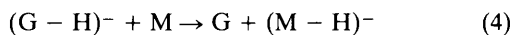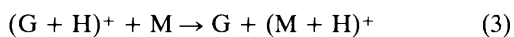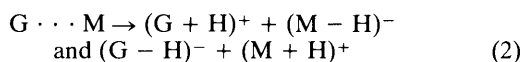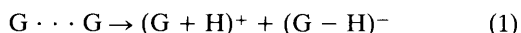# Fast Atom Bombardment (F.A.B.) Mass Spectrometry; Mechanism of Ionisation

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Unusual ions formed by ionisation, electron capture, and hydrogen radical abstraction in the fast atom bombardment mass spectra of some simple molecules (M) indicate these processes may also account for the commonly observed $(M + H)^+$ and $(M - H)^-$ ions.

According to the previously proposed models for fast atom bombardment (F.A.B.) ionisation[1] neutral molecules (M) are ionised by protonation or proton abstraction as shown in equations (1)—(4) (G = glycerol).

$$G \cdots G \rightarrow (G + H)^+ + (G - H)^- \qquad (1)$$

$$G \cdots M \rightarrow (G + H)^+ + (M - H)^-$$
$$\text{and } (G - H)^- + (M + H)^+ \qquad (2)$$

$$(G + H)^+ + M \rightarrow G + (M + H)^+ \qquad (3)$$

$$(G - H)^- + M \rightarrow G + (M - H)^- \qquad (4)$$

Preionised compounds such as salts, strong acids, or bases are dissociated into ion species carrying a net unit charge [equation (5)].

$$M^+ X^- \rightarrow M^+ + X^-$$

$$\text{and } (M^+)_2 X^- + X^-$$

$$\text{and } M^+ + M^+(X^-)_2 \qquad (5)$$
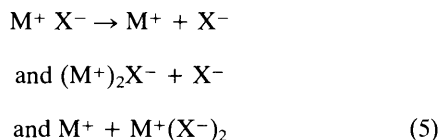
Methyl viologen $[PQ^{2+}(Cl^-)_2$ PQ = paraquat] was therefore expected to give $PQ^{2+}Cl^-$ as the major species in the positive ion spectrum unless dequaternisation to give the N-methylbipyridinium ion occurred. However, the major positive ion[2] is the radical cation $PQ^{\cdot+}$ and both $PQ^{2+}Cl^-$ and N-methylbipyridinium are found in only low abundance. The negative ion spectrum is dominated by Cl^- and $(G + Cl^-)$ but $PQ^{2+}(Cl^-)_3$ and $PQ^{\cdot+}(Cl^-)_2$ are also present. The positive and negative spectra therefore suggest that electrons are involved in F.A.B. ionisation (the solution after bombardment also shows the characteristic deep violet colour of the paraquat radical cation). Further evidence came when (1) gave only radical anions $M^{\cdot-}$ and showed no $(M - H)^-$


(1)

(2)
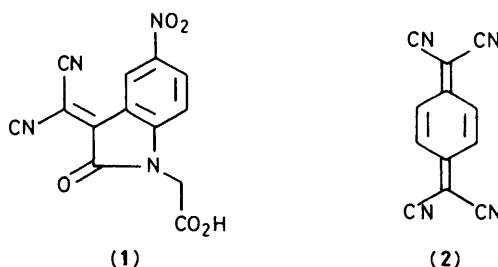
anions. The likeliest explanation was that the $(CN)_2C=$ substituent was acting as an electron capturing group and we therefore obtained the spectrum of tetracyanoquinodimethane (2). Not only did this show the now expected $M^{\cdot-}$ ions, confirming that electrons are involved, but also abundant $(M + H)^-$ ions. Suspecting this reflected the stability of the semiquinone anion we obtained the spectra of quinone and hydroquinone which were almost identical. The major ion was the semiquinone anion (100%) while the quinone radical anion was some 60% of its abundance. There was no evidence of the presence of the hydroquinone radical anion presumably due to its decomposition to the semiquinone ion since simple substituted phenols (Me, Cl, CN) all gave $M^{\cdot-}$ ions in addition to the expected $(M - H)^-$ ions. These phenols also showed abundant $(M + H)^-$ ions which suggested the positive ion spectra should show $(M - H)^+$, $M^{\cdot+}$, and $(M + H)^+$ ions: this proved to be the case.

Since the original models do not predict the existence of $M^{\cdot+}$, $M^{\cdot-}$, $(M + H)^-$, and $(M - H)^+$ ions we propose a new model which we believe also explains the commonly observed $(M + H)^+$ and $(M - H)^-$ ions.

In this mechanism the incoming fast atom either ionises a molecule of sample or glycerol by ejecting an electron or dissociates it by the loss of a hydrogen radical [equations (6) and (7)].

$$M \rightarrow M^{\cdot+} + e \qquad (6)$$

$$M \rightarrow (M - H)^{\cdot} + H^{\cdot} \qquad (7)$$
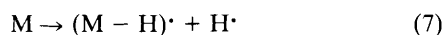
Electron capture by either a molecule or an $(M - H)^{\cdot}$ radical then gives the radical anion $(M^{\cdot-})$ or the commonly observed $(M - H)^-$ ions [equations (8) and (9)].

$$M + e \rightarrow M^{\cdot-} \qquad (8)$$

$$(M - H)^{\cdot} + e \rightarrow (M - H)^- \qquad (9)$$
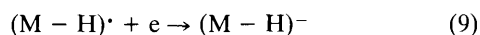
Hydrogen radical abstraction by $M^{\cdot+}$ ions from glycerol gives the commonly observed $(M + H)^+$ and by $M^{\cdot-}$ ions the unusual $(M + H)^-$ ions [equation (10) and (11)].

$$M^{\cdot+} + G \rightarrow (M + H)^+ + (G - H)^{\cdot} \qquad (10)$$

$$M^{\cdot-} + G \rightarrow (M + H)^- + (G - H)^{\cdot} \qquad (11)$$
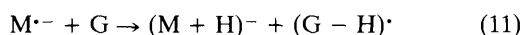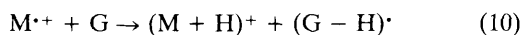
Finally abstraction of a hydrogen radical from $M^{\cdot+}$ gives $(M - H)^+$ ions [equation (12)].

$$M^{\cdot-} + (G - H)^{\cdot} \rightarrow (M - H)^+ + G \qquad (12)$$
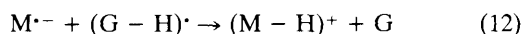
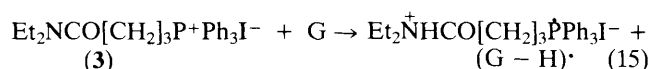The mechanism is not new in that similar cascades of ionisation and hydrogen radical abstraction have long been accepted for radiation chemistry[3] and it is well established that radical cations are formed when dilute solutions of substrate in solvents such as $FCCl_3$ are exposed to ionising radiation at low temperature.[4] Nor do the results show that proton transfer does not occur. However, the proposed model does provide a consistent framework by which all the observed fragments can be readily understood. Thus the initial step in the F.A.B. ionisation of methyl viologen is the capture of an electron to give the radical cation and a chloride ion which then give rise to the observed ions $PQ^{\cdot+}$ and $PQ^{\cdot+}(Cl^-)_2$, equation (13). Similarly (2) and benzoquinone first capture an electron and the resulting radical anion abstracts a hydrogen atom to give
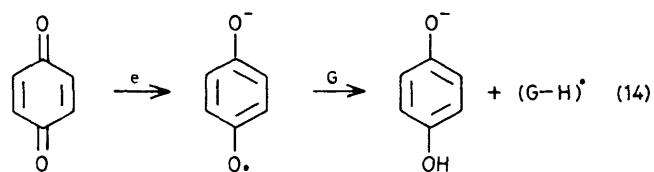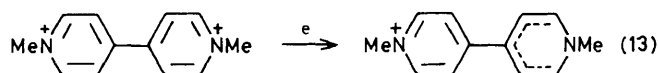
the semiquinone ion, equation (14). Compound (1) is clearly more able to capture an electron to give the radical anion than to form the expected carboxylate anion.

The spectra of some triphenylphosphine salts obtained recently give further confirmation; in addition to the expected cation M^+ the spectrum of (3) shows an equally abundant $(M^+ + H^{\cdot})$ ion. The latter can only be explained by the abstraction of one hydrogen atom from the matrix and an intramolecular electron transfer [equation (15)].

$$Et_2NCO[CH_2]_3P^+Ph_3I^- + G \rightarrow Et_2\overset{+}{N}HCO[CH_2]_3\overset{\cdot}{P}Ph_3I^- + \\ \textbf{(3)} \qquad\qquad\qquad\qquad (G - H)^{\cdot} \qquad (15)$$

We thank Mrs. A. Olsen for the spectrum of (3).

References

1 M. Barber, R. Bordoli, D. Sedgwick, and A. Tyler, *J. Chem. Soc., Chem. Commun.*, 1981, 325; D. Williams, C. Bradley, C. Bojesen, and S. Santikharn, *J. Am. Chem. Soc.*, 1981, **103**, 5700.
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4 H. Chandra and M. Symons, *J. Chem. Soc., Chem. Commun.*, 1983, 29.