

## Density Functional Studies of Ring-Opening Reactions of Li<sup>+</sup>-(ethylene carbonate) and Li<sup>+</sup>-(vinylene carbonate)

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Reaction energies were determined for reductive ring-opening reactions of Li<sup>+</sup>-coordinated ethylene carbonate (EC) and vinylene carbonate (VC) by a density functional method. We have also explored the ring-opening of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC by reaction with a nucleophile (CH<sub>3</sub>O<sup>-</sup>) thermodynamically. Our thermodynamic calculations led us to conclude that the possible reaction products are CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCO<sub>2</sub>Li (O<sub>2</sub>-C<sub>3</sub> cleavage) for Li<sup>+</sup>-EC + CH<sub>3</sub>O<sup>-</sup>, and CH<sub>3</sub>OCHCHOCO<sub>2</sub>Li (O<sub>2</sub>-C<sub>3</sub> cleavage) and CH<sub>3</sub>OCO<sub>2</sub>CHCHOLi (C<sub>1</sub>-O<sub>2</sub> cleavage) for Li<sup>+</sup>-VC + CH<sub>3</sub>O<sup>-</sup>. The opening of VC would occur at the C<sub>1</sub>-O<sub>2</sub> side by a kinetic reason, although the opening at the O<sub>2</sub>-C<sub>3</sub> side is more favorable thermodynamically.

**Key Words :** Density functional calculation, Ring-opening reaction, Lithium-ion battery, Cyclic carbonate, Reductive decomposition

### Introduction

A hybrid lithium-ion battery system is made up of a graphite anode, a non-aqueous organic electrolyte that acts as an ionic path between the electrodes, and a transition metal oxide cathode. Lithium-ion battery electrolytes typically consist of a lithium salt and various additives dissolved in an organic solvent. The most popular solvents are the mixtures of cyclic carbonates, for example, ethylene carbonate (EC), propylene carbonate (PC), and linear carbonates such as dimethyl carbonate (DMC). It is generally recognized that organic electrolytes, particularly cyclic carbonates, are decomposed during the first several lithium intercalations into graphite to form a solid electrolyte interface (SEI) film between the graphite anode surface and the electrolyte. The SEI film plays a crucial role that affects the capacity, cycle life, and safety in the lithium-ion rechargeable battery.<sup>1,2</sup> Thus, the solvent decomposition and subsequent SEI buildup mechanism have been widely studied in the lithium-ion battery electrolyte, both experimentally<sup>3-12</sup> and theoretically.<sup>13-22</sup> It has been demonstrated that electrons would be initially transferred from the polarized electrode to the Li<sup>+</sup>-coordinated solvent (or additive) molecules, forming ion-pair intermediates. Then, a ring-opening would take place on the intermediates to generate radical anions, which participate in termination reactions resulting in proper products in the form of Li organic or inorganic salts, building up the SEI film.<sup>17-22</sup>

The elucidation of reaction mechanisms is a major challenge for theoretical studies. To date, many theoreticians have used quantum chemical methods to gain insights into the initial reactions at the microscopic level.<sup>13-15,17-22</sup> In the present work, Kohn-Sham density functional theory (DFT) calculations were used to investigate the reductive ring-opening reactions of Li<sup>+</sup>-coordinated EC and vinylene carbonate (VC), in order to gain insights into the initial

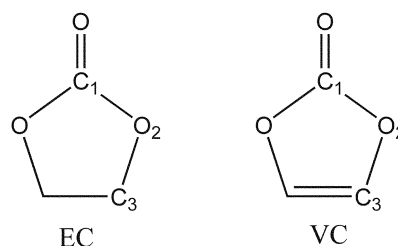


Figure 1. Labelling and molecular structures of EC and VC.

reactions. The molecular structures of EC and VC are depicted in Figure 1. The EC molecule is the electrolyte solvent most widely used in lithium-ion rechargeable batteries. The VC molecule is a reactive additive that reacts on the anode. The spectroscopic studies indicate that VC polymerizes on the lithiated graphite surfaces, thus forming poly alkyl Li-carbonate species that suppress both solvent and salt anion reduction.<sup>23</sup> We have studied the reductive ring-opening reactions by the C<sub>1</sub>-O<sub>2</sub> and O<sub>2</sub>-C<sub>3</sub> bond cleavages for Li<sup>+</sup>-EC and Li<sup>+</sup>-VC kinetically and thermodynamically. Aurbach *et al.*<sup>4</sup> examined the reactions between EC and nucleophiles to explore the major reduction products of EC on lithiated carbons. In the present work, we have also investigated the ring-opening reactions of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC by a nucleophilic (CH<sub>3</sub>O<sup>-</sup>) attack.

### Calculation Details

The equilibrium and transition-state structures were fully optimized by mPW1PW91<sup>24,25</sup> method using 6-311+G(d) basis set, mPW1PW91/6-311+G(d). The transition states were confirmed by the sole imaginary frequency. Single-point energies were calculated at the mPW1PW91/6-311++G(3df,3pd) level of theory. The mPW1PW91 functional gave a good performance for these systems and the 6-311++G(3df,3pd)

basis set was shown to effectively evaluate a basis set limit for these systems.<sup>26</sup> Spin-unrestricted scheme was employed for the odd numbered electron systems. The stationary point wave functions were also checked for spin contamination by evaluation of the  $\langle S^2 \rangle$  values. The  $\langle S^2 \rangle$  values are very close to 0.75, less than 0.761, for all the structures considered. We believe that major conclusions would be affected very little by the spin-contamination errors. The  $\Delta G$  quantities were calculated at 298.2 K using standard rigid-rotor harmonic oscillator partition function expressions. The bulk solvent effects were estimated by single-point calculations using the conductor variant polarized continuum model (CPCM),<sup>27</sup> a self-consistent reaction field (SCRF) method, which simulates the solvent as a continuum of uniform dielectric constant. We adopted the dielectric constant of 77.96, an average value between the dielectric constant of EC (89.78) and PC (66.14), which are the most widely-used solvents in lithium-ion secondary batteries. The GAUSSIAN03<sup>28</sup> program package was employed to perform all the calculations.

### Results and Discussion

For the reductive ring-opening reactions of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC, the mechanisms considered are shown in Figure 2. Table 1 presents the relative energies and Gibbs free energies ( $\Delta G$ ) for the reductive ring-opening reactions of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC including bulk-solvent effects. The  $\Delta G$  value including the solvent effects ( $\Delta G_{solv}$ ) of Li<sup>+</sup>-VC reduced to **2** is 4.8 kcal/mol lower than that of Li<sup>+</sup>-EC, which qualitatively

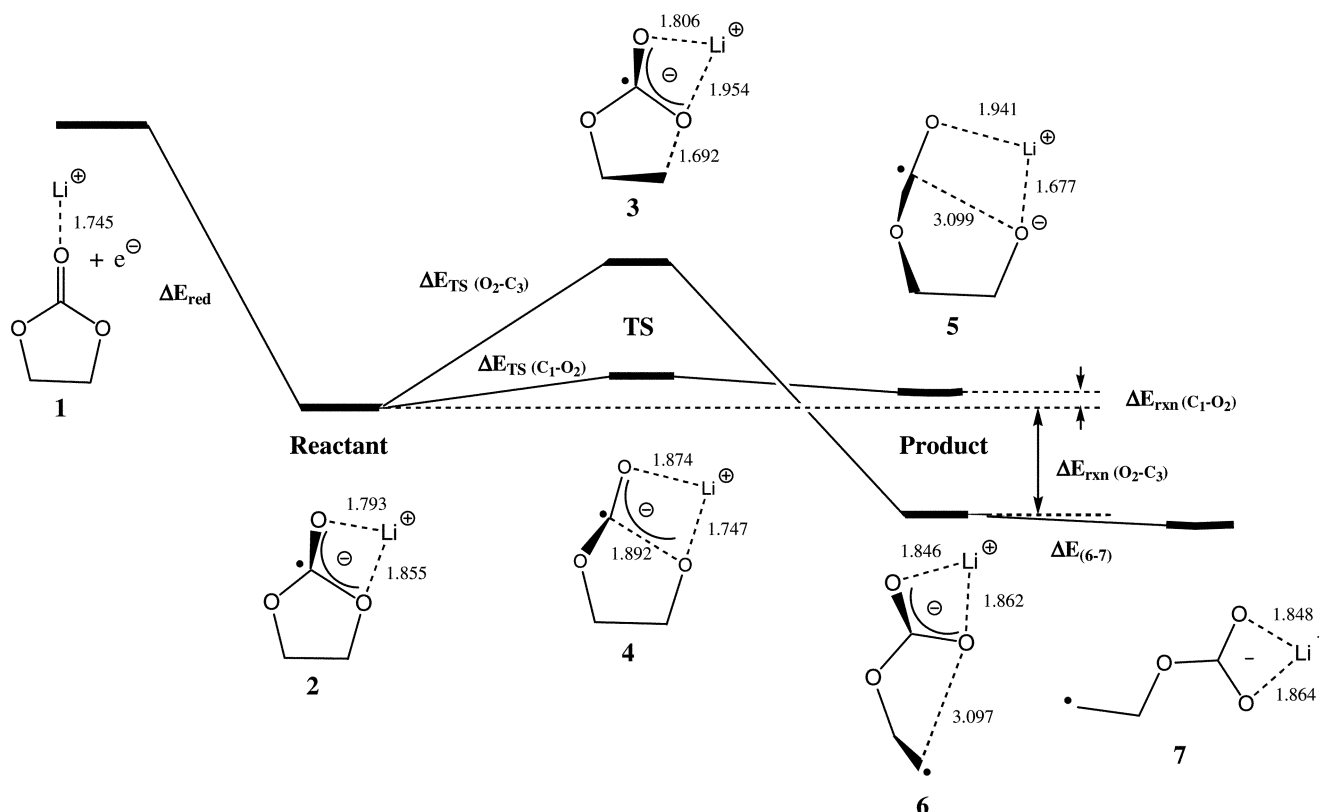
**Table 1.** The reaction energies and Gibbs free energies<sup>a</sup> (in kcal/mol) computed at the mPW1PW91 level of theory for the reductive ring-opening reactions of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC

	$\Delta E_{red}$	$\Delta E_{TS}$ (O <sub>2</sub> -C <sub>3</sub> )	$\Delta E_{TS}$ (C <sub>1</sub> -O <sub>2</sub> )	$\Delta E_{rxn}$ (O <sub>2</sub> -C <sub>3</sub> )	$\Delta E_{rxn}$ (C <sub>1</sub> -O <sub>2</sub> )	$\Delta E$ (6-7)
Li <sup>+</sup> -EC						
$\Delta E$	-90.40	14.75	11.93	-25.67	3.54	-0.12
$\Delta G$	-92.05	12.60	9.63	-29.17	1.81	-0.87
$\Delta G_{solv}$	-45.80	12.48	17.85	-27.26	9.72	-1.06
Li <sup>+</sup> -VC						
$\Delta E$	-94.44	23.64	0.24	-10.72	-4.14	-2.06
$\Delta G$	-96.79	21.68	0.04	-12.61	-5.37	-1.88
$\Delta G_{solv}$	-50.58	21.83	2.18	-10.47	1.72	-1.33

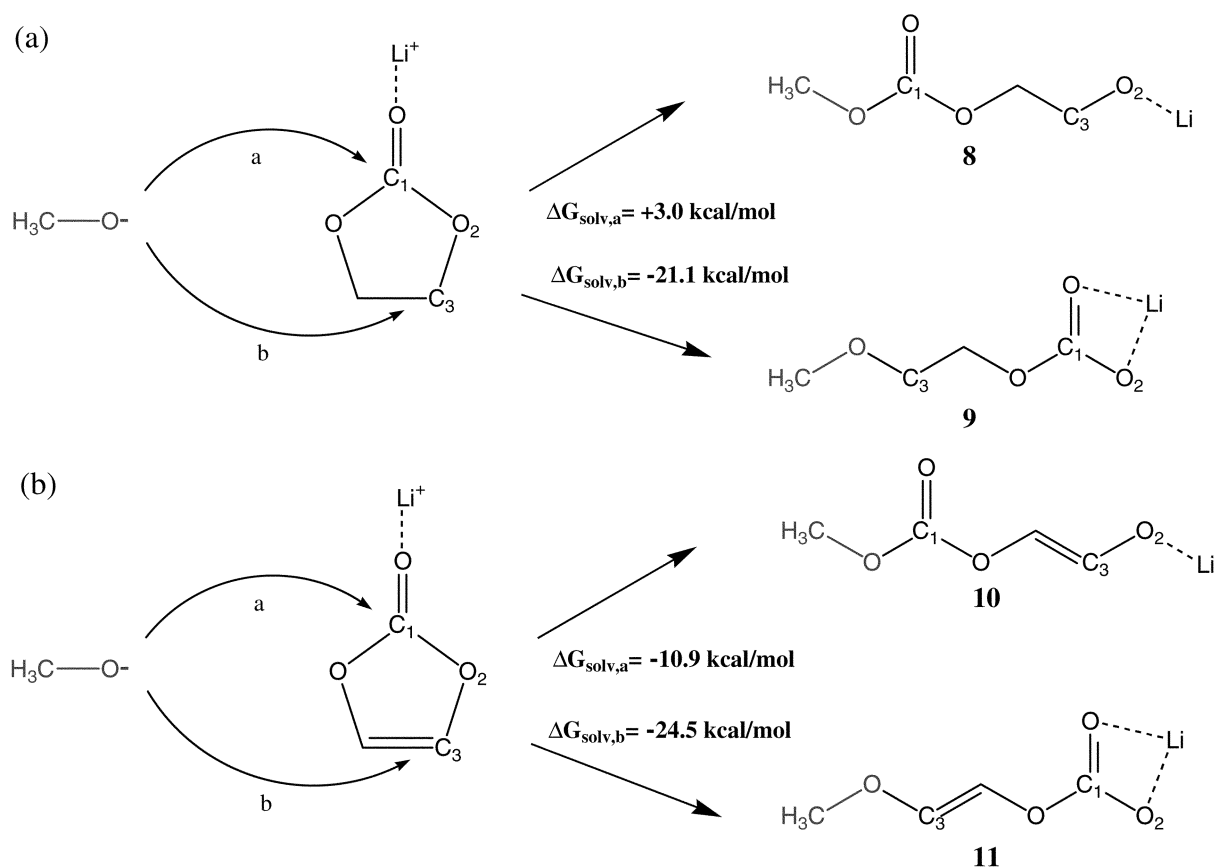
<sup>a</sup>mPW1PW91/6-311++G(3df,3pd)//mPW1PW91/6-311+G(d) results.

reproduces the experimental trend that VC has a more negative reduction potential. For the O<sub>2</sub>-C<sub>3</sub> bond cleavage, the barrier of the ring-opening reaction via TS **3** is 21.8 kcal/mol for Li-VC, much higher than 12.5 kcal/mol of Li-EC, and the formation of radical anion **6** releases 12.0 kcal/mol less energy than that of Li-EC. However, it should be noted that, for Li-VC, the breaking of C<sub>1</sub>-O<sub>2</sub> bond is relatively favorable kinetically and thermodynamically, with respect to Li-EC, implying that the cleavage of C<sub>1</sub>-O<sub>2</sub> bond may occur preferentially in certain reactions.

We have investigated possible reaction products and their thermodynamic stabilities of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC by nucleophilic addition reaction of a nucleophile CH<sub>3</sub>O<sup>-</sup>. In



**Figure 2.** Mechanisms for the reductive ring-opening reactions of Li<sup>+</sup>-EC and Li<sup>+</sup>-VC.



**Figure 3.** Structures of reactants and products and reaction free energies for the reactions (a)  $\text{CH}_3\text{O}^- + \text{Li}^+$ -EC and (b)  $\text{CH}_3\text{O}^- + \text{Li}^+$ -VC.

Figure 3, the reaction free energies along the reaction paths and the structures are summarized. The ring opening can be obtained on the  $\text{C}_1$  (path *a*) and  $\text{C}_3$  carbon (path *b*) atom sides. It was found that the formation of ring-opening products for  $\text{Li}^+$ -VC is thermodynamically more favorable than the formation of those of  $\text{Li}^+$ -EC, which means that VC is more reactive thermodynamically than EC for such nucleophilic attack. The  $\Delta G_{\text{solv},a}$  value is positive (+3.0 kcal/mol) and the  $\Delta G_{\text{solv},b}$  value is negative (-21.1 kcal/mol) for the reaction of  $\text{CH}_3\text{O}^-$  and  $\text{Li}^+$ -EC, indicating that  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCO}_2\text{Li}$  is a dominant compound. The  $\text{O}_2$ - $\text{C}_3$  bond cleavage of EC was confirmed by pyrolysis-gas chromatography-mass spectroscopy.<sup>2</sup> On the other hand, both the  $\Delta G_{\text{solv},a}$  and  $\Delta G_{\text{solv},b}$  values are found to be negative, thermodynamically possible, for the reaction of  $\text{CH}_3\text{O}^-$  and  $\text{Li}^+$ -VC, where the  $\Delta G_{\text{solv},a} = -10.9$  kcal/mol and  $\Delta G_{\text{solv},b} = -24.5$  kcal/mol. Because it can be inferred from the fact that the  $\Delta E_{\text{TS}}(\text{C}_1-\text{O}_2)$  is much lower than  $\Delta E_{\text{TS}}(\text{O}_2-\text{C}_3)$  in the Li-VC calculation results (Table 1), the nucleophilic addition reaction on the  $\text{C}_1$  carbon atom may be kinetically easier than that on the  $\text{C}_3$  atom, although the reverse may be true from a thermodynamic point of view. Once the product **10** is formed, it may become a nucleophile that attacks another  $\text{Li}^+$ -coordinated solvents or additives. If the product **10** would react with another  $\text{Li}^+$ -VC iteratively, the reaction gives rise to oligomers with carbonate-vinylene units. It is known experimentally that the surface film formed by VC consists of polycarbonate

containing  $\text{C}=\text{C}$  bonds,<sup>29</sup> and thus the mechanism is believed to be highly feasible.

## Conclusions

The  $\text{O}_2$ - $\text{C}_3$  bond cleavage for Li-VC is not favorable thermodynamically nor kinetically because of the conjugation group,  $-\text{O}-\text{C}=\text{C}-\text{O}-$  in VC, with respect to Li-EC. However, for the same reason, the  $\text{C}_1$ - $\text{O}_2$  bond cleavage of Li-VC is relatively easier than that of Li-EC thermodynamically and kinetically. The thermodynamic analysis has led us to conclude that the possible reaction products may be  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCO}_2\text{Li}$  ( $\text{O}_2$ - $\text{C}_3$  cleavage) for  $\text{Li}^+$ -EC +  $\text{CH}_3\text{O}^-$  and  $\text{CH}_3\text{OCHCHOCO}_2\text{Li}$  ( $\text{O}_2$ - $\text{C}_3$  cleavage) and  $\text{CH}_3\text{OCO}_2\text{CHCHOLi}$  ( $\text{C}_1$ - $\text{O}_2$  cleavage) for  $\text{Li}^+$ -VC +  $\text{CH}_3\text{O}^-$ . The opening of VC at the  $\text{C}_1$ - $\text{O}_2$  side may be kinetically, but not thermodynamically, more favorable than the opening at the  $\text{O}_2$ - $\text{C}_3$  side. These results imply that such a nucleophilic attack may provide a different-type of ring-opening products and subsequent reaction products for VC, with respect to EC, because of the presence of the conjugation group  $-\text{O}-\text{C}=\text{C}-\text{O}-$  in VC.

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