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Specific Substituent Effects in the Dehalogenation of Halobenzene Derivatives by the Gaseous Bronsted Acid CH_5^+ [1]

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Abstract: In the methane chemical ionization mass spectra of chlorobenzene derivatives containing an electron-donating substituent meta to the chlorine, the protonated molecular ions, MH^+, formed in the initial protonation reaction undergo extensive loss of HCl to form substituted phenyl cations. This dehalogenation reaction is not observed when the substituent is ortho or para to the chlorine (except for the *p*-*N*,*N*-dimethylamino substituent) nor for electron-withdrawing substituents. For fluorobenzene derivatives loss of HF from MH^+ is observed when the substituent is meta or para to the fluorine but not when it is ortho to the fluorine. The origin of these unusual substituent effects is discussed. It is concluded that the substituents act to alter the carbon–halogen bond dipole. This bond dipole in turn exerts a kinetic effect which either alters the activation energy for elimination of the neutral hydrogen halide from MH^+ or, more likely, influences the extent of protonation at the halogen through localized ion–bond dipole interactions in the collision complex.

Introduction

In the methane chemical ionization (Cl) mass spectra of fluorine- and chlorine-substituted benzenes and toluenes moderately abundant fragment ion peaks are observed[2,3] corresponding nominally to protonated toluene or the appropriate protonated xylene. The importance of these product ions decreased through the halogen series with the result that they were of minor importance for the bromo derivatives and were absent for the iodo derivatives.[2,3]

In the Cl studies the formation of these products was attributed[2,3] to the direct reaction

$$CH_5^+ + YC_6H_4X \rightarrow YC_6H_4CH_3 \cdot H^+ + HX \quad (Y = H, CH_3; X = F, Cl) \qquad (1)$$

while from radiolytic[4] and ICR[5] studies the two-step reaction sequence

$$CH_5^+ + YC_6H_4X \xrightarrow{-CH_4} YC_6H_4X \cdot H^+ \xrightarrow{-HX} YC_6H_4^+ \qquad (2)$$

$$YC_6H_4^+ + CH_4 \rightarrow YC_6H_4CH_3 \cdot H^+ \qquad (3)$$

was proposed. Pressure-variation studies[6] under Cl conditions have shown that both the direct reaction (1) as well as the two-step sequence (2) plus (3) are operative, the relative importance of the two pathways being dependent on the identity of the halogen X and the nature and orientation of the substituent Y.

In both Cl[2,3,6] and radiolytic[7] studies of the reaction of H_3^+ (or D_2T^+) with halobenzenes and halotoluenes a similar two-step dehydrohalogenation reaction, (4) plus (5), was observed. In addition, the Cl studies showed that this reaction

$$H_3^+ + YC_6H_4X \xrightarrow{-H_2} YC_6H_4X \cdot H^+ \xrightarrow{-HX} YC_6H_4^+ \qquad (4)$$

$$YC_6H_4^+ + H_2 \rightarrow YC_6H_5 \cdot H^+ \qquad (5)$$

$$H_3^+ + YC_6H_4X \xrightarrow{-H_2} YC_6H_4X \cdot H^+ \xrightarrow{-X} YC_6H_5^{+\cdot} \qquad (6)$$

mode was in competition with the alternative fragmentation of $YC_6H_4X \cdot H^+$ (MH^+) by loss of a halogen atom (reaction 6). Loss of HX from MH^+ was the only fragmentation mode for X = F or Cl, both loss of HX and X were observed when X = Br, while loss of the halogen atom was the only fragmentation mode observed for X = I. In a more recent study[8] of the reaction of H_3^+ with a variety of substituted halobenzenes it was observed that the competition between loss of HX and loss of X· from MH^+ was strongly dependent on the substituent, with electron-releasing substituents enhancing fragmentation by reaction 6. The competition between the two fragmentation modes has been rationalized[3,8] in terms of reaction energetics.

The pronounced effect of substituents on the H_2 Cl mass spectra of substituted halobenzenes[8] indicated that a similar study of substituent effects on the CH_4 Cl mass spectra was desirable. As will be discussed below, unusual substituent orientation effects have been observed in that dehydrohalogenation of chlorobenzene derivatives is observed only when

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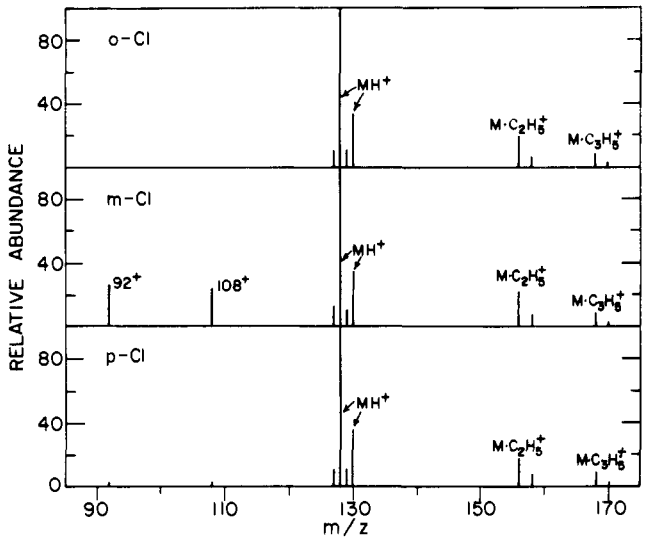


Figure 1. CH_4 Cl mass spectra of chloroanilines.

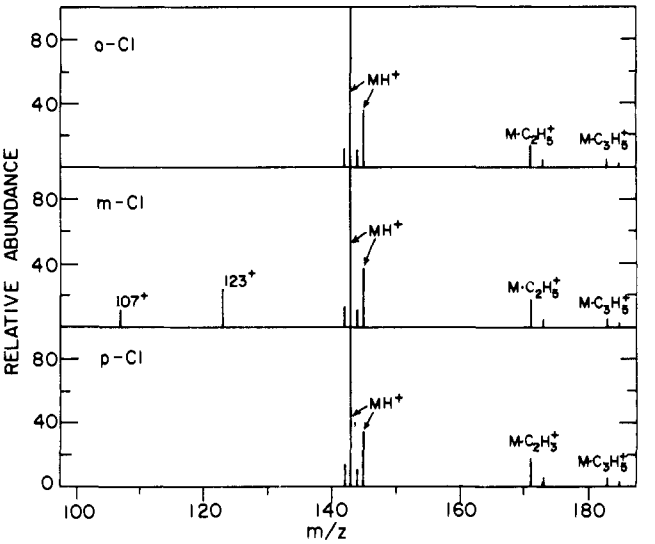


Figure 2. CH_4 Cl mass spectra of chloroanisoles.

electron-donating substituents are meta to the chlorine, while for fluorobenzene derivatives dehydrohalogenation is observed when electron-donating substituents are either meta or para to the fluorine (but not when ortho). These specific effects are not observed in the H_2 Cl spectra and cannot be explained on the basis of energetics effects and alternative explanations are explored.

Experimental Section

The chemical ionization mass spectra were obtained using a Du Pont 21-490 mass spectrometer equipped with a high-pressure chemical ionization source. The source temperature was approximately 150 °C and the ionizing electron energy was 70 eV with the repellers held at cage potential. Reagent gas pressures normally were in the range 0.2–0.5 Torr for the chemical ionization mass spectra reported here. The details of the pressure-variation studies have been given previously.[6] Liquid samples were introduced through a heated inlet system at 120 °C while solid samples were introduced directly from a solids insertion probe.

The compounds used were commercially available and showed no detectable impurities in their electron impact mass spectra. Reagent grade CH_4 (Matheson and Co.) was used without further purification as was the CD_4 (Merck Sharp and Dohme, Montreal).

Results and Discussion

CH_4 CI of Chlorobenzonitriles. No fragmentation was observed in the CH_4 CI mass spectra of these compounds. The MH^+ ion signal was the base peak with significant ion signals for the $M{\cdot}C_2H_5^+$ and $M{\cdot}C_3H_5^+$ clusters also being observed. Low-intensity (<2% of base peak) ion signals corresponding to $M{\cdot}CH_3^+$ also were observed.

CH_4 CI of Chloronitrobenzenes. The MH^+ ion was the base peak for all three isomers. In agreement with the chlorobenzonitriles, no fragment ions were observed corresponding to dehalogenation of the haloaromatic. The only fragment ions observed were low-intensity ion signals (2–3% of base peak) attributable to loss of OH from MH^+. A similar fragmentation reaction has been reported previously[9] in the CH_4 CI of trinitro aromatic compounds.

CH_4 CI of Chloroanilines. The CH_4 Cl mass spectra of the three chloroanilines are shown in Figure 1. For all isomers the protonated molecule, MH^+, is the base peak and there also are significant peaks corresponding to $M^{+\cdot}$ and to the cluster ions $M{\cdot}C_2H_5^+$ and $M{\cdot}C_3H_5^+$.[10] Of particular interest in the present context are the abundant ion signals observed at *m/z* 92 and 108 in the Cl mass spectrum of *m*-chloroaniline. These products are not observed for the ortho isomer and are of extremely low abundance for the para isomer. The *m/z* 92 ion is the product ($H_2NC_6H_4^+$) expected from the dehalogenation reaction (2), while *m/z* 108 ($H_2NC_6H_4CH_3{\cdot}H^+$) is the product expected from the condensation of the aminophenyl cation with methane. Pressure studies for the meta compound, reported elsewhere,[6] have shown that the *m/z* 108 product originates entirely by the two-step reaction sequence (2) plus (3). With CD_4 as reagent gas, the *m/z* 92 product remained unaltered in mass while the *m/z* 108 product shifted to *m/z* 112. This result is consistent with the two-step reaction mechanism, and, in addition, shows that the proton added in forming MH^+ always is lost as the hydrogen in the elimination of HCl. The observation of the products of both reaction 2 and reaction 3 is in agreement with the results reported previously[3,6] for chlorobenzene and the chlorotoluenes. However, the high specificity of the reaction for the meta isomer is quite unexpected.

CH_4 CI of Chloroanisoles. The CH_4 Cl mass spectra of the three chloroanisoles are shown in Figure 2. In agreement with the chloroanilines the dehydrohalogenation product $CH_3OC_6H_4^+$ (*m/z* 107) and its adduct to methane (*m/z* 123) are of significant intensity only for the meta isomer. When CD_4 was used as reagent gas the *m/z* 107 product showed no mass shift while the *m/z* 123 product ion shifted to *m/z* 127. This also is in agreement with the results for the chloroanilines.

CH_4 CI of Chloromethylanilines (Chlorotoluidines). The CH_4 CI mass spectra of six chlorotoluidines are summarized as the first six entries in Table I. The major features of interest are the abundant ion signals corresponding to $[MH^+ - HCl]$ and to its adduct CH_4, $[MH^+ - HCl + CH_4]$, the products of reactions 2 and 3, which are observed when the chlorine is meta to the amino group. By contrast, when the chlorine is ortho or para to the amino group, these fragment ions are of much lower intensity, even though in these cases the chlorine is meta to the methyl group. It is apparent that the dehydrohalogenation reaction (2) is largely specific to those chlorotoluidines with the amino substituent meta to the chlorine. The CD_4 CI mass spectrum of 3-chloro-4-methylaniline was obtained. The product corresponding to $[MH^+ - HCl]$ showed no deuterium incorporation while the $[MH^+ - HCl + CH_4]$ product showed incorporation of four deuterium atoms.

CH_4 CI of Dichloroanilines. The CH_4 CI mass spectra of six isomeric dichloroanilines are summarized as entries 7–12 in Table I. The spectra are similar to those of the chlorotoluidines in that abundant $[MH^+ - HCl]$ ion signals are observed only for those isomers which have at least one chlorine meta to the amino function. For 3,5-dichloroaniline, with both chlorines meta to the amino group, the $[MH^+ - HCl]$ and $[MH^+ - HCl + CH_4]$ ion intensities are particularly pronounced. No

Table I. CH_4 CI Mass Spectra of Substituted Chloroanilines[a]

compd	$M{\cdot}C_3H_5^+$	$M{\cdot}C_2H_5^+$	MH^+	$M^{+\cdot}$	$[MH^+ - Cl]$	$[MH^+ - HCl]$	$[MH^+ - HCl + CH_4]$
2-chloro-4-methyl-	2.3	15.2	100	25.2	2.0	2.3	0
2-chloro-6-methyl-	2.6	15.5	100	20.3	1.4	2.0	0
3-chloro-2-methyl-	5.6	21.4	100	25.7		61.5	13.2
3-chloro-4-methyl-	3.2	18.8	100	21.6	2.6	64.6	8.7
3-chloro-6-methyl-	4.4	20.5	100	29.0	1.8	53.2	14.1
4-chloro-2-methyl-	2.9	14.2	100	35.2	1.8	4.6	0.7
2,4-dichloro-	3.0	12.0	100	29.4	6.9	1.6	
2,6-dichloro-	3.8	13.9	100	15.8			
2,3-dichloro-	5.5	16.3	100	7.9			
2,5-dichloro-	3.3	12.7	100	32.6	3.1	21.2	3.8
3,4-dichloro-	3.0	9.1	100	29.5	7.0	30.7	
3,5-dichloro-	8.7	26.6	100	12.4	3.2	47.4	16.1
N,N-dimethyl-2-chloro-[b]	3.5	17.5	100	25.4	5.6	6.6	
N,N-dimethyl-3-chloro-[b]	4.1	27.8	100	53.0	1.7	1.7	101
N,N-dimethyl-4-chloro-	5.2	16.4	100	67.8		6.8	43.0

[a] Intensities as % of MH^+. [b] $[M - H]^+$ ions also were observed, 8.9% 2-Cl and 5.5% 3-Cl.

Table II. CH_4 CI Mass Spectra of Chlorofluorobenzenes and Difluorobenzenes

compd	$M{\cdot}C_3H_5^+$	$M{\cdot}C_2H_5^+$	MH^+	$M^{+\cdot}$	$[MH^+ - HF]$	$[MH^+ - HF + CH_4]$	*m/e* 107
o-Cl,F	2.9	15.8	100	6.6			
m-Cl,F	3.2	17.9	100	8.8	3.2	16.8	4.0
p-Cl,F	2.5	24.0	100	11.4	1.8	16.0	6.0
o-F_2	1.5	15.4	100	8.5		3.6	
m-F_2	3.9	26.3	100	12.0	2.0	50.9	
p-F_2	1.7	19.0	100	11.4	1.5	42.7	

fragment ions are observed in the mass spectra of the 2,6-dichloro- and 2,3-dichloroanilines, even though the latter has a chlorine meta to the amino group. In the H_2 CI mass spectra these two isomers, which have a 1,2,3 substituent pattern, show[8] a particularly strong MH^+ ion signal, presumably as a result of internal solvation of the added proton. This extra stabilization is sufficient in the CH_4 CI system to suppress all fragmentation.

The remaining isomers show weak ion signals corresponding to $[MH^+ - Cl]$. This fragmentation mode, which appears to be the thermochemically favored reaction channel, is the dominant reaction in the more energetic H_2 CI system.[8]

CH_4 CI of *N,N*-Dimethylchloroanilines. The CH_4 CI mass spectra of the three isomeric *N,N*-dimethylchloroanilines are recorded as the final three entries in Table I. The introduction of the two methyl groups has altered the picture, relative to the chloroanilines, in that abundant ion signals corresponding to $[MH^+ - HCl]$ are observed for both the para and meta isomers, although the intensity is considerably greater for the former. No $[MH^+ - HCl]$ ion signal was observed for the ortho isomer nor were ion signals corresponding to $[MH^+ - HCl + CH_4]$ observed for any of the three isomers.

In addition to low-intensity $[MH^+ - Cl]$ ions signals, low yields of $[M{\cdot}C_2H_5^+ - Cl]$ are observed, indicating that loss of $Cl^{\cdot}$ from the $M{\cdot}C_2H_5^+$ complex is energetically feasible. These reaction channels, forming odd-electron product ions, become of major importance in the CH_4 CI mass spectra of the bromoanilines and bromoanisoles (vide infra). Low-intensity $[M - H]^+$ ion signals also are observed for the ortho and meta isomers; this fragmentation route is the major reaction channel in the H_2 CI mass spectrum of the ortho isomer, while the meta and para isomers show $[MH^+ - Cl]$ as the major fragment ion.[8]

CH_4 CI of Dichlorobenzenes. No fragmentation of the MH^+ ions was observed in the CH_4 CI mass spectra of the three dichlorobenzene isomers. The spectra of all three isomers showed MH^+ as the base peak, the remaining peaks corresponding to low-intensity $M^{+\cdot}$ ion signals, and the usual $M{\cdot}C_2H_5^+$ and $M{\cdot}C_3H_5^+$ cluster ions.

CH_4 CI of Chlorofluorobenzenes. The CH_4 CI mass spectra of the three chlorofluorobenzenes are summarized as the first three entries in Table II. No ion signals corresponding to $[MH^+ - HCl]$ were observed for any of the isomers; however, ion signals corresponding to $[MH^+ - HF]$ as well as to $[MH^+ - HF + CH_4]$ were observed for the meta and para isomers. Pressure-variation studies, similar to those reported previously,[6] showed that the $[MH^+ - HF + CH_4]$ product originated entirely by reaction of $[MH^+ - HF]$ with CH_4, with no contribution from the direct reaction (1). Consequently the relative intensities of these two ions are pressure dependent. Although no $[MH^+ - HCl]$ ions signals were observed, the $[MH^+ - HCl + CH_4]$ product would be isobaric with the $[MH^+ - HF]$ product (*m/z* 111 for ^{35}Cl). Using CD_4 as reagent gas it was found that the *m/z* 111 signal did not show a mass shift, indicating no formation of $[MH^+ - HCl + CH_4]$ and, also, that the added proton is lost with the neutral HF in the fragmentation leading to $[MH^+ - HF]$.

The exclusive loss of HF from protonated chlorofluorobenzene in the CH_4 CI is in contrast to the H_2 CI system, where loss of HCl from MH^+ is almost equal to loss of HF.[8] Using $\Delta H_f°(CH_5^+) = 220$ kcal mol^{-1} ($PA(CH_4) = 127$ kcal mol^{-1} [14]), $\Delta H_f°(FC_6H_4^+) = 227$ kcal mol^{-1},[8] $\Delta H_f°(ClC_6H_4^+) = 264$ kcal mol^{-1},[8] $\Delta H_f°(HF) = -65$ kcal mol^{-1},[11] $\Delta H_f°(HCl) = -22$ kcal mol^{-1},[11] and $\Delta H_f°(C_6H_4ClF) = -33$ kcal mol^{-1},[15] we derive the following:

$$CH_5^+ + C_6H_4FCl \rightarrow ClC_6H_4^+ + HF + CH_4 \qquad \Delta H = -6 \text{ kcal mol}^{-1} \quad (7)$$

$$CH_5^+ + C_6H_4FCl \rightarrow FC_6H_4^+ + HCl + CH_4 \qquad \Delta H = 0 \text{ kcal mol}^{-1} \quad (8)$$

The uncertainty ascribed to these values is at least ±4 kcal mol^{-1} and, consequently, the small difference in the thermochemistry does not appear to be sufficient to explain the specificity for HF elimination from MH^+, nor why this loss is observed only for the meta and para isomers. It is obvious, however, that for fragmentation to be observed almost the entire exothermicity of the initial protonation reaction must be retained as excitation energy of MH^+.

Table III. CH_4 Cl Mass Spectra of Fluoroanilines and Fluoroanisoles

compd	$M{\cdot}C_3H_5^+$	$M{\cdot}C_2H_5^+$	MH^+	$M^{+\cdot}$	$[MH^+ - F]$	$[MH^+ - HF]$	$[MH^+ - HF + CH_4]$
2-F,NH_2	4.3	11.2	100	8.9		3.1	
3-F,NH_2	9.6	33.6	100	17.2	0.9	24.6	22.2
4-F,NH_2	7.9	27.5	100	28.9	5.8	6.7	10.6
2-F,OCH_3	3.0	9.0	100	5.0			
3-F,OCH_3	8.6	29.9	100	8.1		≤1	37.7
4-F,OCH_3	8.9	31.9	100	9.6		≤1	45.1

Table IV. CH_4 Cl Mass Spectra of Bromoanilines and Bromoanisoles

compd	$M{\cdot}C_3H_5^+$	$M{\cdot}C_2H_5^+$	MH^+	$M^{+\cdot}$	$[M{\cdot}C_2H_5^+ - Br]$	$[MH^+ - Br]$	$[MH^+ - HBr]$	$[MH^+ - HBr + CH_4]$
2-Br,NH_2	4.7	6.9	100	11.3	18.2	24.3		
3-Br,NH_2	8.1	4.6	100	16.2	33.2	62.5	10.9	15.9
4-Br,NH_2	2.8	4.1	100	48.5	46.2	171.8	0.3	
2-Br,OCH_3	4.8	3.8	100	7.0	11.0	6.9		
3-Br,OCH_3	6.1	6.4	100	6.6	17.0	15.8		1.7
4-Br,OCH_3	6.5	8.0	100	9.9	20.7	20.8		

A low-intensity ion signal was observed at *m/z* 107 in the CH_4 Cl mass spectra of the meta and para isomers. The mass shift (to *m/z* 113 and 114) when CD_4 was used as reagent gas is consistent with the reaction sequence

$$C_6H_4ClF \cdot H^+ \xrightarrow{-HF} C_6H_4Cl^+ \xrightarrow{+CH_4} CH_3C_6H_4Cl \cdot H^+$$

$$\xrightarrow{-HCl} CH_3C_6H_4^+ \xrightarrow{+CH_4} CH_3C_6H_4CH_3 \cdot H^+ \quad (9)$$

CH_4 CI of Difluorobenzenes. The CH_4 Cl mass spectra of the three difluorobenzenes are presented as the last three entries in Table II. As for the chlorofluorobenzenes the dehydrohalogenation products $[MH^+ - HF]$ and its adduct to CH_4 are of significance only for the meta and para isomers. Using $\Delta H_f^\circ(C_6H_4F_2) = -73$ kcal mol^{-1} [11] and the thermochemical data given above we calculate for the reaction

$$CH_5^+ + C_6H_4F_2 \rightarrow FC_6H_4^+ + HF + CH_4$$
$$\Delta H^\circ = -3 \text{ kcal mol}^{-1} \quad (10)$$

The overall thermochemistry requires that the $C_6H_4F_2{\cdot}H^+$ ion formed initially must acquire almost all of the exothermicity of the proton transfer from CH_5^+ to undergo fragmentation.

CH_4 CI of Fluoroanilines. The CH_4 Cl mass spectra of the three fluoroanilines are presented as the first three entries in Table III. Abundant ions signals corresponding to $[MH^+ - HF]$ and to $[MH^+ - HF + CH_4]$ are observed for the meta isomer with somewhat weaker signals for these two products being observed in the Cl mass spectrum of the para isomer. Pressure-variation studies[6] have shown that for the meta isomer the $[MH^+ - HF + CH_4]$ product originates entirely by the two-step sequence (2) plus (3), while for the para compound there is a significant contribution from the direct reaction (11). These results also show that the $H_2NC_6H_4^+$ ion derived from the meta isomer is much more reactive toward CH_4 (reaction 3) than the ion derived from the para isomer.

CH_4 CI of Fluoroanisoles. The CH_4 Cl mass spectra of the three isomeric fluoroanisoles, presented as the last three entires in Table III, show essentially the same general features as the spectra of the fluoroanilines. Dehydrohalogenation by CH_5^+ is observed only for the meta and para isomers and not for the ortho isomer.

CH_4 CI of Bromoanilines. The CH_4 Cl mass spectra of the three bromoanilines are recorded as the first three entries in Table IV. The spectra of the bromoanilines differ from the spectra of the chloro- and fluoroanilines in showing intense peaks corresponding to the odd-electron species $[M{\cdot}C_2H_5^+ - Br]$ and $[MH^+ - Br]$; indeed the latter is the base peak in the CH_4 Cl mass spectrum of 4-bromoaniline. Low-intensity $[M{\cdot}C_2H_5^+ - Br]$ peaks were observed[3] in the CH_4 Cl mass spectrum of bromobenzene and the bromotoluenes; the increased intensity for the bromoanilines presumably reflects the increased thermochemical stability of the product ion, nominally an aminoethylbenzene molecular ion.

The $[MH^+ - Br]$ fragment ion constitutes the base peak in the H_2 Cl mass spectra of the bromoanilines.[8] The thermochemical data derived[8] from the H_2 Cl indicates that loss of Br from MH^+ is favored over loss of HBr by >25 kcal mol^{-1} for the bromoanilines. In light of this observation it is extremely surprising to find significant ion signals for $[MH^+ - HBr]$ and also for $[MH^+ - HBr + CH_4]$ for *m*-bromoaniline. The formation of these products, specifically for the meta isomer only, cannot be rationalized on thermochemical grounds.

CH_4 CI of Bromoanisoles. The CH_4 Cl mass spectra of the three bromoanisoles are presented as the final three entries in Table IV. As was observed for the bromoanilines, abundant odd-electron $[M{\cdot}C_2H_5^+ - Br]$ and $[MH^+ - Br]$ product ions are observed for all three isomers. The H_2 CI mass spectra of these compounds show[8] $[MH^+ - Br]$ as the dominant fragment ion and the thermochemical data derived from the H_2 Cl study[8] indicate that loss of Br from MH^+ is favored thermochemically over loss of HBr by ~20 kcal mol^{-1}. In contrast to the bromoanilines loss of HBr is not important, even for the meta isomer.

Detailed Mechanistic Considerations. The main features of the results presented above can be summarized as follows. For chlorobenzenes containing an electron-donating substituent in the meta position substantial dehydrohalogenation occurs upon reaction with the Brønsted acid CH_5^+, leading to the appropriate substituted phenyl cation. In many cases, this phenyl cation reacts further in CH_4 to yield $YC_6H_4CH_3{\cdot}H^+$, although in several cases this latter product arises directly from reaction of CH_5^+ with the chlorobenzene derivative. By contrast, for substituted fluorobenzenes, dehydrohalogenation is observed when electron-donating substituents are meta or para to the fluorine. In general, the importance of this dehydrohalogenation reaction is greater when the halogen is fluorine than when it is chlorine. The latter is shown, for example, by a comparison of the CH_4 Cl mass spectrum of fluorobenzene[2] with that of chlorobenzene[3] and by a comparison of the CH_4 Cl mass spectra of the dichlorobenzenes, chlorofluorobenzenes, and difluorobenzenes (vide supra). For substituted bromobenzenes electron-donating substituents favor the elimination of Br from MH^+, although there is some evidence for a specific orientational effect in the observation of $[MH^+ - HBr]$ and $[MH^+ - HBr + CH_4]$ in the CH_4 Cl mass spectrum of *m*-bromoaniline.

A possible rationale for the selective dehydrohalogenation reaction could be based on the thermodynamically favored site

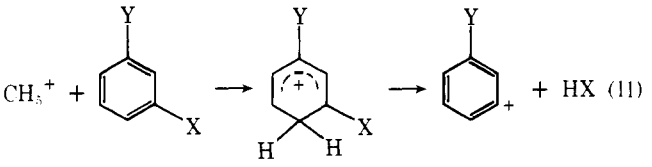
Table V. CNDO/2 Calculated Charge Densities ($\times 10^3$) for Substituted Benzenes

substituents	X[a]	C_1	C_2	C_3	C_4	C_5	C_6	Y[b]
1-Cl	−158	+134	−18	+19	−1	+19	−18	
1-Cl,2-NH_2	−161	+76	+135	−44	+28	−17	+5	−254
1-Cl,3-NH_2	−161	+157	−79	+166	−62	+41	−52	−256
1-Cl,4-NH_2	−166	+102	+6	−42	+148	−42	+6	−256
1-F	−198	+238	−55	+29	−15	+29	−55	
1-F,2-NH_2	−199	+180	+102	−35	+9	−7	−33	−249
1-F,3-NH_2	−199	+259	−117	+175	−75	+51	−89	−256
1-F,4-NH_2	−202	+204	−38	−32	+135	−32	−32	−257

[a] Halogen substituent. [b] Charge on N of substituent.

of protonation. The results using CD_4 as reagent gas, which show that the added proton always is lost as part of the neutral hydrogen halide, require that the initial protonation occurs either at the halogen or at the carbon ipso to the halogen. However, comparison of proton affinities[16] shows that there is no reason to expect that the halogen will be the thermodynamically favored site of protonation for the halogens, let alone that this would be so for specific ring isomers. Similarly, there is no evidence to suggest that ipso protonation would be the thermodynamically favored site of protonation.

Protonation para to an electron-releasing group should be thermodynamically favorable[18] and, indeed, a meta halogen substituent could make this the most favorable protonation site. Protonation in this manner, followed by 1,2 elimination of HX (reaction 11), is ruled out, however, by the observation that, when CD_4 is used as reagent gas, the added deuteron invariably becomes part of the neutral H(D)X eliminated. Reaction 11



would predict that loss of HX and loss of DX should be equally important. Furthermore, this mechanism cannot rationalize the reactivity of the *p*-fluorobenzene derivatives and the lack of reactivity of the *p*-chlorobenzene derivatives.

Similarly, arguments which are based on the relative thermochemical stability of the fragmentation products, $YC_6H_4^+ + HX$, do not appear to be valid. As Speranza et al.[5] have noted, dehydrohalogenation by CH_5^+ is not thermochemically more favorable for fluorobenzene than for chlorobenzene yet the reaction is much more important for the former.[2-4] Theoretical estimates[20] of the heats of formation of substituted phenyl cations show the same, or higher, heats of formation for the meta isomers compared to para isomers. Thus, thermochemical arguments cannot rationalize the specific reactivity of the *m*-chlorobenzene derivatives, while at the same time accommodating the reactivity of both the *m*- and *p*-fluorobenzene derivatives.

From the above discussion it appears that we can rule out the thermodynamically favored site of protonation or the thermochemical favorability of the reaction as the origin of the specific substituent effects observed in the dehydrohalogenation reactions of chloro- and fluorobenzene derivatives by reaction with CH_5^+. One is led, then, to consider possible effects associated with the kinetics of the protonation reaction which can give rise to the observed results. In this regard Cacace and Speranza[7] have suggested that the greater extent of tritiodehalogenation of fluorobenzene compared to other halobenzenes by reaction with D_2T^+ is related to the high polarization of the C-F bond. CNDO/2 calculations[21] of charge densities in benzene derivatives show that the C-F bond in fluorobenzene has a bond dipole moment more than twice that of the C-Cl bond in chlorobenzene. Although Cacace and Speranza[7] suggest that "the incipient cationic nature of the C atom bound to F is expected to favor the formation of a free phenyl cation via HF elimination to a much greater extent than the less polarized bonds involving halogens other than F", this is basically an energetics argument which is not reflected in the thermochemistry but could be reflected in the activation energies for HX elimination from $YC_6H_4X{\cdot}H^+$ if these are greater than the reaction endothermicity. An alternative rationalization is that the higher local bond dipole in fluorobenzene, through ion-dipole interaction with the attacking ion, results in increased protonation at the halogen, the necessary prerequisite to loss of hydrogen halide from the protonated molecule.

To explore the possible role of local bond dipoles in the present system we have calculated, using the CNDO/2 method,[22] charge densities in fluorobenzene, chlorobenzene, the chloroanilines, and the fluoroanilines. The results of these calculations are summarized in Table V. The charge densities for chlorobenzene and fluorobenzene are in good agreement with previous calculations[21] and clearly illustrate the much higher polarity of the C-F bond. Of particular interest in the present context are the results which show that the C-Cl bond polarity is greater for *m*-chloroaniline than for chlorobenzene but is reduced substantially for *o*-chloroaniline and, to a lesser extent, for *p*-chloroaniline. For the fluoroanilines the same trend is observed with the C-F bond polarity being increased for the meta isomer and decreased for both the ortho and para isomers compared to fluorobenzene, although for all the fluoroanilines the C-F bond is more polar than the C-Cl bond of the chlorobenzenes examined.

The calculated bond polarities show the correct changes to rationalize results, although one must assume a very strong dependence on the bond dipole to explain the lack of reactivity of *p*-chloroaniline and the reactivity of *m*-chloroaniline. The failure to observe dehydrohalogenation for the ortho isomers (both chloro and fluoro) may arise from internal solvation by the ortho substituent rather than failure to protonate the halogen substituent. It should be noted that for both *o*-chlorotoluene and *o*-fluorotoluene [$MH^+ - HX$] and the adduct to methane are observed. In these systems the ortho methyl group is not capable of solvating the added proton.

In conclusion, the specific dehydrohalogenation by reaction with CH_5^+ of chlorobenzenes substituted in the meta position by electron-donating substituents and the similar reaction of meta- and para-substituted fluorobenzenes appears to be most readily explained in terms of specific effects arising from the carbon-halogen bond dipole. It is not clear whether the role of this bond dipole is to lower the activation barrier for HX elimination from MH^+ because of the incipient carbonium ion nature of the carbon bonded to halogen or whether the bond dipole plays its role through ion-bond dipole interactions in the collision complex which influence the extent of protonation at the halogen. For both difluorobenzenes and chlorofluorobenzenes significant elimination of HF from MH^+ is observed even though the overall reaction is only slightly (~3 kcal mol^{-1}) exothermic. Not only does this imply that in the initial

protonation reaction the exothermicity of the reaction is retained by the MH^+ product but also it indicates that the fragmentation of MH^+ in these cases cannot have an activation energy significantly greater than the reaction endothermicity. This suggests that the effect of the bond dipole is to influence the site of protonation rather than the activation energy for fragmentation.

The charge distributions in Table V for the haloanilines show that $\mu(C\text{-}N) \simeq (C\text{-}F) > (C\text{-}Cl)$. This suggests that, if ion–bond dipole interactions influence the site of protonation, there should be significant protonation at the amino group. The MH^+ ion, which is the base peak in all spectra, probably represents those cases where protonation occurs at the amino substituent or on the aromatic ring. We suggest only that the magnitude of the carbon–halogen bond dipole determines the fraction of the protonation events which occur at halogen, one of the many possible protonation sites.

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Tosylate Oxygen Scrambling Associated with Ion-Pair Return in the *threo*-3-*p*-Anisyl-2-butyl System

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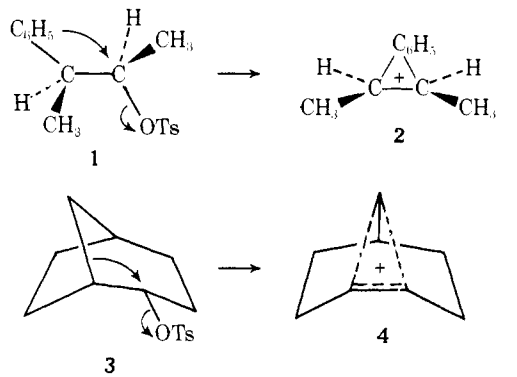
Abstract: Ion-pair return involved in acetolysis of *threo*-3-*p*-anisyl-2-butyl *p*-toluenesulfonate (**6**-OTs) results in racemization of optically active **6**-OTs (k_{rac}) and equilibration of the sulfonate oxygen atoms of ^{18}O-labeled **6**-OTs (k_{eq}). In this system external ion-pair return is involved. Presumably most, if not all, external ion-pair return is eliminated by 0.03 M $LiClO_4$. The oxygen equilibration to racemization (total measurable return) ratio for internal return, $(k_{eq}/k_{rac})_{in}$, is ~0.5 and the ratio for external ion-pair return, $(k_{eq}/k_{rac})_{ex}$, is ~1. Acetolysis of **6**-OTs is accompanied by some exchange with added ^{14}C-labeled *p*-toluenesulfonic acid. Exchange is lowered, but not eliminated, by 0.03 M $LiClO_4$ and does not result in loss of diastereomeric configuration, which rules out an S_N2-type exchange process. The residual exchange in the presence of $LiClO_4$ presumably results from external ion-pair return induced by the accumulating *p*-toluenesulfonic acid produced by acetolysis.

In an earlier investigation[1] we determined the amount of sulfonate oxygen scrambling (eq 4) associated with ion-pair return involved in acetolysis of ^{18}O-labeled *threo*-3-phenyl-2-butyl (**1**) and *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (**3**). These systems were selected because the type of ion-pair return had been characterized previously[2-4] as internal return, and the rate of total ion-pair return can be determined independently. Both **1**[5,6] and **3**[3] give symmetrical cations (**2** and **4**)—initially formed products are racemic. Thus, with optically active substrates the rate of loss of optical activity (eq 1) corresponds to total ionization and the rate of re-formation of racemic substrate (eq 3) corresponds to total ion-pair return (in these cases internal return) providing that the intimate ion pair, as well as the unperturbed cation, is symmetrical. The rate of racemization of the unsolvolyzed ester (eq 3) can be determined indirectly from the difference between rates of ionization (k_α) and solvolysis (k_t, eq 2), i.e., $k_{rac} = k_\alpha - k_t$.[1,3]



The first-order constants for oxygen equilibration (k_{eq}) of ^{18}O-labeled **1** and **3** are about $\frac{1}{2}k_{rac}$. This means that in each case the sulfonate oxygen atoms are not equilvalent in the

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