

# Collisional Heating of Bradykinin Ions in Quadrupole Ion Traps via Ion Acceleration and Bath Gas Temperature Variations

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The dissociation of gaseous ions formed from biomolecules is becoming increasingly important in their structural determination. A variety of methods have been used to dissociate bioions such as single and multiple ion-neutral collisions, ion-surface collisions, and UV and IR photodissociation. Although all have proven useful in providing structural information to some degree, the internal energy distribution of such activated ions often is not well characterized. However, for situations in which the rates of ion activation and deactivation are large relative to unimolecular dissociation, the parent ion internal energy can approach a near Boltzmann distribution. Given such conditions, referred to as rapid energy exchange (REX), reasonably accurate Arrhenius activation parameters can be derived from dissociation rates obtained as a function of parent ion temperature. For large ions having many degrees of freedom, it is possible to establish REX conditions for thermal dissociation in the relatively high pressure environment of quadrupole ion traps and to determine their Arrhenius parameters<sup>1</sup>.

Although ion mobility studies in drift tubes have traditionally been used to obtain ion collision cross-section information via equation 1,

$$\Omega = \frac{3zeE}{16N_{\text{He}}} \sqrt{\frac{\pi}{\mu kT_{\text{eff}}}} \frac{1}{v_E} \quad (1)$$

where  $\Omega$  is the hard-sphere collision cross-section and  $v_E$  is the ion drift velocity, such data also can be obtained from ion trap collision-induced dissociation (CID) despite the fact that ion velocity is not directly measured in such experiments. Using the Arrhenius parameters obtained from thermal dissociation kinetics, effective temperature ( $T_{\text{eff}}$ ) information for corresponding resonance excitation CID experiments can be calculated. Equation 2 can then be used to determine ion velocity,

$$T_{\text{eff}} = T_{\text{He}} + \frac{m_{\text{He}}}{3k} v_E^2 \quad (2)$$

from which collision cross-section information is derived via equation 1.

Figure 1 shows collision cross-section information for dissociating bradykinin ions obtained from ion trap CID kinetics. For each charge state, rate data at fixed excitation voltage were collected over a series of He buffer gas temperatures, and cross-sections subsequently obtained as described above. Table 2 compares cross-section data obtained via CID kinetics with similar data from ion mobility spectrometry. These results suggest that information on the size of activated ions can be extracted from ion trap CID kinetics data.

(1) K.G. Asano; D.E. Goeringer; S.A. McLuckey *Int. J. Mass Spectrom.* 185/186/187, 207 (1999).

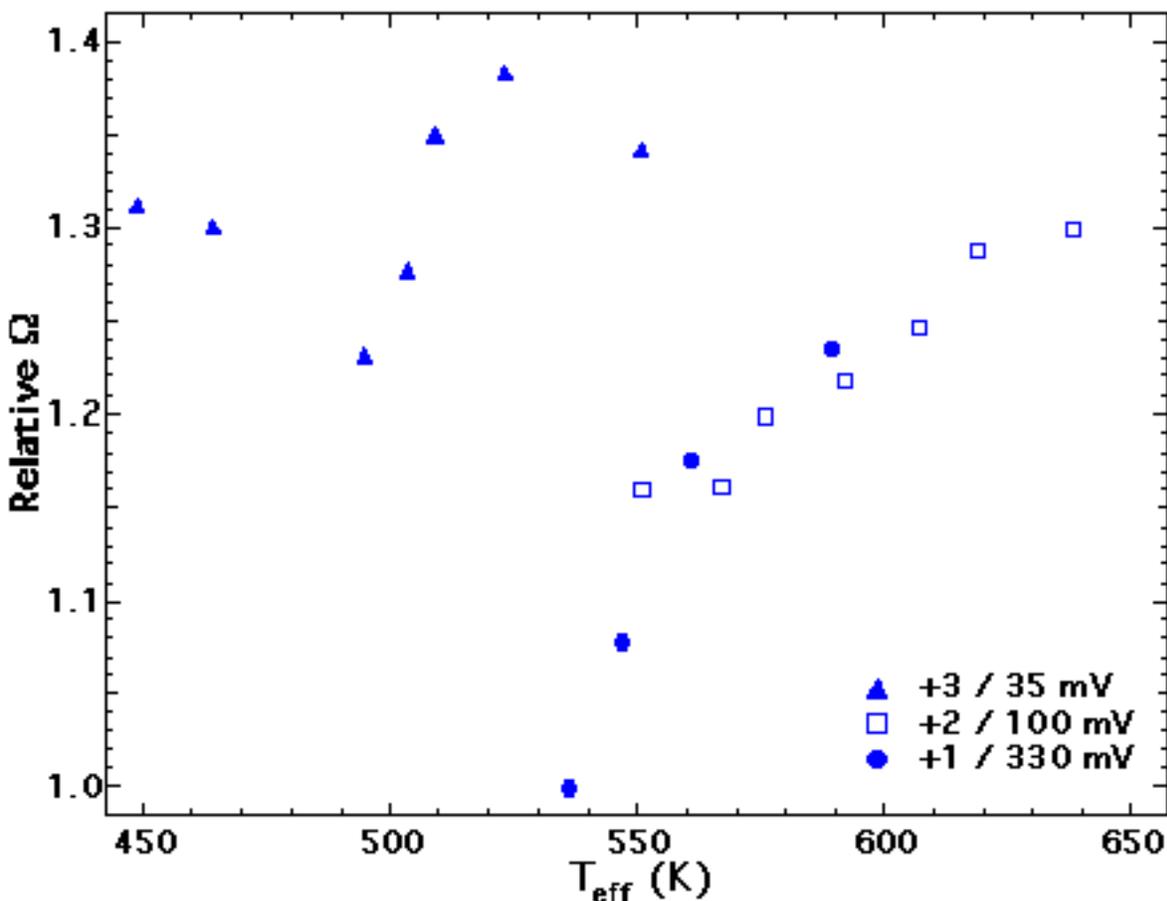


Figure 1 - Relative bradykinin ion collision cross-sections vs effective temperature obtained from quadrupole ion trap dissociation kinetics

Table 1: Gas-phase bradykinin ion collision cross-section data

BK Ion	Ion Mobility <sup>a</sup>			Ion Mobility <sup>b</sup>			Ion Trap <sup>c</sup>		
	T (°C)	(Å <sup>2</sup> )	rel.	T (°C)	(Å <sup>2</sup> )	rel.	T (°C)	(Å <sup>2</sup> )	rel.
(M+H) <sup>+</sup>	25	239	1	250	292	1	274	355	1
(M+2H) <sup>2+</sup>	25	240	1.00	250	319	1.09	278	382	1.08
(M+3H) <sup>3+</sup>	25	284	1.19	250	411	1.41	278	442	1.25

<sup>a</sup> Counterman, Valentine, Srebalus, Henderson, Hoaglund, Clemmer; *J. Amer. Soc. Mass Spectrom.* **9**, 743-759 (1998).

<sup>b</sup> Wu, Klasmeier, Hill; *Rapid Commun. Mass Spectrom.* **13**, 1138-1142 (1999).

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