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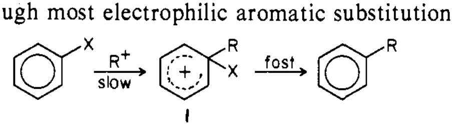
Interconversion of Gas-Phase Arenium Ions and π-Complexes

Robert W. Holman and Michael L. Gross*

Contribution from the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304. *Received November 19, 1987. Revised Manuscript Received August 8, 1988*

Abstract: Arenium ions or σ-complexes are known to be produced as intermediates in electrophilic aromatic substitution (EAS), but the existence of π-complexes is less certain. Evidence is presented in this paper for the coexistence of σ- and π-complexes in the protonation of arenes in the gas phase. Protonation was accomplished in a high-pressure chemical ionization source of a tandem mass spectrometer to give the ethylbenzenium ion, the isomeric propyl- and butylbenzenium ions and five isomeric pentylbenzenium ions. It was established that identical ions are produced by protonation as are by alkylation with stable carbenium ions (i.e., by EAS). The existence of the π-complex is consistent with the observation that the alkyl moieties of secondary butyl- and pentylbenzenium ions isomerize prior to decomposition. The isomerization is directly detectable if it is nearly thermoneutral. Other more exothermic isomerizations (e.g., 1° alkyl → 2° alkyl → 3° alkyl) are only inferred because the energy released causes the π-complex to decompose to benzene and a carbenium ion. The evidence for isomerization was obtained by using collisionally activated dissociation (CAD) and tandem mass spectrometry (MS/MS).

Electrophilic aromatic substitution (EAS), unlike nucleophilic substitution, proceeds largely by a single mechanism.[1] This mechanism, known generally as the arenium ion mechanism, involves electrophilic attack to give an arenium ion (σ-complex) followed by departure of an appropriate leaving group in a final step.[2] Although most electrophilic aromatic substitutions are thought to proceed via the arenium ion mechanism, the participation of π-complex intermediates on the potential energy surface has not been fully established.



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Arenium ions are a class of carbenium ions that are best represented as resonance hybrids, as denoted by structure **1** (eq 1). Although benzenoid ions of this type are intermediate cyclohexadienyl cations and are referred to as Pfeiffer–Wizinger complexes,[3] Wheland intermediates,[4] Brown σ-complexes, or as suggested by Doering,[5] benzonium ions, we will refer to them as arenium ions, the most general classification of these species.

Brown and co-workers[6] showed that a simple linear relationship exists between the relative rates of numerous electrophilic aromatic substitutions and the relative stabilities of the related σ-complexes (arenium ions). Considerable direct experimental evidence has been obtained since then to prove that arenium ion complexes (σ-complexes) do exist as stable intermediates.[7]

Dewar[8] originally proposed that π-complexes also play an important role in EAS. Olah and co-workers[9] then hypothesized that, for reactions of strong electrophiles, the transition state of highest energy resembles that of a π-complex. The rates of nitration with the highly electrophilic NO_2^+, however, correlate no better with π-complex stabilities than with σ-complex stabilities;[10] thus, the generality of π-complex formation being the rate-determining step is questionable.[11] Several studies show that a π-complex does not form at all, or if it does, its formation is not rate limiting.[12-15] Other studies indicate that π-complex formation may be rate determining.[16-22]

One supposition emerging from this debate is that the transition state for EAS is not a rigidly fixed one always resembling the arenium ion. Instead, the transition state may be earlier on the reaction coordinate and resemble starting materials as an oriented π-complex.[16] This hypothesis is in accord with the Hammond postulate as applied to electrophilic aromatic substitution and is rationalized in terms of early and late transition state theory. The existence of a separate π-complex minimum on the reaction coordinate preceding the transition state of highest energy, however, is still equivocal, and the role of π-complex formation in the arenium ion mechanism is still not fully resolved. In fact, the nature of the putative intermediate preceding formation of the arenium ion intermediate is not settled (is it a π-complex?) and has been termed as "encounter complex".[23,24]

The limiting factor in the study of the intermediates in the arenium ion mechanism is the inability to isolate readily such transient species. Although a number of arenium ions were isolated earlier,[25,26] it was not until 1978 that the simplest of arenium

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Table I. CAD Spectra of the Isomeric $(M + D)^+$ Ethyl-, Propyl-, and Butylbenzenium Ions[a]

	m/z														
compd	121	120	106	105	104	93	92	91	80	79	78	77	65	57	43
ethylbenzenium			3	1	2		19		58	5	10		1		
n-propylbenzenium	1	1	2		1	1	24		30	6	5	3	3		23
sec-propylbenzenium	1	<1	12		3		8		41	7	6	1	1		22
n-butylbenzenium	2		4	2	2	9	18	5	11	3	4	1		39	
sec-butylbenzenium	<1		12	2	2	2	8	2	24	5	5	1		50	
1-butylbenzenium	<1		1	1	<1	11	19	5	7	4	4	2		46	
tert-butylbenzenium	41	13	2	1	2	5	5	3	2	3	<1	2		20	

[a] All spectra are presented as the average of 30–40 scans and are reported as percent total ion current (% TIC). The arene ions in this table are $(M + D)^+$ species formed via methane-d_4 chemical ionization of the corresponding alkylbenzene.

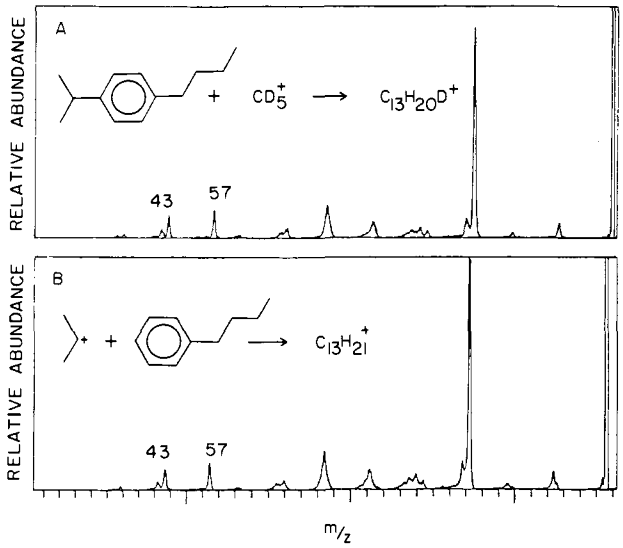


Figure 1. Comparison of the CAD spectra of the isopropyl-*n*-butylbenzenium ion formed via deuteration of isopropyl-*n*-butylbenzene (A) and via the electrophilic attack of the isopropylcarbenium ion on *n*-butylbenzene (B).

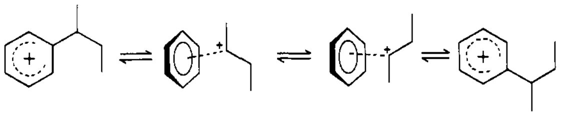
ions, the benzenium ion, was studied by ^{13}C NMR spectroscopy.[27]

The goal of this work is to establish whether π-complex forms of arenium ions exist in the gas phase. The existence of gas-phase arenium ion intermediates does not necessarily mean that π-complexes are accessible on the reaction coordinate for condensed-phase electrophilic aromatic substitution. If π-complex arenium ions do exist as distinct intermediates in the gas phase, then they necessarily must exist on the potential energy surface of isolated arenium ions. This evidence is mandatory in order for Olah's arguments regarding the role of π-complex intermediates in EAS to be valid. Moreover, results of studies of gas-phase ions should reveal the intrinsic (i.e., free of solvent effects) properties of the arenium ions.

It is likely that the properties of arenium ions in the gas phase will not differ markedly from those in the condensed phase because the physical characteristics, relative reactivities, and relative stabilities of stable aliphatic carbenium ions in the condensed phase are subject to relatively minor differential specific solvation and show comparatively little dependence on media change.[28] In addition, a comparison of previous mass spectrometric and calorimetric measurements showed no essential change in enthalpy trends for isomeric gas-phase secondary and tertiary carbenium ions over those seen in the condensed phase or in nonassociating solvents. And finally, the pioneering efforts of Cacace,[32-40] Speranza,[41] and co-workers have shown that gas-phase arenium ion chemistry has common features with condensed-phase studies, thus forging a link that is also important in this work.

Results and Discussion

If gas-phase arenium ions exist as π-complexes, then their dissociation properties, either collisionally activated or metastable, must be in accord with those of a π-complex. If the π-complex forms from a σ-complex, the positive charge must move from the aromatic ring to become localized primarily on the alkyl moiety, allowing for alkyl side chain isomerization (see eq 2). We will seek evidence for this isomerization.


(2)

If isomerism does occur, we have necessary evidence for the existence of a loosely bound carbenium ion/aromatic complex. The evidence may not be sufficient because it does not preclude other intermediates such as a proton-bound carbenium ion complex, for example.

Arenium Ion Formation and Characterization. Mass spectrometric techniques were chosen to investigate the properties of gas-phase arenium ions. The gas-phase arenium ions were produced by protonation (deuteration) of appropriate alkylbenzenes in a chemical ionization mass spectrometer (CIMS) ion source. Chemical ionization mass spectrometry provides a clean, simple way to produce a wide range of arenium ions suitable for study as isolated gas-phase species. Tandem mass spectrometry (MS/MS) was then employed to determine the structure of the arenium ions. These mass spectrometric techniques allow for facile formation, isolation, and detection of such transient species.

In the remainder of this paper we shall focus almost exclusively on the deuterated arenium ion, $(M + D)^+$ (where M is an alkylbenzene), which is formed via methane-d_4 CI. The principal rationale for studying the deuterated instead of protonated arenium

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Table II. Partial CAD Spectra of Isomeric $(M + D)^+$ Pentylbenzenium Ions[a]

compd	149	121	120	119	107	106	105	93	92	91	79	78	71
n-pentylbenzenium	1	1	1	1	1	5	1	13	22	4	5	4	44
2-pentylbenzenium	2	2	3	1	2	8	2	1	9	2	3	3	62
3-pentylbenzenium	2	2	3	1	2	7	2	2	9	2	3	3	62
1,2-dimethyl-1-phenylpropane arene	1		1	1	6	10	3	2	6	1	1	1	64
2-methyl-2-phenyl-butane arene	1	15	8	2	1	1	2	6	8		2	1	51
2,2-dimethyl-1-phenylpropane arene	1	1	1	1	1	1	1	11	11	5	2	2	60

[a] All spectra are presented as the average of 30–40 scans and are reported as percent total ion current (% TIC). The arene ions in this table are $(M + D)^+$ species formed via methane-d_4 chemical ionization of the parent alkylbenzene.

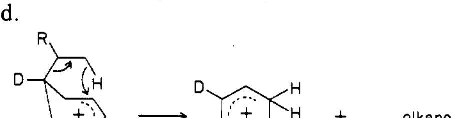
ions is to avoid the problem of isobaric contamination from the ^{13}C-containing radical cation of the parent alkylbenzene. Although the $(M + H)^+$ ion can be separated from its ^{13}C-containing $M^{\bullet+}$ ion at ultrahigh resolution, the resulting CAD spectra will suffer reduced signal-to-noise. For simplicity we shall not repeatedly make the distinction between protonated and deuterated, but instead refer to the $(M + D)^+$ species as the arenium ion. The nomenclature adopted for these species is as follows: ethylbenzenium, *n*-propylbenzenium, *n*-butylbenzenium, etc., for the $(M + D)^+$ arenium ions of ethylbenzene, *n*-propylbenzene, and *n*-butylbenzene, respectively.

It is necessary to establish that gas-phase protonation (deuteration) of neutral alkylbenzenes yields species that are equivalent to those formed via gas-phase EAS. Thus, the CAD spectrum of the $(M + D)^+$ of isopropyl-*n*-butylbenzene is compared to that formed from the electrophilic attack of the isopropylcarbenium ion on *n*-butylbenzene (see Figure 1). That the spectra are nearly identical establishes that protonation (deuteration) of a neutral alkylbenzene is a valid means for forming gas-phase arenium ions equivalent to those formed via gas-phase EAS. Protonation is preferred, however, because it allows for the formation of arenium ions that are at least initially isomerically pure. The formation of arenium ions via gas-phase EAS is complicated by the fact that an unstable free carbenium ion will likely rearrange prior to its electrophilic attack on benzene and, hence, will yield either a mixture of isomeric arenium ions or the arenium ion corresponding to attack by the most stable carbenium ion.

Properties of Gas-Phase Arenium Ions. A characteristic collisionally activated dissociation for all of the arenium ions is to form $C_6H_6D^+$, *m/z* 80, via expulsion of the entire side chain as a neutral alkene (eq 3 and Table I).

$$C_6H_5D\text{-}C_nH_{2n+1}^+ \rightarrow C_6H_6D^+ + C_nH_{2n} \quad (3)$$

The formation of $C_6H_6D^+$ is dominant for the dissociation of the ethylbenzenium ion. Harrison and co-workers[42] observed the loss of neutral C_2H_4 from the dissociation of the *p*-diethylbenzenium ion, an arenium ion formed from $C_2H_5^+$ alkylation of ethylbenzene in the gas phase. Although offering no mechanism for this loss, the authors argued that the nature of the bonding in this arenium ion is that of a σ-complex. One way for a σ-bonded arenium ion to lose a neutral alkene is via a six-center transition state, as depicted in eq 4, although decomposition via a π-complex or a hydrogen-bonded complex of ethylene and benzene cannot be dismissed.



(4)

As the alkyl moiety of the arenium ion becomes larger, the formation of $C_6H_6D^+$ becomes less competitive, and a second fragmentation pathway begins to emerge. This fragmentation pathway is the expulsion of the entire alkyl moiety as a carbenium ion, $C_nH_{2n+1}^+$ (eq 5). For the dissociation of the isomeric propylbenzenium ions, the process is competitive with formation of $C_6H_6D^+$ and becomes increasingly more competitive for the butyl- and pentylbenzenium ions (see Table II). This pathway leads to the formation of $C_3H_7^+$ of *m/z* 43, $C_4H_9^+$ of *m/z* 57, and $C_5H_{11}^+$ of *m/z* 71, for the propyl-, butyl-, and pentylbenzenium ions, respectively. There is little or no detectable incorporation of deuterium into the departing carbenium ion.

$$C_6H_5D\text{-}C_nH_{2n+1}^+ \rightarrow C_nH_{2n+1}^+ + C_6H_5D \quad (5)$$

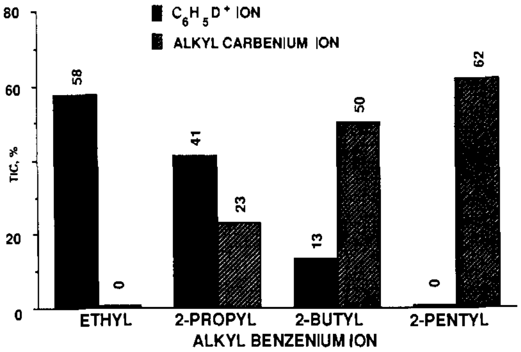


Figure 2. Histogram depicting the two major arenium ion fragmentation processes as a function of alkyl chain length.

The metastable dissociations of gas-phase pentylarenium ions illustrate even more graphically the facile formation of $C_nH_{2n+1}^+$ in these systems. Metastable ion mass spectra are obtained in a similar fashion to CAD spectra except the dissociation is not activated by collision with He (i.e., the arenium ions undergo spontaneous dissociation). Under metastable ion conditions, the only dissociation that is observed for the pentylarenium ions is the cleavage of the entire alkyl moiety to produce the $C_5H_{11}^+$ alkylcarbenium ion. Thus, the dissociation to give $C_5H_{11}^+$ is the lowest energy and most facile mode of fragmentation of pentylarenium ions. These two predominant modes of dissociation are in competition with one another for all arenium ions. The trade-off between $C_6H_6D^+$ formation (eq 3) and alkylcarbenium ion formation (eq 5) as a function of alkyl side chain length is illustrated in Figure 2.

The ability of the alkyl moiety of the arenium ion to accommodate carbenium ion character increases with increasing alkyl chain length in accord with polarizability arguments. It is for this reason that the probability of forming a π-complex becomes much greater as the stability of the incipient carbenium ion increases. The arenium ion of shortest alkyl chain length, the ethylbenzenium ion, possesses dissociation properties principally attributable to a σ-complex, whereas those of the arenium ions with largest alkyl groups, the pentylbenzenium ions, possess the properties primarily attributable to a π-complexed species. All other arenium ions studied here exhibit a continuum of behavior between these two extremes.

Isomerization of Arenium Ions. Although the complex between the π-system of the electron-rich benzene ring and the electrophilic alkyl moiety, which now has considerable carbenium ion character, is likely to be a transition state, we still seek substantial evidence for the π-complex as an actual intermediate. The isomeric propyl-, butyl-, and several isomeric pentylbenzenes were deuterated by reaction with CD_5^+, and the CAD spectra of the resulting arenium ions were obtained (see Tables I and II). The *n*-propyl- and isopropylbenzenium ions give unique CAD spectra, which we interpret to indicate that the *n*-propyl moiety does not undergo any significant rearrangement to the more stable isopropyl moiety prior to dissociation. An examination of the CA dissociations of the isomeric butylbenzenium ions (Table I) reveals that each isomer also possesses a unique CAD spectrum. No evidence exists for primary to secondary, secondary to tertiary, or primary to tertiary isomerization.

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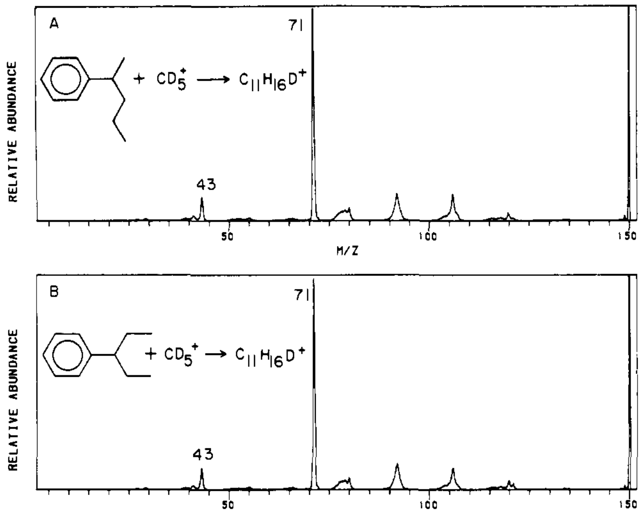


Figure 3. Comparison of the CAD spectra of the isomeric 2- and 3-pentylbenzenium ions, A and B, respectively.

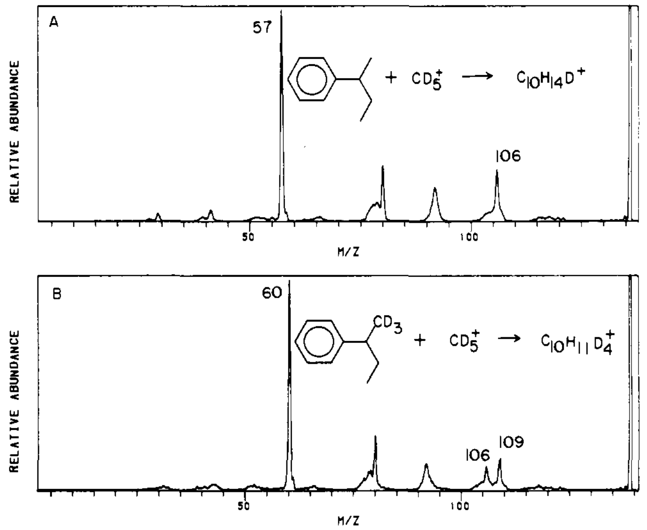


Figure 4. Comparison of the CAD spectra of the s-butylbenzenium ion (A) with that of the C_6H_5–$CH(CD_3)C_2H_5$ benzenium ion (B).

The CAD spectra of the isomeric 2-pentyl- and 3-pentylbenzenium ions, however, contain the first evidence for alkyl side chain isomerization of arenium ions. These benzenium ions undergo nearly identical CA dissociations (see Figure 3), indicating that the two ions possess a common structure. For this to occur, a near thermoneutral 2° = 2° isomerization of the alkyl side chain of the arenium ions takes place.

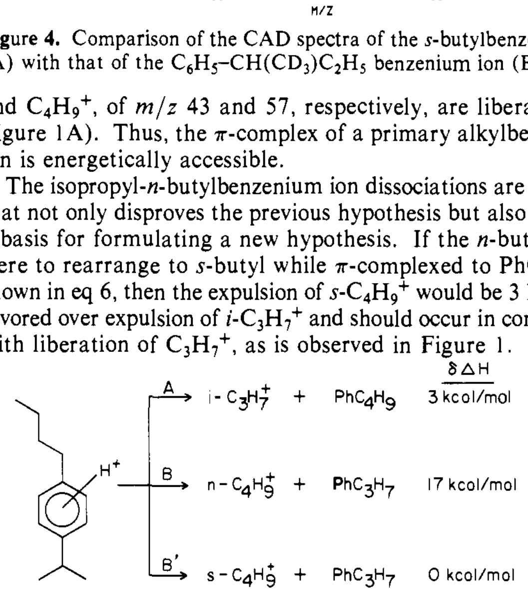
The interconversion of the 2- and 3-pentylbenzenium ions points to the possibility that a similar isomerization takes place for the s-butylbenzenium ion. This isomerization, in the absence of isotopic labeling, is transparent to normal mass spectrometric detection. Thus, an isotopically labeled s-butylbenzenium ion [prepared by D^+ transfer to C_6H_5-$CH(CD_3)C_2H_5$] was studied. In both collisionally activated and metastable dissociations, the unlabeled s-butylbenzenium ion undergoes loss of C_2H_6 to give an ion of m/z 106, whereas the labeled s-butylbenzenium ion competitively loses both C_2H_6 and $C_2H_3D_3$ to give ions of m/z 109 and 106, respectively (see the CAD spectra in Figure 4, parts A and B). It is clear from these spectra that a degenerate 2° = 2° isomerization also takes place for the s-butylbenzenium ion.

We now ask whether collisional activation is required for the isomerization. The dissociation of the labeled s-butylbenzenium ion under metastable ion conditions also provides evidence that 2° = 2° isomerization takes place in the absence of collisional activation. This result makes it clear that it is the property of any gas-phase arenium ions possessing sufficient energy to decompose to undergo a 2° = 2° isomerization, a process that is difficult to explain without invoking a π-complex intermediate.

At first thought, it is perplexing that the 2° = 2° isomerizations occur with little or no thermodynamic driving force, whereas 1° = 2°, or 2° = 3° isomerizations, with significant thermodynamic driving force, seemingly do not occur. If the isomerization of the alkyl moiety takes place only from a π-complex, and secondary σ-complexes are observed to isomerize whereas primary σ-complexes are not, we may hypothesize that secondary σ-complexes can attain π-complex character but primary σ-complexes cannot. The π-complex of a primary carbenium ion would be less stable and hence of higher energy than the π-complex of a secondary or tertiary carbenium ion.

To test directly this hypothesis, the dissociation properties of the arenium ion of isopropyl-n-butylbenzene were studied. This benzenium ion may form π-complexes involving either the isopropyl or n-butyl moiety and, upon collisional activation, dissociate to either the i-$C_3H_7^+$ or the n-$C_4H_9^+$ carbenium ion. The more thermodynamically favored π-complex is that in which the isopropylcarbenium ion interacts with n-butylbenzene. For the aforementioned hypothesis to be valid, this complex should exclusively dissociate to PhC_4H_9 and the i-$C_3H_7^+$ carbenium ion. The isopropyl-n-butylbenzenium ion, however, clearly interconverts with two π-complexes in which both the isopropyl and n-butyl moieties exist as incipient carbenium ions because both $C_3H_7^+$ and $C_4H_9^+$, of m/z 43 and 57, respectively, are liberated (see Figure 1A). Thus, the π-complex of a primary alkylbenzenium ion is energetically accessible.

The isopropyl-n-butylbenzenium ion dissociations are evidence that not only disproves the previous hypothesis but also provides a basis for formulating a new hypothesis. If the n-butyl group were to rearrange to s-butyl while π-complexed to PhC_3H_7, as shown in eq 6, then the expulsion of s-$C_4H_9^+$ would be 3 kcal/mol favored over expulsion of i-$C_3H_7^+$ and should occur in competition with liberation of $C_3H_7^+$, as is observed in Figure 1.



(6)

We now conclude that *all* high-energy isomeric arenium ions undergo side chain alkyl isomerization via π-complex arenium ion intermediates. Those rearrangements that are energy releasing (i.e., the 1° → 2°, 2° → 3° rearrangements) deposit the liberated energy into the release of the alkylcarbenium ion from the parent benzenium ion. The amount of energy released upon isomerization of a primary to a secondary carbenium ion is approximately 15–17 kcal/mol, whereas that for the sequential isomerization of a primary to a tertiary carbenium ion is in excess of 30 kcal/mol. All mass spectral evidence for the isomerization is lost with the departure of the alkylcarbenium ion, and the process is transparent to mass spectrometric detection. Higher order tandem MS experiments (e.g., MS^3) to examine the liberated carbenium ions are futile because these experiments do not permit a distinction to be drawn between isomerization of a π-complex or subsequent isomerization of the free carbenium ion.

The only side-chain isomerizations that are directly observable are those that are nearly thermoneutral (e.g., for the 2- and 3-pentylbenzenium ion, and the degenerate s-butylbenzenium ion rearrangements). In these cases, formation of the π-complex and isomerization of the alkyl side chain take place and are followed by relaxation to a isomerized σ-complex in competition with the direct release of the alkylcarbenium ion.

Alternative Possibilities. Whereas the general properties of arenium ion dissociations are evidence for the existence of π-complex intermediates, these results do not preclude the existence of other loosely bound species such as an H-bonded complex.

The predominant dissociations expected of a H-bonded complex (structure **2**) are those that are observed for the arenium ions; that is, both protonated benzene or a carbenium ion (a protonated alkene) should form (see eq 3 and 5). The preferred ion species is that involving the constituent (benzene or alkene) having the

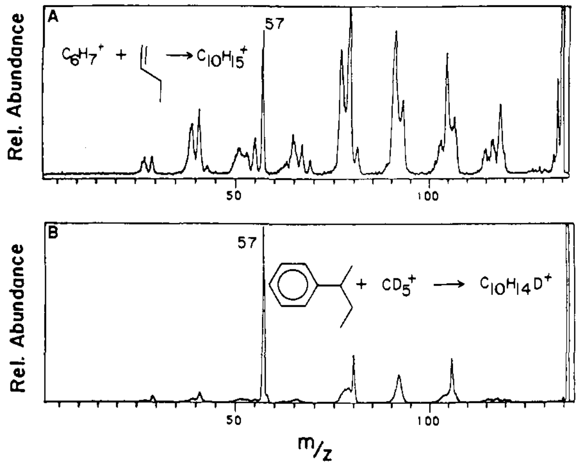
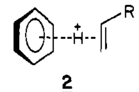


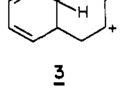
Figure 5. Comparison of the CAD spectra of the C_6H_6–C_4H_9 arenium ion formed via the reaction of $C_6H_7^+$ with 1-butene (A) and the *s*-butylarenium ion formed via deuteration of *s*-butylbenzene (B).

greater proton affinity. The proton affinities of ethylene and propylene are less than that of benzene, whereas the C_4H_8 and C_5H_{10} olefins possess higher proton affinities. As a result, the ethyl- and propylbenzenium ions should dominantly dissociate to $C_6H_6D^+$ and a neutral alkene, whereas all the larger benzenium ions would predominantly give R^+ and neutral benzene, and this is indeed observed.



2

To test whether the processes depicted in eq 5 play a role, we attempted to prepare **2** by reacting $C_6H_7^+$ (formed by loss of CH_2O from benzyl alcohol) and 1-butene. The CAD spectrum of the adduct (Figure 5A) is not consistent with hydrogen-bonded complex (which would give predominantly $C_4H_9^+$ and $C_6H_7^+$) or an arenium ion. Instead, a species is formed, such as structure **3**, in which the positive charge is located on the side chain and directs the extensive fragmentation leading to losses of various alkenes and CH_4.



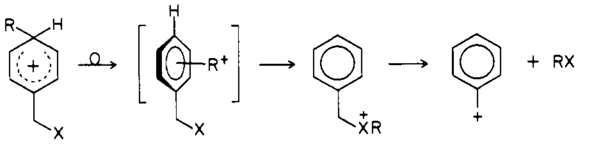
3

Because a hydrogen-bonded complex does not form in the $C_6H_7^+/C_4H_8$ reaction, either this complex is of higher energy than σ- and π-complexes, or there is a kinetic barrier preventing the interconversion of the H-bonded and π-complex. Moreover, if H-bonded complexes were important, they would serve as intermediates in the interconversion of arenium ions and species such as structure **3**. There is no evidence, however, for such interconversions (compare, for example Figure 5, A and B). Furthermore, if H-bonded complexes are accessible, then the H-bonded complex from the *n*-propylbenzenium ion would be identical with that of the isopropylbenzenium ion, and the two benzenium ions would possess identical dissociation properties. The *n*- and isopropylbenzenium ions, however, have unique properties (see Table I), indicating a significant kinetic barrier separating the π-complex and the H-bonded complex. We conclude that H-bonded complexes do not play an important role in arenium ion chemistry.

Further Evidence. Additional evidence in support of the π-complex participation in arenium ion chemistry can be found in the literature and can be broadly categorized into three groups: (1) the migration of incipient electrophiles, (2) the isomerization of alkyl side chains, or (3) the fragmentation of alkyl benzenes.

(1) Migration of Incipient Electrophiles. The general mechanism for this class of reaction involves the migration of an incipient electrophile (R) across a π-system to a suitably disposed nucleophilic substituent (X). This migration is followed by a direct cleavage expelling the electrophile/nucleophile (RX) as a neutral. The intermediate through which this migration takes place is proposed to be a π-complex between the electrophile and the aromatic π-system.

Grützmacher and co-workers[43,44] have described, in separate studies, two different systems that follow the mechanistic chemistry presented in eq 7. The protonated molecular ion of 1-[3-(methoxymethyl)phenyl]ethanol undergoes loss of $HCOOCH_3$ by a gas-phase metastable dissociation. To accommodate this result, the authors propose that the formyl cation (R in eq 7) must migrate across the π-system and associate with the oxygen of the methoxy group (X in eq 7 is OCH_3), followed by cleavage of $HCOOCH_3$ (RX). An identical mechanism was proposed to explain the metastable loss of CH_3COOCH_3 from the protonated molecular ion of *p*-(methoxymethyl)acetophenone (R = CH_3CO, X = OCH_3).[43]



(7)

(2) Isomerization of Alkyl Side Chains. In the high-pressure (100 Torr) gas-phase reaction of the radiolytically formed toluenium ion ($C_7H_9^+$) with neutral *n*-propane, the species formed is a mixture of *n*- and isopropyltoluene.[45] The mechanism proposed for this finding involves the intermediacy of a π-complex between the propylcarbenium ion and the aromatic ring. The isomerization of the propyl moiety takes place during the lifetime of the π-complex. Although the proposed mechanism reinforces our arguments, the analogy must be tempered because the radiolysis conditions used are quite different than those that are employed here.

Bäther and Grützmacher[46] reported on a carbenium ion system in which alkyl side chain isomerization occurs. Gas-phase β-arylethyl arenium ions undergo the metastable loss of an arene molecule. On the basis of indirect evidence (appearance energies), the authors propose that during this dissociation a rearrangement of the β-arylethyl arenium ion to the more stable α-arylethyl arenium ion takes place. The mechanism proceeds via a π-complex intermediate between the arylethyl carbenium ion and the π-system of the aromatic partner.

(3) Fragmentations of Protonated Alkylbenzenes. In an early study, Harrison and co-workers[47] postulated that the gas-phase protonated alkylbenzenes undergo alkyl side chain isomerization. The isomerization is thought to take place on the basis of the extent of $C_3H_7^+$ formation in the full-scan CI mass spectrum of protonated *n*-propylbenzene. Hence, his evidence for isomerization is also indirect. The proposed mechanism involves a π-complex intermediate.

The above evidence is in accord with the existence of gas-phase π-complexes. Each piece of evidence on its own is not sufficient. When taken as a whole and then combined with the observations of side isomerization reported here, however, the evidence for gas-phase π-complexes becomes quite convincing.

Validity of CAD Mass Spectrometry as a Structural Probe. Throughout this paper, we have assumed that collisional activation mass spectrometry is a valid probe of ion structure. Although most of the evidence does not involve strict quantitative comparison of spectra, it is imperative that differences in spectra reflect structural not internal energy differences. In order for CAD mass spectra to be reliable probes of structure, CAD spectra of a given species should not change with changing conditions. Parameters such as source temperature, the extent of collisional stabilization of the ions in the source, and the nature of the deuterating species were tested to see if they affect the spectra and, hence, the interpretation of the results.

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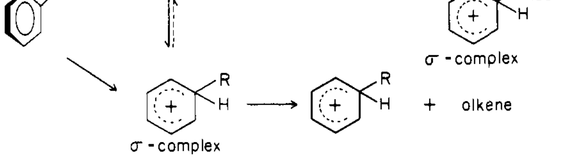
The CAD spectra of the arenium ion formed via methane-d_4 deuteration of neutral *n*-pentylbenzene in an unheated (80 °C) high-pressure source versus that formed in heated sources at 250 °C were compared and found to possess no measurable differences.

By varying the pressure of the reacting media, the extent of collisional stabilization, and hence the internal energy of the adduct ions, was modified. Using this approach, we previously illustrated that the nature of ion–molecule reaction adducts can be tracked as a function of their internal energy.[48-51] The relative abundance of the four dominant fragment ions observed in the CA dissociation of a model arenium ion formed under various pressure conditions was found to be unaffected by the extent of collisional stabilization (relative abundances were constant to within ±1.0%). (See Experimental Section for details.)

Finally, the dissociation properties of the gas-phase arenium ions were measured as a function of the energy of D^+ transfer. The internal energy of the arenium ion formed via bimolecular reaction is directly proportional to the difference in proton affinities of the deuterating reagent and the neutral alkylbenzene. The dissociation properties of the *s*-butylbenzenium ion formed from D^+ transfer from ND_4^+, D_3O^+, and CD_5^+ are an appropriate test. The proton affinities of the neutral, unlabeled precursors NH_3, H_2O, and CD_4 are 205, 173, and 131 kcal/mol, respectively, whereas that for *s*-butylbenzene is 183 kcal/mol. As expected, reacting *s*-butylbenzene with gaseous ND_3 produces no detectable *s*-butylbenzenium ion. The reaction of either D_3O^+ or CD_5^+ with *s*-butylbenzene, however, produces significant amounts of the arenium ions. Their CAD spectra are nearly identical, establishing even more emphatically that CAD spectra are adequate structural probes for arenium ions.

Conclusion

A scheme depicting both σ- and π-complexes as intermediates on the arenium ion potential energy surface is presented in eq 8.



(8)

For arenium ions that possess larger alkyl moieties (i.e., butyl, pentyl), isomerization of the alkyl moiety takes place. The isomerized π-complex either collapses to the corresponding σ-complex or dissociates to form a carbenium ion and benzene. The principal support for this hypothesis comes from the observation that alkyl side chain isomerization can be detected for certain gas-phase arenium ions. Such isomerizations are only possible if significant carbenium ion character resides on the alkyl moiety, as would be expected in a π-complex. Further support for π-complex participation comes from the general properties of gas-phase arenium ion dissociations.

Evidence for the existence of an "early complex" of unknown structure preceding formation of a σ-complex was reviewed recently by Cacace[52] for gas-phase aromatic substitution occurring under radiolytic conditions. The kinetic role of the early complex is identical with that of the "encounter complex" proposed for solution aromatic substitution.[52] The results of this study are interpreted to reveal that the gas-phase early complex is a π-complex, which exists as a distinct intermediate on the potential energy surface of arenium ions. The existence of π-complexes in condensed-phase EAS cannot be decided on the basis of a study of gas-phase ions. The extensive indirect evidence reported by Olah[15-21] coupled with the findings reported here, however, are in accord with the existence of the latter in solution.

Experimental Section

The mass spectrometer used in this study was a Kratos MS-50 Triple Analyzer[53] tandem (MS/MS) system of EB/E configuration. MS-I is a standard Kratos double-focusing MS-50 (ESA-1 and magnetic sector). MS-II is an electrostatic analyzer (ESA-II). A high-pressure chemical ionization source equipped with two reservoir/leak valve systems for sample admission was utilized in this study.

For producing arenium ions, an alkylbenzene was admitted into the high-pressure chemical ionization (CI) source through a controllable leak valve. The chemical ionization reagent gas (CH_4, CD_4) was also admitted into the CI source chamber through the second leak valve system. Protonation by CH_5^+ or deuteration by CD_5^+ of the alkylbenzene to give the arenium ion was conducted in the CI source. All ionic species were accelerated to 8 KeV into the MS-I portion of the tandem mass spectrometer. MS-I was set to allow the passage of only one mass ion, the arenium ion of interest, at a resolution of 2500 (10% valley definition). The arenium ion was activated in field free region III (between the magnet and ESA-II) by collision in a chamber pressurized with sufficient He such that 50% of the main beam intensity was suppressed. The fragment ion mass spectrum (CAD spectrum) was then obtained by scanning ESA-II from zero volts to the main beam voltage. All CAD spectra reported are the average of a minimum of 30 scans.

The metastable ion spectra of the arenium ions were obtained in a similar fashion except He was not admitted to the collision cell in field free region III.

All the unlabeled alkylbenzenes used in this study were obtained commercially from Aldrich Chemical Co., Inc. The alkylbenzenes were distilled prior to use, and their purity was established by mass spectrometric techniques. Research-grade (99.9%) methane-d_4 was obtained from Cambridge Isotopes Inc. and was used without further purification. The deuterated *s*-butylbenzene, $C_6H_5–CH(CD_3)C_2H_5$, was prepared from labeled 2-phenyl-2-butanol via the reduction method described by Small[54] and co-workers. The labeled 2-phenyl-2-butanol was prepared from the reaction of labeled methyl Grignard reagent, CD_3MgBr, with propiophenone. The *s*-propyl-*n*-butylbenzene was prepared in a similar fashion from $CH_3CO–C_6H_5–C_4H_9$, which was formed in the Friedel–Crafts acylation of *n*-butylbenzene. The synthesized compounds were distilled prior to use, and their purity was established by using mass spectrometric techniques.

The gas-phase reaction of $C_6H_7^+$ with C_4H_8 was conducted as follows. The $C_6H_7^+$ was generated via CH_2O loss from benzyl alcohol in a high-pressure CI source in lieu of protonation of benzene to preclude interference from ions formed by reaction of butyl ions and neutral benzene. In the presence of 1-butene, the $C_6H_7^+$/1-butene adduct ion formed and was selected and analyzed by means of the MS/MS technique.

The labeled *sec*-butylbenzenium ion, which was formed at various source pressures to test the effect that source pressure has on ion dissociation properties, was examined as follows. In separate experiments where the partial pressure of the neutral alkylbenzene was held constant at 2×10^{-5} Torr, methane-d_4 was added to total pressures of 4×10^{-5} and 4×10^{-4} Torr, respectively. The lower of the two total pressures represents the minimum pressure required in order for the reaction to take place. The higher pressure represents the upper limit that instrument pumping capacity allowed. The pressures quoted above were measured by a cold cathode gauge located in the source housing, the actual source pressures for these two experiments are approximately 0.05–0.08 Torr for the lower limit and 0.80–1.0 Torr for the upper limit.

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