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Ion–Molecule Reactions of Free Phenyl Cations with Diethylamine in the Gas Phase: Radiochemical Study

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Abstract—Ion–molecule reactions of free phenyl cations with diethylamine in the gas phase were studied radiochemically. The reaction practically totally follows the pathway of proton transfer, which occurs in the intermediate complex not only from the incoming cation ($C_6H_5^+$) but also from the ethyl substituent of the amine. Also, products of the reaction of diethylamine with benzyne (C_6H_4) generated by proton abstraction from the phenyl cation were detected.

Ion–molecule reactions of nuclear-chemically generated alkyl cations with various amines are the subject of our long-term studies. We have elucidated the dependence of the reaction pathway on the nature of the cation [1], nature and number of alkyl substituents in amine [2–4], and substrate vapor pressure [4]. Also we found that the mechanism of this reaction does not change in going to organosilicon analogs of amines [5].

These studies, and also numerous mass-spectrometric works [6–9], showed that in all cases alkyl cations react with amines by the two main pathways, via formation of the condensation complex and proton-transfer complex. The latter pathway prevails in all the reactions studied, although it is energetically unfavorable as compared to the condensation pathway. This fact was explained in [10–12] in terms of the concept of the ion–molecule complex. In this complex a cation and a molecule are held together by ion–dipole interaction forces, with the rotation of the components being almost free. Formation of the ion–molecule complex precedes formation of the condensation and proton-transfer complexes.

In our previous works we studied reactions of amines with alkyl cations of various compositions and structures. In this work we turned to aromatic cations (namely, phenyl cation) with the aim to find whether the proton transfer will remain the prevailing pathway with cations of an essentially different nature.

Phenyl cation is also of interest itself, since the existing data on its geometry, electronic structure, energy state, appearance potentials, and heats of formation are still contradictory [13–20].

Phenyl cation was suggested for the first time as intermediate in decomposition of the diazonium cation $C_6H_5N_2^+$ [16]. However, even its existence was a matter of discussion for a long time. Despite the fact that the phenyl cation was detected in the gas phase by mass spectrometry, its appearance potentials varied in a wide range [17–20], which cast doubt on its aromatic nature.

Later numerous experimental studies [21–24] unambiguously confirmed the existence of the phenyl cation. Theoretical studies performed using modern calculation procedures gave a clear insight into the geometry, electronic structure, and energy state of this cation [14, 25, 26]. In this case the model reaction was considered: Abstraction of hydride ion from benzene. This reaction yields the phenyl cation in the ground singlet state in which the vacant orbital and the π electrons of the aromatic system are mutually orthogonal and do not interact with each other.

The vacant orbital, being initially sp^3-hybrid, tends to reduce the s character. As a result, the $C–C^{\alpha}–C$ angle in the phenyl cation increases from 120° (in benzene) to 144.9°, and the C–C bond length decreases from 1.39 (in benzene) to 1.35 Å. These distortions of the ideal geometry of benzene are due to the tendency of the phenyl cation to maximally delocalize its positive charge by σ hyperconjugation of the carbenium center with the adjacent C–C and C–H bonds and by the shift of the π-electron system toward the carbenoid center.

Another way of delocalization of the positive charge in the phenyl cation is transition of one of the π electrons to the vacant orbital of the carbenoid center. In this case, the aromaticity is distorted, and the triplet state of the cation can arise. Calculation showed that, although in the triplet state the electron directly occupies the vacant orbital, the positive charge still remains on the carbenoid center, and the delocalization is only slightly more efficient than in the singlet species [14]. The enthalpy of formation of the phenyl cation in the ground singlet state, according to [14], is 280 kcal mol^{-1}.[1]

Thus, phenyl cation is an extremely reactive electrophilic species; therefore, it can be expected that ion–dipole interactions involving phenyl cation should be still stronger than those with alkyl cations.

Indeed, mass-spectrometric and radiochemical methods showed that phenyl cations actively react in the gas and condensed phases with hydrocarbons and hydrogen halides [27], ethers [28], alcohols, and water [22–24]. Data on reactions of phenyl cations with nitrogen-containing compounds are scarce, although the reactions of alkyl cations with these compounds are actively studied. Only a few works can be mentioned. For example, Ranasinghe and Glish [23], using mass spectrometry, studied the reaction of phenyl cations with ammonia and its methyl derivatives $(CH_3)_{3-n}NH_n$, where $n = 0$, 1, and 2. Similar to alkyl cations, the reaction with phenyl cations occurred by two competing pathways: condensation and proton transfer, with the latter process prevailing despite its being energetically unfavorable. For example, with dimethylamine the enthalpy of condensation is –98.9 kcal mol^{-1}, and that of proton transfer, –8.9 kcal mol^{-1}, whereas the yields of the products formed by these two pathways are 16 and 81%, respectively.

From the energy standpoint, abstraction of the hydride ion by the phenyl cation from the methyl substituent of the amine molecule is considerably more favorable (–79.1 kcal mol^{-1}) than proton transfer; however, the contribution of this process is as low as 3%, and it becomes appreciable only with trimethylamine (32%). This study shows that in reactions of phenyl cations with amines, too, the major process is proton transfer. The preferableness of this energetically unfavorable process and the increased contribution of hydride abstraction at increased number of methyl groups in the substrate show that reactions of phenyl cations with amines are also controlled by the entropy, rather than enthalpy, factor [10–12].

These results concern only methyl derivatives of amines, studied in the gas phase at low pressure. Furthermore, the mass-spectrometric method used allows observation of only charged reaction products.

In this work we extended the framework of experimental studies. As substrate we took an ethyl-substituted amine, and its vapor pressure in the reaction mixture exceeded by several orders of magnitude the working pressure in [23]. Furthermore, the radiochemical method allows observation of neutral reaction products. All these facts allow more substantiated conclusions about the mechanism of interaction of phenyl cations with amines.

Thus, in this work we studied radiochemically the reactions of nuclear-chemically generated free phenyl cations $C_6T_5^+$ with diethylamine in the gas phase. The observed labeled products and their relative yields (determined from the radioactivity peak areas in chromatograms, taking into account the labeling multiplicity) are given below.

$(C_2H_5)_2NT$	15 ± 4%
$(C_2H_5)_2NC_6T_4H$	13 ± 1%
$C_2H_5NHC_6T_5$	72 ± %

Based on the existing theoretical concepts of reactions of alkyl cations with amines, we can explain the formation of these products as follows. Mutual approach of the cation and amine molecule results in formation of a vibrationally excited ion–molecule complex [10–12] in which all the alkyl (or aryl) groups have the free cation character and can almost freely rotate around the central nitrogen atom. We believe that within the lifetime of this complex (about 10^{-9} s [29]) the excitation energy in it will be redistributed over all the vibrational and rotational degrees of freedom. As a result, the resonance structures can form:

$$\underset{\mathbf{I}}{[C_6H_5^+(C_2H_5)_2NH]} \longleftrightarrow \underset{\mathbf{II}}{[C_2H_5^+\cdot C_6H_5NHC_2H_5]}, \text{ etc.}$$

Thus, proton transfer can occur not only from the phenyl (primary transfer) but also from the ethyl cation (secondary transfer). It is logical to assume that the proton abstraction from the cation exhibiting the lowest moments of inertia and hence the highest rotation rate is the most probable. This assumption is based on the concept that proton can be transferred only when the hydrogen atom of the cation is oriented toward the nitrogen atom [7, 30]. It should be borne in mind, however, that this reasoning is valid only when the excitation energy of the complex is fully redistributed between all alkyl (or aryl) groups. Otherwise the incoming cation will have a higher energy than the alkyl substituents of the amine, making the

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[1] The enthalpy of formation of the most reactive alkyl cation C^+H_3 is 261.3 kcal mol^{-1} [17].

primary proton transfer preferable. According to our estimates, the main moments of inertia (calculated by the SCF MO LCAO method) of the ethyl cation are considerably lower than those of the phenyl cation:

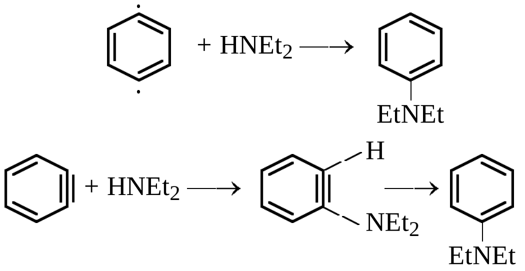
	I_a, au	I_b, au	I_c, au
$C_2H_5^+$	16.97829	67.65190	75.81255
$C_6H_5^+$	261.03984	331.49560	592.53544

This estimate is consistent with the observed predominant proton transfer from the ethyl cation (secondary transfer).[2]

The proton transfer from the resulting protonated amines $(C_2H_5)_2N^+H_2$ and $C_6H_5N^+H_2C_2H_5$ to substrate molecules will yield $(C_2H_5)_2NH$ and $C_6H_5NHC_2H_5$. Indeed, among the products we detected labeled diethylamine and ethylphenylamine, with the latter being formed in a considerably higher yield than the former.

According to the theory of the ion–neutral species complex, ethylphenylamine could also form via the condensation complex. However, it should be emphasized that, although the enthalpy of the decomposition pathway of the condensation complex with elimination of the ethyl cation is –25 kcal mol^{-1}, theoretical studies of the geometry and electronic structure of the ethyl cation [31, 32] and the results of the mass-spectrometric studies [9, 32] show that this decomposition pathway is unlikely (this conclusion also follows from the absence among the reaction products of ethylamine, which could form by monomolecular elimination of the ethyl cation from protonated diethylamine). Another pathway of monomolecular decomposition of the condensation complex, yielding $C_6H_5NHC_2H_5$ (with elimination of ethylene and free proton), is energetically forbidden because of the very high enthalpy of formation of the free proton. The enthalpy of this process is as high as +127 kcal mol^{-1}.

The proton transfer from the phenyl cation to the amine yields C_6H_4 (benzyne). The theoretical studies of the electronic structure of benzyne [33] showed that its *meta* and *para* isomers are diradicals, especially the latter, whereas the *ortho* isomer contains more likely a triple bond than an aromatic C=C bond and resembles dehydrobenzene [34]. Reaction of benzyne (in the biradical or dehydrobenzene state) with the substrate molecule should yield the same product, diethylaniline, which indeed was detected (13%):



Thus, our results show that the reaction of free phenyl cations with diethylamine practically fully follows the proton-transfer pathway. However, in contrast to [23], where only the proton transfer from $C_6H_5^+$ was detected by mass spectrometry, we also observed the proton transfer from the ethyl substituent of the substrate. Furthermore, this process prevails. Also, radiochemical analysis revealed the product of the reaction of C_6H_4 at the N–H bond of the substrate molecule.

EXPERIMENTAL

Products of ion–molecule reactions of phenyl cations with diethylamine were analyzed radiochromatographically with a Tsvet chromatograph equipped with a flow-through proportional counter as detector of tritium β-ray radiation. The tritium-labeled products were identified by comparing their retention times with those of the reference substances under identical chromatographic conditions. The reliability of the results was provided by using two chromatographic columns: (a) 3000 × 2-mm stainless steel column packed with Chromaton N-AW-DDCS + 10% Tridox, carrier gas He, flow rate 30 ml min^{-1}, programmed heating of columns from 60 to 190°C at a rate of 12 deg min^{-1}; (b) 4000 × 2-mm stainless steel column packed with Chromosorb-P + 5% octadecylamine, carrier gas He, flow rate 20 ml min^{-1}, column temperature 80°C. The flow rate of the quenching gas (pentane at 50°C) was 1 ml min^{-1} in both cases; the working voltage of the flow-through proportional counter was 2.4 keV.

The relative yields of the products were determined as the ratios of the activity of the given product to the total activity of all the detected products, taking into account the assumed labeling multiplicity.

Free phenyl cations were generated [35] by β$^-$-decay of tritium in totally tritium-labeled benzene:

$$C_6T_6 \xrightarrow{\beta^-} [C_6T_5^3He]^+ \longrightarrow C_6T_5^+ + {}^3He.$$

Totally tritium-labeled benzene was prepared by the procedure suggested in [36], involving catalytic cyclization of tritium-double-labeled acetylene which,

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[2] In reactions of methyl cations with diethyl- and triethylamines, the prevailing process is proton transfer from the methyl cation (primary transfer) [1, 4].

in turn, was prepared by hydrolysis of lithium carbide with tritium water:

$$T_2 \xrightarrow[\text{CuO}]{450°\text{C}} T_2O \xrightarrow[\text{Li}_2\text{C}_2]{200°\text{C}} C_2T_2 \xrightarrow[\text{catalyst}]{18\text{–}20°\text{C}} C_6T_6.$$

Diethylamine used as substrate and the reference sample of diethylaniline were thoroughly dried over KOH and fractionated.

Reactions of free phenyl cations with diethylamine were studied in the gas phase at a diethylamine vapor pressure of ~40 mm. The procedure for preparing reaction mixtures was described in [37]. Products of ion–molecule reactions were accumulated in 100-ml sealed ampules of molybdenum glass. The activity of benzene introduced into the ampules was 3.7×10^7 Bq. Labeled benzene was dosed using xenon as inert carrier; its pressure in the ampule was about 100 mm. The products were accumulated at room temperature in the dark for 4 months.

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