

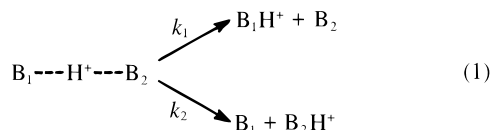
# JMS Letters

Dear Sir,

## Estimation of Heterolytic Bond Dissociation Energies by the Kinetic Method

We report the extension of the kinetic method<sup>1,2</sup> to the estimation of heterolytic bond dissociation energies (HBDEs) of inorganic salts, particularly alkali halides. These species often occur in the form of cluster ions  $[CAC]^+$  and  $[ACA]^-$  ( $C \equiv$  cation,  $A \equiv$  anion) in desorption ionization mass spectra.<sup>3–9</sup> Their structures, reactivities and energetics are all of fundamental interest. Studies of these as well as other metal cluster ions have been extensive.<sup>10–14</sup> This study was designed to test whether their dissociation could be used to measure heterolytic bond dissociation energies of inorganic salts by the kinetic method.

The kinetic method is a procedure for estimating thermochemical quantities based on the rates of competitive dissociations of mass-selected cluster ions.<sup>1,2</sup> It has been used to determine proton affinities as well as affinities towards other ions,<sup>2</sup> including metal ions.<sup>15–22</sup> The method is sensitive to small thermochemical differences (often below 1 kcal mol<sup>-1</sup>) and is applicable to polar and non-polar compounds.<sup>2</sup> In most cases, weakly bound cluster ions are generated, selected by mass/charge ratio and dissociated by collision. In the case of proton-bound dimer of two Brønsted bases  $B_1$  and  $B_2$ , two competitive reactions occur:

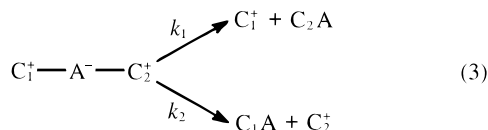


When appropriate conditions are met, the relative proton affinity (PA) of the bases can be determined from the product ion abundance ratio:<sup>2</sup>

$$\ln([B_1H^+]/[B_2H^+]) = \Delta PA / (RT_{\text{eff}}) \quad (2)$$

where  $[B_1H^+]$  and  $[B_2H^+]$  are the product ion abundances and  $T_{\text{eff}}$  is the effective temperature of the activated proton-bound dimers.

The kinetic method does not demand that the precursor ion take the form of a weakly bound cluster ion. As long as the necessary approximations can be satisfied, i.e. equal or zero reverse activation energies, only two competitive primary fragmentations and preferably the absence of secondary fragmentations,<sup>2</sup> the method can be employed. A number of studies have applied the kinetic method to the dissociation of strongly bound covalent ions.<sup>23–29</sup> It seems likely, therefore, that extension to strongly bonded ionic clusters might be possible. In the particular case of alkali halide cluster ions the mixed ionic cluster ions  $[C_1AC_2]^+$  and  $[A_1CA_2]^-$  can be generated readily and are well known from secondary ion mass spectrometry, among other ionization methods. It is expected from previous experiments<sup>3–9,11–13</sup> that cluster ions of this type will dissociate to yield individual alkali metal cations:



Theoretical treatments of the kinetic method<sup>2</sup> assume that dissociation can be described by statistical unimolecular

theory and they lead to the approximate general expression

$$\ln([fragment_1^+]/[fragment_2^+]) \approx [\Delta(\Delta E)] / (RT_{\text{eff}}) \quad (4)$$

where  $[fragment_1^+]$  and  $[fragment_2^+]$  are the abundances of the two monomeric fragments,  $\Delta(\Delta E)$  is the difference in critical energies of the two competing reactions and  $T_{\text{eff}}$  is the effective temperature of the activated parent dimeric ion. In the particular case shown in Eqn (3), the cluster ion has only three degrees of freedom. If, nevertheless, one applies the method, the rates of competitive dissociation of mixed ionic cluster ions to form individual alkali metal cations can be expressed in terms of the difference in heterolytic bond dissociation energies ( $\Delta HBDE$ ) of the two alkali halides:

$$\ln([C_1^+]/[C_2^+]) \approx [\Delta HBDE] / (RT_{\text{eff}}) \quad (5)$$

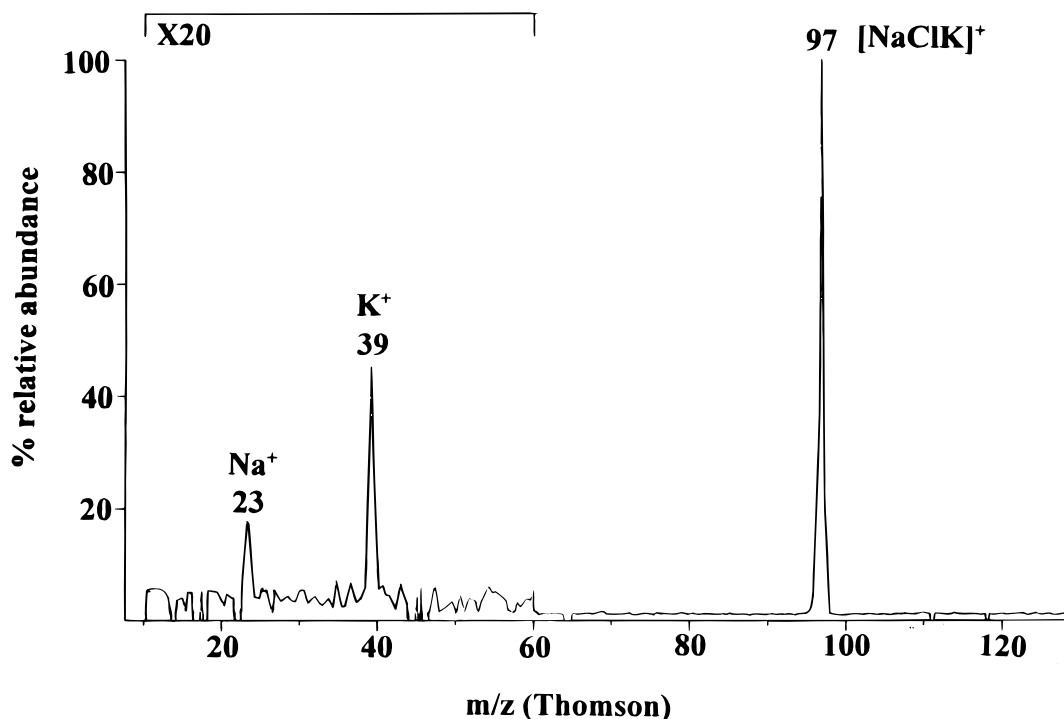
The heterolytic bond dissociation energies estimated by this method are relatively inaccessible quantities.

The approach used in this study is to generate mixed ionic dimeric cations of alkali chlorides by fast atom bombardment (FAB) ionization. The resulting ionic cluster ions are mass selected and fragment upon collisional activation under relatively vigorous (20 eV collision energy) single-collision conditions to yield the individual alkali metal cations. The ratio of the abundances of the two fragment ions is examined for a correlation with the difference in heterolytic bond dissociation energies expressed in Eqn (5).

Experiments were performed using a Finnigan TSQ-700 triple-quadrupole mass spectrometer (Finnigan MAT, San Jose, CA, USA). The manifold temperature and ion source temperature were kept at 40 and 70 °C respectively. The FAB gun (Ion Tech, Teddington, UK) was operated at 5 kV and 3 mA emission current to generate Ar fast atoms. The manifold pressure was  $6.0 \times 10^{-7}$  Torr. In pairwise fashion, inorganic salts (NaCl, KCl, RbCl and CsCl; Aldrich Chemical Co., Milwaukee, WI, USA) were mixed with glycerol and placed on the stainless steel probe tip and bombarded with argon atoms.

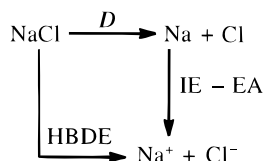
The mixed ionic cluster ions  $[C_1AC_2]^+$  generated in the ion source were mass selected using the first quadrupole mass analyzer. Collisional activation of the cluster ion was achieved in the second quadrupole at a nominal 20 eV collision energy and a nominal argon target gas pressure of 0.20 mTorr. The abundances of the fragment ions were then measured from the product ion mass spectra generated by scanning the third quadrupole. All peak ratios measured were recorded in triplicate and they displayed relative standard deviations of less than 15%. Each set of peak ratios was measured from an average of 50 or more scans.

Figure 1 shows a typical product ion mass spectrum of the mixed ionic cluster ion  $[NaClK]^+$ . The fragments at 23 and 39 Thomson correspond to sodium cation ( $Na^+$ ) and potassium cation ( $K^+$ ) respectively (Thomson = dalton/unit charge<sup>30</sup>). Note that previous studies on alkali halide cluster ions support a symmetrical  $[C_1AC_2]^+$  structure for such cluster ions.<sup>31</sup> The facts that these cluster ions do not fragment at low collision energies (2 eV) and that they fragment to give the individual alkali metal cations at higher collision energy (20 eV) are also consistent with the proposed ionically bound symmetrical structures. The ratio of the ion abundances seen in Fig. 1 indicates that NaCl has a higher heterolytic bond dissociation energy than KCl. There are no direct experimental values for heterolytic bond dissociation energies of these inorganic salts. However, one can utilize the following thermochemical cycle to calculate heterolytic bond dissociation energies using the known values of the homolytic bond dissociation energies ( $D$ ),<sup>32</sup> the ionization energies (IEs) of the



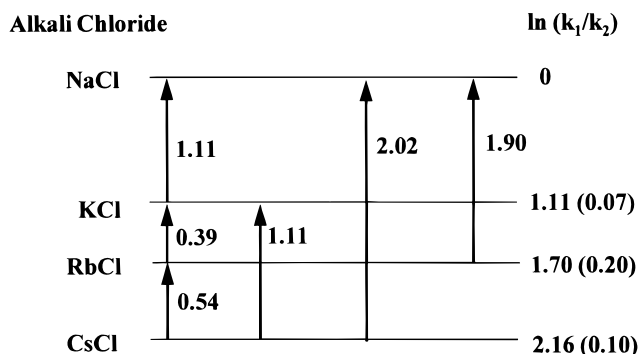
**Figure 1.** Product ion tandem mass spectrum of mass-selected mixed ionic cluster ion  $[\text{NaClK}]^+$ . Activation was achieved with 20 eV collisions using argon as target gas and a nominal pressure of 0.20 mTorr.

alkali metals and the electron affinities (EAs) of the halogen atoms:<sup>33</sup>



Hence  $\text{HBDE} = D + \text{IE} - \text{EA}$ . The calculated  $\text{HBDE}(\text{NaCl}) = 133.6 \pm 2 \text{ kcal mol}^{-1}$  and  $\text{HBDE}(\text{KCl}) = 120.2 \pm 2 \text{ kcal mol}^{-1}$ . The order of these values is in agreement with the experimental observations recorded in Fig. 1.

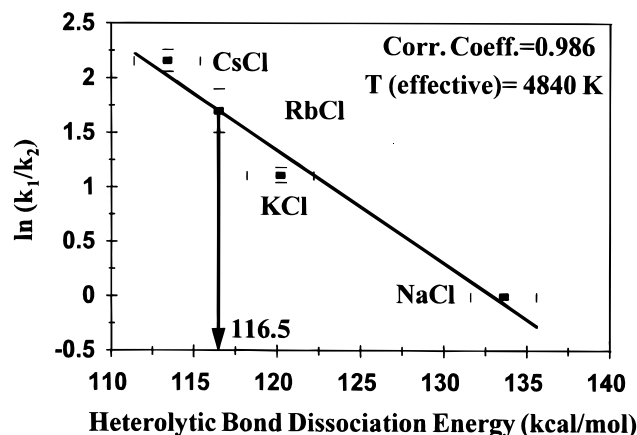
Figure 2 summarizes the results of six measurements of  $\ln(k_1/k_2)$  for cluster ions made up from NaCl, KCl, RbCl and CsCl. The stair-step method was used to cross-check the results by examining different pairs of inorganic salts. It can



**Figure 2.** Measured  $\ln(k_1/k_2)$  ratios from product ion abundances for dissociations of mixed ionic clusters of a group of inorganic salts. Data presented in the  $\ln(k_1/k_2)$  column are the average cumulative values expressed relative to  $\text{Na}^+$ . Data in parentheses are the estimated errors in the abundance ratio.

be seen that the set of data is internally consistent and the results suggest that the kinetic method might be useful for determining the relative values of heterolytic bond dissociation energies for these inorganic salts. The order of the heterolytic bond dissociation energy is  $\text{CsCl} < \text{RbCl} < \text{KCl} < \text{NaCl}$ . In order to obtain numerical values for heterolytic bond dissociation energies of inorganic salts, we utilized Eqn (5) to derive the effective temperature for mixed ionic cluster ions comprised of NaCl ( $\text{HBDE} = 133.6 \pm 2 \text{ kcal mol}^{-1}$ ), KCl ( $\text{HBDE} = 120.2 \pm 2 \text{ kcal mol}^{-1}$ ) and CsCl ( $\text{HBDE} = 113.4 \pm 2 \text{ kcal mol}^{-1}$ ). Note that all these heterolytic bond dissociation energies were obtained from the thermochemical cycle calculations and that the internal consistency of the data provides evidence that the use of a fixed laboratory energy yields acceptable results. A plot of  $\ln(k_1/k_2)$  vs. HBDE has a correlation coefficient of 0.986 and yields an average effective temperature of  $4840 \pm 800 \text{ K}$  (Fig. 3). If we assume that the effective temperatures of all the activated cluster ions are the same under similar ionization and activation conditions, then the heterolytic bond dissociation energy for RbCl can be estimated from the linear regression line shown in Fig. 3. The estimated HBDE value is  $116.5 \pm 3 \text{ kcal mol}^{-1}$ . The uncertainties in both the measured ion abundance ratios and the calculated values for the heterolytic bond dissociation energies of the reference compounds lead to a combined estimated uncertainty of about  $3 \text{ kcal mol}^{-1}$  for the HBDE. This value is within  $1.4 \text{ kcal mol}^{-1}$  of the calculated value using the same thermochemical cycle ( $115.1 \pm 2 \text{ kcal mol}^{-1}$ ), with which it agrees within error.

The effective temperature is a measure of the internal energy of the activated dimer ion.<sup>2</sup> The measured effective temperature (4840 K) is much higher than the values observed in collision-induced dissociation of weakly bound cluster ions, but similar to values found for covalently bound systems activated by collision-induced dissociation.<sup>2</sup> For example, Wenthold and Squires estimated  $\Delta H_{\text{acid}}$  of halogen-substituted aromatic compounds and found effective temperatures on the order of 4400 K.<sup>29</sup> Recently, both Lee and Beauchamp<sup>34</sup> and



**Figure 3.** Linear correlation between  $\ln(k_1/k_2)$  and heterolytic bond dissociation energies of inorganic salts. Vertical error bars represent experimental uncertainties; horizontal error bars are uncertainties in the literature thermochemical values used to arrive at the HBDEs.

Craig *et al.*<sup>35</sup> have shown that the effective temperature is a measure of the excess average number of quanta per degree of freedom in the activated cluster ion. The effective temperature increases with the total number of quanta and as the number of oscillators is decreased. In the present case the ionic cluster ions are activated at a relatively high collision energy (20 eV) and the system has a small number of oscillators (three degrees of freedom). Both factors contribute to the very high effective temperature.

There are a number of issues relating to the activation and dissociation of these ionic clusters which require further investigation. One is the applicability of statistical unimolecular reaction theory to such small clusters. Another is the large difference in frequencies of the dissociating bonds in the activated cluster ion. Yet another is the contribution of the initial internal energy of the cluster ion to its dissociation. This contribution is demonstrated by a plot of fragment ion abundance against collision energy for  $[\text{RbClK}]^+$  which shows a threshold of about 5 eV. The corresponding center-of-mass energy is just 1.25 eV, much less than the HBDE values of the constituent dimers which are both near 5 eV. Finally, the assumption that fixed lab collision energies give a fixed effective temperature is clearly an approximation. However, it is justified by the  $[\text{RbClK}]^+$  experiment just cited which showed the ratio  $[\text{Rb}^+]/[\text{K}^+]$  to change little in the range 20–60 eV (1.8–1.6), although it increased sharply at lower collision energy.

This study has demonstrated the applicability of the kinetic method to the estimation of heterolytic bond dissociation energies of inorganic salts. It is expected that the same methodology may be applied to other alkali halides as well as other ionic systems for estimation of heterolytic bond dissociation energies. Not only are heterolytic bond dissociation energies fundamental properties of the ionic bond, but salt bridges are of growing importance in the mass spectrometry of biological compounds.<sup>36,37</sup> Prior to this work, heterolytic bond dissociation energies were available directly only through studies of lattice energies of large assemblies of ions by study of neutral molecules or through thermochemical cycles of the type discussed above.

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Yours,

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