ^6Li (7.4%) and ^7Li (92.6%). The ion-selection quadrupole mass filter was set to transmit only the $^7Li^+$ isotope and it is the ion chemistry of this species which is reported here.

After mass selection, the Li^+ ions are focused through a Venturi orifice into the instrument flow tube where the reaction chemistry is examined. In all the reactions studied, the helium carrier gas was maintained at a pressure of 0.46 Torr. The reactant neutrals were added through an inlet port located 50.4 cm upstream from the sampling orifice leading to the downstream analyzer quadrupole mass filter. As the number density of ions in the flow tube is always five orders of magnitude less than the reactant neutral, pseudo-first-order kinetics prevails. The slope of the semi-logarithmic plot of I_{Li^+} (I_{Li^+} is the ion count) against neutral reactant flow provides the pseudo-bimolecular rate coefficient. All ions produced in the secondary reactions are monitored. A typical Li^+ decay curve is shown in Fig. 2. All reactions studied in this work were investigated at room temperature (294 ± 4 K).

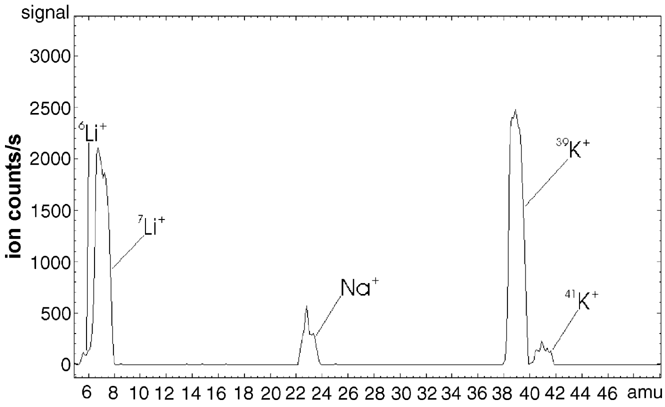

Fig. 1. Typical emission spectrum of a filament coated with β-eucryptite paste.

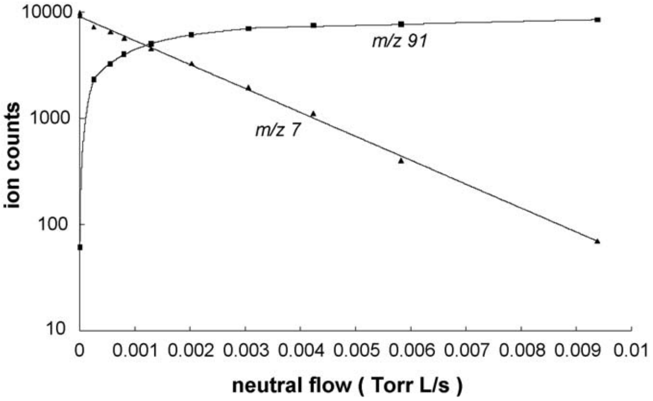

Fig. 2. Semi-logarithmic decay of lithium ion signal through reaction with cyclohexane with corresponding increase in adduct signal.

3. Results and discussion

The rate coefficients of all the reactions of Li^+ ions measured in this study are measured at a single pressure and are reported as pseudo-bimolecular rate coefficients. The rates of many of these reactions, particularly those having pseudo-bimolecular rate coefficients $<1 \times 10^{-11}\,cm^3\,s^{-1}$, will vary linearly with pressure due to the termolecular nature of association reactions. Those reactions that exhibit pseudo-bimolecular rate coefficients approaching the collision rate ($10^{-9}\,cm^3\,s^{-1}$) represent the situation where almost all complexes are stabilized by collision before they can dissociate back to reactants. These near collision-rate reactions will exhibit little or no change in the bimolecular rate coefficient with flow tube pressure. The association rate coefficients measured in this investigation are summarized in Table 1.

As mentioned previously, the rate coefficients summarized in column 3 of Table 1 are the measured pseudo-bimolecular rate coefficients (with uncertainties of ±20%) at 0.46 Torr in a helium bath gas. An approximate termolecular rate coefficient, k_3, is shown for purposes of comparison with the literature values of Spears and Ferguson [7] (column 5) for reactions that have pseudo-bimolecular rate coefficients $<1 \times 10^{-10}\,cm^3\,s^{-1}$. These termolecular rate coefficients in column 4 are approximate as they represent a single point only on a plot of the rate coefficient against pressure. Comparison is possible for just a few compounds with the literature values. The literature result

Table 1
Measured pseudo-bimolecular rate coefficients for the association of Li^+ with the given reactant at 294 K

Reactant	Product	Rate coefficient[a]	Approximated k_3[b]	Literature k_3[b,c]	k_c[d]
CH_4	$Li^+{\cdot}CH_4$	2.2×10^{-13}	1.4×10^{-29}	5.1×10^{-30}	1.7
H_2O	$Li^+{\cdot}H_2O$	9.8×10^{-11}	6.5×10^{-27}		4.0
C_2H_2	$Li^+{\cdot}C_2H_2$	3.4×10^{-12}			1.8
HCN	$Li^+{\cdot}HCN$	2.5×10^{-12}	1.7×10^{-28}		5.9
CO	$Li^+{\cdot}CO$	2.7×10^{-13}	1.8×10^{-29}		1.4
C_2H_4	$Li^+{\cdot}C_2H_4$	4.6×10^{-12}	3.0×10^{-28}	1.9×10^{-28}	2.0
NO	$Li^+{\cdot}NO$	3.3×10^{-13}	2.2×10^{-29}		1.4
C_2H_6	$Li^+{\cdot}C_2H_6$	6.1×10^{-12}	4.0×10^{-28}	2.3×10^{-28}	2.1
CH_2CCH_2	$Li^+{\cdot}CH_2CCH_2$	9.3×10^{-11}	6.4×10^{-27}	$\sim 1.2 \times 10^{-26}$	2.3
CH_3CCH	$Li^+{\cdot}CH_3CCH$	2.9×10^{-10}			2.9
c-C_3H_6	$Li^+{\cdot}c$-C_3H_6	9.8×10^{-11}	6.5×10^{-27}		2.6
CO_2	$Li^+{\cdot}CO_2$	7.4×10^{-13}	4.9×10^{-29}	1.6×10^{-29}	1.6
C_3H_8	$Li^+{\cdot}C_3H_8$	9.7×10^{-11}	6.5×10^{-27}	$\sim 7.2 \times 10^{-27}$	2.4
i-C_4H_{10}	$Li^+{\cdot}i$-C_4H_{10}	3.4×10^{-10}			2.7
SO_2	$Li^+{\cdot}SO_2$	7.6×10^{-12}	5.1×10^{-28}	1.8×10^{-28}	3.7
C_5H_{12}	$Li^+{\cdot}C_5H_{12}$	1.6×10^{-9}			2.9
C_6H_6	$Li^+{\cdot}C_6H_6$	3.2×10^{-9}			3.0
C_5H_5N	$Li^+{\cdot}C_5H_5N$	3.6×10^{-9}			5.2
C_6H_{12}	$Li^+{\cdot}C_6H_{12}$	2.0×10^{-9}			2.0
C_6H_{14}	$Li^+{\cdot}C_6H_{14}$	2.7×10^{-9}			3.2
CH_3Br	$Li^+{\cdot}CH_3Br$	2.2×10^{-11}	1.4×10^{-27}	8.0×10^{-28}	4.1

[a] Pseudo-bimolecular rate coefficient in units $cm^3\ s^{-1}$.
[b] Estimated termolecular rate coefficient in units of $cm^6\ s^{-1}$.
[c] Termolecular rate coefficients from Ref. [7].
[d] Collision rate calculated using the variational transition state model in Ref. [12]. Units are $\times 10^{-9}\ cm^3\ s^{-1}$.

for the smallest rate coefficient, that of $Li^+ + CH_4$, is less than the result we measured which is at the lower limit of our instrument capability. The reason for the higher values measured for CH_4 and CO_2 compared with the early flowing afterglow results is not known but may be attributed in part to contamination by trace amounts of water.

The most significant feature of these measurements shown in Table 1 is that small molecules containing six or fewer atoms, associate only very slowly to Li^+ having termolecular rate coefficients $k_3 < 10^{-27}\ cm^6\ s^{-1}$ or less. Most of the larger molecules that contain 12 atoms or more, exhibit rapid association rates with Li^+. In several cases, the association rate approaches the collision limit. The simple explanation for these results is provided by the RRKM model which predicts that the lifetime of an association adduct with respect to dissociation back to reactants is directly related to the number of degrees of freedom the complex has. A larger number of degrees of freedom and the random distribution of energy into these modes favors longer lifetimes with respect to unimolecular dissociation. Superimposed on this argument is the influence of the Li–X binding energy. Generally the stronger the bond dissociation energy then the longer is the complex lifetime corresponding to the greater density of states that exists above the deeper potential well.

Given that the purpose of this study is to appraise the analytical specificity of Li^+ for SIFT-MS, the most important Li^+ complexes in this work are those with water. This is for the simple reason that almost all samples in SIFT-MS are of ambient air at varying degrees of humidity. Absolute bond dissociation energies (BDEs) for $Li^+{\cdot}(H_2O)_n$ have been measured using the guided ion beam technique by Rodgers and Armentrout who measured the $Li^+{\cdot}H_2O$ BDE as 137 kJ mol^{-1} and also reported successively lower BDEs for each additional water molecule [13]. What happens in the ion-molecule chemistry of mixtures of volatiles in air in which Li^+ ions are used as the reagent ion, then becomes dependent on the relative BDEs of each Li^+-complex as compared to that of $Li^+{\cdot}(H_2O)$. Some specific case studies elaborating on the reaction sequences when water is present, follow. Our observed results for secondary clustering and switching reactions of Li^+ clusters are listed in the relevant reaction equations:

- $Li^+ + C_2H_4$

  The BDE of Li^+-ethylene has been calculated as 82 kJ mol^{-1} [14]. The pseudo-bimolecular association rate of Li^+ and ethylene is very small and was measured as $4.6 \times 10^{-12}\ cm^3\ s^{-1}$ corresponding to a termolecular association rate coefficient of $k_3 \sim 3 \times 10^{-28}\ cm^6\ s^{-1}$. The second and third cluster ions $Li^+{\cdot}(C_2H_4)_2$ and $Li^+{\cdot}(C_2H_4)_3$ are also observed in the flow tube:

$$Li^+ + C_2H_4 + M \rightarrow Li^+{\cdot}C_2H_4 + M,\ k_3 \sim\ 3 \times 10^{-28}\ cm^6\ s^{-1} \tag{4}$$

$$Li^+{\cdot}C_2H_4 + C_2H_4 + M \rightarrow Li^+{\cdot}(C_2H_4)_2 + M,\ k_3 \sim\ 3 \times 10^{-28}\ cm^6\ s^{-1} \tag{5}$$

$$Li^+{\cdot}(C_2H_4)_2 + C_2H_4 + M \rightarrow Li^+{\cdot}(C_2H_4)_3 + M \tag{6}$$

In the presence of water, each of these ethylene molecules in the ion cluster is switched out successively by water at close to the collision rate with the resultant ions being $Li^+{\cdot}(H_2O)_n$:

$$Li^+{\cdot}C_2H_4 + H_2O \rightarrow Li^+{\cdot}H_2O + C_2H_4,\ k = 1.6 \times 10^{-9}\,cm^3\,s^{-1} \tag{7}$$

$$Li^+{\cdot}(C_2H_4)_2 + H_2O \rightarrow Li^+{\cdot}C_2H_4{\cdot}H_2O + C_2H_4,\ k = 2.6 \times 10^{-9}\,cm^3\,s^{-1} \tag{8}$$

$$Li^+{\cdot}C_2H_4{\cdot}H_2O + H_2O \rightarrow Li^+{\cdot}(H_2O)_2 + C_2H_4,\ k \sim 1.8 \times 10^{-9}\,cm^3\,s^{-1} \tag{9}$$

The BDE for the Li^+–C_2H_2 has been calculated as 82.8 kJ mol^{-1} [14] and, although not reported here in detail, a very similar kinetic reaction sequence to that found for ethylene was observed for acetylene, except that acetylene reacts more slowly than ethylene with Li^+.

- $Li^+ + H_2O$

  Water associates slowly with Li^+ forming $Li^+{\cdot}H_2O$ with a pseudo-bimolecular rate coefficient of $k = 9.8 \times 10^{-11}\,cm^3\,s^{-1}$. Reaction of the $Li^+{\cdot}H_2O$ adduct with water produced successive sequential additions of water molecules giving up to five water molecules bonded to a single lithium ion:

$$Li^+ + H_2O + M \rightarrow Li^+{\cdot}H_2O + M,\ k = 9.8 \times 10^{-11}\,cm^3\,s^{-1} \tag{10}$$

$$Li^+{\cdot}(H_2O)_n + H_2O + M \rightarrow Li^+{\cdot}(H_2O)_{n+1} + M \tag{11}$$

- $Li^+ + HCN$

  The binding energy of Li^+ and hydrogen cyanide has been calculated as being slightly larger than that of water at 141 kJ mol^{-1} [15]. Very slow association was observed with hydrogen cyanide to form the Li^+–HCN ion with a pseudo-bimolecular rate coefficient of $k = 2.5 \times 10^{-12}\,cm^3\,s^{-1}$ corresponding to an approximate termolecular rate coefficient of $k_3 \sim 1.6 \times 10^{-28}\,cm^6\,s^{-1}$. Further clustering was observed in the flow tube from sequential addition reactions with up to four hydrogen cyanide molecules attaching to a single lithium ion:

$$Li^+ + HCN + M \rightarrow Li^+{\cdot}HCN + M,\ k = 2.5 \times 10^{-12}\,cm^3\,s^{-1} \tag{12}$$

$$Li^+{\cdot}(HCN)_n + HCN + M \rightarrow Li^+{\cdot}(HCN)_{n+1} + M \tag{13}$$

At higher concentrations of hydrogen cyanide the dominant peak observed was $Li^+{\cdot}(HCN)_3$. The reactions of $Li^+{\cdot}(HCN)_n$ with water were too slow to be measured with a 1.5% water/helium mixture as a neutral reactant, giving a maximum possible switching reaction rate of $\sim 1 \times 10^{-11}\,cm^3\,s^{-1}$:

$$Li^+{\cdot}(HCN)_3 + H_2O \rightarrow Li^+{\cdot}(HCN)_2{\cdot}H_2O + HCN,\ k < 1 \times 10^{-11}\,cm^3\,s^{-1} \tag{14}$$

$$Li^+{\cdot}(HCN)_4 + H_2O \rightarrow Li^+{\cdot}(HCN)_3{\cdot}H_2O + HCN,\ k < 1 \times 10^{-11}\,cm^3\,s^{-1} \tag{15}$$

- Li^+ + benzene

  Li^+ associates rapidly with benzene at the collision rate which is consistent with association rates for large molecules having significant binding energies. The BDE of $Li^+{\cdot}C_6H_6$ has been measured as 164.4 kJ mol^{-1} and that for $Li^+{\cdot}(C_6H_6)_2$ as 103.7 kJ mol^{-1} [16]. The reaction sequence observed for the Li^+/C_6H_6 system is as follows (we show results for benzene addition up to the second cluster only):

$$Li^+ + C_6H_6 + M \rightarrow Li^+{\cdot}C_6H_6 + M,\ k = 3.2 \times 10^{-9}\,cm^3\,s^{-1} \tag{16}$$

$$Li^+{\cdot}C_6H_6 + C_6H_6 + M \rightarrow Li^+{\cdot}(C_6H_6)_2 + M,\ k \sim 8.5 \times 10^{-10}\,cm^3\,s^{-1} \tag{17}$$

In addition to the benzene cluster ions, mixed water–benzene cluster ions were also observed and further experiments were carried out examining the stability of the $Li^+{\cdot}(C_6H_6)_n$ adducts in the presence of water. For these experiments, Li^+ ions were introduced through the Venturi orifice, benzene at a constant flow was added at the upstream inlet (28.0 cm before the downstream reactant inlet and 78.4 cm upstream of the ion sampling orifice) and a helium water mixture in varying controlled amounts was added at the downstream reactant inlet. A typical set of observed ion signals for the $Li^+{\cdot}(C_6H_6)_n/H_2O$ system is shown in Fig. 3. The reactions observed were:

$$Li^+{\cdot}C_6H_6 + H_2O + M \rightarrow Li^+{\cdot}C_6H_6{\cdot}H_2O + M,\ k_3 \sim 7.1 \times 10^{-26}\,cm^6\,s^{-1} \tag{18}$$

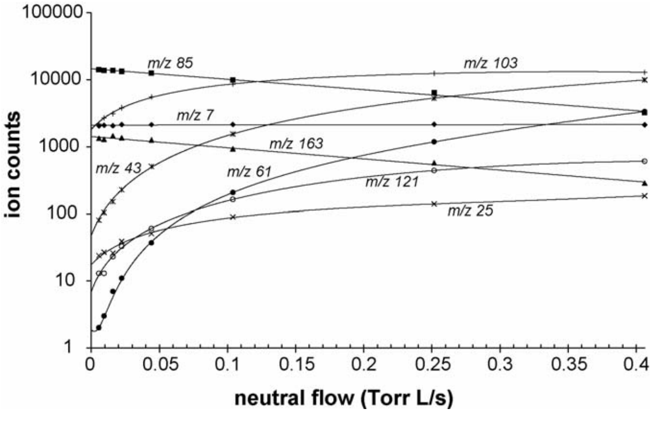

Fig. 3. Characteristic decay curves for the reaction of $Li^+{\cdot}(C_6H_6)$ and $Li^+{\cdot}(C_6H_6)_2$ ions with H_2O and the corresponding growth curves of the product ions. $Li^+{\cdot}C_6H_6$ is represented by m/z = 85; $Li^+{\cdot}C_6H_6{\cdot}H_2O$ by m/z = 103; $Li^+{\cdot}(C_6H_6)_2$ by m/z = 163; $Li^+{\cdot}C_6H_6{\cdot}(H_2O)_2$ by m/z = 121; $Li^+{\cdot}(H_2O)$ by m/z = 25; $Li^+,(H_2O)_2$ by m/z = 43 and $Li^+{\cdot}(H_2O)_3$ by m/z = 61.

$$Li^+{\cdot}(C_6H_6)_2 + H_2O \rightarrow Li^+{\cdot}C_6H_6{\cdot}H_2O + C_6H_6,\ k = 1.1\times10^{-9}\,cm^3\,s^{-1} \quad (19)$$

$$Li^+ + H_2O + M \rightarrow Li^+{\cdot}H_2O + M,\ k_3 \sim 6.5\times10^{-27}\,cm^6\,s^{-1} \quad (20)$$

$$Li^+{\cdot}C_6H_6{\cdot}H_2O + H_2O \rightarrow Li^+{\cdot}(H_2O)_2 + C_6H_6,\ k \sim 2.3\times10^{-9}\,cm^3\,s^{-1} \quad (21)$$

$$Li^+{\cdot}(H_2O)_2 + H_2O + M \rightarrow Li^+{\cdot}(H_2O)_3 + M \quad (22)$$

$$Li^+{\cdot}C_6H_6{\cdot}H_2O + H_2O \rightarrow Li^+{\cdot}C_6H_6{\cdot}(H_2O)_2 + C_6H_6,\ k \geq 4\times10^{-10}\,cm^3\,s^{-1} \quad (23)$$

$$Li^+{\cdot}C_6H_6{\cdot}(H_2O)_2 + H_2O \rightarrow Li^+{\cdot}(H_2O)_3 + C_6H_6,\ k \geq 5\times10^{-10}\,cm^3\,s^{-1} \quad (24)$$

- Li^+ + pyridine

  Li^+ has a higher binding energy with pyridine than with benzene. The $Li^+{\cdot}C_5H_5N$ BDE has been calculated to be 185 kJ mol^{-1} [17] in a study that estimated the BDE of $Li^+{\cdot}C_6H_6$ as 151 kJ mol^{-1}. As noted previously, the BDE for benzene has since been measured as164 kJ mol^{-1} which suggests that the BDE for $Li^+{\cdot}C_5H_5N$ may be even higher than the 1992 calculation [17]. The reactions with Li^+ and C_5H_5N therefore delineate a slightly different system than the Li^+/C_6H_6 system. The association reactions are initiated with a collision rate reaction between Li^+ and pyridine with sequential additions of pyridine leading to larger $Li^+{\cdot}(C_5H_5N)_n$ cluster ions:

$$Li^+ + C_5H_5N + M \rightarrow Li^+{\cdot}C_5H_5N + M,\ k = 3.6\times10^{-9}\,cm^3\,s^{-1} \quad (25)$$

$$Li^+{\cdot}C_5H_5N + C_5H_5N + M \rightarrow Li^+{\cdot}(C_5H_5N)_2 + M,\ k = 2.5\times10^{-10}\,cm^3\,s^{-1} \quad (26)$$

$$Li^+{\cdot}C_5H_5N + H_2O + M \rightarrow Li^+{\cdot}C_5H_5N\cdot H_2O + M,\ k = 7.6\times10^{-10}\,cm^3\,s^{-1} \quad (27)$$

$$Li^+{\cdot}(C_5H_5N)_2 + H_2O \rightarrow Li^+{\cdot}C_5H_5N\cdot H_2O + C_5H_5N,\ k = 1.9\times10^{-10}\,cm^3\,s^{-1} \quad (28)$$

$$Li^+{\cdot}(C_5H_5N)_2 + H_2O + M \rightarrow Li^+{\cdot}(C_5H_5N)_2{\cdot}H_2O + M,\ k = 1.9\times10^{-10}\,cm^3\,s^{-1} \quad (29)$$

$$Li^+{\cdot}C_5H_5N{\cdot}H_2O + H_2O + M \rightarrow Li^+{\cdot}C_5H_5N{\cdot}(H_2O)_2 + H_2O,\ k = 1.8\times10^{-10}\,cm^3\,s^{-1} \quad (30)$$

As with the previous reagents, in SIFT-MS the reactions with background water occur simultaneously with the reactions with pyridine except that here the mixed water–pyridine cluster ions $Li^+{\cdot}(C_5H_5N)_2{\cdot}H_2O$ and $Li^+{\cdot}C_5H_5N{\cdot}(H_2O)_2$ rather than the water cluster ions are the terminal ions.

4. Reaction chemistry summary

The BDE of Li^+ with the various neutral reagents determines the chemistry observed in a lithium ion attachment experiment. Of the four reagents presented as case studies, the BDE of $Li^+{\cdot}C_2H_4$ is less than that of water and the ethylene is efficiently switched out by water leaving only $Li^+{\cdot}H_2O$ clusters. The BDE for hydrogen cyanide is only slightly larger than for water and mixed $Li^+{\cdot}(HCN)_n{\cdot}H_2O$ ($n = 2$ or 3) clusters are formed under high humidity conditions and are the terminal ions. The reaction rate of Li^+ with HCN is too slow for Li^+ to be effective an monitor of small molecules such as HCN in an air sample. The BDE of $Li^+{\cdot}C_6H_6$ at 164 kJ mol^{-1} is considerably larger than the value of 137 kJ mol^{-1} for $Li^+{\cdot}H_2O$ and multiple clusters of Li^+ and benzene are formed which revert to mixed water/benzene clusters before terminating in $Li^+{\cdot}(H_2O)_3$ clusters at high water concentrations. The $Li^+{\cdot}C_5H_5N$ cluster ion exhibited the highest BDE of the four case study compounds examined at ~185 kJ mol^{-1}. In the presence of water, mixed clusters were formed and the reaction sequence terminated with either $Li^+{\cdot}(C_5H_5N)_2{\cdot}H_2O$ or $Li^+{\cdot}C_5H_5N{\cdot}(H_2O)_2$.

5. Conclusions

This study has shown that there are several disadvantages in using Li^+ attachment as a chemical ionization reagent in SIFT-MS. For small molecules the association rate is very slow, thus reducing the sensitivity of the technique: for maximum sensitivity in SIFT-MS, the association reaction with Li^+ should occur at or near the collision rate. For larger molecules that exhibit rapid association, the secondary reactions of the association complex with water decide the ultimate usefulness of the technique. If BDEs between Li^+ and the reagent are <137 kJ mol^{-1}, then water will rapidly switch out the reagent molecule leaving only $Li^+{\cdot}(H_2O)_n$ as terminal ions. This was the situation observed for acetylene and ethylene. For BDEs slightly greater than 137 kJ mol^{-1} as demonstrated by hydrogen cyanide, water can switch out some of the HCN analyte from the clusters. In this case, however, the reactions are very slow and give the mixed cluster ions $Li^+{\cdot}(HCN)_2{\cdot}H_2O$ and $Li^+{\cdot}(HCN)_3{\cdot}H_2O$ (rather than water clusters) as the terminal ions. When the BDE is significantly greater then 137 kJ mol^{-1}, as in the case for benzene, very efficient association occurs of Li^+ to the reagent ion forming multiple clusters. However, water can then add to these clusters via termolecular reactions forming mixed $Li^+{\cdot}C_6H_6{\cdot}H_2O$ complexes and ultimately in these systems the terminal ions are

$Li^+ \cdot (H_2O)_n$. At higher BDEs still, for example with pyridine, water does not switch out the reagent and the terminal ions are mixed cluster ions of the reagent and water. Finally we note that in a situation where Li^+ association is used to monitor analyte concentrations using SIFT-MS, the low mass of the Li^+ ion may lead to differential diffusion losses that would need to be accounted for.

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