here show that the analyst must keep in mind the possibility that with a low exothermicity the sensitivity may be relatively low. Beyond that, to achieve best sensitivity he is advised to operate the mass spectrometer ion source at the lowest temperature that is compatible with the other experimental requirements of the system being investigated.

References and Notes

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Phenylium (C6H5+) Ion–Molecule Reactions Studied by Ion Cyclotron Resonance Spectroscopy

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Abstract: Ion-assisted dehalogenation reactions of halobenzenes provide a convenient source of phenylium ions. Gas-phase reactions of phenylium ions with hydrogen, alkanes, alkyl halides, alkenes, and arenes have been studied by ion cyclotron resonance spectroscopy. Phenylium ions are strong electrophiles, attacking σ as well as π and nonbonding electrons. The reactivity of phenylium ions has carbenoid characteristics.

While relatively little is known about the gas-phase chemistry of phenylium ions $C_6H_5^+$, the literature indicates a renewal of interest in the electronic structure and reactions of this elusive species.

The formation and reactions of phenylium ions in the liquid phase have been reviewed by Richey and Richey.[1] Such reactions as addition of Lewis bases, addition to π-electron systems, and hydride transfer have been reported for aryl cations in solution. However, a mechanistic ambiguity has plagued the solution experiments; alternative pathways which include as reactive intermediates species other than aryl cations, e.g., free radicals and adducts of nucleophiles to diazonium ions, have proven difficult to exclude. The claim has recently been revived that dediazotization of phenyl diazonium ion produces phenyl cations in solution.[2]

Semiempirical SCF calculations of the INDO type have been carried out for the phenylium and 4-aminophenylium ions.[3,4] A singlet ground state with an empty σ orbital has been predicted on the basis of these calculations for the unsubstituted system and nearly degenerate triplet and singlet lowest states for the 4-aminophenylium ion, with vacancies in π and σ orbitals, respectively. Recent ab initio calculations have been interpreted as supporting the assignment of a singlet ground state for the phenylium ion.[5] Stabilization of an empty σ orbital of substituted phenylium ions via "through-bond" interactions has been studied by extended-Hückel molecular orbital calculations.[6]

In order to explain the discrepancy between the ionization potential of phenyl radicals deduced from appearance potentials of $C_6H_5^+$ (8.80 eV) and the value obtained from direct ionization of the radical (9.2 eV)[7] it has been suggested that the $C_6H_5^+$ ion obtained from halobenzenes by electron impact may not possess the phenylium ion structure. Recently, however, collision activation spectra of substituted toluenes have been interpreted as being due to o-, m-, and p-$CH_3C_6H_4^+$.[8] The phenylium ion structure for the $C_6H_5^+$ ion formed by loss of H_2 from protonated benzene has been supported by an elegant argument based on the conservation of orbital symmetry.[9]

We have not, however, found any data describing the gas-phase reactions of the phenylium ion. The report which follows contains several such reactions. In the course of ion–molecule reaction studies designed to shed light on the mechanism of radiation-induced protodehalogenation of halobenzenes,[10] a convenient source of phenylium ions was discovered which prompted this study of their ion–molecule reactions. The reactions of $C_6H_5^+$, with D_2, CH_4, CD_4, CH_3F, CH_3Cl, CH_3Br, CH_2Cl_2, C_2H_6, C_2H_4, propene, cyclopropane, C_6H_5Cl, and C_6H_5F, are reported here.

Experimental Section

The ion cyclotron resonance spectroscopic techniques employed in this study have been described in detail.[11] The experiments were performed with an ionizing electron energy just sufficient to produce the ions of interest (typically 16 to 20 eV). The total pressure in the reaction cell was 10^{-5} Torr. Double resonance experiments were carried out under strong field conditions[12] with an accelerating field of 0.7 V/cm. All gaseous reagents were purchased from Matheson Co. and used without further purification. Liquid reagents were purchased from standard commercial suppliers and purified by

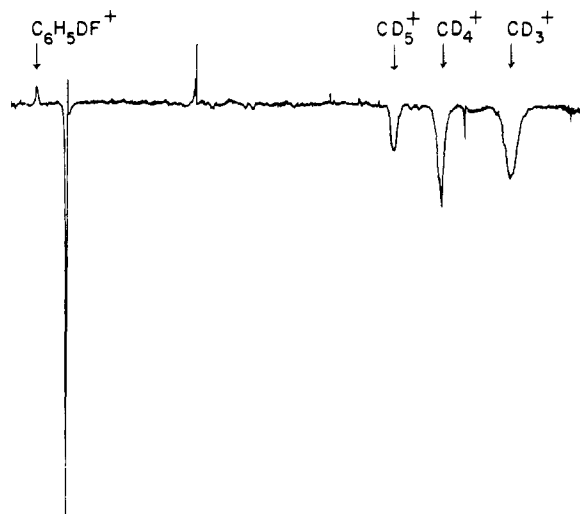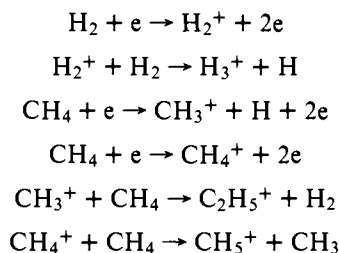* Address correspondence to this author at Washington University.

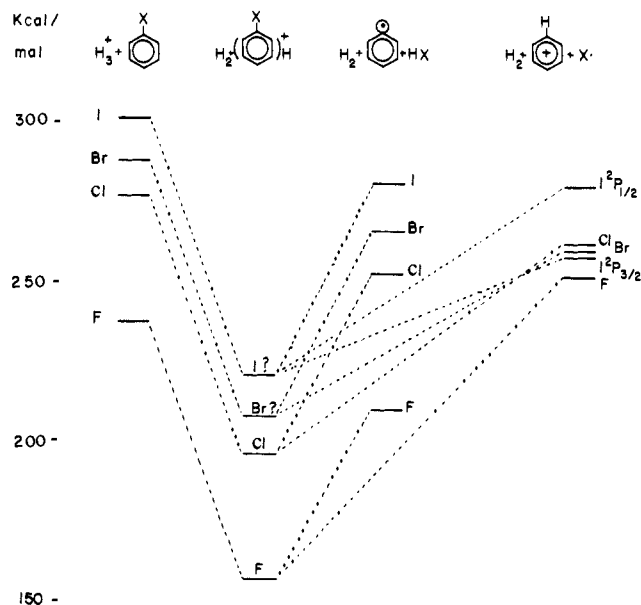Figure 1. Double-resonance spectrum of m/e 77 in CD_4-C_6H_5F mixtures.

Figure 2. Thermochemistry of proton-assisted dehalogenation and protodehalogenation of halobenzenes by H_3^+. Thermochemical data employed are given in Table VI. The proton affinities of bromo- and iodobenzene are assumed equal to those of fluoro- and chlorobenzene.

chromatographic and distillation techniques. In all reaction mixtures a 1:10 ratio of halobenzene to the other reagent was employed.

Formation of Phenylium Ions in Ion–Molecule Reactions

When mixtures of hydrogen o.' methane with halobenzenes are subjected to electron impact in an ion cyclotron resonance spectrometer, $C_6H_5^+$ is a major secondary ion as well as a minor primary ion. Table I gives the single resonance ICR spectra of deuterium–halobenzene mixtures. The large relative magnitude of the m/e 77 $C_6H_5^+$ ion intensity for fluorobenzene in the presence of D_2 is particularly dramatic. The differences in the relative ion abundances for the four halobenzenes will be discussed below in the context of both the formation and reactions of phenylium ions.

In mixtures containing hydrogen or methane, the following well-known ion–molecule reactions and their deuterium counterparts give rise to ions capable of converting halobenzenes into $C_6H_5^+$:

$$H_2 + e \rightarrow H_2^+ + 2e$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

$$CH_4 + e \rightarrow CH_3^+ + H + 2e$$

$$CH_4 + e \rightarrow CH_4^+ + 2e$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$$

In their recently published report of the chemical ionization spectra of halobenzenes Harrison and co-workers observed that the phenylium ion was formed from fluoro-, chloro-, and bromobenzene when hydrogen was employed as the reagent gas but not with methane.[13] These authors estimated that the formation of phenylium ions from CH_5^+ and fluorobenzene is endothermic. Our experiments (see below) indicate that this reaction may be nearly thermoneutral. The failure to observed $C_6H_5^+$ in the methane chemical ionization experiments of Harrison may be due to the rapid consumption of the phenylium ion by reaction with methane. (The rate constant for $C_6H_5^+ + CH_4$ is ca. 0.6×10^{-10} cm^3 molecule^{-1} s^{-1}, i.e. ca. 0.6 times the rate constant for $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$.)

Table II summarizes the ion–molecule reactions we have observed which give rise to phenylium ions. The phenylium ion structure is assigned to the $C_6H_5^+$ produced in these experiments on the basis of the following considerations:

(a) The relatively mild protonating agents CD_3^+, CD_4^+, and

Table I. Single Resonance Spectra of 10:1 D_2–Halobenzene Mixtures[a]

Ion[b]	m/e	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I
$C_6H_5^+$ [c]	77	21.0	20.7	7.8	5.5
$C_6H_4D^+$	78	14.5	18.1	16.8	6.3
$C_6H_5D^+$	79	8.4	11.9	33.9	72.9
$C_6H_4D_2^+$	80	5.5	9.0	19.1	13.6
$C_6H_5D_2^+$	81	34.8	24.9	8.5	1.9
$C_6H_4D_3^+$	82	5.8	15.4	13.8	0

[a] Entries are relative ion abundances, the sum of the ion intensities from m/e 77 to 82 taken as 100. [b] Formulas for the major contributor to each m/e. The entries have not been corrected for contributions from [13]C. [c] When formed directly by electron impact at 18 eV on the halobenzenes, the relative phenylium ion intensities $C_6H_5^+/C_6H_5X^+$ are 0 (X = F), 0.16 (X = Cl), 0.36 (X = Br), and 0.43 (X = I); these data are taken from I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, **91**, 7137 (1969).

CD_5^+ react with fluorobenzene to produce $C_6H_5^+$ with less than 5% $C_6H_4D^+$. In mixtures of CD_4 with chlorobenzene only CD_3^+ converts C_6H_5Cl in $C_6H_5^+$ via an exothermic reaction,[14] again with only a very small amount of $C_6H_4D^+$ formed. (Note that CD_4^+ and CD_5^+ do not appear to react with C_6H_5Cl to produce $C_6H_5^+$.) These observations suggest that in these reactions $C_6H_5^+$ is formed via attack at the halogen atom. The observation of a double resonance signal indicating an endothermic step $C_6H_6X^+ \rightarrow C_6H_5^+ + HX$ is compatible with a two-step mechanism, exothermic proton transfer to the halobenzene followed by dissociation of the $C_6H_5XH^+$. The double-resonance spectrum is shown in Figure 1. Supporting this mechanism are results of ion–molecule reaction studies in the methane–fluorobenzene system. The major product from methane ions and fluorobenzene is protonated fluorobenzene, also observed by Harrison and Lin in the methane chemical ionization mass spectrum of fluorobenzene.[13] Participation by a direct or stripping reaction has not, however, been excluded. The thermochemistry of proton-transfer reactions from CH_5^+ and H_3^+ to halobenzenes is indicated in Figures 2 and 3.

(b) With protonating agents such as D_2^+ and D_3^+, whose reactions with halobenzenes are strongly exothermic, some
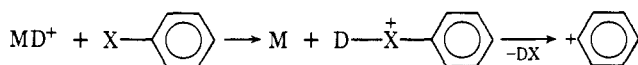
Table II. Ion–Molecule Reactions which Produce Phenylium Ions[a]

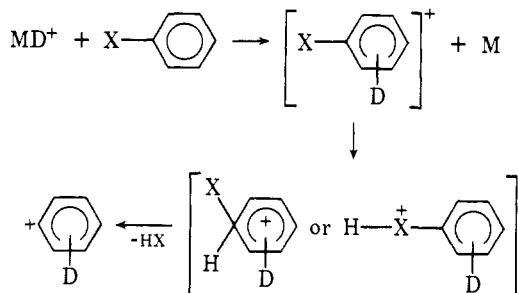|	Reactant ions detected in double resonance experiments[b]									
	H_2^+	H_3^+	D_2^+	D_3^+	CH_3^+	CH_4^+	CH_5^+	CD_3^+	CD_4^+	CD_5^+
Neutral substrates converted to $C_6H_5^+$										
C_6H_5F	X	X	X	X	X	X	X	X	X	X
C_6H_5Cl				X	X			X		
C_6H_5Br				X						
Neutral substrates converted to $C_6H_4D^+$										
C_6H_5F			X	X						
C_6H_5Cl			X	X				X		
Neutral substrates converted to $C_6H_4F^+$										
$p\text{-}C_6H_4F_2$			X	X	X	X	X	X	X	X
$p\text{-}C_6H_4ClF$				X						
$m\text{-}C_6H_4F_2$			X	X	X	X	X	X	X	X
$m\text{-}C_6H_4ClF$				X	X			X		
$o\text{-}C_6H_4F_2$				X	X	X	X	X	X	X
$o\text{-}C_6H_4ClF$				X	X			X	X	
Neutral substrates converted to $C_6H_3DF^+$										
$p\text{-}C_6H_4F_2$			X	X						
$p\text{-}C_6H_4ClF$				X						
$m\text{-}C_6H_4F_2$			X	X						
$m\text{-}C_6H_4ClF$				X						
$o\text{-}C_6H_4F_2$				X						
$o\text{-}C_6H_4ClF$				X						
Neutral substrates converted to $C_6H_4Cl^+$										
$p\text{-}C_6H_4ClF$				X	X	X	X		X	X
$m\text{-}C_6H_4ClF$				X	X	X	X	X	X	X
$o\text{-}C_6H_4ClF$				X		X	X	X	X	X

[a] An X in the table indicates that the reaction was observed in a double resonance experiment. Absence of an X does not necessarily mean that the reaction does not occur. [b] The double resonance spectra were recorded at a pressure of 1×10^{-5} Torr with a double resonance field of 0.7 V/cm.

exchange accompanies dehalogenation, and $C_6H_4D^+$ is formed as well as $C_6H_5^+$ (cf. Table I). The ratio of phenylium ion formation to simple protonation of the halobenzene is much greater with D_n^+ (H_n^+) protonating agents than with CD_n^+ (CH_n^+), although proton and deuteron transfer to the halobenzenes may occur without fragmentation, as indicated by Table III. Therefore it seems plausible that protonation of the halobenzene at the halogen can lead to phenylium ion formation without exchange while attack *at the ring* leads to phenylium ion formation only when there is sufficient internal energy to permit rearrangement and cleavage of the ring-protonated or deuterated halobenzene.[15] Without implying detailed reaction mechanisms, these reactions may be illustrated as follows:

Direct attack on halogen:

$$MD^+ + X\text{—}C_6H_5 \longrightarrow M + D\overset{+}{\text{—}}X\text{—}C_6H_5 \xrightarrow{-DX} {}^+C_6H_5$$

Attack on ring:

$$MD^+ + X\text{—}C_6H_5 \longrightarrow \left[X\text{—}C_6H_5D \right]^+ + M$$

$$\downarrow$$

$${}^+C_6H_5D \xleftarrow{-HX} \left[\begin{array}{c} X \\ \diagdown \diagup \\ H \quad D \end{array} (+) \text{ or } H\text{—}\overset{+}{X}\text{—}C_6H_4D \right]$$

In favor of the unrearranged structure for the phenylium ion formed in proton-assisted dehalogenation of halobenzenes is the fact that ions whose reactions with halobenzenes do *not* lead to exchange of hydrogen accompanying dehalogenation are observed to cause dehalogenation.
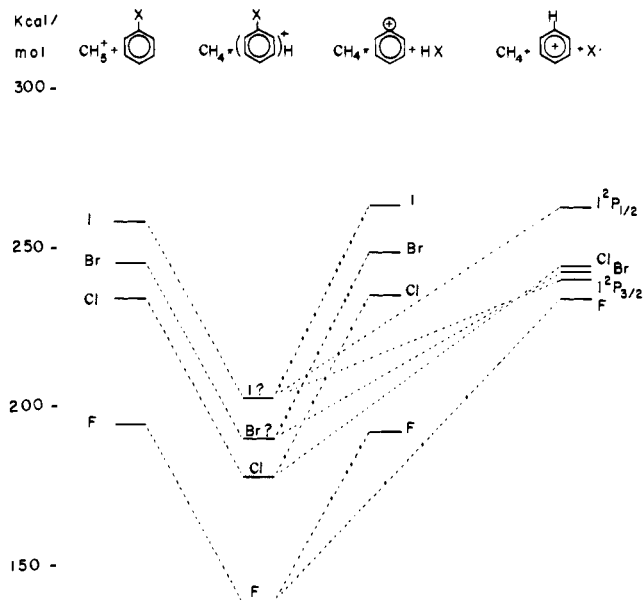

Figure 3. Thermochemistry of proton-assisted dehalogenation and protodehalogenation of halobenzenes by CH_5^+. Thermochemical data employed are given in Table VI. The proton affinities of bromo- and iodobenzene are assumed equal to those of fluoro- and chlorobenzene.

It is interesting to compare the $C_6H_n^+$ relative ion abundances obtained from mixtures of D_2 with each of the four halobenzenes. The data are given in Table I. The *decrease* in the relative abundance of $C_6H_5^+$ in the series $C_6H_5F > C_6H_5Cl > C_6H_5Br > C_6H_5I$ is evidence for the importance of ion-assisted dehalogenation in its formation, since production of $C_6H_5^+$ as a primary ion fragment from electron impact on the halobenzenes *increases* in relative importance in this series.

Table III. Observed Proton and Deuteron Transfers to Halobenzenes[a,b]

c	D_2^+	D_3^+	CH_3^+	CH_4^+	CH_5^+	$C_2H_5^+$	CD_3^+	CD_4^+	CD_5^+	$C_2D_5^+$
C_6H_5F	X	X	X	X	X	X	X	X	X	X
C_6H_5Cl	X	X	X	X	X	X	X	X	X	X
p-$C_6H_4F_2$		X	X	X	X	X	X	X	X	X
p-C_6H_4ClF			X	X	X	X	X	X	X	X
m-$C_6H_4F_2$		X	X	X	X	X	X	X	X	X
m-C_6H_4ClF			X	X	X	X	X	X	X	X
o-$C_6H_4F_2$		X	X	X	X	X	X	X	X	X
o-C_6H_4ClF			X	X	X	X	X	X	X	X

[a] An X in the table indicates that the reaction was observed in a double-resonance experiment. [b] The double-resonance spectra were recorded at a pressure of 1×10^{-5} Torr with a double-resonance field of 0.7 V/cm. [c] Neutral substrate to which proton or deuteron transfer was observed.

Table IV. Observed Product Ions from Phenylium Ion–Molecule Reactions[a,b,c]

Neutral substrate	$C_6H_5^+$ from C_6H_5F	$C_6H_5^+$ from C_6H_5Cl	$C_6H_5^+$ from C_6H_5Br	$C_6H_5^+$ from C_6H_6	$C_6H_4F^+$ from C_6H_5F	$C_6H_4F^+$ from p-$C_6H_4F_2$	$C_6H_4F^+$ from m-$C_6H_4F_2$	$C_6H_4F^+$ from o-$C_6H_4F_2^+$	$C_6H_4F^+$ from p-C_6H_4ClF	$C_6H_4F^+$ from m-C_6H_4ClF	$C_6H_4^+$ from o-C_6H_4ClF
H_2	$C_6H_7^+$										
D_2	$C_6H_5D_2^+$	$C_6H_5D_2^+$	$C_6H_5D_2^+$		$C_6H_4D_2F^{+j}$	$C_6H_4D_2F^+$	$C_6H_4D_2F^+$	$C_6H_4D_2F^+$	$C_6H_4D_2F^+$	$C_6H_4D_2F^+$	$C_6H_3D_3F^{+l}$
CH_4	$C_7H_7^+$ (1.00)	$C_7H_7^+$ (1.00)	$C_7H_7^+$ (1.00)		$C_7H_6F^{+}$	$C_7H_6F^+$ (1.00)	$C_7H_6F^+$ (1.00)	$C_7H_6F^{+d}$	$C_7H_6F^+$ (1.00)	$C_7H_6F^+$ (1.00)	$C_7H_6F^+$ (1.00)
	$C_7H_9^+$ (0.33)	$C_7H_9^+$ (0.20)	$C_7H_9^+$ (0.04)			$C_7H_8F^+$ (0.28)	$C_7H_8F^+$ (0.49)^1	$C_7H_8F^{+d}$	$C_7H_8F^+$ (0.09)	$C_7H_8F^+$ (0.10)	$C_7H_8I^+$ (0.12)
CD_4	$C_7H_5D_2^{+d}$	$C_7H_5D_2^{+d}$	$C_7H_5D_2^{+d}$		$C_7H_4D_2F^+$	$C_7H_4D_2F^+$ (0.35)	$C_7H_4D_2F^{+d}$	$C_7H_4D_2I^{+d}$	$C_7H_4D_2F^+$ (0.42)	$C_7H_4D_2F^+$ (0.33)	$C_7H_4D_2F^+$ (0.39)
	$C_7H_4D_3^+$	$C_7H_4D_3^+$ (1.00)	$C_7H_4D_3^+$ (1.00)		$C_7H_3D_3F^{+d}$	$C_7H_3D_3F^+$ (1.00)	$C_7H_3D_3F^+$	$C_7H_3D_3I^+$	$C_7H_3D_3F^+$ (1.00)	$C_7H_3D_3F^+$ (1.00)	$C_7H_3D_3I^+$ (1.00)
	$C_7H_3D_4^{+f}$	$C_7H_3D_4^{+d}$	$C_7H_3D_4^+$ (0.33)			$C_7H_2D_4I^{+k}$	$C_7H_2D_4I^{+k}$	$C_7H_2D_4I^{+k}$	$C_7H_2D_4I^{+d}$	$C_7H_2D_4F^{+d}$	$C_7H_2D_4F^{+d}$
	$C_7H_5D_2^{+g}$	$C_7H_5D_4^+$ (0.43)	$C_7H_5D_4^{+e}$			$C_7H_4D_4I^{+k}$	$C_7H_4D_4I^{+k}$	$C_7H_4D_4I^{+k}$	$C_7H_4D_4I^+$ (0.14)	$C_7H_4D_4F^+$ (0.18)	$C_7H_4D_4F^{+e}$
C_6H_5F	$C_{12}H_9^{+h}$										
C_6H_5Cl		$C_{12}H_9^{+h}$									
C_2H_6		$C_6H_7^+$									
C_2H_4		$C_8H_7^+$ (1.00)									
		$C_6H_7^+$ (0.85)									
C_3H_6		$C_7H_7^+$									
cyclo-C_3H_6		$C_7H_7^+$								$C_7H_5FCl^+$	
CH_2Cl_2		$C_7H_6Cl^+$									
CH_3F				$C_7H_7^+$ (1.00)							
				$C_7H_6F^+$ (0.01)							
CH_3Cl				$C_7H_7^+$ (1.00)							
				$C_7H_6Cl^{+e}$							
CH_3Br				$C_7H_7^+$							
				$C_7H_6Br^{+i}$							

[a] All product ions in this table were linked with reactant ions by double resonance experiments. The absence of a product from the table does not necessarily mean that the reaction producing it does not occur. [b] The double resonance spectra were recorded at a pressure of 1×10^{-5} Torr with a double-resonance field of 0.7 V/cm. [c] Numbers in parentheses are relative yields for product ions formed from the same reactant ion. [d] Relative yield not determined. [e] Very small yield. [f] Interference from $C_6H_4I^+$. [g] Interference from $C_6H_4DF^+$ and $^{13}CC_5H_5F^+$. [h] Relative yield could not be determined because of other probable product ions too heavy to be detected. [i] Probable product ion not detected because it is too heavy. [j] Interference from deuteration products of C_6H_5F. [k] Interference from ionization products of $C_6H_4F_2$. [l] Very small $C_6H_4D_2I^+$ yield also obtained.

The exothermicity of the reaction $H_3^+ + C_6H_5X \rightarrow H_2 + HX + C_6H_5^+$ decreases in the series $X = F > Cl > Br > I$ as shown in Figure 2. The reaction probability would be expected to decrease with decreasing exothermicity, particularly if there is a contribution from a direct or stripping reaction.

Beauchamp has determined the proton affinities of CH_3X ($X = F, Cl, Br,$ and I) and has found a *decrease* in basicity in the order $CH_3I > CH_3Br > CH_3Cl > CH_3F$.[16] Therefore an order of halogen basicities for the halobenzenes *inverted* from that found for the halomethanes would be required *if* halogen basicity were the dominant factor determining the ease of proton-assisted dehalogenation of the halobenzenes. (A different order of basicities for the halobenzenes might be due to electron release from the π-electron system of the phenyl ring, decreasing in importance with decreasing electronegativity of the halogen in the order $F > Cl > Br > I$, or to electron release from the halogen to the ring, increasing in the order $F < Cl < Br < I$.)

Table I indicates an increase in the relative abundance of m/e 78 ($C_6H_4D^+$) and 79 ($C_6H_5D^+$) in the order $C_6H_5F < C_6H_5Cl < C_6H_5Br < C_6H_5I$ which reflects the increasing basicity of the π-electron system. There is increasing loss of X· relative to the loss of HX with decreasing C–X bond strength, $D(C-F) > D(C-Cl) > D(C-Br) > D(C-I)$.
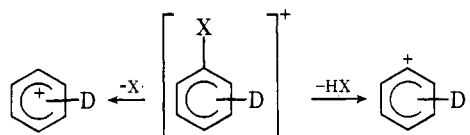

The similarity of the reactivity of $C_6H_5^+$ from proton-assisted dehalogenation of fluorobenzene and $C_6H_5^+$ from electron impact on chlorobenzene provides further evidence that both "primary" and "secondary" $C_6H_5^+$ ions possess the same structure.

Reactions of Phenylium Ions

The observed reactions of phenylium ions, as deduced from double-resonance spectra, are summarized in Table IV. The entries in Table I under m/e 81 and 82 are also products of phenylium ion reactions, $C_6H_5^+$ and $C_6H_4D^+$ react with D_2 to give $C_6H_5D_2^+$ and $C_6H_4D_3^+$, respectively. Table I indicates that the formation of $C_6H_5D_2^+$ correlates well with the formation of $C_6H_5^+$, as expected if our picture of these reactions is correct.

As a simple addition process, the reaction of phenylium ions with deuterium is a rather unusual low-pressure ion–molecule reaction.
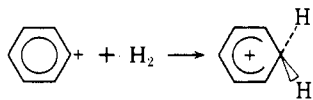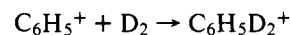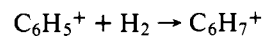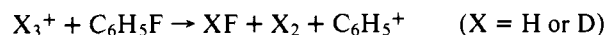

That this addition is symmetry allowed in the Woodward–Hoffmann sense[17] as a concerted process has been deduced from a molecular orbital correlation diagram by Williams and Hvistendahl.[9] These workers observed no release of kinetic energy in the reversal of addition and deduced that 1,1-elimination occurred: $C_6H_7^+ \rightarrow C_6H_5^+ + H_2$. We may thus infer that there is no activation energy barrier to the addition of the phenylium ion to hydrogen. Since addition to form the ground state of protonated benzene is exothermic by an estimated 60 to 80 kcal/mol,[18] a product ion $C_6H_7^+$ of this structure would have to absorb this exothermicity within its internal degrees of freedom in order to survive. If, however, an excited electronic state of product ion $C_6H_7^+$ is formed, or if the product ion has a ring-opened structure, the exothermicity of addition may be much less.[19]

In chemical ionization experiments Harrison and Lin have proposed that $C_6H_5D_2^+$ is formed by a direct fluorine displacement reaction:[13]

$$D_3^+ + C_6H_5F \rightarrow C_6H_5D_2^+ + DF$$
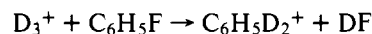
In our ICR experiments a two-step process is clearly indicated by double-resonance spectra, but a contribution from the direct reaction is not excluded. The two-step mechanism is:

$$X_3^+ + C_6H_5F \rightarrow XF + X_2 + C_6H_5^+ \qquad (X = H \text{ or } D)$$

$$C_6H_5^+ + H_2 \rightarrow C_6H_7^+$$

$$C_6H_5^+ + D_2 \rightarrow C_6H_5D_2^+$$

The addition of phenylium ions to deuterium displays an apparent substituent effect. Table V indicates that the ratio of $C_6H_4D_2F^+$ adduct ion to $C_6H_4F^+$ reactant fluorophenylium ion differs for the three neutral precursor molecules *o*-, *m*-, and *p*-chlorofluorobenzene, increasing in the order ortho < meta < para. Our inference is that the differences in product ratios are due to differences in reactivity for the structurally distinct *o*-, *m*-, and *p*-fluorophenylium ions. Differences in the internal energy of the fluorophenylium ions from different precursors may also contribute to the observed product ratios. While the fluorophenylium ions differ in apparent reactivity by less than a factor of 2 from that of the unsubstituted ion, no adduct was observed from the reaction of chlorophenylium ions $C_6H_4Cl^+$.

From reactions of $C_6H_5^+$ with CH_4, both $C_7H_9^+$ and $C_7H_7^+$ product ions are observed. Thus, even when a fragmentation channel is available, simple addition can be observed. Bond rupture without fragmentation may also occur. Williams and Hvistendahl, who found a kinetic energy release of 20 kcal/mol in the loss of H_2 from $C_7H_9^+$, formulated this as a symmetry-forbidden concerted 1,2- or 1,3-hydrogen elimination from a dihydrotropylium ion.[9] This implies an activation energy for hydrogen loss from $C_7H_9^+$ larger than the overall endothermicity, if the methane adduct of the phenylium ion rearranges to the dihydrotropylium ion. It does *not* necessarily imply an activation energy for the addition of phenylium ion to methane, since the initial adduct need not possess the dihydrotropylium structure. In the attack of $C_6H_5^+$ on CD_4, the product ion $C_7H_4D_3^+$ predominates over $C_7H_5D_2^+$. Also in reactions of $C_6H_4F^+$ with CD_4 loss of both HD and D_2 is observed. Since the lost hydrogen molecule does not come exclusively from the methane molecule, rearrangement of a long-lived intermediate prior to hydrogen loss seems to be indicated.

In the reaction of phenylium ion with ethane, the major product ion is $C_6H_7^+$ which could arise from either 1,1- or 1,2-hydrogen transfer. Both processes, if concerted, have small symmetry imposed barriers in the ground singlet electronic state, as indicated by Figures 4 and 5.
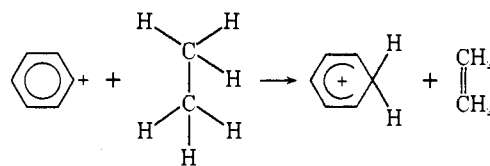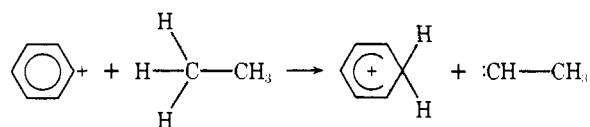
There have, however, been recent reports of ion–molecule reactions occurring by symmetry-forbidden concerted paths,[9,20] and the reactions are symmetry allowed in the lowest triplet electronic states. On thermochemical grounds the 1,2 transfer
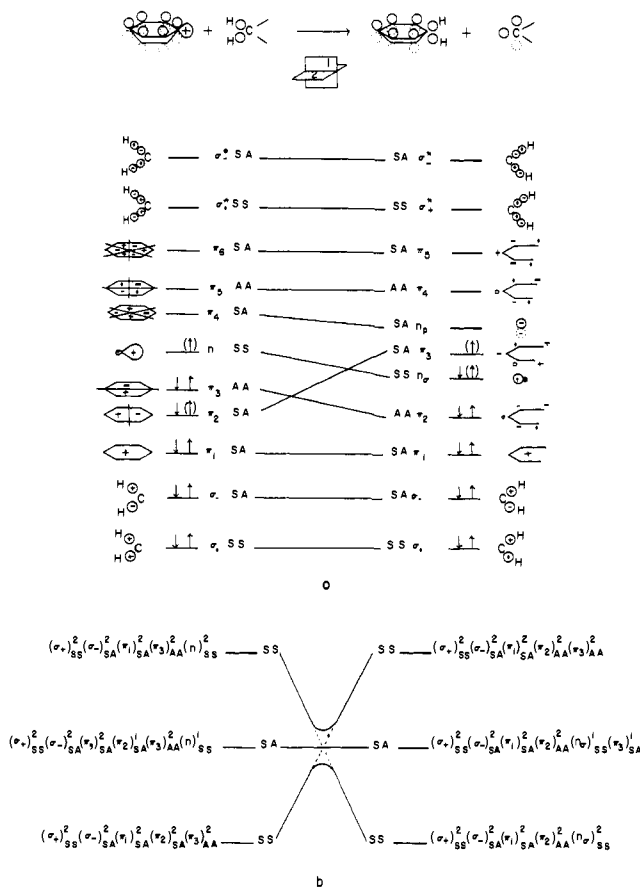
Figure 4. (a) Molecular orbital correlation diagram for 1,1-hydrogen transfer to a phenylium ion. (b) Electronic state correlation diagram for 1,1-hydrogen transfer to a phenylium ion.

Table V. Substituent Effects on Phenylium Ion Reactivity[a]

Phenylium ion precursor	Phenylium ion	Product ion	Ion intensity ratio product ion:phenylium ion
o-C_6H_4ClF	$C_6H_4F^+$	$C_6H_4D_2F^+$	1.0^b
m-C_6H_4ClF	$C_6H_4F^+$	$C_6H_4D_2F^+$	1.2^b
			0.4^c
p-C_6H_4ClF	$C_6H_4F^+$	$C_6H_4D_2F^+$	1.5^b
C_6H_5F	$C_6H_5^+$	$C_6H_5D_2^+$	1.1^b
C_6H_5Cl	$C_6H_5^+$	$C_6H_5D_2^+$	1.2^b
m-C_6H_5ClF	$C_6H_4Cl^+$	$C_6H_4D_2Cl^+$	0^c

[a] All reactions are additions to deuterium: $XC_6H_4^+ + D_2 \rightarrow XC_6H_4D_2^+$. [b] Pressure ca. 5×10^{-5} Torr. [c] Pressure ca. 2×10^{-5} Torr.

is favored. The 1,1-hydrogen transfer is estimated to be endothermic, but the reaction observed is shown to be exothermic by the shape of the double-resonance signal[12] for the process $C_6H_5^+ + C_2H_6 \rightarrow C_6H_7^+ + C_2H_4$. In further support of the occurrence of 1,2-hydrogen transfer in the reactions of phenylium ions with ethane, it should be noted that $C_6H_7^+$ ions are not produced in the reactions of phenylium ions with methane, as might have been expected if 1,1-hydrogen transfer were a facile reaction.

The reactions of phenylium ions with ethylene also produce $C_6H_7^+$ product ions, and again 1,2-hydrogen transfer is believed to occur. A further reaction takes place for whose product it would be premature to assign a structure.

$$C_6H_5^+ + C_2H_4 \rightarrow C_8H_7^+ + H_2$$
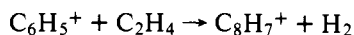
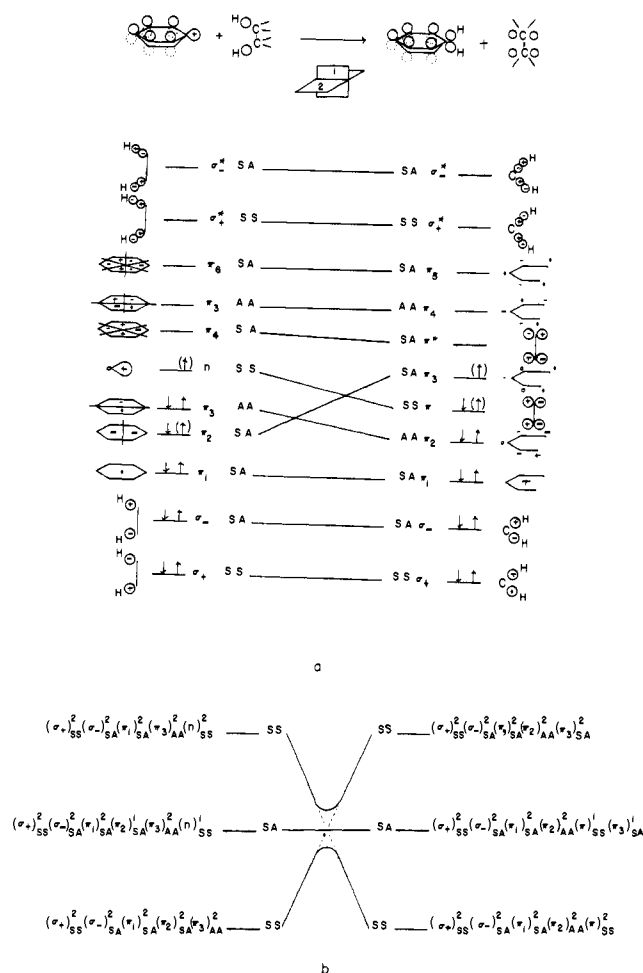With cyclopropane the following ion–molecule reaction is

Figure 5. (a) Molecular orbital correlation diagram for 1,2-hydrogen transfer from an alkane to a phenylium ion. (b) Electronic state correlation diagram for 1,2-hydrogen transfer from an alkane to a phenylium ion.

Table VI. Thermochemical Data for the Dehalogenation of Halobenzenes

Species	ΔH_f (298°), kcal/mol	Species	ΔH_f (298°) kcal/mol	Proton affinity, kcal/mol
H^+	366^a	I ($^2P_{3/2}$)	47.27^a	
H_3^+	264^b	HF	-64.8^a	
CH_5^+	221^c	HCl	-22.062^a	
$C_6H_5^+$	275^d	HBr	-8.70^a	
$C_6H_6^+$	233^a	HI	6.33^a	
CH_4	-17.88^a	C_6H_5F	-26.48^a	182.5^e
F	18.88^a	C_6H_5Cl	12.7^a	182.4^e
Cl	29.082^a	C_6H_5Br	24^a	
Br	26.741^a	C_6H_5I	37^a	
I ($^2P_{1/2}$)	25.535^a	C_6H_6	19.8^a	183.4^e

[a] Reference 19. [b] M. E. Schwartz and L. J. Schaad, J. Chem. Phys., 47, 5325 (1970). [c] W. A. Chupka and J. A. Berkowitz, ibid., 54, 4256 (1971). [d] Reference 7. [e] R. Yamdagni and P. Kebarle, J. Am. Chem. Soc., 98, 1320 (1976).

observed:

$$C_6H_5^+ + C_3H_6 \rightarrow C_7H_7^+ + C_2H_4$$
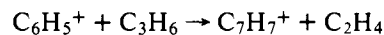
Since a similar reaction is observed between phenylium ions and propene, with nearly the same rate, the temptation to formulate the reaction with cyclopropane as a concerted transfer of a methylene group should be avoided.

Phenylium ions also attack aromatic rings. Reaction of phenylium ions with chloro- and fluorobenzene gives rise to

a $C_{12}H_9^+$ product ion which we formulate as a phenylphenylium ion:

$$C_6H_5^+ + C_6H_5X \rightarrow C_6H_5\text{-}C_6H_4^+ + HX$$
$$(X = Cl, F)$$
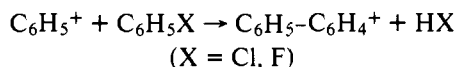
Conclusions

From the reactions reported above it can be seen that phenylium ions appear to be strong electrophiles, attacking σ- as well as π-electron systems. The occurrence of addition without fragmentation as reaction channels for $C_6H_5^+ + H_2(D_2)$ and $C_6H_5^+ + CH_4(CD_4)$ suggests strongly a concerted insertion of the formally divalent carbon atom of the phenylium ion into H–H and C–H bonds. This is a process similar to carbene reactions and suggests the inclusion of an appropriate canonical form in the resonance description of the singlet state of the phenylium ion.
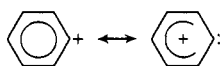
The addition of phenylium ions to hydrogen molecules has some precedent in the formation of a collision complex between methyl cations CH_3^+ and D_2 that is sufficiently long lived for the hydrogens and deuteriums to become equivalent.[21]

In our experiments $C_6H_5^+$ ions are produced both by electron impact and by dehalogenation of halobenzenes by gaseous Bronsted acids. The reactivity of $C_6H_5^+$ does not seem to depend on its mode of formation, suggesting that the same electronic state is formed in both processes, and with similar internal energies.

As a species exhibiting both carbonium ion-like and carbene-like reactivity, the phenyl cation is quite interesting and merits the further study required to elucidate the detailed course of its reactions.

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(14) The reaction $CH_3^+ + C_6H_5Cl \rightarrow CH_3Cl + C_6H_5^+$ is estimated to be exothermic by ca. 7 kcal/mol, while $CH_5^+ + C_6H_5Cl \rightarrow CH_4 + C_6H_5^+$ is estimated to be endothermic by ca. 1 kcal/mol.
(15) Under high-pressure conditions, as in the experiments of Cacace and Speranza (ref 10c), collisional stabilization of the ring-protonated halobenzene may compete effectively with rearrangement followed by loss of HX. Collisional stabilization of a halogen-protonated halobenzene may not be as effective at suppressing dehalogenation, which can occur without rearrangement. This would explain the much smaller extent of tritiodehalogenation found by Cacace and Speranza for $D_2T^+ + C_6H_5Cl$ compared with $D_2T^+ + C_6H_5F$. In the chlorobenzene case the extent of halogen vs. ring attack is smaller than for fluorobenzene and the collisionally deactivated intermediate from ring attack on chlorobenzene loses a proton to become the dominant tritiodeprotonation product in this case.
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