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Comment on: "Reactions of Phenyl Cations with Methanol and Methyl Fluoride"

Maurizio Speranza

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma "La Sapienza", P.le A. Moro, 5-00185 Rome, Italy

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The behavior of the nuclear-decay-formed (nucleogenic) phenylium ion $\mathbf{1_P}$ toward gaseous nucleophiles (NuH)[1,2] (Scheme 1) has been recently re-examined by Ignatyev and Sundius (IS) in the light of the B3LYP/6-31G(d,p)-calculated $[C_6H_5^+,CH_3Y]$ (Y = OH, F) potential energy surfaces (PES).[3,4] In their inquiry, IS call in question the quasidegenerate automerization sequence i of Scheme 1 as being responsible for T scrambling in the TC_6H_4Nu products, without throwing enough light on the supporting experimental evidence.[1,2] To provide a more balanced view of the problem, a brief outline of the 21-year debate on $\mathbf{1_P}$ automerization and a punctual discussion of IS's appraisal of the problem seem in order.

The debate on phenylium ion automerization started in 1980 after the publication of two independent studies by Speranza (Ss)[1] and by Pollack and Herhe (PH).[5] Ss reported that T-anisole formed by the nuclear decay of 1,4-T_2-benzene in gaseous CH_3OH contains the label not only in the original para position but also in the meta and ortho positions. This observation was explained by Ss in terms of partial $\mathbf{1_P}$ automerization before addition to the nucleophile (path i of Scheme 1; NuH = CH_3OH). The same mechanism was proposed by PH to account for the identical dedeuteronation threshold of variously deuterated phenylium cations as measured by ion cyclotron resonance (ICR) mass spectrometry.

Ss's mechanism was immediately questioned by several authors who pointed out that the computed activation barriers of the process (E^*_{isom}) appeared to be too high (44−77 kcal mol^{-1})[6−9] to be overcome by nucleogenic $\mathbf{1_P}$ even, considering the vibrational excitation (E_{def}) arising from its structural relaxation (25−32.3 kcal mol^{-1})[6,9] (Figure 1).

Several alternative explanations of PH's and Ss's results were advanced, all based on multiple H shifts after formation of the adduct between $\mathbf{1_P}$ and the nucleophile (path ii of Scheme 1).[8,10]

Conclusive evidence against this latter mechanistic hypothesis was provided in 1983 by Ss et al. by replacing CH_3OH with CH_3Y (Y = F, Cl, Br), as the gaseous nucleophile NuH.[11] Attack of $\mathbf{1_P}$ on CH_3Y yields isomeric TC_6H_4Y with a distribution unaffected by the nature of the halogen atom Y and similar to that of anisole formed in the methanol systems. These results, coupled with the well-known migratory inaptitude of the F atom in arenium ions, exclude any conceivable isomerization sequences after addition of $\mathbf{1_P}$ to the nucleophile, including sequence ii of Scheme 2, thus supporting the occurrence of the $\mathbf{1_P} \rightleftarrows \mathbf{1_M} \rightleftarrows \mathbf{1_O}$ automerization sequence before addition to the nucleophile (path i of Scheme 1).

After this latter piece of experimental evidence, no other pros and cons for $\mathbf{1_P}$ automerization have been brought on. The controversy among the results of the decay experiments and the theoretical predictions long remained quiescent, until IS tried to reject the $\mathbf{1_P}$ automerization model by reviving another mechanistic option (i.e., sequence i of Scheme 2), already confuted 18 years earlier by Ss.[2] In their paper, IS regard the B3LYP method as inaccurate for predicting transition state energies.[4] Nonetheless they assert that (i) formation of $\mathbf{3_P}$ by insertion of $\mathbf{1_P}$ into the C−Y bond of CH_3Y (Y = F) involves no activation barriers, (ii) the isomerization sequence i of Scheme 2 (Y = F) is energetically allowed since the relevant activation barriers all lie well below the energy level of the $\mathbf{1_P}/CH_3F$ reactants, and (iii) the formation of *meta*- and *ortho*-T-fluorobenzene arises from demethylation of the ipsoprotonated intermediates of path i, e.g., $\mathbf{3_O}$ (henceforth denoted as $\mathbf{3}^*$) (Y = F). The para isomer arises instead from demethylation of intermediates $\mathbf{2_P}$, $\mathbf{3_P}$, and $\mathbf{3_M}$ (Y = F).

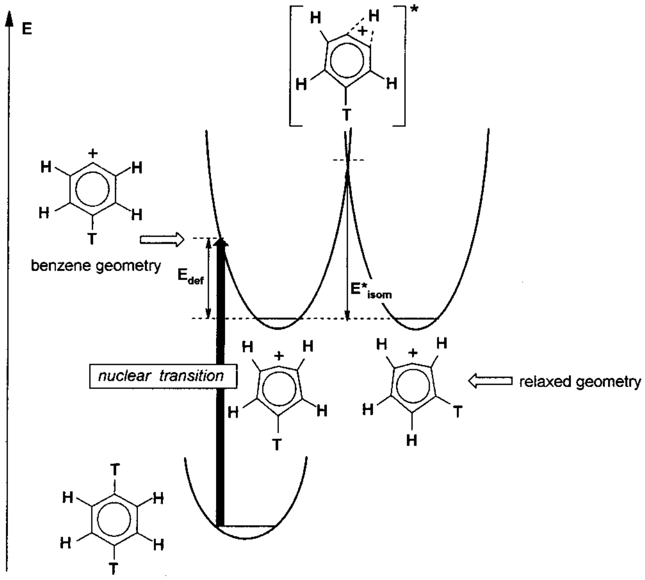
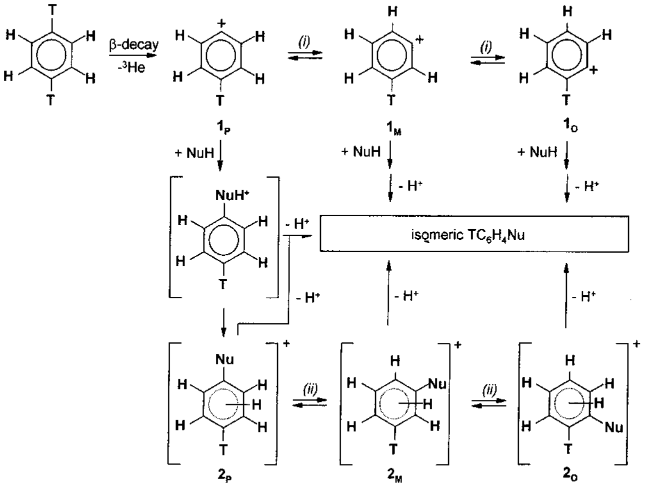


Figure 1. Schematic potential energy profile for the automerization of nucleogenic phenylium ion.

SCHEME 1



Surprisingly enough, IS do not put any emphasis on the following logical consequences of their own calculations: (i) the rearrangement of $\mathbf{3_M}$ is dominated by H-shifts (E^*=ca. 10 kcal mol^{-1}),[3] rather than by CH_3-groups transfers ($E^* > 20$ kcal mol^{-1});[3] (ii) extensive interconversion among the intermediates of path i of Scheme 2 (Y = F) implies that the population of the protonated fluorotoluenes, e.g., $\mathbf{4_O}$, $\mathbf{4_{ipso}}$, and $\mathbf{4'_O}$ (henceforth denoted as $\mathbf{4^*}$), must be at least 2 or 3 orders of magnitude larger than that of the less stable ipsoprotonated isomers $\mathbf{3}^*$; (iii) neutralization of the abundant $\mathbf{4^*}$ isomers yields exclusively

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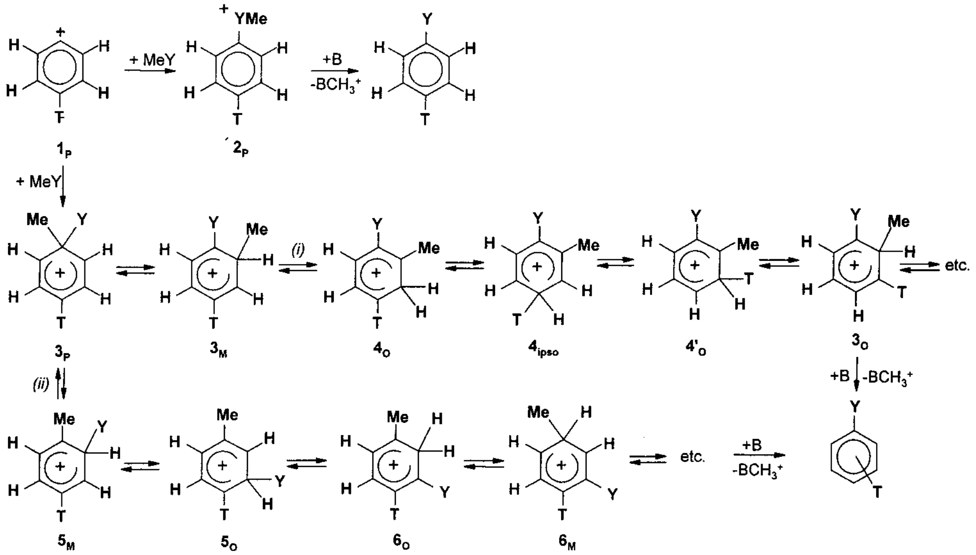
SCHEME 2



fluorotoluenes, whereas the very minor **3*** intermediates undergo deprotonation in competition with demethylation. Since it is known that the first process is kinetically favored over the latter,[12] neutralization of **3*** would yield predominantly T-fluorotoluenes, rather than T-fluorobenzenes. The missing point in IS's reasoning is that path i of Scheme 2 is expected to produce *meta*- and *ortho*-T-fluorobenzene in yields that are many orders of magnitude lower than those of T-fluorotoluenes (19−24%) and, therefore, negligible relative to those measured experimentally (3−9%).[11] The same arguments apply a fortiori to the systems containing CH_3Y ($Y = Cl$, Br).[11] Here, the combined yields of *meta*- and *ortho*-T-halobenzenes (8−15%, $Y = Cl$; 8−18%, $Y = Br$) even exceed those of the corresponding T-halotoluenes (2−3%, $Y = Cl$; 1−3%, $Y = Br$), in striking contrast to the expectations based on IS's mechanistic hypothesis.[3,4]

It is concluded that the mechanism i of Scheme 2, used by IS in opposition to **1**$_{\mathrm{P}}$ automerization, is untenable. Automerization of **1**$_{\mathrm{P}}$ before addition to the nucleophile (path i of Scheme 1) still accounts best for all the experimental results.

The problem is how to reconcile the solid experimental evidence with the available theoretical calculations ($E_{\mathrm{def}} < E^*_{\mathrm{isom}}$). A way could be to consider more carefully (i) the current limitations of the theoretical approaches used for evaluating E^*_{isom} and (ii) all the conceivable sources of excitation of the nucleogenic phenylium ion.

Concerning E^*_{isom}, the available computational data, including IS's, indicate that the description of the transition structures of **1**$_{\mathrm{P}}$ automerization is sensitive to the level of theory employed. Therefore, it may be possible that more refined computations of both E^*_{isom} and E_{def} will further reduce the $E^*_{\mathrm{isom}} - E_{\mathrm{def}}$ gap (ca. 6−8 kcal mol^{-1} at the MP2 level of theory) so as to make the entropically favored gas-phase **1**$_{\mathrm{P}}$ automerization possible.[13]

Concerning the excitation energy imparted to the nucleogenic phenylium ion **1**$_{\mathrm{P}}$ by the β-transition in the 1,4-T_2-benzene precursor, one should consider that the tritium nucleus transmutes into ^{3}He following emission of an antineutrino and of a β^- particle, with a mean energy of 5.6 keV and a maximum energy of 18.6 keV.[14] As pointed out above, nucleogenic phenylium ion **1**$_{\mathrm{P}}$ can be left behind with some degree of vibrational excitation ($E_{\mathrm{def}} < 2$ eV).[15] Further excitation may arise from the collision of the ejected particles (the β^- particle or the ^{3}He atom) with the nucleogenic ion (E_{coll}). Morton et al. pointed out that this latter mechanism may produce ions with a vibrational energy > 2 eV (superexcited ions).[15] In the decay of tritiated ethanol, they estimated as large as ca. 50% the maximum net probability that one of the ejected particles collides with the nucleogenic ions from which it is departing. In other words, a certain fraction of the nucleogenic **1**$_{\mathrm{P}}$ may have an excess energy higher than E_{def} due to the contribution from E_{coll}. It is therefore possible that the gas-phase automerization of phenylium ion, observed in all decay experiments,[1,2,11] involves these superexcited species.[13]

In conclusion, it appears that a greater awareness of all the facets concerning the generation of the nucleogenic **1**$_{\mathrm{P}}$ and its gas-phase automerization,[13] including a more refined theoretical description of the automerization transition structures and an accurate estimate of **1**$_{\mathrm{P}}$'s vibrational energy, is in order before discounting the hard experimental evidence from decay and mechanistic studies.

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