



Graphene metal adsorption as a model chemistry for atmospheric reactions

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ABSTRACT

We propose a mechanism by which chloromethane and dichloromethane decomposition reaction occurs on the surfaces of graphene. To this end we have performed calculations on the graphene surface with metal adsorption on the sheet to reduce the formation of free-radical intermediates.

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1. Introduction

In recent work there has been considerable interest in the ability of nanotubes to alter certain chemical reactions using them as model chemistries for confined space. The nanotube confinement is believed to be important for reducing the energies needed for chemical reactions to take place by reducing the energies of reaction. Other experimental work successfully has found that nanotubes may be used as reaction vessels for the C₆₀O polymerization to yield a linear polymer (C₆₀O)_n [1]. Another study showed that fullerenes may undergo chemical reactions inside of the nanotubes causing linear chains to form [2] as well as other catalytic reactions [3]. In other studies the paper by Halls and Schlegel, revealed the impact of the presence of nanotubes on the Menshutkin SN2 reaction [4] as well as other mechanisms [5–8].

The use of such research maybe in drug delivery [9] and a variety of useful applications. What we have done in this study is to analyze the chemistry of decomposition mechanisms of chloromethanol, dichloromethanol and formyl chloride [10–13] on surfaces of graphene. It has been shown [14] that the adsorption of metals to the graphene surfaces can increase the potential reactivity of adsorbed molecules.

We believe that the decomposition of chlorinated hydrocarbons with and without the presence of water may be improved by the use of highly reactive radicals that may be obtained from hydrogen peroxide or ozone. If we can understand the way by which surfaces (i.e. graphene) can be used to improve the chemical nature of reactions this would be of importance.

We have considered Li adsorption on the opposite side of the graphene as where the proposed chemical reaction is taking place. The reason being that this eliminates any unfavorable reactions of the Li with reactants. As the periodic boundary conditions implied by calculations on the sheet are arbitrary and might influence the outcome qualitatively, the boundary effects are not severe which is the reason we considered a test-bed of finite flakes of graphene bounded by hydrogen.

This allows us to design a model chemistry for atmospheric reactions on graphene sheets. By discussing an important decomposition mechanism can provide insight of how graphene flakes can influence atmospheric mechanisms. If the reactions are in fact hindered by these graphene systems they can potentially be implemented to protect the environment and ozone layer.

As our strategy would be a mechanism to use graphene sheets to eliminate free radicals an understanding of such mechanisms might improve the negative impact of such products to living organisms. We will attempt to analyze different situations where metal adsorption to the surfaces of these graphene sheets improves the decomposition mechanisms of harmful reactions.

2. Computational methods

In this Letter we have used the GAUSSIAN09 suite of packages [15]. We have used the B3LYP [16] method with the STO-3G optimization and 6-311++G** for single point energy calculations. The higher order calculations were performed to eliminate the BSSE error that may be intrinsic to systems of this type.

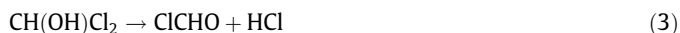
As per the previous Refs. [12,13] we have considered the following reaction path:



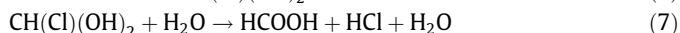
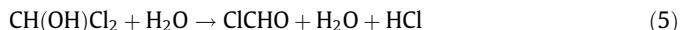
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The latter equation represents the decomposition of dichloromethanol, that can also be described as:



The same reaction can proceed via a different pathway:



As for the graphene surface we have considered a simple system of seven rings for the analysis. This reaction pathway is simple decomposition mechanism that can be used as a test-bed for application to other systems. This reaction was selected in order to test the concept of using Li adsorbed graphene sheets to inhibit specific harmful chemical reactions. In future work we shall consider the effect on chemical reactions of multiple Li adsorption to sheets of varying size.

3. Results and discussion

In Table 1 we display the relative energies (calculated with the B3LYP/6-311++G**//B3LYP/STO-3G method) of reactions (1)–(7) ΔE_I : isolated chemical reactions (1)–(7), ΔE_{II} : reactions (1)–(7) on the graphene surface and ΔE_{III} : reactions (1)–(7) on the Li adsorbed on the graphene complex. Finally, for the sake of comparison ΔE_{IV} represents the MP2/6-31+G** energies of reaction using a confined zigzag (8,0) structure as the base chemistry [13]. The latter calculations were performed previously using the confined cavity of the nanotube for the chemical decompositions.

The corresponding molecular structures were optimized at the B3LYP/STO-3G level of the reactants on the Li + graphene surface are displayed in Figure 1 and the products on Figure 2. The Li atom slightly distorts off the center of the graphene surface a trend that is commonly observed in fullerene structures [17].

Due to space limitations we have not discussed alternative structures or the geometrical optimizations of the adsorption of the reactants/products on the pristine molecular surface.

3.1. Reaction pathway 1: $\text{CH}_2(\text{OH})\text{Cl} \rightarrow \text{HCHO} + \text{HCl}$

From Table 1 it is interesting to note the varying energies of the chemical decompositions. As we can see for the $\text{CH}_2(\text{OH})\text{Cl} \rightarrow \text{HCHO} + \text{HCl}$ (Reaction (1)) we obtain a energy of reaction that is significantly higher on the Li + graphene surface than the free reaction and the non-metal reaction. If we compare to the previous results using nanotube confinement [13] we observe that the calculations suggest that in the presence of such conditions such decompositions are in fact more reactive. While the effect is interesting, for many of these chemical reactions a

higher barrier to reactivity is preferred as it minimizes the production of harmful free-radical intermediates.

As for the chemical structures the position and orientation of $\text{CH}_2(\text{OH})\text{Cl}$ with respect to flake is similar to the case without Li. Measuring the angles between the co-linear carbon atoms of the flake we obtain a bend of around 3° .

For the structure of the products we obtain slightly different results. Compared to case without lithium atom the change is large, whereby molecules are almost out of the flake with a very different orientation. The distance of the lithium atom to the flake is similar in both cases.

3.2. Reaction pathway 2: $\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CH}_2(\text{OH})_2$

If we observe the second reaction $\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CH}_2(\text{OH})_2$ the energy barriers using the tube are in the order of 13 kcal/mol which increase the barrier considerable compared to the isolated reaction. We observe that the reaction on the graphene surface has energy of reaction of -13.48 kcal/mol. When the metal is adsorbed to the sheet we obtain a reaction energy of -17.25 kcal/mol. While these results are better for the nanotube case in the first initiation of the mechanism our energies of reaction will potentially limit the chemical reaction from proceeding to these end products.

Structurally, the reactants and products have interesting chemical formations. For the reactions compared with this case without Li the structures differ, by which the molecules are almost out of the flake. For the products the position and orientation of molecule $\text{CH}_2(\text{OH})_2$ with respect to flake are similar to the non-Li case.

3.3. Reaction pathway 3: $\text{CH(OH)Cl}_2 \rightarrow \text{ClCHO} + \text{HCl}$

In the third mechanism $\text{CH(OH)Cl}_2 \rightarrow \text{ClCHO} + \text{HCl}$ our results using metal adsorption are not as notable as those of the nanotube surface. However, as it is a chain reaction from Eq. (1) the barrier is relatively high to prevent such molecules from forming.

The position and orientation of the reactant CH(OH)Cl_2 with respect to flake is similar in both cases. The angles between the co-linear carbon atoms of the flake yield a bend of 3° . We can consider qualitatively that the molecule is in the center of the flake. For the products the position and orientation of molecules with respect to flake are similar in the case without Li.

3.4. Reaction pathway 4: $\text{ClCHO} \rightarrow \text{CO} + \text{HCl}$

For this reaction the energies with the sheet are rather consistent and higher than the isolated mechanism. However, if we compare the efficacy of inhibiting the reaction on the surface when compared to the nanotube we observe a large difference. The value of the isolated reaction is 4.59 kcal/mol compared to 8.79 kcal/mol and -8.81 kcal/mol for the Li-graphene and nanotube case, respectively.

Table 1
Relative energies (calculated with the B3LYP/6-311++G**//B3LYP/STO-3G method) of the different chemical reactions in kcal/mol whereby ΔE_I : isolated chemical reactions 1–7, ΔE_{II} : reactions 1–7 on the graphene surface and ΔE_{III} : reactions 1–7 on the Li-graphene complex and ΔE_{IV} : reactions 1–7 using the MP2/6-31+G* zigzag (8,0) nanotube [13] for a model of the decompositions in a confined space.

Chemical reactions	No.	ΔE_I	ΔE_{II}	ΔE_{III}	ΔE_{IV}
$\text{CH}_2(\text{OH})\text{Cl} \rightarrow \text{HCHO} + \text{HCl}$	1	6.75	13.56	14.88	-15.51
$\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CH}_2(\text{OH})_2$	2	-8.76	-13.48	-17.25	12.95
$\text{CH(OH)Cl}_2 \rightarrow \text{ClCHO} + \text{HCl}$	3	-5.06	-6.33	-6.76	0.00
$\text{ClCHO} \rightarrow \text{CO} + \text{HCl}$	4	4.59	8.46	8.79	-8.81
$\text{CH(OH)Cl}_2 + \text{H}_2\text{O} \rightarrow \text{ClCHO} + \text{H}_2\text{O} + \text{HCl}$	5	-5.05	-20.41	14.51	-25.23
$\text{ClCHO} + \text{H}_2\text{O} \rightarrow \text{CH(Cl)(OH)}_2$	6	-5.05	4.10	1.13	44.43
$\text{CH(Cl)(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{HCl} + \text{H}_2\text{O}$	7	-1.76	1.02	-4.74	-24.77

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