The Reactions of Some Common Electrophiles, CH_3^+, NO^+, NO_2^+, and $O_2NCH_2^+$, with Monosubstituted Benzenes in the Gas Phase

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The reactions of CH_3^+, NO^+, NO_2^+, and $O_2NCH_2^+$ with monosubstituted benzenes (C_6H_5X where X = H, F, Cl, CF_3, CH_3, and CH_3O) have been studied in the gas phase using a triple quadrupole mass spectrometer. Charge-exchange is the predominant process for all the ions with all the substituted benzenes. No adducts of the Wheland intermediate type were detected as major products but disproportionation products were observed with three of the primary ions [reactions (i)—(iii)]. In addition there were minor processes particular to one substituent with

$$CH_3^+ + C_6H_5X \longrightarrow C_7H_6X \text{ (or } C_7H_7) + H_2 \text{ (or HX)} \quad \text{(i)}$$

$$NO_2^+ + C_6H_5X \longrightarrow C_6H_5XO^{+\cdot} + NO \quad \text{(ii)}$$

$$O_2NCH_2^+ + C_6H_5X \longrightarrow C_6H_5XNO^+ + CH_2O \quad \text{(iii)}$$

one primary ion. The relevance of these gas-phase studies to the interpretation of solution-phase aromatic substitution is briefly discussed.

ELECTROPHILIC aromatic substitution is probably the most studied type of reaction in organic chemistry and one for which qualitative theory has been most extensively developed.[1] Although these reactions occur in solution most theoretical approaches treat the reactants as though they were colliding in free space, and the solvent is usually ignored unless it is invoked to explain some particular facet of the reaction. The present work describes the gas-phase reaction of three common electrophiles, the methyl cation (Friedel–Crafts alkylation), the nitrosonium ion (nitrosation), and the nitronium ion (nitration) with substituted benzenes. In addition the reaction of the nitromethyl ion ($O_2NCH_2^+$) has been included. Besides benzene itself the substituents studied are: the trifluoromethyl group (an electron attractor), the methyl group (an electron repeller), the methoxy-group (an electron donor), and fluorine and chlorine (both electron-attracting donors). The study thus encompasses the extremes of the activating and *ortho–para*-directing methoxy-group and the deactivating, *meta*-directing trifluoromethyl group.

EXPERIMENTAL

The principles of the triple quadrupole mass spectrometer have been discussed in previous papers.[2,3] The primary ions are generated in a conventional ion source, by electron impact on nitromethane. The first quadrupole is used to select the desired ion [$O_2NCH_2^+$ *m/e* 60 ($P - 1$), NO_2^+ *m/e* 46, NO^+ *m/e* 30, and CH_3^+ *m/e* 15]. The second (radio frequency only) quadrupole holds the chosen ion in a stable trajectory and also contains the substituted benzene molecules. The third quadrupole separates the product ions which are detected in a conventional electron multiplier. The instrument has previously been calibrated using the known $Ar^+ + N_2$ reaction.

RESULTS

The cross sections for the reactions of primary ions with the substituted benzenes are in Tables 1—4 (10^{17} Q/cm^2).

TABLE 1

Methyl cation

$CH_3^+ + C_6H_5X$

	X = H	F	Cl	CF_3†	CH_3	CH_3O†
(a) $CH_3^+ + C_6H_5X \longrightarrow CH_3X + C_6H_5^+$	2.3		1.9			0.55 *
(b) $CH_3^+ + C_6H_5X \longrightarrow CH_3 + C_6H_5X^+$	5.71	3.87	3.03	1.01	8.79	4.04
(c) $CH_3^+ + C_6H_5X \longrightarrow HX + C_7H_7^+$	0.45	0.08	0.84			0.53
(d) $CH_3^+ + C_6H_5X \longrightarrow H_2^+ + C_7H_6X^+$	(0.45)	0.37	0.07	0.03	0.42	0.09

* The neutral fragments of this reaction were probably CH_4 and CH_2O. † In addition to the reactions listed in Table 1, $C_6H_5CF_2^+$ and $C_6H_5CF^+$ were observed when X = CF_3 and $C_6H_6^+$ when X = OCH_3, all in low yields.

TABLE 2

Nitrosonium ion

$NO^+ + C_6H_5X$

	X = H	F	Cl *	CF_3	CH_3	CH_3O *
(a) $NO^+ + C_6H_5X \longrightarrow NO + C_6H_5X^+$	4.19	1.05	4.19	0.15	4.61	3.01

* In addition to charge exchange chlorobenzene gave a trace of $C_6H_5^+$ and anisole gave a trace of $C_7H_8^+$.

TABLE 3

Nitronium ion

$NO_2^+ + C_6H_5X$

	X = H	F	Cl	CF_3*	CH_3	CH_3O
(a) $NO_2^+ + C_6H_5X \longrightarrow NO_2 + C_6H_5X^+$	5.37	1.05	6.36	1.05	2.79	3.27
(b) $NO_2^+ + C_6H_5X \longrightarrow NO + C_6H_5XO^+$	0.04	0.01		0.39	0.04	0.02

* In addition benzotrifluoride gave small yield of $C_7H_5F_3NO^+$ and $C_7H_5F_3NO_2^+$. The other aromatic nuclei gave trace amounts of $C_6H_5XNO_2^+$ but these ions represented <1% of the secondary ion current and could not be estimated quantitatively.

TABLE 4

Nitromethyl cation

$O_2NCH_2^+ + C_6H_5X$

X =	H	F	Cl	CF_3	CH_3	CH_3O
(a) $O_2NCH_2^+ + C_6H_5X \longrightarrow O_2NCH_2 + C_6H_5X^+$						
	3.47	2.31	0.74	0.05	2.46	1.66
(b) $O_2NCH_2^+ + C_6H_5X \longrightarrow CH_2O + C_6H_5XNO^+$						
	5.49	3.97	0.46	0.80	0.42	<0.1

DISCUSSION

The first satisfactory study of the gas-phase reactions of simple cations like the methyl cation CH_3^+ and the nitronium ion NO_2^+ with benzene was made by Bursey and his co-workers using ion cyclotron resonance.[4] These workers reported that methyl cations reacted with benzene to give $C_7H_7^+$ and the nitronium ion to give $C_6H_6O^{+\cdot}$. The following year Dunbar and Olah, also using ion cyclotron resonance confirmed that the nitronium ion reacted with benzene to give the ion $C_6H_6O^{+\cdot}$.[5] Both groups reported that an ion of the expected mass for nitration, a Wheland intermediate, namely $C_6H_6NO_2^+$ (*m/e* 122), although not formed by a reaction involving the nitronium ion NO_2^+ was formed by the reaction of $(CH_2ONO_2)^+$ with benzene. Both papers were preliminary communications, but no further work was reported on the gas-phase reactions of the nitronium ion. Instead studies were made on the reactions of ions of the type $(CH_3COX)^+$ and $CH_3OCH_2^+$ with benzene and its derivatives.[6,7] The significant feature of all these studies was that simple additions to the benzene nucleus were very minor processes; instead reactions were detected in which addition to the benzene ring was accompanied by the extrusion of a stable neutral molecule [reactions (1)—(4)].

$$C_6H_6 + O_2NOCH_2^+ \longrightarrow C_6H_6NO_2^+ + CH_2O \quad (1)$$

$$C_6H_6 + CH_3CO(COCH_3)_2^+ \longrightarrow C_6H_6COCH_3^+ + (CH_3CO)_2 \quad (2)$$

$$C_6H_6 + CH_3OCH_2^+ \longrightarrow C_7H_7^+ + CH_3OH \quad (3)$$

$$C_6H_6 + CH_3^+ \longrightarrow C_7H_7^+ + H_2 \quad (4)$$

Attempts by both these groups to study the effect of substituents in the benzene ring were very inconclusive. The next study involved the use of a two-stage ion beam mass spectrometer, and this work established that charge exchange was the principal reaction of the nitronium ion (and the acetylium ion) with benzene in the gas phase.[8]

In an earlier paper we have described the use of a triple quadrupole mass spectrometer to study the ion–molecule reactions of certain organic molecules.[2] The triple quadrupole discriminates in favour of ions formed in a collision against ions formed by simple charge exchange.[3] We confirmed that methyl cations reacted with benzene to give $C_7H_7^+$ [reaction (4)] in addition to charge exchange. In the present work we have again examined the reaction of methyl cations with benzene. In the earlier work the primary ions were generated by electron impact on methane, while in this work they were generated by electron impact on nitromethane. The almost identical reactivity of the methyl cations suggests that the ions from both reactions are in their ground state.

The predominant reaction of the cations with benzene and the substituted benzenes is charge exchange [reaction (5)]. If the ionization potential of R is greater

$$R^+ + C_6H_5X \longrightarrow R + C_6H_5X^+ \quad (5)$$

than or equal to the ionization potential of C_6H_5X the cross section of the charge exchange is to a good approximation dependent only on the structure of $C_6H_5X^+$ and is increased if there is resonance between the LUMO or the SOMO of R and the energy required to reach some level of $C_6H_5X^+$ from the ground state of C_6H_5X; the charge exchange is also dependent on favourable Franck–Condon factors between the initial level of C_6H_5X and the final level of $C_6H_5X^+$. A very close parallel between charge-exchange mass spectra and photoelectron spectra has been observed.[9]

Table 1 shows that the charge-exchange cross section between the methyl cation and the substituted benzenes is greater than 3×10^{-17} cm^2 except for benzotrifluoride which has an ionization potential (9.90 eV) [10] which is substantially greater than the electron recombination potential of methyl (9.84 eV).[10] The large cross section for charge-exchange between the methyl cation and toluene (8.8×10^{-17} cm^2) probably represents a resonance; the first band in the photoelectron spectrum of toluene is broad and represents two transitions, the second of which has an energy close to 9.8 eV.

Apart from charge-exchange the other important process involving methyl cations are reactions (4a and b). When X is fluorine (4a) predominates, while when

$$C_6H_5X + CH_3^+ \longrightarrow C_7H_7^+ + HX \quad (4a)$$

$$C_6H_5X + CH_3^+ \longrightarrow C_7H_6X^+ + H_2 \quad (4b)$$

X is chlorine (4b) predominates. This suggests the strength of the bond broken, *D*(C–X), is more important in determining the course of the reaction than the strength of the bond formed, *D*(H–X).

The electron combination potential of the nitrosonium ion (9.26 eV) [10] is well below the ionization potential of benzotrifluoride (9.60 eV) [10] so that charge-exchange is very small. The other substituted benzenes and benzene itself all take part in charge-exchange with the nitrosonium ion. The nitrosonium ion does not participate in addition reactions or in a general disproportionation reaction although the formation of trace amounts of $C_7H_8^+$ from anisole and $C_6H_5^+$ from chlorobenzene may be the result of disproportionation reactions yielding NO_2 and NOCl respectively as neutral molecules.

As expected from earlier work the nitronium ion (electron combination potential 9.75 eV) [10] takes part in charge-exchange with all the substituted benzenes.[8] The large cross-section for chlorobenzene is probably a resonance between the second (*ca.* 9.71 eV) [11] level of chlorobenzene and the LUMO of the nitronium ion. The disproportionation reaction (6) previously reported

$$C_6H_5X + NO_2 \longrightarrow C_6H_5XO^{+\cdot} + NO \quad (6)$$

by the groups using ion cyclotron resonance,[4,5] is a minor but distinct process for all the substituted benzenes except chlorobenzene. The structure of the adduct ion is uncertain but it is probably the phenol cation $C_6H_4XOH^{+\cdot}$. All the substituted benzenes gave an indication of a trace of the simple adduct in $C_6H_5XNO_2^+$ but the yields were so small that it was impossible to distinguish a real signal from noise except for benzotrifluoride which gave very small but detectable yields of both $C_7H_5F_2NO^+$ and $C_7H_5F_3NO_2^+$.

The electron recombination energy of the nitromethyl cation $O_2NCH_2^+$ is unknown, but the data in Table 4 suggest that it is well below 9.7 eV since there is negligible charge-exchange with benzotrifluoride. The main feature of Table 4 is the large cross section for reaction (7). It is interesting that anisole, which in solution reacts the most rapidly with electrophiles, is the least substituted by this gas-phase reaction.

$$O_2NCH_2^+ + C_6H_5X \longrightarrow CH_2O + C_6H_5XNO^+ \qquad (7)$$

The results of the present work taken together with the earlier results using ion cyclotron resonance provide a very concordant picture. Ions which act as the reactive agents in electrophilic aromatic substitution in solution do not combine with aromatic nuclei in the gas phase to form adduct ions of the Wheland intermediate type. Either simple charge-exchange is observed, or else disproportionation occurs yielding a delocalised ion and extruding a stable neutral molecule. Contrary to the ion cyclotron resonance studies however, the present work shows that the substituents have a major effect on the course of these ion molecule reactions. Their influence depends on the matching of energy levels between the primary ion and the substituted benzene, and not a supposed resonance in a hypothetical intermediate.

Alkylation, nitrosation, and nitration of aromatic nuclei in solution are believed to be effected by alkyl carbocations, nitrosonium ions, and nitronium ions, respectively. The present work and the earlier ion cyclotron resonance studies show that any theoretical discussion of electrophilic aromatic substitution which ignores the role of the solvent bears no relation to the real situation. In solution most of these aromatic substitution reactions are accelerated by increasing the temperature, *i.e. in solution* there is a barrier to be overcome. In contrast the gas-phase reactions are very exothermic and virtually no energy barrier is involved. The energy barrier in the solution-phase reactions is associated with the breaking of a tight solvent shell around the electrophile (or the bonding with a catalyst) and a weaker solvent shell around the aromatic nucleus. In other words, the reactions in solution are largely controlled by solvation. This suggests that the preferred orientation for a reaction involving a *particular* electrophile will be that which requires the least ordering of the solvent in the transition state. The ordering of the solvent will be least when the charge is delocalised to the maximum extent. According to this hypothesis the conventional Wheland intermediate picture currently used in most text books would remain a reasonable approximation. In terms of the hypothesis the intermediate with the most canonical forms is preferred because the charge is more delocalised and the solvation shell is less tightly ordered, rather than because of increased resonance stabilisation.

[0/1963 *Received, 22nd December*, 1980]

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