Formation of Gas-Phase Solvated Br^- and I^- in Ion/Molecule Reactions of Halobenzenes. Revised Heat of Formation of Benzyne

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The formation of gas-phase solvated anions through low-pressure bimolecular ion/molecule reactions has been a recurrent and fascinating aspect of the ion chemistry of negative ions.[1] The scheme for these processes involves in general an elimination-type reaction initiated by attack of a strong gas-phase base (A^-) on an organic substrate containing a mildly acidic site, HXB, as shown in reaction 1. The outcome of reaction 1 has been recognized to be determined by a delicate balance of thermochemical parameters[2] and dynamical properties.[3] These reactions are particularly attractive because they allow for the quantitative determination of gas-phase ion–solvent binding energies through solvent switching equilibria,[4] and for probing the effect of solvation on simple organic reactions in the gas phase.[4d,5]

$$A^- + HXB \rightarrow (AHB)^- + X \qquad (1)$$

We report a novel set of gas-phase reactions of halobenzenes that allow for the specific formation of solvated Br^- and I^- ions. Earlier studies of negative ions with fluorobenzenes established some unusual nucleophilic reactions and helped to bracket the gas-phase acidity of C_6H_5F and C_6H_5Cl somewhere between the acidities of H_2O and CH_3OH.[6] We now find that hydroxide ions generated in an FT-ICR spectrometer react rapidly with bromobenzene and iodobenzene,[7] according to reaction 2. Reaction 2a is surprisingly favored over the simple proton abstraction by almost a factor of 10. The $C_6H_4X^-$ ion in turn reacts extremely fast with H_2O to yield also the solvated ion (reaction 3). Reactions 2 and 3 are not observed for chlorobenzene or fluorobenzene.

$$OH^- + C_6H_5X \rightarrow X^-(H_2O) + C_6H_4 \qquad (2a)$$

$$OH^- + C_6H_5X \rightarrow C_6H_4X^- + H_2O \qquad (2b)$$

$$X = Br, I$$

$$C_6H_4X^- + H_2O \rightarrow X^-(H_2O) + C_6H_4 \qquad (3)$$

Alkoxide ions also react in a similar way to reaction 2a but in a selective fashion (reaction 4). While iodobenzene reacts rapidly with MeO^- and EtO^-, bromobenzene only undergoes facile reaction with MeO^-. With EtO^-, less than 20% conversion to the solvated ion is observed after 3 s of reaction time with bromobenzene at a pressure of 2.6×10^{-5} Pa. Thus, it is likely that reaction 4 is endothermic for this case. Finally, the reaction of a weaker base like F^- with C_6H_5I yields only traces of FHI^-. Given that no proton abstraction is observed in reaction 4, the gas-phase acidity of bromobenzene and iodobenzene must also lie between the acidities of water and methanol.

$$RO^- + C_6H_5X \rightarrow X^-(HOR) + C_6H_4 \qquad (4)$$

The observation of reaction 2a for C_6H_5I is barely compatible on energetic grounds with the available thermochemical data.[8] On the other hand, reaction 4 is consistently predicted to be endothermic for all cases, a fact at odds with the ease of these reactions. Thus, we are led to conclude that the proposed heat of formation of *o*-benzyne of 493 ± 21 kJ mol^{-1}, derived from ICR equilibria experiments,[9] must be too high. A revised heat of formation of *o*-benzyne can be obtained by use of a bracketing technique for the alkoxide reactions with bromobenzene.[10] The bond dissociation energies of the $Br^-(HOR)$ species can be safely assumed to be in the range $D(MeOH \cdots Br^-) = 65 \pm 8$ kJ mol^{-1} and $D(EtOH \cdots Br^-) = 68 \pm 8$ kJ mol^{-1} by comparison with the data available for $Br^-(H_2O)$[11] and the trend observed in the Cl^- and I^- adducts with ROH by high-pressure mass spectrometry.[12] This argument leads us to propose a new value for the heat of formation of benzyne of 440 ± 10 kJ mol^{-1}. This value[13] would then predict reaction 4 to be 5 kJ mol^{-1} exothermic for the reaction of MeO^- and bromobenzene, 5 kJ mol^{-1} endothermic for the corresponding EtO^- reaction, and thermoneutral for F^- with C_6H_5I. This revised value would also predict reactions 2 and 4 to be still substantially endothermic for fluorobenzene and chlorobenzene.

The mechanism of reactions 2 and 4 must bear strong resemblance to that depicted for the general reaction 1. In the present case, the binding energy of the nascent ionic moiety provides the driving force required to dehydrohalogenate the halobenzene and yield the solvated species.

The reactions reported here provide a powerful way to explore the gas-phase stability and reactivity of solvated Br^- and I^- species. These findings and the revised heat of formation of benzyne should also stimulate the recent interest shown in the gas-phase ion chemistry of benzyne.[14]

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Registry No. C_6H_5Br, 108-86-1; C_6H_5I, 591-50-4; OH^-, 14280-30-9; MeO^-, 3315-60-4; EtO^-, 16331-64-9; F^-, 16984-48-8; *o*-benzyne, 462-80-6.

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(7) The general experimental procedure involving the homemade Fourier transform ion cyclotron resonance spectrometer has been described in refs 6b,c. The experiments with OH^- were carried out typically in 1:1 mixtures of H_2O and C_6H_5X at total pressures of 5.3×10^{-5} Pa. The reaction of the alkoxide ions was studied by using a roughly 1:1:1 mixture of N_2O, ROH, and C_6H_5X. Isolation of the reactant ion at variable times up to 500 ms after ionization showed no difference in the observed reactions.

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(10) The fact that the acidities of bromobenzene and iodobenzene are comparable strongly suggests that the slowness of the EtO^- reaction with bromobenzene is not due to a kinetic effect. If such were the case, it would imply an even lower value for the heat of formation of benzyne.

(11) A value of 62 kJ mol^{-1} for $D(Br^- \cdots H_2O)$ has been reported by Burdett and Hayhurst: Burdett, N. A.; Hayhurst, A. N. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2997. A lower value of 53 kJ mol^{-1} was previously suggested by Arshadi et al.: Arshadi, M.; Yamdagni, R.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1475.

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