Mechanism of fullerene hydrogenation by polyamines: Ab initio density functional calculations

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We use ab initio density functional calculations to study the microscopic mechanism underlying the recently demonstrated hydrogenation of the C60 fullerene by diethylenetriamine reagent. Our results indicate that the optimal monoaddition reaction is exothermic, involving an ~0.5 eV high activation barrier associated with the simultaneous docking of the polyamine functional group and H transfer to C60. We calculated vibrational frequencies can be used to experimentally confirm the presence of hydroamination adducts as a necessary prerequisite for successful hydrogenation of C60.

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Chemical functionalization of well defined carbon nanostructures such as C60 is an important direction to obtain a new class of molecules with intriguing properties. Among the many ways to chemisorb atomic hydrogen on C60 and other sp2 bonded nanocarbons, the recently introduced chemical reaction using high boiling polyamines appears as most promising.1-3 Alternative ways of hydrogenation using surfactants leave undesirable residue behind, and physical treatments such as ultrasonication4,5 often cause structural damage. In spite of the demonstrated efficiency of the polyamine-based hydrogenation, the microscopic mechanism underlying this reaction remains obscure.

In this Brief Report, we investigate the microscopic hydrogenation mechanism of C60 by diethylenetriamine (DETA) reagent using ab initio density functional calculations. By exploring the DETA-C60 potential-energy surface, we identify the structural changes and energetics along the optimal monoaddition reaction pathway. We find the hydrogenation to be exothermic, involving an ~0.5 eV high activation barrier associated with the simultaneous docking of the functional group and H transfer to C60. We also provide the vibrational spectrum of the hydroamination adduct to assist in the experimental confirmation of a successful hydrogen transfer to C60.

Our total-energy calculations, as well as global and constrained structure optimization studies, have been performed using the density functional theory (DFT) within the local density approximation (LDA), utilizing first-principles pseudopotentials, as implemented in the DMOL3 (Refs. 6 and 7) and SIESTA (Ref. 8) software. In our DMOL3 (Ref. 6) calculations, we used the parametrization of Perdew and Wang9 for the exchange-correlation energy and a double numerical basis set, including polarization functions on all atoms (DNP). The DNP basis set corresponds to a double-ζ quality basis set with a p-type polarization function added to hydrogen and d-type polarization functions added to heavier atoms, and is comparable to 6–31G** Gaussian basis sets,10 providing a better accuracy at a similar basis set size.6 In the generation of the numerical basis sets, we used a global orbital cutoff of 3.7 Å. The energy tolerance in the self-consistent field calculations was set to 10^-6 hartree. Optimized geometries were obtained without symmetry constraints, using an energy convergence tolerance of 10^-6 hartree and a gradient convergence of 2 × 10^-3 hartree/Å. In our SIESTA (Ref. 8) calculations, we used an optimized double-ζ basis set with polarization orbitals,11 the Perdew-Zunger12 parametrization of the exchange-correlation functional, and norm-conserving ab initio pseudopotentials13 in their fully separable form.14 We used 0.01 eV/Å as a strict gradient convergence criterion during structure optimization.

The optimized geometries of DETA and C60 reagents are shown in Fig. 1(a). In order to better understand the mechanism of hydrogen transfer from DETA to the C60 molecule, we found it convenient to separate the DETA docking process from the hydrogen transfer between the docked polyamine and C60. We considered different docking approaches, with the DETA axis normal or tangential to the C60 surface. We found the latter, corresponding to DETA approaching with its end rather than its center, to provide the most favorable conditions for hydrogen transfer.

Our SIESTA results for the DETA docking process are shown in Fig. 1. To understand the energetics of the reaction, we performed a structure optimization of the DETA-C60

FIG. 1. (Color online) (a) Schematic of DETA docking to the C60 molecule with the distance dCN between the terminal nitrogen of DETA and the closest C atom of the fullerene defining the reaction coordinate. (b) Total-energy change ΔE of the system as a function of dCN, taking the separated system as a reference. (c) Snapshots of the docking process, including the initial, transition, and final states.
complex, constraining the distance between a terminal nitrogen atom in DETA and an atom of the C₆₀ cage, as seen in Fig. 1(a). The total energy of the system as a function of the carbon-nitrogen distance $d_{C-N}$ is depicted in Fig. 1(b). Our results indicate that DETA gains about 0.2 eV as it approaches from infinity and physisorbs near the fullerene. We note that physisorption with the DETA axis tangential to the fullerene, defining the reaction coordinate. (b) Total-energy change $\Delta E$ of the system as a function of $d_{C-H}$, taking the initial-state system as a reference. (c) Snapshots of the hydrogen transfer process, including the initial, transition, and final state.

To better characterize the transition state seen in Fig. 2, we have explored the saddle-point region using the linear synchronous transit (LST) and quadratic synchronous transit (QST) methods as implemented in DMOL3, combined with a standard conjugate gradient optimization of the transition state structure. The transition state has one negative eigenvalue in the Hessian matrix corresponding to an imaginary vibrational frequency of $-1581.7$ cm$^{-1}$. Animation of this frequency shows that this mode corresponds to the vibration of the H atom transiting between the terminal N atom of DETA and the closest C atom of the C₆₀ cage leading to the energetically favored 1,2-hydroamination adduct. The atomic structure corresponding to the transition state was confirmed by an independent intrinsic reaction coordinate calculation.

To explore the possibility of different reaction paths and to decide if the optimum reaction path is a one-step or a multistep process, we investigated the energetics of the system by varying the values of $d_{C-N}$ and $d_{C-H}$ from 1 to 3 Å by performing 400 independent calculations. The potential-energy surface shown in Fig. 3 represents total energies of the DETA-C₆₀ complex that have been optimized with the only constraints being fixed values of $d_{C-N}$ and $d_{C-H}$. Our results indicate that the transition from the physisorbed state of DETA to the final state of the reaction, where a hydrogen atom has been transferred to the C₆₀ cage, may occur either as a single-step process with a slightly higher activation barrier or a two-step process with a lower activation barrier. In particular, the shallow potential well of docked DETA in the $d_{C-H}$ direction suggests an efficient H transfer. Preferred reaction paths are indicated by arrows in Fig. 3.

Careful analysis of our computational results helped us to elucidate the chemical bonding changes associated with hydrogen transfer from DETA to the C₆₀ cage. The recently proposed hydrogenation mechanism of C₆₀ by polyamines suggests the hydrogen transfer to be initiated by an electron transfer from the polyamine to the fullerene followed by a...
proton transfer from the N-H group to C\textsubscript{60}. Close inspection of our results suggests an alternative mechanism, involving neutral hydrogen transfer from DETA to C\textsubscript{60} during a concerted motion reaction. Both in the previously proposed and the present theoretical scenario, the transfer of hydrogen is promoted by the charge-density lobe near the N atom in the nonbonding highest occupied molecular orbital (HOMO) and second highest occupied molecular orbital (HOMO-1) orbitals of the DETA molecule, depicted in Fig. 4. In either case, the final product is a neutral C\textsubscript{60}H radical and a neutral N-centered polyamine radical that is missing one hydrogen.

To allow for an independent confirmation of our findings regarding the formation of a DETA-C\textsubscript{60} complex as a necessary prerequisite of the hydrogenation reaction, we performed a vibrational analysis of this adduct, as well as isolated C\textsubscript{60} and DETA. Calculated frequencies should allow a quantitative comparison with infrared spectra, thus confirming or disproving the presence of the complex. We constructed the Hessian matrix for the final state of the hydrogenation reaction, labeled as DETA-C\textsubscript{60} in Fig. 3, using finite differences of the analytical forces with respect to the atomic positions. The normal modes and their frequencies were obtained by diagonalizing the Hessian matrix in mass-weighted Cartesian coordinates. Calculated vibrational frequency spectra of isolated C\textsubscript{60} and DETA, along with the DETA-C\textsubscript{60} complex, are shown in Fig. 5. The numerical frequency values along with the normal-mode assignments are listed in Table I. Comparison of our calculated vibrational frequencies with observed spectra for C\textsubscript{60} in Table I indicates that the theoretical values can be trusted with an uncertainty $\lesssim 10$ cm\textsuperscript{-1}.

In presence of DETA, successful hydrogen transfer to the C\textsubscript{60} cage cannot be identified by the occurrence of H-related vibrations since both H-C\textsubscript{60} and DETA exhibit similar H-C stretch modes at frequencies near $\approx 3000$ cm\textsuperscript{-1}. Comparison of vibrational modes of the complex in this frequency range, shown in Fig. 5(c), with that of the individual reactants, shown in Figs. 5(a) and 5(b), indicates a frequency shift associated with the coupling between DETA and the C\textsubscript{60} cage.

<table>
<thead>
<tr>
<th>Structure</th>
<th>This work</th>
<th>Expt.\textsuperscript{a}</th>
<th>Vibrational mode</th>
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</thead>
<tbody>
<tr>
<td>C\textsubscript{60}</td>
<td>531.7</td>
<td>521.0</td>
<td>C-C-C bending</td>
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<tr>
<td></td>
<td>575.0</td>
<td>571.8</td>
<td>Radial breathing mode</td>
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<td></td>
<td>1180.3</td>
<td>1178.0</td>
<td>Sym. C-C stretching</td>
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<tr>
<td></td>
<td>1431.4</td>
<td>1424.8</td>
<td>Asym. C-C stretching</td>
</tr>
<tr>
<td>DETA</td>
<td>199.9, 238.6</td>
<td>Twisting of terminal NH\textsubscript{2} groups</td>
<td></td>
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<tr>
<td></td>
<td>419.8</td>
<td>Scissoring of central C-N group</td>
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<td></td>
<td>498.8</td>
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<td>710.0</td>
<td>Wagging of central H atom</td>
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<td></td>
<td>783.2, 809.0</td>
<td>Wagging of terminal NH\textsubscript{2} groups</td>
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<td></td>
<td>1006.5</td>
<td>Asym. C-C stretching</td>
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<td>Asym. stretching of central C-N</td>
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<td></td>
<td>1407.7</td>
<td>Rocking of central H atom</td>
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<tr>
<td></td>
<td>1585.0</td>
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<td>3010.0, 3021.8</td>
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<td></td>
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<td>3528.1</td>
<td>Asym. stretching of terminal N-H</td>
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</table>

\textsuperscript{a}Reference 18.
The frequency shift can be best judged by considering the difference vibrational spectrum between the complex and isolated DETA and C\textsubscript{60} adducts. In the complex, we find the band of H-C modes strongly redshifted by $\approx 500$ cm$^{-1}$.

The coupling between DETA and the C\textsubscript{60} cage is also reflected in the wagging mode of terminal NH$\textsubscript{2}$ groups of the DETA, which are blueshifted by 20–30 cm$^{-1}$ due to the stronger coupling between the terminal N and C\textsubscript{60} in the complex.

So far, we have considered the energetically favorable 1,2-hydroamination adduct as the final state of the reaction. Experimentally, the hydroamination reaction has been reported to lead to C\textsubscript{60}H\textsubscript{18}, suggesting the docking and subsequent desorption of many DETA radicals on a single C\textsubscript{60} cage.\footnote{Present address: Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824-2320, USA.}

If C\textsubscript{60}H\textsubscript{18} is the final product, there must be a way to desorb DETA without significantly detaching the chemisorbed hydrogen or modifying the C\textsubscript{60} cage.

We propose to compare our calculated vibrational frequencies with IR spectra to identify the presence of hydroamination adducts, which we propose as a necessary prerequisite for successful hydrogen transfer to C\textsubscript{60}.

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\bibitem{ref16} In our context, the chemical notation “1,2-hydroamination adduct” means that the DETA amine radical and the transferred H atom are chemisorbed on neighboring C atoms of C\textsubscript{60}.

\bibitem{ref17} Glen P. Miller (private communication).


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