Reactions of Dihalobenzene Radical Cations with Ammonia in the Gas Phase: Reactivity Pattern for Nucleophilic Aromatic Substitution

Detlef Thölmann and Hans-Friedrich Grützmacher*

Contribution from the Fakultät für Chemie der Universität Bielefeld, Postfach 8640, D-4800 Bielefeld, Germany. Received September 10, 1990. Revised Manuscript Received December 13, 1990.

Abstract: The reactions of homo- and heterodisubstituted dibenzyl radical cations with NH₃ were investigated by FT-ICR spectrometry. A halogen atom X (X = Cl, Br, I) is substituted in a gas-phase nucleophilic ipso substitution, yielding halogenanilinium ions. The reaction efficiency, i.e., the percentage of reactive ion-molecule collisions, ranges from <0.006% for 1-chloro-4-iodobenzene radical cations to 18% for 1-bromo-2-chlorobenzene radical cations. The reactivity of the halogenated benzene radical cations was found to be governed by two structural parameters. First, the radical cations with a low ionization energy, i.e., iodobenzene and its derivatives, react especially slowly regardless of the reaction exothermicity. Second, the reactivity of all dibenzyl radical cations is strongly influenced by the substitution pattern. The reactivity of isomeric radical cations is always highest for the 1,2-isomer and lowest for the 1,4-isomer. These results show that the nucleophilic substitution of the halo- and dibenzyl radical cations by NH₃ proceeds by a multistep reaction mechanism with a double-well potential energy surface. The rate-determining step is the addition of NH₃ to the aromatic radical cation in the collision complex. The structural parameters influencing this reaction step can be analyzed by the reactivity model of polar reactions of Shaik and Pross. From this the most important feature of the substitution reaction of mono- and dibenzyl radical cations with NH₃ is the different charge localization in reactants and products. This results in a strong influence of the difference of the ionization energies of the halogenated benzene and NH₃ and of the dipole moment of the halogenated benzene, i.e., the precursor of the ionic reactant, on the activation energy of the addition step.

Introduction

Aromatic radical cations are important reactants and intermediates in condensed-phase aromatic substitution reactions. The radical cations may result from photochemical activation,¹ from electrooxidation,² or from electron transfer of the aromatic compound to strongly oxidizing reagents.³ The extensively studied aromatic nitration is one of the substitution reactions with a charge transfer leading to an aromatic radical cation as the key step of the mechanism.⁴ If the ionization energy (IE) of the aromatic compound is lower than the IE(NO₃), the aromatic reactant is ionized by an outer-sphere electron transfer to NO₃⁺ and the resulting radical cation combines with NO₂.

The substitution pattern resulting from aromatic substitution reactions with intermediate radical cations is often unexpected. In many cases the mechanism of condensed-phase reactions is complex because several electron-transfer steps may be involved, and a study of the mechanism is complicated by side reactions and low yield. In the gas phase the reactions of aromatic radical cations can be investigated much more easily, and it is possible to evaluate their intrinsic reactivity by mass spectrometric techniques, avoiding any disturbance by solvent effects.

A smooth reaction of the radical cations of chlorobenzene, bromobenzene, and nitrobenzene was observed in chemical ionization mass spectrometry with ammonia as the reactant gas [Cl(NH₃)]³ and was further studied by ion cyclotron resonance (ICR) spectrometry.⁶ In these reactions anilinium ions are formed by substitution of the halogen substituent and nitro substituent, respectively. Previously we have shown unambiguously⁷ by using a FT-ICR spectrometer equipped with an external ion source that of the various possible ion–molecule reactions in a ammonia Cl plasma the only reaction yielding anilinium ions is the reaction of halobenzene radical cations with neutral NH₃ (reaction 1).

\[
\text{C}_6\text{H}_4\text{Cl} + \text{NH}_3 \rightarrow \text{C}_6\text{H}_4\text{Cl}^- + \text{NH}_2\text{H}^+ 
\]

(1)

Reaction 1 corresponds to a nucleophilic substitution of an aromatic radical cation carrying a suitable radical leaving group. The investigation of the reaction kinetics showed⁸ that the reaction is strictly second order and that chlorobenzene and bromobenzene radical cations exhibit the same reactivity. However, in both cases the experimental rate constant is distinctly below the collision limit and the reaction efficiency is only 13%. Surprisingly, iodobenzene radical cations react much slower with NH₃, in spite of the smaller dissociation energy of the C–I bond. This interesting effect and the always low efficiency show immediately that the substitution reaction of the halogenated radical cations does not correspond to a direct displacement of the halogen substituent by collision with the nucleophile but involves a long-lived collision complex of the aromatic radical cation with NH₃. This complex may either dissociate into the components or react forward to yield eventually the anilinium ion and the halogen atom. Furthermore, the decoupling of the reaction rate from the dissociation energy of the leaving group, as evidenced most clearly by the small reaction efficiency of the iodobenzene radical cation, proves a multistep reaction mechanism for this process. At least the formation of the C–N bond (addition of NH₃) and the cleavage of the C–X bond (elimination of halogen X) must be separate reaction steps with the addition step determining the total reaction rate. Nevertheless, the displacement of the halogen substituent from the aromatic radical cation corresponds to an ipso substitution. This has been demonstrated by the reaction of the three positional isomers of dichlorobenzene radical cations with NH₃ which form specifically the chloroanilinium ion with the identical orientation

\[
\text{C}_6\text{H}_4\text{Cl}_2 + \text{NH}_3 \rightarrow \text{C}_6\text{H}_4\text{Cl}^- + \text{NH}_2\text{H}^+ 
\]

(2)


The reaction efficiency (eff) is the percentage of the reactive collisions, i.e.,\\[ \text{eff} = \frac{100 k_{\text{exp}}}{k_{\text{ADO}}} \] k_{\text{exp}} is the experimental bimolecular rate constant, and k_{\text{ADO}} is the collision rate constant according to the ADO theory.⁹

References

of the substituents by an ipso substitution of one of the chloro substituents.10

The preliminary investigation of the reactions of the dichlorobenzene radical cations with NH₃ (reaction 2) revealed

\[ \text{X-Cl, Br, I} + \text{NH}_3 \rightarrow \text{X-Cl, Br, I} + \text{H} + \text{NH}_2 \]

another interesting detail of this nucleophilic aromatic substitution. The reactivity of the isomeric dichlorobenzene radical cations depends strongly on the relative orientation of the two chloro substituents. While the ortho isomer exhibits the same efficiency as the monochloro derivative, the efficiency decreases in the order \( o > m > p \)-dichlorobenzene radical cation by more than one order of magnitude.

This unusual positional effect of the second chloro substituent points to a rather special mechanism for the nucleophilic substitution within the collision complex of a dichlorobenzene radical cation and a NH₃ molecule. A better understanding of this mechanism is important with respect to the theory of aromatic reactivity and in particular to the reactivity of halogenated aromatic compounds. So, in the present work the reaction of dihalobenzene radical cations containing identical ("homodisubstitution") and different ("hetertodisubstitution") halogen substituents, respectively, with NH₃ have been studied by FT-ICR spectrometry. From the results a reaction model is presented to explain the reactivities of halobenzene radical cations in nucleophilic substitutions. Such a model predicting the reactivity of a radical cation of a halogenated aromatic compound is not only of theoretical interest. In view of the environmental problems connected with the widespread use of (poly)halogenated aromatics, knowledge of their different reactivities is also important.

In addition, an unambiguous discrimination between positional isomers of polyhalogenated aromatic compounds by mass spectrometric techniques is of interest for analytical purposes.

Experimental Section

The monohalobenzenes and the dichloro-, dibromo-, bromochloro- and bromofluorobenzenes were obtained from Aldrich, Merck, and Ega-Chemie, respectively, and were used without further purification. The chlorofluorobenzenes were prepared by the Sohime reaction11 and the chlorodibenzochlorides by diazotization and iodination12 of the corresponding chloroanilines. The purity of all aromatic halides was better than 99%, as confirmed by gas chromatography.

The FT-ICR measurements were performed on a Spectrion CMS 47X FT-ICR instrument13 equipped with a 4.7-T superconducting magnet, a 24 bit/128 k-word Aspect 3000 computer, a cylindrical cell with a diameter of 6 cm and length of 6 cm, and an external ion source. Ions were generated by electron impact (18-25 eV) from the dihalobenzenes and transferred into the ICR cell. The trapping voltages on the front and back trapping plates were 1 V; the other plate voltages were 0 ± 0.1 V. Selection of the aromatic radical cations was achieved by broad band (frequency sweep) ejection of fragment ions with \( m/z > 50 \). The excitation voltage was attenuated by an attenuator of 6, corresponding to 88 \( V_p \). All ions of masses below \( m/z \) 50 and the isotopomers of the aromatic radical cations containing \(^1{}C\), \(^1{}Cl\), and \(^3{}Br\) isotopes were ejected by "single shot" (fixed frequency radio frequency pulses) of 14 \( V_{pp} \) attenuator 22, and a duration of 1.5 ms per pulse. The total ejection process was finished within 15-20 ms.

Ammonia (Merck, 99.8%) as the reactant gas was introduced continuously by a leak valve; the corrected pressure ranged from 3 \( \times \) 10⁻⁷ to 2 \( \times \) 10⁻⁶ mbar. The ionization gauge was connected close to the diffusion pump of the ICR cell, and the pressure was calibrated by rate measurements of the reactions \( \text{CH}_4^+ + \text{CH}_4 \) (at \( k = 1.5 \times 10^{-4} \text{ cm}^3 \text{s}^{-1} \))15 and \( \text{NH}_3^+ + \text{NH}_3 \) (at \( k = 2.2 \times 10^{-4} \text{ cm}^3 \text{s}^{-1} \)).16 The difference of the sensitivities of the ionization gauge toward methane and ammonia corresponds to the literature values.17

The FT-ICR spectra were obtained with 32K or 64K data for about 20 different reaction times. After exponential multiplication and Fourier transformation, the ion intensities of the magnitude spectra were normalized with respect to the sum of ions formed after the corresponding reaction time. A pseudo-first-order reaction kinetics was obtained from the exponential decaying signal of the dihalobenzene radical cation. To ensure the correct measurement of the true ion abundances, the variation of the sum of the absolute ion intensities with reaction time was examined and compared with the variation of the intensity of trapped unreactive ions at the corresponding delay times ("trapping characteristics"). This method allows a correction of erroneous ion abundance measurements and is described in detail elsewhere.18 If more than two ions are involved in the reaction in higher abundances, i.e., more than one product ion is formed, the method is not reliable, however. Therefore, the determination of the branching ratio in competitive substitutions of two substituents may be less accurate. In these cases special care was taken to avoid "picket-fence" errors19 by suitable exponential multiplication and use of 64K data.

The ions isolated in the ICR cell had more or less excess kinetic energy. A cooling of these ions was achieved by pulsing shortly (opening time of the valve 15 ms) argon into the ICR cell prior to the reaction. The reacting ions were selected by the ejection process described above and cooled by collision with argon. After a delay time of 500 ms to remove the argon from the cell, the fragment ions formed during that time were ejected by single shots (14 \( V_{pp} \), 1 ms). This method diminishes the probability of re-excitation of the reaction ions by the ejection process. Alternatively, \( \text{CF}_4 \) has been used as collision gas instead of argon because of its better deactivation property. The pulse

### Table I. Reaction of Halobenzene Radical Cations with NH₃

<table>
<thead>
<tr>
<th>Compound</th>
<th>IE* eV</th>
<th>( k_{ex} ) ( \times 10^{11} ) cm³ s⁻¹</th>
<th>( k_{ex} ) %</th>
<th>( \Delta H_f^o ) kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>9.06</td>
<td>21</td>
<td>13</td>
<td>-23</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>8.98</td>
<td>22</td>
<td>13</td>
<td>-76</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>8.69</td>
<td>0.38</td>
<td>24</td>
<td>-112</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>9.22</td>
<td></td>
<td></td>
<td>+92</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>9.08</td>
<td>24</td>
<td>15</td>
<td>-21</td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>9.11</td>
<td>12</td>
<td>7</td>
<td>-20</td>
</tr>
<tr>
<td>1,4-Dichlorobenzene</td>
<td>8.99</td>
<td>0.7</td>
<td>0.4</td>
<td>-4</td>
</tr>
<tr>
<td>1,2-Dibromobenzene</td>
<td>8.8</td>
<td>28</td>
<td>17</td>
<td>-56</td>
</tr>
<tr>
<td>1,3-Dibromobenzene</td>
<td>8.85</td>
<td>8.1</td>
<td>5</td>
<td>-61</td>
</tr>
<tr>
<td>1,4-Dibromobenzene</td>
<td>8.7</td>
<td>1.8</td>
<td>1.1</td>
<td>-52</td>
</tr>
<tr>
<td>1-Chloro-2-Fluorobenzene</td>
<td>9.18</td>
<td>25</td>
<td>15</td>
<td>-35</td>
</tr>
<tr>
<td>1-Chloro-3-Fluorobenzene</td>
<td>9.21</td>
<td>17</td>
<td>10</td>
<td>-30</td>
</tr>
<tr>
<td>1-Chloro-4-Fluorobenzene</td>
<td>9.01</td>
<td>4.7</td>
<td>2.8</td>
<td>-9</td>
</tr>
<tr>
<td>1-Bromo-2-Fluorobenzene</td>
<td>9.55</td>
<td>1.9</td>
<td>28</td>
<td>0.5</td>
</tr>
<tr>
<td>1-Bromo-3-Fluorobenzene</td>
<td>9.56</td>
<td>5.6</td>
<td>3.4</td>
<td>1.5</td>
</tr>
<tr>
<td>1-Bromo-4-Fluorobenzene</td>
<td>9.28</td>
<td>29</td>
<td>18</td>
<td>3.3</td>
</tr>
<tr>
<td>1-Chloro-2-Iodobenzene</td>
<td>9.11</td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>1-Chloro-4-Iodobenzene</td>
<td>9.14</td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>1-Chloro-3-Iodobenzene</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td>&lt;0.006</td>
</tr>
</tbody>
</table>

* Data from ref 24; proton affinities estimated for o-haloanilines.

† Data from ref 8. ‡ ±25% (see text). † Data rate of disappearance of radical cations by sum of substitution processes.

Figure 1. Pulse sequence for the FT-ICR measurements using collisional deactivation.

---


(17) Bartmess, J. E.; Georgiadis, M. Vacuum 1983, 33, 149.

Table II. Distribution of Substitution Products in the Reaction (2) of Dihalobenzene Radical Cations with NH₃

<table>
<thead>
<tr>
<th>compound</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-bromo-2-chlorobenzene</td>
<td>47%</td>
<td>53%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-bromo-3-chlorobenzene</td>
<td>33%</td>
<td>67%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-bromo-4-chlorobenzene</td>
<td>7%</td>
<td>93%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-chloro-2-iodobenzene</td>
<td>17%</td>
<td>44%</td>
<td>39%</td>
<td></td>
</tr>
<tr>
<td>1-chloro-3-iodobenzene</td>
<td>19%</td>
<td>48%</td>
<td>33%</td>
<td></td>
</tr>
<tr>
<td>1-chloro-4-iodobenzene</td>
<td>12%</td>
<td>59%</td>
<td>29%</td>
<td></td>
</tr>
</tbody>
</table>

*Approximate values; the reaction is extremely slow, and very little product is formed.*

sequence used in these ICR experiments is shown in Figure 1.

Results

Reaction Products. The dihalobenzenes studied are listed in Table I, which includes for comparison also the values for the reactions of the monohalobenzenes studied previously. An analogously the radical cations of the dihalobenzenes exchange only one halogen atom by the NH₃⁺ group. In heterodisubstituted benzenes either of the two substituents may be exchanged with exception of a fluor substituent. The substitution reaction of fluorobenzene radical cations with NH₃ is endothermic and not observable under FT-ICR conditions. Similarly, the loss of F from the radical cations of the chlorofluoro- and bromofluorobenzenes is endothermic. Hence, only the substitution of the other halogen atom is possible in these heterodisubstituted radical cations. However, for the other heterodisubstituted dihalobenzene radical ions both reaction pathways are possible and in fact are observed. The individual branching ratio is shown in Table II.

Usually haloanilinium ions, i.e., protonated even-electron species, are formed exclusively. However, the chloroiodobenzene radical cations and NH₃ yield additionally odd-electron iodoaniline radical cations by substitution with elimination of HCl (reaction 3c). Compared to reaction 3b, reaction 3c is energetically favorable because the IE of the resulting aniline is low.

![Figure 2](image-url)  
*Figure 2. Reaction of o-dibromobenzene radical cations with ammonia [p(NH₃) = 5.8 × 10⁻² mbar (a)/4.4 × 10⁻² mbar (b)]. Kinetics without (a) and with (b) collisional deactivation.*

The radical cations of chlorobenzene and bromobenzene react with NH₃, showing nearly identical reaction efficiencies. Hence, a ratio of approximately 1:1 is expected for the loss of Cl and Br, respectively, from the radical cations of the bromochlorobenzenes. However, this ratio is observed only for the 1-bromo-2-chlorobenzene radical cations (Table II). The 1,3-isomer and in particular the 1,4-isomer exhibit a distinct preference for the substitution of the bromo substituent. As will be shown below, the reaction efficiency decreases in the order 1,2- > 1,3- > 1,4-isomer by a factor of 12. Thus, in the case of the isomeric bromochlorobenzene radical ions a decrease of the reactivity is accompanied by an increase in the selectivity.

In contrast, the radical cations of the isomeric chloroiodobenzenes react always by a preferred loss of I, and this selectivity shows no clear dependence on the relative orientation of the two halogen substituents. The reaction efficiency for the substitution of these aromatic radical cations with NH₃ is always rather low, however, although again a decrease of the reactivity is observed in the series 1,3- < 1,2- < 1,4-isomer. In addition, the radical cations of the chloroiodobenzenes react also by substitution with loss of HCl, and this additional reaction path may influence the branching ratio for the loss of Cl and I, respectively. Thus, it is difficult to decide why the radical cations of bromochlorobenzenes and chloroiodobenzenes show a different behavior for the effect of the orientation of the substituents on the selectivity of the substitution reaction with NH₃.

Kinetic Studies. The substitution reaction of all halogenated aromatic radical cations studied shows a negative temperature dependence; i.e., the reaction rate decreases with increasing kinetic energy of the ions. Hence, the kinetic energy of the ions resulting from the transfer process and/or the ejection procedure gives rise to an induction period at the beginning of the measurement (Figure 2a). In addition, some NH₃⁺ radical cations are formed in the early reaction period by an endothermic charge transfer from the kinetically excited ions which subsequently react very fast with NH₃ to yield NH₄⁺. A direct formation of NH₄⁺ by proton transfer from the haloanilinium product ions is endothermic and is feasible only for excited ions. The reaction rates of thermal aromatic radical cations can be determined by considering only the last part of the kinetic curves after kinetic relaxation of the ions. If the reaction efficiency is below 10%, the ions thermalize by nonreactive collisions before a substitution. In case of a higher reaction efficiency, the ions have to be kinetically deactivated by the admission of argon or CF₂ as an inert collision gas prior to the substitution reaction. It was shown¹⁹ that this is an efficient technique to thermalize the ions leading to a constant reaction rate over the whole reaction time (Figure 2b). Furthermore, it is easily possible to control the reactant pressure during the experiment, because the argon gas is pumped away quickly and the pressure returns to the original constant value of the reactant gas. Thus, the pulsed introduction of the inert collision gas has great advantages over a continuous introduction by a leak valve.

The reaction rates were determined very accurately by this method, and for the reactions of the chloro-, bromo-, and 1,3-

---

¹⁹ Thölmann, D. Unpublished results from this laboratory.
dichlorobenzene radical cations (eff 13%, 13%, and 7%, respectively) the values obtained are identical with the previously published rates. This shows that the flow of the reactant gas through the ICR cell and its partial pressure are not influenced by the admittance of a pulse of argon or CF\textsubscript{4}. The fast reactions of all 1,2-dihalobenzene radical cations were examined and with collisional deactivation. The efficiencies obtained after collisional deactivation are usually 10–20% higher than those determined without deactivation.

Table 1 shows the experimental bimolecular reaction rates, \( k_{\text{exp}} \) and the efficiencies, \( \text{eff} \), for the reactions of NH\textsubscript{3} with the radical cations of all halobenzenes and a selection of homo- and hetero-disubstituted dihalobenzenes. The error of the experimental rate constant is ±15%, and the corresponding collisional rates were calculated according to the ADO theory. During the experiments using collisional deactivation, especially at a higher NH\textsubscript{3} pressure, some nonreactive ions with the mass of 1,2-dichlorobenzene were observed, indicating some isomerization. Note, however, that during the delay time of 500 ms to pump off the collision gas, 50–75% of the initially present 1,2-dichlorobenzene radical cations had already reacted, leading to an enrichment of the unreactive isomer. Taking this into account, it was estimated that about 5% of the aromatic radical cations initially present had isomerized. This amount is independent of the nature of the collision gas (argon and CF\textsubscript{4}, respectively). This excludes an isomerization induced by the collision gas because argon and CF\textsubscript{4} behave rather differently in these gases. Obviously, some 1,2-dichlorobenzene molecules isomerize to an unreactive \( C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2} \) species during the electron impact ionization.

**Discussion**

**Isomerization of Dihalobenzene Molecular Ions.** The electron impact (EI) mass spectra of dihalobenzenes show losses of X and HX (X = Cl, Br, I) as the main fragmentations. The relative abundances of these fragmentations depend on the nature of X, but the mass spectra of positional isomers of the dihalobenzenes are not very different, prohibiting an unequivocal identification of these isomers by EI mass spectrometry. It is generally assumed that nearly identical EI mass spectra of isomeric disubstituted benzenes arise from a fast isomerization of the molecular ions prior to decomposition. Olesik et al. have studied the rate for the loss of Cl from the isomeric dichlorobenzene radical cations by PEPCICO and have obtained identical rates for all three isomers. This agrees with the isomerization of the molecular ions, probably to the 1,4-isomer.21 Obviously some 1,2-dichlorobenzene molecules isomerize to an unreactive \( C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2} \) species during the electron impact ionization.

**Kinetic Scheme and Reaction Mechanism.** As mentioned in the introduction, the low efficiency of the reaction of monohalogenated benzene radical cations with NH\textsubscript{3} shows that this nucleophilic substitution occurs within a long-lived collision complex. As Brauman et al. have shown, slow exothermic ion–molecule reactions have to proceed by a multistep mechanism with a multwell potential energy surface. Figure 3 presents the proposed reaction mechanism and the kinetic scheme derived therefrom together with a schematic reaction energy profile for the reaction of the isomeric dichlorobenzene radical cations with NH\textsubscript{3}. By application of the steady-state approximation to the concentration of the collision complex C and the addition complex D, eq 4 has been obtained for the experimental bimolecular rate constant \( k_{\text{exp}} \).

\[
k_{\text{exp}} = k_1 k_2 k_3/p \left( k_+ + k_p (k_2 + k_p) - k_p k_2 \right) \quad \text{(4)}
\]

where \( k_1 \) corresponds to the collision rate which can be calculated by the ADO results and \( k_2 \) is the rate constant for the back dissociation of the collision complex C. For an ion–molecule reaction of a low efficiency \( k_1 \), is always much larger than the rate constant \( k_p \) of the forward reaction. In the limiting case \( k_1 \gg k_p \), eq 5 is obtained:

\[
k_{\text{exp}} = (k_1/k_p) k_2 p \quad \text{(5a)}
\]

\[
\text{eff} = k_{\text{exp}}/k_1 = (1/k_1 k_2) k_3/p \quad \text{(5b)}
\]

As long as ion–molecule reactions of different ions with identical neutral molecules are compared, the first term of eq 5a \( (k_1/k_p) \) is constant. By the principle of microscopic reversibility all factors influencing the rate of formation of the collision complex C will affect in a similar way also the rate of the dissociation of C. According to the ADO theory the collision rate constant \( k_1 \) depends only on the dipole moment \( \mu \) and the polarizability \( \alpha \) of the neutral component. Hence, \( k_1/k_p \) is identical for the reactions of all radical cations of halogenated benzenes with NH\textsubscript{3}. Consequently, the variation of \( k_{\text{exp}} \) with the type of the halogen substituent must be due to a variation of the rate constant \( k_2 \) of the addition of NH\textsubscript{3} to the aromatic radical cation, and the term \( k_3/p (k_2 + k_3) \) of eq 5a which corresponds to the fraction of the addition complexes D decomposing to the reaction products P. This has already been discussed for the monohalobenzenes. The

---

reaction of the radical cations of the dihalobenzenes with NH₃
exhibits the same characteristic features (Table I). In particular,
the efficiency of the substitution reaction is always small, so that
the kinetic scheme of Figure 3 and eq 5 can be also applied to
these reactions.

The preceding discussion makes clear that the effect of the type
of halogen substituents and of their relative orientation on the
amination rate constant kₐ of mono- and dihalogenated benzene
radical cations has to be explained by a dependence of k₂ and of
k₃/(k₂ + k₃) on these structural parameters. The main effects
emerging from the data of Table I are a strong decrease of the
substitution rate for the iodochlorobenzene radical cations, in close
analogy to the reduced reactivity of the iodobenzene radical
cations and a decrease of the rate for all isomeric dihalobenzene
radical cations in the order 1,2- > 1,3- > 1,4-substitution.

The term k₃/(k₂ + k₃) is expected to increase for the iodinated
radical cations because of an increase of k₃ with the small dis-
association energy of the C=I bond. Thus, this term cannot be
responsible for the decrease of kₐ for these ions. Moreover,
in the case of the isomeric homodisubstituted benzene radical
cations an identical C-X bond is always cleaved in the final
reaction step. It is not very likely that k₃ depends so much on
the relative orientation of the two halogen substituents to account
for the positional effect on kₐ. Thus, the effects observed in Table
I are mainly due to a variation of k₂ with the type of the halogen
substituents and with their relative positions at the aromatic ring
of the dihalogenated radical ions.

It is rather unexpected that the addition of the nucleophilic NH₃
to an electron-deficient radical cation is slow. The geometry
and the heat of formation, ΔHf, of the collision complex C and of the
addition complex D, respectively, have been calculated by
MNDÖ28 for the reaction of the radical cations of chlorobenzene
and of the three isomeric dichlorobenzenes with NH₃ (Table III
and Figure 3).

The geometries of the two complexes C and D are very different.
In the most stable structure of the collision complex C of the
radical cations of chlorobenzene as well as of the three isomeric
dichlorobenzenes the NH₃ molecule is located vertically above
the center of the chlorinated benzene ring at a distance of about
3.5 Å. Furthermore, the stabilization energy E₆ of the complex
C (eq 6) is not very different for chlorobenzene and all isomers

![Figure 4](https://example.com/figure4.png)

> Figure 4. Detailed description of the addition step C → D according to
the curve-crossing model of Shaik and Pross28 (see text).

In the addition complex D the original NH₃ is covalently bonded
as a positively charged NH₃⁺ group to the C atom carrying the
chloro substituent. Thus, the NH₃⁺ is located outside the ring.
The heat of formation of the addition complex D for chlorobenzene
and all dichlorobenzenes is below that of the corresponding collision
complex C, and the addition step is exothermic. However, the
rather different geometries of C and D may create a considerable
energy barrier which makes the addition a slow process. Note
from Table III that the ipso complex D is not the most stable
addition complex, but the addition of NH₃ to any other C atom
besides those carrying the halogen substituent gives rise to a
complex reacting only by a back dissociation.27 It appeared
possible in view of the geometric differences of C and D that the
"bulkiness" of the halogen substituent may hinder the addition
of NH₃ and that this steric effect is the origin of the low reactivity
of the iodobenzene radical cations. However, although the ef-
ficiency of the reaction of the radical cations of all three isomers
is as small or even smaller than that of the iodobenzene radical
cation (Table I), the chloriodo derivatives nevertheless lose
predominantly I as expected by the small C-I bond dissociation
energy Table II. This excludes a steric effect of the halogen
substituent on its substitution rate.

Another important difference between the collision complex
C and the addition complex D is the distribution of the charge
and the radical electron. In C both are located at the aromatic
π-system, while D corresponds to a cyclohexadienyl radical sub-
stituted by a NH₃⁺ group at the sp²-C atom and is in fact a distonic
ion with the positive charge localized at the NH₃⁺ substituent.
Consequently, the transformation C → D corresponds to the net
transfer of one electron from the NH₃ molecule to the aromatic
radical cation. Hypothetically, the generation of D from C can be
divided into two steps (Figure 4): (i) the transfer of the electron
from NH₃ to the radical cation and (ii) formation of the C–N
bond by coupling of the unpaired electron of radical cation NH₃⁺
with one of the π-electrons of the neutral halogenated benzene.

This view of the nucleophilic addition to an electrophilic radical
cation corresponds to the reactivity model of Shaik and Pross.28

![Figure 3](https://example.com/figure3.png)

> Figure 3. Geometries of the two complexes D, C, and the radical cation.


(27) The most stable addition complex is formed by addition of NH₃ para
to the chloro substituent. The loss of H from this complex (and the other
complexes) is endothermic and cannot occur. A rearrangement of this
complex into complex D by migration of H and Cl, respectively, is forbidden
by the orbital symmetry rules and can be excluded by the experimentally proven
selective formation of the ipso substitution product in the case of the
dichlorobenzene radical cations.29

According to this curve-crossing model for polar reactions between an electron donor and an electron acceptor, the transition state can be described mainly by a resonance between the electronic configurations of the starting and final state of the reacting system, and the potential energy of the system along the reaction coordinate can be modeled by an avoided crossing between these two states. Then the activation barrier $E^*$ is formulated as a fraction $f$ of the difference between the energy of that excited state of the reactants, which has the electronic configuration of the products but still the ground-state geometry, and the energy of the ground state of the reactants. This energy difference is named the initial energy gap $E_g$. In addition, $E^*$ is lowered by the avoided crossing constant $\beta$:  

$$E^* = fE_g - \beta$$  

(7)

This model has already been used to discuss the reactions of radical cations and can be used conveniently to analyze the structural parameters that influence the reactivity of halogenated aromatic radical cations toward NH$_3$. The relevant excited electronic states of the reactants with the electron configuration of the addition complex correspond to the radical cation NH$_3^+$ and the neutral halogenated benzene with two unpaired electrons, i.e., the triplet state of the halogenated benzene. From these excited states the complex D is formed by the approach of NH$_3^+$ to the halogen-substituted C atom and the coupling of its unpaired electron with one of the unpaired electrons of the triplet benzene. Thus, $E_g$ of this reaction is determined by the difference of the ionization energy (IE) of NH$_3$ and the recombination energy (RE) of the aromatic radical cations and by the triplet energy ($E_T$) of the neutral halogenated benzene:  

$$E_g = \text{IE(NH}_3\text{)} - \text{RE(C}_6\text{H}_8\text{}\text{X}_a) + \text{E}_T(C_6\text{H}_8\text{}\text{X}_a)$$  

(8)

The RE of the radical cation can be approximated by the IE of the corresponding benzene derivative. The difference between IE(NH$_3$) = 10.15 eV and the IE of a halogenated benzene (8–9 eV) see Table I is quite large, resulting in a large value of $E_g$. The bond-forming process along the reaction coordinate diminishes this energy difference, leading to a curve crossing for the states corresponding to the charge-transfer process and the bond formation as schematically depicted in the lower part of Figure 4. However, the bond formation between NH$_3^+$ and triplet benzene involves a delocalized π-electron and diminishes the energy demand for the electron transfer rather late on the reaction coordinate, leading to a late curve crossing and a large value of $f$ in eq 7. These factors predict that the activation energy $E^*$ for the nucleophilic addition of NH$_3$ to the radical cation of a benzene derivative should be quite large and should increase with decreasing IE and increasing $E_g$ of the benzene derivative. The influence of the IE on $E^*$ explains the low reaction efficiency of the radical cation of iodobenzene because of its distinctly lower IE. The IE values of the chlorobenzodienes are not known, but should be again lower than the IE of the other dihalobenzenes, explaining also the low reaction efficiency of these radical cations. The strong influence of the IE of the halogenated aromatic compound on the reaction rate of their radical cation with NH$_3$ is also seen in the case of the three isomeric bromoanilines [IE-(4-bromoanilne) = 8.1 eV] and of 1-bromo- and 2-bromonaphthalene (IE = 8.1 eV) whose radical cations do not react with NH$_3$. However, the radical cations of these compounds do give substitution products with CH$_3$NH$_2$ (IE = 8.97 eV) because the lower IE(CH$_3$NH$_2$) results in a decrease of the initial energy gap $E_g$ and leads to a considerably enhanced rate compared to the reaction with NH$_3$.  

The data of Table I show, however, that other structural parameters besides the IE influence the reaction efficiencies of the radical cations of the dihalobenzenes for a nucleophilic substitution. This is seen clearly by comparing the reactions of the radical cations of chlorobenzene, dichlorobenzene, and chlorofluorobenzene, which react exclusively by substitution of a chlorine substituent. The IE values of these compounds are accurately known, and in each series of the dihalobenzenes the 1,3-isomer exhibits the highest IE, and the lowest rate constant $k_{obs}$ is observed for the 1,2-isomer and the rates decrease always in the order 1,2- > 1,3- >> 1,4-isomer. The strongly reduced efficiencies of the 1,4-isomers cannot be explained by the decrease of the IE. Similar differences of ca. 0.1 eV are observed between the IE values of, for example, chlorobenzene, 1,2-dichlorobenzene, and 1-chloro-2-fluorobenzene, but nevertheless the efficiencies for the reactions of these radical cations are almost identical (13%, 15%, and 15%, respectively).

In the case of the radical cations of 1,4-dichloro- and 1-chloro-4-fluorobenzene the low reaction efficiency could be attributed to the rather small exothermicity of 4 and 9 kJ mol$^{-1}$, respectively (Table I). However, a different heat of reaction, $\Delta H^\circ$, cannot be the origin of the positional substituent effect on the substitution rate. An identical positional effect as with the chloro derivatives is observed for the dibromo- and bromofluorobenzenes (Table I), although neither the IE nor the $\Delta H^\circ$ values of the isomeric dibromobenzenes are very different.

It is seen from eq 8 that the initial energy gap $E_g$ and hence the substitution rate of the aromatic radical cations is also influenced by the triplet energy $E_T$ of the corresponding halogenated benzene. For the compounds studied $E_T$ is not known, but the UV–vis spectra of isomeric dihalobenzenes are not very different. Thus, it is not very likely that $E_T$ varies strongly and systematically in the order 1,2- > 1,3- >> 1,4-substitution in each set of positional isomers of dihalogenated benzenes, and $E_T$ cannot be used to explain this order of the decreasing substitution rate. However, a molecular property which varies systematically in that order is the dipole moment, $\mu$, of the halogenated benzenes. An effect of $\mu$ on the rates of the radical cations of dihalogenated benzenes with NH$_3$ becomes also apparent when the rates of related 1,4-homo- and 1,4-heterodisubstituted derivatives are compared. For 1,4-homodisubstituted benzenes $\mu = 0$, whereas $\mu > 0$ for 1,4-heterodisubstituted benzenes. The relevant compounds of Table I are the radical cations of 1,4-dichloro- and 1-chloro-4-fluorobenzene, both reacting only by substitution of a Cl, and of 1,4-dibromo- and 1-bromo-4-fluorobenzene, losing only a Br. In both cases the substitution rate for the 1,4-heterodisubstituted derivatives is distinctly larger.

The effect of the dipole moment $\mu$ of the neutral precursor of an ion on the rate of an ion–molecule reaction is rather unusual. It is expected in cases where charge or proton transfer takes place during the encounter, resulting in an equilibrium between two or even more ion–molecule complexes. However, in the present case the formulation (NH$_3^+$C$_6$H$_8$X$_a$) represents an excited state of the complex, which is energetically not accessible under the reaction conditions. By the ADO theory $\Delta H^\circ$ the rate of an ion-molecule reaction depends on the dipole moment and the polarizability of the neutral reaction partner. However, this is an effect on the attractive electrostatic forces and the collision rate between the reactants, whereas in the present case an effect on the rate within the collision complex is observed. This effect can be understood within the frame of the curve-crossing model of Shaik and Pross, if the electrostatic interaction of both components of the complex in its ground state and in the relevant excited state is taken into account.
Reactions of Dihalobenzene Radical Cations

Table IV. Stabilization Energies $E_\Delta$ (equation 6) of Ion–Molecule $\sigma$-Complexes [C$_6$H$_5$Cl-NH$_3$]$^+$ Relative to Separated Compounds$^a$

<table>
<thead>
<tr>
<th></th>
<th>$\mu_p$</th>
<th>$a_p,\sigma$</th>
<th>$E_\Delta$</th>
<th>$E_\Delta^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-C$_6$H$_5$Cl$_2$NH$_3^+$</td>
<td>2.54</td>
<td>14.2</td>
<td>-126</td>
<td></td>
</tr>
<tr>
<td>m-C$_6$H$_5$Cl$_2$NH$_3^+$</td>
<td>1.72</td>
<td>14.2</td>
<td>-106</td>
<td></td>
</tr>
<tr>
<td>p-C$_6$H$_5$Cl$_2$NH$_3^+$</td>
<td>0.00</td>
<td>14.5</td>
<td>-67</td>
<td></td>
</tr>
<tr>
<td>NH$_3$C$_6$H$_5$Cl$_2^+$</td>
<td>1.47</td>
<td>2.26</td>
<td>34</td>
<td>-45</td>
</tr>
</tbody>
</table>

$^a$ Calculated according to the ADO theory$^{20}$ assuming a distance of 3.5 Å (distance from MNDO calculations); dipole moments $\mu_p$ and polarizabilities $a$ are given for the neutral components.

The curve-crossing model relates the activation energy $E^*$ of the chemical reaction within the encounter complex to $E_\Delta$, defined as the energy difference between the excited state of the system relevant for the reaction and the ground state. The energies of these two states depend not only on the properties of the separated components, however. This is well-known from solvent effects $E$, and $E^*$ hitherto has been neglected. The reaction of the radical cations of halogenated benzenes with NH$_3$ is clearly a case with a different charge distribution of the relevant states of the long-lived collision complex (Figure 4). In the ground state the positive charge resides on the benzene and the stabilization energy $E_\Delta$ of the encounter complex depends on the dipole moment $\mu$ and the polarizability $a$ of NH$_3$. However, in the excited state the positive charge is localized on the ammonia (as in the product, the anilinium ion) and now $E_\Delta^*$ of the excited state depends on $\mu$ and $a$ of the neutral halogenated benzene. $E_\Delta$ and $E_\Delta^*$ are clearly different, and this energy difference $\Delta E_\Delta = E_\Delta^* - E_\Delta$ has to be included for the determination of the initial energy gap $E_\Delta$ of the reaction:

$$E_\Delta = \text{IE(NH}_3) - \text{RE(C}_6\text{H}_5\text{-X}_n) + E_\Gamma(\text{C}_6\text{H}_5\text{-X}_n) - \Delta E_\Gamma(\text{C}_6\text{H}_5\text{-X}_n;\text{NH}_3)^+\ + \text{(7a)}$$

Assuming a distance of 3.5 Å between the halogenated benzene and NH$_3$ in the collision complex C as calculated by MNDO, the values for $E_\Delta$ and $E_\Delta^*$ presented in Table IV are obtained for the radical cations of the isomeric dichlorobenzenes, using, as a first approximation, the polarizability $a$ and the dipole moment $\mu$ of the singlet moleules. The effect of $\Delta E_\Delta$ on $E_\Delta$ is quite large and may be of the same order of magnitude as the difference between the IE of the halogenated benzene (or more correctly the IE of the corresponding radical cation) which alters accordingly the activation energy $E^*$ of the NH$_3$ addition. The positional effect of two halogen substituents can be linked to the dipole moment $\mu$ of the dihalobenzene. The curve-crossing activity model predicts that the initial energy gap $E_\Delta$ of the stabilization of the encounter complex in the excited state depends on the reaction rate is a general effect, in particular for the IE of the halogenated benzene (or more correctly the RE of the corresponding radical cation) which alters accordingly the activation energy $E^*$ of the NH$_3$ addition. Thus, the stabilization energy $E_\Delta^*$ of the excited complex depends strongly on the dipole moment $\mu$ and the polarizability $a$ of the dihalogenated benzene. An increase of the absolute value of $E_\Delta^*$ by an increasing value of $\mu$ of the dihalogenated benzene decreases $E_\Delta$ and $E^*$ and enhances the reaction rate considerably. This unexpected effect of the dipole moment $\mu$ and the polarizability $a$ of the neutral precursor of the ion of a (slow) chemical reaction within a long-lived collision complex of an ion–molecule reaction has not been discussed before. Our results show that this effect is in agreement with the reactivity model of Shaik and Pross.$^{28}$ It is predicted that this structural effect of an ion on the reaction rate is a general effect, in particular for large organic ions, and that this effect is large for all ion–molecule reactions with a different charge distribution in the reactant state and in the product state.

Acknowledgment. This work has been supported by gift of an ICR spectrometer and additional financial support by the Deutsche Forschungs gemeinschaft. Further financial assistance by the Fonds der Chemischen Industrie is gratefully acknowledged.

Conclusion

Our study of the reactions of radical cations of mono- and dihalogenated benzenes with NH$_3$ show that this nucleophilic substitution of aromatic radical cations is a slow two-step reaction within a long-lived collision complex C. The two elementary reaction steps are the addition of the nucleophile NH$_3$ to the radical cation and the elimination of the halogen substituent X (or elimination of HX) from the addition complex D. The addition step is slow, and the total rate $k_{exp}$ of the substitution reaction is determined by the rate constant $k_2$ of the addition step modified by the probability $k_2/(k_1 + k_2)$ for the dissociation of the addition complex D to the products. The reaction efficiency of the substitution process depends strongly on the type of the halogen substituent and on the relative orientation of two substituents in the radical cation. These structural effects on the reactivity can be understood by using the curve-crossing model of Shaik and Pross$^{28}$ to analyze the parameters influencing the activation energy of the addition step. This analysis reveals that the effect of the type of halogen substituent is mainly due to a general substituent effect on the IE of the halogenated benzene (or more correctly the IE of the corresponding radical cation) which alters accordingly the activation energy $E^*$ of the NH$_3$ addition. The positional effect of two halogen substituents can be linked to the dipole moment $\mu$ of the dihalobenzene. The curve-crossing activity model predicts that the initial energy gap $E_\Delta$ of the stabilization of the encounter complex in the excited state $C^*$ and the ground state $C$ (Figure 4) by the electrostatic interactions between its components. The neutral component of the relevant excited state of the encounter complex of the addition of NH$_3$ to the radical cation is the corresponding neutral halogenated benzene. Thus, the stabilization energy $E_\Delta^*$ of the excited complex depends strongly on the dipole moment $\mu$ and the polarizability $a$ of the dihalogenated benzene. An increase of the absolute value of $E_\Delta^*$ by an increasing value of $\mu$ of the dihalogenated benzene decreases $E_\Delta$ and $E^*$ and enhances the reaction rate considerably.

...