Evidence for Interionic Reactions in the Mass Spectrometer

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THE mass spectrum of the 3β,20α-diaminopregn-5-ene[1] ($M^+ = 316$) shows, in addition to classical peaks at *m/e* 44 and 56 induced by the amino-group,[2] the presence of peaks at $M-43$ and $M-55$ due to the loss of the same fragments with rearrangement of one hydrogen atom. We demonstrate that this phenomenon is caused by an "interionic" mechanism.

The peak at *m/e* 273 ($M-43$) is accompanied by peaks at *m/e* 258 (loss of Me•), 256 (loss of NH_3), and 241 (loss of Me• and NH_3). The peak at *m/e* 261 ($M-55$) is accompanied by a peak at *m/e* 244 (loss of NH_3). All these transitions are established by the presence of clear metastable peaks.

These peaks become more prominent when the spectra are obtained at low voltage (12 ev) (*m/e* 273 becomes the base peak). On the other hand, only a weak variation in intensity of these peaks has been observed when the sample pressure in the ion source is changed.

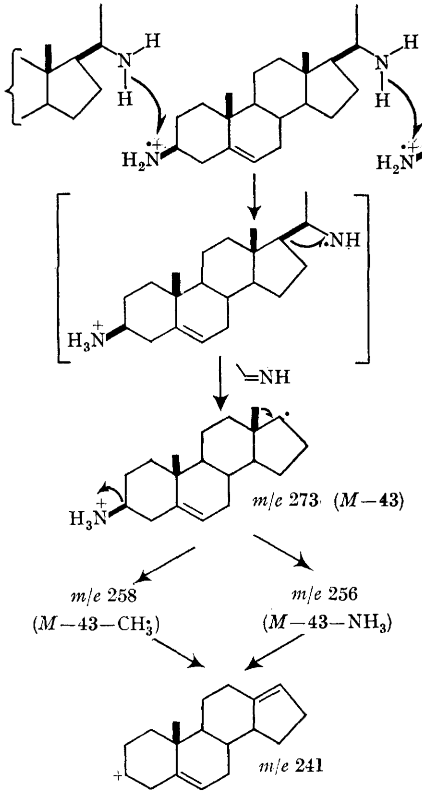
The mass spectrum of the deuteriated derivative (obtained by exchange of the hydrogen atoms of the amino groups using D_2O) shows the incorporation of up to 4 deuterium atoms into the molecule ($M^+ = 320$).

Peaks at *m/e* 273 and 261 are shifted to *m/e* 276 and 264, showing the presence of three deuterium atoms in the corresponding ions. Peaks at *m/e* 256, 244 (and 241) are not shifted and metastable peaks are present at *m/e* 237·4 and 225·5 demonstrating that they are due to loss of ND_3 (276 → 256 and 264 → 244).

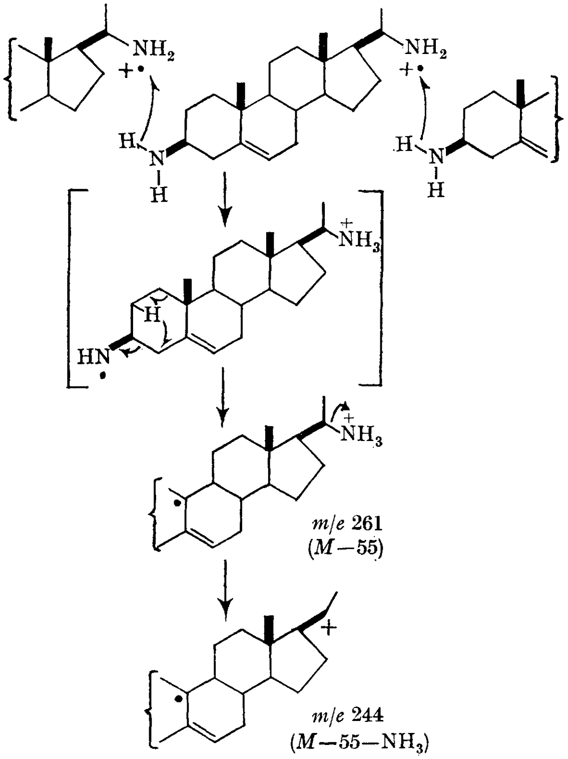
The rearranged hydrogen atom, therefore, comes from one of the amino-groups and goes to the other. This fact cannot be reasonably interpreted in terms of a unimolecular process, and it therefore seems probable that it is due to a "chain" reaction according to the mechanisms suggested in Schemes 1 and 2.

The molecules, after the ionization of one of the amino-groups, may behave as dipoles, forming chains by "head to tail" linkages (Schemes 1 and 2). One of the hydrogen atoms of an amino-group migrates to the charge- and radical-bearing nitrogen atoms of a neighbouring molecular ion leading to the formation of an ammonium ion. The radical site, therefore, is displaced from one nitrogen atom to the next, and this induces characteristic fragmentations.

A number of steroidal diamines have been examined. Further details will be published[3] in a full paper. The following are a few conditions on which this phenomenon depends.



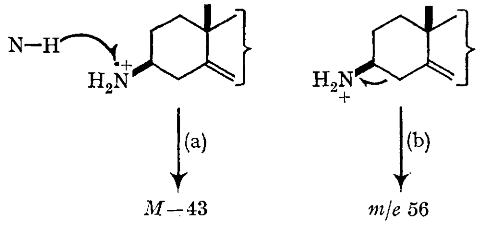
SCHEME 1



SCHEME 2

(1) The ionized molecules have to carry electron-rich functions (n or π) in two distinct centres ("poles"). (2) The ionized group is the hydrogen acceptor. Therefore, the other group must be able to donate a hydrogen atom (this fragmentation does not take place in the case of tertiary diamines). If both groups bear hydrogen atoms (as in the above example), the mechanism works in both ways (Schemes 1 and 2). It has been observed that imino-groups are very good hydrogen acceptors. (3) As is generally true for any fragmentation, this process must not be overshadowed by other more favoured cleavages. In particular, in the case of amines, this mechanism (Scheme 3a) which is in competition with the "classical" unimolecular fragmentation[1] (Scheme 3b), is more important in the case of primary amines in which the molecular fragmentation process is less strongly induced.

(4) This phenomenon is not apparent in the case of the 5,6-saturated derivative. Therefore, the 5,6-double bond plays an important role in stabilizing the charge or radical in the ions formed. Without this double bond, the fragmentation probably goes further producing ions which are masked in the low-mass region of the spectrum.



SCHEME 3

A different position of the double bond (or the presence of other functions) can induce other characteristic fragmentations.

This type of fragmentation involving what one might call an "interionic" reaction seems to be very widespread. The mass spectra of numerous compounds, for instance nucleosides,[4] some indole alkaloids,[5] halfordinol,[6] etc. could be better explained by the application of this general "interionic" mechanism.

Finally, this phenomenon appears to be a new and strong argument in favour of "charge localization".[7]

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