

THE STRUCTURE OF THE HIGH ENERGY (M-KETENE)⁺ IONS FROM ACETANILIDE.¹

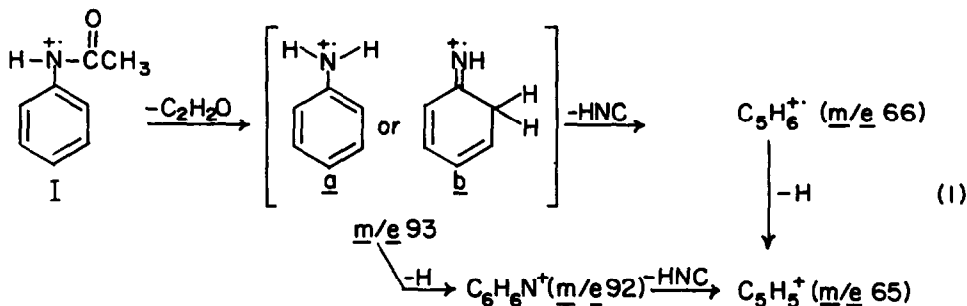
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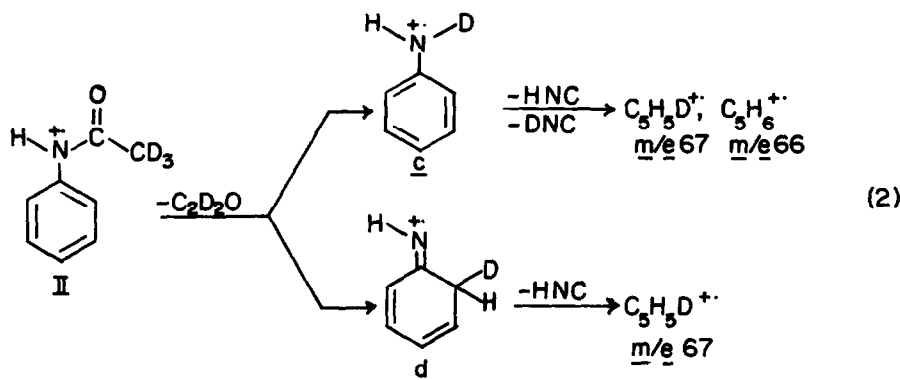
The base peak in the mass spectrum of acetanilide (I) is at m/e 93 and arises via hydrogen transfer from the acetyl group to the anilino moiety with expulsion of ketene (Eq. 1).

If the itinerant hydrogen is transferred to nitrogen via a four-membered transition state the product ion will have an aniline structure (a). Alternatively, the itinerant hydrogen may be transferred to carbon through a six-membered transition state to form product ions with a cyclohexadienimine structure (b). The mass 93 ion subsequently decomposes by expulsion of HNC or H followed by loss of H or HNC respectively.^{2,3}



Recent reports based on metastable ion data from labeled acetanilides indicate that those (M-ketene)⁺ ions from acetanilide which decompose in the field-free regions of the mass spectrometer possess structure a rather than b.^{4,5}

By examining the relative abundances of the $C_5H_5D^+$ and $C_5H_6^+$ ions produced in the mass spectrum of 2,2,2-d₃-acetanilide (II) it is possible to determine the structure of the (M-ketene)⁺ ions decomposing in the source, since the labeled aniline ion (c) will expel both HNC and DNC, while the labeled cyclohexadienimine ion (d) will expel only HNC (Eq. 2).



The presence, however, of $[M-(C_2H_2O+H+HNC)]^+$ and $[M-(C_2H_2O+HNC+H)]^+$ ions has hitherto prevented the direct measurement of the $C_5H_6^{+}/C_5H_4D^{+}$ doublet at m/e 66.

With the current availability of super-high resolution instruments possessing the ability to resolve this doublet (e.g., Varian MAT 711 mass spectrometer), this roadblock has been removed. We have now investigated the intensities of the $C_5H_6^{+}$ (m/e 66.04948) and $C_5H_5D^{+}$ (m/e 67.05323) ions in the mass spectrum of II and our data are summarized in the table.

High Resolution Measurements for 2,2,2-d₃-Acetanilide

m/e	Composition	Intensity ^{a,b}	% of Low Resolution Peak ^c
65	C_5H_5	8.90	93
66	C_5H_4D	1.45	18.7
	C_5H_6	5.90	72
67	C_5H_5D	5.65	97

^a Based on m/e 94 as 100% and corrected for isotopic purity.

^b $\pm 5\%$.

^c Includes all N and C^{13} containing ions.

The $C_5H_6^{+}/C_5H_5D^{+}$ ratio of 0.96 is consistent only with the loss of ketene involving deuterium transfer to nitrogen (c) rather than to carbon (d) to form ions with sufficient energy to decompose further in the source. This result is in agreement with the earlier metastable ion data.^{4,5} Since those $(M\text{-ketene})^{+}$ ions containing sufficient energy to decompose further in the source and the field-free regions are of structure c, it is most likely that the non-decomposing ions are also of this structure. Definitive evidence for the structure of

the non-decomposing (M-ketene)⁺ ions may be found by ion cyclotron resonance spectrometry, and experiments in this direction are under investigation.

The data in the table also indicate that the ratio of C₅H₅⁺ to C₅H₄D⁺ ions formed by successive expulsion of HNC (DNC) and D· or H· from the (M-ketene)⁺ ion is 6:1. This ratio is consistent only with a majority of the ions expelling both hydrogens (deuterium) initially on the nitrogen. Mechanisms involving the ortho or all of the ring hydrogens would lead to ratios ranging from 3:1 to 1.4:1.

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