J. Am. Chem. Soc. **1991**, *113*, 3281-3287

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

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Received September 10, 1990. Revised Manuscript Received December 13, 1990

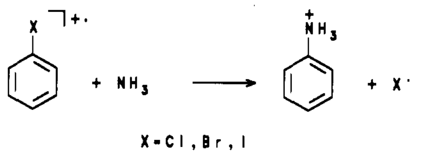
Abstract: The reactions of homo- and heterodisubstituted dihalobenzene radical cations with NH_3 were investigated by FT-ICR spectrometry. A halogen atom X (X = Cl, Br, I) is substituted in a gas-phase nucleophilic ipso substitution, yielding haloanilinium ions. The reaction efficiency, i.e., the percentage 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 dihalobenzene 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 dihalobenzene radical cations by NH_3 proceeds by a multistep reaction mechanism with a double-well potential energy surface. The rate-determining step is the addition of NH_3 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 dihalobenzene radical cations with NH_3 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 NH_3 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(NO_2), the aromatic reactant is ionized by an outer-sphere electron transfer to NO_2^+ and the resulting radical cation combines with NO_2.

The substitution pattern resulting from aromatic substitution reactions with intermediate radical cations often is 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 [CI(NH_3)][5] 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 unambiguously[7] by using a FT-ICR spectrometer equipped with an external ion source that of the various possible ion-molecule reactions in a ammonia CI plasma the only reaction yielding anilinium ions is the reaction of halobenzene radical cations with neutral NH_3 (reaction 1).



(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 showed[8] 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[9] is only 13%. Surprisingly, iodobenzene radical cations react much slower with NH_3 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 NH_3. 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 NH_3) 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 NH_3 which form specifically the chloroanilinium ion with the identical orientation

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(9) The reaction efficiency (eff) is the percentage of the reactive collisions eff (%) = $100k_{exp}/k_{ADO}$. k_{exp} is the experimental bimolecular rate constant, and k_{ADO} is the collision rate constant according to the ADO theory.[20]

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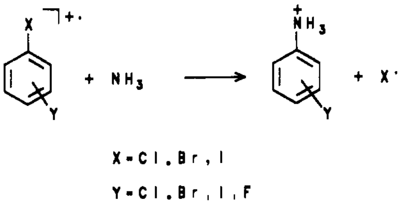
of the substituents by an ipso substitution of one of the chloro substituents.[10]

The preliminary investigation of the reactions of the dichlorobenzene radical cations with NH_3 (reaction 2) revealed



(2)

another interesting detail of this nucleophilic aromatic substitution.[10] 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 NH_3 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 ("heterodisubstitution") halogen substituents, respectively, with NH_3 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 Schiemann reaction[11] and the chloroiodobenzenes by diazotation and iodination[12] 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 Spectrospin CMS 47X FT-ICR instrument[13] 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.[14]

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-p}. All ions of masses below m/z 50 and the isotopomers of the aromatic radical cations containing ^{13}C, ^{37}Cl, and ^{81}Br isotopes were ejected by "single shots" (fixed frequency radio frequency pulses) of 14 V_{p-p}, 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 3×10^{-7} to 2×10^{-6} mbar. The ionization gauge is connected close to the diffusion pump of the ICR cell, and the pressure was calibrated by rate measurements of the reactions $CH_4^{\cdot+} + CH_4$ ($k = 1.5 \times 10^{-9}$ cm^3 s^{-1})[15] and $NH_3^{\cdot+} + NH_3$ ($k = 2.2 \times 10^{-9}$ cm^3 s^{-1}).[16] The difference of the sensitivities of the ionization gauge toward methane and ammonia corresponds to the literature values.[17]

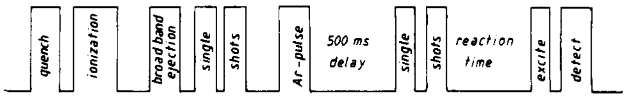


Figure 1. Pulse sequence for the FT-ICR measurements using collisional deactivation.

Table I. Reaction of Halobenzene Radical Cations with NH_3

compound	IE,[a] eV	k_{exp},[d] 10^{-11} cm^3 s^{-1}	eff, %	ΔH_r°,[a] kJ mol^{-1}
chlorobenzene[b]	9.06	21	13	−23
bromobenzene[b]	8.98	22	13	−76
iodobenzene[b]	8.69	0.38	0.24	−112
fluorobenzene[b]	9.22	no		+92
1,2-dichlorobenzene	9.08	24[c]	15	−21
1,3-dichlorobenzene	9.11	12	7	−20
1,4-dichlorobenzene	8.99	0.7	0.4	−4
1,2-dibromobenzene	8.8	28	17	−56
1,3-dibromobenzene	8.85	8.1	5	−61
1,4-dibromobenzene	8.7	1.8	1.1	−52
1-chloro-2-fluorobenzene	9.18	25	15	−35
1-chloro-3-fluorobenzene	9.21	17	10	−30
1-chloro-4-fluorobenzene	9.01	4.7	2.8	−9
1-bromo-2-fluorobenzene		28	17	
1-bromo-3-fluorobenzene		15	9	
1-bromo-4-fluorobenzene		5.6	3.4	
1-bromo-2-chlorobenzene		29	18	
1-bromo-3-chlorobenzene		11	7	
1-bromo-4-chlorobenzene		2.4	1.5	
1-chloro-2-iodobenzene		3.3	2.0	
1-chloro-3-iodobenzene		0.2	0.12	
1-chloro-4-iodobenzene		<0.01	<0.006	

[a] Data from ref 24; proton affinities estimated for *o*-haloanilins. [b] Datafrom ref 8. [c] ±25% (see text). [d] Rate of disappearance of radical cations by sum of substitution processes.

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.[8] 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" errors[18] 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_{p-p}, 1.5 ms). This method diminishes the probability of re-excitation of the reacting ions by the ejection process. Alternatively, CF_4 has been used as collision gas instead of argon because of its better deactivation property. The pulse

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Table II. Distribution of Substitution Products in the Reaction (2) of Dihalobenzene Radical Cations with NH_3

compound	substitution of Cl	substitution of Br	substitution of I	substitution of HCl
1-bromo-2-chlorobenzene	47%	53%		
1-bromo-3-chlorobenzene	33%	67%		
1-bromo-4-chlorobenzene	7%	93%		
1-chloro-2-iodobenzene	17%		44%	39%
1-chloro-3-iodobenzene	19%		48%	33%
1-chloro-4-iodobenzene	12%[a]		59%[a]	29%[a]

[a] Approximate values; the reaction is extremely slow, and very little product is formed.

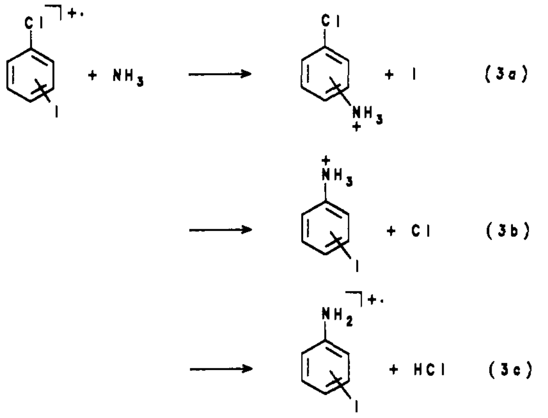
sequence used in these ICR experiments is shown in Figure 1.

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.[8]

Dichlorobenzene radical cations react with NH_3 under FT-ICR conditions by substitution of only *one* chloro substituent.[10] Analogously the radical cations of the dibromobenzenes exchange only *one* bromine atom by the NH_3^+ group. In heterodisubstituted benzenes either of the two substituents may be exchanged with exception of a fluoro substituent. The substitution reaction of fluorobenzene radical cations with NH_3 is endothermic and not observable under FT-ICR conditions.[8] 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 NH_3 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.



The radical cations of chlorobenzene and bromobenzene react with NH_3, 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 NH_3 is always rather low, however, although again a decrease of the reactivity is observed in the series 1,2- > 1,3- ≫ 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 NH_3.

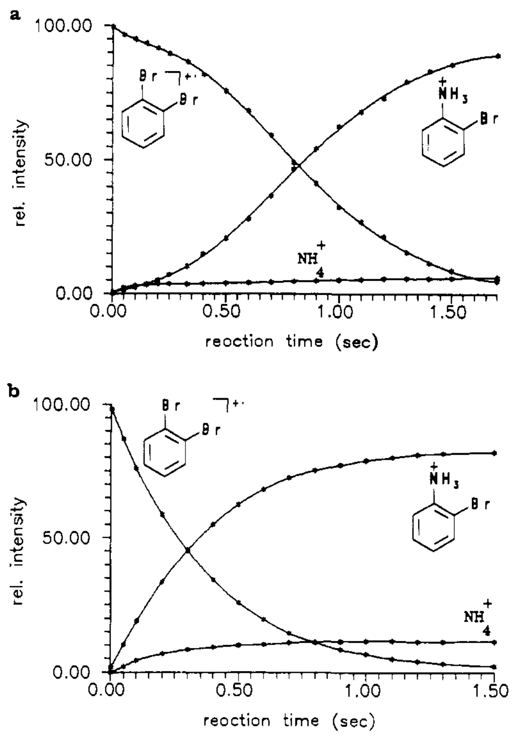


Figure 2. Reaction of *o*-dibromobenzene radical cations with ammonia [$p(NH_3) = 5.8 \times 10^{-7}$ mbar (a)/4.4×10^{-7} mbar (b)]. Kinetics without (a) and with (b) collisional deactivation.

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 $NH_3^{\bullet+}$ 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 NH_3 to yield NH_4^+. A direct formation of NH_4^+ 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 later 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 CF_4 as an inert collision gas prior to the substitution reaction. It was shown[19] 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-

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[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.[8,10] 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_4. The fast reactions of all 1,2-dihalobenzene radical cations were examined without and with collisional deactivation. The efficiencies obtained after collisional deactivation are usually 10–20% higher than those determined without deactivation.

Table I shows the experimental bimolecular reaction rates, k_{exp}, and the efficiencies, eff, for the reactions of NH_3 with the radical cations of all halobenzenes and a selection of homo- and heterodisubstituted dihalobenzenes. The error of the experimental rate constants is ±15%, and the corresponding collision rates were calculated according to the ADO theory.[20]

During the experiments using collisional deactivation, especially at a higher NH_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_4, respectively). This excludes an isomerization induced by the collision gas because argon and CF_4 behave rather differently as collision gases.[21] Obviously some 1,2-dichlorobenzene molecules isomerize to an unreactive $C_6H_4Cl_2^{\bullet+}$ 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,[22] 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.[23] have studied the rate for the loss of Cl from the isomeric dichlorobenzene radical cations by PEPICO and have obtained identical rates for all three isomers. This agrees with an isomerization of the molecular ions, probably to the 1,4-isomer.[21] In contrast to this, our results exclude any extensive isomerization of the molecular ions of isomeric dihalobenzenes. For all dihalobenzene radical cations each isomer reacts with NH_3 with a typical rate constant which decreases in the order 1,2- > 1,3- ≫ 1,4-isomer by factors of about 1:0.5:0.1. In particular, any admixture of a substantial amount of the 1,4-isomer should have been detected by a deviation from the expected simple pseudo first order of the reactions. This is not the case. Furthermore, generation of each of the isomeric dichlorobenzene radical cations in the external ion source of the ICR spectrometer by energies of the ionizing electrons between 20 and 70 eV and by charge exchange with benzene molecular ions (IE = 9.21 eV[24]) has no effect on the characteristic rate constants of the isomers. Only in one experiment with 1,2-dichlorobenzene radical cations under the rather irregular conditions discussed in the previous section were a few percent of ions isomeric to 1,2-dichlorobenzene ions detected. However, these isomeric ions are unreactive toward NH_3 and probably correspond to open-chain isomers. Thus, the *stable* molecular ions of isomeric dihalobenzenes observed in the FT-ICR spectrometer at lifetimes >1 ms do not mutually interconvert, and any isomerization observed in the EI mass spectra must be due to highly energized *fragmenting* ions.

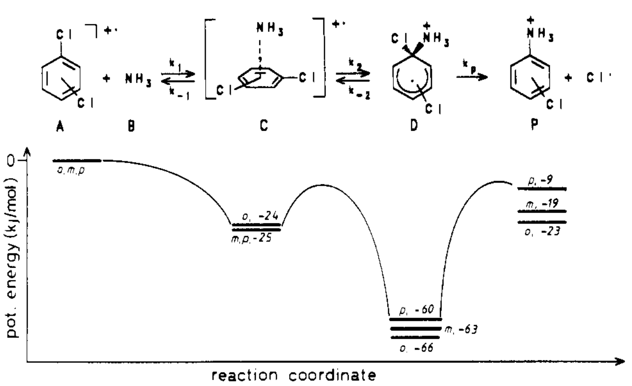

Figure 3. Reaction mechanism of the isomeric 1,2-, 1,3-, and 1,4-dichlorobenzene radical cations with ammonia (potential energies calculated by MNDO).

The structural stability of the molecular ions of halogenated benzene in the FT-ICR spectrometer and the strong dependence of their bimolecular reactivity on the relative orientation of the substituents is of interest with respect to an unambiguous identification of the isomers in this class of compounds. The analysis of polychlorinated biphenyls (PCB) and related compounds is an important issue of environmental chemistry, and our results indicate that certain ion–molecule reactions under standard conditions of CI mass spectrometry may be used for this analysis.

Kinetic Scheme and Reaction Mechanism. As mentioned in the introduction, the low efficiency of the reaction of monohalogenated benzene radical cations with NH_3 shows that this nucleophilic substitution occurs within a long-lived collision complex. As Brauman et al.[25] have shown, slow exothermic ion–molecule reactions have to proceed by a multistep mechanism with a multiwell 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_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_{exp}:[8]

$$k_{exp} = k_1 k_2 k_p / [(k_{-1} + k_2)(k_{-2} + k_p) - k_2 k_{-2}] \quad (4)$$

k_1 corresponds to the collision rate which can be calculated by the ADO theory,[20] and k_{-1} 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_2 of the forward reaction. In the limiting case $k_{-1} \gg k_2$, eq 5 is obtained:

$$k_{exp} = (k_1/k_{-1})k_2[k_p/(k_{-2} + k_p)] \quad (5a)$$

$$\mathrm{eff} = k_{exp}/k_1 = (1/k_{-1})k_2[k_p/(k_{-2} + k_p)] \quad (5b)$$

As long as ion–molecule reactions of different ions with identical neutral molecules are compared, the first term of eq 5a (k_1/k_{-1}) 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 μ and the polarizability α of the neutral component. Hence, k_1/k_{-1} is identical for the reactions of all radical cations of halogenated benzenes with NH_3. Consequently, the variation of k_{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_3 to the aromatic radical cation, and the term $k_p/(k_{-2} + k_p)$ 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.[8] The

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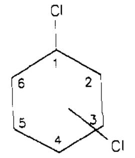
Table III. Relative heat of formation $\Delta\Delta H_f$[a] of the Cation Radical σ-Complexes of Chloro- and Dichlorobenzenes with NH_3, respectively, and the Separated Aromatic Radical Cations and NH_3

site of NH_3 attachment[b]	$\Delta\Delta H_f$, kJ mol^{-1}			
	C_6H_5Cl	1,2-	1,3-	1,4-$C_6H_4Cl_2$
ipso (**D**)	-56	-66	-63	-60
2	-74		-86	-72
3	-68	-78		-72
4	-75	-79	-88	
5	-68	-79	-75	-72
6	-74	-78	-88	-72

[a] Calculated by MNDO. [b] Numbering according to



reaction of the radical cations of the dihalobenzenes with NH_3 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 k_{exp} of mono- and dihalogenated benzene radical cations has to be explained by a dependence of k_2 and of $k_p/(k_{-2} + k_p)$ on these structural parameters. The main effects emerging from the data of Table I are a strong decrease of the substitution rate for the chloroiodobenzene 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 $k_p/(k_{-2} + k_p)$ is expected to increase for the iodinated radical cations because of an increase of k_p with the small dissociation energy of the C–I bond. Thus, this term cannot be responsible for the decrease of k_{exp} for these ions. Furthermore, 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 k_p depends so much on the relative orientation of the two halogen substituents to account for the positional effect on k_{exp}. Thus, the effects observed in Table I are mainly due to a variation of k_2 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 NH_3 to an electron-deficient radical cation is slow. The geometry and the heat of formation, ΔH_f, of the collision complex **C** and of the addition complex **D**, respectively, have been calculated by MNDO[26] for the reaction of the radical cations of chlorobenzene and of the three isomeric dichlorobenzenes with NH_3 (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 NH_3 molecule is located vertically above the center of the chlorinated benzene ring at a distance of about 3.5 Å. Furthermore, the stabilization energy E_s of the complex **C** (eq 6) is not very different for chlorobenzene and all isomers

$$E_s = \Delta H_f(C) - \Delta H_f(C_6H_{6-n}X_n^{\bullet+}) - \Delta H_f(NH_3) \qquad (6)$$

of dichlorobenzene, and the values of E_s obtained by MNDO agree with those predicted by the classical electrostatic forces.[20] These results corroborate the assumption that the rate constants k_1 and k_{-1} for the formation and the back dissociation of **C** are not influenced by the type and position of the halogen substituents at the aromatic ring of the radical cations.

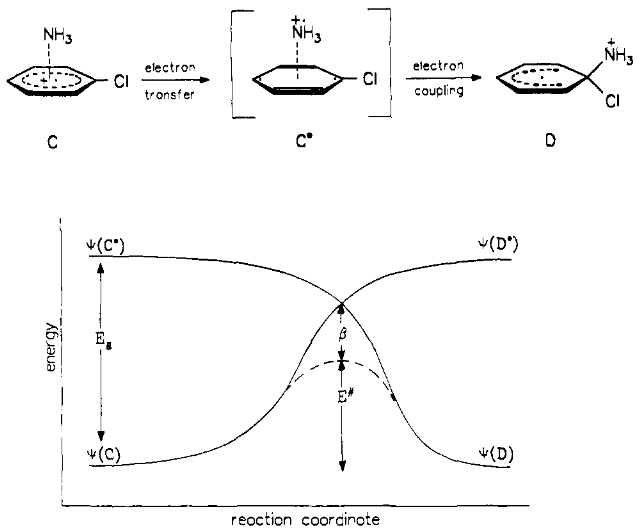


Figure 4. Detailed description of the addition step **C** → **D** according to the curve-crossing model of Shaik and Pross[28] (see text).

In the addition complex **D** the original NH_3 is covalently bonded as a positively charged NH_3^+ group to the C atom carrying the chloro substituent. Thus, the NH_3^+ 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 NH_3 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 NH_3 and that this steric effect is the origin of the low reactivity of the iodobenzene radical cations. However, although the efficiency 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 chloroiodo 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 substituted by a NH_3^+ group at the sp^3-C atom and is in fact a distonic ion with the positive charge localized at the NH_3^+ substituent. Consequently, the transformation **C** → **D** corresponds to the net transfer of one electron from the NH_3 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 NH_3 to the radical cation and (ii) formation of the C–N bond by coupling of the unpaired electron of *radical cation* $NH_3^{\bullet+}$ 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]

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(26) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(27) The most stable addition complex is formed by addition of NH_3 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.[10]

(28) (a) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (b) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 2708. (c) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (d) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. (e) Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537. (f) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1989**, *111*, 4306. (g) Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205.

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 β:[28]

$$E^* = fE_g - \beta \tag{7}$$

This model has already been used to discuss the reactions of radical cations[28f] 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* $NH_3^{\bullet+}$ 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 $NH_3^{\bullet+}$ 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 cation[29] and by the triplet energy (E_T) of the neutral halogenated benzene:

$$E_g = \mathrm{IE}(NH_3) - \mathrm{RE}(C_6H_{6-n}X_n) + E_T(C_6H_{6-n}X_n) \tag{8}$$

The RE of the radical cation can be approximated by the IE of the corresponding benzene derivative. The difference between $\mathrm{IE}(NH_3) = 10.15$ eV[24] and the IE of a halogenated benzene (8–9 eV,[24] 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 process as schematically depicted in the lower part of Figure 4. However, the bond formation between $NH_3^{\bullet+}$ 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.[28g] 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_T of the benzene derivative. The influence of the IE on E^* explains the low reaction efficiency of the radical cation of iodobenzene[8] because of its distinctly lower IE. The IE values of the chloroiodobenzenes 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 bromoanisoles [IE(4-bromoanisole) = 8.1 eV[24]] 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_3NH_2 (IE = 8.97 eV) because the lower $\mathrm{IE}(CH_3NH_2)$ 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.[30]

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, dichlorobenzenes, and chlorofluorobenzenes, which react exclusively by substitution of a chloro substituent. The IE values of these compounds are accurately known,[24] and in each series of the dihalobenzenes the 1,3-isomer exhibits the highest IE. Nevertheless, the largest rate constant k_{exp} 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, ΔH_r, 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 ΔH_r 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[31] 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*, μ, of the dihalogenated benzenes. An effect of μ on the rates of the radical cations of dihalobenzenes 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 μ 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.[32] However, in the present case the formulation ($NH_3^{\bullet+}\cdot C_6H_{6-n}X_n$) represents an excited state of the complex, which is energetically not accessible under the reaction conditions. By the ADO theory[20] 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.*

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(29) More correctly the *vertical* IE and RE should be used. However, these are usually approximated by the adiabatic values.

(30) The reactions of these and other radical cations of aromatic compounds with CH_3NH_2 and related nucleophiles will be discussed in detail in a forthcoming paper.

(31) See the UV–vis spectra of chlorinated benzenes in: Hall, K. R.; Wilhout, R. C.; Ferguson, A. M. *Selected Ultraviolet Spectral Data*; Beach, L. B., Ed.; Thermodynamics Research Center: College Station, TX, 1981; Vol. II.

(32) (a) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641. (b) Ausloos, P.; Lias, S. G. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 165. (c) Squires, R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185.

(33) (a) Moore, E. M.; Hobbs, M. E. *J. Am. Chem. Soc.* **1949**, *71*, 411. (b) Groves, L. G.; Sugdan, S. *J. Am. Chem. Soc.* **1934**, *56*, 1782.

(34) Landolt-Börnstein. *Atom- und Molekularphysik*, 6th ed.; Springer Verlag: West Berlin, 1951; Vol. 1, Part 3.

(35) Clary, D. C. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 139.

Table IV. Stabilization Energies E_s (equation 6) of Ion–Molecule π-Complexes $[C_6H_4Cl_2{\cdot}NH_3]^{\bullet+}$ Relative to Separated Compounds[a]

	μ_D,[32] D	α,[33] Å^3	E_s, kJ mol^{-1}	E_s^*, kJ mol^{-1}
o-$C_6H_4Cl_2{\cdot}NH_3^{\bullet+}$	2.54	14.2		−126
m-$C_6H_4Cl_2{\cdot}NH_3^{\bullet+}$	1.72	14.2		−106
p-$C_6H_4Cl_2{\cdot}NH_3^{\bullet+}$	0.0	14.5		−67
$NH_3{\cdot}C_6H_4Cl_2^{\bullet+}$	1.47[34]	2.26[34]	−45	

[a] Calculated according to the ADO theory[20] assuming a distance of 3.5 Å (distance from MNDO calculations); dipole moments μ_D and polarizabilities α are given for the neutral components.

The curve-crossing model relates the activation energy $E^{\ddagger}$ of the chemical reaction within the encounter complex to E_g, 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 on the rates of polar reactions in solution. Analogously, in the gas phase one has to take into account the electrostatic interactions between the reactants in the collision complex in both its excited and its ground state. The stabilization is very different for both states if the charge distribution between the reactants is different in the ground state and the relevant excited state. This effect on E_g and $E^{\ddagger}$ 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 halogenated benzene and the stabilization energy E_s of the encounter complex depends on the dipole moment μ and the polarizability α 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_s^* of the excited state depends on μ and α of the neutral halogenated benzene. E_s and E_s^* are clearly different, and this energy difference $\Delta E_s = E_s^* - E_s$ has to be included for the determination of the initial energy gap E_g of the reaction:

$$E_g = \mathrm{IE}(NH_3) - \mathrm{RE}(C_6H_{6-n}X_n) + E_T(C_6H_{6-n}X_n) - \Delta E_s[(C_6H_{6-n}X_n;NH_3)^{\bullet+} \quad (7a)$$

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_s and E_s^* presented in Table IV are obtained for the radical cations of the isomeric dichlorobenzenes, using, as a first approximation, the polarizability α and the dipole moment μ_D of the singlet molecules. The effect of ΔE_s on E_g is quite large and may be of the same order of magnitude as the difference between IE(NH_3) and RE($C_6H_{6-n}X_n$) for 1,4-dihalobenzene. Furthermore, the IE values of the dichlorobenzenes differ only by 0.12 eV (11 kJ mol^{-1}), while the ΔE_s differ by 59 kJ mol^{-1}. In the case of 1,4-dichlorobenzene radical cations the smaller value of both the IE and the ΔE_s increase the E_g and $E^{\ddagger}$ so that the reaction efficiency decreases considerably. The same effects operate very likely also in the reactions of the other 1,4-dihalobenzene radical cations. The IE values of the 1,3-dihalobenzenes regularly exceed that of the other isomers and thus partly compensate the decrease of ΔE_s. Consequently, the efficiencies of the reactions of the 1,2- and 1,3-disubstituted benzene radical cations differ only by a factor of ca. 2.

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 $k_p/(k_{-2} + k_p)$ 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 of the RE of the corresponding radical cation) which alters accordingly the activation energy $E^{\ddagger}$ of the NH_3 addition. The positional effect of two halogen substituents can be linked to the dipole moment μ of the dihalobenzene. The curve-crossing reactivity model predicts that the initial energy gap E_g, which represents the energy difference between the excited state and the ground state involved in the reaction, determines $E^{\ddagger}$ of the reaction. In a modified reactivity model for polar reactions E_g depends inter alia on the difference ΔE_s 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_s^* of the excited complex depends strongly on the dipole moment μ and the polarizability α of the dihalogenated benzene. An increase of the absolute value of E_s^* by an increasing value of μ of the dihalogenated benzene decreases E_g and $E^{\ddagger}$ and enhances the reaction rate considerably.

This unexpected effect of the dipole moment μ and the polarizability α 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 Forschungsgemeinschaft. Further financial assistance by the Fonds der Chemischen Industrie is gratefully acknowledged.