

Intrinsic Affinities of Alkali Cations for 15-Crown-5 and 18-Crown-6: Bond Dissociation Energies of Gas-Phase M^+ –Crown Ether Complexes

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Received July 2, 1998

Abstract: Bond dissociation energies (BDEs) of $M^+[c-(C_2H_4O)_5]$ and $M^+[c-(C_2H_4O)_6]$ for $M = Na, K, Rb,$ and Cs are reported. The BDEs are determined experimentally by analysis of the thresholds for collision-induced dissociation of the cation–crown ether complexes by xenon measured by using guided ion beam mass spectrometry. In all cases, the primary and lowest energy dissociation channel observed experimentally is endothermic loss of the ligand molecule. The cross section thresholds are interpreted to yield 0 and 298 K BDEs after accounting for the effects of multiple ion–molecule collisions, internal energy of the complexes, and unimolecular decay rates. For both 18-crown-6 and 15-crown-5, the BDEs decrease monotonically with increasing cation size. These results indicate that the intrinsic affinity of $c-(C_2H_4O)_5$ and $c-(C_2H_4O)_6$ for M^+ is determined principally by the charge density of the cation not by the ratio of the ionic radius to the cavity size. The BDEs reported here are in fair agreement with recent ab initio calculations at the MP2 level with 6-31+G* basis sets. The experimental values are systematically smaller than the computed values by 8 ± 2 kJ/mol per metal–oxygen interaction. The existence of less strongly bound isomers in the experimental apparatus for $Rb^+(15\text{-crown-5})$ and $Cs^+(15\text{-crown-5})$ appears likely, but their absence for Na^+ and K^+ complexes indicates interesting metal-dependent dynamics to the formation of such isomers.

Introduction

Macrocyclic polyethers (crown ethers) are multidentate ligands that exhibit selectivity for specific metal ions in solutions containing other chemically similar ions. They have become model systems for understanding molecular recognition and ligand selectivity due to the enzyme-like specificity in their interactions with cations. Thus a wide variety of data on these systems has been obtained and analyzed.¹ In many cases, the observed selectivity has been rationalized by considering the relative sizes of the metal ions and the cavity of the macrocyclic ligand. However, even for simple homologous crown ethers, a more comprehensive model is required to explain all of the data.² This suggests the need for a more detailed understanding of the noncovalent interactions between ions and neutral molecules and for accurate values of the critical parameters, to develop models of molecular recognition and related phenomena in complex chemical and biochemical systems with broad predictive capabilities.³ Crown ethers are also interesting from a practical point of view because of their potential utility in

advanced chemical separations⁴ and analytical methods.⁵ Computational methods capable of predicting ligand selectivity in a variety of condensed-phase environments would be valuable tools for the advancement of separation technologies. Such methods, currently under development, require accurate models of the relevant noncovalent interactions and suitable experimental data to benchmark the calculations.

One approach to achieving a detailed understanding of noncovalent interactions is the study of isolated ion–molecule complexes. Measurements and calculations on isolated complexes allow separation of intrinsic interactions from effects due to solvation and solvent-induced phenomena. Obtaining accurate data on complexes of cations with simple macrocyclic ligands and determining the level of theory required to accurately model these complexes are the first steps toward developing reliable models of the interaction between cations and more complex macrocycles.

Crown ethers, in particular 18-crown-6, have been the focus of a number of studies based on molecular mechanics, molecular dynamics, and Monte Carlo calculations. Extended basis set ab initio electronic structure calculations have been performed on isolated crown ether–alkali cation complexes by Glendening, Feller, and Thompson⁶ and microsolvated crown ether–alkali

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cation complexes by Feller.⁷ Complexes of crown ethers with alkali cations have also been studied previously in the gas phase by Dearden and co-workers using Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) and tandem quadrupole mass spectrometry^{8,9} and by Brodbelt and co-workers using tandem mass spectrometry.¹⁰ In these studies, relative selectivities were obtained by the kinetic method, relative rates of complexation, and bracketing reactions. Some of the relative affinities derived from the aforementioned studies are in conflict and do not agree with conventional ideas of electrostatic ligation of gas-phase ions. The conflicting results appear to be dependent on the method of species generation (e.g., fast atom bombardment vs ion–molecule chemistry) and the method of study (e.g., the kinetic method vs bracketing reactions). Dearden and co-workers surmised that different isomers may have been generated in the different ion sources used in the various experiments and this could alter the apparent selectivity of a crown ether for a given alkali cation.⁹ They also suggested that the necessary conditions for accurate application of the kinetic method were not being met by the ion–molecule complexes studied. Semiquantitative bond dissociation energies (BDEs) have also been estimated from collision-induced dissociation (CID) measurements made in an FTICR/MS by Katritzky et al.¹¹ These estimates differ significantly from the BDEs computed by Glendening, Feller, and Thompson.⁶ These same calculations yield geometries consistent with recent determinations of the conformations of the complexes of 18-crown-6 with Li⁺, Na⁺, K⁺, and Cs⁺ via ion chromatography.^{12,13}

We have previously measured CID cross sections of alkali ion–ether complexes using a guided ion beam mass spectrometer (GIBMS) specifically designed for measurements of the kinetic energy dependence of collision-induced phenomena. BDEs for complexes of dimethyl ether (DME), 1,2-dimethoxyethane (DXE), and 12-crown-4 (12c4) with Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ were obtained by a detailed analysis of these cross sections.^{14–18} The BDEs determined from these studies are consistent with conventional ideas of electrostatic ligation of gas-phase ions and recent ab initio calculations. In the present work, we report BDEs of the complexes of Na⁺, K⁺, Rb⁺, and Cs⁺ with 15-crown-5 (15c5), *c*-(C₂H₄O)₅, and 18-crown-6 (18c6), *c*-(C₂H₄O)₆, from analysis of the kinetic energy dependence of the CID cross sections. Goals of this work include providing accurate experimental data to resolve the discrepancies

in the previous experimental work, to benchmark calculations, and to facilitate development of suitable models of the noncovalent interactions operative in molecular recognition, ligand selectivity, and related phenomena.

Experimental Section

General. Complete descriptions of the apparatus and the experimental procedures are given elsewhere.^{19–21} The production of M⁺(L) (L = 15c5 and 18c6) complexes is described below. Briefly, ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. Mass selected ions are retarded to a desired kinetic energy and focused into an octopole ion guide that radially traps the ions. The octopole passes through a static gas cell containing xenon, used as the collision gas, for reasons described elsewhere.^{22,23} After exiting the gas cell, product and unreacted reactant ions drift to the end of the octopole where they are focused into a quadrupole mass filter for mass analysis and subsequently detected by a secondary electron scintillation ion counter using standard pulse counting techniques. Raw ion intensities are converted to absolute cross sections as described previously.²⁰ Absolute uncertainties in cross section magnitudes are estimated to be ±20% and relative uncertainties are ±5%.

Ion kinetic energies in the laboratory frame are related to center-of-mass (CM) frame energies by $E(\text{CM}) = E(\text{lab}) m/(M + m)$ where M and m are the ion and neutral reactant masses, respectively. All energies cited below are in the CM frame unless otherwise noted. Sharp features in the observed cross sections are broadened by the thermal motion of the neutral gas²⁴ and the distribution of ion energies. The zero of the absolute energy scale and the full width at half maximum (fwhm) of the ion energy distribution are measured by a retarding potential technique described elsewhere.²⁰ The ion beam energy distribution was typically 0.5–0.8 eV fwhm (lab) for these experiments. The uncertainty in the absolute energy scale is ±0.05 eV (lab).

The complexes are formed in a 1 m long flow tube²¹ operating at a pressure of 0.4–0.7 Torr with a helium flow rate of 4000–9000 standard cm³/min. Alkali ions are generated in a continuous dc discharge by argon ion sputtering of a cathode consisting of a carbon steel “boat” containing Na or K metal, or RbCl or CsCl salt. Complexes are formed by associative reactions with the ligand introduced to the flow tube 5 cm downstream from the dc discharge. Typical operating conditions of the discharge are 3 kV and 30 mA in a flow of ~3% argon in helium. The flow conditions used in this source provide approximately 10⁵ collisions between the ions and the buffer gas, which should thermalize the complexes both rotationally and vibrationally to 300 K, the temperature of the flow tube. Armentrout and co-workers,^{25–28} have shown that this assumption is reasonable and no evidence for nonthermal ions was observed in this work.

Results

Experimental cross sections for the collision-induced dissociation (CID) of M⁺(15c5) by xenon are shown in the Supporting Information, Figure A, parts a through d, for M = Na, K, Rb, and Cs, respectively. Supporting Information, Figure B, shows analogous results for the M⁺(18c6) complexes. Figure 1 gives the representative example of Na⁺(18c6). The only

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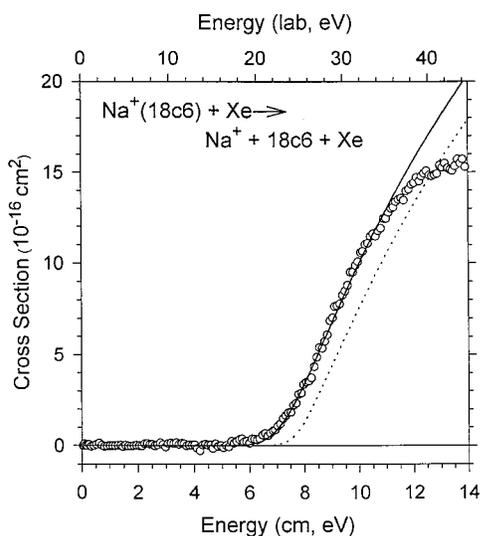


Figure 1. Cross sections for reactions of $\text{Na}^+(18\text{c}6)$ with xenon as a function of kinetic energy in the center of mass frame (lower x axis) and the laboratory frame (upper x axis). The best fits to the data using the model of eq 1 incorporating RRKM modeling for the reactants with an internal temperature of 0 K are shown as dotted lines. Solid lines show these models convoluted over the neutral and ionic kinetic and internal energy distributions.

processes observed for the collision energies studied (typically 0 to 15 eV) were the loss of the intact crown and the formation of $M^+(\text{Xe})$ by ligand exchange. The cross sections for ligand exchange were small and data for these channels were not collected. The apparent threshold energy for the loss of 15c5 from the $M^+(15\text{c}5)$ complexes is greatest for the Na^+ complex, ~ 5 eV, and monotonically decreases to ~ 0.5 eV for the Cs^+ complex. For the $M^+(18\text{c}6)$ complexes, the apparent thresholds for the loss of 18c6 decrease monotonically from ~ 6 eV for the Na^+ complex to ~ 2 eV for the Cs^+ complex.

The maximum cross sections have magnitudes that are large, 40–80 \AA^2 for the 15c5 systems and about half that for the 18c6 systems. Collision cross sections that reflect the size of the alkali metalated crown ethers have been measured by Bowers and co-workers.^{12,13} It should be realized that the CID cross sections determined here represent a convolution of these collision cross sections with the efficiency of energy transfer and the probability for dissociation (which is governed by the dissociation energy and the size of the system). Hence the CID cross sections for the 15c5 complexes are larger than those of the 18c6 complexes because the former systems have lower threshold energies and the smaller complexes dissociate more rapidly. Similar variations as the alkali is changed can be similarly explained although the absolute magnitudes of both K^+ complexes appear anomalously large.

Thermochemical Analysis

Cross sections are modeled in the threshold region with eq 1,

$$\sigma(E) = \sigma_0 \sum_i g_i (E + E_i + E_{\text{rot}} - E_0)^n / E \quad (1)$$

where σ_0 is an energy independent scaling factor, E is the relative translational energy of the reactants, E_0 is the threshold for reaction of the ground rotational, vibrational, and electronic state, and n is an adjustable parameter. The summation is over i , which denotes the rovibrational states of the complex, g_i is the population of those states ($\sum_i g_i = 1$), and E_i is the excitation energy of each rovibrational state. Because the complexes studied here have many low-frequency vibrational modes, the populations of excited vibrational levels are not

negligible at 298 K. The Beyer–Swinehart algorithm²⁹ is used to calculate the population of the vibrational levels with use of the frequencies listed in Table A, Supporting Information. Scaled (85, 90, and 100%) vibrational frequencies for the $M^+(18\text{c}6)$ complexes and free 18c6 are taken from theoretical calculations of Glendening et al.⁶ Scaled (85, 90, and 100%) frequencies for 15c5 were taken from Wasada et al.³⁰ Frequencies for the $M^+(15\text{c}5)$ complexes were obtained by grouping frequencies according to atomic motions of analogous $M^+(12\text{c}4)/12\text{c}4$ ³¹ and $M^+(18\text{c}6)/18\text{c}6$ ⁶ systems and interpolating by using the frequencies for free 15c5.³² The form of eq 1 is expected to be appropriate for translationally driven reactions³³ and has been found to reproduce cross sections well in a number of previous studies of both atom–diatom and polyatomic reactions^{34,35} including CID processes.^{14–18,23,26–28}

The presence of nonthermal ions, pressure effects, and the lifetime of the complex after collisional excitation must be considered and treated properly in the analysis of CID thresholds. These topics are treated as follows. First, excess internal excitation is unlikely because the ions that traverse the 1 m flow tube are thermalized by the 10^5 collisions they undergo with the buffer gases. Second, pressure effects due to multiple collisions with Xe are examined by performing the experiments at three different pressures. Pressure effects are eliminated, following a procedure developed previously,³⁶ by linearly extrapolating the cross sections to zero-pressure, rigorously single collision conditions. It is these cross sections that are further analyzed.

The lifetime effect is examined by incorporating RRKM theory into eq 1 as previously detailed^{26,37} employing the *phase space limit* transition state (PSL TS) model. The additional information necessary to implement this theory is the set of vibrational frequencies for the transition state (TS) associated with the dissociation. This choice is reasonably straightforward because the TS should be fairly loose and similar to the CID products. Thus, most of the frequencies for the PSL TS model are those of the products, $M^+ + L$, which are listed in Table A, Supporting Information. The transitional mode frequencies (those affected most severely as the ligand is removed) are chosen as follows. One $M^+–L$ stretching frequency is chosen as the reaction coordinate and removed. The remaining transitional modes are assigned as free rotors of the products as described elsewhere.^{37,38}

Before comparison with experimental data, the model of eq 1 is convoluted with the kinetic energy distributions of the reactants.²⁰ The parameters σ_0 , n , and E_0 are then optimized with a nonlinear least-squares analysis to give the best fit to the data. An estimate of the error in the threshold energy is obtained from variations in E_0 for different data sets, variations in the parameter n , variations associated with uncertainties in the vibrational frequencies, and the error in the absolute energy scale. We also determine a threshold energy for a “tight” TS, $E_0(\text{tight})$, and a threshold energy without RRKM lifetime modeling, $E_0(\text{no RRKM})$, to quantify the kinetic shift. Parameters for the *tight* TS are determined by removing only the reaction coordinate frequency and leaving the other frequencies unchanged from those of the reactant. Uncertainties listed with the $E_0(\text{PSL})$ and $E_0(\text{tight})$ values

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Table 1. Threshold Energies at 0 K, Modeling Parameters for Eq 1, and Entropies of Activation at 1000 K for $M^+(15c5)$ and $M^+(18c6)^a$

species	$E_0(\text{noRRKM})$, eV	$\sigma_0(\text{PSL})$	$n(\text{PSL})$	$E_0(\text{PSL})$, eV	$\Delta S^\ddagger(\text{PSL})$, J/(mol K)	$E_0(\text{tight})$, eV	$\Delta S^\ddagger(\text{tight})$, J/(mol K)
$\text{Na}^+(15c5)$	6.11(0.39)	34(15)	1.4(0.3)	3.05(0.19)	92	2.11(0.19)	-34
$\text{K}^+(15c5)$	3.95(0.25)	114(68)	1.1(0.2)	2.12(0.15)	51	1.55(0.15)	-23
$\text{Rb}^+(15c5)$	1.71(0.08)	56(5)	1.1(0.2)	1.18(0.07)	44	0.92(0.07)	-21
$\text{Cs}^+(15c5)$	1.47(0.10)	18(7)	1.7(0.1)	1.04(0.06)	33	0.81(0.06)	-22
$\text{Na}^+(18c6)$	7.37(0.24)	28(7)	1.3(0.1)	3.07(0.20)	64	2.23(0.20)	-25
$\text{K}^+(18c6)$	5.95(0.16)	112(64)	0.9(0.2)	2.43(0.13)	40	1.78(0.13)	-27
$\text{Rb}^+(18c6)$	4.56(0.22)	34(9)	1.0(0.1)	1.98(0.13)	18	1.49(0.13)	-28
$\text{Cs}^+(18c6)$	3.53(0.11)	26(4)	1.2(0.1)	1.74(0.09)	51	1.31(0.09)	-28

^a Uncertainties (one standard deviation) are listed in parentheses.

also include errors associated with variations in the time assumed for dissociation (10^{-4} s) by a factor of one-half and two.

One useful measure of the dissociation process is the change in entropy in going from the energized molecule to the activated complex during this process, ΔS^\ddagger . These values are listed in Table 1 for a temperature of 1000 K, often used as a standard.^{39,40} The range of values obtained is similar to the results of a theoretical study on the dissociation dynamics of $\text{Na}^+(18\text{-crown-6})$ by Hase et al.⁴¹ This investigation studied the complexation kinetics and dynamics of Na^+ with the D_{3d} and C_i conformations of 18-crown-6 with canonical variational transition-state theory. At 300 K, Hase et al. computed ΔS^\ddagger as 35 J/(mol K) for the D_{3d} state and 62 J/(mol K) for the C_i state. In our work, the calculated ΔS^\ddagger at 300 K for dissociation of $\text{Na}^+(18c6)$ is 83 J/mol K for our PSL TS and -15 J/(mol K) for our tight TS. The similar ranges obtained in these two studies support the validity of our assumptions regarding the TS frequencies. They also point to a loose TS as being most reasonable for describing the dissociation of sodium ion-crown ether complexes.

Results from analysis of the cross sections shown in Figures A and B, Supporting Information, with eq 1 are provided in Table 1. In previous work with $M^+(12c4)$, $M = \text{Na},^{16} \text{K},^{17} \text{Rb}, \text{Cs},^{18}$ and Li^+ with a variety of small alcohols and one through six water molecules,^{38,42} we have found that thresholds obtained assuming the PSL TS, the loosest TS that we can reasonably imagine, provide the most accurate thermochemistry. The tight TS values provide very conservative limits to the correct thermodynamics, while values obtained with no RRKM modeling provide very conservative upper limits.

Because the rotational, vibrational, and translational energy distributions are explicitly included in our modeling, the threshold energies determined with eq 1 correspond to 0 K. Threshold energies for CID reactions are converted into 0 K bond dissociation energies (BDEs) by assuming that E_0 represents the energy difference between the reactants and the products at 0 K.⁴³ This requires that there are no activation barriers in excess of the endothermicity. This is generally true for ion-molecule reactions;^{34,44} however, this assertion needs more careful consideration for ligands such as 15c5 and 18c6 where the conformation of the ligand may change in going from the lowest energy state of the complex to the lowest energy form of the products. The barriers separating these conformations in the absence of the metal ion are likely to be small. We believe that the energy of complexation with the metal ion can overcome any such barriers to rearrangement. In essence, dissociation of the lowest energy conformation of the complex to the products should have no barriers in excess of the bond energy as long as the interaction between the metal cation and the ligand in its lowest energy conformation is attractive at long range. This presumes that barriers between conformations of the complex are less than the binding

energy of the metal ion to the ligand; exceptions seem unlikely. Thus, the question of conformations moves from an energetic one to a kinetic one, namely, in the presence of multiple conformations, what is the rate at which the excited complex moves along the lowest energy dissociation path. Given the flexibility of the empirical model used to determine the threshold for dissociation, it seems likely that the true thresholds are still accurately located even if the unimolecular rate constant does not include such an effect explicitly. In the end, comparison of the thermochemistry measured here to theoretical work provides some test of this conclusion. This is discussed below.

Comparison to Theoretical Results. Table 1 compares the 0 K BDEs of the alkali cation-crown complexes determined without RRKM lifetime modeling and with the two versions of the lifetime effects included. The threshold energies obtained without any lifetime analysis, $E_0(\text{no RRKM})$, are the greatest and the $E_0(\text{tight})$ values are the smallest. This is expected because these modeling procedures represent the shortest and longest lifetimes of the dissociating complexes, respectively. The $E_0(\text{PSL})$ values fall between these values. To assess which of the three models is most appropriate, we compare the $M^+(18c6)$ BDEs with the theoretical values taken from the work of Glendening et al.⁶ after adjusting these values to 0 K. In this theoretical work, equilibrium gas-phase geometries were optimized with a 6-31+G* modified basis set⁴⁵ at the restricted Hartree-Fock (RHF) level of theory. Electron correlation corrections were evaluated with second-order Møller-Plesset perturbation theory applied to the optimized geometries. Basis set superposition errors in the calculated bond energies were estimated through the use of the counterpoise correction.

Neither the $E_0(\text{no RRKM})$ values nor the $E_0(\text{tight})$ values for the $M^+(18c6)$ BDEs agree well with theory, showing average deviations of 2.57 ± 1.08 eV above theory and 1.08 ± 0.23 eV below theory, respectively. Consistent with the observations made for the $M^+(12c4)$, $M = \text{Na}, \text{K}, \text{Rb},$ and Cs complexes,¹⁶⁻¹⁸ the $E_0(\text{PSL})$ values agree much better with the theoretical results. These show an average deviation of 0.48 ± 0.14 eV below theory (0.08 ± 0.02 eV below when normalized by the number of oxygen atoms in the dissociating ligand). Note that both the absolute deviations and the dispersion in the differences are smaller for the $E_0(\text{PSL})$ values, indicating that the trends in the experimental and theoretical BDEs agree better than for the other models. We conclude that the $E_0(\text{PSL})$ BDEs represent our best experimental values.

It is possible that the $M^+(18c6)$ experimental BDEs are lower than the theoretical BDEs because of inadequacies in our treatment of the calculated unimolecular dissociation rates. To obtain better agreement, these rates would have to increase, leading to a smaller kinetic shift and a higher threshold. However, the PSL model already represents the loosest TS that is reasonable. Nevertheless, if the experimental data are modeled to attain BDEs that agree precisely with theory, we obtain ΔS^\ddagger values of 105, 124, 123, and 123 J/mol for $M^+(18c6)$, for $M = \text{Na}, \text{K}, \text{Rb},$ and Cs , respectively, at 300 K. These entropies of activation are about twice as large as those obtained with the PSL model (38 J/(mol K) for $\text{Rb}^+(18c6)$ to 83 J/(mol K) for $\text{Na}^+(18c6)$ at 300 K) and well above those calculated by Hase et al.,⁴¹ 35 and 62 J/(mol K) at 300 K for the association of Na^+ with 18c6 in the D_{3d} and C_i state, respectively. Nevertheless, the extent of the kinetic shift in these systems clearly indicates that the BDEs determined here are strongly model dependent. As additional information regarding the character of these

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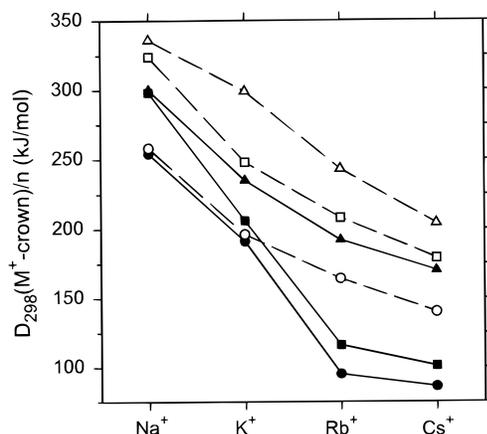
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Table 2. Bond Dissociation Enthalpies at 298 K and Enthalpy Shifts from 0 to 298 K of $M^+(12c4)$,^a $M^+(15c5)$, and $M^+(18c6)$ in kJ/mol^b

species	$\Delta H_{298}(\text{CID})$	$\Delta H_{298}(\text{MP2})^c$	$\Delta H_{298}(\text{ICR})^d$	$\Delta H_{298} - \Delta H_0$
$\text{Na}^+(12c4)$	254(13)	258		2
$\text{K}^+(12c4)$	191(11)	196		1.9
$\text{Rb}^+(12c4)$	95(13)	164/105 ^e		2.2
$\text{Cs}^+(12c4)$	86(9)	140/81 ^e		1
$\text{Na}^+(15c5)$	298(18)	324		3.4
$\text{K}^+(15c5)$	206(14)	248		1.4
$\text{Rb}^+(15c5)$	116(6)	208		1.4
$\text{Cs}^+(15c5)$	101(6)	179		0.8
$\text{Na}^+(18c6)$	300(19)	336		4
$\text{K}^+(18c6)$	235(13)	299	167	1.2
$\text{Rb}^+(18c6)$	192(13)	243		1.9
$\text{Cs}^+(18c6)$	170(9)	204	134	0.8

^a Values are PSL model values taken from refs 15, 16, and 17.^b Uncertainties (one standard deviation) are given in parentheses and include variations in all quantities described in the text for the PSL model. ^c Values are taken from refs 6, 31, and 47. ^d Values are taken from ref 11. ^e Values for structures in which 12c4 is constrained to have S_4 symmetry; taken from ref 31.**Figure 2.** Experimental (closed symbols) and theoretical (open symbols) BDEs of $M^+(12c4)$ [circles], $M^+(15c5)$ [squares], and $M^+(18c6)$ [triangles] for $M = \text{Na}, \text{K}, \text{Rb},$ and Cs at 298 K. All values are taken from Table 3.

dissociations becomes available, the precision and accuracy of the modeling could be improved.

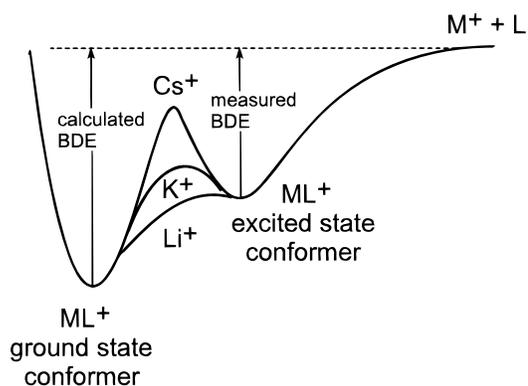
Discussion

To compare with literature thermochemistry, we convert our 0 K BDEs to values at 298 K using standard formulas for the temperature dependence of the enthalpy.⁴⁶ This temperature correction is given in Table 2 along with the 298 K BDEs including previously determined values for $M^+(12c4)$ complexes. This information is also plotted in Figure 2. It is evident from these data that the BDEs for all the metal ion crowns increase with increasing metal ion charge density, i.e., as the alkali ion gets smaller. It is also evident that for a given metal ion, the BDEs increase for 12c4 to 15c5 to 18c6 complex. (The near equality of the BDEs of $\text{Na}^+(15c5)$ and $\text{Na}^+(18c6)$ is discussed below.) Both of these trends are in accord with conventional ideas of electrostatic ligation.

The BDEs computed for $M^+(12c4)$, $M^+(15c5)$, and $M^+(18c6)$ at 298 K by Feller and co-workers are also given in Table 2.^{6,31,47} The computed BDEs exceed the experimental values for all

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**Figure 3.** A potential energy diagram describing the formation of the alkali cation–ligand complexes, $M^+(L)$, in the ground state and a low-lying conformation starting from the separated alkali cation, M^+ , and ligand, L .

complexes studied here. The discrepancies range from 34 to 64 kJ/mol for the $M^+(18c6)$ complexes. The $\text{Na}^+(15c5)$ and $\text{K}^+(15c5)$ complexes show similar discrepancies (24 and 42 kJ/mol), while $\text{Rb}^+(15c5)$ and $\text{Cs}^+(15c5)$ exhibit much larger differences between theory and experiment (92 and 78 kJ/mol). These latter two cases are discussed separately below. When normalized by the number of oxygen atoms in the ligand, the average discrepancy for the 18c6 complexes is 8 ± 2 and 7 ± 2 kJ/mol for $\text{Na}^+(15c5)$ and $\text{K}^+(15c5)$, respectively. These normalized discrepancies are similar to those between theory and experiment for monodentate (dimethyl ether), bidentate (1,2-dimethoxyethane), and tetradentate (12c4) ligands complexed with the alkali metals: 8 ± 5 , 7 ± 5 , 5 ± 3 , 11 ± 8 , and 9 ± 7 kJ/mol per metal–oxygen interaction for the Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ complexes, respectively.^{14–18,31,48} Thus, this difference appears to be an intrinsic difference between experiment and theory even in cases such as the dimethyl ether complexes where dissociation lifetimes do not affect the experimental results.

As noted above, the experimentally and theoretically determined BDEs of $\text{Na}^+(15c5)$ and $\text{Na}^+(18c6)$ are nearly equal. This appears to be a result of the ability of the O atoms to get substantially closer to Na^+ in 15c5. This is indicated by ab initio calculations, which obtain an average Na^+-O bond length of 2.33 Å in $\text{Na}^+(15c5)$ and 2.74 Å in $\text{Na}^+(18c6)$.^{6,47} For all of the other metal ions studied, the $M^+-\text{O}$ bond lengths in $M^+(15c5)$ differ from those in $M^+(18c6)$ by less than 0.15 Å.

The discrepancies between experimental and theoretical BDEs for $\text{Rb}^+(15c5)$ and $\text{Cs}^+(15c5)$ are quite large: 18 ± 1 and 16 ± 1 kJ/mol per $M-\text{O}$ interaction, respectively. Comparison of the experimentally derived BDEs and the computed BDEs for $\text{Rb}^+(12c4)$ and $\text{Cs}^+(12c4)$, reported previously¹⁸ and included in Table 2, show similarly large discrepancies: 17 ± 3 and 14 ± 2 kJ/mol per $M-\text{O}$ interaction. These discrepancies were attributed to the presence of a higher energy conformer (with a lower BDE) in the experimental apparatus. For this to be plausible, the higher energy conformer must be formed easily from the separated metal ion and ligand and there must be a barrier that prevents the higher energy conformer from rearranging to the minimum energy conformation as the complexes are thermalized.

Such a situation, shown schematically in Figure 3, seems plausible for complexes containing 12c4. When uncomplexed, 12c4 has a ground-state geometry with S_4 symmetry that is quite

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different from the C_4 geometry of 12c4 when it is complexed to Na^+ , K^+ , Rb^+ and Cs^+ .³¹ A critical difference between these two geometries is the orientation of the oxygen atoms in the ring. The S_4 geometry has alternate oxygens pointing to opposite sides of the ring, such that the oxygen dipoles interact weakly with one another. In the C_4 geometry, all of the oxygen atoms lie on one side of the ring, such that an alkali cation can interact strongly with all four oxygen atoms. In generating the alkali ion–crown complexes in our flow tube source, we imagine that the metal ion interacts with the 12c4 with S_4 symmetry and is then stabilized by three-body collisions. It seems reasonable that if the alkali ion is small, the electrostatic field pulling the oxygens toward the ion could be sufficiently strong that the barrier to rearrangement can be overcome. Thus, the $M^+(12c4)$ complexes with smaller alkalis, e.g. Na^+ and K^+ , are formed efficiently in their minimum energy conformation. When the alkali ion is larger, e.g. Rb^+ or Cs^+ , however, the electrostatic field is weaker and more diffuse, such that the barrier to rearrangement may be difficult to overcome. This allows thermalizing collisions to trap the complex in a higher energy conformation. This conclusion is corroborated by calculations of the BDEs of $Rb^+(12c4)$ and $Cs^+(12c4)$ by Feller and co-workers for complexes in which 12c4 is constrained to S_4 symmetry.³¹ These calculations obtain BDEs that agree with those determined experimentally, Table 2.

It is probable that a similar scenario applies to the complexes of 15c5 with Rb^+ and Cs^+ leading to anomalously low experimentally determined BDEs. As for $M^+(12c4)$, the minimum energy structures for $Rb^+(15c5)$ and $Cs^+(15c5)$ are pyramidal with all oxygens on the same side of the crown. As in 12c4, the ground state conformation of uncomplexed 15c5 minimizes dipole–dipole interactions by directing at least one oxygen atom to one side of the crown and the rest to the other side. It is plausible that Rb^+ and Cs^+ cannot effect the change in conformation that leads to the minimum energy conformer under the experimental conditions even though 15c5 is more flexible than 12c4.

As for the smaller crowns, the minimum energy structure of free 18c6 has four of its six ether oxygens directed inward from the ether backbone and the other two directed outward. Likewise, the minimum energy structures of $Rb^+(18c6)$ and $Cs^+(18c6)$ are pyramidal with all oxygens directed toward the same side of the ether backbone. In contrast to the $M^+(12c4)$ and $M^+(15c5)$ complexes, however, comparison of the experimental and theoretical BDEs for the $M^+(18c6)$ complexes (average discrepancy of 8 ± 2 kJ/mol per M–O interaction) is uniformly reasonable for all metals. This suggests that the experimentally derived BDEs correspond to the minimum energy conformers and that even the largest alkali metal cations can effect a change in conformation. This is similar to the cases of $M^+(12c4)$ and $M^+(15c5)$ for $M = Na$ and K . This is presumably because 18c6 has more degrees of freedom and is more flexible.

Comparison to Previous Experiments. We are aware of only one other experimental study that has attempted to determine the absolute BDEs of alkali cation–crown ether complexes. Katrizky et al.¹¹ performed CID of these complexes in an ICR mass spectrometer. Their results for the BDEs of $K^+(18c6)$ and $Cs^+(18c6)$ are listed in Table 2. Both of the BDEs are considerably smaller than the present experimental and theoretical BDEs. The large differences between these previous results and the present experiments can be accounted for by difficulties in the previous experiments and analysis. In particular, the previous studies were probably not able to thermalize

the alkali cation–crown complexes completely (conditions leading to approximately 60 thermalizing collisions are used) and effects of multiple collisions and dissociation lifetimes are not explicitly considered.

Brodbelt and co-workers¹⁰ have reported the relative affinities of 18c6 and 15c5 toward alkali cations. The relative affinities were determined by application of the kinetic method.⁴⁹ Ion complexes of crown ethers with two different alkali metals and a halide were generated by using liquid secondary ion mass spectrometry. After isolation, the bis(alkali metal) halide–crown ether complexes underwent high-energy CID that produced primarily alkali–crown ether adduct ions and presumably an alkali halide. The relative fragment peak intensities from the high-energy CID were correlated to the relative affinities of the crown ethers for the alkali cation. From these experiments, Brodbelt and co-workers reported that the relative affinities of 15c5 are $Li^+ \gg Na^+ > K^+ > Cs^+$, and for 18c6 the relative affinities are $Na^+ > K^+ > Li^+ > Rb^+ > Cs^+$.^{10a} However, in the more recent paper,^{10b} Brodbelt and co-workers reported the relative affinities for 18c6 were $Na^+ > K^+ > Li^+ > Cs^+ > Rb^+$, although no new data were presented.

Our results affirm Brodbelt's 15c5 relative affinities but our results for complexes containing 18c6 are not in agreement with the most recent results of Brodbelt and co-workers. Instead, we find that the BDE of $Rb^+(18c6)$ is greater than that of $Cs^+(18c6)$. We note that our results are in accord with conventional ideas of electrostatic ligation and the ab initio results of Feller and co-workers. It should also be noted that the BDEs for $Li^+(15c5)$ and $Li^+(18c6)$ obtained by Feller and co-workers are greater than those of $Na^+(15c5)$ and $Na^+(18c6)$, respectively, in accord with conventional ideas of electrostatic ligation but not in accord with the results of Brodbelt and co-workers.

In a study by Dearden and co-workers,⁹ the selectivities of the alkali cations for several crown ethers were determined by using the kinetic method. In these experiments, complexes containing two crown ethers and one alkali cation were created via ion molecule reactions and made to undergo CID at high pressure and high energy. The results indicated that for Na^+ , K^+ , Rb^+ , or Cs^+ bound to a pair of crown ethers, the relative product peak intensity was always greatest for the peak that contained the alkali cation bound to the larger of the crown ethers. These results were used to infer that the alkali cations bond more strongly to the larger 18c6 followed by 15c5 and 12c4, consistent with the results reported here. This phenomenon is not surprising, because the larger crown ethers have two advantages over the smaller crown ethers. First, the larger crowns have more oxygen sites for interaction with the metal ion. Second, the larger crowns have more degrees of freedom, and thus are more flexible, facilitating the formation of a more favorable conformation for the crown–cation interaction.

Comparison of $M^+(18c6)$ Selectivity in the Gas Phase and Aqueous Environment. Both the results presented here and previous theoretical work⁶ have determined that the selectivity of 18c6 is greatest for Na^+ followed by K^+ , Rb^+ , and Cs^+ . These trends indicate that the charge density of the cation is the critical feature controlling the bonding. Smaller alkali cations have greater charge density and can get closer to the crown to create a stronger electrostatic field to bind the electron-donating ligands. In contrast, in an aqueous environment, K^+ is the most

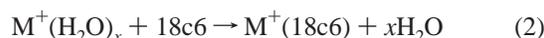
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Table 3. Total Bond Dissociation of $M^+(H_2O)_x$ for $M = Na, K, Rb,$ and Cs^a and the Enthalpy of Reaction 2 at 298 K

x	$Na^+(H_2O)_x$	$\Delta H(Na^+)$	$K^+(H_2O)_x$	$\Delta H(K^+)$	$Rb^+(H_2O)_x$	$\Delta H(Rb^+)$	$Cs^+(H_2O)_x$	$\Delta H(Cs^+)$
0	0	300	0	235	0	192	0	170
1	-100	200	-75	160	-66	125	-57	113
2	-183	117	-142	93	-123	69	-110	60
3	-249	51	-197	38	-174	18	-156	13
4	-307	-7	-247	-12	-221	-29	-201	-31
5	-359	-59	-292	-56	-265	-73	-242 ^b	-72
6	-403	-103	-333	-98	-306 ^c	-114	-281 ^c	-111

^a Total bond dissociation energies of $M^+(H_2O)_x$ for $M = Na, K, Rb,$ and Cs taken from ref 49. ^b The BDE for $Cs^+(H_2O)_5$ is assumed to equal 0.94 of the BDE for $Cs^+(H_2O)_4$, the same ratio found in the analogous Rb^+ complexes.⁴⁹ ^c The BDEs for $M^+(H_2O)_6$ for $M = Rb$ and Cs are assumed to equal 0.94 of the BDE for $M^+(H_2O)_5$ for $M = Rb$ and Cs , respectively, the same ratio found in the analogous K^+ complexes.⁴⁹

strongly complexed to 18c6 followed by Rb^+ , Cs^+ , and Na^+ .⁵⁰ We can gain insight into this aqueous selectivity by considering the competition between the solvation of alkali cations and the complexation by crown ethers, reaction 2.



A similar analysis has been conducted by Glendening et al.⁶ using theoretical information exclusively. They concluded that the aqueous selectivity of 18c6 could be mimicked with as few as four water molecules. Here, we reexamine the energetics of reaction 2 given the experimental information now available.

Table 3 lists the total gas-phase bond energies of $M^+(H_2O)_x$ for $M = Na, K, Rb,$ and Cs for $x = 1-6$,⁵¹ and the reaction enthalpy for reaction 2. For $x = 1-4$, the reaction enthalpy indicates that the selectivity of 18c6 is unaltered from its gas-phase selectivity, but the differences in the reaction enthalpies for the different alkali cations become much closer. At $x = 5$ and 6, the selectivity of the 18c6 changes to favor K^+ over Na^+ such that the new order is $K^+ > Na^+ > Rb^+ \approx Cs^+$. Thus, as x gets larger, the reaction enthalpies begin to more closely reproduce the selectivity of aqueous 18c6. However, reaction 2 has also become endothermic as the initial solvation of the metal ion increases. To understand the aqueous equilibria, we also need to consider the sizable entropic contribution to this reaction, which clearly favors products. However, the entropic term is approximately the same for all metal ions such that the relative selectivities observed in the enthalpies should be retained in calculations of the free energies.

Another consideration in determining the true aqueous selectivities which cannot be assessed by these gas-phase studies is the extent to which the $M^+(18c6)$ complex is also solvated. Theoretical calculations⁶ show that Na^+ is enveloped by 18c6 in the gas phase, such that solvation of this complex will not involve direct interaction of the solvent with Na^+ . However, K^+ , Rb^+ , and Cs^+ are large enough that the 18c6 ligand does not completely block access to surrounding solvent molecules,⁶ such that these complexes will be differentially stabilized by solvation.

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Conclusion

Kinetic energy dependent collision-induced dissociation in a guided ion beam mass spectrometer is used to determine the absolute bond dissociation energies of sodium, potassium, rubidium, and cesium cations with 18-crown-6 and 15-crown-5. Analysis of the kinetic energy dependence of these cross sections, including considerations of the effects of multiple collisions, internal energies of the complexes, reactant translational energy distributions, and dissociation lifetimes, led to the desired bond energies. The experimental bond dissociation energies obtained here are in reasonable agreement with results of ab initio calculations of Feller and co-workers.^{6,47} The average discrepancy between the experimental and theoretical BDEs is about 8 ± 2 kJ/mol per metal-oxygen interaction. Discrepancies outside of this range are obtained for $Rb^+(15c5)$ and $Cs^+(15c5)$ and are attributed to the presence of less strongly bound isomers in the experimental apparatus. Comparisons of $M^+(12c4)$, $M^+(15c5)$, and $M^+(18c6)$ for $M = Na, K, Rb,$ and Cs reveal that alkali cation-crown BDEs are greatest for 18c6 followed by 15c5 and 12c4. Na^+ is bound most strongly to all of the crowns followed by K^+ , Rb^+ , and Cs^+ in that order, indicating that the intrinsic metal ion affinity of the crowns is determined principally by the charge density of the cation.

Acknowledgment. We thank S. E. Hill, D. Feller, and E. D. Glendening for sharing results of their calculations prior to publication. Funding for this work was provided by the National Science Foundation under Grant No. CHE-9530412 (P.B.A.) and by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (M.B.M., D.R.). Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Supporting Information Available: Figure A, kinetic energy dependent cross sections for CID of $M^+(15c5)$ ($M = Na, K, Rb,$ and Cs with Xe), Figure B, kinetic energy dependent cross sections for CID of $M^+(18c6)$ ($M = Na, K, Rb,$ and Cs with Xe), and Table A, vibrational frequencies and average internal energies at 298 K of 15c5, 18c6, $M^+(15c5)$, and $M^+(18c6)$ complexes for $M = Na, K, Rb,$ and Cs (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.