Gas-Phase Aromatic Substitution. Isomerization of Gaseous Arenium Ions from the Attack of D_2T^+ on Dihalobenzenes

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Abstract: The isomerization of gaseous, unsolvated arenium ions from the attack of radiolytically formed D_2T^+ on dihalobenzenes was investigated in the gas phase at atmospheric pressure, irradiating with the ^{60}Co γ radiation homogeneous systems containing an excess of D_2 gas labeled with DT and low concentrations of the aromatic substrate and a thermal radical scavenger (O_2). The isomeric composition of the tritiated products from difluorobenzenes, dichlorobenzenes, chlorofluorobenzenes, and bromofluorobenzenes was determined by radio gas chromatography. The results show that gas-phase tritiodeprotonation of dihalobenzenes by D_2T^+ is invariably accompanied by isomerization, whose rate depends markedly on the nature of the substituents, the migratory aptitude of the halogens increasing in the order: $F \ll Cl < Br$. The position of the substituents has also a significant effect, as the meta isomer of a given dihalobenzene is found to undergo appreciably less extensive halogen migration than the ortho and para isomers. The results suggest that the isomerization process is of *intramolecular* nature, involving consecutive $1 \rightarrow 2$ halogen shifts of the gaseous arenium ions formed from the exothermic triton transfer from D_2T^+ to dihalobenzenes. The mechanism of the isomerization is discussed and compared with those of similar reactions promoted in solution by strong Bronsted acids.

Introduction

The isomerization of halogen-substituted arenium ions, in particular the migratory aptitude of the halogens, has been the subject of considerable interest and extensive investigation, especially in connection with the general problem of electrophilic halogenation of aromatic molecules.[2-5]

Till now, however, all studies have been restricted to condensed phases, using variously promoted Friedel-Crafts catalysts, and the interpretation of their results has been considerably hampered by the occurrence of various side processes, including disproportionation of the substrate, halogen exchange with the catalyst, intermolecular halogen transfer, Friedel-Crafts arylation and polymerization, etc., in addition to the complicating phenomena of solvation and ion pairing invariably encountered in solution.

In a previous paper[6] we have reported on the gas-phase reactions of radiolytically formed D_2T^+ ions on halo- and dihalobenzenes, describing in particular the ambident behavior of these substrates toward the strong gaseous electrophile and identifying two major reaction channels, i.e., tritiodeprotonation and tritiodehalogenation. The experimental technique[7,8] employed in these studies allows the determination of the isomeric composition of the tritiated products, thus affording the possibility to investigate the isomerization of the gaseous, unsolvated arenium ions formed in the exothermic triton transfer from D_2T^+ to the halobenzenes, which represents the first step of the tritiodeprotonation.

In the present paper we report on the isomerization of difluoro-, dichloro-, chlorofluoro-, and bromofluoroarenium ions obtained from the attack of D_2T^+ on the corresponding dihalobenzenes and studied in highly diluted gaseous solutions, under conditions where solvation, ion pairing, intermolecular halogen shifts, and other complicating factors are entirely eliminated.

Experimental Section

The D_2T^+ reagent was obtained by irradiating with the ^{60}Co γ radiation D_2 gas containing a tracer activity of DT, in the presence of the aromatic substrate and of O_2, used as a radical scavenger. Typical experimental conditions were: D_2, 760 Torr; DT, 40 mCi; dihalobenzenes, 1-2 Torr; O_2, 1 Torr; radiation dose, 3.5 Mrad; irradiation temperature, 37.5 °C.

Full experimental details of the techniques used for the purification of the reagents, the preparation and irradiation of the gaseous samples, and the radio gas chromatographic analysis of the tritiated products, including a complete account of the columns employed, have been given elsewhere.[6] Blank irradiations were carried out using systems containing no DT, but otherwise identical with those employed in the actual runs, in order to evaluate the extent of the radiation-induced isomerization of dihalobenzenes. Analysis of the products, carried out with a Perkin-Elmer Model 800 gas chromatograph equipped with a FID detector, demonstrated that in all cases less than 1% of the initial dihalobenzene underwent isomerization in the blank irradiations.

Results

The isomeric composition of the tritiated products from the gas-phase tritiodeprotonation of selected dihalobenzenes by the D_2T^+ reagent is given in Table I. The percentages listed represent the mean values of the data obtained from several separate irradiations carried out under the same conditions, and their standard deviation is of the order of 10%, except for the lowest values, e.g., those referring to difluorobenzenes, characterized by a somewhat lower precision. Most of the data listed were obtained at a radiation dose of 3.5 Mrad. Separate irradiations of the individual dihalobenzenes at different doses, ranging from 1 to 14 Mrad, indicate that the isomeric composition of the tritiated products is in general essentially independent of the dose, at least within the range investigated.

The major features of the experimental results can be summarized as follows:

i. The extent of isomerization depends on the nature of the halogen substituents, the migrating ability of the halogens increasing in the order: $F \ll Cl < Br$. Thus, while isomerized tritiated products are barely detectable in the tritiodeprotonation of difluorobenzenes, they account for over 20% of the total yield in the tritiodeprotonation of *o*-bromofluorobenzene.

ii. The position of the halogen substituents affects considerably the rate of isomerization. In particular, the *m*-dihalobenzenes undergo considerably less extensive isomerization than the corresponding ortho and para dihalobenzenes.

iii. In general, the ortho isomer formed from *p*-dihalobenzenes and inversely the para isomer from *o*-dihalobenzenes are accompanied by higher yields of the meta isomer, the only

Table I. Isomeric Composition of Products from the Gas-Phase Tritiodeprotonation of Dihalobenzenes with D_2T^+

Substrate	Isomeric composition of tritiodeprotonation products, %		
	Ortho	Meta	Para
o-Difluorobenzene	98.7	1.1	0.2
m-Difluorobenzene	0.4	99.2	0.4
p-Difluorobenzene	0.1	0.6	99.3
o-Chlorofluorobenzene	93.1	4.7	2.1
m-Chlorofluorobenzene	1.2	96.8	1.9
p-Chlorofluorobenzene	1.2	6.3	92.5
o-Bromofluorobenzene	77.8	10.0	12.2
m-Bromofluorobenzene	1.7	96.0	2.3
p-Bromofluorobenzene	2.2	13.0	84.8
o-Dichlorobenzene	89.5	9.1	1.4
m-Dichlorobenzene	0.7	98.2	1.1

exception being observed in the tritiodeprotonation of *o*-bromofluorobenzene.

iv. Isomerization of *m*-dihalobenzenes proceeds preferentially to the para, rather than to the ortho isomer.

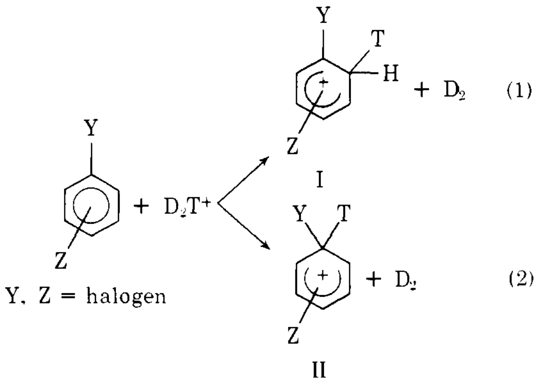
Discussion

Nature of the Isomerization Process. Discussion of the isomerization mechanism requires preliminary consideration of two basic experimental features. In the first place, the relatively insignificant rate of isomerization measured in the blank runs rules out the possibility that labeled isomerized products are formed either via the tritiation of radiolytically isomerized dihalobenzene molecules, or inversely via the radiolytic isomerization of already tritiated, but not isomerized, dihalobenzene molecules.

In the second place, the composition of the gaseous reaction environment, where dihalobenzene is diluted by a large excess of D_2 gas and no monohalobenzene is present, suggests that isomerization must be *intramolecular*, as no appreciable formation of *tritiated* isomerized dihalobenzenes can occur via intermolecular halogen shifts. This view is supported by the observation that the rate of isomerization is not reduced by the presence of gaseous base (MeOH) in concentrations equivalent to that of the aromatic substrate.

The above considerations indicate that isomerization is an intramolecular process related to the attack of the D_2T^+ reagent on the substrate.

Isomerization Mechanism. It is suggested that the formation of tritiated isomerized products involves the attack of the D_2T^+ ions, produced in the radiolysis of the D_2/DT mixture and thermalized by a large number of unreactive[9] collisions with deuterium molecules, on the aromatic ring of dihalobenzene. A fraction of the ion attacks, in particular, the ring positions bearing the halogen substituent, yielding the arenium ion (II) tritionated in the "ipso" position and excited by the exothermicity of the reaction.[10] The excited intermediate undergoes, in addition to the fast[4,11-13] 1 → 2 hydrogen shifts (3), slower 1 → 2 intramolecular halogen shifts (4), followed by the loss of a proton to a gaseous base, either added deliberately to the system, or formed from its radiolysis, that leads to the formation of the tritiated isomerized dihalobenzenes. It should be noted that, owing to the fast intramolecular proton shifts that are likely to occur before deprotonation of III, tritium atoms are not expected to remain bound exclusively to the ring position occupied by the halogen atom before its migration.[14]



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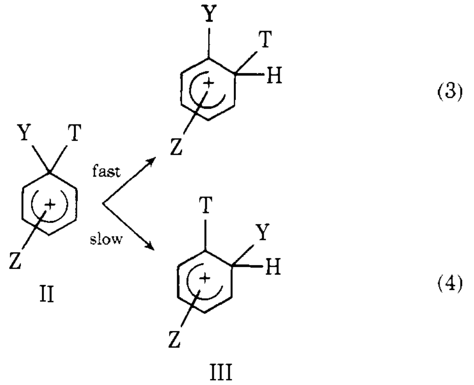

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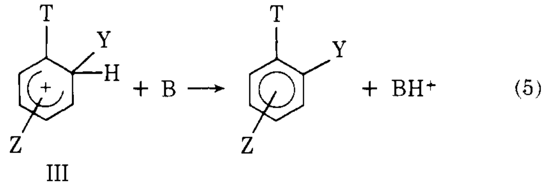

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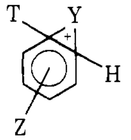
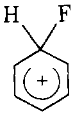
According to the mechanism outlined in eq 1 to 5, isomerization of dihalobenzenes can be characterized as a particular process following the attack of the D_2T^+ electrophile to the aromatic ring, the major reaction channel responsible for tritiodeprotonation identified in previous kinetic[7,8,16,17] and mass spectrometric[18,19] investigations.

The mechanism suggested for isomerization appears to account for the major features of the experimental results.

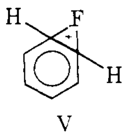
In the first place, the migratory aptitude of the halogens, increasing in the order F ≪ Cl < Br, can be rationalized taking into account the nature of the suggested transition state, where the shifting halogen is necessarily characterized by a certain degree of positive polarization. Thus, the activation energy for isomerization is expected to depend critically on the ability of the halogen to become positively polarized, which is lowest for F and increases passing to Cl and Br.



In this connection, recent calculations,[15] referring to fluorobenzenium ions, indicate that structure V, corresponding to the transition state of the 1 → 2 halogen shift, is less stable by more than 40 kcal mol^{-1} with respect to the "ipso" protonated structure IV. Such a large activation energy accounts satisfactorily for the lack of appreciable F migration observed in the present study. Furthermore, the stronger −I effect of F



IV

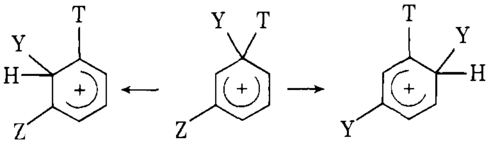


V

with respect to other halogens is expected to depress the nucleophilicity of the F-substituted ring position(s), thus decreasing its relative rate of protonation in the competition between reactions 1 and 2.

Another significant feature of the experimental results, i.e., the comparatively low rate of isomerization of *m*-dihalobenzenes, is also consistent with the suggested mechanism. In fact, assuming that isomerization requires the D_2T^+ attack on the ring position bearing the halogen atom that subsequently shifts, the positions that are ortho and para to the other halogen substituents are expected to be more reactive toward the gaseous electrophile than the meta position, owing to conjugative activation.

Furthermore, the observation that isomerization of *m*-dihalobenzenes gives invariably higher yields of para, rather than of ortho isomers, is consistent with the expected influence of the −I effect of the halogens, that is much weaker in the para than in the ortho position, thus decreasing the relative nucleophilic reactivity of the latter in the competing processes. Finally, the higher yields of meta isomer that generally accompany the formation of the ortho isomer from *p*-dihalobenzenes, and of the para isomer from *o*-dihalobenzenes, support the postulated 1 → 2 nature of the halogen shifts.



Comparison with Solution Chemistry Data. When comparing the present results with those obtained from conventional studies on Friedel-Crafts isomerization of dihalobenzenes, it is hardly necessary to underline the profound differences of the reaction environments. In fact, the gaseous dihalobenzenium ions are studied in a very diluted D_2 gas solution, in the absence of solvents, counterions, catalysts, and especially of monohalobenzenes from disproportionation reactions. As a consequence, the gaseous reaction environment is kinetically much cleaner and excludes the confusing and frequently indistinguishable intermolecular processes that almost invariably superimpose, in solution chemistry studies, on the intramolecular halogen migration. Nevertheless, if comparison is restricted to those solution chemistry investigations where secondary processes could be eliminated, or at least their influence could be evaluated, a remarkable agreement with the present gas-phase data is obtained. Indeed, the inability of F to undergo intramolecular (or, for that matter, intermolecular) migration has been long established, either under Friedel-Crafts conditions[2,3] or in superacid solutions.[11,12] Furthermore, the occurrence of intramolecular 1 → 2 shifts of Cl and Br atoms has been frequently postulated in order to account for the isomerization of protonated dichlorobenzenes, chlorofluorobenzenes, dibromobenzenes, bromofluorobenzenes, and bromochlorobenzenes,[2] even if frequently the comparatively slow intramolecular shift was obscured by faster intermolecular isomerization. While a precise comparison is difficult, it appears that the *intramolecular* migratory aptitude of Br was generally recognized to exceed that of Cl in the Friedel-Crafts isomerization of halobenzenes.

Finally, it should be mentioned that solution chemistry investigations have allowed, in several systems, to measure the thermodynamic (or equilibrium) composition of isomeric dihalobenzenes. From the preceding discussion it is apparent that no such feat could be reached in the gas phase, and that the data reported in the present study are of strictly kinetic nature, reflecting the (initial) rates of the processes leading to thermodynamical equilibrium among the protonated dihaloarenium ions.

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