Gas-phase electrophilic aromatic substitution of electron-rich and electron-deficient aromatic compounds

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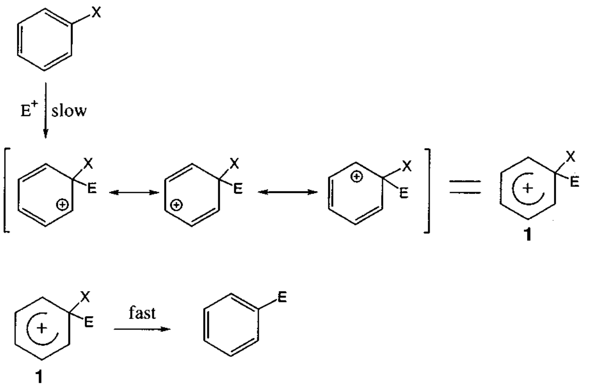
The first step in gas-phase electrophilic aromatic substitution (EAS) reactions of alkyl carbenium ions with fluoro-, chloro- and bromo-benzene, furan, thiophene and pyrrole, has been investigated by using high-pressure, chemical-ionization and tandem mass spectrometry (MS/MS). Collisionally activated dissociation (CAD) and tandem mass spectrometry, MS/MS, have been utilized for ion-structure determination. The coexistence of σ and π complexes in these reactions is a means of rationalizing the results. It has been established that the extent of π-complex formation decreases with an increased capability of the aromatic to donate electron density. Semi-empirical computations indicate that as π-electron density within the aromatic moiety increases, the energy difference between the more stable σ complex and the π complex increases, which is also consistent with experimental observations. The extent of bonding between the alkyl group and the aromatic of certain π complexes is sufficiently weak that isomerization of the alkyl moiety takes place.

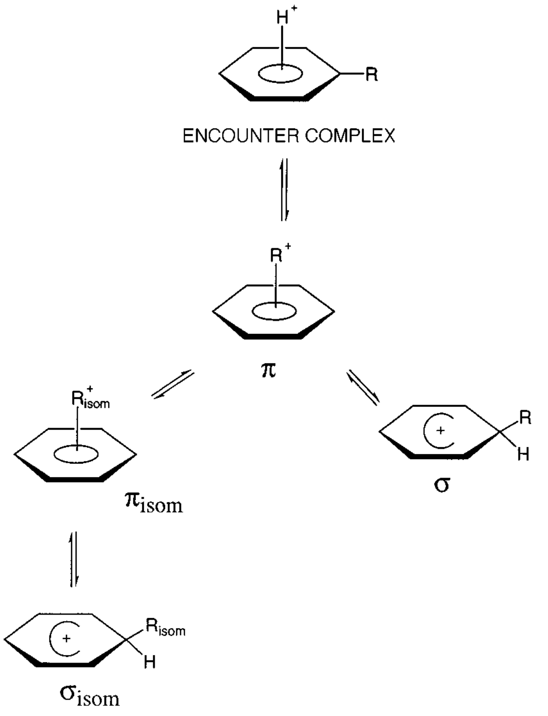
Introduction

Arenium ions, or σ complexes, are produced as intermediates in electrophilic aromatic substitution (EAS) of benzenoid species.[1,2] The long-accepted mechanism involves electrophilic attack to give an arenium ion, **1** (Scheme 1), followed by the departure of an appropriate leaving group in a final step.



Scheme 1

As early as 1946, Dewar[3] proposed that π complexes also play an important role in EAS. In the later pioneering work of Olah and co-workers,[4,5] convincing arguments were forwarded that the arenium ion mechanism indeed does involve π-complex intermediacy. Significant contributions from experiments involving gas-phase ions have come from the laboratories of Grützmacher,[6] Audier[7] and others.[8–11] In our own earlier work, we presented evidence indicating that σ and π complexes coexist as interconvertible species when arenes are protonated in the gas phase.[12] This finding, coupled with the insight gained from the other related work, led us to propose a modified arenium-ion mechanism that invokes an early π complex that can then collapse to a σ complex[12] (Scheme 2). There was no evidence of a face-protonated *vs.* edge-protonated encounter complex, and the former is presented as a matter of convenience.



Scheme 2

Although evidence for π-complex intermediacy was convincing, many concluded that π complex formation is not rate-determining and that formation of the σ complex is the slow step,[13–18] whereas others concluded that the formation of the π complex is rate determining.[4,5] One conclusion emerging from this debate is that π-complex intermediates do exist on the potential-energy surface of benzenoid EAS and are energetically accessible in some reactions and not in others (depending on the strength of the electrophile, extent of free-cation character in the attacking electrophile and the nature of the catalyst interaction with the electrophile).

Although the nature of the reactive intermediates involved in the gas-phase EAS of benzene has received much attention, less has been paid to the EAS of substituted aromatic and heterocyclic aromatic compounds. Whether π complexes form between electrophiles and substituted aromatic or heterocyclic aromatic species is uncertain. Further, if π complexes are involved, the interplay between σ and π complexes would be intriguing to investigate, especially in the light of what is known about the benzenoid systems. We show in this article that the concept of σ and π complexes allows us to rationalize the properties of arenium ions formed from substituted and heterocyclic aromatic compounds in the gas phase.

The limiting factor in the study of the intermediates formed in EAS in the condensed phase is the inability to isolate readily such transient species. The investigation of these intermediate(s) in the gas phase, however, is not subject to this limitation. For example, the ionic intermediate(s) can be readily formed within the source of a tandem mass spectrometer and analysed within the same instrument. Further, catalysts are not necessary for the promotion of the reaction, and the chemistry is simplified without solvent and more amenable to theory than solution chemistry. The difficulty with measurements in the gas phase is that spectroscopic techniques are not readily applied.

The strategy is to establish the structure(s) of the initially formed species when substituted aromatic and heterocyclic aromatic species react with alkyl carbenium ions in the gas phase. Two classes of aromatics were chosen. The first set is substituted aromatics that are electron-deficient, and include fluoro- chloro- and bromo-benzene. The second set includes the heterocyclic aromatic species pyrrole, furan and thiophene, which were chosen as representatives of electron-rich aromatics. Specific interest lies in assessing the role that π complexes play in this chemistry and in comparing and contrasting the chemistry of the aromatics within each of the two groups.

Because the physical characteristics, relative reactivities and relative stabilities of aliphatic carbenium ions in the condensed phase depend very little on media change,[19] the properties of these ionic species in the gas phase are relevant to those in the liquid phase. A comparison of mass spectrometric and calorimetric measurements shows no essential change in enthalpy trends for isomeric gas-phase secondary and tertiary carbenium ions over those in the condensed phase. Furthermore, the work of Cacace and Speranza[20–29] and their co-workers has shown that the chemistry of gas-phase arenium ions has common features with those in solution, thus forging an important link in this work. Further discussions of the literature are in several excellent reviews of this research area, which were recently published.[30,31]

Results and discussion

The nature of the ions formed in the gas-phase alkylation of substituted benzenoid and the heteroaromatic species pyrrole, furan and thiophene were determined by using tandem mass spectrometry, the methodology employed earlier in a study of the EAS of benzene.[12] Specific emphasis in this article is in determining the structure of the ion(s) by using collisional activation and tandem mass spectrometry.

I. Ion formation, dissociation and characterization

The gas-phase halo and heteroaromatic arenium ions were produced *via* electrophilic aromatic substitution (EAS). The reactions of the appropriate alkyl carbenium ions, which were generated from their corresponding alkyl iodides, with neutral aromatic species were conducted in the high-pressure, chemical-ionization (CI) source of a tandem mass spectrometer. Tandem mass spectrometry (MS/MS) was then employed to determine the structures of the ionic species.

As in earlier work centering upon the dissociations of the ions generated from the reaction of benzene and alkyl carbenium ions,[12] we rationalized the results by invoking a mixture of σ- and π-complexes (Scheme 2). The extent to which the π complex is accessed within the ion mixture is linked to the extent of R^+ formation observed upon collisional activation. The governing assumption then, and now, is that loss of the alkyl moiety as a carbenium ion (R^+) proceeds through the π complex.

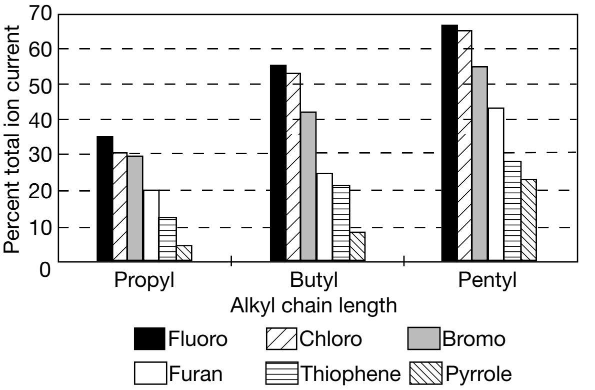


Fig. 1 Histogram representing the fraction of product-ion abundance constituted by R^+ as a function of alkyl chain length for the CAD of arenium ions formed in the reaction of R^+ and the designated aromatic species

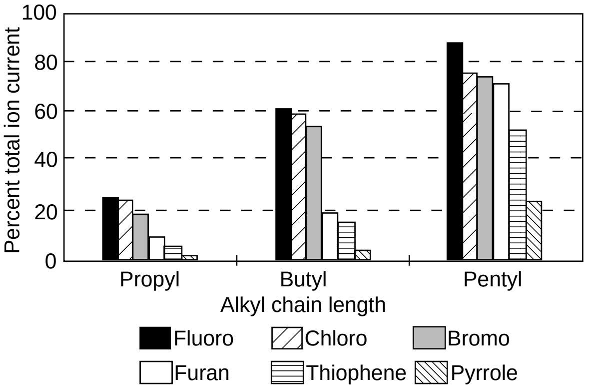


Fig. 2 Histogram representing the fraction of product-ion constituted by R^+ as a function of alkyl chain length for the metastable ion decompositions of arenium ions formed in the reaction of R^+ and the designated aromatic species

Histograms (Figs. 1 and 2) comparing the extent of R^+ formation in both the CAD and metastable-ion mass spectra of the ions generated in the reactions between the aromatic species and alkyl carbenium ions of various alkyl chain length show that each of the haloarenium complexes dissociates to R^+ to a greater extent than any of the heteroarenium ion complexes. For the haloaromatics, the amount of R^+ formation is greatest when the halogen is fluorine, and least when the halogen is bromine. For the heterocyclic aromatics, the formation of the alkyl carbenium ion with respect to that of all other fragment ions steadily decreases in the order of furan > thiophene > pyrrole. The extent of R^+ formation is greater in the electron-deficient systems and decreases when going to the electron-rich species, and this is established as a clear trend.

In the gas-phase EAS reactions involving benzene, the extent of arenium ion dissociation to R^+ increases as the chain-length of the alkyl group increases.[9,12] The ability of the alkyl moiety to accommodate carbenium ion character increases with increasing alkyl chain length in accord with polarizability arguments. For this reason, energy barriers on the proposed π-complex pathway would decrease as the stability of the incipient carbenium ion increases. The current results are in accord with those observed in the earlier investigations of the gas-phase EAS of benzene[12] and are consistent with π-complex formation in both halo and heterocyclic aromatic EAS.

II. Alkyl side-chain rearrangements

To test for alkyl side-chain rearrangements in the haloaromatic/carbenium ion complexes, it is necessary to start with an arenium ion of defined structure. Because the reacting carbenium ion in gas-phase EAS is free to rearrange prior to reacting with the aromatic species, it is difficult to distinguish rearrangements within the complex(es) from those of the free carbenium ion itself. The effect of the side-chain structure with-

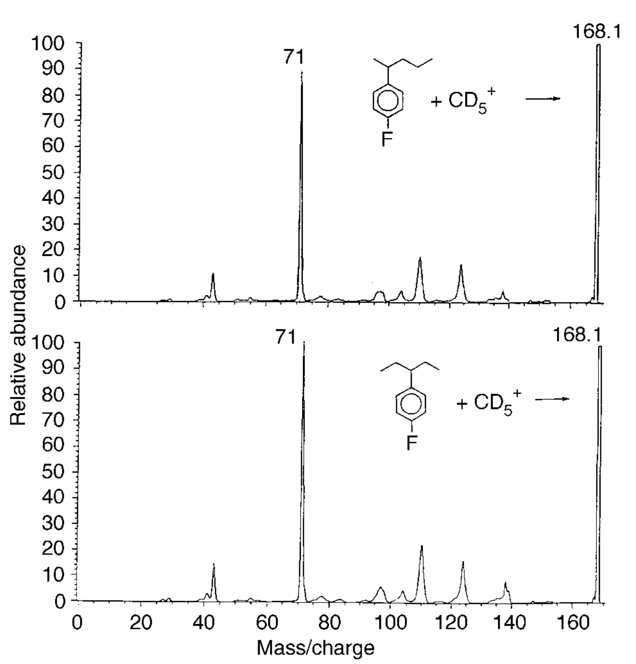


Fig. 3 The CAD spectrum of deuteriated 2-(*p*-fluorophenyl)pentane compared to that for 3-(*p*-fluorophenyl)pentane

in these complexes can be probed, however, when the complex is generated *via* addition of D^+ to an alkyl substituted aromatic of known structure. A comparison of the CAD spectra of the $[M + D]^+$ of 2-(*p*-fluorophenyl)pentane *vs.* that for 3-(*p*-fluorophenyl)pentane (Fig. 3), provides good evidence that the two ions are nearly identical (we analysed the $[M + D]^+$ ions rather than $[M + H]^+$ so as to minimize overlap and coselection of ^{13}C and $[M + H]^+$ when protonated molecules are studied). Similar side-chain isomerizations were documented previously[12] and must also occur for 2-(*p*-chlorophenyl)pentane and 3-(*p*-chlorophenyl)pentane and for 2-(*p*-bromophenyl)pentane and 3-(*p*-bromophenyl)pentane because the product-ion spectra of the $[M + D]^+$ ions of these isomeric pairs are also nearly identical. There is an interconversion of structure of the alkyl side chain; for this isomerization to occur, a significant extent of carbenium-ion character must exist on the side chain. A π complex meets this criterion. The assumption is that for those ions containing the requisite internal energy, the arenium ion (a σ complex) is interconverting with a π complex, and that isomerization of the alkyl group takes place within the lifetime of the more loosely bound π complex.

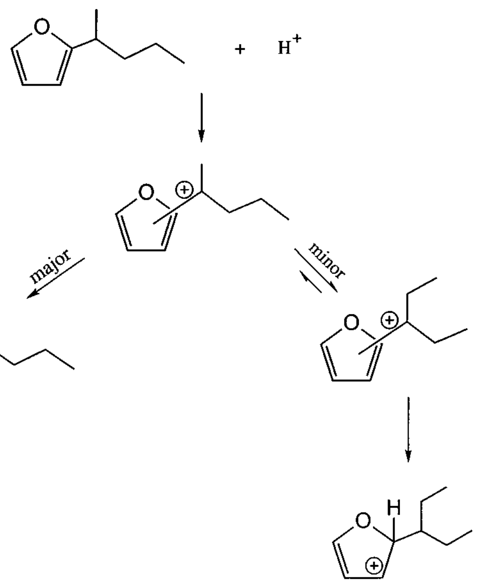
The CAD spectrum of deuteriated 2-(2-pentyl)furan, on the other hand, is similar, but not identical to that for the $[M + D]^+$ ion of 2-(3-pentyl)furan. Both isomeric ions fragment *via* competitive pathways to give abundant deuteriated furan and $C_5H_{11}^+$. The interesting feature of the spectra, however, is the abundance ratio for fragments losing 2-carbon *vs.* 3-carbon neutrals for the $[M + D]^+$ ion of 2-(2-pentyl)furan *vs.* that of 2-(3-pentyl)furan: the former is 1 : 3 whereas the latter is 1 : 1. We surmise that the ions exist as different structures or different mixtures of structures, and that isomerization within the alkyl side chain does not occur or is incomplete. Because 2-carbon and 3-carbon losses occur for both deuteriated isomers, we favor the argument that isomerization of the side chain is incomplete. If there were no isomerization, we would predict that the $[M + D]^+$ of 2-(2-pentyl)furan would expel predominantly neutrals containing 3 carbon atoms whereas that from 2-(3-pentyl)furan would eject neutrals containing 2 carbon atoms. Nevertheless the argument for partial isomerization is not completely satisfying because we have no reference CAD spectra for the pure isomers.

Table 1 Percent total ion current deposited in R^+ formation, proton affinity and σ^+ value for each aromatic species

	R^+ (% TIC)	PA/kcal mol^{-1}	σ^+
Fluorobenzene	36	182.2 ± 2	−0.07
Chlorobenzene	31	181.9 ± 2	+0.11
Bromobenzene	30	182.4 ± 2	+0.15
Furan	20	189.8 ± 2	−0.95[a]
Thiophene	12	196.5 ± 2	−0.85[a]
Pyrrole	4	205.9 ± 2	−1.90[a]

[a] Reference 32.

To test the prediction that the extents for losses of 2- and 3-carbon neutrals are sensitive to alkyl side-chain isomerization, the radical cations of 2-(2-pentyl)furan and 2-(3-pentyl)furan were studied. For the radical cations, there is little driving force for side-chain isomerization. Although comparing the dissociations of these radical cations with those of arenium ions is not entirely justified, the abundance ratios for 2-carbon and 3-carbon neutrals can provide support for our prediction. The abundance ratio of fragments produced by losing 2-carbon *vs.* 3-carbon neutrals for 2-(2-pentyl)furan radical cation is 1 : 7 whereas that for the 2-(3-pentyl)furan radical cation is 9 : 1. The corresponding abundance ratios for the $[M + D]^+$ ions show trends that are similar, affirming that side-chain isomerization does take place but is not complete (Scheme 3).

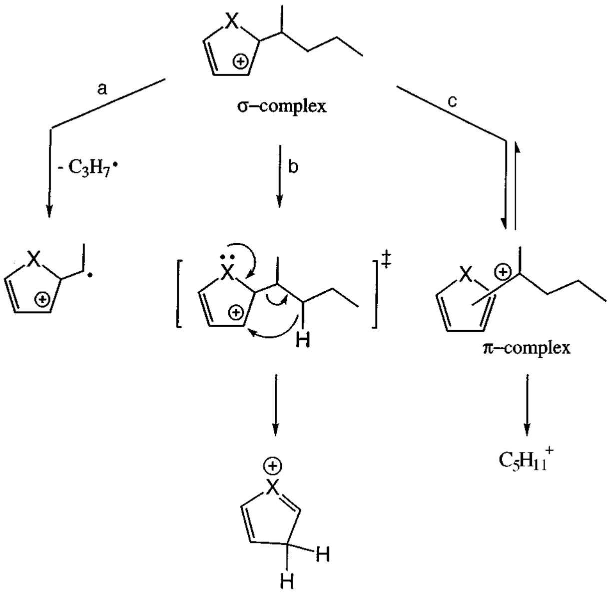


Scheme 3

III. Existence and role of π complexes in the decompositions of arenium ions

Several properties of the aromatic moiety within the π complex can be correlated with the above-mentioned ion-dissociation properties. First, the amount of R^+ formation upon collisional activation of the arenium ions smoothly decreases as the π-electron density increases within the aromatic species (*i.e.*, $FC_6H_5 > ClC_6H_5 > BrC_6H_5 >$ furan > thiophene > pyrrole). Correspondingly, the extent of alkyl side-chain losses and ArH_2^+ formation increases with increasing aromatic π-electron density. Second, the amount of R^+ formation in the CAD spectra of the arenium ions smoothly decreases as the proton affinities (PA) of the aromatic species increase (Table 1). Finally, a parallel, but poorer, relationship exists between R^+ formation and the σ^+ value.[32] The haloaromatics, with σ^+ values near zero or positive, generate substantially more R^+ than the heterocyclic aromatics, for which the σ^+ is much more negative (see Table 1).

The starting point for the interpretation of these results is the relative stability of the σ complex. Because σ complexes should be more stable than π complexes, the predominant species that is submitted to collisional activation is a σ complex. The decomposition channels of the σ complex include (a) fragmentation from the side chain (*e.g.*, to expel methyl, methane, ethyl, ethane, *etc.*), (b) the formation of $(Ar\text{-}H_2)^+$ species by loss of a neutral alkene, and (c) the formation of R^+ and a neutral aromatic, presumably *via* the π complex, which may also collapse back to the σ complex, or rearrange to an isomerized π complex (Scheme 4). We propose that the branching between the three decomposition channels depends on the π-electron density of the aromatic species. As the π-electron density increases (*i.e.*, in going from the halo- to the heterocyclic aromatic species), the energy difference between the σ complex and π complex increases, reducing the competitiveness of decompositions that occur through the π complexes. The heteroatoms of the electron-rich heterocyclic aromatics are capable of donating electron density from lone-pairs to stabilize the positive charge within the ring and, as a consequence, to stabilize increasingly the σ complex with respect to the π complex. Further, decompositions that yield positive charge within the ring (formation of $Ar\text{-}H_2^+$ and losses of alkyl side-chains) also become increasingly favored as the aromatic π-electron density donation increases.



Scheme 4

IV. Molecular modeling computations

To test further the proposal, we calculated the enthalpies of formation for the isolated starting materials (the neutral aromatic and the free carbenium ion), the σ complexes, the π complexes and the ArH^+ ion plus neutral alkene. We chose the AM1 semiempirical method because we wished to corroborate trends within a class (*i.e.*, differences between σ complexes, π complexes, *etc.*) rather than calculate absolute enthalpies.[33] From the data, we determined the enthalpy differences ($\Delta\Delta H$) for the σ and π complex, for the σ complex and $(Ar\text{-}H_2)^+$ plus neutral alkene, and for the π complex and R^+ plus ArH (see Table 2). As a check for the validity of our calculations, we compared computed values for the enthalpy change, ΔH_{rxn}, for the reaction $R^+ + ArH \longrightarrow ArH_2^+ +$ alkene with experimentally determined values taken from known enthalpies of formation and proton affinities.[34] The average absolute difference between calculated and experimental values for the eighteen reactions evaluated is *ca.* 2 kcal mol^{-1}, which gives credibility to the calculations.

Several salient trends are apparent from the data in Table 2. First, as the aromatic becomes increasingly electron-rich (going from fluorobenzene to pyrrole), the σ complexes become increasingly more stable with respect to π complexes, as was proposed in the previous section. The π complexes are less sensitive than are σ complexes to the electron density of the aromatic compound. Second, for the haloaromatics, the π complexes are more stable than the corresponding protonated aromatics $(Ar\text{-}H_2)^+$/alkene products, whereas the stability order is reversed for the electron-rich heterocyclic aromatics. Finally, the endothermicity for R^+ formation from the π complex increases as the aromatic becomes more electron-rich.

The experimental results for each aromatic system show that R^+ formation becomes more favored as the size of the alkyl group increases. For fluorobenzene through thiophene, the experimental trend has as a basis the depth of the potential-energy well of the σ complex. The stability of the π complex with respect to the σ complex increases as alkyl group size increases, except for pyrrole. For pyrrole, the major difference is that the endothermicity for R^+ formation from the π complex decreases to the greatest extent with increasing alkyl chain-length whereas the enthalpy requirement for formation of the π complex is relatively insensitive to the alkyl substituent.

The π-electron density in the aromatic determines not only the amount of π complex that can form, but also the nature of the π complex itself. In the calculations of the π-complex energies in Table 2, an optimal distance between the carbenium ion and the aromatic was determined by systematically varying the distance between the ring and the carbenium ion and evaluating the corresponding energies in search of a minimum value. Upon finding the optimal distance, we discovered that the π complex formed from the heterocyclic aromatics is much more tightly bound (*i.e.*, the alkyl group is much closer to the aromatic ring within the complex) than that formed with the haloaromatics. Further, the calculated charge on the central carbon of the propyl group in a π complex with fluorobenzene, chlorobenzene, and bromobenzene (+0.61, +0.54 and +0.57, respectively) is greater than that for π complexes with furan, thiophene and pyrrole (+0.52, +0.48 and +0.50, respectively).

These findings corroborate our interpretations of the experimental data that the alkyl moieties within π complexes of haloaromatics possess sufficient positive charge that the carbenium ion can isomerize. For the π complexes of the electron-rich heterocyclic aromatics, the carbenium ion is more tightly bound and isomerization is incomplete.

V. Potential energy surface

A partial potential energy surface has been constructed to illustrate the major features for the two extremes of the aromatic species studied, the fluorobenzene/propyl carbenium ion (representing the electron-deficient haloaromatics) and the pyrrole/propyl carbenium ion (representing the electron-rich heterocyclic aromatics) (Fig. 4). Transition state energies are not included.

We omitted the loosely bound H-bonded complex between $Ar\text{-}H_2^+$ and an alkene $(Ar\text{-}H\cdots H\cdots \text{alkene})^+$, the existence of which has been convincingly demonstrated by Audier and co-workers,[35] because the focus of this work centers upon EAS. Entry onto this surface by $Ar\text{-}H_2^+$ reacting with an alkene does not produce the σ complex of interest,[12] and the $(Ar\text{-}H\cdots H\cdots \text{alkene})^+$ intermediate does not relate directly to the interplay between σ and π complexes in the EAS mechanism. The energy of $(Ar\text{-}H\cdots H\cdots \text{alkene})^+$ complex tracks that for isolated $Ar\text{-}H_2^+$ and alkene; it is higher in energy than the π complex for the haloaromatics, and lower in energy than the π complex for the heterocyclic aromatics. We suggest that the $(Ar\text{-}H\cdots H\cdots \text{alkene})^+$ complex is a local minimum en route to an exit channel (the production of isolated $Ar\text{-}H_2^+$ and alkene).

The following reaction scenarios can be envisioned upon the study of the potential energy surface and Table 2. As the carbenium ion R^+ associates with the aromatic ring to form a π complex, a small amount of energy (typically 3–6 kcal mol^{-1}, depending upon the alkyl group) is released, except for pyrrole

Table 2 Calculated $\Delta\Delta H$ values for various intermediates on the potential energy surface for the gas-phase EAS of halo and heteroatomic species. The ΔH_{rxn} data is the enthalpy change for the reaction $R^+ + ArH \longrightarrow ArH_2^+ +$ alkene. The experimental data (in kcal mol^{-1}) are from the enthalpies of formation and proton affinities.[34] The calculated values (in kcal mol^{-1}) are from the semi-empirical methodology that we employed.

Aromatic	Alkyl	$\Delta\Delta H$ ($\sigma \longrightarrow \pi$)	$\Delta\Delta H$ ($\pi \longrightarrow R^+$)	$\Delta\Delta H$ ($\sigma \longrightarrow ArH_2^+$)	ΔH_{rxn} calc.	ΔH_{rxn} exp.
Fluorobenzene	Propyl	+19.9	+2.9	+21.8	−1	−3
	Butyl	+18.0	+2.8	+20.9	0	−2
	Pentyl	+15.3	+3.2	+16.5	−2	0
Chlorobenzene	Propyl	+17.4	+4.6	+20.6	−1	−2
	Butyl	+17.1	+3.9	+17.6	−3	−2
	Pentyl	+14.2	+3.4	+16.2	−1	+1
Bromobenzene	Propyl	+14.0	+5.2	+21.6	+1	−3
	Butyl	+13.2	+3.8	+17.4	0	−2
	Pentyl	+11.5	+3.4	+16.3	+1	0
Furan	Propyl	+33.2	+6.8	+25.9	−14	−10
	Butyl	+32.6	+5.3	+22.8	−15	−10
	Pentyl	+26.3	+4.0	+15.3	−15	−7
Thiophene	Propyl	+34.5	+5.7	+22.2	−18	−17
	Butyl	+31.2	+4.3	+20.2	−15	−16
	Pentyl	+27.8	+4.9	+18.6	−14	−14
Pyrrole	Propyl	+36.1	+14.1	+24.5	−26	−26
	Butyl	+37.3	+11.1	+21.0	−27	−26
	Pentyl	+38.7	+8.8	+21.3	−26	−23

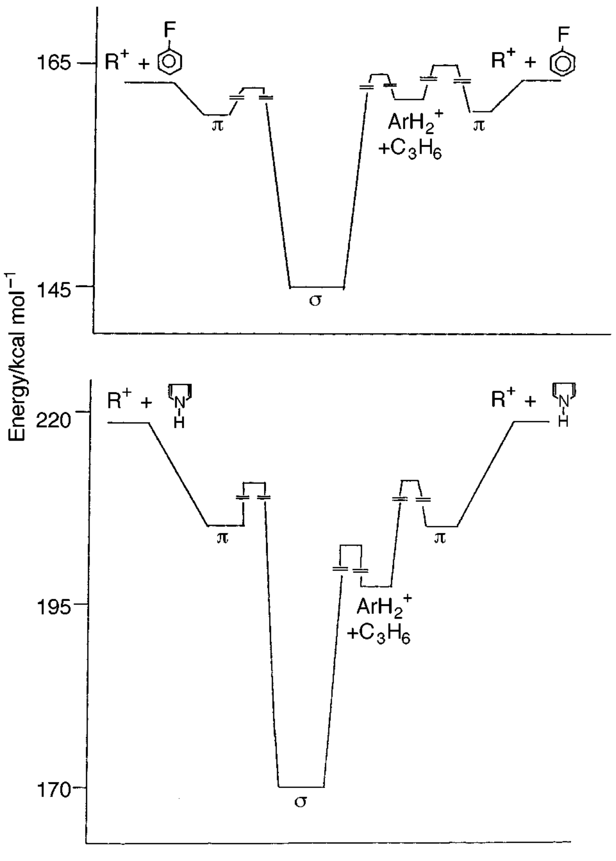


Fig. 4 Schematic potential energy surfaces for the gas-phase reaction of the 2-propyl carbenium ion with fluorobenzene (top) and pyrrole (bottom)

where the release is 9–14 kcal mol^{-1}. The structure of the π complex has more in common with those of the starting carbenium ion and aromatic than with that of the σ complex. This is apparent because as the π complex rearranges to the σ complex, considerably more energy is released (26–39 kcal mol^{-1} for the electron-rich and 12–20 kcal mol^{-1} for the electron-poor aromatics), indicating stronger bonding in the σ complex.

Once formed, the σ complex may fragment by returning to starting materials or by eliminating an olefin to give a protonated aromatic. For electron-poor aromatics, the energy required for the production of olefin/protonated aromatic is comparable to that for producing the carbenium ion and neutral aromatic. For electron-rich aromatics, the energy is less, an observation in accord with the higher proton affinities of the electron-rich aromatics. For all complexes, fragmentation to the protonated aromatic always has a lower energy demand for the systems containing and releasing larger olefins. This is due, in part, to the greater stabilities of the larger olefins (*e.g.*, pent-2-ene is *ca.* 13 kcal mol^{-1} more stable than propene). The reaction to give the protonated aromatic, Ar-H_2^+, must have an appreciable reverse activation barrier because the forward reaction of protonated benzene and but-1-ene does not give a complex.[12] Further, if a substantial barrier did not exist, the arenium ion formed between $C_3H_7^+$ and pyrrole would not fragment to give back $C_3H_7^+$.

Both the π and σ complexes of the electron-rich aromatics are more stabilized with respect to the entry point (isolated R^+ + aromatic) than are those for electron-poor aromatics. The extent of stabilization for the σ complex, however, far exceeds that of the π complex. The difference in energy between the σ and π complexes for the haloaromatics is *ca.* 18 kcal mol^{-1} whereas that for the heteroaromatics is *ca.* 35 kcal mol^{-1}. The factors that determine the stability of the σ complex (*i.e.*, proton affinity, aromatic π-electron density) also determine the stability of the Ar-H_2^+ ion. This is also the case for the ions generated from σ-complex fragmentation (*i.e.*, ions generated from Branch a, Scheme 4). This is reasonable because each of the ions (the σ-complex, the Ar-H_2^+ ion, and the cations formed by losses of portions of the side-chain) possesses significant positive charge within the ring. For the electron-rich aromatics, the Ar-H_2^+ ions are more stable than the π complexes, owing to the stabilizing effects of electron donation to the ring-bound cation in the Ar-H_2^+ ion. For electron-deficient aromatics, on the other hand, Ar-H_2^+ is less stable than the π complex.

The difference in energy between the σ complex and the Ar-H_2^+ ion decreases with the increasing size of the alkyl substituent (pentyl > butyl > propyl), owing largely to the enhanced stability of the neutral alkene that is formed alongside the Ar-H_2^+ ion. The π complex is also stabilized by the same factors, but to a much lesser extent.

Finally, an appreciable barrier must exist between Ar-H_2^+/alkene and the σ complex. This is supported by the observation that when protonated benzene was reacted with but-1-ene, no σ complex was formed.[12] Further, if a substantial barrier did not exist between the σ complex and Ar-H_2^+ outlet, the arenium ion formed between $C_3H_7^+$ and pyrrole would not give any R^+.

Conclusions

We suggest, on the basis of experiment and theory, that π complexes are formed with σ complexes in the gas-phase EAS of both halo and heteroaromatic species. The extent of π-complex formation decreases as the extent of electron density within the aromatic moiety of the complex increases (*i.e.*, $FC_6H_5 > ClC_6H_5 > BrC_6H_5$ > furan > thiophene > pyrrole). Aromatic electron density also increases the interaction between the alkyl group and the aromatic ring for π complexes formed between carbenium ions and electron-rich aromatics. For these systems, the aromatic moiety possesses greater positive charge than that for the electron-poor aromatics.

Alkyl side-chain rearrangements occur within the lifetime of the π complex. The alkyl groups are loosely-bound in the π-complexes formed between haloaromatics and carbenium ions, and the alkyl moieties within these π-complexes possess extensive carbenium ion character. As a result, complete side-chain isomerization occurs. Incomplete interconversion, however, occurs for the $[M + D]^+$ ions of 2-(2-pentyl)furan and 2-(3-pentyl)furan. This may be a characteristic of heterocyclic aromatic arenium ions where tight π-complexes, whose alkyl groups have relatively little carbenium ion character, are formed.

Perrin and co-workers[36] have proposed an alternative mechanistic explanation for certain aromatic substitutions. They convincingly report that when reactive aromatics are nitrated, electrophilic attack onto a neutral aromatic (EAS) does not occur, but rather, an electron transfer takes place to yield an aromatic radical cation/NO_2 radical intermediate, which rapidly collapses to yield the nitrated aromatic. In the reactions reported upon here, even with those of the reactive heterocyclic aromatics, we do not see evidence for electron transfer or radical-cation intermediacy. If a radical cation/alkyl radical complex were involved, the alkyl moiety would possess radical character rather than carbenium-ion character, and side-chain isomerizations would have to be explained by 1,2 hydrogen atom shifts, which are very unlikely for radicals. Furthermore, electron transfer from the neutral aromatic to the alkyl carbenium ion is endothermic for the systems reported in this article, and, therefore, is unlikely to occur.

Experimental

Mass spectrometry

All CAD mass spectra were obtained with a Kratos MS50 triple-analyser mass spectrometer,[37] which consisted of a Nier–Johnson geometry, high-resolution mass spectrometer followed by an electrostatic analyser (ESA). The ions formed in the ion source were mass selected at a mass resolving power of 2500–3500 (10% valley definition) by using MS-1 (ESA-1 and the magnetic sector). The ions were then activated by collisions with helium gas in the second collision cell; sufficient helium was added to suppress the ion beam by 50%. The second ESA was scanned to give the CAD spectrum of the resulting fragment ions. In a typical CAD experiment, 20–40 scans were acquired and then signal averaged. The precision for all peak heights was *ca.* 5% relative, as determined by replicate experiments. The CI source was operated at 280 eV with a total emission current of 500 μA. The ion accelerating voltage was 8000 V.

The gas-phase EAS experiments were carried out by simultaneously admitting, *via* separate glass inlets and controllable leak valves, the aromatic species and an alkyl bromide into the CI source. The alkyl bromide served as the precursor to the alkyl carbenium ion. All ionic species were accelerated into the first stage of the tandem mass spectrometer, and CAD or metastable-ion spectra were recorded as described above.

To produce the deuteriated aromatics, the alkylaromatic was admitted into the high-pressure chemical ionization (CI) source through a controllable leak valve. The chemical ionization reagent gas (CH_4 or CD_4) was also admitted into the CI source through a second leak valve. Deuteriation by CD_5^+ of the alkylaromatic occurred in the CI source, and all ionic species were analysed as described above.

Computations

All computations were performed on a Hewlett-Packard Apollo Unix-based hardware system utilizing the Spartan 4.1 molecular modeling program produced by Wavefunction Incorporated. All computations were performed at the AM1 semi-empirical level.

Syntheses

The syntheses of the alkylhaloaromatics were carried out in multiple steps, using modifications of textbook and literature procedures. The general procedure was as follows: the appropriate halobenzene was acylated with either propionyl chloride or acetyl chloride, then reacted with ethylmagnesium bromide or propylmagnesium bromide, respectively, in diethyl ether, and the product was submitted to the Small reduction[38] utilizing Li/NH_3 and NH_4Cl.

3-(*p-Chlorophenyl*)*pentane*. ^{13}C DEPT NMR: CH_3 carbons (16.5 ppm), CH_2 carbons (23.3 ppm), CH carbons (49.2, 129.0 and 130.3 ppm), C carbons (129 and 132 ppm).

2-(*p-Chlorophenyl*)*pentane*. ^{13}C DEPT NMR, CH_3 carbons (14.8, 22.9 ppm), CH_2 carbons (21.2, 41.0 ppm), CH carbons (39.0, 128 and 131 ppm), C carbons (129 and 133 ppm).

2-(*p-Fluorophenyl*)*pentane*. ^{13}C DEPT NMR, CH_3 carbons (15.3 and 24.1 ppm), CH_2 carbons (20.6 and 39.8 ppm), CH carbons (38.4, 129.1 and 132 ppm), and C carbons (128.5 and 133.3 ppm).

3-(*p-Fluorophenyl*)*pentane*. ^{13}C DEPT NMR, CH_3 carbon (18.4 ppm), CH_2 carbon (20.3 ppm), CH carbons (48.2, 127.9 and 131.3 ppm), and C carbons (128.3 and 133.8).

The general procedure for alkylfuran synthesis involved the formation of the lithiofuran utilizing *n*-butyllithium in THF under nitrogen at 0 °C. The solution was allowed to warm to room temperature, and then the appropriate iodopentane was slowly added. The solution temperature was raised to 55 °C, and the solution was stirred for 5 h. The product was rinsed with water, extracted into fresh diethyl ether, the solvent removed, and the product was distilled in a vacuum. The furans were identified *via* ^{13}C DEPT NMR.

n-Pentylfuran. CH_3 carbons (14.1 ppm), CH_2 carbons (22.3, 27.9, 28.1, 31.5 ppm), CH carbons (104.7, 110.1, 140.5 ppm), C carbons (156.7 ppm).

2-*Pentylfuran*. CH_3 carbons (16.2 and 22.6 ppm), CH_2 carbons (27.1 and 28.5 ppm), CH carbons (36.5, 123.6, 127.1, and 127.3 ppm), C carbons (146.8 ppm).

3-*Pentylfuran*. CH_3 carbons (12.6 ppm), CH_2 carbons (25.6 ppm), CH carbons (45.8, 122.4, 125.1, and 127.5 ppm), C carbons (138.6 ppm).

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