

Gas-phase proton transfer from dications: Coulombic repulsion between reaction products in $C_{60}H^{2+} + B$ ($B = C_3H_3N$, HCN and CO)

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Received 27 October 2005; received in revised form 2 December 2005; accepted 2 December 2005

Available online 9 January 2006

This paper is dedicated to the memory of Chava Lifshitz.

Abstract

B3LYP/6-311+G**/B3LYP/6-31G* calculations are carried out on C_{60}^{z+} species ($z = 0-3$), $C_{60}H^+$, $C_{60}H^{2+}$ and on the potential energy surfaces for proton transfer from $C_{60}H^{2+}$ to CH_2CHCN , HCN and CO. Reasonable agreement is obtained with experiment for the C_{60} species, although the second and third ionization potentials are too low. The calculated potential energy surfaces account for observed reactivity. Analysis of the charge distribution in the TS for proton transfer to HCN helps explain the origin of the Coulombic barrier.

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Keywords: Dication; Proton transfer; Computation; Electronic structure

1. Introduction

The ion chemistry of carbon clusters such as C_{60} is a particularly rich area of mass spectrometry, and was the subject of a recent review by Lifshitz [1]. Typical reactions of fullerene ions involve loss of C_2 fragments. Where the initial cluster bears more than one positive charge, such processes can lead to Coulombic explosion through production of C_2^+ . These processes are identified through the large kinetic energy release of the fragments.

Another very interesting charge fission reaction of fullerene derivatives has been studied in detail by Petrie et al., namely transfer of a proton from the dication $C_{60}H^{2+}$ [2] and trications $C_{60}XH^{3+}$ (where XH is, e.g., NH_3 , OH_2) [3] to bases of varying strength. These ions are in some respects surprisingly unreactive, with $C_{60}H^{2+}$ unable to transfer a proton to neutrals such as CS_2 or C_2H_4 , despite the fact that these are expected to have a higher proton affinity than C_{60}^+ . This was explained by the presence of a Coulombic barrier to dissociation to form the protonated base and the fullerene monocation, which is only surmounted when the base has a considerably larger proton affinity than required for exothermic reaction. This feature of the potential energy sur-

face, typical in reactions of multiply charged ions [4], is shown schematically in Fig. 1. The reaction proceeds through initial formation of an ion–molecule complex between the dication and the neutral, followed by proton transfer and charge separation. The height of the latter barrier with respect to the products can be rationalized using a model in which one charge is localized on the proton being transferred, and the other is located on the opposite side of the fullerene cage. Assuming that the TS is located close to the encounter complex $C_{60}H^{2+} \cdots B$, then this leads to a charge–charge distance of $8.0 \pm 0.7 \text{ \AA}$ [2]. Given that the charges interact roughly in vacuo, this leads to a predicted reverse barrier of $42 \pm 4 \text{ kcal/mol}$. This value can then be used to correct the apparent proton affinity (or gas-phase basicity) of $C_{60}H^{2+}$ to give the ‘correct’ thermodynamic value.

Proton transfer was observed to occur slowly for $CH_2(CN)_2$, CH_2O and HCN, which have respective gas-phase basicities of 167.4, 164.3 and 163.8 kcal/mol, whereas no reaction was observed with CS_2 (GB = 158 kcal/mol) and other weaker bases. This corresponds to an apparent gas-phase basicity of $166 \pm 4 \text{ kcal/mol}$ [2]. Using the estimated barrier due to Coulomb repulsion discussed above, this can be translated into a ‘real’ gas-phase basicity of $124 \pm 8 \text{ kcal/mol}$, much lower than the apparent one. However, this value is dependent on the accuracy of the model. It is of interest to see how well this model describes reactivity in this type of system, as it can also yield

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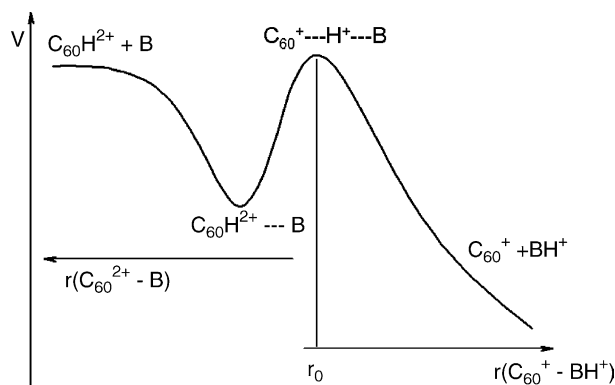


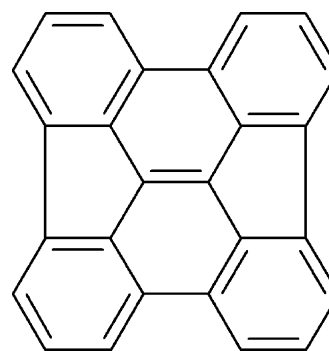
Fig. 1. Potential energy surfaces involved in gas-phase proton transfer from a dication such as $C_{60}H^{2+}$ to a neutral base.

insight into gas-phase deprotonation reactions of other multiply charged ions, especially the highly charged protein ions which are formed in electrospray ionization processes. We note that the experimental work expresses proton affinities as gas-phase basicities, that is, gas-phase free energies at room temperature for the reaction $C_{60}H^{2+} \rightarrow C_{60}^+ + H^+$. With some assumptions about entropic contributions, the proton affinity (enthalpy of the same reaction) can be derived as 134 ± 8 kcal/mol [2]. We will use proton affinities rather than free energies in the results section of this work.

We are interested in using computation to assess the structure, energetics and reactivity of gas-phase dications and other multiply charged ions [5–10]. In particular, we have examined potential energy surfaces for proton transfer from NeH^+ to the LaO^+ cation to form the dication $LaOH^{2+}$ [6]. Although this proton transfer is exothermic, it is unlikely to occur due to the large Coulombic repulsion as the two reactants approach each other. In this work, we examine proton transfer from $C_{60}H^{2+}$ to three bases studied in the experimental work of Petrie et al. [2], namely $CH_2=CH-CN$, HCN and CO . These species have proton affinities of respectively 187.5, 170.4 and 140.0 kcal/mol [11], and were observed to undergo respectively efficient, slow and no proton transfer [2]. We have also studied the series of ions C_{60}^{z+} ($z = 0-3$), and examined the electronic structure of the proton transfer TSs to elucidate whether or not the model proposed in the experimental study is accurate. Previous computational work has addressed C_{60} and some of its ions using semiempirical [12] and DFT [13] methods, but none to our knowledge has addressed $C_{60}H^{2+}$ or its reactions.

2. Computational details

All calculations have been carried out at using the standard B3LYP hybrid density functional as implemented in the Jaguar 4.0 program [14]. The unrestricted ansatz (UB3LYP) was used for all open-shell species. All geometries were optimized using the 6-31G* basis on all atoms, and single-point calculations were then carried out at these optimized geometries using the larger 6-311+G** basis. Due to computational restrictions, it was not possible to carry out frequency calculations on the large C_{60} system, so unless mentioned otherwise, reported ener-



Scheme 1.

gies are based on electronic energies only. However, in some cases, zero point energy corrections are included, and these were obtained either directly, or, for C_{60} and its derivatives, from B3LYP/6-31G* frequency analysis of a model compound, the bowl-shaped fullerene fragment $C_{26}H_{12}$ (diindeno[1,2,3,4-defg,1',2',3',4'-mnop]chrysene, [15]) shown in Scheme 1. Population analysis was carried out using single-point calculations at the B3LYP/6-311G** level.

3. Results

We have first computed ionization potentials for C_{60} , C_{60}^+ , C_{60}^{2+} and $C_{60}H^+$, as shown in Table 1. In all cases, the larger basis set leads to a better description of the species with lower charge, and hence to a higher ionization energy. B3LYP is in very good agreement with experiment for the first ionization potential of C_{60} when using the larger basis set. The second ionization potential, corresponding to formation of triplet C_{60}^{2+} , is less accurate, as it is too small by ca. 0.7 eV. The tendency of DFT methods to underestimate second ionization potentials for hydrocarbons has been noted before [16], and can be attributed to errors associated with electron self-interaction and the incorrect behaviour of the long-range potential for the electron. The third ionization potential, leading to quartet C_{60}^{3+} , is smaller than the experimental value by as much as 2 eV, which even though the experimental error bar is fairly large represents a huge margin of error. $C_{60}H^+$ is a closed-shell species, so better agreement with experiment for its ionization potential might be expected, and is indeed observed. It is to be noted, however, that the experimental value shown here is derived from the proton affinity of C_{60}^+ through the use of a thermodynamic cycle, and is thereby to be taken with caution as the proton affinity itself depends on the accuracy of the model discussed above.

Table 1
Computed and experimental ionization energies (eV) of C_{60} species

	B3LYP/6-31G*	B3LYP/6-311+G** ^a	Experimental
C_{60}	7.41	7.72	7.61 ± 0.02 [17]
C_{60}^+	10.37	10.68	11.39 ± 0.05 [18]
C_{60}^{2+}	13.64	13.79	15.6 ± 0.5 [19]
$C_{60}H^+$	10.28	10.55	10.70 ± 0.4 [2]

^a Single-point energy at the B3LYP/6-31G* geometry.

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