The Internal Energy Distribution in Fast Atom Bombardment/Liquid Secondary Ion Mass Spectra

Dudley H. Williams* and Stephen Naylor

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

An alternative analysis of previously published data is used to show that the internal energy distribution in a liquid secondary ion mass spectrum extends over a few electron volts (*ca.* 0—4 eV).

The advent of liquid matrix fast atom bombardment (f.a.b.)[1] and liquid matrix secondary ion mass spectrometry (s.i.m.s.) has revolutionised our ability to obtain the mass spectra of large and polar molecules. In a recent paper[2] we have used rather indirect arguments to deduce that the internal energy distribution of ions after they have left a typical f.a.b. matrix (*e.g.* glycerol) lies in the range 0—3 eV. In developing our arguments, we assumed, with supporting evidence, that after atom impact into the matrix, analyte and matrix molecules which are initially strongly excited make multiple collisions which serve to spread the collision energy over many molecules. The number of such collisions may not be sufficient to establish a Maxwell–Boltzmann distribution, but appears to be sufficient to equilibrate at least partially an energy in the range 0—3 eV between translational and vibrational modes.

If the foregoing assumptions are correct, then an approximate internal energy distribution should be derivable experimentally by examining the fraction of MH^+ ions which undergo a series of fragmentation reactions of known activation energy.[3] Suppose the internal energy distribution were assumed to correspond to the curve shown in Figure 1, where the probability of an ion possessing an internal energy E is $P(E)$ (plotted vertically) and the internal energy E, extending from 0 to x eV (1 eV = 96.5 kJ mol^{-1}), is plotted horizontally. Thus, a fragmentation reaction possessing an activation energy (E_a) of $x/2$ eV would give similar abundances of MH^+ and the fragment ion; and one possessing an activation energy $x/4$ eV would give a [fragment]/[MH^+] ratio of *ca.* 7 : 1.

De Pauw *et al.*[3] have approached the problem of the internal energy distribution in liquid s.i.m.s. by the use of [fragment]/[MH^+] ratios for a series of benzylpyridinium (**1**) salts substituted on the phenyl ring. They assumed that the fraction of non-decomposing ions is essentially determined by changes in the ionisation potentials of compounds (**1**) as R is varied. Although this is a good approximation in some instances,[4] it may not be the case for the observed liquid s.i.m.s. fragmentation of (**1**) to (**2**), in particular where *para*-substitutents R can strongly stabilise or destabilise the substituted benzyl cation (**2**). Although we did not anticipate that a more rigorous treatment of the data would change fundamentally the conclusion of de Pauw *et al.*[3] that the internal energy distribution has a half-width of *ca.* 1.3 eV, we now report our approach which recognises that the abundance ratio [(**2**)]/{[(**1**)] + [(**2**)]} is essentially determined by the activation energy for (**1**) → (**2**).

If the activation energy for (**1**) → (**2**) is x when R = H and y when R is a specific substituent, then equations (1)—(3) apply. These equations assume that the reactions (**1**) → (**2**) occur without reverse activation energy. This should be a good approximation since the forward reaction is a single bond cleavage, and additionally we note that in the reverse reaction it is a reasonable expectation that as a nitrogen lone pair of pyridine approaches a carbocation, the developing interaction should be continuously bonding.

$$\Delta H_f(\mathbf{1};\ \mathrm{R} = \mathrm{H}) + x = \Delta H_f(\mathbf{2};\ \mathrm{R} = \mathrm{H}) + \Delta H_f(\text{pyridine}) \tag{1}$$

$$\Delta H_f(\mathbf{1};\ \mathrm{R} \neq \mathrm{H}) + y = \Delta H_f(\mathbf{2};\ \mathrm{R} \neq \mathrm{H}) + \Delta H_f(\text{pyridine}) \tag{2}$$

$$\therefore\ y - x = [\Delta H_f(\mathbf{2};\ \mathrm{R} \neq \mathrm{H}) - \Delta H_f(\mathbf{2},\ \mathrm{R} = \mathrm{H})] - [\Delta H_f(\mathbf{1};\ \mathrm{R} \neq \mathrm{H}) - \Delta H_f(\mathbf{1};\ \mathrm{R} = \mathrm{H})] \tag{3}$$

Thus, the change in activation energy caused by the introduction of the substituent is given by the change in heat of formation of the fragment ions minus the change in heat of formation of the reactants. The change in the heats of

Table 1. Changes in activation energies and abundance ratios.

R	($y - x$)/kJ mol^{-1} [a]	Ratio [(**2**)]/{[(**1**)] + [(**2**)]} Obs.	Calc.[b]
p-CN	80	0.19	0.1(5)
m-CN	100	0.24	0.1
p-Cl	40	0.43	0.3
(H)	0	0.50	0.5
p-Me	−5	0.44	0.5(5)
m-OMe	30	0.44	0.3(5)
p-OMe	−55	0.70	0.8

[a] Values rounded to nearest 5 kJ mol^{-1}. [b] On the basis of the internal energy distribution shown in Figure 1, and an activation energy for (**1**) → (**2**) of 150 kJ mol^{-1} when R = H.

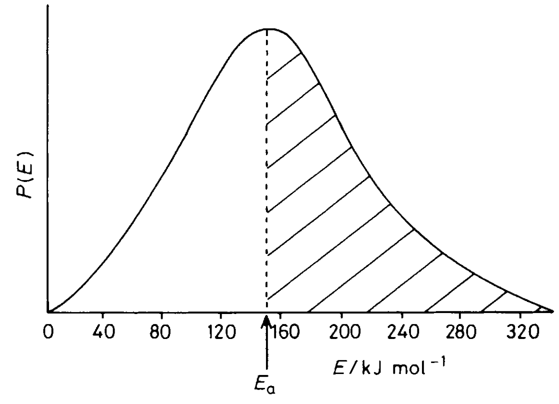
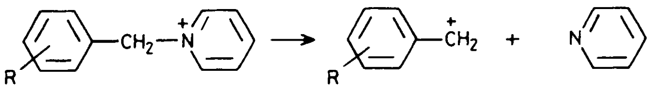


Figure 1. Energy distribution used to fit the experimental data of de Pauw *et al.*[3] for the conversion (**1**) → (**2**) induced by desorption with a Cs$^+$ primary beam from a glycerol matrix.



(**1**) (**2**)

formation of benzyl ions upon substitution is known in many cases with relatively good precision from the measurement of the ionisation potentials of substituted benzyl radicals.[5] The changes in heats of formation of (**1**) as R is varied are not known. However, since the structural variation in (**1**) is simply the substitution of a benzene ring which is well isolated from the charge, these changes can be well approximated simply by using the difference $\Delta H_f(RC_6H_5) - \Delta H_f(C_6H_6)$.[6] The resulting data, and the ion abundance ratios $[(\mathbf{2})]\{[(\mathbf{1})] + [(\mathbf{2})]\}$ reported by de Pauw,[3] are given in Table 1.

The significance of the values $y - x$ is that if the vertical line drawn from E_a (for R = H) in Figure 1 is moved along the horizontal energy scale by this value, then the width and shape of the energy distribution has to be such that the change in area of the shaded portion of the energy distribution (which leads to product ions) relative to the whole area under the curve is in reasonable accord with the ratios given in column 3 of Table 1. We find that the experimental data can be accommodated satisfactorily (see Table 1, column 4) if the energy distribution shown in Figure 1 extends over *ca.* 340 kJ mol^{-1} (0—3.5 eV), and if E_a for the dissociation (**1**) → (**2**) is *ca.* 150 kJ mol^{-1} when R = H (which seems a physically reasonable value). This conclusion is essentially the same as that derived by de Pauw *et al.*[3] in their elegantly conceived experiments, but we believe that our analysis gives additional physical insight.

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