Reactions of Phenyl Cations with Methanol and Methyl Fluoride

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Benzenium ions formed by the interaction of the phenyl cation with methanol and methyl fluoride as well as the transition states for their rearrangement were optimized at the B3LYP/6-31G(d,p) level of theory. Among the reactant complexes $[C_6H_5{\cdot}CH_3X]^+$ corresponding to the different sites of the phenyl cation attack on the CH_3X molecules (X = OH,F) the addition complex (O-protonated anisole) was the most stable one for X = OH, followed by the CH insertion complex (*ipso*-protonated benzyl alcohol), while for X = F the CF insertion complex had the lowest energy. Addition and insertion complexes may transform into the ring protonated isomers. Barrier heights for subsequent proton migrations in the arenium ions studied were in the 1−23 kcal/mol range and those for methyl migrations were in the 5−28 kcal/mol range. All these rearrangements were allowed, since their barriers were substantially lower than the complexation energy (67 kcal/mol for X = OH and 42 kcal/mol for X = F). The global minimum was *para*-protonated anisole for X = OH and *meta*-protonated *ortho*-fluorotoluene for X = F. These theoretical predictions were compared with experimental results in studies of nucleogenic phenyl cation reactions with methanol and methyl fluoride. Low barriers for methyl migrations, especially that of CH_3 shift from *ipso*- to *ortho*-positions relative to F in the phenyl cation−methyl fluoride encounter complex, relieved objections to proton shifts in arenium ions as a mechanism of the observed H/T scrambling.

Introduction

In our previous communication,[1] we have confirmed predictions earlier made by the MINDO/3 [2] and ab initio [3] methods that the barrier for automerization (hydride shifts around the ring) in phenyl (and substituted phenyl) cations is too high to be overcome by the excess energy of the free nucleogenic phenyl cation. The possibility of automerization of phenyl cations was debated in the 1980's while discussing the interpretation of experimental data on reactions of phenyl cations produced by the β-decay of tritium atoms in ditritiated benzene.[4−6] The study of the reaction of these cations with methanol in the gas phase has shown that neutral products of the reaction contain the tritium atom not only in the *para*-position (as it was in the precursor molecule) but also in *meta*- and *ortho*-positions. Angelini, Fornarini, and Speranza suggested that the tritium scrambling occurs in the free phenyl cation before interacting with methanol. However, this proposal contradicts theoretical predictions of the automerization barrier height. Schleyer, Kos, and Raghavachari [3] argued that it cannot be overcome by the excess "deformation" energy of the nucleogenic phenyl cation.

Dewar and Reynolds [2] suggested that hydrogen (tritium) migration may occur in the protonated anisole formed by the reaction between the phenyl cation and methanol. The mechanism proposed by these authors implies initial formation of O-protonated anisole with subsequent proton transfer from oxygen to the ring and proton shifts in ring protonated anisoles. They have shown by the MINDO/3 method that barrier heights for these shifts do not exceed 26 kcal/mol and that these barriers may be easily overcome with the excess energy obtained from the extremely exothermic addition of methanol to the phenyl cation (MINDO/3 estimate is 45 kcal/mol).

However, the Speranza group presented additional evidences against this mechanism.[6] They studied reactions of the nucleogenic phenyl cation with methyl halides. The authors found a close correspondence between the tritium distribution within the halobenzenes and anisole and suggested that these findings indicate that the tritium scrambling is governed by the same mechanism both in phenyl−methanol and phenyl−methyl halide systems. Since in the latter system there is no hydroxyl proton which plays a key role in the mechanism proposed by Dewar and Reynolds [2] and the migratory inaptitude of fluorine is well-known, Speranza et al. argued that the sole mechanism consistent with these experimental data is the automerization of the free phenyl cation. As mentioned above, this mechanism contradicts all theoretical predictions. In view of this challenge to theoretical methods, the aim of the present study was to revisit the mechanism proposed by Dewar and Reynolds [2] at a more sophisticated level of theory including electron correlation for X = OH and to elucidate whether this mechanism may not be applicable for the case of X = F.

Theoretical Approach

In the present work the hybrid HF/DFT method known as B3LYP was used. This method combines Becke's three parameter exchange functional [7] with the Lee−Yang−Parr correlation functional.[8] The basis set was the standard 6-31G-(d,p). Both the method and the basis set were used as realized in Revision E.2 of the Gaussian 94 program.[9] In the previous

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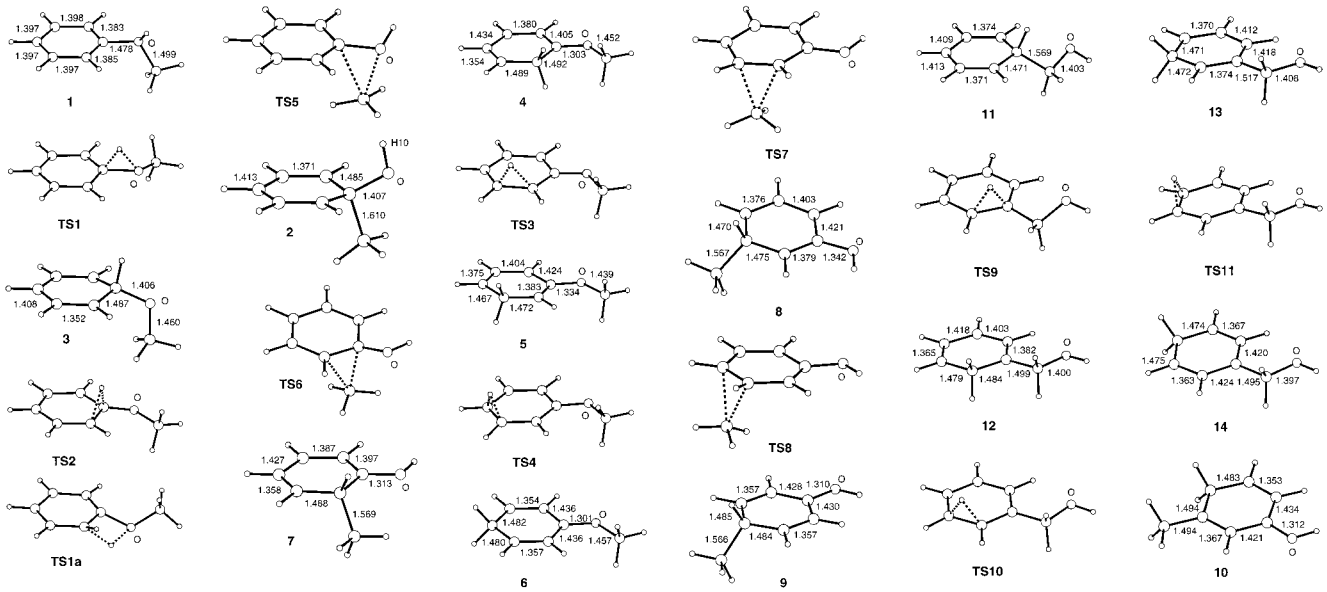

Figure 1. The molecular geometries of the equilibrium structures of isomers in the $C_6H_5^+ + CH_3OH$ system.

quantum chemical studies of the phenyl[10] and tolyl[11] cations the B3LYP method led to good predictions of geometrical parameters and energies of these systems: superior to MP2 and approaching those of CCSD(T) and CASSCF. The last methods, however, can hardly be employed for the scanning of the potential energy surface for the systems studied.

Results and Discussion

Phenyl Cation + Methanol. There are four plausible ways the phenyl cation can interact with the methanol molecule. The most probable site of attack, which was the only one considered in the previous mechanistic interpretations,[2,5,6] is the addition of the phenyl cation to the oxygen lone pairs. Here we also examine the three other channels, i.e., insertion of the cation into the CO, CH, and OH bonds of methanol. No barrier for any of these processes is found. The optimized structures of the adduct **1** and three insertion products **2, 3, 11** are depicted in Figure 1. As expected the most stable of them is the adduct, i.e., O-protonated anisole (**1,** Table 1, and Figure 1). The products of the insertion into the CH bond (*ipso*-protonated benzyl alcohol **11**, Figure 1), into the CO bond (*ipso*-methylated phenol **2**), and into the OH bond (*ipso*-protonated anisole **3**) are less stable than the adduct by 1.9, 7.6, and 15.7 kcal/mol (Table 1, ΔH_{298} values hereafter). The OH insertion complex **3** is of the highest energy among these isomers, however a facile way of the rearrangement of the most stable isomer **1** into **3** by the oxonium proton shift through **TS1** exists (Figure 1). This process has a high barrier (39.9 kcal/mol), but it may be surpassed with the excess complexation energy.

While the isomerization of **1** into *ipso*-protonated anisole **3** is endothermic, the exothermic process (−12.4 kcal/mol) exists with nearly the same barrier height (40.2 kcal/mol). It leads through **TS1a** directly to *ortho*-protonated anisole **4** (Figure 1). This isomer may also be achieved from **3** by the proton shift through the transition state **TS2** with a very low barrier (0.5 kcal/mol). The ring protonated anisoles formed by the rearrangements discussed may undergo further isomerization by a chain of H shifts around the ring with higher barriers (**TS3**, 22.8 kcal/mol; **TS4**, 7.2 kcal/mol). The most stable form of protonated anisoles is **6** in which proton is in the *para*-position to the methoxy group (Figure 3).

TABLE 1: Total Energies (E_e, hartree), Relative Energies (ΔE_e, kcal/mol) and Enthalpies (ΔH_0, ΔH_{298}, kcal/mol) of Cations Formed by the Interaction of the Phenyl Cation with Methanol

	HF/3-21(d)		B3LYP/6−31(d,p)			
	E_e	ΔE_e	E_e	ΔE_e	ΔH_0	ΔH_{298}
$C_6H_5^+ + CH_3OH$	−342.86248	0	−346.99523	0	0	0
1	−343.00607	−90.1	−347.10027	−65.9	−60.4	−61.4
TS5	−342.92190	−37.3	−347.02915	−21.3	−18.5	−20.1
TS1	−342.89287	−19.1	−347.03067	−22.2	−20.3	−21.5
TS1a	−342.89505	−20.4	−347.02902	−21.2	−20.1	−21.2
			OH insertion			
3	−342.95439	−57.7	−347.07261	−48.6	−44.7	−45.7
TS2	−342.93371	−44.7	−347.06965	−46.7	−43.9	−45.2
4	−343.00011	−86.4	−347.11902	−77.7	−72.7	−73.8
TS3	−342.93925	−48.2	−347.07920	−52.7	−49.7	−51.0
5	−342.97397	−70.0	−347.09790	−64.4	−60.2	−61.2
TS4	−342.94715	−53.1	−347.08407	−55.8	−52.7	−54.0
6	−343.00837	−91.5	−347.12429	−81.0	−75.9	−77.0
			CO insertion			
2	−342.96881	−66.7	−347.08636	−57.2	−52.8	−53.8
TS6	−342.95338	−57.0	−347.07725	−51.5	−47.6	−48.8
7	−343.00902	−92.0	−347.12870	−83.8	−78.3	−79.5
TS7	−342.95605	−58.7	−347.08215	−54.5	−50.2	−51.5
8	−342.98024	−73.9	−347.10679	−70.0	−65.6	−66.6
TS8	−342.95936	−60.8	−347.08495	−56.3	−51.8	−53.2
9	−343.01126	−93.4	−347.13170	−85.6	−80.3	−81.4
10	−343.01865	−98.0	−347.14323	−92.9	−88.2	−89.1
			CH insertion			
11	−342.98004	−73.8	−347.09608	−63.3	−58.5	−59.5
TS9	−342.94455	−51.5	−347.08068	−53.6	−50.6	−51.9
12	−342.98423	−76.4	−347.10503	−68.9	−64.7	−65.5
TS10	−342.94289	−50.4	−347.08072	−53.6	−50.8	−52.0
13	−342.98131	−74.6	−347.10104	−66.4	−62.1	−63.0
TS11	−342.94448	−51.5	−347.08135	−54.0	−51.2	−52.5
14	−342.98755	−78.5	−347.10836	−71.0	−66.8	−67.8

These theoretical predictions are in agreement with the results of studies of anisole protonation in superacid media by NMR spectroscopy.[12] Olah and Mo[12] have shown that the site of protonation (O− *vs* C−) depends on the acidity of the medium, but the predominant site at higher temperatures is C-protonation. Carbon shifts indicated partial charge delocalization to the oxygen atom leading to partial double-bond character in the

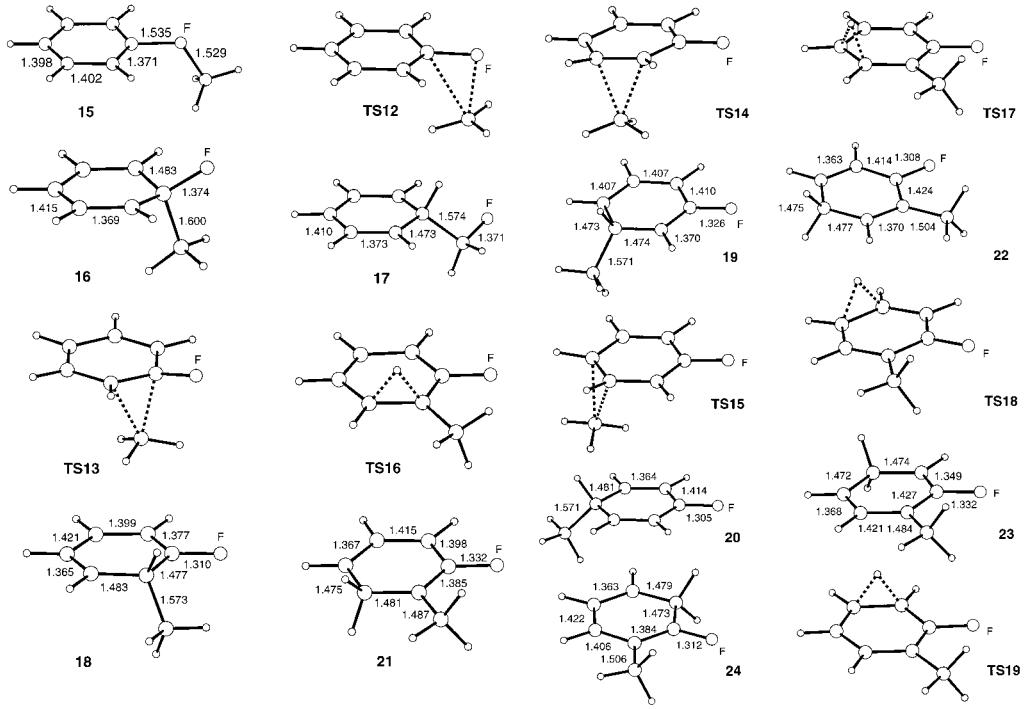

Figure 2. The molecular geometries of the equilibrium structures of isomers in the $C_6H_5^+ + CH_3F$ system.

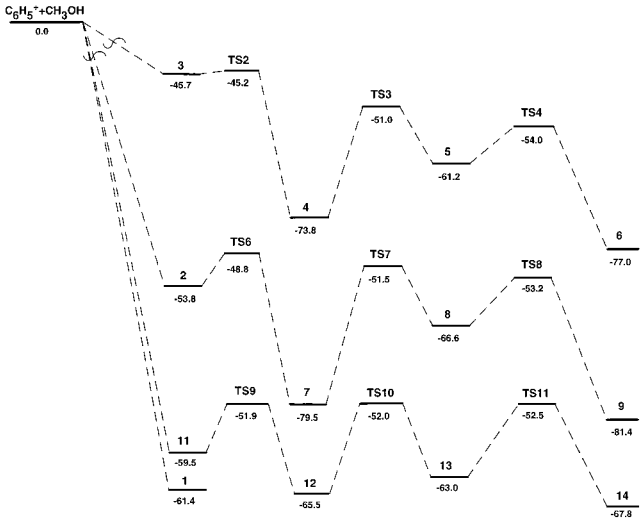

Figure 3. Potential energy diagram for stationary points in the $C_6H_5^+ + CH_3OH$ system.

CO bond. The equilibrium structures of protonated anisoles predicted in the present study are consistent with these findings: *para*-C-protonated anisole **6** is by 15.6 kcal/mol more stable than the O-protonated form **1**. The CO bond length of 1.301 Å in **6** indicates partial double-bond character (compare the equilibrium CO bond lengths in formaldehyde, 1.207 Å, and anisole, 1.367 Å, optimized at the same theory level).

Insertion of the phenyl cation into the CO bond of methanol leads to *ipso*-hydroxylated toluene **2** (Figure 1). It lies 7.6 kcal/mol above O-protonated anisole **1** and may be produced also from **1** by a methyl shift from the oxygen atom to the ring carbon through the **TS5** barrier (Figure 1). However, this barrier is substantially high (41.3 kcal/mol). The 1,2-methyl shift gives *ipso*-protonated *ortho*-cresol **7** (Figure 1) with the barrier (**TS6**) height of only 5 kcal/mol above **2**. Structure **7** in contrast to **2** is considerably more stable than **1** (by 18.1 kcal/mol). The subsequent methyl group shifts lead to *ipso*-protonated *meta*-cresol **8** and *ipso*-protonated *para*-cresol **9** (Figure 3). The barriers for these transformations are 28.0 kcal/mol (**TS7**) and 13.4 kcal/mol (**TS8**). Note, that the barriers for the methyl migration around the ring are of similar heights to those for the H-migration in anisole. Structure **9** (Figure 1) is the most stable among *ipso*-protonated cresols. However, the most stable among the products of insertion of the phenyl cation into the CO bond of methanol (the global minimum in the whole phenyl cation−methanol system as well) is *para*-protonated *ortho*-cresol **10** (Figure 1). It is lower in energy than O-protonated anisole **1** by 27.7 kcal/mol. Note that experimental results indicate that the site of protonation of *ortho*-cresol is on the ring carbon *para*- to the hydroxy group.[12]

The fourth plausible way of phenyl cation interaction with the methanol molecule is insertion into the CH bond. It produces *ipso*-protonated benzyl alcohol **11** (Figure 1). It is the second most stable reactant complex among four complexes (**1, 2, 3, 11**) and it is only 1.9 kcal/mol above the most stable one (**1**). Proton migrations around the ring give three other position isomers of this arenium ion, i.e., *ortho*- (**12**), *meta*- (**13**), and *para*-protonated benzyl alcohol (**14**, Figure 1 and Figure 3). Barrier heights for these migrations are of the same order of magnitude as in protonated anisoles (**TS9**, 7.6 kcal/mol; **TS10**, 13.5 kcal/mol; **TS11**, 10.5 kcal/mol). Similar to sequence of the OH insertion isomers (**3**−**6**) and the CO insertion isomers (**7**−**10**), where structures with protonation sites in *para*-position to the oxygen containing group are the most stable ones, *para*-protonated benzyl alcohol **14** is the most stable of the CH insertion isomers (Figure 1).

These results suggest that the barriers for methyl migration around the ring in arenium ions are of the same order of magnitude as for hydrogen migrations. This is in contrast with the prevalent opinion that hydrogen atoms have high mobility with respect to methyl groups in gaseous arenium ions.[6] This opinion was based on the experimental estimate of the barriers for hydrogen (ca. 10 kcal/mol) and methyl (ca. 20 kcal/mol) migrations in methylbenzenium ions[13] and on the fact that methyl shifts were not observed for xylenes in $HF-SbF_5-SO_2ClF$ solution below 0°.[14] Our results show that the first step for

H migration from *ipso*-protonated anisole **3** and benzyl alcohol **11** as well as for CH_3 migration from *ipso*-methylated phenol **2** has low barriers (0.5−7.7 kcal/mol). The highest barriers are **TS3** and **TS10** for H-shifts (22.8 kcal/mol in anisoles and 13.5 kcal/mol in benzyl alcohols) and for the CH_3 (27.9 kcal/mol) shift from *ortho*- to *meta*-positions (**TS7**).

These theoretical predictions allow us to discuss the scope of experimental results obtained in the study of the neutral products of gas- and liquid-phase reactions of nucleogenic T-labeled phenyl cations with methanol.[5] The observed neutral labeled products are formed by deprotonation (or less probable demethylation) of the intermediate arenium ions, i.e., products of interaction between the phenyl cation and the methanol molecule. Although the experimental conditions significantly affect relative yields of the aromatic labeled products the main products of reaction between phenyl cations and methanol are anisole, cresol, benzyl alcohol, phenol, and toluene. The yield of anisole is invariably predominant and increases from 76% to 94% with the partial pressure of methanol in the gas phase. The analysis of the tritium distribution shows a mixture of *para*-, *meta*-, and *ortho*-anisoles (with respect to the tritium position in the ring). The initial benzene has two tritium atoms in the *para*-position and therefore the nascent nucleogenic ion is the *para*-phenyl cation. The relative yield of *para*-anisole, however, increases with the methanol pressure from 72% to 80% and becomes 100% in the liquid phase. Phenol and cresol have comparatively high yields at low pressure but they substantially decrease at high pressures and in the liquid phase. In contrast the yields of benzyl alcohol and toluene increase in the liquid phase.[5]

The predominance of anisole among the observed neutral products may be rationalized taking into account not only the fact that adduct **1** is the most stable encounter complex (Table 1), but that the oxygen *n*-center is the most obvious site of interaction of phenyl cations. The last factor, i.e., the orientation of the positively charged particles to the oxygen lone pair due to ion−dipole interactions, plays a decisive role at low pressures. Note that, practically, only two products were observed in the low-pressure experiments, i.e., anisole and phenol (95% of the total yield of aromatic products at the lowest pressure, 5 Torr). They may both be derived from adduct **1** through intermediate structures **3** (anisole by deprotonation) and **2** (phenol by demethylation). Deprotonation, as a more facile process predominates, especially at higher pressures. Note that **2** is also a direct CO insertion complex.

A similar mechanism may be responsible for the small decrease of the cresol yield (from 3% to 1%). Cresol may also be derived from **2**, but an additional step is required, that is, methyl migration through the barrier **TS6** from *ipso*- (**2** to *ortho*-position (**7**). Deprotonation of **7** may produce cresol.

It is interesting to note that in contrast to anisole, the H/T scrambling in benzyl alcohol is also observed in the liquid phase.[5] The distribution of the *para*-, *meta*-, and *ortho*-isomers of benzyl alcohol is 85/13/2 in the liquid phase while only the *para*-isomer of anisole was found. This observation may be rationalized by comparing the barriers for H-migration from encounter complexes **1** and **11**. The barrier height for the H-shift from the oxygen atom of the adduct **1** to the ring is about 40 kcal/mol (**TS1**) and in the liquid phase where the energy dissipation is higher and the adduct lifetime is shorter the proton may be lost from **1** before it migrates to the ring. In contrast to **TS1** the barrier height for H-migration from the *ipso*- to the *ortho*-position in protonated benzyl alcohols (**TS9**) is much lower (7.7 kcal/mol). Further H-migrations to the *para*-position have also low barriers (12.5 and 10.5 kcal/mol) and the probability of these migrations before deprotonation is much higher. This interpretation is an additional argument against the H/T migration in free phenyl cations proposed by Angelini, Fornarini, and Speranza.[5]

TABLE 2: Total Energies (E_e, hartree), Relative Energies (ΔE_e, kcal/mol) and Enthalpies (ΔH_0, ΔH_{298}, kcal/mol) of Cations Formed by the Interaction of the Phenyl Cation with Methyl Fluoride

	HF/3-21(d)		B3LYP/6−31(d,p)			
	E_e	ΔE_e	E_e	ΔE_e	ΔH_0	ΔH_{298}
$C_6H_5^+ + CH_3F$	−366.74635	0	−371.00955	0	0	0
15	−366.83438	−55.2	−371.06805	−36.7	−32.9	−33.5
TS12	−366.78777	−26.0	−371.02723	−11.1	−9.1	−9.8
16	−366.84315	−60.7	−371.09420	−53.1	−48.9	−49.8
17	−366.85357	−67.3	−371.10407	−59.3	−54.3	−55.4
TS13	−366.82402	−48.7	−371.08012	−44.3	−40.5	−41.8
18	−366.86616	−75.2	−371.11994	−69.3	−64.5	−65.5
CH_3 migration from **18**						
TS14	−366.82596	−50.0	−371.08130	−45.0	−41.0	−42.2
19	−366.85280	−66.8	−371.10788	−61.7	−57.6	−58.5
TS15	−366.82926	−52.0	−371.08439	−47.0	−42.9	−44.2
20	−366.86764	−76.1	−371.12173	−70.4	−65.8	−66.8
H migration from **18**						
TS16	−366.82657	−50.3	−371.09944	−56.4	−54.1	−55.3
21	−366.86386	−73.7	−371.12223	−70.7	−67.3	−68.0
TS17	−366.82668	−50.4	−371.10154	−57.7	−55.6	−56.7
22	−366.87097	−78.2	−371.13012	−75.7	−71.6	−72.5
TS18	−366.82843	−51.5	−371.10249	−58.3	−56.1	−57.3
23	−366.86742	−76.0	−371.12453	−72.2	−68.7	−69.5
TS19	−366.82366	−48.5	−371.09862	−55.9	−53.8	−54.9
24	−366.86628	−75.2	−371.12635	−73.3	−69.3	−70.0

Phenyl Cation + Methyl Fluoride. The main argument of the Speranza group [6] against the proposals of Dewar and Reynolds [2] that automerization takes place not in free phenyl cations, but rather in complexes with substrates, is that it is observed in the reaction of phenyl cations with methyl halides. The possibility of methyl migration in the complex was rejected. However, in the first part of the present communications we have shown that the predicted barrier heights for methyl migrations in the complexes between the phenyl cation and methanol are comparable to those for hydrogen migration and they are all significantly lower than the complexation energy. Below we shall discuss these procceses for reactions with methyl fluoride.

There are three plausible ways of the phenyl cation interaction with the methyl fluoride molecule: addition to the fluorine lone pairs, and insertion to the CF and CH bonds. In contrast to the phenyl cation−methanol system, the addition complex to CH_3F **15** (Figure 2) is not one of the lowest energy. The insertion complexes to the CF bond **16** and to the CH bond **17** (Figure 2) are more stable by 16.3 and 21.9 kcal/mol (Table 2). This is in keeping with the results of the site selectivity study of phenylation of alcohols and alkyl chlorides.[15] It was shown that the oxygen *n*-center is the preferential site of attack by the phenyl cation, while in alkyl halides insertion into the C−Hal bond is predominant.

However, the CF insertion complex **16** may also be produced from the addition complex **15** by methyl migration (through **TS12**) with a barrier height (23.7 kcal/mol) below the complexation energy of the adduct **15** (33.5 kcal/mol). The preferential formation of **16** may be due to this fact. Although **17** is more stable than **16** by 5.6 kcal/mol there are no obvious ways of isomerization of **15** to **17**. And as in the case of methanol we believe that the *n*-center is the most attractive site for interaction with phenyl cations provided that they are free to reorientate.

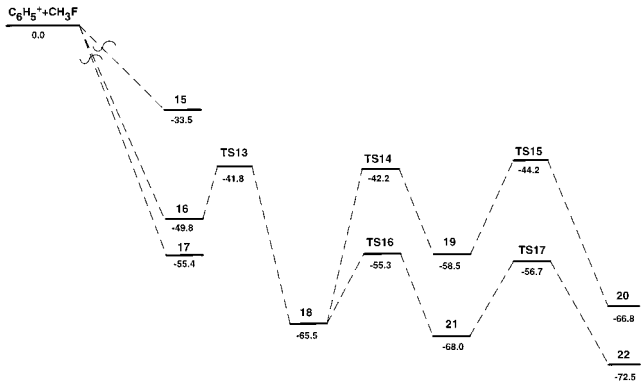

Figure 4. Potential energy diagram for stationary points in the $C_6H_5^+ + CH_3F$ system.

The *ipso*-methylated fluorobenzene cation **16** may undergo methyl migration to form *ipso*-protonated *ortho*-fluorotoluene **18** (Figure 2 and Figure 4). The barrier height for this process (**TS13**) is only 8 kcal/mol (41.8 kcal/mol below reactants). This is a decisive step, the probable high barrier for which was the main argument of the Speranza group[5,6] against proposition of Dewar and Reynolds.[2] One can see that after this step there is no difference in the behavior of arenium ions (proton ring migrations) formed either from phenyl cation−methanol or from phenyl cation−methyl fluoride interactions.

The further isomerization of this cation may go either by methyl migration (through **TS14** to **19**, Figure 2) or by proton migration through **TS16** to **21**, Figure 2). The latter channel has a barrier with a height of 10.2 kcal/mol, while methyl migration has a higher (23.3 kcal/mol) barrier. The subsequent proton shifts produce different isomers of protonated *ortho*-fluorotoluene (**22**, **23,** and **24**, Figure 2) with structure **22** corresponding to the global energy minimum of the system. The barrier heights for these transformations are 11.3 kcal/mol (**TS17**), 15.3 kcal/mol (**TS18**), and 14.6 kcal/mol (**TS19**).

Methyl shifts produce *ipso*-protonated *meta*- **19** and *para*-fluorotoluenes **20**. The barriers for CH_3 migration are 23.3 kcal/mol (**TS14**) and 14.3 kcal/mol (**TS15**). Although the barriers for methyl shifts are higher than those for H shifts, all these barriers are substantially below the complexation energy.

Four neutral tritiated aromatic products were observed in the gas chromatographic study of the reactions between nucleogenic phenyl cations and methyl fluoride,[6] i.e., fluorobenzenes, toluene, fluorotoluene, and benzyl fluoride. The last product which obviously originates from deprotonation of the CH insertion complex **17** gives 4−7% relative yield under all experimental conditions, but the distribution of the first three products strongly depends on the methyl fluoride pressure and the presence of the base (NH_3). Without the base, fluorobenzenes and toluene have nearly equal yields, while addition of NH_3 results in the predominant formation of fluorobenzenes. Fluorotoluene has almost constant yield (19−24%) under all experimental conditions. These three products (C_6H_5F, $C_6H_5CH_3$, and $FC_6H_4CH_3$) may originate from **16** which is the encounter CF insertion complex, but also may be produced from the most probable encounter complex **15** (adduct). Loss of the methyl group of this cation gives fluorobenzene (note, that it is the predominant product in the presence of a base). However, the low barrier for the CH_3 shift (8 kcal/mol) allows it to isomerize to **18**. The constant presence of $FC_6H_4CH_3$ which may be produced by deprotonation of **18** shows that this step is available under all experimental conditions. Moreover protonated *ortho*-fluorotoluene is much more stable than any of the encounter complexes **15**−**17**. That is why it may be considered as a key structure for the formation not only of $FC_6H_4CH_3$, but also C_6H_5F at low pressures. More difficult is to rationalize the appearance of the labeled toluene within this mechanism. However, the significant drop in its yield with addition of the base may indicate withdrawal of fluorine by some electrophiles.

The observed appearance of fluorobenzene isomers, in which the tritium label is in a different position in the ring from the nascent phenyl cation, and the decrease of their yield with pressure growth may be explained by the same mechanism as proposed for anisole. Low barriers (ca. 10 kcal/mol) for hydrogen shifts allow the proton to travel from *ipso*-position **18** to *para*- **23** and back (note that **18** and **23** have similar energies). In the low-pressure experiments the vibrationally excited complex has a sufficient lifetime for the subsequent H-shifts which may produce the T-position isomers of fluorobenzene observed in the experiment.[6] Thus, the predicted potential surface of isomerization in the $C_6H_5CH_3F$ system can explain all observed products including T-isomers of fluorobenzene the observation of which was believed to be the main argument in favor of automerization in the free phenyl cation.[6]

Conclusions

1. From the four plausible ways of phenyl cation interaction with the methanol molecule the addition complex (adduct) is of the lowest energy, while in the phenyl cation−methyl fluoride system the insertion complex (into the CF bond) is by 11 kcal/mol lower than the adduct. The barrier heights for isomerization of the adduct by the CH_3 group shift to the CO(F) insertion complex are 42 kcal/mol (CH_3OH) and 24 kcal/mol (CH_3F). These values are substantially lower than the exothermicity of the addition of the phenyl cation to the methanol molecule (67 kcal/mol) and methyl fluoride (33.5 kcal/mol).

2. In the methanol system the hydroxyl group H of the adduct may migrate to the phenyl ring carbon forming *ipso*-protonated anisole with a 40 kcal/mol barrier height. Further H-migration into *ortho*-, *meta*-, and *para*-positions have barrier heights of 0.5, 23, and 7 kcal/mol.

3. The CO(F) insertion complex may also undergo further isomerization by CH_3-shift from the *ipso*- into the *ortho*-position forming protonated cresols (the methanol system) and protonated fluorotoluenes (the methyl fluoride system). The barrier heights are 5 and 8 kcal/mol, correspondingly.

4. H-ring migration barrier heights in protonated fluorotoluenes are 11 and 15 kcal/mol, while for CH_3 migrations these are 23 and 14 kcal/mol. Thus the barrier heights for methyl migrations do not significantly exceed those for proton migrations and they may all be overcome with the excess complexation energy stored in the system. These results counter the earlier objections that methyl migrations cannot occur in the phenyl cation−methyl fluoride system.

5. The global minimum in the $C_6H_5^+ + CH_3OH$ system is *para*-protonated anisole and in the $C_6H_5^+ + CH_3F$ system *meta*-protonated *ortho*-fluorotoluene. In both these structures the position of protonation is *para*- toward the O(F) atom.

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