The Gas-phase $C_6H_4X^-$ Ion ($X^- = Br^-, I^-$): a Halide–Benzyne Complex

Harrald V. Linnert and José M. Riveros*

Instituto de Química, Universidade de São Paulo, CP 20780, São Paulo, Brazil CEP 01498-970

The gas-phase $C_6H_4Br^-$ and $C_6H_4I^-$ ions react with more acidic substrates than either bromo- or iodo-benzene by halide transfer rather than by proton abstraction, a behaviour consistent with an ion structure corresponding to a halide–benzyne complex.

High reactivity and unusual features have made benzyne a well explored and useful intermediate of organic reactions[1] and as a ligand of transition metal ions.[2] Yet, the elusive nature of this species has proved to be an experimental challenge for its direct characterization. A fresh approach towards the understanding of the energetics of the dehydrobenzenes has recently emerged from gas-phase studies of ion chemistry.[3–6]

We now report the novel observation that the gas-phase $C_6H_4Br^-$ and $C_6H_4I^-$ ions display the characteristics of halide–benzyne complexes and can easily transfer a halide ion to other neutral substrates.

The gas-phase acidities of the halobenzenes are known to lie between those of water and of methanol[7–9] with relative ordering $C_6H_5F<C_6H_5Cl<C_6H_5CN$, while bromo- and iodobenzene are presumably somewhat higher but definitely below methanol. Nevertheless, the gas-phase conjugate bases of these latter acids show a unique reactivity pattern. Different $C_6H_4X^-$ ions† were generated in our homemade Fourier transform ion cyclotron resonance (FT-ICR) spectrometer[10] by eqn. (1).

$$NH_2^- + C_6H_5X \rightarrow NH_3 + C_6H_4X^- \qquad (1)$$

For X = F, Cl, CN, NO_2, these $C_6H_4X^-$ species were found to be unreactive towards ammonia, or the parent C_6H_5X, but to readily abstract a proton from the more acidic alcohols. By comparison, $C_6H_4Br^-$ and $C_6H_4I^-$ undergo fast reaction with the parent halobenzene through eqn. (2).

$$C_6H_4X^- + C_6H_5X \rightarrow C_6H_4 + C_6H_5X_2^- \qquad (2)$$
$$(X = Br, I)$$

A more significant observation is the fact that these $C_6H_4X^-$ anions fail to abstract a proton from the more acidic alcohols but instead promote rapid halide ion transfer, see eqns. (3*a*,*b*).

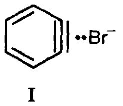
$$C_6H_4Br^- + MeOH \rightarrow C_6H_4 + MeOHBr^- \qquad (3a)$$
$$\nrightarrow C_6H_5Br + MeO^- \qquad (3b)$$

The ability of the $C_6H_4Br^-$ and $C_6H_4I^-$ anions to transfer a halide ion to a number of polar substrates has been well verified in our laboratory. By comparison, no bromide transfer is observed to C_6H_6 at benzene pressures as high as 1.33×10^{-4} Pa and reaction times of 2 s, while transfer to ammonia under similar conditions proceeds to less than 10%. This latter observation is consistent with recent calculations predicting very low cluster energies for species similar to $Br^-(NH_3)$.[11]

Our results strongly suggest that the $(C_6H_4)Br^-$ and $(C_6H_4)I^-$ anions are species akin to a halide–benzyne complex **I** with the charge residing on the polarizable halide atom. This is in marked contrast to similar anions containing a first- or second-row electron-withdrawing group, *i.e.* $C_6H_4Cl^-$ **II**.

Such halide–benzyne complexes are strongly reminiscent of the recent findings of simple gas-phase carbene–anion complexes.[12] The presence of a second electron-withdrawing group in substituted bromobenzenes reverts the reactivity of the corresponding anions to that of structure **II**. For example, $C_6H_3FBr^-$ ions generated from different isomers of C_6H_4FBr through eqn. (1) act as typical gas-phase bases abstracting a proton from more acidic substances.

An upper limit of 50 kJ mol^{-1} can be safely estimated for the stability of the benzyne–Br^- complex by assuming a ΔH_{acid} in the range of 1600 kJ mol^{-1} for C_6H_5Br and by comparison



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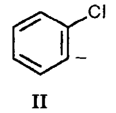

II

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† Spectra were acquired at 1.0 or 1.25 T and processed by an IonSpec Data System. The NH_2^- were generated at 6 eV from NH_3 maintained typically at 2×10^{-5} Pa while the partial pressure of the halobenzene was kept around 8×10^{-6} Pa. The reactions of the $C_6H_4X^-$ ions were studied by isolating this ion after 400 ms of reaction with selective ejection of all other ions.

with the gas-phase acidity data recently reported by Nibbering.[9] This estimate is consistent with the ease of eqn. (3*a*) and with the recent value of 58 kJ mol^{-1} reported for the Br$^-$ (MeOH) cluster energy.[13]

The stability of the putative species **I** must be equated with charge donation from the halide ion to the LUMO of benzyne. *Ab initio* calculations[14–19] are consistent with the recent photoelectron spectrum[20] of *o*-benzyne, which shows the HOMO to be close in energy to the degenerate π-orbital of benzene and the second E_i to correspond to the removal of an electron from an orbital associated primarily with the in-plane bonding of *o*-benzyne. On the other hand, the electrophilicity of benzyne has been proposed to arise from a substantial lowering of its LUMO[21–24] (the in-plane $8b_2$ orbital in particular) when compared with benzene. Symmetry considerations and the lowering of the LUMO thus allow for a favourable interaction of the bromide (or iodide) ion *p*-orbital. This qualitative picture is in good agreement with our experimental observations. A more quantitative explanation will require higher level calculations to address the question of the halide specificity for complex formation and the peculiarities of the benzyne system.

The present results provide a fascinating outlook on benzyne gas-phase chemistry and pave the way for the study of cluster energies for larger halide ions.

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