allyl iodide efficiently scavenges H atoms on H-precovered Al surfaces to form propylene at 500 K, a temperature over 100 K above where hydrogen atoms recombine to form H_2 on Al surfaces (Figure 5D), we infer that the equilibrium described above greatly favors the saturated form.

It should be emphasized that this allyl/metallacycle equilibrium does not necessarily lie along the olefin-forming reaction coordinate. Several other pathways can be envisioned as outlined in Scheme III.

Pathway 1 shows a concerted 1,2-hydrogen shift,[19] pathway 2 a β-hydride elimination coupled to a reductive elimination, and pathway 3 reductive elimination followed by β-hydride elimination. This latter mechanism requires hydrogen atoms (from the metallacycle/allyl equilibrium, for example) for initiation, with the overall reaction regenerating hydrogen necessary to perpetuate the chain process. While we cannot determine from our data which pathway is operative, the important observation to note is that each pathway contains either a hydrogen shift or a reductive elimination step, chemistries *not* observed for either the *n*-alkyls or the C_4 metallacycle on aluminum. The fact that the kinetics for C_3 metallacycle decomposition are similar to those for β-hydride elimination suggests that either ring strain in the C_3 metallacycle or π-allyl character in the propenyl intermediate enhance the rate of one of these new processes.

5. Conclusions

Surface metallacycles can be prepared on aluminum in ultrahigh vacuum by the low-temperature dissociative adsorption of suitable dihaloalkanes. Bromo- and iodoalkanes yield similar results, suggesting that the nature of the halogen does not significantly affect the surface reaction chemistry. The C_3 metallacycles derived from 1,3-dihalopropanes or 1,3-dibromobutane yield alkanes at ~500 K, while C_4 species formed by dissociative adsorption of 1,4-dihalobutanes produce predominantly butadiene. The observed rates are very similar for these two mechanistically distinct processes. The predominant formation of butadiene by C_4 metallacycles can be accounted for by sequential β-hydride elimination reactions. With regard to the C_3 metallacycle, the products as well as the results of isotope exchange studies suggest that the thermal decomposition of this species must involve additional surface chemistries, most notably reductive elimination and/or 1,2-hydrogen atom shifts.

Stabilities of Complexes of Br^- with Substituted Benzenes (SB) Based on Determinations of the Gas-Phase Equilibria Br^- + SB = $(BrSB)^-$

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada. *Received July 12, 1990*

Abstract: Equilibria involving some forty substituted benzenes (SB) and the bromide ion ($SB + Br^- = SBBr^-$) in the gas phase were determined with a pulsed electron, high-pressure mass spectrometer (PHPMS). The resulting $-\Delta G_1^\circ$ provide information on the stabilities of the $SBBr^-$ complexes. Previous work, involving gas-phase thermochemical data for X^- (CH_3O^-, F^-, Cl^-, Br^-, I^-) and quantum chemical calculations, indicate that the most stable $SB{\cdot}X^-$ complexes might have a variety of structures, depending on X^- and the nature of the substituents. Thus X^- may engage in hydrogen bonding to an aromatic hydrogen atom, or lead to a σ-bonded (Meisenheimer) complex, or form a complex where X^- is on an axis perpendicular to the benzene plane. A Taft substituent analysis of the $\delta\Delta G_1^\circ$ indicates that Br^- and Cl^- form aromatic C-H hydrogen-bonded complexes with all singly substituted benzenes. The field effects of the substituents provide the dominant contribution to the bonding in these complexes. Similar conclusions are reached also for the singly substituted nitrobenzenes and Br^-. A clearcut analysis of the bonding to Br^- when triply substituted benzenes with strongly electron withdrawing substituents like CF_3, CN, and NO_2 are present could not be obtained. In these cases all three bonding structures mentioned above may have similar stabilities.

Introduction

The formation of complexes between X^- (CH_3O^-, F^-, Cl^-, Br^-, and I^-) and substituted benzenes (SB) is of interest in gas-phase ion chemistry and condensed-phase organic chemistry.

The formation energies of complexes $(XSB)^-$ from X^- and SB can be obtained by measurement of equilibria 1 and 2 in the gas phase with suitable mass spectrometric apparatus.[1] Many

$$X^- + SB = (XSB)^- \qquad (1)$$

$$(XSB')^- + SB'' = (XSB'')^- + SB' \qquad (2)$$

measurements involving X^- and particularly F^- and Cl^- and a variety of compounds other than substituted benzenes have been reported by this[2] and other laboratories.[3,4] In the present work, we restrict the discussion to substituted benzenes. Furthermore we will exclude substituents which have protic hydrogens such as CO_2H, OH, and NH_2, which engage in strong hydrogen bonding to X^-. These benzoic acids, phenols, and amines represent a different class of compounds which are considered elsewhere.[5]

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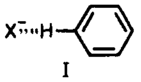
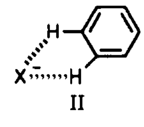
The complexes dealt with here are those in which X^- bonds to the benzene moiety. Since the equilibrium determinations provide information on the energetics but not on the structure of the complexes, quantum mechanical calculations have been essential for the understanding of the type of bonding and structures that are present. Depending on the nature of the substituents and X^- an interesting variety of most stable structures can occur. The most important ones, I–IV, are shown below. For simplicity the substituent(s) have been omitted from the structures.



I



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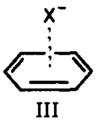
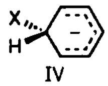


III



IV

Earlier work[2d] on equilibria 1 involving Cl^- and a few substituted benzenes, which included also minimal basis set (STO-3G) calculations, indicated that structure I is the most stable one for benzene and singly substituted benzenes. π-donor, σ-acceptor substituents lead to complexes I where Cl^- interacts with the C–H hydrogen in a position meta to the substituent although the interaction with the para C–H is only slightly weaker. Recent calculations with larger basis sets (3-21G) by Hiraoka, Mizuse, and Yamabe[6] for F^-, Cl^-, Br^-, and unsubstituted benzene also predict structure I to be the most stable, while structure II is predicted to be most stable for the I^- complex with benzene.

Mulliken electron population analysis[6] indicates significant electron transfer from X^- to C_6H_6 only for $F^-\cdot C_6H_6$. The extent of electron transfer decreases rapidly for Cl^-, Br^-, and I^-. The bonding structure I for F^-, Cl^-, and Br^- can be considered as a $C–H\cdots X^-$ hydrogen bond, while that for I^- and structure II is a bifurcated H bond.[6] The bonds become progressively more electrostatic from F^- to I^- and the bifurcated H bond with I^- is a classical electrostatic structure. The tendency for I^- to form bifurcated H bonds has been observed also in complexes with other molecules.[2g]

Strongly π and σ electron accepting substituents like NO_2 can be expected to increase the $C–H\cdots X^-$ bond strength; however, in the presence of such substituents and for small X^- like F^- and CH_3O^- which can form strong covalent bonds, the most stable structure may not be I but the σ bonded complex IV. σ bonded complexes like IV are well-known. Thus, multiple NO_2 substitution as in 1,3,5-trinitrobenzene and F^- and CH_3O^- leads to stable σ bonded complexes (Meisenheimer–Jackson complexes) which are well-characterized in solution.[7] σ complexes of this type are of special interest in the gas phase[8] as well as in solution,[7] since they are probable intermediates in aromatic substitution reactions involving nucleophiles X^-.

Recent calculations[9] dealing with the complex formed by F^- and nitrobenzene, using 3-21G plus polarization basis sets, predict structure I to be the most stable and the C–H involved in the bond is in the position para to the nitro group. The σ complex, structure IV, where F^- inserts in the para position to the nitro group, is only somewhat less stable. The bond energies, $-\Delta E_1$, in the two structures are predicted as ~27 and ~22 kcal/mol.[9] This is much higher than $-\Delta E_1 \approx -\Delta H_1 \approx 15$ kcal/mol for the $C–H–F^-$ bonded complex with unsubstituted benzene.[6]

The complex III, where X^- lies on an axis perpendicular to the benzene plane, is not a charge transfer complex. While electron transfer from X^- to the LUMO of benzene might appear to be a distinct possibility, the relatively high electron affinity of X and electrostatics[10] hinder the formation of a π complex. Thus the negative quadrupole moment of benzene, $Q_{zz} = -8.7 \times 10^{-26}$ esu,[11] which is perpendicular to the plane of benzene, leads to a significant electrostatic repulsion between X^- and benzene and a low stability of the axial complex III, when unsubstituted benzene is involved.[10] However structures III have been predicted by Hiraoka, Mizuse, and Yamabe[12a] to be the most stable complexes when the highly substituted benzene, C_6F_6, and $X^- = Cl^-$, Br^-, and I^- are involved. On the other hand F^- and CH_3O^- form a σ complex with hexafluorobenzene.[12b,13]

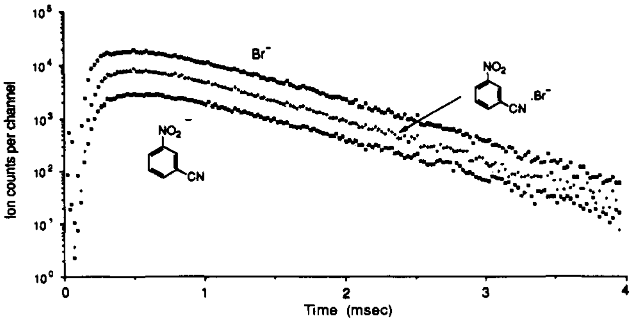


Figure 1. Ion intensities, presented as ion counts per 10 μs channel width, observed after ~20 μs electron pulse. Gas mixture in ion source: 2.8 Torr of CH_4 (bath gas), 2.1 mtorr of CH_2Br_2, 0.65 mtorr of *m*-cyanonitrobenzene (*m*-CNNB). Ion source temperature 423 K. Br^- association equilibrium Br^- + *m*-CNNB = *m*-CNNB·Br^- establishes after ~0.5 ms. The *m*-cyanonitrobenzene radical anion, which does not participate in the equilibrium, is due to direct electron capture by *m*-CNNB. The three ions shown represent ~95% of the total ions. The observed slow decrease of ion intensities with time is due to ion diffusion to walls of the ion source.

The stability of the axial structures III of C_6F_6 and Cl^-, Br^-, and I^- is due to the high electronegativity of the fluorine substituent. The experimentally measured quadrupole moment[11] Q_{zz} in C_6F_6 is $Q_{zz} = +9.5 \times 10^{-26}$ esu, i.e. reversed when compared to that of C_6H_6, and attractive to negative ions. This reversal must be due to the strong effect of the large $C^+–F^-$ bond dipoles in C_6F_6. The axial $X^-C_6F_6$ complex is described as being largely electrostatically bonded.[12a] Other strong electron withdrawing substituents like CN, CF_3, and NO_2, when present in multiple substitution in benzene, also should promote the formation of the axial electrostatic complex III with the larger nucleophiles, Cl^-, Br^-, I^-.

From the discussion presented above it becomes evident that structures I–IV could be occurring with different X^- and differently substituted benzenes and that some effort is required to arrive at a prediction for the most stable complex under certain given circumstances. In the present paper experimentally determined bond energies based on determination of equilibria 1 with $X^- = Br^-$ and singly, doubly, and triply substituted benzenes are reported. The singly substituted benzene complexes are subjected to substituent effect analysis following Taft.[14] This analysis provides very useful supplementary information which, when combined with the structural information discussed above, permits bonding structural assignments to be made. These extend also over complexes involving Cl^- and NO_2^- whose equilibria were measured in previous work. Experimental data and theoretical calculations involving F^-, Cl^-, Br^-, singly substituted perfluorobenzenes and Br^-, and perfluoroquinones and tetracyanoethylene will be reported in subsequent publications.[9]

Experimental Section

The measurement of equilibria 1 with $X^- = Br^-$ was performed with a pulsed high-pressure mass spectrometer (PHPMS). The apparatus and methodology have been described previously.[1,5,15]

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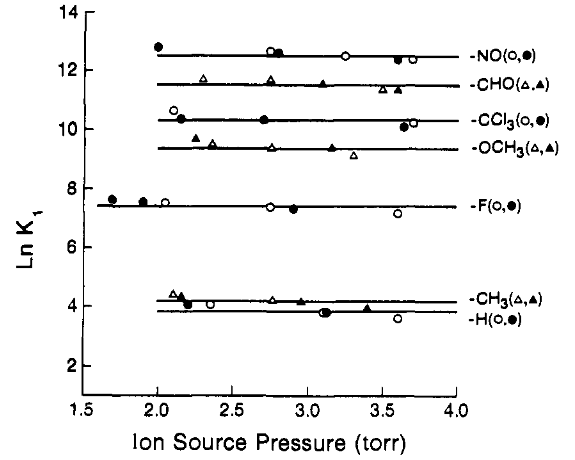

Figure 2. Representative results for equilibrium constants K_1 of the reaction $Br^- + YC_6H_5 = YC_6H_5{\cdot}Br^-$ at different total ion source pressures. Empty and full symbols for a given YC_6H_5 correspond to K_1 determined at two different C_6H_5Y/methane ratios. Generally, the ratio was changed by a factor of ~4.

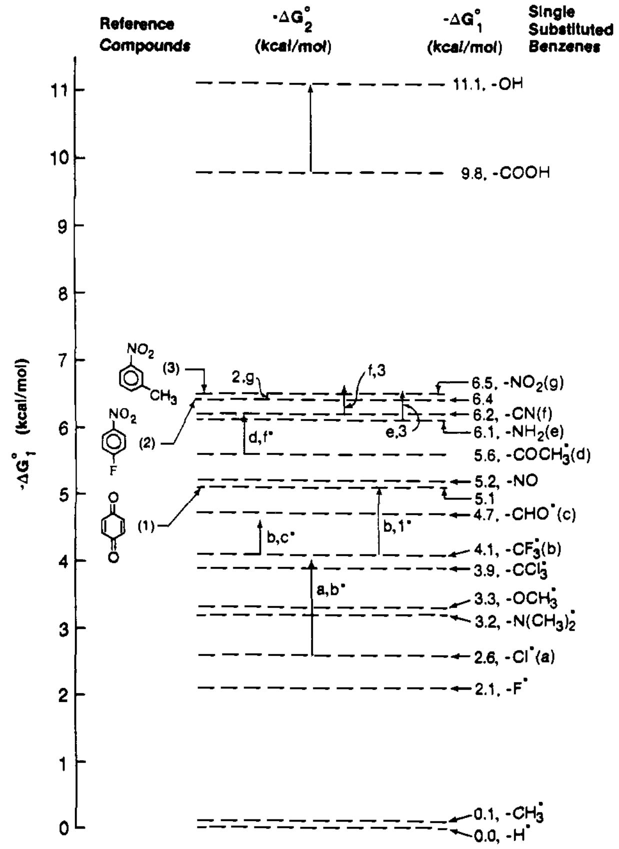

Figure 3. Scale of $-\Delta G_1^\circ$ ($X-Br^-$) for singly substituted benzenes. The ΔG_1° values of weakly bonded complexes were measured at 303 K and recalculated to 423 K with use of $\Delta S_1^\circ = -20.2$ cal deg^{-1} mol^{-1}. Values obtained in this manner are indicated with an asterisk. All other ΔG_1° values were determined at 423 K. Vertical arrows shown in the figure correspond to ΔG_2° obtained from measurements of Br^- transfer equilibria 2. Numbers and letters beside the arrows identify molecules participating in equilibrium 2.

Table I.[a] Free Energy Change, ΔG°, for Reaction 1 ($Br^- + YC_6H_5 = YC_6H_5{\cdot}Br^-$)

Y	$-\Delta G_1^\circ$(423 K), kcal/mol	Y	$-\Delta G_1^\circ$(423 K), kcal/mol
H	0.0[b]	CHO	4.7[c]
CH_3	0.1[c]	NO	5.2[c]
F	2.1[c]	$COCH_3$	5.6[c]
Cl	2.6[c]	NH_2	6.1
$N(CH_3)_2$	3.2[c]	CN	6.2
OCH_3	3.3[c]	NO_2	6.5
CCl_3	3.9[c]	COOH	9.8
CF_3	4.1[c]	OH	11.1

[a] Data from Figure 3. C_6H_5Y are substituted benzenes. Standard state 1 atm (423 K). Approximate $-\Delta H_1^\circ$ values can be obtained from $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$ and ΔS° values given below. [b] Bond free energy determined at 303 K. $-\Delta G_1^\circ(C_6H_6)$ at 423 K estimated with $-\Delta S_1^\circ = 17.0$ cal deg^{-1} mol^{-1}, see text. [c] Bond free energy determined at 303 K. $-\Delta G_1^\circ$ at 423 K estimated with $-\Delta S_1^\circ$(NB) = 20.2 cal deg^{-1} mol^{-1}, see Figure 5.

Table II.[a] Free Energy Change, ΔG°, for Reaction 1 ($Br^- + SB = SB{\cdot}Br^-$) Involving Singly and Doubly Substituted Nitrobenzenes

SB	$-\Delta G_1^\circ$(423 K), kcal/mol	SB	$-\Delta G_1^\circ$(423 K), kcal/mol
2-CH_3NB	6.1[b]	2-CHONB	9.1
3-CH_3NB	6.5	3-CHONB	10.3
4-CH_3NB	6.8[b]	2-CNNB	11.5
NB	6.5	3-CNNB	11.1
2-FNB	8.2	4-CNNB	9.2
3-FNB	7.9	2-NO_2NB	11.6
4-FNB	6.4	3-NO_2NB	10.9
2-ClNB	7.7	4-NO_2NB	9.2
3-ClNB	8.1	3,5-$(CF_3)_2$NB	8.2
4-ClNB	6.7	3-NO_2-5-CF_3NB·	10.4
2-CF_3NB	9.8	3-NO_2-5-CNNB	12.2
3-CF_3NB	9.1	3,5-$(NO_2)_2$NB	13.1
4-CF_3NB	7.0		

[a] Data from Figure 4. Standard state 1 atm. Approximate $-\Delta H_1^\circ$ values can be obtained from $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$ and $\Delta S^\circ \approx 22.3$ cal deg^{-1} mol^{-1}. [b] Bond free energy determined at 303 K. $-\Delta G_1^\circ$ estimated with $-\Delta S_1^\circ$(3-CF_3NB) = 22.3 cal deg^{-1} mol^{-1}, see Figure 5.

In order to be able to obtain data for a large number of substituted benzenes, the majority of the equilibrium determinations were performed at a constant temperature: 303 K for the more weakly bonded complexes and 423 K for the strongly bonded ones. Typical data leading to the evaluation of the equilibrium constant K are shown in Figure 1. Secondary electrons produced by the ionization of the bath gas CH_4 with a pulse of electrons led to Br^- by dissociative electron capture involving CH_2Br_2. Equilibrium 1 establishes rapidly and K_1 can be evaluated from the mass spectrometrically determined equilibrium concentration ratio of $SBBr^-$ and Br^- and the known concentration of SB in the ion source. For every given SB compound, it was established that K_1 was invariant with the SB/methane partial pressure ratio and with changes of total pressure at a constant SB/methane ratio. For some typical results see Figure 2. Additional data are included in ref 16.

The free energy changes $-\Delta G_1^\circ$ obtained with eq 3 were combined in

$$-\Delta G_1^\circ = RT \ln K_1 \tag{3}$$

scales of gradually increasing $-\Delta G_1^\circ$ values. These are shown in Figure 3 for singly substituted benzenes and Figure 4 for singly and doubly substituted nitrobenzenes.

In order to examine the consistency of the results some Br^- transfer equilibria involving two given SB, see eq 2, were determined also. The resulting ΔG_2° provide differences of the ΔG_1° involving the corresponding two SB. It is clear from Figures 3 and 4 that the ΔG_2° are consistent with the difference of the ΔG_1° values to within ~0.2 kcal/mol.

The entropy changes ΔS° for a series of related association reactions like (1) are often found to be relatively independent of the nature of the molecule. In order to verify this, the temperature dependence of equilibria 1 with Br^- and nitrobenzene and *m*-(trifluoromethyl)nitrobenzene was determined. The van't Hoff plots obtained from these data are shown in Figure 5, and the resulting ΔH_1° and ΔS_1° are given in the figure caption. The ΔS_1° are -20.2 (nitrobenzene) and -22.3 (*m*-(trifluoromethyl)nitrobenzene) cal deg^{-1} mol^{-1}.

The ΔS_1° values determined above are fairly close and this indicates that good estimates of the ΔG_1° values at the same temperature (423 K) can be obtained by assuming the same ΔS_1° for the whole series of com-

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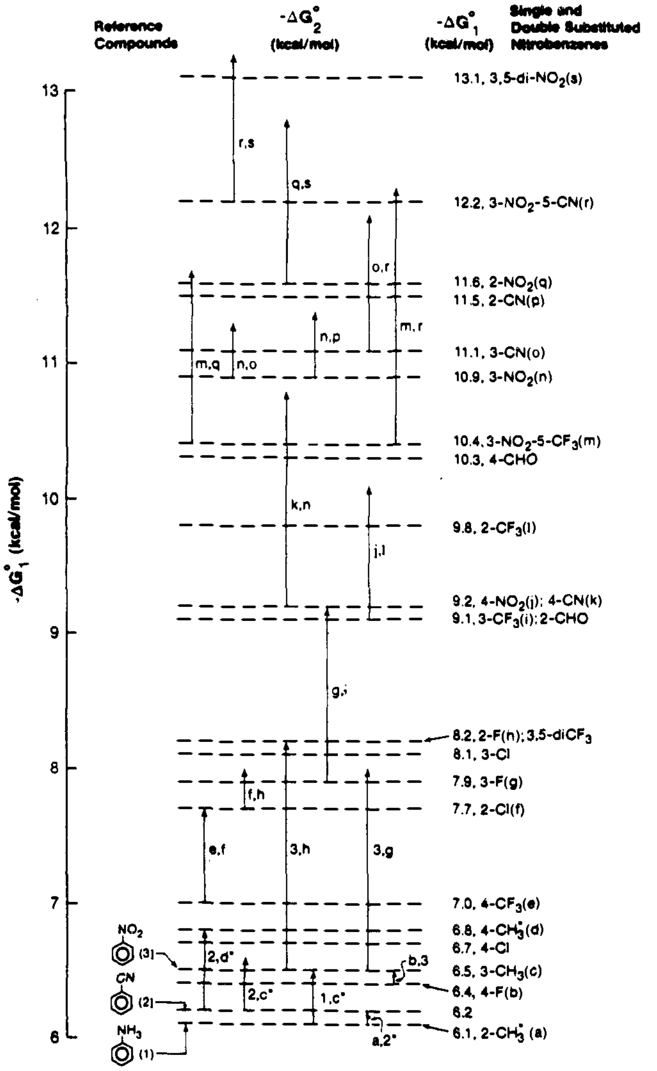


Figure 4. Same as Figure 2 but for substituted nitrobenzenes.

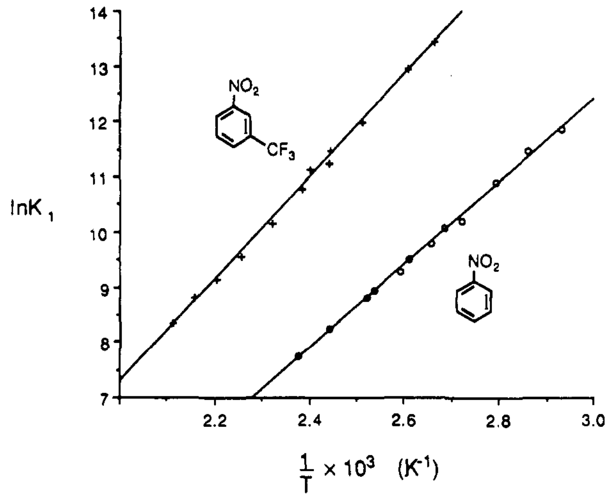


Figure 5. van't Hoff plots of equilibrium constants K_1 for equilibria of Br^- with nitrobenzene and m-(trifluoromethyl)nitrobenzene. Slope and intercept lead to $\Delta H^\circ_1(NB) = -15.0$ kcal/mol, $\Delta S^\circ_1(NB) = -20.2$ cal/(deg mol) and $\Delta H^\circ_1(m\text{-}CF_3NB) = -18.4$ kcal/mol, $\Delta S^\circ_1(m\text{-}CF_3NB) = -22.3$ cal/(deg mol).

pounds. The ΔG°_1 obtained at 303 K for the singly substituted benzenes were recalculated to 423 K by using $\Delta S^\circ_1 = -20.2$ cal deg^{-1} mol^{-1} for all of these compounds (see Figure 2). Benzene has a high rotational symmetry number, $\sigma = 12$, and is the only compound for which formation of the Br^- complex, presumed to be of structure I and $\sigma = 2$, leads to a large rotational entropy symmetry change: $\Delta S = R \ln 6 = 3.5$ cal deg^{-1} mol^{-1}. Therefore, only for benzene the ΔG°_1 from 303 to 423 K was recalculated by using $\Delta S^\circ_1 = -17$ cal deg^{-1} mol^{-1}.

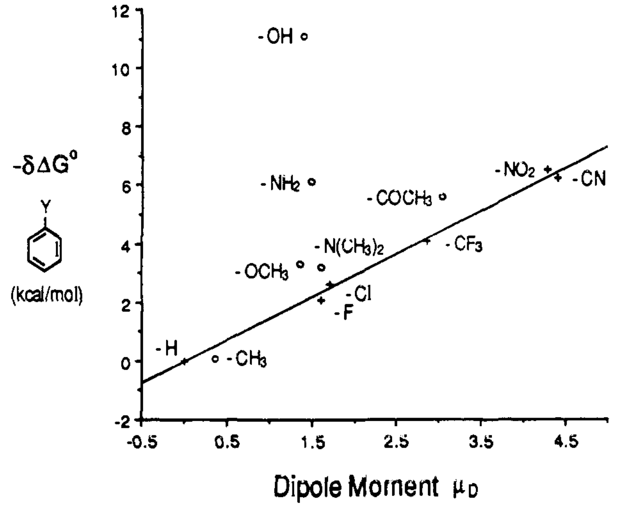


Figure 6. Bond free energies ($\delta\Delta G^\circ_4$ at 423 K (for the reaction $C_6G_6Br^0 + YC_6H_5 = C_6H_6 + YC_6H_5{\cdot}Br^-$ versus dipole moments of substituted benzenes, C_6H_5Y. Substituents Y are given in the figure. The results for hydrogen bonding substituents, OH and NH_2 are from Paul.[5b]

The ΔG°_1 data are summarized in Tables I and II. Approximate ΔH°_1 values can be obtained from $\Delta H = \Delta G + T\Delta S$ and the ΔG°_1 values given in Tables I and II by assuming $\Delta S^\circ_1 = -20$ cal deg^{-1} mol^{-1} for all compounds in Table I except benzene, where $\Delta S^\circ_1 = -17$ cal deg^{-1} mol^{-1}. For the compounds in Table II, $\Delta S^\circ_1 = -22$ cal deg^{-1} mol^{-1} may be more appropriate.

The $-\Delta G^\circ_1$ value for Br^- and C_6H_6 is 1.8 kcal/mol lower than the value reported by Hiraoka et al.[6] The reason for this discrepancy is not known.

Discussion

(a) Singly Substituted Benzenes. The experimentally determined bond free energies, ($-\Delta G^\circ_1$, Table I) for the complexes between Br^- and C_6H_5Y are seen to increase as the substituent Y becomes more strongly electron withdrawing. Extrapolating the theoretical result[9] for $NO_2C_6H_5{\cdot}F^-$ which predicted the most stable structure to be the $C\text{-}H{\cdots}F^-$ hydrogen bonded complex I, see Introduction, where F^- is interacting with the C–H hydrogen in the position para to the NO_2, we assume that all the singly substituted benzene Br^- complexes are C–H hydrogen bonded, i.e. have structure I. Since Br^- has a much lower tendency to form σ bonds when compared to F^-, the theoretical result[9] certainly excludes the σ bonded structure IV as a possibility for $YC_6H_5{\cdots}Br^-$.

The $\delta\Delta G^\circ_1$ relative to Y = H as substituent, corresponding to the free energy change for reaction 4, and evaluated from the ΔG°_1

$$C_6H_6{\cdot}Br^- + YC_6H_5 = C_6H_6 + YC_6H_5{\cdot}Br^- \qquad (4)$$

data in Table I are shown in Figure 6 plotted versus the dipole moment of the substituted benzenes. A fair straight line correlation is observed, when the strongly H bonding substituents[5] OH and NH_2 are excluded. The relationship is consistent with $C\text{-}H{\cdots}X^-$ hydrogen bonding and indicates that the field effect of the substituent will be the dominant substituent effect.

In the following discussion we will make use of the substituent effect concepts developed by Taft et al.[14] In eq 5, the total energy change, $-\delta\Delta G$, due to a given substituent is separated into con-

$$\delta\Delta G^\circ = \rho_R\sigma_R + \rho_F\sigma_F + \rho_\alpha\sigma_\alpha \qquad (5)$$

tributions due to the resonance ($R = \rho_R\sigma_R$), the field effect ($F = \rho_F\sigma_F$), and its polarizability ($P = \rho_\alpha\sigma_\alpha$), and the σ parameters are constants for the given substituent and are tabulated[14] while the ρ values are dependent at the given reaction series and are determined by best fit regression analysis to the experimental $-\delta\Delta G$ values.

The experimentally determined $\delta\Delta G^\circ_1$ versus the calculated $\delta\Delta G^\circ_1$, with the best fit parameters, are shown in Figure 7. A very good correlation (correlation coefficient $r = 0.990$) is ob-

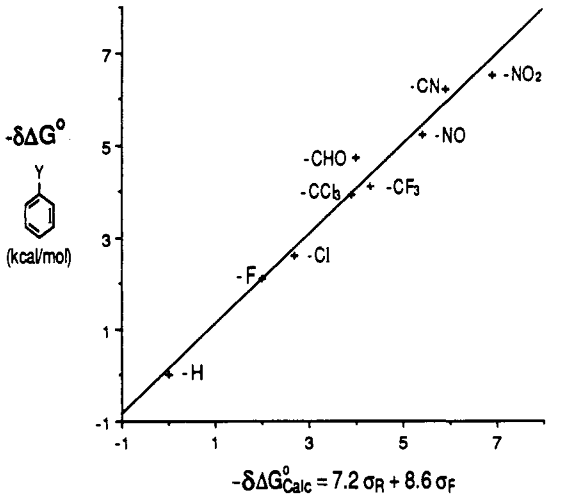


Figure 7. Comparison of experimental and evaluated (see eq 5) $\delta\Delta G°$ at 423 K, for singly substituted benzenes and Br^-. Values of ρ_R and ρ_F are also given in the figure. For a summary of ρ values see Table III.

Table III. Values for Resonance (ρ_R), Field (ρ_F), and Polarizability (ρ_α) Parameters, Taft Equation 5[a]

reaction	ρ_R	ρ_F	ρ_α	r^b	origin of data
$YC_6H_5 \cdot Br^-$ [a]	7.2 ± 0.8	8.6 ± 0.3	0	0.987	Table I
	7.0 ± 0.8	8.3 ± 0.5	−0.5 ± 0.6	0.990	
$YC_6H_5 \cdot Cl^-$ [a]	6.6 ± 0.6	9.1 ± 0.2	0	0.998	Table V
	6.4 ± 0.5	8.9 ± 0.4	−0.5 ± 0.7	0.999	
4-$YPhCO_2H$ [c]	14.6 ± 0.7	15.0 ± 0.6	0.1 ± 1.0	0.997	Taft[14]
4-YPhOH [c]	49.0 ± 1.5	18.6 ± 0.5	0.6 ± 0.8	0.999	Taft[14]
π acceptors					

[a] ρ values obtained from a linear regression analysis of eq 5, where $\delta\Delta G°$ corresponds to experimentally determined $\Delta G°$ for the reaction $YC_6H_5 + C_6H_6 \cdot X^- = YC_6H_5 \cdot X^- + C_6H_6$ ($X^- = Br^-, Cl^-$). [b] Correlation coefficient. [c] Gas-phase acidities.

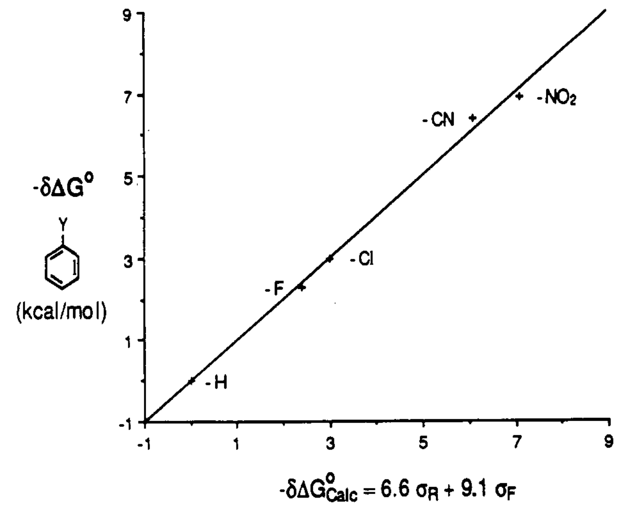


Figure 8. Comparison of experimental and evaluated (see eq 5) $\delta\Delta G°$ at 423 K, for singly substituted benzenes and Cl^-. Values of ρ_R and ρ_F are also given in the figure. For a summary of ρ values see Table III.

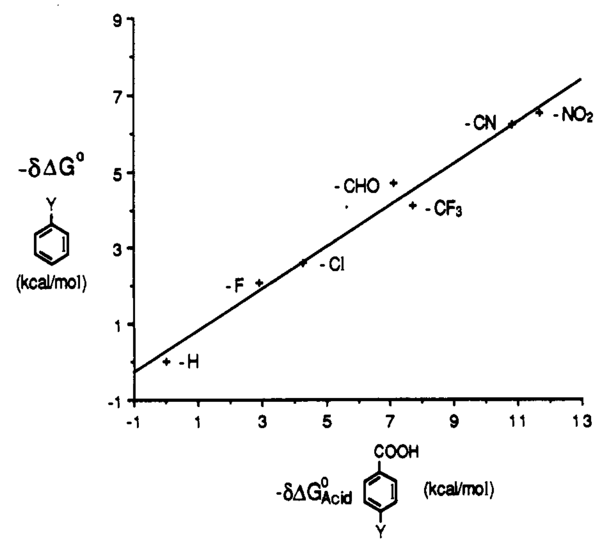


Figure 9. Comparison of substituent effects on bonding in complexes of Br^- with C_6H_5Y and on acid dissociation ($YC_6H_5CO_2H = YC_6H_5CO_2^- + H^+$) in the gas phase.

served. The ρ values obtained from the fit are given in Table III. It was found that inclusion of the polarizability term improved the fit very little and had only a very small effect on the ρ_R and ρ_F values (see Table III). Therefore, for simplicity, the discussion will be based on the field and resonance effects only.

In order to provide an illustration of the actual magnitude of the energy contribution of the resonance and field effect to the binding free energies, the evaluated $R = \rho_R\sigma_R$ and $F = \rho_F\sigma_F$ are given in Table IV. Examination of these data shows that even for substituents like NO_2, which are strong π acceptors, the R energy term is close to five times smaller than the F term. This result, which shows that electrostatic field effects dominate the bond interactions, is in line with the dependence on the dipole moments observed in Figure 6.

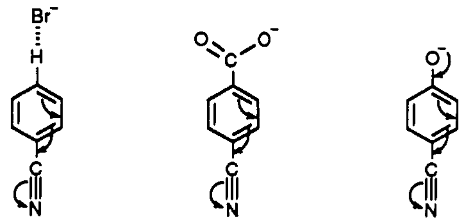
More limited data for the $\Delta G°_1$, $X^- = Cl^-$, shown in Table V, are available from previous determinations performed in this laboratory. These were used to obtain the plot shown in Figure 8. The bonding energies of Cl^- to the substituted benzenes are only slightly larger than those for Br^-, and this is reflected in the similarity of the resulting ρ values obtained from the two sets of data (see Figures 7 and 8 and Tables III and IV).

Also given in Table III for comparison are the ρ values for the gas phase acid dissociation eq 6 of benzoic acids and phenols obtained from the corresponding $\delta\Delta G$ values.[14] The acid dis-

$$AH = A^- + H^+ \qquad (6)$$

sociation reactions have played an important role in the development of the treatment of substituent effects.[14] The ρ_R and ρ_F values, Table III, are ~7 and ~9 fo Cl^- and Br^-, ~14 and ~15 for para-substituted benzoic acids, and ~49 and 19 for the para-substituted phenols. Thus, the ratio ρ_R/ρ_F for the Cl^- and Br^- complexes is very similar to that for the acidities of benzoic acids while the resonance effect is relatively much larger for the phenols. Correspondingly a good linear correlation is observed between the substituent effect on the Br^- bond energies and the acidities of benzoic acids (See Figure 9, correlation coefficient $r = 0.991$), while a much poorer correlation $r = 0.956$ is obtained from a plot of the same bond energies versus the phenol acidities (plot not shown).[17]

The similarity in the relative F and R effects of the Cl^-, Br^- bonding energies with those for the acidities of the benzoic acids is expected on the basis of the major contributing resonance structures for the anions occurring in these systems, shown below for the CN substituent as example. These resonance structures are very much less important than the direct into the ring conjugation occurring for the phenoxide anion, see below.



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[17] Only the σ acceptor, π acceptor substituents (CF_3, CHO, NO, CN, NO_2) were used in the plot of phenol acidities, since π donor substituents lead to a separate correlation.[14]

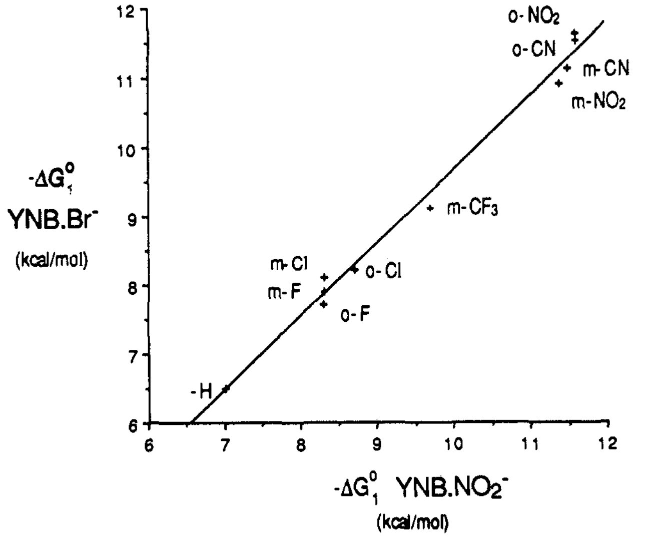


Figure 10. Correlation between bond free energies in complexes of Br$^-$ and of NO_2^- with substituted nitrobenzenes (YNB). ΔG_1° values at 423 K.

The contribution of resonance to the bonding in the Cl$^-$, Br$^-$ complexes with YC_6H_5 and particularly where strongly π accepting substituents like CN, NO_2, and CHO are involved can be viewed as consisting of two parts. One is the favorable charge distribution induced in the neutral YC_6H_5. The second part would be the enhancement of the same type of resonance structure on approach of the negative ion.

The application of the Taft relationship in eq 5 to the Br$^-$ and Cl$^-$ bonding to the singly substituted benzenes implies that the position of the C–H···X$^-$ hydrogen bond relative to that of the substituent remains constant and we assume that for strongly electron withdrawing σ and π acceptor substituents CF_3, CHO, CN, and NO_2 the C–H···X$^-$ bond forms in the position para to the substituent. For π donor substituents like F and Cl, the bond will be para to the substituent only if the field effect is completely dominant. However, since π donation by the substituent increases the negative charge in the para position, H bonding meta to the substituent cannot be excluded. In fact, as mentioned in the Introduction, the STO-3G calculations[1d] predict for fluorobenzene and Cl$^-$ that the meta C–H bond is slightly stronger, $-\Delta E_1 = 10.8$ kcal/mol, than that for the para position, $-\Delta E_1 = 10.3$ kcal/mol. The difference is very small and essentially compatible with near dominance of the field effect. Therefore, the fact that the most stable C–H bond may actually be in the position meta to the π donor substituents does not invalidate the use of the Taft relationship. This is also indicated by the relatively good fit observed in the plots, Figures 7 and 8.

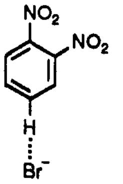
The fact that a good correlation is obtained with Taft's substituent effect relationship strongly suggests that the type of bonding, i.e. structure I for the $YC_6H_5{\cdot}X^-$ (X^- = Cl$^-$, Br$^-$), is preserved throughout the whole series of singly substituted benzenes. That is, not only a change over to the σ bonded complexes IV but also a change over to the axial electrostatic complexes III can be excluded for this series.

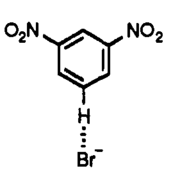
(b) Multiply Substituted Benzenes. The experimental bond free energies $-\Delta G_1^\circ$ for Br$^-$ and multiply subsituted benzenes are summarized in Table II. All the doubly substituted benzenes have one NO_2 substituent, i.e. are singly substituted nitrobenzenes (YNB).

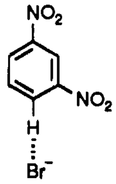
The bonding trends with the relative position of the substituents depend on the nature of the second substituent. Thus for the strongly σ and π accepting substituents, increases are observed to occur in the order para, meta, ortho, as illustrated by the $-\Delta G_1^\circ$ values, in kcal/mol, quoted below:

p-CF_3NB	m-CF_3NB	o-CF_3NB
7.0	9.1	9.8
p-CNNB	m-CNNB	o-CNNB
9.2	11.1	11.5
p-NO_2NB	m-NO_2NB	o-NO_2NB
9.2	10.9	11.6

As was shown in section a, the field effect for these substituents was dominant. On this basis, the order para < meta < ortho could have been expected since the alignment of the substituent-produced dipoles with the negative ion becomes progressively more favorable in the above order. This is illustrated in structure V for the o-NO_2NB·Br$^-$ complex. It is also likely that for m-NO_2NB, structure VI which maximizes the field effect is slightly more stable than VII which maximizes the resonance stabilization.


V

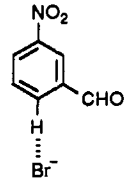

VI

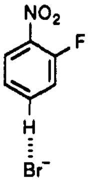

VII

It is interesting to note that the CHO-substituted nitrobenzene shows the higher bond energy (kcal/mol) for the meta rather than for the ortho isomer:

m-CHONB	o-CHONB
10.3	9.1

For the complex of m-CHONB with Br$^-$, structure VIII may be expected. The bond energy order meta > para and structure VIII are consistent with the known[14] large resonance and small field contribution of the CHO substituent. Therefore for CHO a structure like VIII which maximizes the resonance contribution while the dipole orientation is less favorable appears most likely.


VIII


IX

The order of Br$^-$ bonding energies for F–NB is para < meta ≤ ortho (Table II). This indicates a structure as in IX. The result ortho < meta observed for ClNB is difficult to understand.

The Br$^-$ bonding to methyl-substituted nitrobenzenes increases in the order ortho < meta < para (see Table II). Clearly the situation here is very different. Probably, the Br$^-$ bonds not to a benzene but to one of the methyl hydrogens. The early STO-3G calculations[1d] for bonding of Cl$^-$ to toluene predicted that bonding to the methyl hydrogen is only slightly less favorable than that to the aromatic H. The presence of the nitro group in the present case can be expected to make bonding to the methyl hydrogen more favorable and particularly so for the p-MeNB, and this conforms to the observed order in Table II.

Equilibria and $-\Delta G_1^\circ$ values were determined in earlier work of this laboratory[18] for substituted nitrobenzenes and $X^- = NO_2^-$. A comparison of the bond free energies in the complexes YNB·Br$^-$ and YNB·NO_2^- is provided by the plot of Figure 10. A close correlation is observed. Furthermore, the $-\Delta G_1^\circ$ values for Br$^-$ and NO_2^- are seen to be very close. The close correlation suggests that the type of bonding is the same for both negative ions. The negative charge in NO_2^- is delocalized over the two oxygen atoms, and from an electrostatic standpoint, NO_2^- may be viewed as an ion with a radius similar to that of Br$^-$. The similarity of bonding is thus not surprising.

In the discussion above, it was assumed that aromatic C–H, hydrogen bonding, see structure I, occurs for the singly substituted nitrobenzenes, except for the nitrotoluenes. This assumption is also supported by the magnitudes of the observed changes of the bond free energies $-\Delta G_1^\circ$ on double substitution with the same substituent. The changes in kcal/mol, are shown in Scheme I.

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(18) Grimsrud, E. P.; Chowdhury, S.; Kebarle, P. *Int. J. Mass Spectrum. Ion Proc.* **1986**, *68*, 57.

Table IV. Resonance (*R*) and Field (*F*) Contributions of Substituents[a]

	$YC_6H_5{\cdot}Br^-$ [b]		$YC_6H_5{\cdot}Cl^-$ [c]		4-YPhOH[d]		$4\text{-}YPhCO_2H$ [d]	
substituent	*R*	*F*	*R*	*F*	*R*	*F*	*R*	*F*
NO_2 [f]	1.3	5.6	1.2	5.9	8.8	12.1	2.6	9.8
CN[f]	0.7	5.2	0.7	5.5	4.9	11.2	1.5	9.0
CHO[f]	1.3	2.7			9.3	5.8	2.8	4.7
CF_3 [f]	0.5	3.8			3.4	8.2	1.0	6.6
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cl[g]	−1.2	3.9	−1.1	4.1	*e*	*e*	−2.5	6.8
F[g]	−1.8	3.8	−1.7	4.0	*e*	*e*	−3.7	6.6

[a] Contribution: $R = \rho_R\sigma_R$ and $F = \rho_F\sigma_F$ in kcal/mol to $\delta\Delta G°$, see eq 5, for given substituent. [b] $\delta\Delta G_1^\circ$ for reaction 1, $X^- = Br^-$, involving singly substituted benzenes. [c] $\delta\Delta G_1^\circ$ for reaction 1, $X^- = Cl^-$, involving singly substituted benzenes. [d] $\delta\Delta G°$ for gas-phase acidities of phenols and benzoic acids. [e] π donor substituents require a separate fit, see Taft.[14] [f] π acceptor substituent. [g] π donor substituent.

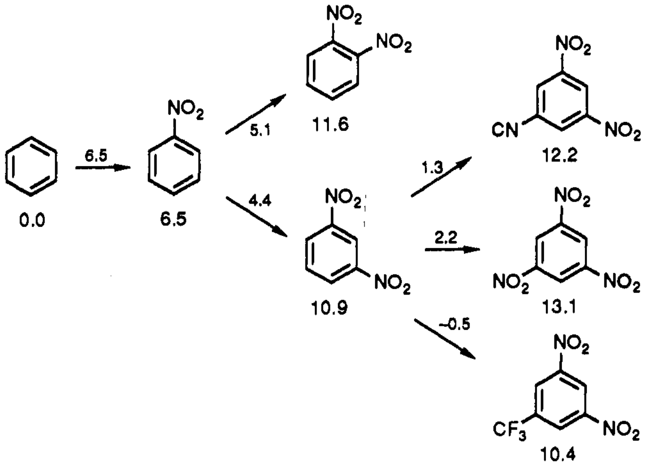
Table V. Thermochemical Data for the Reaction $Cl^- + YC_6H_5 = YC_6H_5Cl^-$

Y	$-\Delta G°$(300 K), kcal/mol
H[d]	3.6,[a] (4.0),[b] 3.8[c]
F	5.9[c]
Cl	6.6,[a] 6.5[c]
CN	10.0[a]
NO_2	10.5[a]

[a] Ph.D. Thesis, Swapan K. Chowdhury, Kinetics and Equilibria of Electron Transfer Reactions. Department of Chemistry, University of Alberta, Edmonton, 1987. [b] Hiraoka et al.[6] [c] French et al.[1d] [d] $-\Delta H° = 9.4$ kcal/mol, $-\Delta S° = 17.9$ cal. deg^{-1} mol^{-1} from Hiraoka et al.[6]

It is seen that the effect of the NO_2 substituent on second substitution is attenuated but not by much, i.e. from 6.5 to 5.1 kcal/mol. This is expected if C–H···X⁻ bonding carries on and the dominant stabilization is the field effect, since it is generally observed that stabilization due to the field effect attenuates much more slowly than that due to resonance.[19,20]

Scheme I



Also given in Scheme I is the bond energy change on introduction of a third substituent. The stabilization due to the third substituent is seen to be strongly attenuated. Assuming that C–H···Br⁻ bonding still leads to the most stable structure in the triply 1,3,5-substituted benzenes, the large decrease of stabilization can be explained as due to the removal, by the third substituent, of the last C–H position, for which the substituent dipoles are still favorably oriented. In the 1,3,5-substituted benzenes, the C–H···Br⁻ bond must occur ortho to two of the substituents and only the resonance stabilization operates for these positions. Furthermore resonance stabilization attenuates significantly with multiple substitution.[19,20]

The discussion, just given, shows that the observed energy changes are consistent with C–H···Br⁻ bonding also in the triply substituted benzenes shown in Scheme I. However, since the tendency toward σ bonded complexes IV and the axial electrostatic complexes III is expected to increase with multiple substitution with CN, CF_3, and NO_2, probably the energies of these Br⁻ complexes come quite close to that of the C–H···Br⁻ complex for the triply substituted benzenes, and for these complexes all three forms of bonding become competitive.

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(19) Taft, R. W.; Abboud, L. M.; Anvia, F.; Berthelot, M.; Fujio, M.; Gal, J. F.; Headley, A. D.; Henderson, W. G.; Koppel, I.; Derian, J. H.; Mishima, M.; Taagepera, M.; Vegi, S. *J. Am. Chem. Soc.* **1988**, *110*, 1797.

(20) Chowdhury, S.; Kishi, H.; Dillow, G. W.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 603.