

Structure and Reactions of the $C_6H_7N^+$ and $C_6H_5N^+$ Ions Formed from Phenylurethane on Electron Impact*

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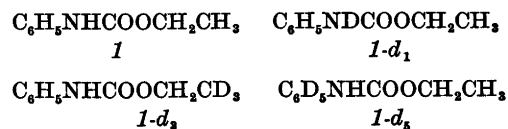
Dedicated to Professor K. A. Jensen on his 70th birthday

The $C_6H_7N^+$ fragment ions from $C_6H_5NHCOOC_2H_5$ and $C_6H_5NHCSOC_2H_5$ are formed with an aniline-like structure despite indications to the contrary in literature spectra of deuterium labeled phenylurethanes. An earlier suggestion that pivalanilide likewise generates $C_6H_7N^+$ ions with an aniline-like structure has been confirmed. $C_6H_5NH^+$ ions formed by elimination of C_2H_5OCO from phenylurethane do not undergo extensive hydrogen scrambling prior to decomposition, in contrast to $NH_2C_6H_4^+$ ions.

A number of recent studies have established that the abundant $C_6H_7N^+$ fragment ions formed by elimination of small neutral molecules from the molecular ions of acetanilides,¹⁻⁴ higher anilides,⁵ and formanilides⁶ are formed with an aniline-like structure. The published mass spectra of phenylurethane (ethyl *N*-phenylcarbamate)^{7,8} and higher esters of *N*-phenylcarbamic acid show that these compounds likewise give rise to abundant $C_6H_7N^+$ fragment ions, and *a priori* it would appear reasonable to assume that the initial structure of these ions is also aniline-like. However, a comparison of the mass spectra of phenylurethane and some labeled analogs ($C_6H_5NHCOOCH_2CD_3$ and $C_6H_5NHCOOC_2D_5$)^{7,8} with the spectra of acetanilide and acetanilide-*d*₃ ($C_6H_5NHCOC_3D_3$)⁹ does not lend

immediate support to this assumption. For acetanilide, ketene elimination from the molecular ions gives rise to *m/e* 93 ions ($C_6H_7N^+$); these decompose by loss of HNC, leading to *m/e* 66 ions which again eliminate H with formation of *m/e* 65 ions. In the spectrum of acetanilide-*d*₃, the corresponding peaks are *m/e* 94 ($C_6H_5DN^+$), *m/e* 67 and *m/e* 66 (elimination of HNC and DNC from *m/e* 94), and *m/e* 66, 65 (H/D loss from *m/e* 67 and 66). The spectrum of phenylurethane is almost identical to that of acetanilide in the *m/e* 60–100 region, showing peaks at *m/e* 93, 66 and 65. However, the published spectra^{7,8} of the *d*₃ and *d*₅ analogs of phenylurethane show the expected shift of *m/e* 93 to 94, but the abundant *m/e* 65 peak is *not* shifted to *m/e* 66. One possible explanation would be that the D-atom transferred from the ethyl group in the reaction leading to $C_6H_5DN^+$ (*m/e* 94) is completely lost in the subsequent fragmentation (*i.e.*, exclusive loss of DNC), in which case the decomposing $C_6H_7H^+$ ions of phenylurethane would be structurally different from the corresponding ions formed from the aniline derivatives previously examined.¹⁻⁸

In order to resolve this problem, we have re-examined the mass spectra of phenylurethane and some labeled analogs hereof.

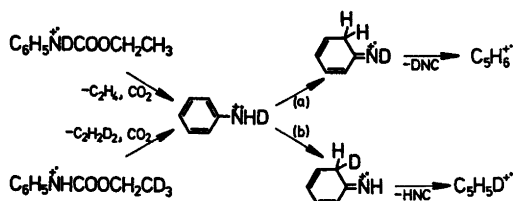


* A preliminary account of this work was presented at the VIIth Triennial Mass Spectrometry Conference, Firenze, Italy, Aug. 30–Sept. 3, 1976 (*Adv. Mass Spectrom.* 7. *In press*).

As shown previously,^{1,2,5,6} the course of the hydrogen migration leading to $C_6H_7N^+$ ions may be established through a study of the decomposition of metastable $C_6H_6DN^+$ ions. These ions were in the present case formed by expulsion of $C_2H_4 + CO_2$ from $1-d_1$ or of $C_2H_2D_2 + CO_2$ from $1-d_3$ (Scheme 1). In the field-free region between the electric and magnetic sectors these ions decompose by elimination in both cases of HNC and DNC in equal amounts, as shown by the relative areas of the corresponding metastable peaks:

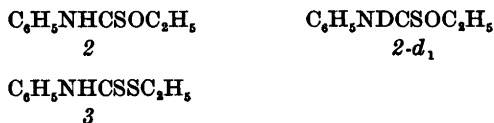
Precursor	$1-d_1$	$1-d_3$	$1-d_5$	$2-d_1$	$7-d_1$
m_{HNC^+}/m_{DNC^+}	1.0	1.05	4.8	1.0	1.25

This shows that the rearranged hydrogen atom (from the terminal CH_3) has become chemically equivalent to the hydrogen originally on nitrogen prior to the subsequent decomposition by HNC (DNC) elimination, *i.e.*, that the hydrogen transfer must occur to *nitrogen*; transfer of the migrating hydrogen atom to the ring would not allow (only) these two hydrogen atoms to become equivalent. This then strongly suggests that the $C_6H_7N^+$ is formed with an aniline-like structure.



Scheme 1.

To complement this result, the mass spectra of the sulfur analogs, 2 and 3, of phenylurethane were studied.



However, 3 does not decompose to give abundant $C_6H_7N^+$ ions; instead $C_6H_7S^+$ ions are formed, after migration of the phenyl group from N to S as previously described for similar systems.⁹ The mono-thio compound, 2, decomposes very much like 1; in particular,

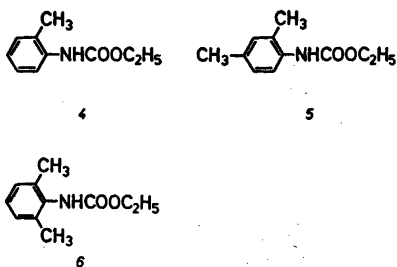
the course of the hydrogen rearrangement leading to formation of $C_6H_7N^+$ is not affected by the exchange of oxygen for sulfur. The metastable $C_6H_6DN^+$ ions formed from $2-d_1$ eliminate HNC and DNC in equal amounts (see above), showing again that the rearranged hydrogen atom has become equivalent to the hydrogen on the nitrogen atom prior to HNC (DNC) loss.

It has previously been shown¹ for aniline molecular ions that limited interchange occurs between the hydrogen atoms of the $-NH_2$ group and the *ortho* hydrogen atoms (reversibility of paths *a* and *b* in Scheme 1). For $C_6H_5NHD^+$ ions this should increase the probability for loss of HNC relative to DNC. At the same time, there is an isotope effect on the hydrogen transfer step that precedes HNC elimination, which favors retention of D on nitrogen (path *a* in Scheme 1) and hence should cause preferential loss of DNC. Elimination of HNC and DNC in equal amounts from the $C_6H_6DN^+$ ions of $1-d_1$, $1-d_3$, and $2-d_1$ shows that the two effects in these cases, as for acetanilides^{1,2} and formanilides,⁶ are of the same order of magnitude. In the decomposition of $C_6D_5NH_2^+$ ions the two effects should reinforce each other, leading to significant DNC loss, which is indeed observed for the $C_6H_5D_5N^+$ ions formed from $1-d_5$ (see above).

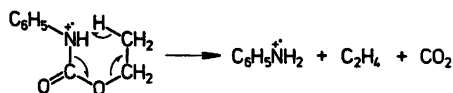
Previous studies of the decomposition of acetanilide¹⁰ and pivalanilide¹¹ (see also below) have shown that the reaction leading to the $C_6H_7N^+$ fragment ions is not inhibited by the presence of *ortho* substituents. The relative abundances of the corresponding ion ($Q = M - C_2H_4 - CO_2$) and its daughter ions ($Q' = Q - H^+$; and $Q'' = Q - CH_3^+$) in the mass spectra of the tolyl- and xylylurethanes 4–6 show that methyl groups in one or both *ortho* positions do not inhibit the elimination of $C_2H_4 + CO_2$:

Compound	1	4	5	6
M/base peak	72	83	100	78
Q/M	1.4	0.5	0.4	0.3
$(Q + Q' + Q'')/M$	2.0	2.0	1.5	1.9

The absence of steric hindrance for the hydrogen transfer reaction corroborates the conclusion that hydrogen transfer occurs to nitrogen rather than the aromatic ring.

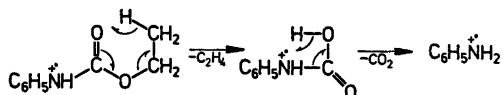


It is not clear whether the formation of C₆H₇N⁺ from 1 occurs as a one-step elimination of C₂H₄ + CO₂ with hydrogen transfer to nitrogen in a six-membered cyclic transition state, as depicted in Scheme 2, or if the reaction occurs stepwise, with initial transfer of hydrogen



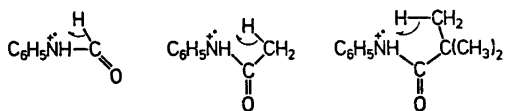
Scheme 2.

to oxygen in a six-membered cyclic transition state and elimination of C₂H₄ (a McLafferty rearrangement), followed by transfer of the same hydrogen from oxygen to nitrogen in a four-membered cyclic transition state with loss of CO₂, as shown in Scheme 3.

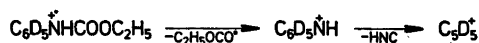


Scheme 3.

A comparison with the processes leading to formation of C₆H₇N⁺ ions from other aniline derivatives does not provide a clue to the size of the transition state, inasmuch as the hydrogen transfer in formylanilides takes place in a three-membered cyclic transition state, while the transition state for acetanilides is four-membered, and for pivalanilides the hydrogen atom is transferred in a five-membered cyclic transition state.



A number of investigations^{2,13} of the decomposition of aniline and simple aniline derivatives have provided strong evidence that many even-electron C₆H₇N⁺ ions undergo extensive scrambling of both hydrogen and carbon atoms prior to decomposition. However, this appears not to be the case for the C₆H₅NH⁺ ions formed from phenylurethanes by loss of the C₂H₅OCO radical. In the spectrum of 1-d₅, the metastable peak for HNC elimination from C₆D₅NH⁺ is about five times as intense as that for DNC elimination, indicating a high degree of retention of the amino hydrogen on nitrogen even for the metastable ions.



Scheme 4.

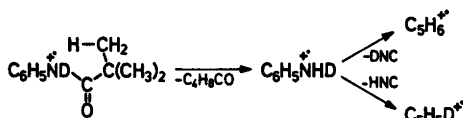
In the spectrum of 1-d₁, the metastable peak for DNC elimination from C₆H₅ND⁺ is more intense than that for HNC loss, confirming the preferential retention of D on nitrogen. A quantitative measure of the ratio of DNC to HNC loss is in this case precluded by the presence of C₆H₅NH₂⁺ ions (same nominal mass as C₆H₅ND⁺) that also eliminate HNC. A similar specificity has been observed for the C₆H₅NH⁺ ions formed from phenylhydrazines.¹³

These observations provide the reason why *m/e* 65 is not partially shifted to *m/e* 66 in the spectra of C₆H₅NHCOOCH₂CD₃ and C₆H₅NHCOOC₂D₅.^{7,8} Apparently, most C₆H₅⁺ ions (*m/e* 65) are formed by fragmentation without scrambling of the C₆H₅NH⁺ ions generated by loss of C₂H₅OCO[•] from the molecular ions and will hence not incorporate any of the atoms originating in the -NHCOOC₂H₅ group (*cf.* Scheme 4).

The reason for the differing behaviour with respect to scrambling of the C₆H₅N⁺ ions described in the literature^{2,12} and those of the present study may well be that most of the previously examined C₆H₅N⁺ ions have been generated as NH₂C₆H₄⁺ (*e.g.*, by loss of NO₂ from nitroaniline), whereas the initial structure of the C₆H₅N⁺ ions from phenylurethanes will be C₆H₅NH⁺. Apparently, for NH₂C₆H₄⁺ the energy of activation necessary to reach the reacting configuration for HNC loss is higher than that needed for scrambling of the hydrogen

atoms, while the reverse relationship exists for $C_6H_5NH^+$.

The conclusion that the $C_6H_5N^+$ ion formed by loss of C_4H_6CO from pivalanilide (7) has an aniline-like structure was based on the observation¹¹ that the *ortho* bromine atoms of 2,4,6-tribromopivalanilide do not inhibit the elimination of C_4H_6CO . To confirm this conclusion we have studied the mass spectrum of pivalanilide-*N-d*₁ (7-*d*₁). This compound decomposes with formation of abundant $C_6H_5DN^+$ ions, which subsequently fragment by loss of either HNC or DNC.



Scheme 5.

Again, the metastable peaks for HNC and DNC loss are of similar intensity (see above), supporting the conclusion that the $C_6H_5N^+$ fragment ions are formed *via* hydrogen migration to nitrogen. The ratio of the metastable peak intensities (1.25) is, however, sufficiently different from that observed for other aniline derivatives to leave open the possibility that more than one mechanism is operating.

EXPERIMENTAL

The mass spectra were recorded by Ms E. Wolff-Jensen with an AEI MS-902 mass spectrometer operating with an ion source temperature of 100 °C, using the direct insertion probe. Phenylurethanes 1, 1-*d*₅, 4, 5, and 6 were prepared from ethyl chloroformate and the appropriate aniline;¹⁴ 1-*d*₃ was obtained by addition of 2,2,2-trideuterioethanol to phenyl isocyanate.¹⁵ The sulfur analogs, 2 and 3, were prepared by previously described methods.^{16,17} Pivalanilide, 7, was prepared from aniline and pivaloyl chloride. The *N-d*₁ compounds, 1-*d*₁, 2-*d*₁, and 7-*d*₁ were obtained by repeated recrystallizations of the unlabeled compounds from 10% CH_3COOD in D_2O ; back exchange in the inlet system of the mass spectrometer was minimized by introduction of D_2O prior to introduction of the sample. The isotopic purity of the labeled compounds (determined from low-voltage mass spectra) were as follows: 1-*d*₁: 84% *d*₁; 1-*d*₃: 96% *d*₃, 4% *d*₂; 1-*d*₅: 96% *d*₅, 4% *d*₄; 2-*d*₁: 89% *d*₁; 7-*d*₁: 61% *d*₁.

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Received July 26, 1977.