# Concerning the Mechanism of Dehalogenation of Halobenzene Derivatives by Gaseous Brønsted Acids

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Abstract: The formation of protonated benzene derivatives ($YC_6H_5 \cdot H^+$, Y = H or CH_3) by reaction of the gaseous Brønsted acid H_3^+ with halogenated benzene derivatives is shown to occur by a two-step mechanism involving formation of phenyl cations ($YC_6H_4^+$) followed by addition of these ions to H_2, rather than by direct reaction of H_3^+ with the neutral molecule. By contrast, the formation of $YC_6H_4CH_3 \cdot H^+$ ions from reaction of CH_5^+ with YC_6H_4X (X = halogen) is shown to occur both by direct reaction of CH_5^+ with the halobenzene derivative and by the two-step sequence involving formation of the appropriate phenyl cation which adds to CH_4. The relative importance of the two reaction mechanisms depends strongly on the halogen and other substituents present. Although tolyl ions react with both H_2 and CH_4, benzyl and tropylium ions do not, thus providing an approach to determining the structure of gaseous $C_7H_7^+$ ions.

In the H_2 chemical ionization (CI) mass spectra of fluoro- and chlorobenzenes and the related ring-substituted fluoro- and chlorotoluenes abundant fragment ions are observed[2,3] corresponding nominally to protonated benzene ($C_6H_7^+$) and protonated toluene ($C_7H_9^+$), respectively. Similarly, in the CH_4 CI mass spectra of the same compounds significant fragment ion peaks are observed[2,3] corresponding nominally to the appropriate protonated toluene ($C_7H_9^+$) and protonated xylene ($C_8H_{11}^+$), respectively. The relative importance of these product ions in the chemical ionization mass spectra was found to decrease through the halogen series (F > Cl > Br > I), with the result that such products are of minor importance for the bromo derivatives and are absent for the iodo derivatives. Based largely on the mass shift when deuterated reagent gases (D_2 or CD_4) were used, the formation of these dehalogenated products was attributed to the direct reaction of the reagent ion AH_2^+ (A = H or CH_3) with the relevant halobenzene derivative:

$$AH_2^+ + XC_6H_4Y \rightarrow AC_6H_4Y \cdot H^+$$
$$+ HX \quad (Y = H \text{ or } CH_3) \quad (1)$$
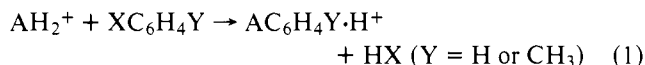
By contrast, in a study of the gas-phase reactions of radiolytically produced D_2T^+ with halobenzenes, Cacace and Speranza[4] observed tritiodehalogenation as well as tritiodeprotonation products, particularly for fluorine-substituted benzenes. They attributed the tritiodehalogenation process to the two-step reaction sequence 2 plus 3 (written for simplicity with H_3^+ as reactant).

$$(2)$$

$$(3)$$
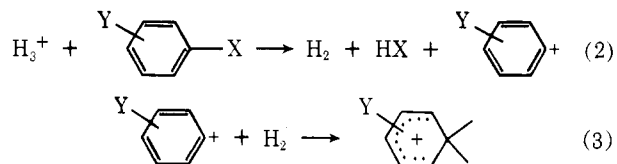
The product ion in eq 3 is the same as that observed in the chemical ionization studies and on proton transfer to a suitable base will yield the neutral dehalogenated product observed in the radiolytic work. In a related study of the γ-radiolysis of methane–halobenzene mixtures, where the major reactions involve attack of CH_5^+ and $C_2H_5^+$ on the halobenzene substrate, Speranza and Cacace[5] observed methyldehalogenated products, which, they proposed, were formed by an analogous reaction sequence 4 and 5, with eventual neutralization of the ionic product by proton transfer in the radiolytic system.

These two-step reaction sequences (2 plus 3 and 4 plus 5), leading to dehalogenation of halobenzene derivatives by the gaseous Brønsted acids H_3^+ and CH_5^+, are supported by an ICR study[6] which shows that $C_6H_5^+$ (presumably phenyl)

$$(4)$$

$$(5)$$
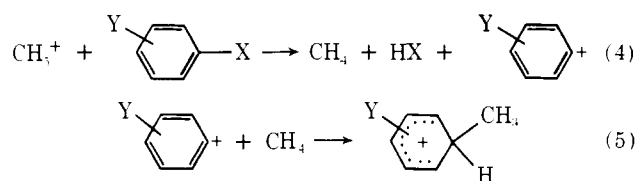
cations, produced by electron impact ionization of halobenzenes, react by addition to H_2 to yield $C_6H_7^+$ and with CH_4 to yield $C_7H_9^+$. These radiolytic and ICR results suggest, although they do not prove, that the two-step mechanisms rather than the direct reaction 1 may be responsible for the dehalogenation reactions initiated by H_3^+ and CH_5^+ in the chemical ionization systems which result in the formation of protonated benzene derivatives.

More recent chemical ionization studies in this laboratory have shown that $C_6H_7^+$ is the base peak in the H_2 CI mass spectra of dichlorobenzenes (Figure 1a) and the chlorobenzoic acids (Figure 1b) and also is a major peak in the H_2 CI of the fluorobenzoic acids (Figure 1c), as well as being a major product ion in the H_2 CI of the simpler halobenzenes. Obviously, formation of $C_6H_7^+$ in the spectra of the compounds of Figure 1 cannot be interpreted in terms of a single-step reaction analogous to 1 but must involve a sequence of reactions similar to that proposed from the radiolytic work. These results and the divergent conclusions reached in the chemical ionization and radiolytic studies have led us to carry out more detailed pressure studies to elucidate the mechanism(s) by which protonated benzene derivatives arise by dehalogenation of haloaromatic derivatives through reaction with the gaseous Brønsted acids H_3^+ and CH_5^+.

H_2 Chemical Ionization Systems. Figure 2 shows a plot of the normalized ion intensities observed (excluding H_3^+) in the H_2–m-chlorobenzoic acid system as a function of H_2 source pressure at a constant pressure of the acid. Quantitative interpretation of the results is difficult because there are many different factors affecting the relative intensities. At the lowest H_2 pressures there is a large contribution from direct electron impact ionization of m-chlorobenzoic acid, as shown by the large $M^{+\cdot}$ intensity. In addition, the H_3^+ reactant ions initially are formed with considerable excess internal energy[7,8] and with increasing H_2 pressure collisional deexcitation of the H_3^+ reactant ions as well as collisional stabilization of the ions produced by chemical ionization can lead to changes in the relative importance of the various reaction channels.

At least qualitatively the pressure dependence of the chemical ionization spectrum can be explained by the reaction sequence of Scheme I. A detailed study[9] of the H_2 CI mass spectra of substituted benzoic acids has shown that the two
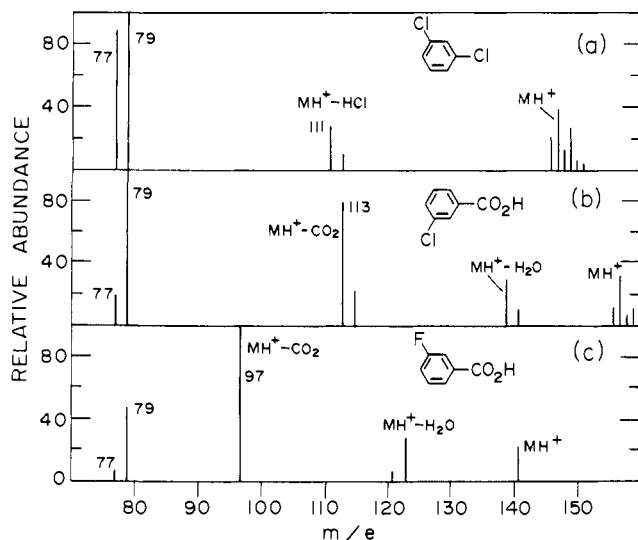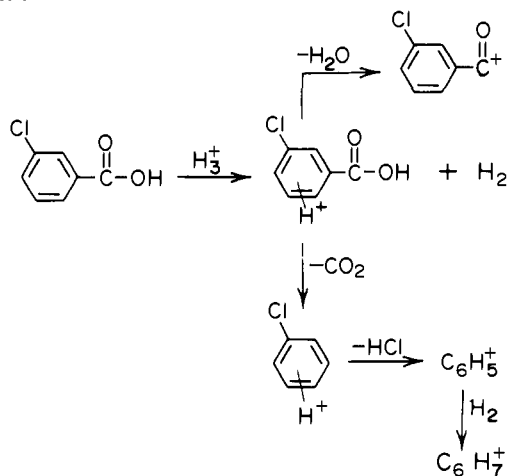
Figure 1. H_2 chemical ionization mass spectra of (a) *m*-dichlorobenzene, (b) *m*-chlorobenzoic acid, and (c) *m*-fluorobenzoic acid.

Figure 2. Pressure dependence of *m*-chlorobenzoic acid H_2 CI spectrum.

Scheme I

Figure 3. Intensity ratios as function of H_2 pressure *m*-chlorobenzoic acid ($\Sigma(MH^+$-$CO_2) = ClC_6H_5^+ + C_6H_7^+$).

Scheme II

major decomposition channels of the protonated molecule involve loss of H_2O and loss of CO_2 leading, in the present case, to $ClC_6H_4CO^+$ (which is also a major electron impact fragmentation product) and to protonated chlorobenzene ions, at least some of which retain sufficient internal energy to fragment further to $C_6H_5^+$ + HCl. The $C_6H_5^+$ (phenyl) ion intensity initially increases with increasing H_2 pressure but decreases at higher pressure with a concomitant increase in the $C_6H_7^+$ ion signal, indicative of the occurrence of reaction 3. In support of the proposed reaction scheme, Figure 3 shows that although the $(C_6H_5^+ + C_6H_7^+)/ClC_6H_5\cdot H^+$ ratio initially decreases with increasing H_2 pressure (through collisional deactivation processes) it then levels off while the ratio of $C_6H_7^+$ to $C_6H_5^+$ continues to increase. Collisional stabilization effects also are apparent in the decrease in the $\Sigma(MH^+$-$CO_2)/MH^+$ ratio with increasing H_2 pressure. It is apparent that the $C_6H_7^+$ ions formed in this system originate entirely by the reaction of $C_6H_5^+$ with H_2. A pressure study of the fluorobenzoic acid system indicated a similar mechanism for formation of $C_6H_7^+$. The pressure studies on the H_2–$Cl_2C_6H_4$ system also indicated that $C_6H_7^+$ originated by reaction of $C_6H_5^+$ with H_2, with the $C_6H_5^+$ ion originating by reaction of $ClC_6H_4^+$ with H_2 (Scheme II). No $ClC_6H_5\cdot H^+$ ions which would result from the latter reaction were observed and it appears that they undergo a facile loss of HCl.

The results discussed above show, in agreement with the ICR study,[6] that $C_6H_5^+$ cations react moderately rapidly with
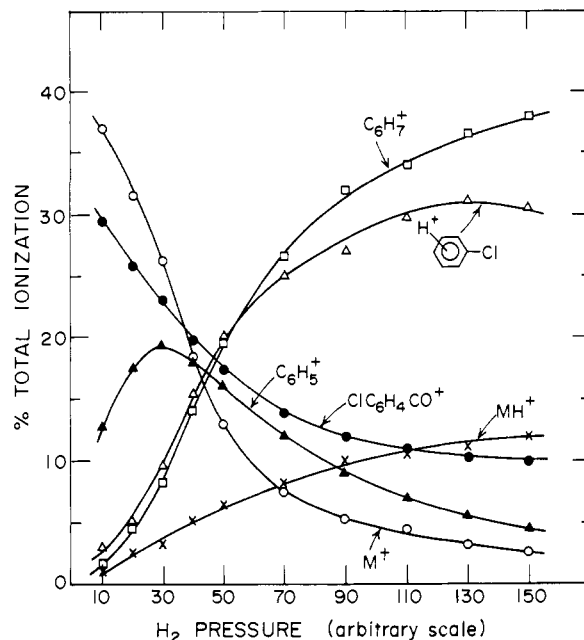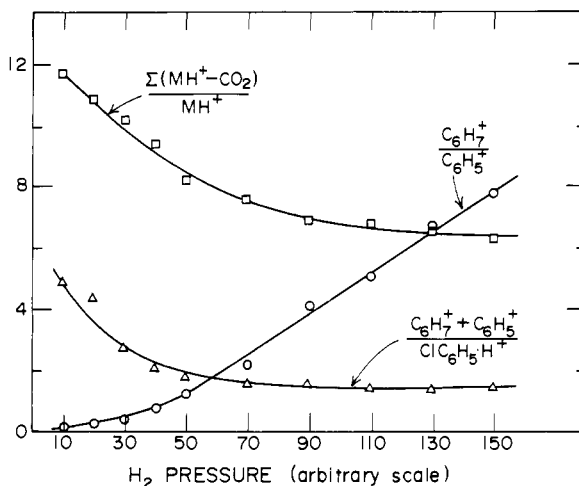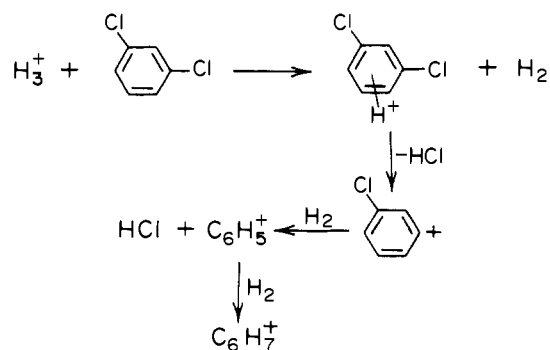
H_2 to form $C_6H_7^+$ and suggest that the two-step mechanism 2 plus 3 rather than the direct reaction 1 may be responsible for the formation of protonated benzene derivatives by dehalogenation of the simpler halobenzenes and halotoluenes studied in the earlier CI work.[2,3] We have therefore examined the pressure dependence of the H_2 CI mass spectra of a number of these compounds.
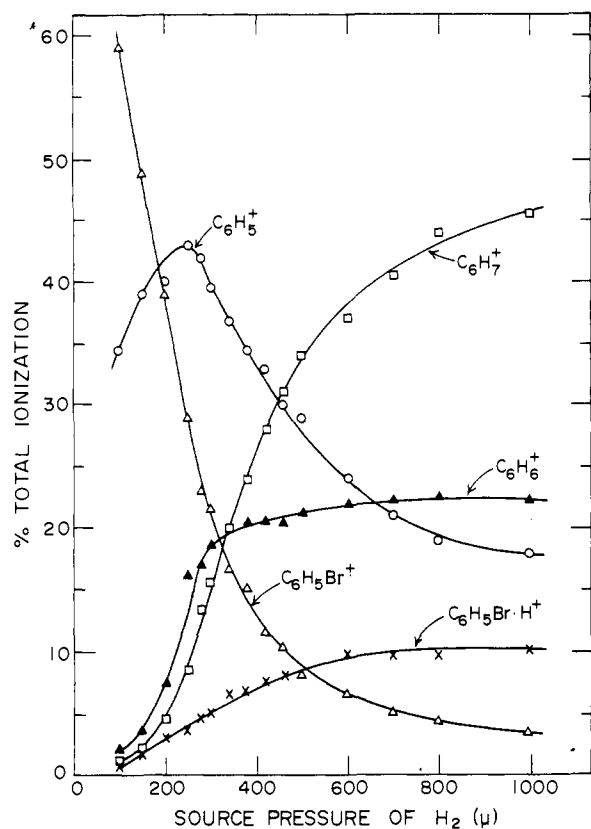
Figure 4. Pressure dependence of bromobenzene H_2 Cl spectrum.

Figure 5. $YC_6H_5 \cdot H^+/MH^+$ ratios as a function of H_2 pressure.

Figure 6. $YC_6H_4CH_3 \cdot H^+/MH^+$ ratios as a function of CH_4 pressure.

Figure 4 shows the variation of the relative ion intensities with H_2 pressure for the H_2–C_6H_5Br system. The major primary products from reaction of H_3^+ with bromobenzene are $C_6H_5BrH^+$, $C_6H_6^+$, and $C_6H_5^+$, as identified previously.[3] Clearly the $C_6H_5^+$ ion reacts rapidly with the H_2 reagent gas to produce $C_6H_7^+$; the reaction appears to be bimolecular and we estimate a rate constant between 10^{-11} and 10^{-12} cm³ molecule⁻¹ s⁻¹. As shown in Figure 5 the $C_6H_7^+/C_6H_5BrH^+$ ratio initially increases with H_2 pressure as expected for the reaction sequence 2 followed by 3. The direct reaction 1, in competition with simple proton transfer, should lead to a $C_6H_7^+/MH^+$ ratio independent of H_2 pressure. The dependence on the H_2 pressure and the observation that the $C_6H_7^+/C_6H_5BrH^+$ ratio extrapolates to zero at zero H_2 pressure indicates that there is no contribution to $C_6H_7^+$ formation by reaction 1 (for contrasting results see the CH_4 Cl results below). Also shown in Figure 5 are typical results obtained for the fluorobenzene, and chlorotoluene systems which show the same dependence of the $YC_6H_5 \cdot H^+/MH^+$ ratio on H_2 pressure as the bromobenzene system. This behavior was noted for all the systems investigated and we conclude that the mechanism of protiodehalogenation of halobenzene derivatives by H_3^+ is the two-step mechanism 2 followed by 3, as proposed by Cacace and Speranza.[4] There appears to be no contribution from the direct reaction 1.[10]

Methane Chemical Ionization Systems. Dehalogenation of the aromatic substrate leading to protonated benzene derivatives is particularly evident in the methane CI mass spectra of fluorobenzene, the ring-fluorinated toluenes,[2] and the ring-chlorinated toluenes.[3] If this dehalogenation reaction occurred by the direct reaction of CH_5^+ with the neutral molecule (reaction 1), as assumed in the original CI work,[2] the product ion $YC_6H_4CH_3 \cdot H^+$ should have the same dependence on CH_4 pressure as the protonated molecule MH^+. On the other hand, if the overall reaction occurs by the two-step sequence 4 and 5, proposed by Speranza and Cacace,[5] the $YC_6H_4CH_3 \cdot H^+$ yield should be at least one order higher in CH_4 pressure than
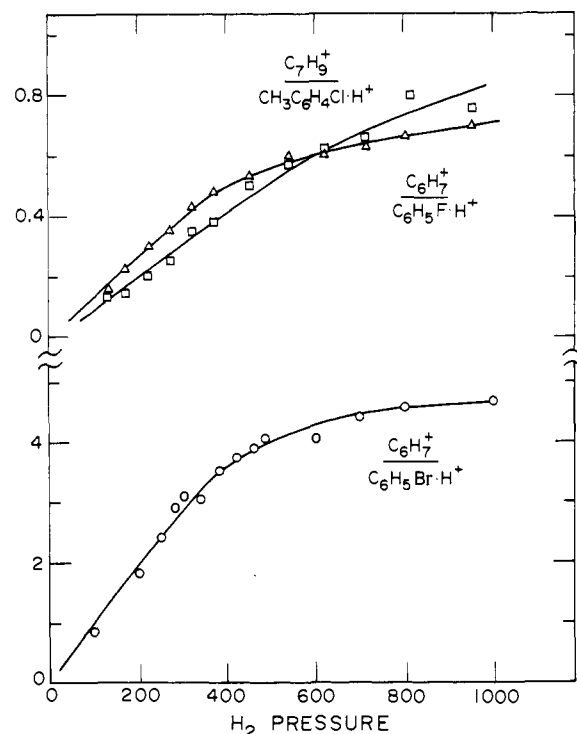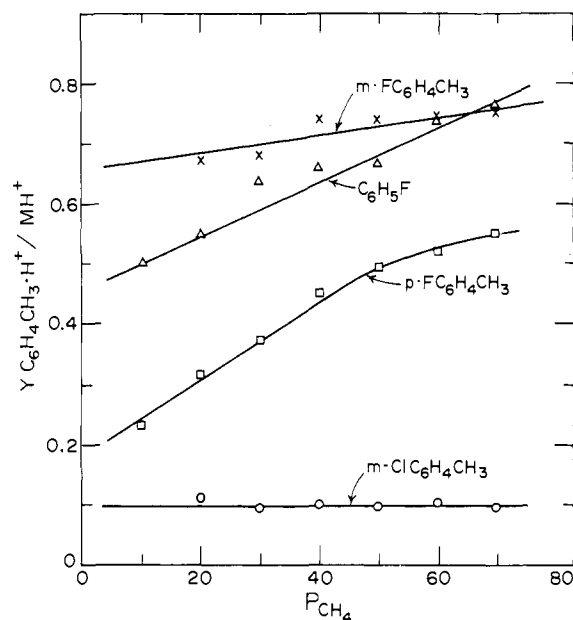
the MH^+ yield. Accordingly we have examined the dependence of the $YC_6H_4CH_3 \cdot H^+/MH^+$ ratio on the CH_4 pressure for a number of these systems. The results are shown in Figure 6. (Similar plots for the H_2 CI systems are shown in Figure 5 and have been discussed above.)

For the CH_4–*m*-chlorotoluene system the CH_3C_6-$H_4CH_3 \cdot H^+/MH^+$ ratio is independent of CH_4 pressure. This is consistent with formation of $CH_3C_6H_4CH_3 \cdot H^+$ by the direct reaction of CH_5^+ with the chlorotoluene, in competition with simple proton transfer to yield MH^+. The zero slope indicates that there is no contribution from the two-step sequence 4 plus 5. For fluorobenzene and the fluorotoluenes the $YC_6H_4CH_3 \cdot$ H^+/MH^+ ratio increases with increasing CH_4 pressure in agreement with the predictions of the Speranza and Cacace mechanism. However, in no case does the ratio extrapolate to
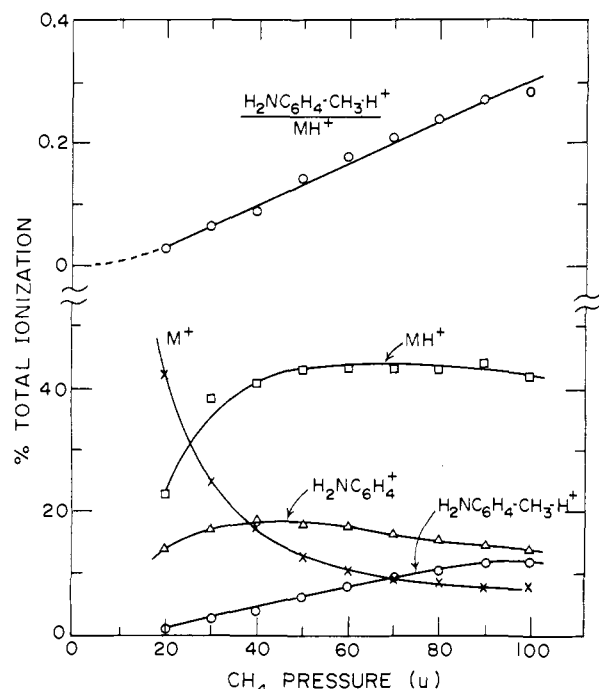
Figure 7. Pressure dependence of *m*-chloroaniline CH_4 CI spectrum.

Figure 8. Pressure dependence of *m*-fluoroaniline CH_4 CI spectrum.

Figure 9. Pressure dependence of *p*-fluoroaniline CH_4 CI spectrum.

zero at zero CH_4 pressure indicating that there also is a contribution from the direct reaction 1. The intercepts and slopes (in the latter case multiplied by the CH_4 concentration) should be related to the relative importance of the two mechanisms for formation of $YC_6H_4CH_3 \cdot H^+$. In view of the approximate pressure measurements made in the present work quantitative interpretation does not appear justified; however, it is evident that the two-step mechanism is more important than the direct mechanism for *p*-fluorotoluene while the reverse is true for *m*-fluorotoluene. It should be noted that in all cases the abundances of the $YC_6H_4^+$ ions, which are intermediates in the two-step reaction, were of extremely low abundance, indicating that they must react quite rapidly with CH_4. In summary, the present results for the chloro- and fluoro-substituted benzenes and toluenes show that both the direct reaction 1 and the two-step sequence 4 and 5 lead to formation of $YC_6H_4CH_3 \cdot H^+$ ions in the reaction of the Brønsted acid CH_5^+ with simple halobenzenes YC_6H_4X (Y = H or CH_3).

In recent work in this laboratory[12] we have observed that both $H_2NC_6H_4^+$ and $H_2NC_6H_4CH_3 \cdot H^+$ ions are of appreciable abundance in the CH_4 CI mass spectra of *m*-chloroaniline, *m*-fluoroaniline, and *p*-fluoroaniline. The $H_2NC_6H_4^+$ ion is the intermediate in the two-step sequence 4 and 5 and it was of interest to determine the origin of the $H_2NC_6H_4CH_3 \cdot H^+$ ions observed. Figure 7 shows the variation of relative ion abundances with CH_4 pressure in the CH_4–*m*-chloroaniline system. At the lowest pressures there is a considerable contribution from electron impact ionization of the amine as shown by the high $M^{+} \cdot$ abundance. However, the behavior with increasing CH_4 pressure shows clearly that $H_2NC_6H_4^+$ reacts with CH_4 to produce $H_2NC_6H_4CH_3 \cdot H^+$. Indeed, the plot of the $H_2NC_6H_4CH_3 \cdot H^+ / MH^+$ ratio vs. CH_4 pressure, also shown in Figure 7, establishes that the $H_2NC_6H_4CH_3 \cdot H^+$ ion arises entirely by this reaction and that there is no contribution from the direct reaction of CH_5^+ with the chloroaniline. The observation that the plot of the intensity ratio extrapolates to zero at a finite CH_4 pressure presumably reflects the CH_4 pressure necessary to generate the CH_5^+ and $C_2H_5^+$ reactant ions in the chemical ionization system.

Figures 8 and 9 show the variation of relative ion abundances with CH_4 pressure for the *m*-fluoroaniline and *p*-fluoroaniline
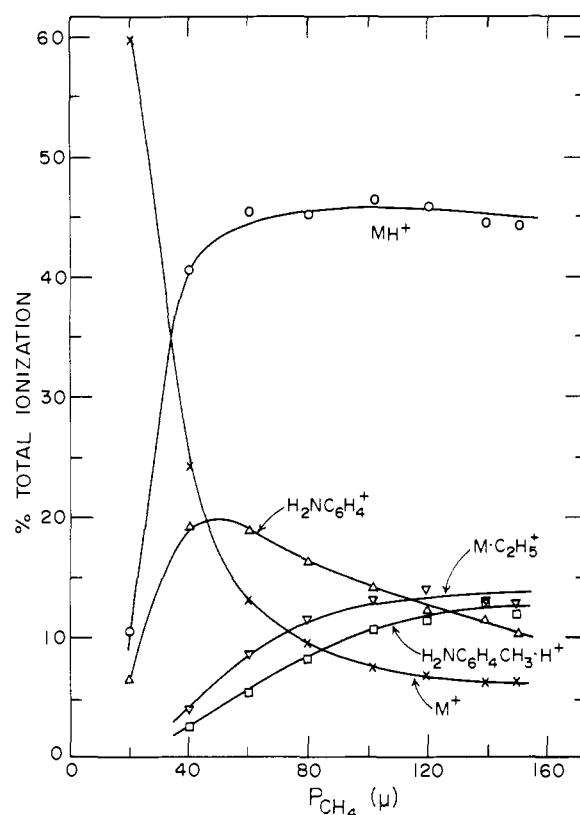
systems. It is obvious that there is a considerable difference in the behavior of the two systems. The $H_2NC_6H_4^+$ ion formed in the *m*-fluoroaniline system reacts moderately rapidly with CH_4 to produce $H_2NC_6H_4CH_3 \cdot H^+$, a reaction already observed in the *m*-chloroaniline system. As the pressure depen-
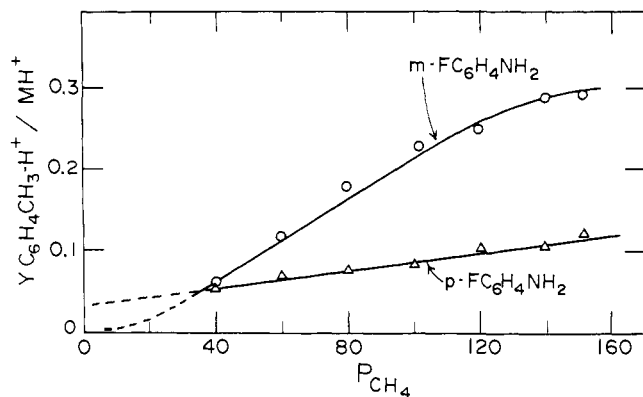
Figure 10. $YC_6H_4CH_3 \cdot H^+/MH^+$ ratios as function of CH_4 pressure for *m*- and *p*-fluoroaniline.

Figure 11. H_2 and CH_4 Cl mass spectra of methoxycycloheptatriene and benzyl methyl ether.

dence of the $H_2NC_6H_4CH_3 \cdot H^+/MH^+$ ratio (Figure 10) shows the formation of $H_2NC_6H_4CH_3 \cdot H^+$ can be explained entirely in terms of the reaction of $H_2NC_6H_4^+$ with CH_4 (reaction 5, $Y = NH_2$). By contrast, the $H_2NC_6H_4^+$ ion formed from *p*-fluoroaniline reacts only very slowly with CH_4 and as the intensity ratio plot in Figure 10 shows that there is a significant contribution to $H_2NC_6H_4CH_3 \cdot H^+$ formation by the direct reaction of CH_5^+ with the fluoroaniline, while the two-step sequence 4 and 5 is of only minor importance.

From the above it is obvious that formation of methyl dehalogenated arenium ions $(YC_6H_4CH_3 \cdot H^+)$ by the reaction of the Brønsted acid CH_5^+ with haloaromatic compounds (YC_6H_4X) occurs by the direct mechanism, reaction 1, originally proposed from chemical ionization studies,[2] and by the two-step mechanism 4 and 5, originally proposed from radiolysis studies.[5] The relative importance of the two processes obviously depends on the CH_4 pressure and also, as the present work has shown, is critically dependent on the haloaromatic compound investigated. With our present understanding of the mechanistic details, speculation as to the structural features which favor one mechanism over the other would be futile. In contrast to the results obtained for CH_5^+, the analogous reaction initiated by the Brønsted acid H_3^+ occurs only by the two-step sequence 2 and 3 proposed by Cacace and Speranza[4] and does not occur by the direct reaction 1 proposed in our earlier CI studies.[2,3]

The present work has largely reconciled the divergent conclusions reached from the chemical ionization studies[2,3] and the radiolytic studies.[4,5] However, one discrepancy remains and that is the failure of Cacace and Speranza[4] to observe significant amounts of tritiodehalogenation products from the reaction of D_2T^+ with chlorobenzene. Our chemical ionization study has shown that $C_6H_5^+$ is a major product ion from the reaction of H_3^+ with chlorobenzene and that this $C_6H_5^+$ ion reacts to produce $C_6H_7^+$ by reaction 3. Yet Cacace and Speranza[4] observed only 0.4–1.1% tritiodehalogenation product (98.9–99.6% tritiodeprotonation product) compared to ~42% tritiodehalogenation product from the reaction of D_2T^+ with fluorobenzene. Our chemical ionization results would not predict such a large difference.

Implications for Ion Structure Determination. The structures of the $C_7H_7^+$ ions formed from toluene and derivatives of toluene by dissociative electron impact ionization have long been of considerable interest.[13] From collisional activation studies McLafferty and Winkler[14] have identified benzyl, tropylium, tolyl, and norbornadienyl ions as stable, nondecomposing (after 10^{-5} s) $C_7H_7^+$ ions formed from appropriate precursors. More recently, using ICR techniques, Jackson et al.[15] have observed two distinct $C_7H_7^+$ species formed from toluene and halogen-substituted toluenes. One of these reacted with *p*-diethylbenzene at essentially every collision and was
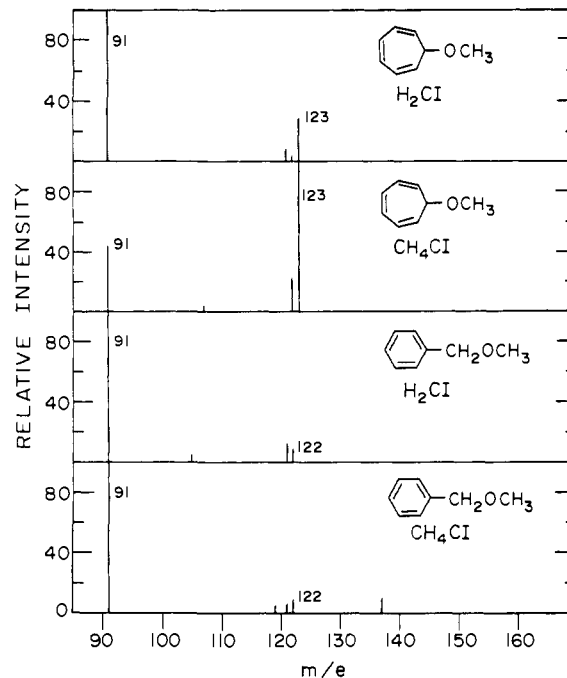
assigned the benzyl structure while the second was unreactive toward *p*-diethylbenzene and was assigned the tropylium structure. They found no evidence for stable tolyl ions on the time scale $(10^{-2}–10^{-1}$ s) of their experiments.

The present work, in conjunction with the previous chemical ionization studies,[2,3] has shown that $C_7H_7^+$ ions produced in the H_2 CI of ring-halogentated toluenes react by addition to H_2. In the absence of rearrangement these ions should have the tolyl structure. The abundant $C_7H_7^+$ (presumably benzyl) ions formed in the H_2 CI of benzyl halides are unreactive toward H_2.[2,3] In addition the H_2 CI mass spectrum of 7-methoxycycloheptatriene shows an abundant $C_7H_7^+$ ion at m/e 91 but no m/e 93 (Figure 11) indicating that this $C_7H_7^+$ structure (presumably tropylium) also is unreactive toward H_2. An abundant $C_7H_7^+$ ion (presumably benzyl) also is observed in the H_2 CI mass spectrum of benzyl methyl ether (Figure 11) and, as expected, does not react with H_2. The present work also has shown that $C_7H_7^+$ ions formed by the CH_4 CI of ring-halogenated toluenes are reactive toward CH_4 while the $C_7H_7^+$ ions observed in the CH_4 CI mass spectra of benzyl halides are unreactive toward CH_4[2,3] as are the $C_7H_7^+$ ions observed (Figure 11) in the CH_4 CI mass spectra of 7-methoxycycloheptatriene and benzyl methyl ether. It thus appears that the reactivity of $C_7H_7^+$ ions toward H_2 and CH_4 is characteristic of the tolyl structure and that, on the time scale of the chemical ionization experiments $(\sim10^{-5}$ s), isomerization to the unreactive benzyl or tropylium structures has not occurred. The reactivity of tolyl ions toward H_2 and benzyl ions toward *p*-diethylbenzene, combined with the unreactivity of tropylium ions toward either, should provide an extremely useful technique for elucidating the structures of gaseous $C_7H_7^+$ ions and may have applications to higher homologues.

Experimental Section

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 70 eV, with the repellers held at cage potential. Liquid samples were introduced through a heated inlet system at ~100 °C while solid samples were introduced directly from a solids insertion probe.

Approximate source pressures were measured by inserting, in place of the solids probe, a probe consisting of a calibrated thermocouple gauge on a 25-cm length of stainless steel tubing with a Teflon end machined to fit the source opening for the solids probe. The thermocouple gauge was separately calibrated with both H_2 and CH_4 against a capacitance micromanometer. This arrangement permitted establishment of the (approximately linear) relation between the reagent gas pressure behind the reagent gas inlet leak and the source pressure. This was used to estimate source pressures when the solids probe was used.

All samples used were commercially available except 7-methoxycycloheptatriene which was prepared by the reaction of tropylium tetrafluoroborate with sodium methoxide.[16]

References and Notes

(1) Author to whom correspondence should be addressed.
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Steric Effects in S_N2 Reactions

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Abstract: Steric effects for S_N2 reactions of the classical alkyl series have been calculated by molecular mechanics using full relaxation and a force field based on reasonable estimates for the several special constants required. The results show appreciable differences from earlier calculations based on static models and questionably weak nonbonded functions. As expected, agreement is good for the β series (Et, *n*-Pr, *i*-Bu, neo-Pe) for a modest range of variations in the force field constants, and the observed relative rates can be explained wholly from steric effects. Formal requirements which justify the equating of ΔH values with steric energy differences are not properly met in the α series, and in fact agreement between calculated and observed rates is poor for this series (Me, Et, *i*-Pr, *t*-Bu). Thus methyl halides are reported to react 60 times faster than ethyl bromide while steric effects predict the much larger factor of 35 000. *tert*-Butyl bromide, on the other hand, has such a high steric interference in the S_N2 transition state that the C_α-$Br^{1/2}$ bonds are greatly elongated. Even so the predicted rate is much smaller than the observed rate. Whether such a reaction is to be classified as S_N2 or something else, it needs a large accelerating polar factor to overcome the steric hindrance. Steric hindrance in the transition state is relieved in part by bending the $Br^{-1/2}$-C_α-$Br^{-1/2}$ bond in primary and secondary systems. With complete relaxation the total strain becomes distributed throughout the molecule. Although the relative degree of strain is ultimately due to H···Br and C···Br nonbonded contacts, the transition state models do not show unusually short contacts; nor is there any simple parallel with total hindrance. The shortest H···Br distance found in the classical alkyl series is in Br-*i*-Bu-Br where the α-H eclipses one bromine atom and is only 2.4 Å distant. Experimental data for the classical alkyl series have been reevaluated to provide a suitable data set for comparison with calculated steric energies. The molecular mechanics computations have utilized transition state models which either directly or indirectly force the two C_α-Br distances to remain equal and other models which do not force quasi-symmetry. Since the quasi-symmetric models have the higher energies, our force field treats them as transition states rather than stable complexes.

Introduction

Substitution reactions are subject to steric retardation and acceleration.[1-3] Detailed studies by Schleyer's group based on molecular mechanics have provided a good account of steric effects in the solvolysis reaction.[3-6] Much less is known about steric effects in S_N2 substitution despite the fact that it is one of the first reactions to be treated theoretically.[1] In an important pioneering study Ingold's group performed hand calculations on models of the transition state (Figure 1). To make the task manageable they adopted a single appropriate rigid conformation for the transition state for each alkyl group and calculated the H···Br nonbonded distances. For all shorter than the expected van der Waals contact distance they calculated the repulsive energy. The sum of these repulsive energies was taken as the steric energy; the starting alkyl halides were assumed to be strain free. The study included the classical series of alkyl groups: methyl, ethyl, *n*-propyl, isobutyl, neopentyl, isopropyl, and *tert*-butyl. It proved necessary to allow the C_α···Br semibond distances to vary, or else *tert*-butyl was out of line with other groups. Remarkably enough this primitive model gave a reasonably quantitative account of the relative rates.

In a series of papers published some years later the calculations were refined and the experimental base was greatly expanded.[7-15] The classical alkyl series was treated, but in greater detail. In the extended model the Br···C_α···Br axis was allowed to bend as well as stretch and entropy effects were treated in detail.[15]

A more recent study has examined both front-side and back-side attack using simplified stiff models and grouped interactions.[16]