

Evidence for Intramolecular Interaction between Ionic and Neutral Fragments in the Mass Spectrometer†

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Summary Apparent 'long distance' H-transfers in the fragmentation of steroidal diamines under electron impact result from 'intramolecular' ion-molecule reactions between ionic and neutral fragments in the mass spectrometer.

THE electron impact mass spectra of steroidal diamines show, in addition to well known nitrogen-containing ions x ,

normally observed in the spectra of the corresponding monoamines,¹ ions $M - x + 1$ representing the loss of the elements of x ions except for a hydrogen which is rearranged in the process.^{2,3} For example, the 3,20-diaminopregnane shown in the Scheme produces, under electron impact, not only an abundant fragment ion of mass 44 (as do all 20-amino pregnanes),¹ but also $M - 43$ ions whose formation requires the presence of both functional groups.^{2,3}

† This work was presented at the EUCHEM conference on the chemistry of ion beams held at Lunteren (Holland), April 1—4, 1980.

The formation of $M - x + 1$ ions has been shown (i) to involve a direct H-transfer from one group to the other (D-labelling experiment),^{2,3} (ii) to be unimolecular (independent of sample pressure),³ (iii) to involve no rearrangement of rings b and/or c of the molecular ion, because it shows a similar intensity in cases where such a rearrangement is highly improbable (aromatic ring c), and (iv) to concern mainly parent ions of a low internal energy (the relative abundance of $M - x + 1$ ions increases at low ionizing energy and their formation is largely predominant in the metastable time frame).^{2,3}

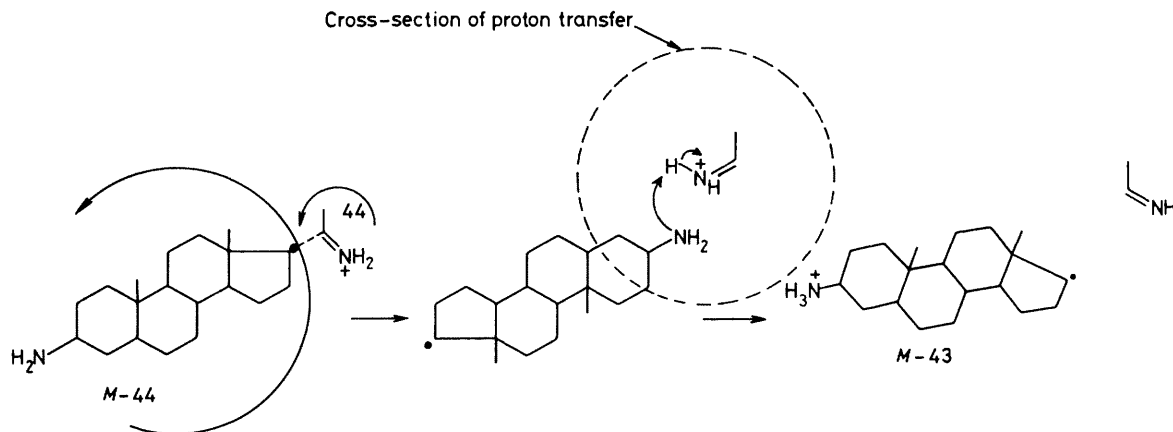
Clearly, x and $M - x + 1$ ions have closely related mechanisms of formation, the only difference being the H rearrangement implied by the latter.

We now propose an explanation for this apparently 'long distance' (*ca.* 10 Å) intramolecular and interfunctional H-transfer which is compatible with all the above experimental observations and which also may have a wider field of application in the chemistry of organic ions in the gas phase.

for interaction before their mutual separation exceeded the radius of the cross-section of this reaction.

For example, in the case of the diamine shown in the Scheme, as soon as the fragmentation leading to ion 44 is accomplished, the fragments (ion 44 and neutral $M - 44$) rotate independently. For a certain fraction of these ions, the mutual separation of the fragments is slow enough to permit a π -turn of the neutral fragment bringing its 3-amino group into the sphere of interaction of the ion, *i.e.* to a distance allowing a proton transfer from the ion 44 to the neutral $M - 44$ fragment and giving rise to an $M - 43$ ion. Of course this proton transfer should be thermodynamically favourable [the proton affinity (P.A.) of ethyldieneamine, 891 kJ/mol,⁴ is probably lower than the P.A. of the neutral fragment $M - 44$ (as an indication, the P.A. of cyclohexylamine is 920 kJ/mol).⁵

The possibility of such a mechanism may be verified by an approximate calculation of the energies and times involved. The rotational energy of the molecular ion (318 m.u.) is almost entirely conserved by the neutral fragment (275 m.u.)



SCHEME. Mechanism of formation of x and $M - x + 1$ ions after electron impact of steroidal diamines.

When an ion decomposes in the mass spectrometer, the total translational kinetic energy (K.E.), *i.e.* the K.E. of the parent ion, plus the K.E. released in the reaction coordinate, is shared between the fragments (ionic and neutral) in proportion to their mass. The velocity of the fragments, however, results from the vectorial addition of the velocity of the parent plus a velocity component (due to the K.E. release) in the direction of separation of the fragments. The latter component is the only factor responsible for this separation (in the absence of any external electric or magnetic field). If it is weak, ionic and neutral fragments may separate slowly from each other and remain in close proximity long enough to permit the occurrence of ion-molecule reactions between them. Moreover, the rotational kinetic energy of the molecular ion is shared between the fragments according to their specific rotational momenta. Therefore, the fragments rotate independently and consequently, an eventual ion-molecule reaction between fragments may involve functional groups which originally were distant in the intact molecular ion and which were brought, by the rotations, to a position suitable

and the angular velocity of the latter may be approximated assuming its mass to be situated uniformly at a distance $r = 2.5 \text{ \AA}$ from a central rotational axis.

The rotational moment is $I = Mr^2 = ca. 2 \times 10^{-20} \text{ kg m}^2$. The rotational energy for one degree of freedom is $E_r = \frac{1}{2} I \omega^2 = \frac{1}{2} RT$ (ω = angular velocity, R = gas constant, T = absolute temperature) and gives $\omega = 3.5 \times 10^{11} \text{ rad/s}$ at 300 K.[†] So, the time for a π -turn of the neutral fragment, π/ω , is about 10^{-11} s .

One can now evaluate the maximum distance of the fragments after 10^{-11} s within which a proton transfer is still possible. Cross sections for ion-molecule proton transfers are usually about $50\text{--}150 \text{ \AA}^2$ (ref. 6) which correspond to interaction radii of $4\text{--}7 \text{ \AA}$. Therefore the separation velocity should not exceed $40\text{--}70 \text{ m/s}$ for the reaction to be possible. This velocity originates from K.E. releases in the reaction co-ordinate of $35\text{--}110 \text{ J/mol}$.

These values appear quite plausible. In fact, only parent ions with a small excess of energy in the reaction co-ordinate give rise to $M - x + 1$ ions. Those for which this excess of energy is higher than a certain value give rise

[†] The temperature is not a crucial factor since a variation of 200 K leads to the same order of magnitude for ω .

to ions x since they separate too rapidly from the neutral fragment and are too far away after 10^{-11} s to react with it.

The relatively high abundance of $M - x + 1$ ions in many cases^{2,3} indicates that an important fraction of the parent ions decomposes with a small translational energy in the reaction co-ordinate. This may be regarded as a consequence of a highly populated ground electronic state of the molecular ion of complex diamines, and also of the large number of oscillators among which the internal energy is distributed.

Moreover, the cross-section of the proton-transfer reaction may be large owing to the existing ion dipole interaction between the ion and neutral fragment which may notably increase the duration of interaction.

Reactions other than proton transfer might probably be observed in other circumstances between ions and neutral species; proton transfers are probably good candidates because of their high cross-section.

(Received, 13th May 1980; Com. 520.)

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