The Question of Ring Expansion in the Electron Impact-induced Fragmentation of Aromatic Amines

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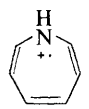
THE demonstration by Meyerson and his co-workers that the toluene molecular ion decomposes *via* a tropylium ion[1] raises the question of whether ring-expansion to azatropylium species is a pathway in the fragmentation pattern of aromatic amines. Our recent studies on ^{13}C-labelled nitrogen heterocycles are consistent with ring-expansion during the fragmentation of those compounds.[2]

On consideration of the mass spectra of aniline,[3] acetanilide,[4] and sulphanilamide,[5] an azatropylium ion such as (I) may be written for the molecular ion from aniline (*m/e* 93, base peak), and also for the odd-electron fragment of identical composition, $C_6H_7N^+$, that generates the base peak for acetanilide by loss of keten from the molecular ion. An


(I)


(II)

azatropylium ion (II) has been postulated[5] for the even-electron ion $C_6H_6N^+$ responsible for the intense peak at *m/e* 92 in the spectrum of sulphanilamide. These ions decompose further to hydrocarbon fragments of mass 66 and 65 respectively by loss of the elements of HCN. This reaction permits a decisive test for the presence of azatropylium structures by specific ^{13}C-labelling of aniline, acetanilide, and sulphanilamide at C(1). If ring expansion does not occur, the C–N bond should retain its identity and all the labelled carbon in the enriched species would be expelled as $H^{13}CN$. To the extent that azatropylium structures are involved, some retention of the labelling in the hydrocarbon product would be observed since $H^{12}CN$ and $H^{13}CN$ should be lost with similar probabilities.

[1-^{13}C]Aniline hydrochloride of 44% enrichment was prepared from sodium [1-^{13}C]acetate by the method used for the synthesis of [1-^{14}C] aniline.[6] Correspondingly-labelled acetanilide and sulphanilamide were prepared from it by standard methods.[7] Mass spectra were obtained using the direct insertion probe of an A.E.I. MS-9 instrument. The aniline was handled as its hydrochloride for ease of manipulation on a small scale; spectra of the free base and its salt are identical above *m/e* 40.

A qualitative conclusion can be drawn from the metastable peaks. For labelled aniline and acetanilide, metastable signals corresponding to equations (1) and (2) were observed, but there was no comparable signal for equation (3). Therefore the label loss from these compounds is essentially specific, and azatropylium forms such as (I) cannot contribute to the structure of the ion radical $C_6H_7N^+$.

$$\underset{(m/e\ 93)}{{}^{12}C_6H_7N} \xrightarrow{-H^{12}CN} \underset{(m/e\ 66)}{{}^{12}C_5H_6} \quad *(46{\cdot}8) \qquad (1)$$

$$\underset{(m/e\ 94)}{{}^{13}C^{12}C_5H_7N} \xrightarrow{-H^{13}CN} \underset{(m/e\ 66)}{{}^{12}C_5H_6} \quad *(46{\cdot}3) \qquad (2)$$

$$\underset{(m/e\ 94)}{{}^{13}C^{12}C_5H_7N} \xrightarrow{-H^{12}CN} \underset{(m/e\ 67)}{{}^{13}C^{12}C_4H_6} \quad *(47{\cdot}8) \qquad (3)$$

$$\underset{(m/e\ 92)}{{}^{12}C_6H_6N} \xrightarrow{-H^{12}CN} \underset{(m/e\ 65)}{{}^{12}C_5H_5} \quad *(45{\cdot}9) \qquad (4)$$

$$\underset{(m/e\ 93)}{{}^{13}C^{12}C_5H_6N} \xrightarrow{-H^{13}CN} \underset{(m/e\ 65)}{{}^{12}C_5H_5} \quad *(45{\cdot}4) \qquad (5)$$

$$\underset{(m/e\ 93)}{{}^{13}C^{12}C_5H_6N} \xrightarrow{-H^{12}CN} \underset{(m/e\ 66)}{{}^{13}C^{12}C_4H_5} \quad (*46{\cdot}8) \qquad (6)$$

On the other hand, the labelled sulphanilamide produced metastable signals corresponding to equations (4), (5), and (6). Therefore some loss of $H^{12}CN$ from the ^{13}C-enriched species must occur. This demands an intermediate such as (II) in which the unique identity of the labelled position disappears. However the *m/e* 46·8 peak is noticeably smaller than the 45·4 peak, so that reaction (5) predominates over reaction (6). If an azatropylium type contributes to the structure of the even-electron ion $C_6H_6N^+$, there must still be a proportion of unrearranged species in which the integrity of the label is unimpaired.

Quantitative analysis of the mass spectral data is complicated, and details will be presented in a full paper. The signals in the *m/e* 65 region all contain several components including satellites of adjacent

peaks and those from nitrogen-containing fragments; all components have been characterized by mass-matching. Within experimental error, the intensities of the relevant peaks in the spectra of [1-^{13}C]aniline and [1-^{13}C]acetanilide correspond to specific loss of H^{13}CN [equation (2)], and equation (3) need not be invoked. For the enriched sulphanilamide species, the contribution of equation (6) is 20—25% that of equation (5). If the ion $C_6H_6N^+$ is regarded as a mixture of unrearranged and azatropylium forms, the relative concentration of the latter species would be 40—50%, since equation (6) represents only half the ring-expanded ions present.

The present results indicate that postulation of ring-expanded structures without adequate support from isotopic labelling experiments is unwarranted. It should be noted that all species for which ring-expansion has been demonstrated (sulphanilamide as well as examples in refs. 1 and 2) are of an even-electron character.

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