Graphene Multi-Protonation: a New Mechanism for Proton Permeation

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Abstract

The interaction between protons and graphene is attracting a large interest due to recent experiments showing that these charged species permeate through the 2D material quite easily. Various authors have computed the flipping of a chemisorbed proton (rotation of the C-H\(^+\) bond from one to the other side of the membrane) and found so far that the energy barriers (around 3.5 eV) are too high to explain the experimental findings. Contrarily to the previous approach that assumes an isolated proton, in this work we consider protonated graphene at high coverage and explore the role played by nearby chemisorbed protons in the permeation process. By means of density functional theory calculations on a large molecular model for graphene (circumcoronene, C\(_{54}\)H\(_{18}\)) it is found that the permeation barrier can be reduced down to 1.0 eV when various protons are adsorbed on the same carbon (benzenic) ring. The process comprises a transition state where, basically, two protons are bound to two consecutive carbon atoms and one of the protons inserts into the C-C bond while the carbon atoms adopt sp\(^2\)-like hybridizations, a feature that contributes to the lowering of the activation barrier. This new mechanism involving low energy barriers might be considered as an alternative interpretation of the experimental observations.

Graphical TOC Entry
Introduction

This work is motivated by recent experimental work on the permeation at room temperature of protons through graphene. In that study, Geim and coworkers reported conductance and mass spectroscopy measurements of proton transport through pristine graphene and found that, in a temperature range of 270-330 K, the process exhibits an Arrhenius-type behavior with a rather low activation energy (about 0.8 eV). Moreover, protons permeate through this two-dimensional crystal about ten times faster than deuterons. These discoveries were absolutely unexpected since graphene was believed to be completely impermeable to all atoms and molecules under ambient conditions. A number of works have subsequently appeared—both experimental and theoretical—not only stimulated by the promise of important applications in hydrogen technology but also with the aim to uncover the microscopic mechanisms underlying these observations.

As far as we are aware, a satisfactory understanding of the processes that lead to such a facile permeation of protons through graphene has not been given yet and there is some debate about a possible role of defects in the transport process. Some works have emphasized the role of quantum tunneling in effectively lowering the energy barrier and on isotope selectivity, using models that assume that protons/deuterons are free particles. In the experiments, however, protons are initially moving within an aqueous media (hydrated Nafion or HCl solution), so in other works protons are considered to be bound to water (as H$_3$O$^+$) in the reactants states. As Shi et al indicate, two possible modes for the penetration of a hydrated proton can be distinguished. The first one (dissociation-penetration) involves the removal of the proton from the water network as it crosses the graphene membrane through the hollow of a carbon ring. It has been found that this mechanism is unlikely due to the large proton affinity of water. Interestingly, Feng et al have recently found, by means of first principles calculations, that the proton transport can be largely facilitated if various carbon atoms of the graphene layer (close to the crossing region) are in sp$^3$ configurations due to hydrogenation. In the second mechanism (adsorption-penetration), a
proton is transferred from the aqueous media to the graphene surface, where it becomes chemisorbed at the top of a carbon atom and, in a second step, it flips through the hollow from the original chemisorbed site to a related one on the other side of the layer. Previous works\textsuperscript{14} indicate that the barrier for proton transfer from water to a chemisorbed state is small and therefore the first step appears to be feasible at ambient conditions. However, the chemisorbed state is very stable, hence the barrier for the proton flipping becomes extremely high (\( \sim 3.5 \text{ eV} \)).

In this work, we assume that the chemisorbed proton is not initially isolated but surrounded by a number of protons that are chemisorbed as well and, in this way, we aim to explore the role of these neighbors on the flipping process. In other words, it is supposed that protons have been already transferred from the water network to a set of chemisorption sites so that the graphene sheet becomes partially protonated on one of its sides. It is found that, if two protons respectively attach to two consecutive carbon atoms, the permeation mechanism is completely different to that of an isolated chemisorbed proton. First, the energy barrier drops quite significantly (down to about 1.0 eV). Second, in contrast with the isolated case, where the reaction path goes through a planar transition state near the center of the carbon ring, the path for the multiprotonated case involves the insertion of the flipping proton into the middle of an effectively broken C-C bond. This bond is restored once the flipping process comes to an end, therefore preserving the stability of the membrane. It is worth noting that this mechanism bears significant similarities with a process reported some time ago by Lee et al.\textsuperscript{17} in their study of the electrochemical storage of hydrogen within single-walled carbon nanotubes, where a low energy reaction path was identified for a hydrogen atom flipping from the external to the internal side of the nanotube. We propose that the mechanism presented here provides an alternative interpretation of the experimental observations\textsuperscript{14} to that presented by Feng et al.\textsuperscript{14} that could also provide clues for the understanding of the properties of hydrogenated graphene\textsuperscript{18,19} and of processes of astrochemical interest involving interactions between hydrogen/protons and carbonaceous surfaces.\textsuperscript{20,21}
The paper is organized as follows. Computational methods are described in the following section. Next, results are presented and discussed, starting with an analysis of the stability of protonated graphene and continuing with a study of the permeation process as a function of the number of chemisorbed protons along a carbon ring. The report closes with a summary where further lines for research are indicated.

**Computational Methods**

We have performed electronic structure calculations of the interaction between a number of protons ($n = 1 - 6$), all chemisorbed along a given carbon ring of graphene, using a molecular model of that material. In previous works the coronene molecule was found to be a sufficiently accurate model for the study of the physical adsorption of single atoms or the sticking of hydrogen atoms to graphene. Here, a larger molecular prototype is required to correctly describe a more complex process involving a larger number of adsorbed species and, to this end, we have found that the use of circumcoronene ($C_{54}H_{18}$) is sufficiently adequate for the present purposes.

DFT calculations have been performed for the optimization of the protonated circumcoronene structures by using the PBE functional together with the cc-pVTZ basis set. These calculations were found to be in good agreement with benchmark MP2/aug-cc-pVTZ computations carried out for a smaller carbon plane prototype such as coronene. Additional calculations involving a larger prototype ($C_{96}H_{24}$) were carried out with a reduced 6-311+G basis set. We have verified that, in the case of coronene, this smaller set provides energy variations that are in good agreement (within few percents) with those obtained with the cc-pVTZ basis set. All reported energies correspond to stationary points whose correct nature has been verified by carrying out harmonic frequency calculations, used in turn to estimate zero-point energy and thermal corrections (at 298 K and 1 atm) to thermodynamic properties. Intrinsic reaction coordinate calculations have been employed to check that reactants
and products are indeed connected with the transition states for various of the permeation processes.

All DFT computations have been performed by using the Gaussian 09 code.  

Results and Discussion

First, we address the question about the affinity of graphene to chemically adsorb protons. Structures of circumcoronene after the sequential sticking of protons above its central ring are illustrated in the upper part of Fig. 1. In the lower part of Fig. 1 we report the energy variation between the protonated and unprotonated graphene prototype as a function of the number of chemisorbed protons. It can be seen that the consecutive addition of a proton to a graphenic ring is a likely process since, after the chemisorption of the first proton, the successive addition of protons is energetically favorable for up to four protons. Moreover, when a larger graphene molecular prototype as circumcircumcoronene (C_{96}H_{24}) is taken into account (see solid line in Fig. 1), we observe a remarkable stabilization (of about 26-27 eV) for the chemisorption of up to 5-6 protons. These results suggest that the saturation of a graphenic ring with protons is in principle energetically possible and we can expect that even more favorable chemisorption energies could be found if a larger graphene molecular prototype would be considered.

We have noticed that once the C-H\(^+\) bond is formed the proton character is lost and the partial charge on hydrogen is that typical of an usual C-H bond; however, to remind the reader that only protons are added, the positive charge on the hydrogen atoms will be retained.

Having established the stability of the graphene prototypes when several protons are chemisorbed on a benzenic ring, we start studying the permeation process for one and two chemisorbed protons. In Fig. 2 the proton penetration from one side to the other side of the carbon plane is compared for the case of a single chemisorbed proton (n = 1) and that
Figure 1: Upper part: sequential protonation of a graphenic single ring. Lower part: corresponding energy variation with respect to the unprotonated graphene molecular prototype. The dashed and solid lines correspond to the \( \text{C}_{54}\text{H}_{18} \) (circumcoronene) and \( \text{C}_{96}\text{H}_{24} \) (circumcircumcoronene) prototypes, respectively.
Figure 2: Most favorable proton flipping mechanisms for the consecutive protonation (up to two protons) of a graphenic single ring. The first row shows the reactants configuration with adjacent protons chemisorbed on the same side of the carbon plane. The second row shows the transition state (TS) configuration. For $n=2$, carbon atoms bound to the flipping proton ($C_a$) and to the adjacent proton ($C_b$) are indicated. The last row shows the products configuration with one proton flipped on the other side of the carbon plane. The corresponding electronic energy and enthalpy balances are reported in Table I.
Figure 3: As in Fig. 2 but with five and six protons chemisorbed on the graphenic single ring.

of two protons attached to two consecutive carbon atoms ($n = 2$). For the isolated proton the transition state (TS) corresponds to a planar structure: the C-H$^+$ bond rotates to locate near the center of the ring (termed as “hollow” TS) and continues the rotation to end up in an equivalent chemisorption state at the other side. Notice that at the TS the original C-H$^+$ bond has been broken. The corresponding activation energy ($\Delta E_a$) is quite high and close to 3.5 eV as reported in Table 1. Similar results have already been obtained from previous calculations at the DFT level. However, for two nearby chemisorbed protons the reaction path is quite different: the related TS is not planar and we observe the insertion of the proton through the middle of the C-C bond connecting to the closest chemisorbed additional proton (“insertion” TS). For this to occur, the length of that C-C bond changes from 1.55 (reactants) to 2.39 Å (TS), so the bond effectively breaks. Interestingly, this breaking of the C-C bond does not provoke a large energetic penalty as could be expected. On the contrary, as shown in Table 1 the corresponding activation energy is about 2.8 eV, lower than that of the single chemisorbed proton. In part this is due to the fact that, during
insertion, the C-H bond is preserved as opposed to the \( n = 1 \) case where such a bond is broken.

Table 1: Electronic energy and enthalphy variations associated to the most favorable single proton flipping process for an increasing number (\( n \)) of adjacent chemisorbed protons on a graphenic carbon ring. The cases of \( n=1,2,5 \) and 6 are illustrated in Figs. 2 and 3. The first two columns show the energy balances between reactants (R) and transition state (TS) while the last columns, those between reactants and products (P). The last line reports the values for the arrangement of five protons on a ring plus one proton on a surrounding ring (Fig. 5), leading to the lowest activation energy. Values are in eV.

| chemisorbed protons | \( \Delta E_a \) | \( \Delta H_a \) | \( \Delta E_r \) | \( \Delta H_r \) |
|---------------------|-----------------|-----------------|-----------------|-----------------|
| \( n=1 \)           | 3.44            | 3.24            | 0.00            | 0.00            |
| \( n=2 \)           | 2.77            | 2.65            | -0.39           | -0.39           |
| \( n=3 \)           | 2.29            | 2.17            | -0.38           | -0.42           |
| \( n=4 \)           | 1.76            | 1.69            | -0.37           | -0.37           |
| \( n=5 \)           | 1.53            | 1.44            | -0.46           | -0.47           |
| \( n=6 \)           | 1.61            | 1.50            | -1.21           | -1.20           |
| \( n=5+1 \)         | 1.01            | 0.95            | -0.55           | -0.56           |

To get insight into this new mechanism, we have examined in detail the structures of the corresponding stationary points (right panel of Fig. 2). Let us denote \( H_a^+ \) and \( H_b^+ \) as the flipping and adjacent protons, respectively, and \( C_a \) and \( C_b \), as the carbon atoms linked to those protons (see right central panel of Fig. 2). Initially, these carbon atoms exhibit four bonds in a sp\(^3\)-like hybridization (i.e., \( C_a \) is bound to \( H_a^+ \), to \( C_b \) and to two other adjacent carbon atoms of the graphenic network, the corresponding C-C distances, 1.50-1.55 Å, being typical of single bonds). At the TS, the \( C_a-C_b \) bond is broken but the \( C_a \) atom keeps its bonding with the three remaining atoms, showing, however, quite different bond distances and angles (C-C distances are reduced to 1.36 Å). Indeed, these four atoms nearly exhibit a planar geometry (with \( C-C_a-H_a^+ \) and \( C-C_a-C \) angles of 113° and 134°, respectively), indicating that the \( C_a \) atom approximately adopts a sp\(^2\) configuration. Analogously, the three remaining bonds around the \( C_b \) atom have transformed towards a trigonal planar geometry (angles \( C-C_b-H_b^+ \) and \( C-C_b-C \) being 118.5° and 122°, respectively), thus
showing also C_b an sp^2 configuration. Although the distance between the flipping proton and the opposite carbon atom at the TS, H_a^+-C_b, is short (1.32 Å) it does not correspond to a bonding interaction but rather to a repulsive one. This is to be expected considering that, as stated before, the proton character in the C_aH_a^+ bond has been lost and therefore it can only experience a steric repulsion with the C_b atom. This will be further confirmed below as a correlation between the H_a^+-C_b distances and the barrier heights.

Therefore, as a qualitative explanation for the relatively low activation energy of this insertion process, it can be said that the cost of breaking the C-C bond at the TS is compensated by the transformation of the remaining bonds to stronger sp^2-type ones. We have checked that, when additional adsorbed protons are added to the same ring of carbon atoms, the penetration process occurs through the same kind of insertion TS, as can be seen, for instance, in Fig. 3 for the case of five and six protons.

Additional adsorbed protons have been consecutively added along the central ring of the circumcoronene molecule and the results for the proton permeation are collected in Table 1 and in Fig. 4. Note that the flipping proton is that located at the end of the row of chemisorbed protons, as indicated schematically in the upper part of Fig. 4. It is found that the activation energy further decreases with the protonation degree, reaching a minimum of $\Delta E_a=1.53 \text{ eV}$ for $n = 5$ (less than half of the value for $n=1$) and then slightly increasing to 1.61 eV for $n = 6$. The corresponding enthalpies are roughly 0.10 eV smaller than the activation energies, in accordance with the finding that the zero point energy is larger for reactants than for the TS. On the other hand, as seen in Fig. 4 (middle panel), the C_a-C_b distance in the reactants state monotonously increases with $n$ up to $n = 5$. This is a consequence of the amplification of the ring area, in turn due to the increasing number of single C-C bonds and effects of steric repulsion between hydrogens. This feature probably facilitates a larger C_a-C_b distance in the TS (as indeed seen in the lower panel of Fig. 4) and therefore an easier insertion of the proton between the two carbon atoms (a lower energy barrier). In fact, the C_b-H_a^+ distance increases from 1.32 Å for $n = 2$ to 1.52 Å for $n = 6$. }

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| Number of protons | 1   | 2   | 3   | 4   | 5   | 6   |
|------------------|-----|-----|-----|-----|-----|-----|
| Reactants        |     |     |     |     |     |     |
| Transition State |     |     |     |     |     |     |
| Ca - Cb distance (Å) |     |     |     |     |     |     |
|                  | 1.00 | 2.00 | 3.00 | 1.55 | 1.60 |     |

**Figure 4:** Upper panel: Activation energy $\Delta E_a$ (in eV) for the permeation of a proton through a graphene prototype (circumcoronene) as a function of the number of chemisorbed protons along the central carbon ring. Initial configurations of the protons are schematically depicted in the upper part of the figure, where red and dark blue circles represent flipping ($H_a^+$) and adjacent ($H_b^+$) protons. Middle panel: distances between the corresponding carbon atoms $C_a$ and $C_b$ in the reactant state. Lower panel: same as middle panel for the transition state.
whereas the $C_a$-H$_a^+$ distance stays in the range of 1.07-1.08 Å in the whole $n$ range studied.

From Table 1 it can also be seen that (except for $n$=1 where initial and final states are equivalent) the flipping process is exothermic with electronic energy and enthalpy variations ($\Delta E_r$ and $\Delta H_r$) ranging between -0.4 to -0.5 eV for $n$=2-5. This result is not surprising as in related systems as hydrogenated graphene the most stable states involve adjacent carbon atoms, each one linking hydrogen atoms at opposite sides of the layer. Moreover, note that $\Delta E_r$ drops to about -1.20 eV for $n$ = 6, indicating that the permeation process is globally more favorable when the graphenic ring protonation is complete. In this case a sp$^3$ configuration of the carbon atom bound to the flipped proton appears to be even more feasible as it is connected with two carbon atoms supporting protons on the other side, in an arrangement that is more similar to the typical chair conformation of graphane.

Interestingly, we have found that the permeation process exhibits different activation barriers and exothermicities depending on the position of the proton within a given row along a carbon ring. For instance, we have studied the case where the flipping proton is the central one in a row of five protons (Fig. S1) and compare the results with those of the $n$ = 5 case reported above, which shares the same reactant state but where the flipping proton is the one at the end of the row (right panel of Fig. 3). The process occurs through the same kind of insertion TS (middle panel of Fig.S1) but the activation energy is considerably larger (2.54 eV vs. 1.53 eV). We have noticed that at the TS the $C_a$-$C_b$ distance is smaller than in the previous case; there are also some other differences in size, shape and flatness of the central and adjacent rings between the two TS being compared. In addition, exothermicity of this process is larger (-0.83 eV) than for the flipping of the external proton (-0.46 eV). As already discussed for $n$=6, the greater stability of the products can be related with a larger feasibility of the carbon atom linking the flipped proton to be arranged in a sp$^3$ geometry (lower panel of Fig.S1).

As can be foreseen from the previous results, it is a real challenge to identify the optimum configuration for the proton transport among a large number of different initial proton
Figure 5: Same as in Figs. 2 and 3 for the case of five protons on a ring plus another one on a nearest neighbor ring.
distributions. We have analyzed some more candidates and in Table 1 we show the obtained optimum configuration, named $5 + 1$, corresponding to five protons adsorbed on the central ring plus another one on a nearest neighbor ring, as reported in Fig. 5. The related activation energy is only 1.0 eV which already can be considered consistent with the experimental determination\textsuperscript{1}, especially taking into account that a further reduction when properly including tunneling effects could be expected. This brings strong support to the newly proposed mechanism as a consistent explanation for the experimental findings.

There have been two previous theoretical studies which deserve special mention in connection with the present work, both of them already briefly mentioned in the Introduction. First we recall the work of Feng \textit{et al}\textsuperscript{14} where the importance of locally saturating carbon chemisorption sites via hydrogenation together with the associated change in carbon hybridization proved crucial in determining lower barriers for proton transport. We would like to stress some important differences with our proposed new mechanism. First, our model strictly includes the addition of protons as opposed to hydrogen atoms thus lending our approach closer to the proton permeation experimental conditions. Second and most important we propose a qualitatively different path, not through the center of the carbon hexagon but rather an insertion into a C-C bond. This path is analogous to the flip-in hydrogen insertion mechanism in single-walled carbon nanotubes reported by Lee \textit{et al}\textsuperscript{17} using periodic density-functional tight-binding calculations. They found a low energy path (with $\Delta E_a = 1.51$ eV) where a hydrogen atom inserts into the middle of a very stretched C-C bond (details about the structure of the transition state were not provided), a bond that is exothermically recovered after the hydrogen atom has flipped-in. However, they note that the flip-in process is efficient only if the nanotube is completely saturated, while an analogous conclusion for protonated graphene is not suggested from the present explorations (eg. Fig.S2). Also, the authors report even lower activation barriers for the flipping-in of a hydrogen atom nearby another one already on the inner surface of the nanotube, a finding that is opposite to the test reported in Fig.S3. Of course, the distinct structure of a carbon nanotube as compared
with graphene and the use of hydrogen atoms in their simulations instead of protons may be at the origin of these different features.

**Summary and Outlook**

To summarize, we have reported DFT calculations of the permeation (flipping) of a proton through multiprotonated graphene, using circumcoronene as its molecular prototype. A new mechanism involving relatively low energy barriers (down to about 1.0 eV) has been found to occur when there is at least one other chemisorbed proton next to the flipping one. The corresponding transition state is characterized by the insertion of the proton into the middle of a C-C bond and a rearrangement of the hybridizations of the involved carbon atoms, with a recovering of that bond after the flipping is completed. The nature of this transition state as well as the enlargement of the C-C distances in the initial state is at the origin of the reduced activation energy as compared with the flipping of an isolated chemisorbed proton.

The lowest reported energy barrier is close to the experimentally measured activation energy (0.8 eV), and some contributions not taken into account in the present work -such as solvent effects, nuclear quantum effects and bias potential- could actually play a role in further decreasing it. In the context of these experiments and within the frame of the adsorption-penetration model mentioned in the Introduction, it would be also important to study the multiprotonation of graphene by proton transfer from the aqueous environment. Moreover, we believe that it is worth to investigate whether related systems such as hydrogenated graphene or hydrogenated/protonated hexagonal boron nitride exhibit permeation processes with mechanisms analogous to those here reported. Work along some of these directions is in progress.
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**Supplementary Material**

Cases where the flippling proton is central in the row of chemisorbed protons or there is a secondary protonated ring, or there are two protons flipping, are shown in the Supplementary Material.

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**Supplementary Material**
Figure 6: **Flip of the central proton of a five-proton row.** Mechanism for the flipping of the central proton in a row of five chemisorbed protons along a carbon ring. Reactants, transition state and products configurations are showed in the upper, middle and lower panels, respectively. Activation energy and exothermicity are $\Delta E_a = 2.54\,\text{eV}$ and $\Delta E_r = -0.83\,\text{eV}$, respectively, to be compared with $\Delta E_a = 1.53\,\text{eV}$ and $\Delta E_r = -0.46\,\text{eV}$ for the case where the flipping proton is the one located at the end of the row. All calculations have been performed as detailed in the main article.
Figure 7: **Protonation of a second adjacent ring.** Same as Fig. 6 for ten protons chemisorbed covering the central ring of the prototype as well as an adjacent ring. The corresponding energy balances are $\Delta E_a = 1.73$ eV and $\Delta E_r = -1.65$ eV, to be compared with the case of the chemisorption on only one ring (with $n=6$), where $\Delta E_a = 1.61$ eV and $\Delta E_r = -1.21$ eV. It is seen that, although the process becomes globally more favourable when adjacent rings are also saturated, the related activation energy is slightly higher.
Figure 8: **Flipping of a second proton.** Same as Fig. 6 for the flipping of a second proton in the case of a fully protonated graphenic ring ($n=6$), once a neighboring one has already migrated to the other side of the carbon plane. The most favourable second proton to be flipped is the second nearest neighbor, as seen in the Figure. The related $\Delta E_a$ is 2.07, larger than that corresponding to the flipping of the first proton ($\Delta E_a$=1.61 eV). Also, exothermicity is smaller for the second flipping proton ($\Delta E_r$=-0.55) than for the first one ($\Delta E_r$=-1.21).