# Variation of Relative Ion Abundances with Accelerator Potential in the Mass Spectrometer

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VALID kinetic studies on the unimolecular decomposition of a gaseous organic ion in the mass spectrometer require a quantitative correlation between the relative concentrations of parent and fragment ions reaching the collector and the rate constant for fragmentation. The steady-state approximation ventured by Bursey and McLafferty[1] has been recently used to explain a number of substitution effects.[2] The derived correlation requires that "the recorded intensities are proportional to the concentrations of ions in the source".[1]

The steady-state treatment has been applied only to ions in the source, so an important factor in determining the relative abundances of ions at the collector is the time, $t_2$, for flight of a molecular ion from the exit slit of the ion chamber to the collector in relation to the time, $t_1$, spent in the ion chamber. The time $t_1$ is difficult to evaluate, but for most mass spectrometers lies in the range 1—5 $\mu$sec.[3] In the AEI MS9 mass spectrometer, for an ion of mass 100, $t_2$ is 15 $\mu$sec. when operating at the normal accelerating voltage of 8 kv. These time periods can be used, along with the fundamentally correct unimolecular decay kinetics of the molecular ion to show that the relative abundances of parent and fragment ions reaching the collector are a function of $t_2$.

The simplest case of unimolecular decomposition is that of a molecular ion, $M^+$, decaying to a daughter ion, $A^+$, with rate constant $k_A$, where $M^+$ has only this one decay pathway and $A^+$ is not fragmenting to any appreciable extent. If a number, $M_0^+$, of molecular ions are produced in the source at time $t = 0$, after a further time $t$ these ions will have been removed together (due to influence of the various fields) to some other point along the flight pathway. Due to unimolecular decay, the number of molecular ions remaining at this point will be $M_0^+.\exp(-k_At)$ (neglecting possible radiative transitions and loss of $M^+$ by instrumental parameters) and the number of ions $M^+$ reaching the collector will be $M_0^+.\exp(-k_A[t_1 + t_2])$. Since daughter ions $A^+$ will be recorded only if they are produced in the ion chamber, the number of ions $A^+$ (derived from the original molecular ions $M_0^+$) which reach the collector will be independent of $t_2$ and is given by $M_0^+.[1 - \exp(-k_At_1)]$ (again neglecting radiative transitions and instrumental losses). This exponential variation of $[M^+]$ and $[A^+]$ with rate constant has been previously recognised.[3,4] Therefore, the relative abundance $[A^+]/[M^+]$ is given by:

$$\frac{[A^+]}{[M^+]} = \frac{1 - \exp(-k_At_1)}{\exp(-k_A[t_1 + t_2])}$$

Thus, for any given decomposition of this type an increase in $t_2$ will lead to an increase in $[A^+]/[M^+]$. This may be readily understood on a qualitative basis without consideration of precise unimolecular decay kinetics, since the longer $M^+$ has to decompose, the smaller the amount surviving at the collector.

We have used an AEI MS9 mass spectrometer to investigate the variation of $[A^+]/[M^+]$ with $t_2$, by altering the accelerator potential $V$ (for an ion of given mass, $t_2 \propto 1/\sqrt{V}$). Changing $V$ from 8 to 2 kv will thus alter $t_2$ for an ion of mass 100 from 15 $\mu$sec. to 30 $\mu$sec. Compounds were chosen which, at low electron-beam energies, give largely two ions in the mass spectrum. The results are summarised in the Table.

TABLE

*Variation of* [A+]/M+] *with accelerator potential for some compounds at low* ev[a]

| Parent molecule | Fragment ion ($A^+$) | Neutral fragment | $[A^+]/[M^+]$ 8 | 6 | 4 | 2 kv |
|---|---|---|---|---|---|---|
| Pyridine | $C_4H_4^+$ | HCN | 0·076 | 0·086 | 0·185 | 0·39 |
| Bromobenzene | $C_6H_5^+$ | Br | 0·062 | 0·090 | 0·22 | 0·25 |
| Benzyl bromide | $C_7H_7^+$ | Br | 5·3 | 5·7 | 7·0 | 7·3 |
| Benzyl chloride | $C_7H_7^+$ | Cl | 0·70 | 0·87 | 0·91 | 0·98 |
| *p*-Bromotoluene | $C_7H_7^+$ | Br | 0·13 | 0·15 | 0·17 | 0·18 |
| Iodobenzene | $C_6H_5^+$ | I | 0·07 | 0·10 | 0·13 | 0·15 |
| n-Butyl bromide | $C_4H_9^+$ | Br | 8·7 | 8·9 | 9·4 | 10·7 |
| Acetone | $C_2H_3O^+$ | $CH_3$ | 0·34 | 0·36 | 0·42 | 0·60 |

[a] The electron-beam energy (16—18 ev) and source temperature (~200°) were not necessarily exactly the same for different compounds, but remained the same within each run of accelerating voltages; the kv values are nominal only.

Qualitatively, the results support the reasoning previously discussed; the $[A^+]/[M^+]$ values increase without exception with decreasing accelerating voltage. The shortcomings of a steady-state approach[1] are thus borne out. In changing from 8 to 2 kv, the $[A^+]/[M^+]$ ratio varies by a factor of 1·2 for n-butyl bromide through to a factor of 5 for pyridine.

However, the derived equation for $[A^+]/[M^+]$ is nothing more than a useful expedient. A complication arises because there is an energy distribution in the molecular ion and hence a range of rate constants.[5] Since ions of higher internal energy decompose faster, there will be a shift to lower mean energy, and hence to lower rate of decay, as time of flight through the spectrometer increases. The basic rate equation, $-\mathrm{d}[M^+]/\mathrm{d}t = k_A[M^+]$, is thus complicated by the fact that $k_A$ is a function of $t$. Quantitative interpretations of $[A^+]/[M^+]$ will thus require a knowledge of energy and rate constant distributions within the molecular ion.†

The results presented here must cast doubt on the validity of absolute $\rho$ values calculated in using the steady-state approach to evaluate substituent effects.[1,2] The basic assumption[1] that the recorded intensities are proportional to the concentrations of ions in the source does not hold. More work will be necessary to evaluate the magnitude of the error involved for a wide variety of compounds, but clearly the ratio $Z/Z_0$[1] is a function of the accelerating voltage. Since the extent of decay of the molecular ion between $t_1$ and $t_2$ will vary with $k$ and the distribution of $k$-states,[5] the error involved in the steady-state approach will vary with $k$ and the distribution of $k$-states, and will be different from one substituent to another when there is a substituent effect on these parameters.

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† There is evidence of this complication from the data in the Table. If the fastest reactions were naïvely regarded as those giving the largest $[A^+]/[M^+]$ ratios, then one would expect the greatest change in $[A^+]/[M^+]$ ratios with accelerator potential for such reactions. The data in the Table show that this conclusion is incorrect. The detailed significance of the data will be the subject of a subsequent paper.

[1] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 529.

[2] (a) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 4484; (b) M. M. Bursey and F. W. McLafferty, *ibid.*, 1967, **89**, 1; (c) P. Brown and C. Djerassi, *ibid.*, p. 2711.

[3] W. A. Chupka, *J. Chem. Phys.*, 1959, **30**, 191.

[4] B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, 1961, **34**, 189.

[5] See, for example, J. Hertel and Ch. Ottinger, *Z. Naturforsch.*, 1967, **22a**, 40.