Conclusions

Analysis of the chemical shifts of derivatives **1–9** indicates that polarization of the intervening π-electron system is a significant mechanism of transmission of polar substituent effects in all of these derivatives.

Calculations based on the Buckingham equation indicate that direct field effects are important only in 4-substituted fluorobenzenes and 10-substituted 9-fluoroanthracenes. The relative insensitivity of ^{19}F chemical shifts to direct field effects arises because direct field effects act primarily by polarizing the C–F σ bonds while ^{19}F chemical shifts are mainly sensitive to variation in π-electron density.[30]

Experimental Section

Chemical shift measurements and molecular orbital calculations were carried out using previously reported procedures.[7,8]

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(1) (a) Research supported by a grant from the National Research Council of Canada; (b) Department of Chemistry, McGill University, Montreal, Quebec.

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Aromatic Substitution in the Gas Phase. Ambident Behavior of Halo- and Dihalobenzenes toward D_2T^+. Tritiodeprotonation vs. Tritiodehalogenation

Fulvio Cacace*[1a] and Maurizio Speranza[1b]

Contribution from the Università di Roma, 00100 Rome, Italy, and the Laboratorio di Chimica Nucleare del CNR, 00016 Monterotondo Stazione, Rome, Italy.

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Abstract: The gas-phase electrophilic attack of radiolytically formed D_2T^+ ions on halo- and dihalobenzenes was investigated in homogeneous systems formed by a large excess (760 Torr) of D_2 labeled with DT and containing at low concentrations (ca. 1 Torr) the aromatic substrate and a thermal radical scavenger (O_2). Analysis of the labeled products demonstrated two major reaction pathways, i.e., tritiodeprotonation, yielding the tritiated substrate or its isomers, and tritiodehalogenation. The relative rate of the two competing reactions is mainly determined by the nature of the halogen atom(s) contained in the substrate, the extent of dehalogenation increasing in the order Br $\leq$ Cl $\ll$ F. The results suggest two distinct mechanisms for the major reaction channels, as tritiodeprotonation appears to depend on the attack of D_2T^+ on the aromatic π system, while tritiodehalogenation requires the attack of the gaseous electrophile to the *n* center(s) of the substrate. The above conclusions, independently supported by appropriate ion cyclotron resonance and chemical ionization mass spectrometric data, are compared with the results obtained with different gaseous electrophiles and in related reactions occurring in solution.

Introduction

Novel experimental techniques[2-4] that allow the isolation of the final products and the determination of the *substrate* and *positional* selectivity of the electrophile have been extensively applied to the study of aromatic substitutions in the gas phase, i.e., in a reaction environment entirely free from the complicating effects of solvation and ion pairing that invariably affect the investigations carried out in solution. The unsolvated cations of precisely defined structure employed as electrophiles in the gas phase include HeT^+,[5-7] D_2T^+,[8,9] CH_4T^+,[10] $^{80}Br^+$,[11] and several alkyl cations.[12-16] Among the substrates investigated, halobenzenes have received particular attention, as the reactivity pattern of these molecules containing distinct nucleophilic centers, i.e., the π system of the aromatic ring and the *n* electrons of the substituent(s), toward the comparatively indiscriminate attack of the extremely strong electrophiles available in the gas phase was expected to provide direct evidence of ambident behavior. Actually, the study of the gas-phase attack of the HeT^+ on fluorobenzene, chlorobenzene, and bromobenzene[6] failed to demonstrate any significant reaction channel other than tritiodeprotonation, as the corresponding tritiated halobenzenes represented by far the predominant product, and formation of minor amounts of benzene-*t*, increasing in the *inverse* order of the C-X bond strength ($C_6H_5F \ll C_6H_5Cl < C_6H_5Br$) could be reasonably traced to the fragmentation of a little fraction of the arenium ions that are formed in an excited state from the strongly exothermic attack of HeT^+. On the other hand, use of D_2T^+ in a drastically different reaction environment, revealed an unexpectedly remarkable difference in the behavior of fluorobenzene and chlorobenzene, as the former substrate was observed to undergo extensive tritiodehalogenation, giving high yields of benzene-*t*.[9] This interesting result suggested a systematic investigation of the reactions of selected halo- and dihalobenzenes toward D_2T^+, in order to assess their ambident behavior and to evaluate the relative reactivity of the π-type and *n*-type nucleophilic centers of these molecules toward the gaseous electrophile. In addition, the possibility of gathering hitherto inaccessible information on the isomerization (in particular, intramolecular halogen shifts) of gaseous arenium ions was considered of interest. The results obtained along this second research line are reported in the following paper of this issue.

Experimental Section

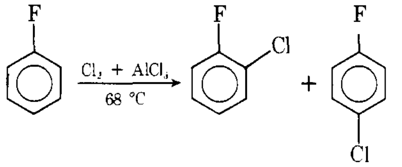
Materials. Deuterium gas, a research grade product from Fluka AG, with a stated D_2 content exceeding 99.8 mol %, was passed through molecular sieves traps cooled at -196 °C for further purification. Deuterium tritide was prepared from T_2 gas (CEA, France) diluted with a large excess of D_2 and subjected to Tesla discharges at reduced pressure. The isotopic composition of DT was determined by radio GSC using a ferric oxide activated silica column at -196 °C,[17] connected to a flow ionization chamber.[18]

Research grade O_2 (SIO Co., Milano) with a stated purity of over 99.9 mol % was used without further purification. Samples of halo- and dihalobenzenes from Fluka AG were purified on the following columns: C_6H_5F, 5-m diisodecyl phthalate column at 70 °C; C_6H_5Cl, 2-m DC 550 silicone oil column at 110 °C; $C_6H_4F_2$, 4-m Bentone 34 column at 70 °C; C_6H_4FCl, 4-m Bentone 34 column at 110 °C; C_6H_4FBr, 4-m Bentone 34 column at 125 °C; $C_6H_4Cl_2$, two consecutive separation steps, respectively with a 2-m Bentone 34 column at 120 °C and with a 4-m DC 550 silicone oil column at 130 °C. Helium was used as the carrier gas and acid-washed Chromosorb W as the solid support in all separations that were performed on a modified[19] Model DC Erba gas chromatograph and repeated until the purity of the recovered samples, as determined by analytical GLC, exceeded 99.99 mol %.

Procedure. Pyrex bulbs (1 l.), connected to a greaseless vacuum line, were outgassed and evacuated to 10^{-5} Torr, then filled with D_2 (760 Torr, containing ca. 40 mCi of DT), O_2 (1 Torr), and the aromatic substrate (ca. 10 mg). The bulbs were irradiated with the ^{60}Co γ rays in a 220 Gammacell (Atomic Energy Canada Ltd.) at 37.5 °C, at a dose rate of 0.7 Mrad h^{-1}. After receiving doses ranging from 1 to 14 Mrad, as determined with a Fricke dosimeter, the samples were added with exactly weighed amounts of appropriate inactive carriers, then connected to the vacuum line, cooled to -130 °C, and carefully outgassed with a Toepler pump, collecting the uncondensed gases into a separate bulb. The recovered aromatics were purified by preparative GLC on the following columns: C_6H_6 and C_6H_5F: 7.5-m β,β'-oxydipropionitrile column at 25 °C and 5-m diisodecyl phthalate column at 70 °C; C_6H_6, C_6H_5F, and anisole: 5-m diisodecyl phthalate column at 70 °C; C_6H_6 and C_6H_5Cl: 2-m DC 550 silicone oil column at 110 °C and 2-m Bentone 34 column at 110 °C; C_6H_5F and $C_6H_4F_2$ isomers: 4-m Bentone 34 column at 70 °C, 5-m diisodecyl phthalate column at 90 °C, and 7.5-m β,β'-oxydipropionitrile column at 65 °C; C_6H_5F, C_6H_5Cl, and C_6H_4FCl isomers: 2-m Bentone 34 column at 110 °C and 4-m tricresyl phosphate column at 110 °C; C_6H_5F, C_6H_5Br, and C_6H_4FBr isomers: 2-m Bentone 34 column at 125 °C and 4-m tricresyl phosphate column at 120 °C; C_6H_5Cl and $C_6H_4Cl_2$ isomers: 2-m Bentone 34 column at 120 °C and 4-m DC 550 silicone oil column at 130 °C. Each labeled product was repeatedly passed through the appropriate column(s) until its specific activity, measured with a Mark I Nuclear Chicago liquid scintillation spectrometer, reached a constant value.

In order to evaluate the extent of the radiation-induced dehalogenation and isomerization of the substrates, blank runs were carried out by irradiating, under exactly the same conditions, samples which did not contain any DT and assaying the products by analytical GLC, using a Model 800 Perkin-Elmer gas chromatograph equipped with a FID detector. The blank irradiations indicated that less than 0.3% of the starting halobenzenes was dehalogenated and/or isomerized under the conditions used in the actual runs.

Preparation of Substituted Derivatives of Fluorobenzene. The distribution of tritium within the labeled fluorobenzene formed from the D_2T^+ induced tritiodehalogenation reaction on p-$C_6H_4F_2$ was determined by measuring the decrease of the molar radioactivity caused by replacement of hydrogen atoms by suitable inactive groups. Chlorination of fluorobenzene gave a mixture of *o*- and *p*-chlorofluorobenzene which was resolved by preparative GLC on a 2-m Bentone 34 column at 110 °C, and the activity of the purified isomers was measured. The tritium content of the meta positions was determined by difference.



Ion Cyclotron Resonance Mass Spectrometric Experiments. ICR experiments were performed by bombarding with 16-eV electrons, emitted by a heated rhenium filament, a $[D_2]$:[halobenzene] = 10:1 mixture in the source region of the cell of a modified Varian Associates ion cyclotron resonance mass spectrometer (Syrotron).

Results

The tritiated products from the gas-phase attack of the D_2T^+ ions on selected halo- and dihalobenzenes are listed in the Table I. Only the relative yields of the tritiated products, i.e., the ratio $A_i/\Sigma_{i=1}^{N} A_i$, where A_i is the total activity of the *i*th product and $\Sigma_{i=1}^{N} A_i$ is the combined activity of all tritiated products identified, are reported because the measure of the *absolute* yields is largely approximate, owing to the difficulty of measuring with sufficient accuracy the *absolute* activity of the DT gas used as a tracer. However, even the low accuracy level of the *absolute* yields measurements allows detection of a peculiar feature that sets apart the halo- and dihalobenzenes from other substrates. In fact, in the case for instance of arenes,[8] the *absolute yields* could be usually calculated from the radiation dose absorbed by the D_2/DT mixture, the initial DT activity, and the known[20] $G_{X_3^+}$ value, assuming the lack of isotope effects both in the formation of the X_3^+ (X = D, T) ions and in their X^+ transfer to the substrate. The results of these calculations, while largely approximate, were nevertheless reasonably close to the experimental yields, indicating that the radiolytically formed D_2T^+ reagent was indeed the only significant precursor of the tritiated products. In the present work, however, the experimental yields usually exceed by a factor of 1.5 to 2 the values calculated with the above assumptions, suggesting that the final tritiated products arise not only from the reactions of the radiolytically formed D_2T^+ ions, but also from the molecular DT contained in the gaseous mixture.

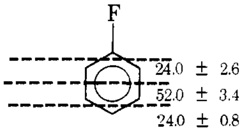
Table I. Tritiated Products from the Gas-Phase Attack of X_3^+ (X = D, T) on Halo- and Dihalobenzenes

	System composition					Relative yields of tritiated products,[a] %	
Substrate	D_2, Torr	DT, mCi	O_2, Torr	Substr, Torr	Dose, Mrad	Tritiodeprotonation product	Tritiodehalogenation product
Fluorobenzene[b]	760	43	1.0	1.3	3.5	Fluorobenzene, 57.8	Benzene, 42.1
Fluorobenzene[c]	760	43	1.0	1.9	3.5	Fluorobenzene, 56.5	Benzene, 42.1; anisole 1.4
Fluorobenzene	760	40	1.0	1.9	3.5	Fluorobenzene, 58.9	Benzene, 41.1%
Chlorobenzene[b]	760	92	1.5	1.3-1.6	1-10	Chlorobenzene, 99.6	Benzene, 0.4
Chlorobenzene	760	40	1.0	1.6	1	Chlorobenzene, 98.9	Benzene, 1.1
o-Difluorobenzene	760	40	1.0	1.5	3.5	Isom. difluorobenzenes, 54.2	Fluorobenzene, 45.8
m-Difluorobenzene	760	40	1.0	1.5	3.5	Isom. difluorobenzenes, 44.6	Fluorobenzene, 55.4
p-Difluorobenzene	760	40	1.0	1.5	3.5	Isom. difluorobenzenes, 61.5	Fluorobenzene, 38.5
o-Chlorofluorobenzene	760	40	1.0	1.3	3.5	Isom. chlorofluorobenzenes, 75.9	Fluorobenzene, 3.3; chlorobenzene, 20.8
m-Chlorofluorobenzene	760	40	1.0	1.3	3.5	Isom. chlorofluorobenzenes, 65.2	Fluorobenzene, 7.2; chlorobenzene, 27.7
p-Chlorofluorobenzene	760	40	1.0	1.3	3.5	Isom. chlorofluorobenzenes, 77.3	Fluorobenzene, 2.4; chlorobenzene, 20.2
o-Bromofluorobenzene	760	40	1.0	1.1	3.5	Isom. bromofluorobenzenes, 79.3	Fluorobenzene, 9.2; bromobenzene, 11.4
m-Bromofluorobenzene	760	40	1.0	1.1	3.5	Isom. bromofluorobenzenes, 67.1	Fluorobenzene, 4.5; bromobenzene, 28.4
p-Bromofluorobenzene	760	40	1.0	1.1	3.5	Isom. bromofluorobenzenes, 74.3	Fluorobenzene, 2.4; bromobenzene, 23.2
o-Dichlorobenzene	760	40	1.0	1.2	1-10	Isom. dichlorobenzenes, 98.1	Chlorobenzene, 1.9
m-Dichlorobenzene	760	40	1.0	1.2	1-10	Isom. dichlorobenzenes, 89.4	Chlorobenzene, 10.6

[a] Referred to the combined activity of all tritiated aromatic identified; standard deviation ca. 10%. [b] Reference 9. [c] Irradiation carried out in the presence of CH_3OH (1.2 Torr).

The percentages listed in the Table I represent the mean values from several separate irradiations carried out under the same conditions, and their standard deviation is of the order of 10%. Most of the data listed were obtained at a radiation dose of 3.5 Mrad. Separate irradiations of several halobenzenes at doses ranging from 1 to 14 Mrad indicate that the distribution of the tritiated products is, in general, essentially independent of the dose, at least within the dose range investigated.

The distribution of tritium within the labeled fluorobenzene produced by the D_2T^+ attack on *p*-$C_6H_4F_2$ is given below:



Each value is the average of several determinations on samples from two different experiments carried out under identical conditions. The standard deviation of the data is of the order of 10%.

The major features emerging from the experimental data can be summarized as follows.

i. The extent of tritiodehalogenation vs. tritiodeprotonation is strongly dependent on the nature of the leaving halogen, increasing in the order: Br $\simeq$ Cl $\ll$ F. Thus, while benzene-*t* accounts for only 1% of the final tritiated products from the tritiodechlorination of chlorobenzene, it represents the major labeled product from the D_2T^+ attack on the fluorobenzene.

ii. In addition to the nature of the leaving halogen, the extent of tritiodehalogenation of dihalobenzenes is somewhat affected by the nature of the other halogen.

iii. The relative rate of tritiodehalogenation vs. tritiodeprotonation of dihalobenzenes is considerably affected by the position of the two halogens. In particular, *m*-dihalobenzenes undergo considerably more extensive dehalogenation than the corresponding ortho and para isomers.

iv. The presence of a gaseous base (MeOH) deliberately added to the systems in concentrations equivalent to that of the aromatic substrate does not affect the *relative* yields of the final labeled products, although their *absolute* yields are strongly depressed. Besides, a small amount of tritiated anisole is formed.

v. The tritium atom, contained in the molecule of fluorobenzene produced by the tritiodefluorination of *p*-difluorobenzene, is not bound exclusively to the para position, but also to the meta and, to a smaller extent, to the ortho positions.

Discussion

Nature of the Dehalogenation Process. Discussion of the mechanism of dehalogenation can usefully proceed from the following preliminary considerations. In the first place, the insignificant fraction of halo- and dihalobenzenes which undergoes dehalogenation in the blank irradiations rules out both the secondary tritiation of radiolytically dehalogenated halobenzenes and the secondary radiolytic dehalogenation of previously tritiated halobenzenes as significant channels to the formation of the tritiated, dehalogenated products. This conclusion is consistent with the observation that the relative rate of tritiodehalogenation increases in the order: F $\gg$ Cl $\simeq$ Br, which is exactly opposite to the trend expected for a radiolytic dehalogenation, whose extent should *decrease* with the strength of the C–halogen bond, i.e., in the order: Br > Cl $\gg$ F. This expectation is supported by the mass spectrometric data on the fragmentation of halobenzenes induced either by electron impact,[21-24] or by dissociative attachment of quasithermal electrons,[25] showing that the abundance of dehalogenated species is negligible for fluorinated substrates and increases significantly passing to chlorobenzenes and bromobenzenes.

In conclusion, the results of the blank irradiations, taken together with the relative extent of tritiodehalogenation (F $\gg$ Cl $\simeq$ Br) and with the available mass spectrometric data, exclude the *direct* radiolysis of the substrate as a significant route to the labeled dehalogenated products and suggest that tritiodehalogenation must be somehow related to the attack of the X_3^+ ions (X = D, T), the major species formed from the radiolysis of the bulk constituent of the system, on the aromatic substrate.

Mechanism of the Electrophilic Attack. The results outlined in the previous sections and the supporting mass spectrometric evidence (vide infra) can be best rationalized assuming an ambident behavior of the halobenzenes toward the X_3^+ ($X =$ D, T) ions formed from the radiolysis of the D_2/DT mixture (henceforth indicated as X_2), that represents the bulk constituent of the gas:

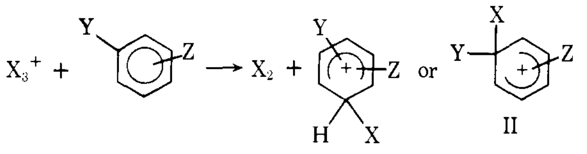
$$X_2 \rightsquigarrow X_2^+ + e \qquad (1)$$

$$X_2^+ + X_2 \rightarrow (X_3^+)^* + X \qquad (2)$$

and thermalized by a large number of unreactive[26] collisions with X_2 molecules

$$(X_3^+)^* \xrightarrow[>100 \text{ collisions}]{+X_2} X_3^+ \qquad (3)$$

A. Attack to the π system of the ring, leading to the formation of isomeric haloarenium ions, e.g., I or II



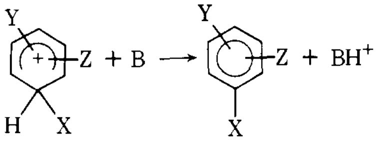
(4)

I

II

Y = halogen, Z = H or halogen

The arenium ions formed are excited by the exothermicity of the reaction, that can be calculated, at least for the species I from fluorobenzene, chlorobenzene, and *m*-difluorobenzene, using very recent *PA* values determined by Yamdagni and Kebarle,[27] which lead to $\Delta H°$ values of ca. −73 kcal mol^{-1} for all these substrates. Before collisional stabilization, the excited ions I and II are likely to undergo fast intramolecular proton shifts and, for Y = Cl or Br, slower 1 → 2 halogen shifts. Eventually the halobenzenium ions loose a proton to a gaseous base, either deliberately added to the system (MeOH), or formed from its radiolysis. The available thermochemical data, which refer to fluorobenzenium, chlorobenzenium, and *m*-difluorobenzenium ions, show that proton transfer (5) to



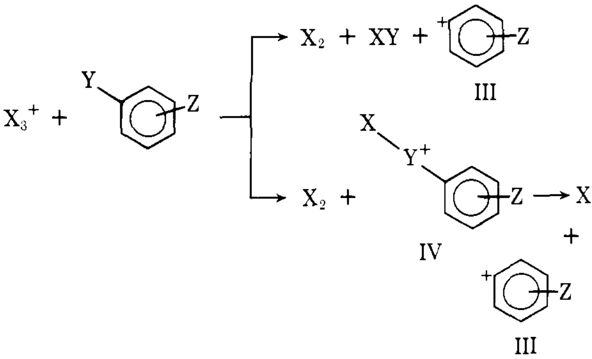
(5)

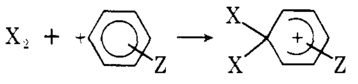
MeOH is almost exactly thermoneutral. Since a fraction of the X_3^+ ions, and therefore of the intermediates I and II, contains T atoms, the reaction sequence initiated by the X_3^+ attack on the ring provides a *direct* route to tritiated products identical, or isomeric, with the starting halobenzene and can be therefore characterized as a *tritiodeprotonation* process. The intramolecular halogen shifts that can occur within intermediates I, and especially II, provide an example of a gas-phase isomerization of unsolvated haloarenium cations, and their mechanism will be discussed elsewhere.

B. Attack to the *n* electrons of the halogen substituent, competitive with the attack to the ring (4). Halonium ions and neutral halogen atoms (particularly F and Cl) are poor leaving groups, and their elimination must be therefore ruled out on energetic grounds. Considering the attack of X_3^+ on F-substituted arenes, the substrates that undergo the most extensive dehalogenation, direct formation of C_6H_6 from fluorobenzene, with release of a free F^+ ions, would be endothermic by more than 200 kcal mol^{-1}, and formation of a $C_6H_6^+$ ion, with elimination of a F atom, would also be endothermic by ca. 24 kcal mol^{-1}. In this case, the only leaving group whose release is compatible with energetic requirements appears to be a hydrogen halide molecule. In fact, the overall process:

$$C_6H_4YZ + X_3^+ \rightarrow C_6H_4Z^+ + XY + X_2 \qquad (6)$$

can be shown to be slightly exothermic in all cases (monohalobenzenes, *m*-difluorobenzene) where the available thermochemical data allow $\Delta H°$ calculations.[27] Experimental confirmation of reaction 6 cannot be achieved by actual isolation of the labeled hydrogen halides XY, owing to the highly exchangeable nature of the tritium atoms contained in these products. Nevertheless, formation of phenyl ions from the dehalogenation of halobenzenes promoted by X_3^+ attack finds direct experimental support in the mass spectrometric results that will be discussed in a following section. Reaction 6 can proceed either via *direct* halide ion abstraction (6a), or via the dissociation of an intermediate phenylhalonium ion (IV) formed from the attack of the electrophile on the halogen substituent (6b). Whatever their source, the phenyl ions III are suggested to efficiently attack the X_2 gas, the only nucleophile contained in high concentrations in the system, yielding dehalogenated arenium ions, excited by the exothermicity of the process, whose $\Delta H°$ value ranges from −78 kcal mol^{-1} for the unsubstituted phenyl cation to −106 kcal mol^{-1} for the fluorophenyl cation.[27] Eventually, the arenium ions from reaction 7 which escape fragmentation undergo a de-





(7)

V

protonation process analogous to reaction 5, yielding tritiated products containing one halogen atom less then the starting halobenzene. The tritium distribution in the neutral dehalogenated products, where the radioactive atoms are bound predominantly, but not exclusively, to the ring position formerly occupied by the halogen, can be explained either by the isomerization of the phenyl ions III via intramolecular hydride ion shifts, or by 1 → 2 proton shifts within the arenium ions V. The latter mechanism, which is characterized by a low activation energy in halobenzenium ions,[28] seems to be preferred, especially considering the high excitation energy of the intermediates (V) from the strongly exothermic reaction 7. The reaction sequence initiated by the X_3^+ attack on the halogen substituent of the substrate represents an *indirect* labeling route to dehalogenated products and can be therefore characterized as a *tritiodehalogenation* process. It should be noted that tritiated dehalogenated products can be formed even from *inactive* phenyl ions reacting with the DT molecules contained in the X_2 gas, a feature that would account for the experimental observation of overall yields exceeding those calculated on the assumption that D_2T^+ ions are the only source of the tritium atoms incorporated into the products. The results of the radiolytic experiments do not allow to discriminate between the direct halide ion abstraction (6a) and the intermediacy of the phenylhalonium cation (6b). However, isolation of minute amounts of tritiated anisole from the protonation of fluorobenzene carried out in the presence of MeOH indicates that a certain fraction of the phenyl ions III does indeed contain tritium, suggesting the intervention of an adduct, such as IV, sufficiently long lived to allow some degree of isotopic scrambling. The conclusion that dehalogenation does not proceed *exclusively* via halide ion abstraction is independently supported by mass spectrometric evidence.

The occurrence of dehalogenation can be regarded as compelling, if indirect, evidence for the ambident behavior of halobenzenes toward X_3^+, i.e., for the attack to *n* electrons of the halogen substituent competing with the attack to the π electrons of the aromatic ring which leads to tritiodeprotonation. In fact, irrespective of its detailed mechanistic pathway (direct halide ion abstraction vs. formation of a phenylhalonium intermediate, etc.), dehalogenation necessarily requires formation of a hydrogen halide, i.e., bonding of one hydrogen atom of the reagent to the leaving halogen, as dictated by energetic constraints and indicated by mass spectrometric results. Consequently, dehalogenation necessarily affects the n electrons of the halogen substituent, underlining the ambident behavior of the substrate toward the gaseous electrophile.

Mass Spectrometric Evidence. In their chemical ionization (CI) study, Harrison and Ping-Huang Lin[29] identified *all the intermediates* postulated by the mechanism outlined in the previous section as the most abundant ionic products from the attack of X_3^+ (X = H, D) ions on fluorobenzene and fluorotoluenes. Thus, the protonated substrate $(M + X)^+$, corresponding to intermediates I and II, is the most abundant (ca. 40%) ion, demonstrating efficient collisional stabilization even at relatively low X_2 pressures. Phenyl ions $(M - Y)^+$, corresponding to intermediates III, and dehalogenated arenium ions $(M - Y + X_2)^+$, corresponding to intermediates V, were detected with comparable (ca. 20%) abundances. However, formation of V is ascribed by Harrison and Ping-Huang Lin to a single-step process, unrelated to the intermediacy of a phenyl ion precursor, e.g.,

$$C_6H_5F + X_3^+ \rightarrow XF + C_6H_5X_2^+ \qquad (8)$$

It should be noted, however, that, in the lack of a pressure-dependence study, CI spectra taken at a fixed and rather low (0.3 to 0.5 Torr) X_2 pressure do not allow to resolve the elementary steps of consecutive ion–molecule reactions, and that the CI results appear entirely consistent with the consecutive processes 6 and 7 as well.

This and other central mechanistic points have been brought to a sharper focus by an extensive ion cyclotron resonance (ICR) study on the attack of X_3^+ (X = H, D) ions on a variety of halo- and dihalobenzenes, carried out in the pressure range from 10^{-6} to 10^{-4} Torr.[21] The conclusions most relevant to the present discussion can be summarized as follows.

i. Attack of X_3^+ on halobenzenes yields, as a major *secondary* ion, the protonated substrate $[M + X]^+$, corresponding to intermediates I and II.

ii. Phenyl ions $[M - Y]^+$, corresponding to intermediates III, are also abundant *secondary* species formed from the attack of X_3^+ on halobenzene.

iii. Dehalogenated arenium ions $[M - Y + X_2]^+$, corresponding to the intermediates V, are major *tertiary* ions, arising from the attack of the corresponding phenyl ions III on the X_2 molecules. Double resonance experiments confirm that the phenyl ions $[M - Y]^+$ are the precursors of the $[M - Y + X_2]^+$ arenium ions, thus supporting the two-step mechanism based on reactions 6 and 7.

iv. Finally, the ICR data show that a fraction of the phenyl ions III from the attack of D_3^+ on fluorobenzenes contains deuterium, indicating that dehalogenation does not proceed *exclusively* via direct halide ion abstraction.

Finally, the attack of the D_3^+ reagent on the *n* electrons of halobenzenes, which is particularly relevant in the case of fluorobenzenes, finds interesting analogies with the ICR results of Ridge and Beauchamp,[30] who demonstrated the occurrence and the chemical consequences of strong hydrogen bonding involving gaseous Bronsted acids and *fluorinated* substrates.

As a whole, the mass spectrometric evidence provides strong support to the mechanism outlined in the previous sections and confirms the most significant result obtained at atmospheric pressure, namely the occurrence of extensive defluorination following the X_3^+ attack.

Competition of Tritiodeprotonation with Tritiodehalogenation. The extent of dehalogenation depends essentially on the nature of the halogen, increasing in the order Br $\simeq$ Cl $\ll$ F. The trend cannot be rationalized on energetic grounds, since the C–halogen and C–hydrogen bond energies undergo roughly equivalent changes, and consequently the overall energetic balance of process 6 remains essentially unaffected in passing from F to Cl and Br. Kinetic explanations based on the highly selective character of the electrophilic attack on the F atom(s) of the substrate appear also inadequate, owing to the well-established indiscriminate reactivity of the X_3^+ cation, largely demonstrated on a wide variety of substrates.[8,9]

A possible explanation can rather be based on the pronounced polarization of the C–F bond, whose *individual* dipole moment in C_6H_5F exceeds that of the C–Cl bond in C_6H_5Cl by a factor greater than 2, according to a recent analysis of ^{13}C chemical shifts.[31]

In the critical competition between the reaction channels opened by the exothermic X_3^+ attack, 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.

The suggested correlation between the rate of dehalogenation and the positive polarization of the halogen-substituted ring C would also explain the effects of an additional halogen substituent in the aromatic molecule and of its position with respect to F. In fact, polarization of the C–F bond should be highest in C_6H_5F and should be reduced by the presence of substituents capable of increasing by conjugative stabilization the electron density at the F-substituted C. Thus, one would expect that the relative rate of defluorination is highest in C_6H_5F and decreases passing to C_6H_4ClF and C_6H_4BrF, which agrees with the experimental trend. Furthermore, the effects of Cl and Br should be higher in the ortho and para than in the meta position, and therefore, for a given dihalobenzene, the highest defluorination rate should be expected for the meta isomer, again in agreement with the experimental results.

The *reverse* effect should be observed for dechlorination (debromination). In fact, owing to the strong electron-withdrawing effect of F, the polarization of the C–Cl (C–Br) bond should be *increased* by F substitution, thus *enhancing* the rate of dechlorination (debromination) in fluorochlorobenzenes (fluorobromobenzenes) with respect to that of C_6H_5Cl (C_6H_5Br), an expectation supported by the experimental data.

Such interpretation finds also interesting analogies in solution chemistry, where the *arylating* ability of halobenzenes under Friedel-Crafts conditions is known to increase in the order $C_6H_5Br < C_6H_5Cl \ll C_6H_5F$, a trend traced to the increasing polarization of the C–halogen bond and to the incipient cationic nature of the phenyl group in fluorobenzene.[32,33]

Comparison with Related Reactions in the Gaseous and in the Liquid Phase. HeT^+, the only gaseous Bronsted acid whose aromatic substitutions have been extensively investigated, reacts with halobenzenes giving high yields (67 to 76%) of the corresponding tritiodeprotonation products.[6] Tritiated benzene, the tritiodehalogenation product, is not formed from C_6H_5F, and its yield increases from 3.7 to 8.1% passing from C_6H_5Cl to C_6H_5Br. The trend follows the inverse order of the C–halogen bond strength and is opposite to the one observed in the case of X_3^+ reagent. However, this apparent discrepancy does not imply any fundamental diversity in the inherent reactivity of HeT^+ with respect to X_3^+, but it is likely to arise exclusively from the extremely different reaction environment prevailing in the two investigations. In fact, HeT^+ were generated from the decay of T_2 within the pure gaseous substrates at a pressure of 250 Torr, at a typical [halobenzene]:[T_2] ratio of 2.10^5:1. Under such conditions, no appreciable tritiodehalogenation can be expected based on the mechanism suggested in the present report, as the unlabeled phenyl cations formed from a possible reaction similar to processes 6, e.g.,

$$HeT^+ + C_6H_5F \rightarrow He + C_6H_5^+ + TF \qquad (9)$$

$$\Delta H^\circ = -77 \text{ kcal mol}^{-1}$$

cannot react at any significant rate with T_2, contained at extremely low concentrations in the gas, and will rather attack the halobenzene molecules present in a large excess, according to phenylation processes well established in solution chemistry,[33] yielding no tritiated benzene. The only possible source of C_6H_5T, under these conditions, can be some reaction sequence initiated by the decomposition of the highly excited arenium ions formed from the exothermic triton transfer from HeT^+ to the halobenzenes, thus explaining the observed *decrease* of the C_6H_5T yields with the strength of the C–halogen bond, which increases in the order $Br < Cl < F$.

The gas-phase protodehalogenation of halobenzenes, established as a major reaction channel in the present study, finds only partial analogies in solution chemistry. In fact, while examples of protolytic dehalogenation of iodo-, chloro-, and bromobenzenes are known, no protodefluorination has been observed, even when fluorobenzenes are dissolved in the strongest Bronsted acids. In fact, while protonation at the *n* electrons of F has been *postulated* in recent studies,[34] only ring protonation and subsequent proton shifts could be experimentally observed in NMR investigations on superacid solutions of fluorobenzenes without detectable defluorination or F migration.[28,35,36]

On the other hand, protonation of nonbonded electron pairs of halogens has been demonstrated in the case of iodo-, chloro-, and bromobenzene, but not of fluorobenzene.[34] Furthermore, Lewis acids, such as aluminum halides, are known to promote halogen-exchange reactions requiring the fission of the C–halogen bond in halobenzenes. While the mechanistic pathway of these processes is not definitely established, as the presence of traces of Bronsted acids, even in the so called anhydrous aluminum halides, cannot be safely excluded, it is interesting to note that the rate of the exchange processes increases in the order of increasing polarity of the C–halogen bonds.[33]

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