

H4P: Quantum Chemistry of Lithium-Graphene Interactions: Catalytic Activity of the Phenolate

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Interest in the fundamental aspects of lithium-graphene interactions has grown tremendously over the past several decades, as their applications evolved from intercalation compounds [1] to char and biomass gasification catalysis [2,3]. Lately, the focus is on carbon-based energy storage in rechargeable batteries, where phenolic surface groups presumably play an important role in improving the capacity of reduced graphene oxide [4]. Here we report the results of our ongoing studies, using density functional theory (DFT), 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.

The Gaussian quantum chemistry software [5] is used to study the interaction of O₂ with a free zigzag site in prototypical graphene molecules [6] that have an -OLi group in its vicinity. 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.

Chemisorption is found to be 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.* 13 to *ca.* 6.0 kcal/mol, as a consequence of Li-O attraction. Finally, the mechanistic pathway found for oxygen reaction in the presence of lithium phenolate is analogous to the mechanism when alkali phenolate is absent. But, when lithium is present there is a path that leads to desorption of CO, rather than CO₂, in remarkable analogy to what has been suggested [7] to proceed in the absence of alkali phenolates.

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QUANTUM CHEMISTRY OF LITHIUM-GRAPHENE INTERACTIONS

Influence in the gasification process



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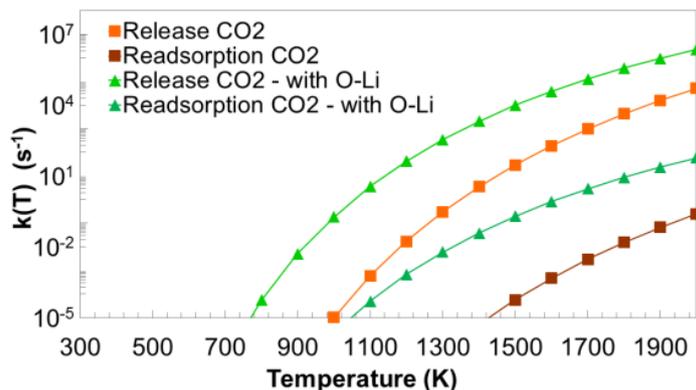
Background:

Interest in fundamental aspects of lithium-graphene interactions has grown tremendously, as their applications evolved from gasification catalysis [1] and graphite intercalation to carbon-based energy storage in rechargeable batteries [2]. To understand the mechanistic pathways of chemisorption, surface rearrangement and desorption of oxygen in the presence of alkali phenolates is crucial for maximizing their beneficial effects (e.g., catalytic activity).

Results and Discussion:

Among the many identified steps in the graphene-O₂ interaction, several are crucially affected by the presence of the alkali phenolate.

Without C-OLi (orange)		kcal/mol		With C-OLi Release of CO ₂ (green)		kcal/mol	
		ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
1 → 2		-59.4	-47.6	1 → 2		-52.1	-40.5
2 → 3		-10.0	-9.9	2 → 3		10.5	10.6
3 → 4		-54.8	-55.2	3 → 4		-60.4	-60.1
4 → 5		-11.4	-16.7	4 → 5		0.4	-5.0
Overall:		-135.6	-129.4	Overall:		-101.5	-95.0
E_a^f [kJ/mol]	368	A [s ⁻¹]	1.9×10^{14}	E_a^f [kJ/mol]	269	A [s ⁻¹]	2.2×10^{13}
E_a^r [kJ/mol]	415	A [s ⁻¹]	1.6×10^{10}	E_a^r [kJ/mol]	282	A [s ⁻¹]	1.3×10^9



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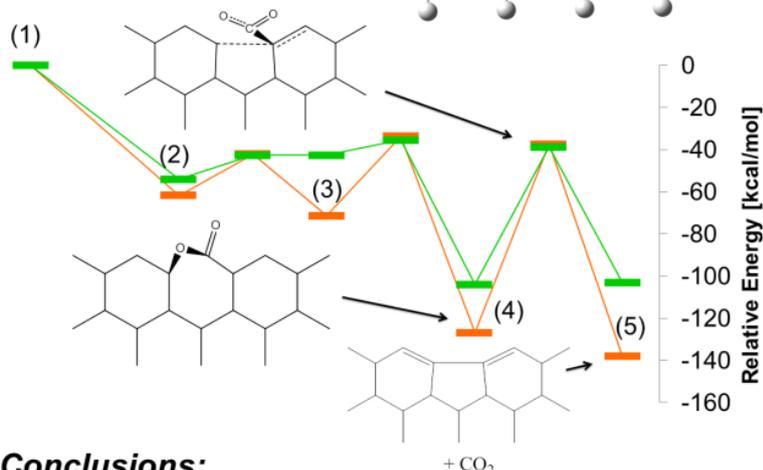
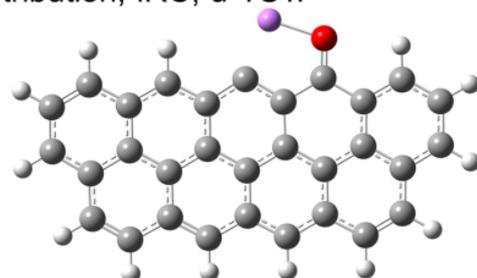
Objectives:

- Compare the reactivity of an active zigzag site in the presence and absence of alkali phenolates.
- Reveal the mechanism of evolution of CO₂ and analyze the influence of C-OLi.

Methodology and Models:

Computational quantum chemistry (Gaussian03, DFT, B3LYP/6-31G(d)): spin multiplicity analysis, electron density distribution, IRC, u-TST.

$$k = \frac{k_B T}{h} \frac{Q_{TS}^\ddagger}{Q_R} e^{\left(\frac{-\Delta E_0}{k_B T}\right)}$$



Conclusions:

- Chemisorption and surface rearrangement is exothermic in both cases.
- The overall process is thermodynamically favorable even in the absence of phenolate.
- The C-OLi group reduces the activation energy of CO₂ desorption by 99 kJ/mol, benefiting the gasification process at lower temperatures.
- The MEP leads to a stable 7-member lactone group formation, followed by CO₂ and simultaneous NSD. This is the RDS.