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Proton elimination in charge-separation reactions with hydrogen halides driven by chemical-bond formation with triply-charged C_{60} cations

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Abstract

Experimental results are reported which demonstrate the efficient elimination of protons in charge-separation reactions of $C_{60}^{\cdot 3+}$ with HCl and HBr at room temperature. Two mechanisms are observed for the production of protons in these ion/molecule reactions: dissociative electron transfer and halide transfer with concomitant chemical-bond formation. Both occur in the reaction with HBr which produces protons in all reactive collisions.

The remarkable stability and ready availability of multiply-charged fullerene cations provides the very rare opportunity to explore the chemistry of cations as a function of charge state. We have shown previously that new chemical pathways become accessible in the gas phase at room temperature to reactions of C_{60} cations as the charge state is increased from 1 to 2 to 3 [1]. Here we report the observation of a remarkable onset in the chemical reactivity of C_{60}^{n+} at $n = 3$ which results in the elimination of protons from hydrogen halide molecules due to chemical-bond formation with $C_{60}^{\cdot 3+}$. One of these reactions, that of $C_{60}^{\cdot 3+}$ with HBr, produces protons in all reactive collisions at room temperature due to the onset, also, of dissociative electron transfer.

The authors are aware of only a few previous observations of proton production in gas-phase chemical reactions. F^+ has been reported to react with H_2 to produce H^+ and HF in 2% of the reactive encounters at room temperature [2]. This reaction channel, which may be viewed as H^- transfer, is favoured by the relatively high enthalpy of formation of F^+ ($\Delta H^0_{298} = 420.7$ kcal mol^{-1} [3]) and the strong F^+–H^- bond ($D^0_{298} = 520$ kcal mol^{-1} [3]). Also, observations of analogous D^- transfer reactions with D_2 involving chemical-bond formation with the doubly-charged cations CF^{2+}, CF_2^{2+}, CF_3^{2+}, CO_2^{2+} and COS^{2+} at laboratory kinetic energies between 30 and 50 eV have been reported more recently [4]. The authors are not aware of reports of other proton-formation reactions involving chemical-bond formation. However, protons can also be produced in dissociative electron-transfer reactions as has been shown in experimental studies of the reactions of the doubly-charged rare-gas cations Ne^{2+} and Kr^{2+} with H_2 at 300 K [5]. The production of protons in reactions of $C_{60}^{\cdot 3+}$ is driven by the high enthalpy of formation of this cation which has been estimated to be 1433 ± 13 kcal mol^{-1} [6] and 1397 ± 12 kcal mol^{-1} [7] based on a value for the third adiabatic ionization energy

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