Appearance Potentials of Metastable and Normal Ions and the Kinetic Shift

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Summary Within experimental error, we could find no differences in the appearance potentials of corresponding metastable and normal ions in mass spectrometric decompositions of benzonitrile, benzene, and aniline and hence no evidence for any measurable kinetic shift.

IT has been suggested that a partial measure of the kinetic shift, the excess of energy required for mass spectrometric fragmentation to be observed, can be obtained from the difference between the appearance potentials of metastable and normal fragment ions.[1] Whilst we appreciate the reasons for this proposal, we have been surprised by some of the large reported differences in appearance potentials. We have discussed[2] the use of the semi-log plot method for measuring these appearance potentials and have suggested that the IE/EDD method gives more accurate and reproducible results.[3] The IE/EDD technique is a computer-assisted method for acquisition of ionization efficiency data with mathematical smoothing and analysis of the resulting curves. Recently, Occolowitz has reported that a critical slope method gave no difference in the appearance potentials of normal and metastable ions for a number of fragmentations.[4] It is interesting that we have been able to show how the EDD method is essentially also a critical slope method.[5] We have now measured appearance potentials for metastable and normal ions for a number of fragmentations using the IE/EDD approach to compare with the values found by other workers using the semi-log plot method. With the IE/EDD technique we did not find any significant differences in appearance potentials, unlike the large differences found by the semi-log method.

Ottinger, using the semi-log method, has shown[6] that the appearance potential for the normal C_6H_4 ion in fragmentation (1, Table) is 1·3 eV greater than that of the metastable C_6H_4 ion. In ion cyclotron resonance work, it was shown that the appearance potential for the normal C_6H_4 ion was the same as Ottinger found for the metastable ion.[7] With the IE/EDD method we find that, within experimental error, there is no difference in the appearance potentials of metastable and normal C_6H_4 ions. It is probable that the higher values found previously by others for the appearance potentials of normal fragment ions were due to systematic errors (for example, insensitivity of the semi-log method at the 1% level), coupled with the difficulty of separating signal from noise near the foot of an ionization efficiency curve. The results of Hickling and Jennings[1] and Brown[8] agree well with each other and suggest reasonable reproducibility in the semi-log method. Our appearance potential measurements by the IE/EDD method are in good agreement with the appearance potential determined by ion cyclotron resonance spectroscopy of longer-lived ions.[7] Other processes for which appearance potentials were determined by the IE/EDD method are shown

Appearance potentials of fragment ions (eV)

	Normal[a]	Metastable[b]	Difference	Method[c]	Ref.
(1)	$C_6H_5CN^{+\cdot} \longrightarrow HCN + C_6H_4^{+\cdot}$				
	15·2	13·9	1·3	S.L.	6
			0·7	S.L.	1
	15·2	14·44	0·66	S.L.	8
	13·80 (± 0·06)	13·9 (± 0·2)	<0·2	IE/EDD	This work
	13·92			I.C.R.	7
(2)	$C_6H_6^{+\cdot} \longrightarrow H\cdot + C_6H_5^+$				
	13·8			P.I.	12
			0·28	S.L.	9
	13·97(±0·06)	13·95(±0·1)	<0·2	IE/EDD	This work
	14·44(±0·05)			S.L.	10
(3)	$C_6H_6^{+\cdot} \longrightarrow H_2 + C_6H_4^{+\cdot}$				
	14·04(±0·06)	13·95(±0·1)	<0·2	IE/EDD	This work
	14·09(±0·07)			S.L.	10
(4)	$C_6H_5NH_2^{+\cdot} \longrightarrow HCN + C_5H_6^+$				
	12·45	12·05	0·40	S.L.	8
	12·13(±0·06)	12·2(±0·1)	<0·2	IE/EDD	This work
	12·3(±0·1)			P.I.	11

[a] Lifetime $\leqslant 1$ μs. [b] Lifetime $\simeq 10$ μs. [c] S.L. = semi-log; EDD (see ref. 3); I.C.R. = ion cyclotron resonance with S.L.; P.I. = photoionisation.

in the Table. In no case is there a significant difference between the appearance potentials of normal and metastable ions.

As the maximum lifetime of a normal fragment ion (*ca.* 1 μs) is similar to that of a metastable ion, one might not expect that a sensitive, accurate measurement of appearance potentials of metastable and normal ions should differ by more than 0·2 eV. Our results suggest that the measurable kinetic shift for normal ions of lifetime 1 μs may be quite small. If this conclusion could be extrapolated to mean there was little total kinetic shift for slowly decomposing ions, it would greatly increase the prospect of using thermochemical calculations to deduce information about structures and energies of ions from mass spectrometric reactions. We feel this sort of extrapolation should be viewed cautiously at the moment since all that has been demonstrated by this work is that a measure of kinetic shift does not appear feasible from measurements on the appearance potentials of normal and metastable ions.

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