

Gaseous Arenium Ions at Atmospheric Pressure: Elementary Reactions and Internal Solvation Effects

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Introduction

Mechanistic studies of ionic processes in the gas phase are directed toward two major goals. The first is to understand reaction pathways operative in the upper atmosphere, interstellar space, plasmas, and flames. The second one is to assess reactivity patterns unaffected by the presence of solvents, counterions, solutes, or catalysts.^{1–3a} This effort requires, however, overcoming problems peculiar to gas-phase reactivity studies performed in the low-pressure regime (from 10^{-8} to a few Torr) typical of most mass spectrometric approaches. Under these conditions, most ionic reactions occur in a single collision event, with the reagent species retaining their initial energy content throughout the route to products. Because the formation of encounter complexes from the isolated partners invariably releases electrostatic binding energy, the ensuing reaction pattern will be dominated, in general, by chemically activated species.³ Within this framework, the route to products will be influenced by the internal energy content of the ion–neutral intermediate, which will depend, in turn, on its specific formation route.

It is thus frequently found that ion–molecule reactions, conceivably leading to the same ionic intermediate, may, in fact, take a different course, depending on their different exothermicity. As an example, one may consider the gas-phase nitration of arenes (ArH). Nitration adducts (NO_2ArH^+) are observed only from the reaction of $\text{ArH}^{+\bullet}$ with NO_2 , whereas the reaction of NO_2^+ with neu-

tral ArH proceeds by charge and oxygen-atom transfer.⁴ This result is likely due to the overall energy content of the ArH/NO_2^+ pair, which lies 12 kcal mol⁻¹ higher than the $\text{ArH}^{+\bullet}/\text{NO}_2$ pair, opening alternative high-energy pathways. The drawback of an ill-defined temperature that is attached to ionic processes in dilute gas phase is circumvented by a radiolytic methodology of generating ions at higher pressures (up to several atmospheres), where the greater frequency of unreactive collisions may quench "hot" ion–neutral complexes and ionic intermediates, bringing them to thermal equilibrium with the surroundings.⁵ This condition needs to be checked, however, for each specific system under investigation.

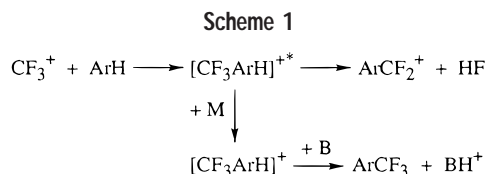
The effect of a different pressure regime on ionic processes is exemplified by the CF_3^+ reaction with arenes, which at a pressure of ca. 10^{-3} Torr yields ArCF_2^+ as the major product by an addition–elimination process.⁶ The same reaction proceeds in a different way in CF_4 at atmospheric pressure, yielding ArCF_3 as the major neutral product from the electrophilic addition of CF_3^+ at a ring carbon, followed by neutralization of the charged intermediate by proton transfer to a base (B in Scheme 1).⁷ Characteristics of the radiolytic technique are outlined with reference to Scheme 1. In the first place the different reaction pattern prevailing at atmospheric pressure is ascribed to an efficient collisional thermalization by the bath gas (M), which removes the excess energy released by the exothermicity of the association of CF_3^+ with ArH to form $[\text{CF}_3\text{ArH}]^{+\bullet}$, which, unless efficiently thermalized, undergoes fragmentation. Unreactive collisions with M occur with pseudo-first-order rate constants in the range of 10^{10} – 10^{11} s⁻¹ and are followed by the slower proton transfer to B, present at typical partial pressures on the order of 1 Torr.

The base neutralizes $[\text{CF}_3\text{ArH}]^+$ ions that have undergone an average of 10^3 unreactive collisions with M and which are therefore truly thermalized species. It may be further pointed out that the concentration of B determines the lifetime of $[\text{CF}_3\text{ArH}]^+$, setting a "clock" to time the rate of possible unimolecular rearrangement processes. Finally, the reaction sequence yields a neutral product, which may be assayed and characterized by techniques such as GLC-MS and NMR.

The title species, of paramount importance as key intermediates of electrophilic aromatic substitution reactions,⁸ are amenable to mechanistic studies by mass spectrometric and radiolytic techniques.⁹ They have proven to be versatile benchmark models for the study of elementary processes such as proton migration, which may occur in both intra- and intermolecular fashions. This Account primarily focuses on proton migration reactions involving arenium ions. Additionally, we shall attempt to evaluate the effect of a second unsaturated ring bound by an aliphatic chain of variable length on the stability and the reactivity of the arenium ion. A "spectator" phenyl ring is expected to provide some electrostatic stabilization by the interaction of its π electron system

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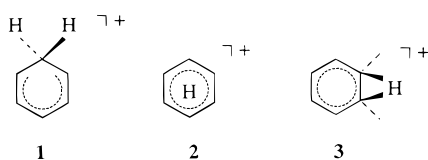
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with the positively charged moiety, thus behaving like a neighboring molecule of an aromatic solvent.¹⁰

The Protonation of Simple Aromatics

The protonation of benzene occurs at one of the six equivalent carbon atoms to form C_6H_7^+ benzenium ions having the σ -complex structure **1**.¹¹ Experimental evidence that confirms **1** to be the most stable gas-phase structure for protonated benzene has been gathered recently.¹² The unimolecular dissociation and the bimolecular neutralization by strong bases of $\text{C}_6(\text{H},\text{D})_7^+$ ions of varying D content has been studied by FA-SIFT, showing that all seven H/D atoms have become equivalent in the experimental time frame (10^{-3} s), pointing to a H/D randomization process that is fast compared to subsequent reactions. The benzenium ion structure **1** has been supported by the formation of $\text{C}_6\text{D}_5\text{H}$ (deuterated benzene incorporating a H atom) from the reaction of $\text{CH}_5^+/\text{C}_2\text{H}_5^+$ ions, formed by radiolysis of methane, with benzene- d_6 . In no case has any evidence been obtained in favor of a proposed face-protonated π complex **2** for ground-state, protonated benzene, where the proton delivered by the acid would retain a unique position.¹³ Theoretical calculations have contributed to settling this problem, showing that **1** is more stable than **2** by 47.6 kcal mol⁻¹.¹⁴ A third structure (**3**) lies 7.9–8.3 kcal mol⁻¹ above **1** and corresponds to the transition state for the 1,2-hydrogen migration process.^{14,15}



Simple aromatics, such as monosubstituted benzenes, present more than one basic site. Assessing the site of protonation in polyfunctional compounds has presented a challenge, owing to the limited ability of conventional mass spectrometric techniques to distinguish between relatively complicated structures differing only in the position of a proton. We have approached the problem by the radiolytic technique, studying the protonation of deuterated arenes. The protonation of toluene- d_8 by $\text{CH}_5^+/\text{C}_2\text{H}_5^+$ ions leads to incorporation of one H atom on the ring with the following distribution, established by ¹H NMR analysis of the product: 44% ortho, 37% meta, and 19% para.¹⁶ The nearly statistical distribution is consistent with an unselective protonation of toluene by the powerful Brønsted acids, a process exothermic by 58 (for CH_5^+) and 27 (for C_2H_5^+) kcal mol⁻¹, respectively. Alternatively, the protonation of aromatics can be performed in an indirect way, that is, by generating an

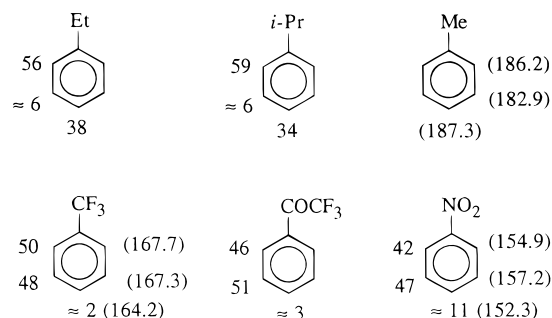
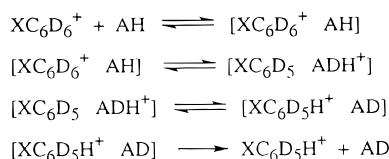


FIGURE 1. Hydrogen distribution within $\text{XC}_6\text{D}_4\text{H}$, from H/D exchange between XC_6D_6^+ and H_2O (ca. 1 Torr) in radiolytic experiments at 40 °C and 1 atm. Theoretical PA values for PhMe,¹⁹ PhNO₂,²⁰ and PhCF₃^{7a} are in parentheses.

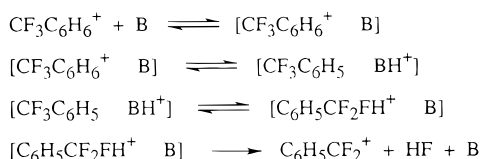
Scheme 2



arenium ion and allowing it to react with a base containing an exchangeable hydrogen and having a proton affinity (PA) lower than that of the arene. Under these conditions, the use of D-labeled reagents results in a H/D exchange process, outlined in Scheme 2.^{16,17} The reagent arenium ions XC_6D_6^+ are formed by “X+” attack on benzene- d_6 , a procedure that may be extended to all charged electrophiles that may be formed by gas-phase radiolysis.

The sequence outlined in Scheme 2 is initiated by collision of the reagents forming an ion–neutral complex, $[\text{XC}_6\text{D}_6^+ \text{AH}]$, where hydron (H^+/D^+) transfer events occur, which take advantage of the electrostatic energy released in the ion–molecule encounter to overcome the barrier associated with the endothermic D^+ transfer from XC_6D_6^+ to AH. The H/D exchange reaction is thus an example whereby elementary reactions take place within chemically activated ion–neutral complexes, prior to their thermal equilibration with the surroundings.¹⁸ The key step involves the protonation of XC_6D_5 , formed within the complex, by ADH^+ ions, behaving as mild Brønsted acids. The H distribution found within $\text{XC}_6\text{D}_4\text{H}$, illustrated in Figure 1,¹⁷ bears a close relationship to the site-specific PA evaluated by theoretical calculations.^{7a,19,20} Ethyl- and *i*-propylbenzene show a distinct preference for protonation at the ortho/para positions, consistent with the higher basicity of these sites, in contrast with the statistical protonation of toluene by the strong $\text{CH}_5^+/\text{C}_2\text{H}_5^+$ acids. In the presence of electron-withdrawing groups, such as CF_3 and NO_2 , the ring H incorporation is limited and is characterized by an ortho/meta distribution. Thus, CF_3 and NO_2 do not behave as simple meta-orienting groups toward electrophilic attack in the gas phase, in contrast with the reactivity observed in solution.²¹ Protonation at the ortho position with respect to $\text{X} = \text{CF}_3$, COCF_3 , and NO_2 appears to benefit from the interaction of the hydrogens on the tetrahedral carbon with the electronegative atoms on the substituent.

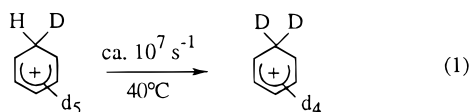
Scheme 3



Electron-withdrawing substituents represent alternative protonation sites, which may be favored thermodynamically with respect to the ring carbons. An example is provided by $\text{CF}_3\text{C}_6\text{H}_5$, where the fluorine atoms have a PA of $170.3 \text{ kcal mol}^{-1}$ as compared with $167.7 \text{ kcal mol}^{-1}$ for the most basic ring carbons.^{7a} Nevertheless, ring-protonated $\text{CF}_3\text{C}_6\text{H}_6^+$ ions can be formed in the cell of a FT-ICR instrument using unselective Brønsted acids, such as CH_5^+ , C_2H_5^+ , and SO_2H^+ .^{7a} These $\text{CF}_3\text{C}_6\text{H}_6^+$ ions undergo a slow thermal decomposition to $\text{C}_6\text{H}_5\text{CF}_2^+$, losing HF in a process that may proceed via isomerization to $\text{C}_6\text{H}_5\text{CF}_2\text{FH}^+$. The presence of weak bases promotes the formation of $\text{C}_6\text{H}_5\text{CF}_2^+$ ions, possibly through "proton-transport" catalysis.²² The base-catalyzed isomerization-fragmentation process illustrated in Scheme 3 is one of the few examples reported for gas-phase ions.

1,2-Hydrogen Shifts in Arenium Ions

The radiolytic approach to the study of unimolecular rearrangements of gaseous ions examines shorter time scales than do conventional mass spectrometric techniques. Fast hydrogen scrambling within arenium ions is known to occur both in solution and in the gas phase.^{9,11} For example, the benzenium ion undergoes complete equilibration of the seven hydrogens in the gas phase prior to unimolecular loss of H_2 within 10^{-5} s . A radiolytic study of the D^+ transfer reaction from $\text{C}_6\text{D}_6\text{H}^+$ ions has provided useful estimates of the temperature dependence of the H/6D equilibration rate within $\text{C}_6\text{D}_6\text{H}^+$.^{12b} At $120 \text{ }^\circ\text{C}$ this process is complete within 10^{-7} – 10^{-8} s , whereas at $40 \text{ }^\circ\text{C}$ D^+ shifts on the aromatic ring occur at an estimated rate of ca. 10^7 s^{-1} (eq 1).



The degenerate rearrangement of benzenium ions has provided only qualitative data. More quantitative studies of alkylated arenium ions, where 1,2-hydron shifts can occur in a nearly degenerate way between positions of comparable basicity, have been undertaken.²³ This condition obtains in the alkylation of toluene by Me_3C^+ ions from the radiolysis of $i\text{-C}_4\text{H}_{10}$, where the para-substituted product has nearly the same PA values for the alkylated and unsubstituted ring positions. 1,2-Hydron shift processes have been revealed by the use of labeled reagents. Thus, *tert*-butylation at the para position of $p\text{-MeC}_6\text{DH}_4$ shows that retention of the D-atom in the substitution product depends on the presence of a strong base, increasing with decreasing partial pressure of piperidine,

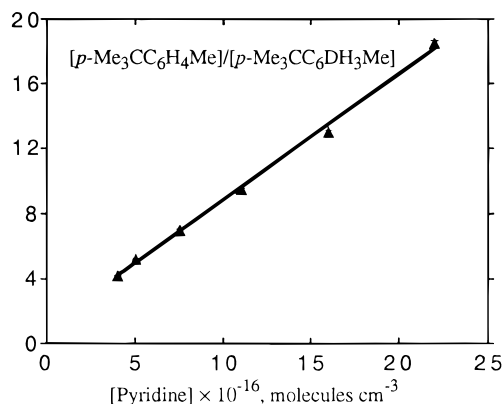
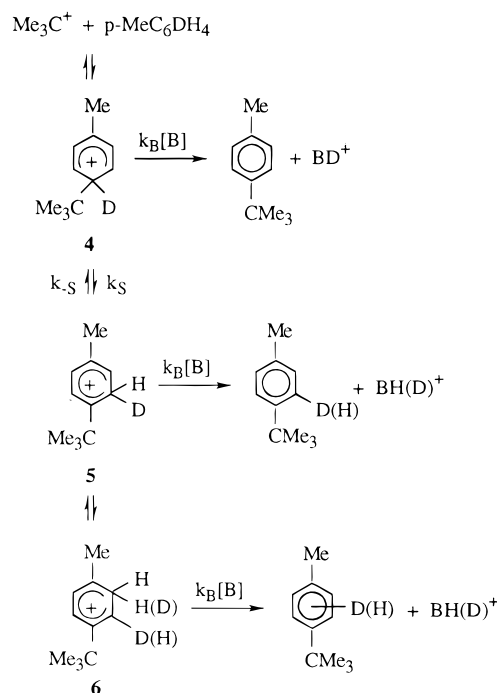


FIGURE 2. Dependence of the relative yield of unlabeled to deuterated products from the Me_3C^+ reaction with $p\text{-MeC}_6\text{DH}_4$ on the concentration of pyridine at $40 \text{ }^\circ\text{C}$.

Scheme 4



[B]. Scheme 4 accounts for the effect of base concentration, which affects the lifetime of the primary arenium intermediate **4**. Deprotonation of **4**, rapid at high [B], yields mostly unlabeled *p-tert*-butyltoluene. As the lifetime of **4** becomes longer, an increasing fraction of ions isomerizes to **5** by 1,2-deuteron shift. The 1,2-hydron shift could conceivably proceed as far as **6**, though this step is not detected under the prevailing experimental conditions, as demonstrated by the nearly complete retention of deuterium in the *p-tert*-butyltoluene formed upon alkylation of $o\text{-MeC}_6\text{DH}_4$. The kinetic analysis of the mechanistic pattern leads to a linear dependence (eq 2) of the relative yield of deuterated and unlabeled products on the piperidine partial pressure, [B] (Figure 2).

$$\frac{[p\text{-Me}_3\text{CC}_6\text{H}_4\text{Me}]}{[p\text{-Me}_3\text{CC}_6\text{DH}_3\text{Me}]} = \frac{2(k_{-S} + k_B[\text{B}])}{k_S} + 1 \quad (2)$$

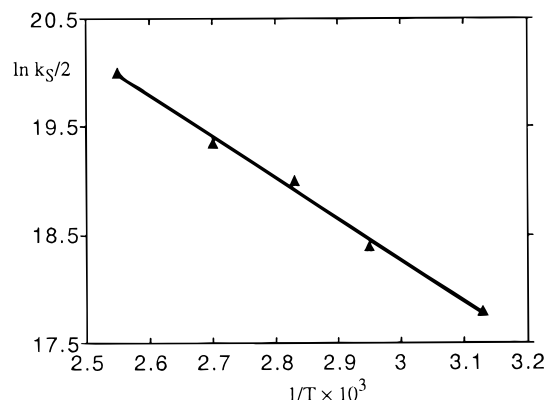


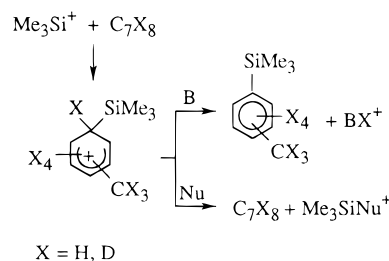
FIGURE 3. Arrhenius plot showing the dependence of k_5 on $1/T$ (K^{-1}).

Table 1. Rate Constants for Hydron Migrations in Gaseous Arenium Ions at 47 °C

Process	Kinetic Data (k , s^{-1})
	$1.0 \pm 0.2 \times 10^8$ (Ref. 23)
	$8.8 \pm 4.0 \times 10^8$ (Ref. 23)
	$> 10^9$ (Ref. 23)
	$< 10^6$ (Ref. 23)
	$2.9 \pm 0.6 \times 10^6$ (Ref. 24)

The slope of the plot gives the rate constant for the 1,2-deuteron shift, assuming that neutralization by the strong base is fast and unaffected by any kinetic isotope effect (KIE) (an assumption that has been tested and proven to be correct). The k values obtained at different temperatures are drawn in an Arrhenius plot (Figure 3) yielding $E_a = 7.6 \pm 0.2$ kcal mol $^{-1}$ and $\log A = 12.9 \pm 0.4$. The E_a value obtained for a nearly thermoneutral 1,2-deuteron shift process within **4** is comparable to the experimental value of 10 ± 1 kcal mol $^{-1}$ for the activation energy of 1,2-H shift in benzenium ion in superacid solution¹¹ and also to the calculated energy difference between **1** and **3**.^{14,15} Table 1 summarizes a few typical data concerning the kinetics of hydron migration involving gaseous arenium ions. The comparison of the first two

Scheme 5



entries, related to the *p*-*tert*-butyltoluenium system, shows that a distinct primary KIE is involved in the 1,2-hydron shift. It is a fortunate circumstance that the rates of thermoneutral 1,2-hydron shifts fall within the observation time window of the radiolytic technique. As evident from Table 1, the process becomes exceedingly fast when energetically favored (Table 1, entry 3), whereas no 1,2-hydron migration is observed from a silylated carbon (Table 1, entry 4). It is known from both theoretical and experimental studies that a silyl group confers an enhanced basicity on the adjacent aromatic carbon, thus rendering the ipso hydrogen unwilling to migrate. It is remarkable that no 1,2-hydron shift takes place even if the migration terminus is activated by a para methyl group. Indeed, the reverse reaction should occur, as reported for arenium ions obtained from protonation or alkylation of trimethylsilylbenzenes.²⁵ The last two entries in Table 1 introduce the following related issues.

Mechanistic Role of the Deprotonation of Intermediate Arenium Ions

The reluctance of a hydron to migrate from a silylated carbon is responsible for the major problem encountered in accomplishing aromatic silylation by R_3Si^+ ions, namely, the requirement for a strong, preferably hindered, nitrogen base to deprotonate the silylated arenium ion. If this condition is not met, no neutral silylated products can be formed, because the silylated arenium ion is prone to undergo an easy desilylation channel, promoted by nucleophiles.²⁶ As shown in Scheme 5, the product determining step involving hydron removal from the silylated intermediate competes with nucleophilic desilylation. If this mechanistic pattern is correct, a primary KIE is expected to arise from a faster rate of H^+ versus D^+ transfer to a suitable base, both competing with a desilylation process that is less affected by the isotopic substitution.

This hypothesis was tested in the competitive silylation of toluene/toluene- d_8 mixtures in the presence of amines of varying basicity.²⁷ The highest k_H/k_D values of ca. 4 were obtained in the presence of NH_3 , the least basic compound that can still lead to some silylated products. The minor role played by secondary KIEs was confirmed by the silylation at the meta position of *m*- MeC_6DH_4 , displaying k_H/k_D ratios comparable to those obtained from the toluene/toluene- d_8 mixture.

The facile nucleophilic desilylation of silylated arenium ions, which limits the formation of silylated aromatic

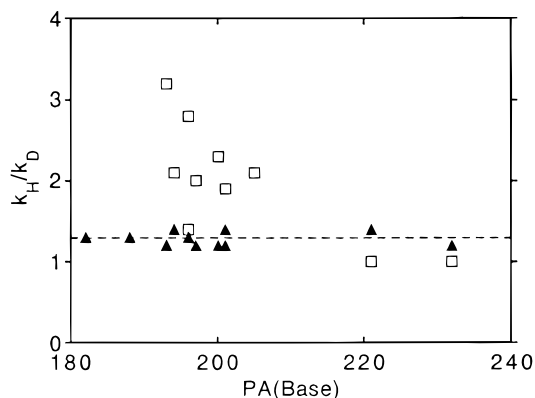
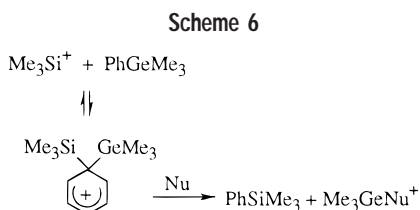


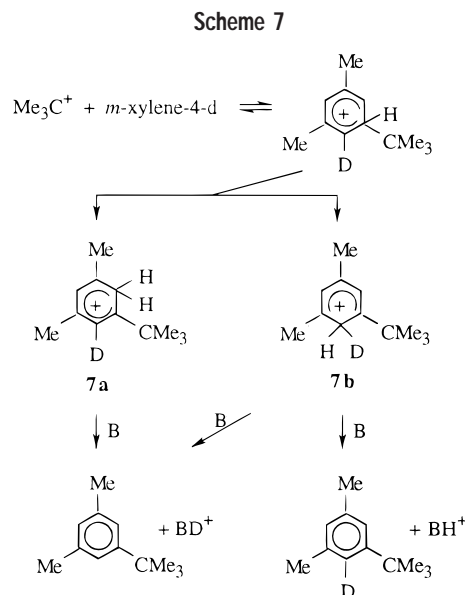
FIGURE 4. k_H/k_D values for the *tert*-butylation at the 5 position of *m*-xylene/*m*-xylene- d_{10} mixtures (triangles) or *m*-xylene- d_4 (open squares) vs PA of the added base.



products, is related to the “super-proton” character of $\text{Me}_3\text{-Si}^+$. In this view, the key to obtaining silylated products lies in the choice of a group endowed with superior leaving ability as cationic moiety. Because the rate of protolytic cleavage of PhYMe_3 increases from $\text{Y} = \text{Si}$ to $\text{Y} = \text{Ge}$, PhGeMe_3 was selected as a substrate for radiolytic silylation. No base was required to obtain silylated aromatic products that arose primarily from Me_3Si^+ attack at the germylated carbon via Me_3Ge^+ displacement (Scheme 6).²⁸

Unimolecular 1,2-hydron shifts and hydron transfer to an external base may both control the reactivity of arenium ions as exemplified by the intermediates obtained from the alkylation at the 5 position of *m*-xylene by Me_3C^+ ions.²⁹ The kinetic role of these two processes in the overall electrophilic substitution reaction was uncovered using KIE as a mechanistic tool. The relative reactivities of *m*-xylene and *m*-xylene- d_{10} in the formation of the *tert*-butylated products at the 5 position are constant (triangles, Figure 4), irrespective of the PA of the added base. By contrast, a base-dependent KIE affects the formation of *tert*-butylated products at the 5-position of *m*-xylene- d_4 (open squares, Figure 4). The combined information on the different dependence of k_H/k_D ratios versus PA of the base corroborate the mechanistic pattern shown in Scheme 7.

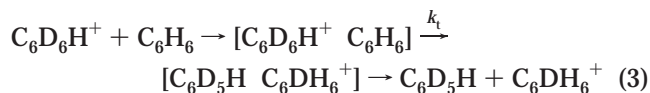
The arenium ion from Me_3C^+ attack at the 5 position of *m*-xylene is not significantly resonance-stabilized by the two meta methyl groups. Hence, it is prone to undergo either back dissociation or 1,2-hydron shift to yield the most stable isomer **7**. Formation of **7** is irreversible; therefore, the 1,2-hydron shift is the rate-determining step of the reaction and should display a primary KIE. The relative reactivity of *m*-xylene versus *m*-xylene- d_{10} should not be affected by the PA of the base. The base is needed,



however, to neutralize **7** and a base dependent KIE will be observed if H^+ and D^+ transfer occur in competition, as in the case of **7b**. In this case, the observed KIE affects the product-determining step.

Internal Solvation of Arenium Ions by a “Spectator” Phenyl Ring

The last entry in Table 1 shows that a phenyl group attached to an alkylated arenium ion by an ethylene chain partakes to an interannular hydron exchange process whose rate, activation parameters, and KIE have been characterized by the radiolytic approach.^{24,30} The early studies on this system employed mass spectrometric techniques based on the metastable loss of benzene.^{9a} Complete scrambling of the 11 ring H/D atoms in protonated $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{D}_5$ was observed, thus showing that the time scale of the experimental technique adopted does not allow the kinetic study of the process. Kinetic information was indeed obtained by the radiolytic approach. It is interesting to compare the rate constant for the interannular D^+ transfer, $k = 3 \times 10^7 \text{ s}^{-1}$ at 120°C , with the value of $k_t \approx 1 \times 10^9 \text{ s}^{-1}$ obtained at the same temperature for the process involving benzenium ion and neutral benzene within the $[\text{C}_6\text{D}_6\text{H}^+ \text{ C}_6\text{H}_6]$ complex (eq 3).^{12b} The intramolecular transfer is clearly disfavored by



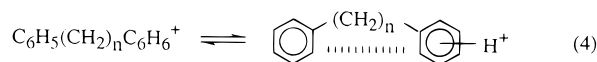
conformational constraints that do not affect the benzenium–benzene reaction, which therefore proceeds at a faster rate.

The interannular hydron migration process reveals a bias that comes from folding a polymethylene chain. The positively charged ring seeks internal solvation by the π electron density of the “spectator” ring. The chain length effect is revealed by thermodynamic and kinetic studies

Table 2. Gas-Phase Basicity of Selected Diphenylalkanes³¹

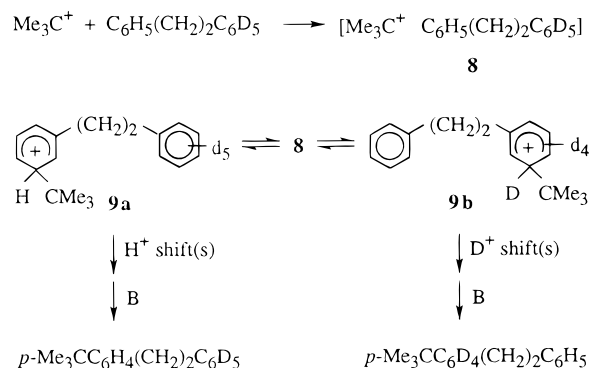
compound	GB ₃₀₀ (kcal mol ⁻¹)
Ph ₂ CH ₂	184.5
Ph(CH ₂) ₂ Ph	185.8
Ph(CH ₂) ₃ Ph	188.4
Ph(CH ₂) ₄ Ph	187.0
Ph(CH ₂) ₅ Ph	187.5
Ph(CH ₂) ₆ Ph	187.9
<i>trans</i> -1,4-diphenylcyclohexane	185.1
<i>trans</i> -1,4-dibenzylcyclohexane	185.4

of the gas-phase chemistry of a series of α,ω -diphenylalkanes. The gas-phase basicity (GB) of Ph(CH₂)_{*n*}Ph (*n* = 1–6) and of other selected diaryl compounds have been measured by FT-ICR.³¹ As Table 2 summarizes, (i) diphenylalkanes display GB values that are consistently higher than that of toluene, despite the similar electron-releasing effect of methyl and phenylalkyl groups; (ii) Ph(CH₂)₃Ph has a higher GB than its higher and lower homologues; and (iii) phenyl groups separated by a rigid link (as in 1,4-diphenyl- and 1,4-dibenzylcyclohexane) have GB values ca. 2 kcal mol⁻¹ lower than α,ω -diphenylalkanes in which the phenyl groups are separated by the same number of C–C bonds. This evidence suggests that under the prevailing conditions (25 °C and 10⁻⁷–10⁻⁸ Torr) protonated α,ω -diphenylalkanes attain a bent structure where the uncharged phenyl ring lends electrostatic stabilization to the arenium ring (eq 4). If the entropy loss in



the conformational equilibrium shown in eq 4 is estimated on the basis of the frozen rotations at the C–C bonds, a value of $\Delta H^\circ = -10$ kcal mol⁻¹ is derived, which agrees with the 11 kcal mol⁻¹ binding energy of the [benzenium benzene] complex, the intermolecular model of the intramolecular phenyl ring/arenium ring interaction.

Gas-phase alkylation of conformationally flexible α,ω -diphenylalkanes exhibits distinct rate-determining and product-determining steps. The presence of two phenyl rings enhances the stability of initially formed noncovalent ion–neutral complexes, where the attacking ion benefits from the interaction with two π electron densities. This effect may exert a major influence on reactivity. An example is the alkylation of α,ω -diphenylalkanes of varying chain length by radiolytically formed Me₃C⁺ ions.³² Ph(CH₂)₂Ph and higher homologues react at the same rate, whereas a decreasing reactivity is shown by PhCH₂Ph and toluene. There is no selectivity between *m*-MeC₆H₄(CH₂)₂Ph and Ph(CH₂)₂Ph in a mixture. Nevertheless, attack at the methylated ring of *m*-MeC₆H₄(CH₂)₂Ph is favored by a factor of 2 over attack at the unsubstituted ring. These observations imply that the electrophilic attack by Me₃C⁺ (which is sensitive to the electron-donating effect of a methyl group on the aromatic ring) follows a rate-determining collision event. The same conclusion is supported by experiments with deuterium-labeled substrates. Me₃C⁺ attacks Ph(CH₂)₂Ph and C₆D₅(CH₂)₂C₆D₅ with equal efficiency but the unlabeled ring of C₆H₅(CH₂)₂C₆D₅ is more rapidly substituted than the deuterated

Scheme 8

one. Scheme 8 shows a mechanism for *tert*-butylation at the para position of C₆H₅(CH₂)₂C₆D₅ that accounts for these data.

The encounter complex **8** shows a negligible tendency to back dissociate since two phenyl rings stabilize the Me₃C⁺ ion. The reaction proceeds by reversible C–C bond formation: return to **8** competes with 1,2-hydron shift within **9**, which is eventually followed by neutralization. An intramolecular KIE arises from the different rate of H⁺ versus D⁺ shift, favoring the formation of substitution products at the unlabeled ring. The major reactivity difference, as compared to that for monocyclic aromatic compounds (such as toluene) or diphenyl compounds lacking conformational flexibility (such as PhCH₂Ph), lies in the “microsolvated” environment that positive ions experience within ion–neutral complexes resulting from polarizable π electron density from the two aromatic rings. Interconversion of ions **9a** and **9b** is confirmed by forming ions of type **9** via an alternative route.³³ Alkylation of *p*-Me₃C–C₆H₄(CH₂)₂C₆D₅ yields products exhibiting interannular Me₃C⁺ transfer. Products involving loss of Me₃C were also observed. Their yield is small, though, relative to the corresponding products from model substrates with a single aromatic ring, depending on the exothermicity of the alkylation step. In the framework of Scheme 9, ions **9** cleave reversibly to give **8** and the latter species is resistant to dissociation.

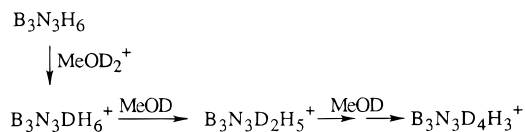
To summarize, the additional phenyl ring in Ph(CH₂)_{*n*}Ph provides electrostatic stabilization to charged species within ion–neutral complexes and to a linked arenium moiety. It may behave as a base leading to interannular hydron transfer, and it may also display chelating properties with respect to metal ions whose coordination demand is not exhausted by the first aryl ring.³⁴ This type of reactivity was displayed in a comparative study of the reactivity of Cr(I) ions with simple aromatics and with selected α,ω -diphenylalkanes. Kinetic evidence has been obtained by FT-ICR indicating that, for appropriate values of *n*, a sandwich-type structure is achieved allowing simultaneous coordination of Cr⁺ with the two phenyl rings of Ph(CH₂)_{*n*}Ph.

Inorganic Arenium Ions?

Compounds such as B₃N₃H₆ (borazine), B₃O₃H₃ (boroxine), and B₃P₃Ph₆ (a boron phosphorus analogue of borazine)

share some features in common with benzene, though their supposed aromaticity is a matter of debate. Among the cited compounds borazine is the most likely candidate to display aromatic character. It is therefore of interest to ascertain the reactivity behavior of protonated borazine as related to benzenium ion. Deuteron transfer from MeOD_2^+ to borazine is followed by a H/D exchange sequence (Scheme 9) that ends with the formation of $\text{B}_3\text{N}_3\text{D}_4\text{H}_3^+$.³⁵

Scheme 9



This finding shows that only three sites in the molecule are involved in the protonation process and that 1,2-hydron shifts do not occur. Moreover, an analogue of an alkylbenzenium ion is the likely intermediate in the reaction pathway leading to *N*-methylborazine from the radiolytic methylation of borazine by Me_2F^+ ions.³⁵

Concluding Remarks

The chemistry of arenium ions in a dense gaseous environment exhibits a compromise between the complexity of condensed media and highly dilute gaseous environments, where the temperature of reacting ions is not well defined. Hydron migration processes involving arenium ions have been studied and characterized by their rate constants, activation parameters, and KIE's under conditions of thermal equilibration. By excluding the leveling effect of solvent, gas-phase studies allow insight into the effects of specific interaction with single solvent molecules or with remote functional groups covalently attached to the ionic site of interest. The operation of this effect has been identified in the internal solvation provided by a phenyl group linked by a polymethylene chain to a positively charged arenium moiety. It is expected that gas-phase studies may further uncover the role of intramolecular noncovalent interactions, such as those responsible for the specificity of the folding and recognition properties of biopolymers.

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