Variation of Relative Ion Intensities with Accelerating Potential in Mass Spectrometers

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EXPERIMENTAL data and theoretical arguments have recently been advanced which suggest that the recorded intensities of mass-spectral peaks do not accurately reflect true ion-concentrations in the spectrometer source.[1] The experimental data were large variations in relative ion-intensities (with resulting variation in Z values[2]) when the ion accelerating-potential was varied under conditions of low ionizing voltage. We have approximately reproduced these results at constant meter readings (between 16 and 18 v) on both an AEI MS902 instrument and a Hitachi RMU6E instrument. In the most striking case,[1] that of pyridine, the 52 : 79 ratio was decreased by a factor of two when the accelerating potential of the RMU6E was quadrupled under conditions similar to those of the previous study.[1] Using the MS902, the ratio varied by a factor of less than two in the same direction. The exact factor is undoubtedly a function of the ionizing potential chosen, since the original report quoted a factor of five for an MS9 instrument.

In the same experiments, however, the intensity of the ^{84}Kr peak measured at low ionizing voltage (constant meter reading) was found to vary in comparison to the intensity at 70 or 75 ev, depending on whether the experiment was carried out at low or high accelerating potentials. The fractional intensities of rare-gas ions have been used in several well-established methods for the determination of ionization potentials, which give these data on different instruments with a reproducibility of $\pm 0{\cdot}1$ ev.[3,4] We have found that the slope of the relative ionization-efficiency curve is invariant with accelerating potential in the linear portion of the curve; but the intercept of the linear portion on the (meter reading) energy axis is a function of the accelerating potential. This variation of the mean energy of the ionizing electrons with accelerating potential, not detectable by the meter reading for the potential of the filament with respect to the ion block, may be understood if one considers penetration of the source by the field of the accelerator.[5] The magnitude of this penetration will depend on the value of the accelerating potential;† on our MS902 a change of 6000 v in the accelerating potential changed the mean value of the ionizing beam by

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† Even the sign of the perturbation induced in the energy of the ionizing electrons should be a function of the geometry of the source.

Variation in intensity ratios (Z) *and log* (Z/Z_0) *values for* m/e 105 *in substituted benzophenones at* 75 ev

Y	Z, V_{acc} 540 v	Z, V_{acc} 1070 v	Z, V_{acc} 2150 v
H ($Z/2$)	1·20	1·30	1·35
p-CH$_3$O	0·40	0·46	0·48
m-NO$_2$	3·5	3·9	3·9
p-Br	1·7	1·9	1·9
	log (Z/Z_0), 540 v	log (Z/Z_0), 1070 v	log (Z/Z_0), 2150 v
H	0·00	0·00	0·00
p-CH$_3$O	−0·48	−0·45	−0·45
m-NO$_2$	+0·47	+0·48	+0·46
p-Br	+0·17	+0·16	+0·18

about 3 v, since the meter reading required to produce a 31% fractional intensity of ^{84}Kr relative to its 70 v value varied from 14 v at 8000 v to 17 v at 2000 v. This small (0·05%) penetration of the source would nevertheless have a large effect on relative ion intensities when the ionizing voltage is close to the appearance potential of the daughter ion. We have commented before on the necessity of including an internal standard for low-voltage intensity measurements,[6,7] though the importance of field penetration when comparing data obtained at different accelerating potentials had not been considered.

By correcting for penetration by the accelerating potential field by taking values at constant fractional intensities of the ^{84}Kr peak, new values for the magnitude of the variation of the relative ion intensities at different accelerating voltages have been determined. At a fractional ^{84}Kr intensity of 24% in the RMU6E instrument, the 52 : 79 ratio of pyridine varied from 0·24 at V_{acc} 540 v to 0·27 at V_{acc} 2150 v; at 31% in the MS902, it varied from 0·33 at V_{acc} 2000 v to 0·31 at V_{acc} 8000 v. The values on each instrument were nearly invariant within our ability to reproduce the voltage settings and the reproducibility of the recording system, for this most sensitive of test cases.

The observation that the dependence on accelerating potential is small is not therefore consonant with Howe and Williams' equation relating the intensity ratio to lifetime in the source t_1 and time before arriving at the detector t_2.[1] If the rate constant K_A were uniform during the time interval under consideration then there would be in fact a very strong dependence of $[A]/[M]$ on the residence time of the ions in the analyser. But as was pointed out by these authors, K_A is not constant but decreases rapidly as t increases. (K_A will change from at least 10^8 sec.$^{-1}$ to 10^7 sec.$^{-1}$ in going from $0 \rightarrow t_1$ to $t_1 \rightarrow t_2$, where t_1 and t_2 are each of the order of magnitude of 10^{-6} sec.) Thus the expression for the number of daughter ions observed at the collector should be written as $M_0\exp(-K_At_1 - K'_At_2)$, where K_A and K_A are ths mean values of the rate constants for the intervale $0 \rightarrow t_1$ and $t_1 \rightarrow t_2$ respectively. Since $(K'_A/K_A) < 10^{-2}$, the expression reduces very nearly to $M_0\exp(-K_At_1)$, which was our original assumption.[2] Our results show that doubling of the length of the interval $t_1 \rightarrow t_2$ changes the ratio only very slightly, as this model predicts. In addition, it is common knowledge that metastable-ion intensities, another measure of ions decomposing in perhaps 20% of the $t_1 \rightarrow t_2$ interval, are very small relative to normal mass-spectrometric peaks.

We[7,8] have followed the lead of many others[9] in noting that the rates of mass-spectral reactions have different statistical mechanical origins from reactions at thermal equilibrium. Mass-spectral k values which might be calculated by our original treatment[2] cannot be compared with ordinary rate constants; but they can be compared with other mass-spectral k values, as in the log Z/Z_0 relationships.[2] A relative k value is a weighted mean of a distribution of individual rate constants, and the entire distribution must be taken into account in determining the value whether the ion decomposes in the allotted time span or not. Only the true precursors should be enumerated.[8] Activation energies affected by molecular characteristics will still be reflected in the relative k values obtained; but the statistics will differ, and so the ρ values for mass-spectral reactions cannot be compared with solution ρ values, or be considered absolute values, as Howe and Williams point out.

They can, however, be compared with other mass-spectral ρ values. Since experimental evidence indicates only a small effect for accelerating potential on Z values and since the earlier theory[1] can be improved to predict this observation, the manipulations of the kinetic approach[2]—taking logarithms of ratios of Z values which fluctuate slightly in the same direction with V_{acc}—should almost completely obscure the accelerating-potential effect. To demonstrate this point, several of the benzophenones used in the original study[2] were also studied at 75 v on the RMU6E instrument.

Results for the $105/M$ ratio in compounds spanning a σ range of one log unit are given in the Table. A maximum variation of 15% in Z values was obtained. The direction of the variation was opposite to that predicted by the model,[1] but this merely indicates that the model is oversimplified at higher ionizing voltages. Since all the Z values varied in the same direction, the log (Z/Z_0) values were almost the same at every accelerating potential, and showed no trend in their deviations. The slope of the correlation line, therefore, is independent of accelerating potential, within the small error calculated in the original experiment.

To summarize: the effect of accelerating potential on ion-intensity ratios is, in fact, quite small; (theory actually predicts this) and the use of log (Z/Z_0) instead of Z diminishes whatever effect there may be to within reproducibility of data at a given V_{acc}. Our original assumption—that ion intensities are proportional to concentrations of species within the source—can still be used as a good approximation for the calculations employed in studies in conventional mass spectrometers.‡ Howe and Williams' theory ought to predict results for a different time scale. Perhaps, if analysis within 10^{-9} to 10^{-10} sec. could be obtained, k_A in the range $t_1 \rightarrow t_2$ would be sufficiently similar to k_A in the range $0 \rightarrow t_1$ so that strong dependence of Z values on accelerating potential would be observed; the present commercial instruments have too long a t_1.

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‡ We have noticed, incidentally, that on several double-focussing commercial instruments, relative ion-intensities vary greatly from one end of a spectrum to another, depending, for example, on the final lens potentials after maximizing ion, current factors which might be expected to affect mass discrimination.

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