

AROMATIC SUBSTITUTION OF HALOBENZENES IN THE GAS PHASE: A KINETIC STUDY BY FT-ICR SPECTROMETRY

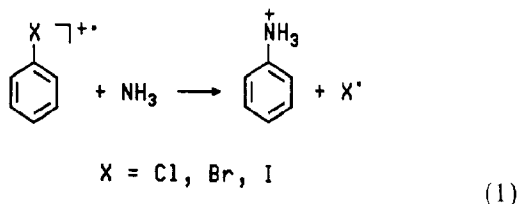
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Ion-molecule reactions of halobenzene radical cations with ammonia were carried out in a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer. Chloro-, bromo- and iodo-benzene radical cations react with ammonia in an ipso substitution yielding anilinium ions. Fluorobenzene radical cations do not react. The reaction rates show a strong dependence on the kinetic energy of the ions. The unimolecular rate constants are $(2.1 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ($X=\text{Cl}$), $(2.2 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ($X=\text{Br}$) and $(3.8 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ($X=\text{I}$).

Halobenzenes react with ammonia and other nucleophiles under chemical ionization conditions [1,2] by an ipso substitution of the halogen substituent, as proven for the reaction of the isomeric dichlorobenzenes with ammonia [3]. It was shown by FT-ICR spectrometry that the reaction



of the aromatic radical cations with the neutral nucleophile is the only reaction leading to substitution in the system chlorobenzene/ammonia as well as in the system dichlorobenzene/ammonia. Neither NH_4^+ [2] nor NH_3^+ [4] ions react with chlorobenzene by substitution, in contrast to the report of van der Hart et al. [2].

In view of the interesting substituent effects in reactions of dichlorobenzene radical cations with ammonia we have examined the kinetics of the reactions of the different halobenzene radical cations under low-pressure conditions (3×10^{-7} – 3×10^{-6} mbar) in a FT-ICR cell.

The ions were generated by electron impact ionization in the external ion source of a Bruker CMS

47X FT-ICR spectrometer and transferred into the ICR cell (for a detailed discussion of the external ion source see ref. [5]). The fragment ions were ejected by broad band ejection in the higher mass range ($m/z > 50$) and by "single shots" (fixed frequency rf pulses) at low masses. The isotopomers of the ions to be studied were also ejected by single shots. The excitation amplitude of these rf pulses, $14 \text{ V}_{\text{p-p}}$, was kept low to avoid excitation of the reacting ions. The time needed for the whole ejection process was about 10–15 ms. The intensities of the ions participating in reaction (1) are shown in fig. 1 as a function of the reaction time. The intensities (magnitude spectra) are normalized with respect to the sum of all the peak intensities of a spectrum.

It has already been pointed out that the technique used to measure ion intensities has an important influence on the reliability of the reaction rates determined by FT-ICR spectrometry [6]. Differences in the sensitivity for the detection of ions of different m/z values influence the determination of the reaction kinetics. The main problem is the need to normalize ion intensities with respect to the sum of all ion intensities despite the dependence of the sensitivity on the position of the ions in the z direction of the ICR cell. In general, the signal intensity of trapped ions increases in the first instance because of collisional damping of their z motion [7].

In our experiments, the same Lorentzian shape of

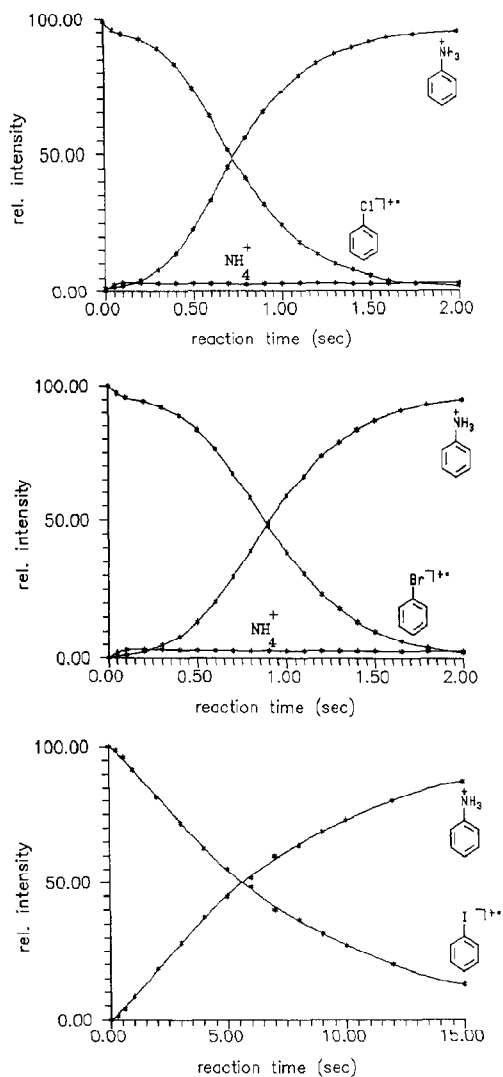


Fig. 1. Ion abundance versus reaction time for the reactions of the halobenzene radical cations with ammonia. The pressure of NH_3 is 5.8×10^{-7} mbar during the reactions of chloro- and bromobenzene, respectively, and 1.5×10^{-6} mbar for iodobenzene.

all peaks after Fourier transformation is achieved by suitable exponential multiplication of the time domain signal [8]. This ensures proportionality of peak height and area. Furthermore the ICR spectrometer configuration is adjusted to give the correct isotope ratios in the EI spectra of halobenzenes. Under these conditions identical temporal dependences of the trapped ion intensities (trapping characteristics) were obtained for the isolated halobenzene radical

cation as well as for the sum of all ions in the ion-molecule reaction (fig. 2). The trapping potentials were kept at 1 V in each case.

The similarity of the trapping characteristics shows that both chlorobenzene ions (m/z 112) and anilinium ions (m/z 94), respectively, are determined with the same sensitivity. Otherwise, the sum of all ion intensities would deviate considerably from the value expected from the trapping characteristics of the isolated ions in nitrogen, especially near the end of the reaction, when all chlorobenzene ions are converted into anilinium ions.

The pseudo-first-order rate constants for reaction (1) are evaluated from the exponential decay of the concentration of the halobenzene radical cations. These are converted into second-order rate constants k_{exp} by taking into account the corrected $^{\#1}$ ammonia pressure (table 1).

In the case of chloro- and bromo-benzene an induction period is observed. The constant reaction rate of the (thermalized) ions is reached after 500 ms ($p = 5.8 \times 10^{-7}$ mbar).

The induction period indicates that the rate of reaction (1) decreases with increasing kinetic energy of the ions. To study this effect, the halobenzene radical cations were kinetically excited by a rf pulse of 14 V_{p-p}, 80 μs , after 500 ms reaction time at a pressure of 5.8×10^{-7} mbar (fig. 3). The maximum ki-

^{#1} The pressure is corrected by considering the reactions $\text{CH}_4^+ + \text{CH}_4$ ($k = 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) and $\text{NH}_3^+ + \text{NH}_3$ ($k = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). The difference of the sensitivities of the ionization gauge toward methane and ammonia corresponds to the values given by ref. [8].

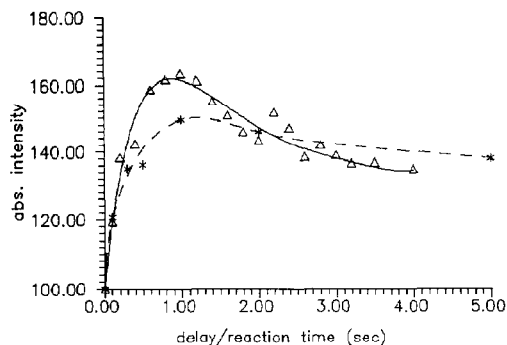


Fig. 2. Trapping characteristics of chlorobenzene radical cations (*) in nitrogen, $p = 5.0 \times 10^{-7}$ mbar, and of the sum of all ions (Δ) in the reaction with ammonia, $p(\text{NH}_3) = 2.9 \times 10^{-7}$ mbar.

Table 1
Rate constants for the reactions of the halobenzene radical cations with ammonia

C ₆ H ₅ X	k_{exp} (cm ³ s ⁻¹)	k_{ADO} [10]	Eff. (%)
X=Cl ^{a)}	2.1×10^{-10}	1.67×10^{-9}	13
X=Br ^{a)}	2.2×10^{-10}	1.64×10^{-9}	13
X=I ^{b)}	3.8×10^{-12}	1.62×10^{-9}	0.24

^{a)} $p(\text{NH}_3) = 2.9/5.8 \times 10^{-7}$ mbar.

^{b)} $p(\text{NH}_3) = 1.5/2.9 \times 10^{-6}$ mbar.

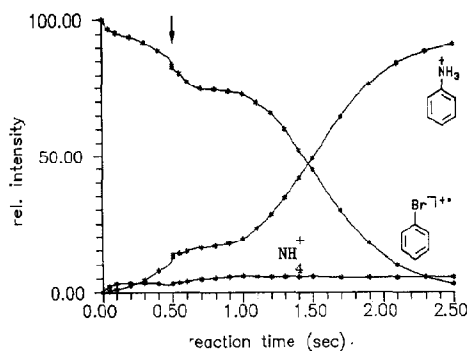
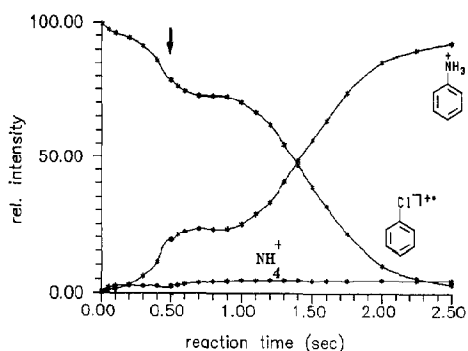
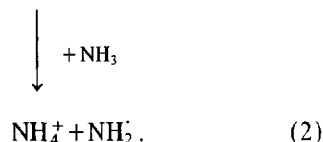
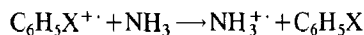


Fig. 3. Reaction of chloro- and bromo-benzene radical cations with ammonia, $p = 5.8 \times 10^{-7}$ mbar. The halobenzene ions were excited after a reaction time of 500 ms by an rf pulse of 14 V_{p-p} for 80 μ s.

netic energy imparted into the ions was 36 eV in the case of chlorobenzene (m/z 112) and 26 eV in the case of bromobenzene (m/z 156). It can be seen from fig. 3 that, indeed, the reaction rate decreases dramatically following the excitation. The same constant value as for k_{exp} without excitation was observed, however, 700 ms after the excitation pulse.

The concentration of ammonium ions, m/z 18, increases slightly for about 100 ms after the ion exci-

tation and remains constant thereafter. The use of the external ion source ensures that halobenzene radical cations and neutral ammonia are present exclusively in the ICR cell at the beginning of the experiment. So ammonium ions must be formed according to the following reaction:



The charge exchange reaction (2) is endothermic by about 1 eV ($\text{IE}(\text{NH}_3) = 10.15$ eV, $\text{IE}(\text{C}_6\text{H}_5\text{Cl}) = 9.07$ eV, $\text{IE}(\text{C}_6\text{H}_5\text{Br}) = 8.98$ eV, $\text{IE}(\text{C}_6\text{H}_5\text{I}) = 8.74$ eV [11]). So charge exchange can occur only for the ions with excess energy. In the present case there is obviously some kinetic energy of the ions resulting from the transfer line.

It can be seen from table 1 that k_{exp} is clearly lower than the collision rate predicted by ADO theory [10] for all reactions. The fluorobenzene radical cations do not react at all in accord with the corresponding high reaction endothermicity (see table 2). A comparison of the reaction efficiencies (eff.) shows that chloro- and bromo-benzene exhibit nearly the same reactivity, while iodobenzene reacts slower by nearly a factor of 60. The individual reaction efficiencies cannot be explained by the different reaction exothermicities.

A discussion of these results and of the reaction mechanism must take into account the formation of ion-neutral complexes (K_1 and K_2) (fig. 4) prior to the previously established ipso attack of the ammonia molecule [2] and after the elimination of X[•],

Table 2

Ionization energies (IE), enthalpies and efficiencies of the reactions of the halobenzene radical cations with ammonia^{a)}

C ₆ H ₅ X	IE (eV)	ΔH_f° (kJ/mol)	Eff. (%)
X=Cl	9.07	-23	13
X=Br	8.98	-76	13
X=I	8.73	-112	0.24
X=F	9.22	+92	no reaction

^{a)} The enthalpies and ionization potentials were obtained from ref. [10], the proton affinity of aniline is 876.5 kJ/mol [12].

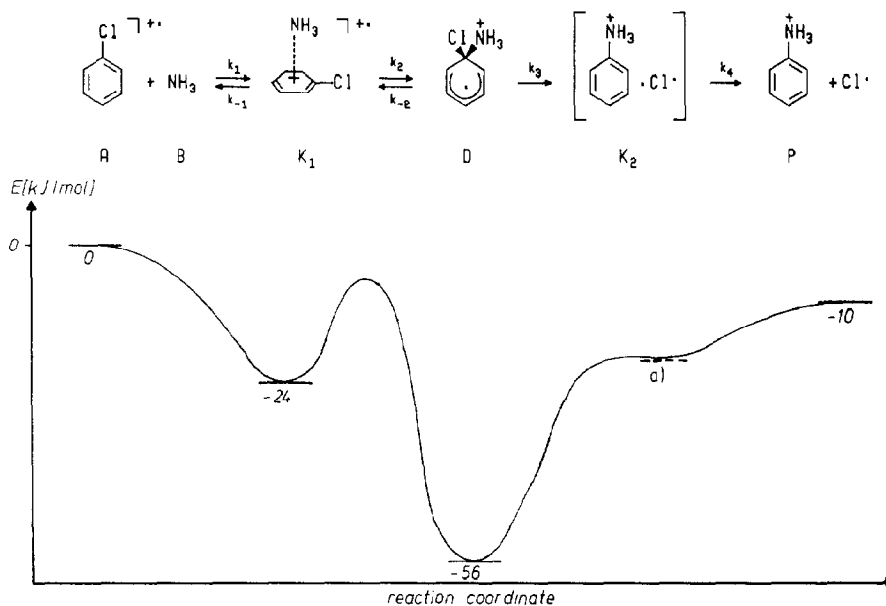
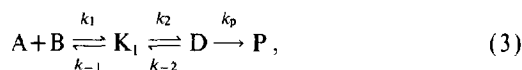


Fig. 4. Triple-well potential of the reaction of the chlorobenzene radical cations with ammonia; energies and geometries from MNDO calculations. (a) No minimum found by MNDO; but the stabilization energy of K_2 is predicted to be 11 kJ/mol ($\alpha(\text{Cl}^\cdot) = 2.3 \text{ \AA}^3$, $r = 3.5 \text{ \AA}$) using classical electrostatic forces [10].

respectively. We suppose a triple-well potential in analogy to the multi-potential model developed by Brauman [13] for ion-molecule reactions with low reaction efficiencies.

An MNDO study of the complexes K_1 and D (fig. 4) show that they correspond to minima in the potential energy surface of the system $[\text{C}_6\text{H}_5\text{Cl}/\text{NH}_3]^+$, whereas a minimum is not found for the complex K_2 . This indicates that K_2 is unstable, if it exists at all, and that it has no effect on the reaction kinetics, because the halogen atom is lost irreversibly. The following kinetic scheme is obtained; where k_1 corresponds to the collision rate,



$$d[\text{P}]/dt = k_{\text{exp}}[\text{A}][\text{B}].$$

Applying the steady-state approximation to the concentrations of K_1 and D, which are too low to be detected in the experiment, results in the following expression for k_{exp} ,

$$k_{\text{exp}} = \frac{k_1 k_2 k_p}{(k_{-1} + k_2)(k_{-2} + k_p) - k_2 k_{-2}}. \quad (4)$$

Two limiting cases can be distinguished:

(a) $k_2 \gg k_{-1}$. In this case the "chemical" reaction within the ion-neutral complex K_1 is much faster than the back-dissociation. This condition leads to

$$k_{\text{exp}} = k_1, \quad \text{efficiency} = 1. \quad (5a)$$

In the reactions of the halobenzene radical cations this collision limit is never reached, however.

(b) $k_2 \ll k_{-1}$. In this case one obtains

$$k_{\text{exp}} = \frac{k_1}{k_{-1}} k_2 \frac{k_p}{k_{-2} + k_p},$$

$$\text{eff.} = \frac{1}{k_{-1}} k_2 \frac{k_p}{k_{-2} + k_p}. \quad (5b)$$

The reaction rate is determined by the ratio k_1/k_{-1} , by the forward reaction rate k_2 of complex K_1 and by the fraction $k_p/(k_{-2} + k_p)$ of complexes D reacting to products.

We do not expect from ADO theory the ratio k_1/k_{-1} to be very different for the halobenzenes, because the stabilization energies of the collision complexes should be nearly identical for equal distances between each of the halobenzene radical cations and

ammonia. In the most stable conformation (from MNDO calculations) of the collision complex K_1 (fig. 4) the NH_3 molecule is located vertically above the center of the aromatic ring at a distance of about 350 pm and the positive charge is totally located at the halobenzene. Analogous centered and charge-localized conformations are expected for the complexes of bromo- and chloro-benzene radical cations, respectively. So the distance between the components and the stabilization energy of the complex should not differ much for the individual halobenzenes.

The fraction $k_p/(k_{-2}+k_p)$ of the forward reacting complexes D is expected to increase along the series chloro-, bromo- and iodo-benzene, because the strength of the C-X bond decreases and k_p increases in that sequence. Hence, by eq. (5b) and assuming constant k_2 , k_{exp} should also increase in that order. This is not observed, however. Consequently, the rate constant k_2 of the ipso attack of the ammonia molecule must decrease in going from chlorobenzene to bromo- and iodo-benzene.

To explain the experimental results, the increase of $k_2/(k_{-2}+k_p)$ and the decrease of k_2 have to compensate in the case of chloro- and bromo-benzene. In the case of iodobenzene the reaction rate is dominated by the low reaction rate k_2 . These kinetic effects of the different halogen substituents at the benzene ring are not yet fully understood. We suppose that the IE differences between the halobenzenes (see table 2) and ammonia (10.15 eV [11]) may control the rate constant k_2 . The π -complex K_1 has the positive charge located at the halobenzene, whereas in the σ -complex D the charge is located at the NH_3^+ substituent. Consequently, at some stage of the reaction between K_1 and D a charge transfer has to oc-

cur from the aromatic ring to the NH_3 group, which should be more favourable for the complexes of chloro- and bromo-benzene ($\Delta IE=1.08$ and 1.17 eV, respectively) than for iodobenzene ($\Delta IE=1.44$ eV).

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