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Bonding Energies in Association Ions of Aromatic Compounds. Correlations with Ionization Energies

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Abstract: Enthalpies of dissociation, ΔH°_D (kcal mol⁻¹), were measured by temperature studies on the equilibria $(B_1B_2)^+ \rightleftharpoons B_1^+ + B_2$ (B_1 and B_2 = benzene and substituted benzenes). It is observed that ΔH°_D is largest (16 ± 1) in symmetric association ions ($B_1 = B_2$) and decreases to 10 ± 1 as the difference in the ionization potentials of B_1 and B_2 (ΔIP , kcal mol⁻¹) increases. For example, for $(C_6H_6 \cdot C_6H_6)^+ \Delta IP = 0$, $\Delta H^\circ_D = 17.0$; for $(C_6H_6 \cdot C_6F_6)^+ \Delta IP = 16.7$, $\Delta H^\circ_D = 10.5$. Similarly, for $(1,3,5-C_6H_3(CH_3)_3 \cdot 1,3,5-C_6H_3(CH_3)_3)^+ \Delta IP = 0$, $\Delta H^\circ_D = 17.2$; while for $(1,3,5-C_6H_3(CH_3)_3 \cdot C_6H_6)^+ \Delta IP = 19.1$, $\Delta H^\circ_D = 10.6$. Weak bonding ($\Delta H^\circ_D = 11.0$) is also observed in $C_6H_7^+ \cdot C_6H_6$ where the reactant ion is not a radical and in $C_6H_6^+ \cdot c-C_6H_{12}$ ($\Delta H^\circ_D = 9.9$), where the neutral reactant lacks a π system. It is suggested that weak bonding of about 10 kcal mol⁻¹ in the latter association ions and in association ions with large ΔIP is due to electrostatic interactions, while in the aromatic association ions additional bonding of as much as 6 ± 1 kcal mol⁻¹ results from electron delocalization. The measurements were done by pulsed high-pressure mass spectrometry, utilizing soft chemical ionization by charge transfer from CS_2^+ , which should yield cyclic benzene ions in the electronic ground state.

Introduction

Bonding between radical ions and neutral aromatic molecules is of obvious interest in gaseous ion chemistry and mass spectrometry, but it is also of considerable interest in condensed phase chemistry. For example, ion-neutral interactions play a role in determining ionization potentials (IP) in the condensed phase; ionized states, in turn, contribute to conductivity in organic semiconductors.¹ Dimer cations of benzene, naphthalene, perylene, and other aromatic hydrocarbons have been observed in solutions subjected to pulse radiolysis.^{2,3} Benzene and substituted benzenes constitute an obvious and experimentally tractable model for the investigation of relationships between structure and ion-molecule interaction energies in dimer cations of aromatic compounds.

The benzene dimer cation, $(C_6H_6)_2^+$, has been observed in the gas phase by a number of research groups.⁴⁻⁶ Quantitative investigations concerning this ion dealt with the kinetics of the association of $C_6H_6^+$ with C_6H_6 ,⁷⁻⁹ as well as with the enthalpy of dissociation (ΔH°_D) of $(C_6H_6)_2^+$. ΔH°_D was measured by Field and co-workers¹⁰ to be 15 kcal mol⁻¹ using high-pressure mass spectrometry ($P = 0.5-1.5$ Torr) with a continuous mode of ion production and detection. Tiernan and co-workers,⁸ using continuous ionization and somewhat lower pressures ($P = 0.1-0.2$ Torr), obtained a value of $\Delta H^\circ_D = 8 \pm 2$ kcal mol⁻¹. Wexler and Pobo⁷ identified a negative activation energy of 10 kcal mol⁻¹ which they found in the kinetics of the formation of $(C_6H_6)_2^+$ with a lower limit for ΔH°_D . In the condensed phase, ΔH°_D was measured to be 14.8 kcal mol⁻¹ by Badger and Brocklehurst¹¹ using spectroscopic data for the transition between attractive and repulsive states of the dimer cation in solution. The difference between the reported gas-phase values of ΔH°_D may be due in part to failure to achieve equilibrium in either or both of the previous mass spectrometric measurements. Our recent experience has been that the continuous ionization methods used are notoriously unreliable. In addition, the specific identity of the $C_6H_6^+$

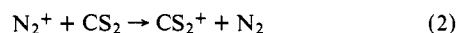
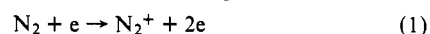
monomer ion, which may be a cyclic ion in either the electronic ground state or an excited state, or an acyclic ion in an undefined electronic state,^{8,12} was ambiguous in previous measurements.

We have redetermined the value of ΔH°_D for the benzene ion dimer by making a temperature study of the association equilibrium $C_6H_6^+ + C_6H_6 \rightleftharpoons (C_6H_6)_2^+$ using a time-resolved high-pressure mass spectrometric technique with which equilibrium can generally be achieved. Furthermore, to increase confidence in the identity of the $C_6H_6^+$ ion, we produced it using a mild chemical ionization method which should yield the ion with a cyclic structure in the ground electronic state. Finally, we extended these measurements to other aromatic ions and molecules.

Experimental Section

Our measurements were performed by pulsed high-pressure mass spectrometry using the Rockefeller University Chemical Physics Mass Spectrometer.^{13,14} Mixtures of the aromatic compounds of interest in a carrier gas were prepared in a gas handling system and allowed to flow into the ion source. Ionizing pulses of 600 V electrons with a duration of 20 μ s initiated reaction sequences leading to the equilibria of interest. The course of the reactions and the attainment of equilibria were monitored by recording the intensities of ions issuing from the source as a function of reaction time.

The reagent gas used was a mixture of 15-30% CS_2 and N_2 . The total pressure ranged from 0.5 to 1.5 Torr, with most measurements made at ~ 0.8 Torr. The sample of interest was an aromatic compound or a mixture of two aromatic compounds. The concentration(s) of aromatics ranged from 0.05 to 5% of the gas mixture, and they were empirically selected so that equilibrium concentrations of the ions of interest were within the dynamic range of the mass spectrometer. With these conditions, ions of the aromatic compounds are generated by the following sequence of chemical ionization processes:



where B is benzene or a substituted benzene. Other processes, such as the direct ionization of CS₂ and the aromatic compounds by electron impact as well as the ionization of the aromatic compounds by N₂⁺, also occur to small extents. However, because of the relative concentrations of the components of the reaction mixture, ionization of the aromatics will be predominantly by reaction 3. Furthermore, the CS₂⁺ reactant ion will collide 20–100 times with N₂ or CS₂ before reacting with the aromatic compounds; thus the aromatic ions are generated by charge transfer from thermalized CS₂⁺. For the reaction of ground-state CS₂⁺ with C₆H₆ the exothermicity is 23.1 kcal mol⁻¹ when the product is benzene ion in the ²E_{1g} ground state. This energy is insufficient to generate C₆H₆⁺ in the ²E_{2g} state, which is 50.8 kcal mol⁻¹ above the ²E_{1g} state, to generate C₆H₆⁺ ions in more highly excited states, or to generate the noncyclic C₆H₆⁺ ions whose appearance potential was measured as 12.8 ± 0.5 eV (296 kcal mol⁻¹) by Tiernan and co-workers.⁸ For the substituted benzene compounds used in the study the exothermicity of charge transfer from CS₂⁺ is 42 kcal mol⁻¹ or less; the ions produced may also be expected to be in their ground electronic states and have cyclic structures. Furthermore, these aromatic ions can undergo 10 000–20 000 collisions with the carrier gas in the course of establishing the association equilibrium. This figure is obtained from considerations of the pressure and the fact that ion residence times of 500 μs or more can be observed in our apparatus. We confidently believe that the association reactions that we observed involved thermalized ground-state aromatic ions.

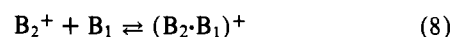
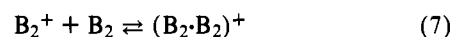
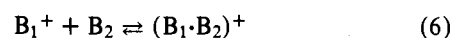
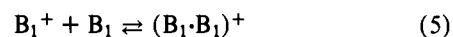
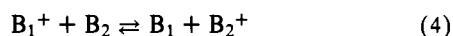
A further indication that chemical ionization by CS₂ produces ground-state cyclic ions can be derived from a previous study from our laboratory.¹⁵ In that work we observed charge transfer equilibria between benzene and substituted benzenes in CS₂ as carrier gas. These equilibria yielded relative ionization energies in good agreement with photoionization values, which indicates that no excited states or acyclic structures were involved.

Benzene and the methylbenzenes used in this work were purchased from Chemical Samples Co. These materials were supplied at purities of 99% or higher and used as supplied. Fluorobenzenes were supplied by PCR Research Chemicals and were of purity 98% or higher. In some experiments where the sample compounds were benzene and fluorobenzenes we observed impurity ions of *m/e* 92 (C₆H₅CH₃⁺) and 106 (C₆H₄(CH₃)₂⁺). The intensities of these ions relative to the intensities of sample ions increased with reaction time, owing to charge transfer from the sample ions. In all instances experiments were conducted under conditions where the buildup of impurity ions was slow compared with the establishment of equilibria in the sample ions. The presence of the impurities thus did not affect the measured equilibrium constants.

Results and Discussion

1. Considerations Concerning Attainment of Equilibrium.

Under the conditions which obtained in our experiments, reactions 1–3 are completed within a few microseconds after the ionizing electron pulse. In those cases where two aromatics (B₁ and B₂) are present, the relative amounts of B₁⁺ and B₂⁺ formed are proportional to the concentrations of B₁ and B₂. These were chosen to make one concentration (that of B₁, let us say) approximately ten times that of the other, and the following scheme is an adequate representation of the reactions occurring:



The charge transfer process 4 is reversible under the present conditions only if the ionization potentials (IP) of the aromatic compounds are sufficiently similar, i.e., within ca. 4 kcal mol⁻¹ of each other. In addition to the formation of symmetric dimer cations in reactions 5 and 7, an asymmetric association ion is formed in reactions 6 and 8. A reversible association of aromatic ions with CS₂ to form (B·CS₂)⁺ is also observed in some cases. Exchange reactions involving the dimer ions are also

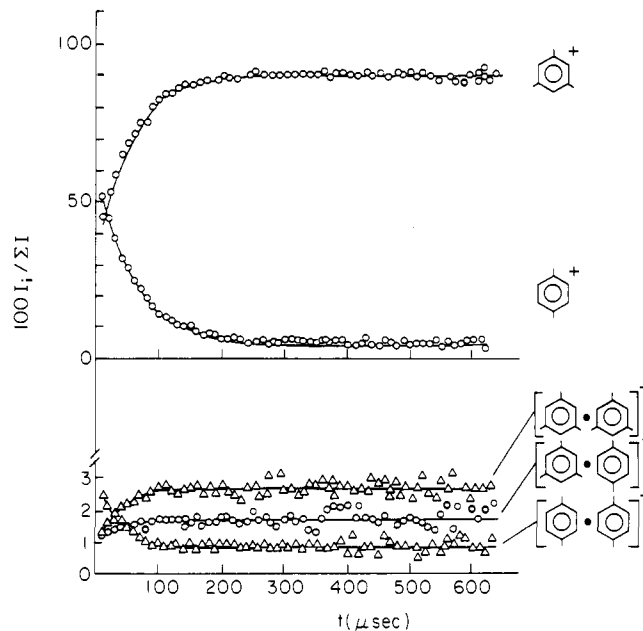
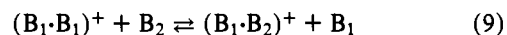


Figure 1. Normalized ion intensities in a mixture of 0.1% 1,3,5-C₆H₃(CH₃)₃ and 1.1% 1,4-C₆H₄(CH₃)₂ in a carrier gas of 30% CS₂ in N₂ at a total source pressure of 0.8 Torr, *T* = 341 K. Some scattering of normalized intensities occurs at long reaction time (*t* > 400 μs) owing to decreased absolute intensities.

possible; for example



The presence of multiple equilibria should not, of course, affect ion concentrations at thermodynamic equilibrium. We wish to point out that in the remainder of this paper we shall for rhetorical simplicity (although with some loss of chemical accuracy) refer to ions like those on the left side of eq 5–8 as reactant ions and to ions like those on the right side of eq 5–8 as association ions. These will sometimes be abbreviated by R⁺ and A⁺, respectively.

The variation of relative ion concentrations as a function of reaction time is determined by the rates of reactions 4–8, and such a variation of normalized ion intensities with reaction time in a sample reaction system is shown in Figure 1. The achievement of constant concentrations of the reactant and association ions after 250 μs indicates that equilibrium is reached in the reaction system. We thus used ion intensities taken from the horizontal, time-independent portions of the ion intensity plots for equilibrium calculations. Equilibrium constants are calculated from the expression

$$K = \frac{I_{B_1 \cdot B_2^+}}{(I_{B_1^+})(P_{B_2})} \quad (10)$$

For one-component systems, B₂ must be replaced by B₁.

The attainment of equilibrium in the formation of association ions was also tested by pressure studies. The results of a pressure study in a system of 1,3,5-C₆H₃(CH₃)₃ and 1,3-C₆H₄(CH₃)₂ is shown in Figure 2. For two of the equilibria shown, *K*_{obsd} values are independent of source pressure between 0.2 and 1.5 Torr. *K*_{obsd} for the formation of (1,3,5-C₆H₃)₂⁺ decreases slightly with pressure. Decrease in *K*_{obsd} at high pressures may be caused by the collisional dissociation of the association ion outside the ion exit slit. This process will convert a fraction of the association ions issuing from the source into reactant ions. Kebarle¹⁶ pointed out that the error that this process introduces into the measured A⁺/R⁺ ratio increases with the value of the ratio. This provides a rationalization of the decrease in *K*_{obsd} found for the reaction producing (1,3,5-C₆H₃(CH₃)₃)₂⁺, which had a high A⁺/R⁺ ratio under

Table I. Thermodynamic Quantities for Association of Benzene Ion with Neutral Molecules, B

$C_6H_6^+ + B \rightleftharpoons (C_6H_6 \cdot B)^+$						
reaction no.	neutral B	$-\Delta H^\circ \pm 1.5,$ kcal mol $^{-1}$	$-\Delta S^\circ \pm 4,$ cal mol $^{-1}$ K $^{-1}$	$-\Delta G^\circ_{300} \pm 1.5,$ kcal mol $^{-1}$	IP of B, kcal mol $^{-1}$	IP(B) - IP(C $_6$ H $_6$), kcal mol $^{-1}$
1	C $_6$ H $_6$	17.0	27	8.9	213.2 ^a	0.0
2	C $_6$ H $_5$ F	17.0	30	8.1	213.4 ^b	0.2
3	1,2-C $_6$ H $_4$ F $_2$	(15.2) ^c	(27)	6.3 ₃₃₀ ^d	214.7 ^a	1.5
4	1,3-C $_6$ H $_4$ F $_2$	13.9	26	6.2	216 ^e	3
5	1,3,5-C $_6$ H $_3$ F $_3$	12.4	28	3.9		
6	1,2,4,5-C $_6$ H $_2$ F $_4$	12.0	27	3.9	217.4 ^b	4.2
7	1,2,3,5-C $_6$ H $_2$ F $_4$	(11.2)	(27)	3.1	220.2 ^a	7.0
8	C $_6$ HF $_5$	(11.2)	(27)	3.1	226.9 ^a	13.7
9	C $_6$ F $_6$	(10.5)	(27)	4.0	229.9 ^a	16.7
10	c-C $_6$ H $_{12}$	(9.9)	(27)	3.2 ₂₉₅	227.8 ^a	14.6
11	CS $_2$	12.2	24	4.9	232.4 ^a	19.2

^a Ionization potentials from ref 24. ^b Ionization potentials from ref 15. ^c Enthalpies in parentheses represent values obtained from the measurement of ΔG° at one temperature and assuming that $-\Delta S^\circ = 27$ cal mol $^{-1}$ K $^{-1}$. ^d ΔG° values given correspond to 300 K, except if specified otherwise by subscript. ^e This ionization potential was obtained from a charge transfer equilibrium observed in this work.

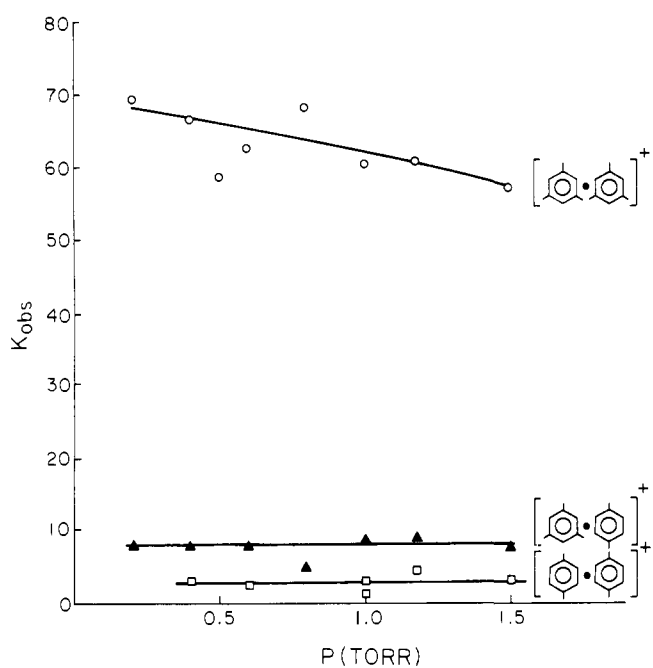


Figure 2. Observed equilibrium constants for the formation of the association ions indicated in the figure as a function of the pressure in a mixture of 0.11% 1,3,5-C $_6$ H $_3$ (CH $_3$) $_3$ + 0.83% 1,4-C $_6$ H $_4$ (CH $_3$) $_2$ in N $_2$ + 21.7% CS $_2$ at $T = 300$ K.

the conditions of Figure 2; i.e., $I(1,3,5-C_6H_3(CH_3)_3)_2^+ / I(1,3,5-C_6H_3(CH_3)_3)^+ = 1.0$ at $P = 1.2$ Torr. This high A^+/R^+ ratio is an atypical extreme case in the present set of measurements. A smaller value of A^+/R^+ , namely, 0.41, obtained in the experiments on 1,4-C $_6$ H $_4$ (CH $_3$) $_2$ referred to in Figure 2, and one can see from Figure 2 that K_{obsd} obtained in this system is independent of pressure. Consequently, to eliminate or minimize the effects of collisional dissociation we performed the equilibrium measurements at low pressures (0.6–1.0 Torr) and mostly under conditions where the A^+/R^+ ratio was kept below 0.5.

For some of the reactions studied, a further check on the attainment of equilibrium was obtained by the determination of the equilibrium constant in a number of different reaction mixtures. Thus, the formation of $(C_6H_6)_2^+$ was observed in reaction mixtures where only benzene was added to the carrier gas and the only equilibrium observed was the association of $C_6H_6^+$ with benzene. Then the formation of $(C_6H_6)_2^+$ was observed in eight reaction mixtures containing benzene and

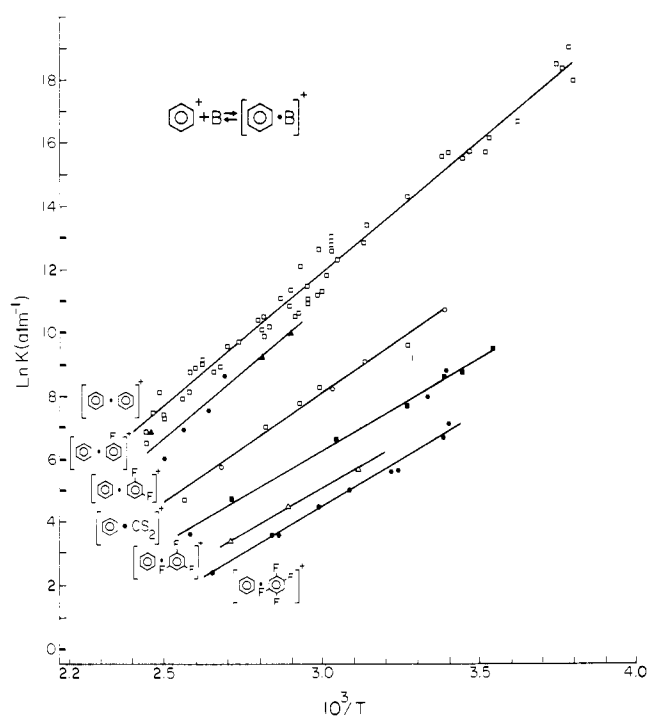


Figure 3. van't Hoff plots for the association of $C_6H_6^+$ with molecules to form the association ions indicated in the figure.

one of the fluorobenzenes listed in Table I. In these mixtures the multiple equilibria described in reactions 4–8 occur. Equilibrium constants for the formation of $(C_6H_6)_2^+$ measured in all of the mixtures were consistent with the van't Hoff plot shown in Figure 3. Similarly, the formation of $(1,3,5-C_6H_3(CH_3)_3)_2^+$ in seven different reaction systems yielded equilibrium constants consistent with the van't Hoff plot shown in Figure 4. Thus equilibrium in the formation of association ions was confirmed by the attainment of constant ion ratios with reaction time and by the constancy of K_{obsd} when the source pressure or the composition of the reaction mixture was varied.

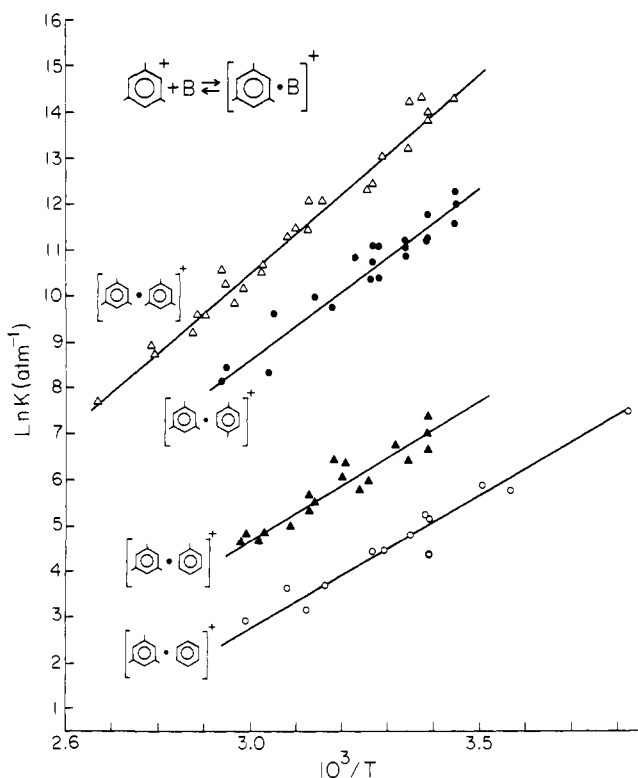
In the present set of measurements we performed temperature studies on 13 association reactions between ions and neutral molecules of aromatic compounds, on the association of $C_6H_6^+$ with CS $_2$, and on the association of the even-electron protonated benzene ion $C_6H_7^+$ with C_6H_6 (Figures 3–5 and Tables I–III). We observed that the $-\Delta S^\circ$ values of all the reactions were in the range 27 ± 3 cal mol $^{-1}$ K $^{-1}$ (except re-

Table II. Thermodynamic Quantities for the Association of 1,3,5-Trimethylbenzene Ion with Neutral Molecules, B

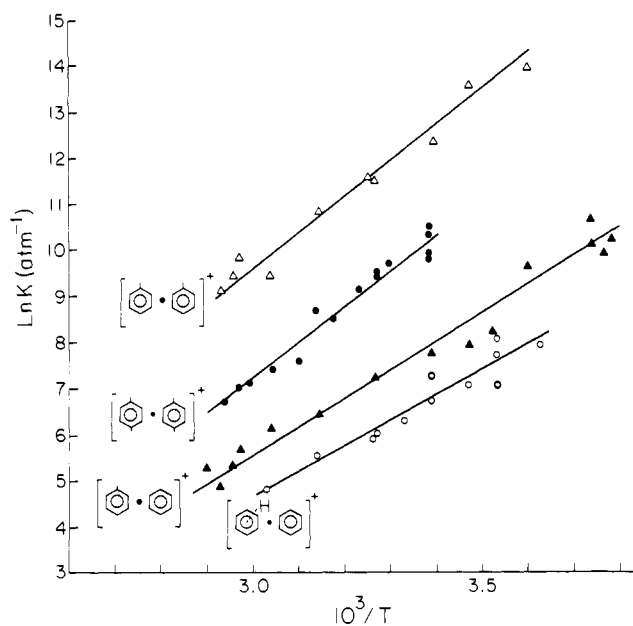
1,3,5-C ₆ H ₃ (CH ₃) ₃ ⁺ + B ⇌ (1,3,5-C ₆ H ₃ (CH ₃) ₃ ·B) ⁺						
reaction no.	neutral, B	-ΔH° ± 1.5, kcal mol ⁻¹	-ΔS° ± 4, cal mol ⁻¹ K ⁻¹	-ΔG° ₃₀₀ ± 1.5, kcal mol ⁻¹	IP of B, kcal mol ⁻¹	IP(B) - IP(C ₆ H ₃ (CH ₃) ₃), kcal mol ⁻¹
12	1,3,5-C ₆ H ₃ (CH ₃) ₃	17.2	30	8.0	194.1 ^b	0.0
13	1,4-C ₆ H ₄ (CH ₃) ₂	14.9	28	6.6	195.6 ^a	1.5
14	1,3-C ₆ H ₄ (CH ₃) ₂	(14.3)	(27)	6.2	197.4 ^a	3.3
15	C ₆ H ₅ CH ₃	12.0	27	4.0	204.1 ^b	10.0
16	C ₆ H ₅ Cl	(11.0)	(27)	2.9	210.1 ^b	16.0
17	C ₆ H ₆	10.6	26	2.8	213.2 ^a	19.1

^{a,b} See Table I.**Table III.** Thermodynamic Quantities for the Association of Various Ions with Various Molecules

reaction no.	reactant ion	reactant neutral	-ΔH° ± 1.5, kcal mol ⁻¹	-ΔS° ± 4, cal mol ⁻¹ K ⁻¹	-ΔG° ₃₀₀ ± 1.5, kcal mol ⁻¹
1	C ₆ H ₆ ⁺	C ₆ H ₆	17.0	27	8.9
17	1,3,5-C ₆ H ₃ (CH ₃) ₃ ⁺	C ₆ H ₆	10.6	26	2.8
18	C ₆ H ₅ CH ₃ ⁺	C ₆ H ₆	12.4	26	4.6
19	C ₆ H ₅ Cl	C ₆ H ₆	14.0	26	6.2
20	C ₆ H ₇ ⁺	C ₆ H ₆	11.0	24	3.9
21	C ₆ H ₅ CH ₃ ⁺	C ₆ H ₅ CH ₃	16.0	29	7.3
22	1,4-C ₆ H ₄ (CH ₃) ₂ ⁺	1,4-C ₆ H ₄ (CH ₃) ₂	15.6	32	5.9
23	C ₆ H ₅ F ⁺	C ₆ H ₅ F	(14.1)	(27)	5.3 ₃₅₆
24	1,3-C ₆ H ₄ F ₂ ⁺	1,3-C ₆ H ₄ F ₂	(13.2)	(27)	5.2 ₂₉₅

**Figure 4.** van't Hoff plots for the association of 1,3,5-C₆H₃(CH₃)₃⁺ with molecules to form the association ions indicated in the figure.

action 22 (Table III), for which $-\Delta S^\circ$ was slightly higher, 32 cal mol⁻¹ K⁻¹). In addition to the temperature studies we performed measurements on equilibria in several additional systems where ΔG° was measured only at one temperature. Since there is no reason to expect that the entropy of these reactions is significantly different from those where temperature studies were performed, we assumed the value of $\Delta S^\circ = -27$ cal mol⁻¹ K⁻¹ for these reactions and calculated the

**Figure 5.** van't Hoff plots for association equilibria producing the association ions indicated in the figure. From top to bottom, reactions 21, 22, 18, and 20 of Table III.

enthalpies accordingly. Values of ΔH° obtained in this manner are indicated by parentheses in Tables I-III.

Calculations were made of the standard deviations of the slopes and intercepts of the van't Hoff plots of four typical representatives of the systems studied. The average standard deviations for the corresponding ΔH° and ΔS° values are 0.6 kcal mol⁻¹ and 2.0 cal mol⁻¹ K⁻¹, respectively. To allow for the possibility of unrecognized systematic errors in the measurements, the quantities given in Tables I-III are assigned uncertainties of 1.5 kcal mol⁻¹, 4 cal mol⁻¹ K⁻¹, and 1.5 kcal mol⁻¹ for ΔH° , ΔS° , and ΔG° , respectively.

Of the reactions presented in Tables I-III, only the formation of (C₆H₆)₂⁺ was investigated previously. The value of

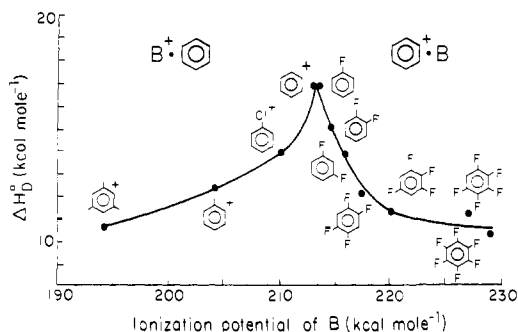


Figure 6. Relation between enthalpy of dissociation (ΔH°_D) and the difference between the ionization potentials of the reactants, in the association of $C_6H_6^+$ with neutral molecules ($C_6H_6^+ \cdot B$) and in the association of ions with neutral benzene ($B^+ \cdot C_6H_6$).

$-\Delta H^{\circ}$ given in Table I may be identified with the quantity ΔH°_D referred to previously, and our present value is higher than any of the earlier values (8–15 kcal mol $^{-1}$, *vide supra*). We consider the new value to be most reliable of the gas-phase results because it was obtained with time-resolved experimental measurements. The rather close agreement with the condensed phase value of ΔH°_{D11} is interesting. Badger and Brocklehurst¹¹ predicted that π electron interactions should contribute to bonding in the $(C_6H_6)_3^+$ ion, as well as in $(C_6H_6)_2^+$. We looked for $(C_6H_6)_3^+$, but only traces were observed even at 250 K, $P_{C_6H_6} = 1$ Torr. Under these conditions $I_{(C_6H_6)_3^+}/I_{(C_6H_6)_2^+} \leq 0.01$. For the reaction $(C_6H_6)_2^+ + C_6H_6 \rightleftharpoons (C_6H_6)_3^+$, $K_{250} \leq 1.3 \times 10^{-5}$, $-\Delta G^{\circ}_{250} \leq 1.0$ kcal mol $^{-1}$, and, assuming $\Delta S^{\circ} = -25$ cal mol $^{-1}$ K $^{-1}$, $-\Delta H^{\circ} \leq 7$ kcal mol $^{-1}$. These results suggest that C_6H_6 is held to $(C_6H_6)_2^+$ only by weak electrostatic bonding.

2. Bonding Energies in the Association Ions and the Relation between ΔH°_D and the Ionization Energies of the Reactants. One of the important objectives of this work was to investigate the effects of physical properties of the reactants on the bonding in the association ions. For these purposes the majority of our results may be divided into three sets. In one set, we give the energies of association of a series of different molecules with the benzene cation. van't Hoff plots are given in Figure 3, and thermodynamic values are given in Table I. In the second set the reactant ion, 1,3,5- $C_6H_3(CH_3)_3^+$, is kept constant, and the neutral reactants are varied. The results are shown in Figure 4 and Table II. In the third set various ions react with various neutrals (Figure 5 and Table III), and this set includes a subset wherein a single neutral reactant, benzene, reacts with several different ions.

Early in the course of making the measurements it became evident that the magnitude of the bonding in the association ions ($\Delta H^{\circ}_D = -\Delta H^{\circ}$) is related to the difference in ionization potentials of the neutral substances B and the substances R from which R $^+$ are derived. All of the measurements made confirm this relationship, and in particular one sees in Tables I and II that for the A $^+$ ions formed from $C_6H_6^+$ ions and a series of aromatic molecules (reactions 1–9, Table I) and for the A $^+$ ions from 1,3,5- $C_6H_3(CH_3)_3^+$ ions and a series of aromatic molecules (reactions 12–17, Table II) the values of ΔH°_D decrease monotonically as ΔIP increases. These results are shown graphically in Figure 6 (reactions of $C_6H_6^+$ ions with B molecules to right of cusp; reactions of B $^+$ ions with C_6H_6 molecules to left of cusp) and Figure 7. From the tables and figures one observes that the largest value of ΔH°_D (~ 17.0 kcal mol $^{-1}$) is obtained for $(C_6H_6)_2^+$ ($\Delta IP = 0$), 1,3,5- $C_6H_3(CH_3)_3^+$ ($\Delta IP = 0$), and $(C_6H_6 \cdot C_6H_5F)^+$ ($\Delta IP = 0.2$). As ΔIP increases, ΔH°_D decreases and asymptotically approaches the value 10 ± 1 kcal mol $^{-1}$.

Previous measurements^{16,19,20} of ΔH°_D of protonated as-

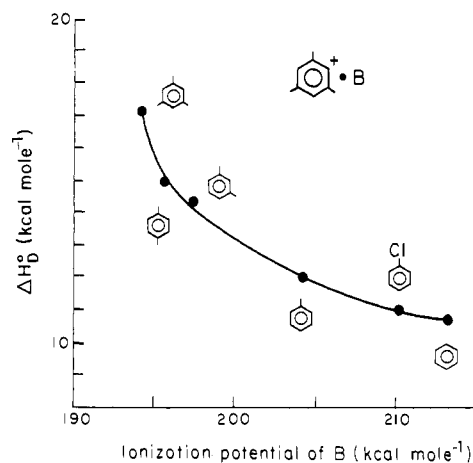


Figure 7. Relation between enthalpy of dissociation (ΔH°_D) and the difference between the ionization energies of the reactants, in the association of 1,3,5- $C_6H_3(CH_3)_3^+$ with neutral reactants.

sociation ions (the so-called proton bound association ions) indicate that electrostatic ion–neutral interactions and, where possible, hydrogen bonding interactions contribute to the bonding energies. However, we have observed¹⁷ that bonding in the radical association ions $N_2 \cdot N_2^+$ and $CO \cdot CO^+$ is significantly stronger than bonding in the analogous protonated association ions $N_2 \cdot N_2H^+$ and $CO \cdot COH^+$, which have an even number of electrons. We suggested that energetic effects due to electron delocalization contribute to the bonding in the radical association ions in addition to the electrostatic interactions which are common to both types of ions. We suggest that both electron delocalization and electrostatic interactions contribute to the bonding in the radical association ions studied here. Furthermore, we believe that the observed relationship between ΔH°_D and ΔIP constitutes strong support for the validity of the suggestion.

It is generally accepted^{8,10,11,21,22} that association ions of aromatic molecules have a sandwich structure, i.e., the two benzene rings are parallel. In these structures a bonding orbital can be formed in the usual way as

$$\bar{\Psi} = \psi(B_1^+)\psi(B_2) + \psi(B_1)\psi(B_2^+) \quad (11)$$

where $\psi(B)$ and $\psi(B^+)$ are the π molecular orbitals of the aromatic entities.¹¹ In terms of resonance theory the resonance structures $B_1^+ \cdot B_2$ and $B_1 \cdot B_2^+$ will both contribute to the wave function of the association complex. Electron delocalization, resulting in a lowering of the energy and hence stronger bonding, requires that the resonance structures have comparable energies. The effect will be maximized for association ions where the resonance structures $B_1^+ \cdot B_2$ and $B_1 \cdot B_2^+$ have identical energies. The effect will diminish in significance as ΔIP increases because in association ions composed of molecules with markedly different ionization potentials the charge may be expected to be localized almost entirely on the molecule with the lower ionization potential. In the limit of very high ΔIP values only electrostatic interactions should contribute to the bonding.

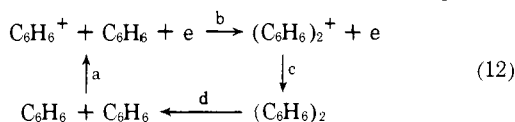
In order further to define the contributions of electrostatic bonding in the association ions, we measured association enthalpies in two cases where electron delocalization involving interactions between the π electrons of a neutral molecule and a vacancy in the π orbitals of an ion are not possible. In one case the neutral reactant, cyclohexane, has no π electrons available for bonding; ΔH°_D for the association ion $(C_6H_6 \cdot c-C_6H_{12})^+$ is 9.9 kcal mol $^{-1}$ (Table I). In another case the reactant ion is not a radical but an even-electron species, protonated benzene. In this case, ΔH°_D for $(C_6H_7 \cdot C_6H_6)^+$ is 11.0 kcal mol $^{-1}$. The

low bonding energies observed in these ions are similar in magnitude to ΔH°_D of association ions with large ΔIP , such as in $C_6H_6^+ \cdot C_6F_6$ ($\Delta H^\circ_D = 10.5 \text{ kcal mol}^{-1}$) or $1,3,5-C_6H_3(CH_3)_3^+ \cdot C_6H_6$ ($\Delta H^\circ_D = 10.6 \text{ kcal mol}^{-1}$). These observations support the generalization that electrostatic bonding contributes about 10 kcal mol^{-1} to bonding in association ions of benzene compounds. Our observations are in accord with the broader generalization of Beauchamp²⁰ that nonspecific weak interactions in ion-molecule complexes are usually of the strength 10 kcal mol^{-1} or less.

The generalization that the stability of symmetric association ions is enhanced by electron delocalization is further supported by measurements of ΔH°_D in the symmetric association ions $(C_6H_5CH_3)_2^+$ and $(1,4-C_6H_4(CH_3)_2)_2^+$. ΔH°_D in these ions is 16.0 and $15.6 \text{ kcal mol}^{-1}$, respectively. These values are identical within the combined experimental uncertainty with the ΔH°_D values for $(C_6H_6)_2^+$ and $(1,3,5-C_6H_3(CH_3)_3)_2^+$ ions, namely, 17.0 and $17.2 \text{ kcal mol}^{-1}$. Thus ΔH°_D of all symmetric association ions of the methylbenzenes are higher by $6\text{--}7 \text{ kcal mol}^{-1}$ than ΔH°_D in ions where bonding by electron delocalization is impossible or unfavorable. The fact that bonding in all of the symmetric association ions of methylbenzenes is of about equal strength shows that steric interference by the presence of the methyl groups and changes in symmetries of the reactants by methyl substitution have no significant effect on bonding. However, fluorine substitution appears to decrease somewhat the stability of symmetric association ions (reactions 23 and 24, Table III), possibly due to partial charge localization on the fluorine substituents.

It is also interesting to note that the dipole moment of the neutral reactant does not seem to affect the bonding. Thus the progression in the bonding of benzene and fluorobenzenes to B^+ in Figure 6 seems to be determined only by ΔIP , although C_6H_6 , $1,2,4,5-C_6H_2F_4$, and C_6F_6 are nonpolar, while the other neutrals are polar molecules. This observation supports the sandwich structure of the association ions. Ion-dipole interactions would give a perpendicular structure in which ΔH°_D would increase with the dipole moment of the neutral reactant.

3. Applications in the Condensed Phase. As a conclusion of this discussion we wish to consider the possible application of the present data for condensed-phase ion chemistry. Molecular dimers are sometimes considered as an approximation to crystals.¹ Ionization energies of molecular dimers may therefore be of some interest in relation to the energy of formation of ionized states in crystals. Adiabatic ionization energies of the molecular dimers may be calculated from the thermodynamic cycle, shown for the benzene dimer as an example.



ΔH°_a , the ionization energy of benzene, is $213.2 \text{ kcal mol}^{-1}$;²⁴ ΔH°_b is the association enthalpy measured here as $-17.0 \text{ kcal mol}^{-1}$. The enthalpy of dissociation of the neutral benzene dimer, ΔH°_d , may be calculated as $0.6 \pm 0.2 \text{ kcal mol}^{-1}$ using the Lennard-Jones parameters quoted by Hirschfelder et al.²³ Using these values we calculate the adiabatic ionization energy of the neutral benzene dimer as $-\Delta H^\circ_c = 196.8 \text{ kcal mol}^{-1}$. The ionization potential for the dimer is lowered as compared with the monomer, mostly by the bonding in the dimer ion, since bonding in the neutral dimer is weak.

To the extent that ion-neutral bonding energies measured in the gas phase are applicable in crystals, the difference between bonding in symmetric and in asymmetric association ions may be applied to the solid state. The result will be that ion-neutral interactions in the crystal will lower the IP of a host molecule more than the IP of an impurity molecule. This results from the fact that an ionized host molecule will form a symmetric dimer with a neighboring host molecule. The ion of the host molecule may therefore be stabilized by electron bonding in addition to the polarization forces which will apply in the interaction of the impurity ion with host molecules.

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