

# Quantum Chemistry of Lithium-Graphene Interactions: Catalytic Activity of the Phenolate

Adolfo Salgado<sup>1</sup> and Ljubisa R. Radovic<sup>1,2</sup>

<sup>1</sup>Department of Chemical Engineering, University of Concepción, Concepción, Chile

<sup>2</sup>Department of Energy & Mineral Engineering, Penn State University, USA

\*lradovic@udec.cl, lrr3@psu.edu

## INTRODUCTION

Interest in the fundamental aspects of lithium-graphene interactions has grown tremendously over the past several decades, as their applications evolved from char gasification catalysis and graphite intercalation to carbon-based energy storage in rechargeable batteries. Here we report the results of our ongoing studies, using density functional theory, to gain an improved mechanistic understanding of chemisorption, surface rearrangement and desorption pathways for oxygen when an alkali phenolate is present at varying distances from a reactive zigzag site in graphene.

## METHODOLOGY

The Gaussian quantum chemistry software [1] is used to study the interaction of O<sub>2</sub> with a free zigzag site in prototypical graphene molecules that have an –OLi group in its vicinity (see Figure 1). The DFT model chemistry selected was B3LYP with the 6-31G(d) basis set; special care was exercised in the analysis of the spin multiplicity (M) of both ground and transition states. Transition-state structures were sought using the QST2 and/or QST3 procedures and confirmed using the intrinsic reaction coordinate (IRC) analysis.

## RESULTS AND DISCUSSION

Figure 2 shows a key portion of the path that is analogous to that of O<sub>2</sub> interaction with a metal-free graphene. The rearrangement is 6.8 kcal/mol uphill and CO<sub>2</sub> is eventually formed upon consecutive rupture of the C–C14–C bonds. In contrast, Figure 3 illustrates a path that may lead to desorption of CO, rather than CO<sub>2</sub>, even though it involves the (temporary) insertion of O to form a seven-member ring. The final ground-state structure in both cases, subsequent to CO<sub>2</sub> or CO desorption and nascent site deactivation [2], contains a pentagon, but the former path is more favorable by 37.5 kcal/mol.

## CONCLUSIONS

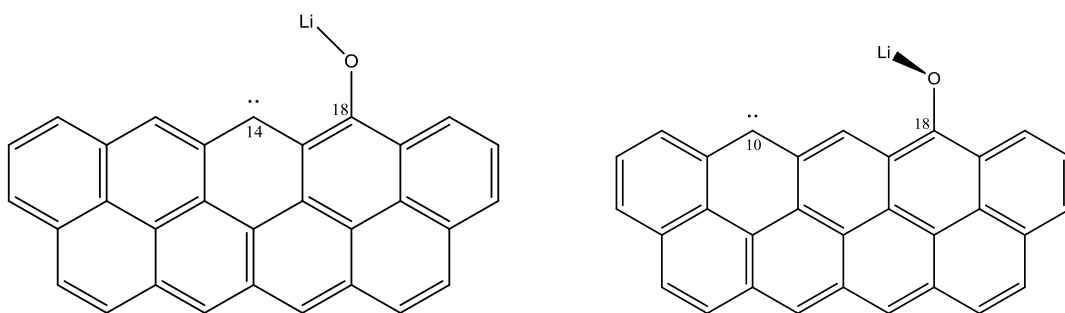
Chemisorption is exothermic in all cases and it is barrierless in the presence of lithium phenolate. Surface rearrangement is endothermic in the absence of the phenolate, and becomes exothermic in its presence. Furthermore, the highest barrier, for the cleavage of the bond between adsorbed O atoms, is reduced from ca. 35 to ca. 6.0 kcal/mol, as a consequence of Li-O attraction. Finally, several desorption pathways were characterized, including formation of both CO and CO<sub>2</sub>; the latter are analogous to those that have been suggested [3] to proceed in the absence of alkali phenolates.

## ACKNOWLEDGMENTS

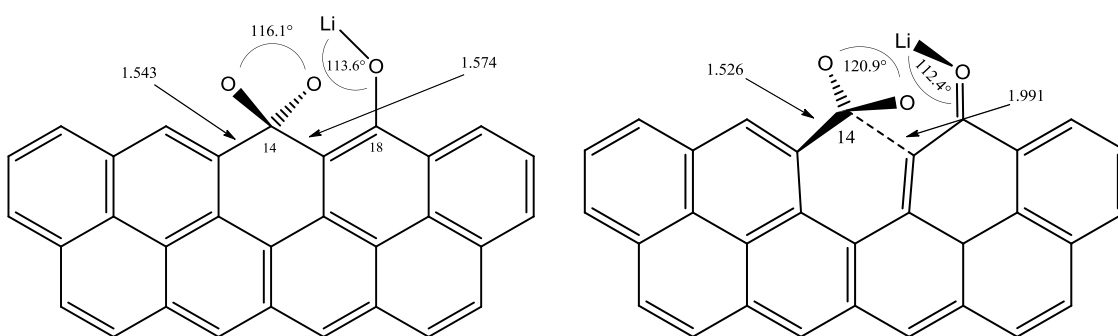
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## REFERENCES

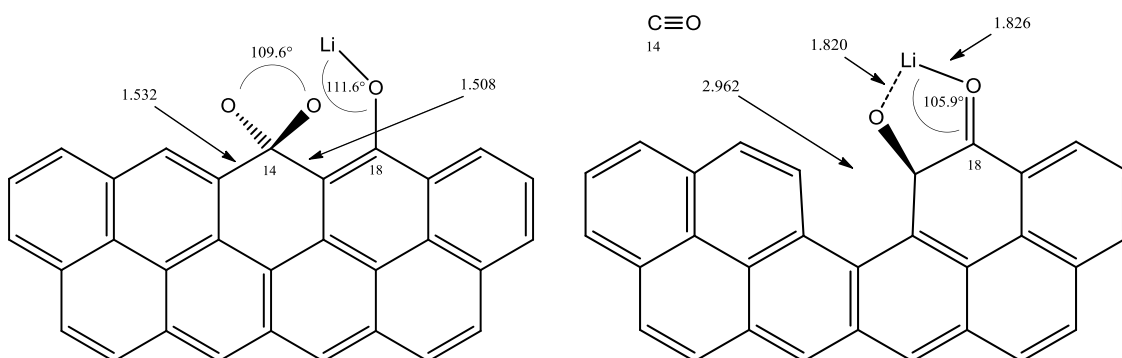
1. Frisch MJ *et al.*, Gaussian Inc., Wallingford CT, 2009.
2. Radovic LR *et al.*, *Carbon* (2011), 49, 3471-3487.
3. Radovic, LR, *J Amer Chem Soc* (2009), 131(47), 17166-17175.



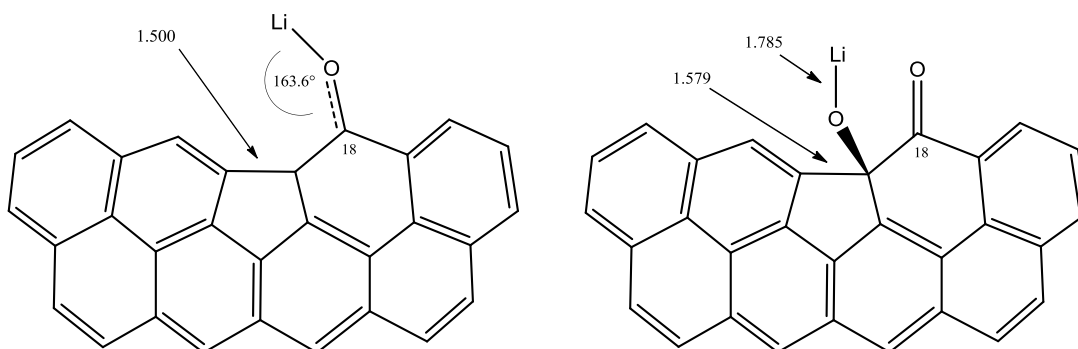
**Figure 1.** Graphene molecules used as models for analysis of electron density distribution upon interaction with  $O_2$  in the presence ( $C_{31}H_{13}OLi$ ) and absence ( $C_{31}H_{14}$ ) of a phenolate group.



**Figure 2.** Intermediate ground state (left,  $M=3$ ) and transition state (right,  $M=3$ ) leading to  $CO_2$  desorption.



**Figure 3.** Intermediate transition state (left,  $M=1$ ) and ground state (right,  $M=3$ ) leading to  $CO$  desorption.



**Figure 4.** Final ground states that result in desorption of  $CO_2$  (left,  $M=1$ ) and  $CO$  (right,  $M=3$ ) upon interaction of  $O_2$  in the presence of lithium phenolate.