

Quantum Chemical Calculation of Reactions Involving C_{20} , C_{60} , Graphene and H_2O

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Calculations of chemical reactions between C_{20} , C_{60} , hydrogen and water molecules are carried out using the PM3 method. Reactions with a hydrogen release at room temperature and atmospheric pressure are identified by the Gibbs energy change. The hydrogen release can be raised by increasing the number of water molecules in chlorine-assisted decomposition of fullerenes. Calculations of the Gibbs energy of chemical reactions involving water molecules between two parallel curved graphene sheets are carried out using DFT with the functional UB3LYP. During pumping between plates of an electric capacitor designed from curved graphene sheets, the water vapor with the assistance of external illumination is enriched by electrically neutral hydroxyl groups (OH)⁰.

Keywords: PM3 method; DFT calculation; fullerene; graphene; hydrogen; water; hydroxyl group.

1. Introduction

Interaction of hydrogen, oxygen and water molecules with carbon low-dimensional systems is in focus of many researchers.^{1–5} For example, graphene is often used as a photocatalyst⁶ because of its unique two-dimensional conjugated structure and electronic properties.⁷ In addition, fullerenes and carbon nanotubes are useful in nanotechnology, biotechnology and medicine. The study of chemical reactions accompanied by the decomposition of

water molecules on graphene sheets with the formation of electrically neutral hydroxyl groups (OH)⁰ as bactericidal agent is relevant for applications in biomedicine.

The fullerene C_{20} can be effectively hydrogenated up to $C_{20}H_{20}$ unlike the fullerene C_{60} , which is typically hydrogenated to $C_{60}H_{36}$ molecule.⁸ The advantages of fullerene derivatives such as chlorinated $C_{60}Cl_{30}$ for different applications are also studied.^{9,10}

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The purpose of this paper is to demonstrate possible reactions involving C_{20} and C_{60} fullerenes, graphene, water, hydrogen and also chlorine, which provide release of hydrogen, hydroxyl groups (OH)⁰ and associated gases (carbon monoxide, oxygen, chlorine) by estimating the Gibbs energy ΔG within the quantum chemical approaches.

2. Methodology

All calculations were carried out using the Gaussian 09 package.¹¹ At each temperature in the range of 278–528 K (5–255°C), the complete optimization of the reactant molecules was performed using the quasi-Newton ion relaxation implemented in the method of Broyden–Fletcher–Goldfarb–Shanno (BFGS).¹² In our calculations, we used both the semi-empirical PM3 method and density functional theory (DFT)¹³ with the hybrid exchange-correlation energy functional UB3LYP with three unrestricted mixing parameters and the 6-31G (*d*, *p*) basis set. Using the larger basis set, such as 6-311G (*d*, *p*), is impractical since it leads to energy changes of $\sim 10^{-3}$ hartree per carbon atom.

To assess the possibility of a chemical reaction, the change in the Gibbs free energy $\Delta G = \Delta H - T\Delta S$ as a function of the absolute temperature T was estimated, where ΔH is the enthalpy change and ΔS is the entropy change. The enthalpy (or heat) of reactions ΔH is a function of temperature:

$$\begin{aligned}\Delta H &= H_f(\text{products}) - H_f(\text{reactants}) \\ &= \Delta G + T\Delta S,\end{aligned}$$

where H_f is the heat of formation. A reaction can occur spontaneously at $\Delta G < 0$. A negative sign for the heat of reaction ($\Delta H < 0$) corresponds to an energy release, whereas a positive sign for the heat of reaction ($\Delta H > 0$) corresponds to an energy absorption in the reaction.

Gibbs energy and enthalpy calculations for reactions with C_{60} , $C_{60}Cl_{20}$, $C_{60}Cl_{60}$, H_2O and other reactant molecules were carried out using the PM3 molecular orbital method. The DFT/UB3LYP method was used for reactions with graphene and water molecules, H^0 , $(OH)^-$, $(H_2O)^-$, $(2\cdot H_2O)^-$. [The reactant $(2\cdot H_2O)^-$ is a dimer of two water molecules, which has a negative electric charge.]. We have considered only those reactions that are chemically possible with high probability and are of practical interest.

3. Results and Discussion

3.1. Thermochemical analysis of reactions involving C_{20} , C_{60} and H_2O

Changes of the Gibbs energy (ΔG) between products and reactants for different reactions with C_{20} are shown in Fig. 1. Full saturation of C_{20} with chlorine atoms is likely to occur since the addition of atomic chlorine to C_{20} is energetically preferable (Fig. 1, reactions 2 and 5). By increasing the number of chlorine atoms attached to C_{20} , the Gibbs energy change ΔG becomes lower and thus reaction 2 has the higher probability. Reaction 7 (hydrogenation of C_{20}) can occur at $T < 1200$ K (see also Ref. 14). Reaction 4 (interaction of $C_{20}H_{20}$ and water with the release of H_2) is also possible.

Figure 1 also shows that reaction 1, accompanied by reaction 2 of $C_{20}Cl_{20}$ synthesis, can occur where $C_{20}Cl_{20}$ interacts with water ($20H_2O$) leading to the release of CO, H_2 and Cl_2 . The hydrogen yield ($20H_2$) is lower than that in reaction 4 ($30H_2$) with hydrogenated fullerene $C_{20}H_{20}$. Reaction 3 is shown for comparison indicating the higher probability of water decomposition ($40H_2O$) by chlorinated fullerene $C_{20}Cl_{20}$ with higher hydrogen yield ($40H_2$).

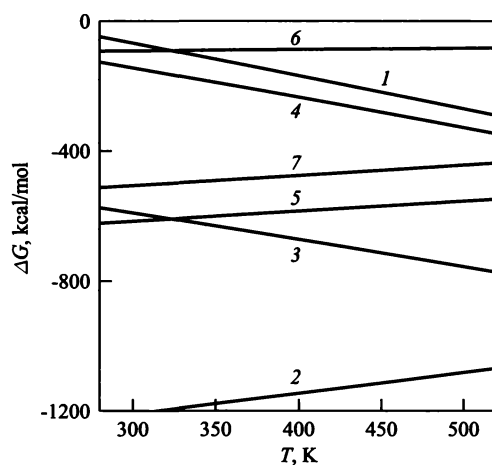


Fig. 1. Temperature dependences of the Gibbs energy change $\Delta G = \Delta H - T\Delta S$ in the reactions 1–7 with the participation of C_{20} .

Reactions:

- 1: $C_{20}Cl_{20} + 20H_2O \rightarrow 20CO + 10Cl_2 + 20H_2$ (+10.21 eV)
- 2: $C_{20} + 20Cl \rightarrow C_{20}Cl_{20}$ (−60.7 eV)
- 3: $C_{20}Cl_{20} + 40H_2O \rightarrow 20CO_2 + 10Cl_2 + 40H_2$ (−14.8 eV)
- 4: $C_{20}H_{20} + 20H_2O \rightarrow 20CO + 30H_2$ (+5.73 eV)
- 5: $C_{20} + 10Cl \rightarrow C_{20}Cl_{10}$ (−30.7 eV)
- 6: $C_{20} + O_2 \rightarrow C_{20}O_2$ (−4.48 eV)
- 7: $C_{20} + 10H_2 \rightarrow C_{20}H_{20}$ (−26.06 eV).

The heat of reaction ΔH is indicated in parentheses, the minus sign means energy release (exothermic reaction), the plus sign means energy absorption (endothermic reaction), 1 kcal/mol = 43.36 meV = $6.948 \cdot 10^{-21}$ J.

The Gibbs energy changes ΔG in the reactions 1–11 with fullerene C_{60} are shown in Fig. 2. It is evident that all reactions 3–6 of interaction of $C_{60}Cl_{60}$ with water are energetically favorable with the release of H_2 . However, reaction 1 occurs only at $T > 378$ K. Reactions 2 and 7 are also possible and show that chlorine atoms can be easily attached to C_{60} even at room temperature. In reactions 5 and 6 (having approximately the same Gibbs energy changes ΔG), chlorinated C_{60} fullerene is not decomposed, suggesting that the chlorine plays a role of a catalyst for hydrogen generation. From reactions 1, 3, 4 and 11, it can be seen that water can decompose C_{60} derivatives with a hydrogen release. In reactions 5 and 6, hydrogen and oxygen can be released, and then oxygen can be added to fullerene (reaction 8), forming the $C_{60}O_2$ molecule with a low probability by energy (cf. reaction 6 of $C_{20}O_2$ formation in Fig. 1).

Note that in reaction 6 partially chlorinated $C_{60}Cl_{20}$ fullerene can form. This compound can

instantly collapse (see reaction 1) in the presence of water vapor. In reactions 1 and 4, CO is released which can interact with water to form CO_2 in the reaction cycle with the release of hydrogen (reaction 9). Reaction 10 of $C_{60}H_{20}$ production is energetically unfavorable ($\Delta G > 0$) confirming ineffectiveness of C_{60} fullerene hydrogenation.⁸

It can be seen that reactions 2–10 with participation of C_{60} (Fig. 2) are exothermic, whereas reactions 1 and 11 are endothermic. In contrast, for chemical reactions with participation of C_{20} (Fig. 1), energy is released in reactions 2, 3, 5, 6 and 7, whereas reactions 1 and 4 are endothermic.

By common analysis of the both reaction series for C_{20} and C_{60} , we may conclude that the larger the number of water molecules interacting with chlorinated fullerenes, the more energetically preferable hydrogen release becomes (see reactions 1 and 3 in Fig. 1 and reactions 3 and 4 in Fig. 2). The occurrence of reactions 3 and 4 (Fig. 2) is most probable in terms of energy. The destruction of fullerenes is unfavorable for technological processes, since new C_{60} fullerenes are then needed in the cyclic process. Therefore, these reactions lead to possible hydrogen generation with consumption of chlorinated fullerenes. In order to increase the probability of reactions 5 and 6 that can preserve undestroyed fullerenes and suppress reactions 3 and 4, it is necessary to limit the amount of water molecules reacting with chlorinated fullerenes.

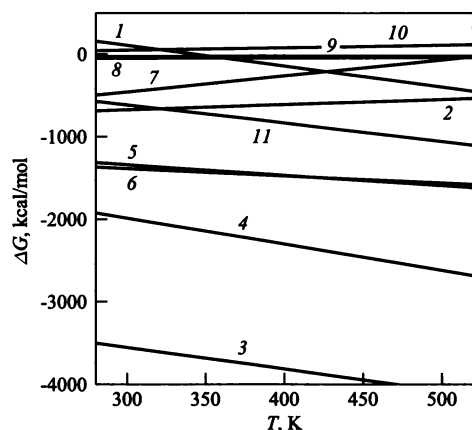


Fig. 2. Temperature dependences of the Gibbs energy change $\Delta G = \Delta H - T\Delta S$ in the reactions 1–11 with the participation of C_{60} .

Reactions:

- 1: $C_{60}Cl_{20} + 60H_2O \rightarrow 60CO + 20Cl + 60H_2$ (+37.9 eV)
- 2: $C_{60} + 20Cl \rightarrow C_{60}Cl_{20}$ (-37.2 eV)
- 3: $C_{60}Cl_{60} + 120H_2O \rightarrow 60CO_2 + 30Cl_2 + 120H_2$ (-119.9 eV)
- 4: $C_{60}Cl_{60} + 60H_2O \rightarrow 60CO + 30Cl_2 + 60H_2$ (-44.9 eV)
- 5: $C_{60}Cl_{60} + 2H_2O \rightarrow C_{60} + O_2 + 30Cl_2 + 2H_2$ (-41.7 eV)
- 6: $C_{60}Cl_{60} + 2H_2O \rightarrow C_{60}Cl_{20} + O_2 + 20Cl_2 + 2H_2$ (-48.7 eV)
- 7: $C_{60} + 60Cl \rightarrow C_{60}Cl_{60}$ (-45.1 eV)
- 8: $C_{60} + O_2 \rightarrow C_{60}O_2$ (-2.62 eV)
- 9: $CO + H_2O \rightarrow CO_2 + H_2$ (-1.25 eV)
- 10: $C_{60} + 10H_2 \rightarrow C_{60}H_{20}$ (-1.84 eV)
- 11: $C_{60}H_{20} + 60H_2O \rightarrow 60CO + 70H_2$ (+3.90 meV).

The heat of reaction ΔH is indicated in parentheses, the minus sign means energy release (exothermic reaction), the plus sign means energy absorption (endothermic reaction), 1 kcal/mol = 43.36 meV = $6.948 \cdot 10^{-21}$ J.

3.2. Thermochemical analysis of reactions involving curved graphene and H_2O

We propose the curved capacitor model (Fig. 3) consisting of two graphene sheets.¹⁵ The graphene sheets are connected by two electrodes to an external source of electrical voltage: a positive potential is applied to the concave graphene plate, whereas a negative potential is applied to the convex plate.

A local electric dipole moment can occur in this model on curved graphene sheets (see the bottom part of Fig. 3) due to asymmetrically extended π -bonds of carbon atoms (the direction of the electric moment is determined by the density of π -electron states, which is larger at the convex side of the graphene sheet).^{16,17} Therefore, the curved graphene surface can attract water molecules¹⁶ and it can be considered as an element of straintronics.¹⁸

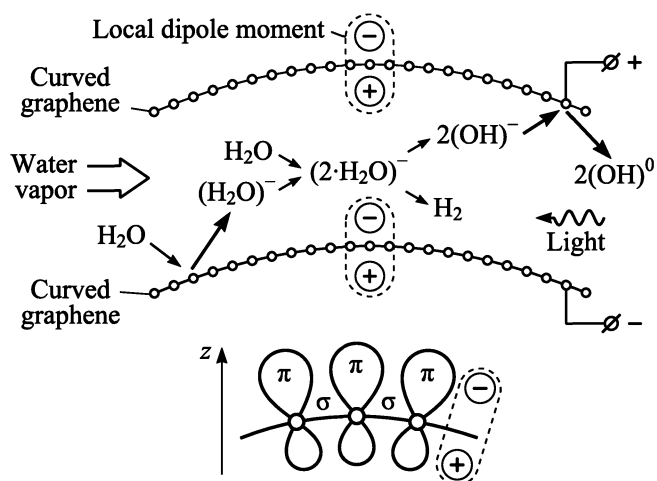


Fig. 3. Top: scheme of generation of the hydroxyl group $(\text{OH})^0$ between the convex and concave surfaces of graphene during water vapor injection. (A cross-section of curved graphene electrodes is shown.) Bottom: scheme of the occurrence of a local dipole moment on the graphene surface due to deformation of σ -bonds (which determine the mechanical strength of graphene) and redistribution of electron density for π -orbitals of carbon atoms along the z -axis (perpendicular to the graphene surface).

Figure 4 shows the results of the thermochemical calculations of the Gibbs energy change ΔG in reactions 1–5. This is the closed cycle of reactions that are chemically possible using external electromagnetic radiation (photochemical processes) pre-generating free ions and atomic hydrogen. In accordance with our calculations (Fig. 4), reactions 2–4 are possible ($\Delta G < 0$). They can be the primary reactions that lead to extraction of negatively charged hydroxyl groups $(\text{OH})^-$. Therefore, we present the roadmap of the main stages for production of hydroxyl group:

- (1) H_2O molecule in the water vapor flow (Fig. 3) colliding with the negatively charged curved graphene sheet can acquire a negative charge.
- (2) An electrically neutral H_2O molecule in the water vapor interacts with a negatively charged $(\text{H}_2\text{O})^-$ molecule (reaction 3) and produces a negatively charged water dimer $(2\cdot\text{H}_2\text{O})^-$.
- (3) The latter, $(2\cdot\text{H}_2\text{O})^-$, decomposes (reaction 4) into H_2 and two negatively charged hydroxyl groups $(\text{OH})^-$. The charge from $(\text{OH})^-$ can be transferred to the positive curved graphene anode. As a result, the electrically neutral hydroxyl groups $(\text{OH})^0$ can be formed.

In addition, water vapor with negatively charged water molecules can be exposed to external

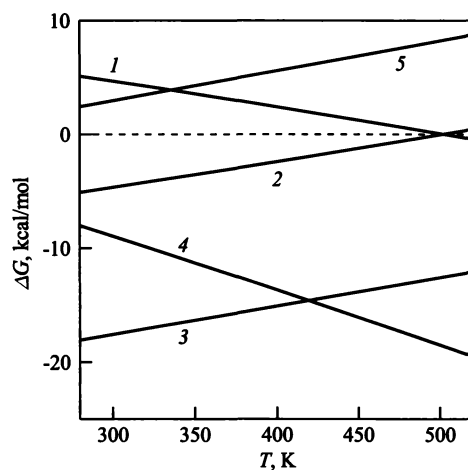


Fig. 4. Temperature dependences of the Gibbs energy change $\Delta G = \Delta H - T\Delta S$ in the reactions 1–5 with the participation of water.

Reactions:

- 1: $(\text{H}_2\text{O})^- \rightarrow \text{H}^0 + (\text{OH})^-$ (+0.50 eV)
- 2: $\text{H}^0 + (\text{OH})^- \rightarrow (\text{H}_2\text{O})^-$ (−0.50 eV)
- 3: $\text{H}_2\text{O} + (\text{H}_2\text{O})^- \rightarrow (2\cdot\text{H}_2\text{O})^-$ (−1.09 eV)
- 4: $(2\cdot\text{H}_2\text{O})^- \rightarrow \text{H}_2 + 2(\text{OH})^-$ (+31.91 eV)
- 5: $\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow (2\cdot\text{H}_2\text{O})^0$ (−0.22 eV)

The heat of reaction ΔH is indicated in parentheses, the minus sign means energy release (exothermic reaction), the plus sign means energy absorption (endothermic reaction), 1 kcal/mol = 43.36 meV = $6.948 \cdot 10^{-21}$ J, temperature 273.15 K = 0°C.

illumination. Then, reaction 1 can occur. Reaction 5 can proceed at room temperature leading to the formation of neutral water dimers $(2\cdot\text{H}_2\text{O})$. These dimers $(2\cdot\text{H}_2\text{O})$ can acquire a negative charge, by colliding with the curved and negatively charged cathode (Fig. 3), thereby increasing the number of negatively charged dimers $(2\cdot\text{H}_2\text{O})^-$ between graphene electrodes that are necessary for initiating reaction 4. As a result, the yield of negatively charged hydroxyl groups is increased. Under the above conditions, reactions 1 and 5 proceed at temperatures close to the room temperature.

The Gibbs energy change ΔG is a criterion for the reaction possibility. According to the results shown in Fig. 4, in the entire temperature range under consideration reactions 2–4 are energetically permissible ($\Delta G < 0$) with the release of $(\text{H}_2\text{O})^-$ and $(2\cdot\text{H}_2\text{O})^-$ ions as well as H_2 and $(\text{OH})^-$. However, reaction 1 occurs only at $T > 478$ K, while at room temperature it can require some external energy (provided, e.g., by illumination). Reactions 2, 3 and 5 proceed with the release of thermal energy ($\Delta H < 0$), and reactions 1 and 4, in contrast, are endothermic ($\Delta H > 0$).

4. Conclusion

Possible chemical reactions in a gas mixture of fullerenes C_{20} or C_{60} with water vapor leading to hydrogen release are revealed at temperatures close to 300 K. Reactions 2, 5, 6 and 7 in Fig. 2 constitute a closed cycle of reactions in which chlorine acts as a catalyst for hydrogen generation with low consumption of C_{60} fullerenes. In reactions 1, 2, 3, 5 in Fig. 1 and 1, 3, 4, 11 in Fig. 2, fullerenes C_{20} and C_{60} can be decomposed with the hydrogen release. The larger the number of water molecules involved, the higher is the probability of the hydrogen release.

Reactions 1–5 in Figs. 3 and 4 constitute the closed cycle of reactions in which negatively charged hydroxyl groups $(OH)^-$ can be produced. Reactions 3 (with the heat release) and 4 (with the heat absorption) are main reactions resulting in the formation of $(OH)^-$ ions at room temperature. Reactions 1 and 5 are possible at room temperature with an assistance of external illumination. Electric neutralization of $(OH)^-$ groups can be achieved by their contact with the positively charged graphene electrode.

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