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Theoretical studies of the solvent decomposition by lithium atoms in lithium-ion battery electrolyte

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Abstract

We have carried out density functional and ab initio calculations on the structure and stability of $M-Li_n$ ($n=0, 1$, and 2) complexes, where the M = ethylene carbonate (EC), propylene carbonate (PC), vinylene carbonate (VC), ethylene sulfite (ES), and glycol sulfate (GS). Although the molecules are geometrically similar, it is found that the reactions with lithium atoms may provide various reaction products depending upon the structures and stabilities. Reductive decomposition by lithium atoms appears to be in order of the most energetically favorable, $ES \sim GS > EC \sim PC > VC$, and $GS > PC \sim EC \sim VC > ES$ for the first and second lithium atom addition reactions to the molecules, respectively. The transition states are also determined and discussed for EC, VC, and ES. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Electrochemical reactions involving solvent (or additive) decompositions at the electrode–electrolyte interface play a crucial role that affects capacity, cycle life, and safety in lithium-ion rechargeable battery. The solvent decomposition mechanism has been widely studied in the lithium-ion battery electrolyte, both experimentally [1–10] and theoretically [11–15]. However, these reactions are very complicated, and are not well understood. In terms of overall battery performance, an un-

derstanding of the initial reactions is essential because they directly affect the charge–discharge efficiency, and can lead to subsequent decomposition.

In the present work, density functional theory (DFT) and ab initio Møller–Plesset second-order perturbation (MP2) [16] calculations were used to investigate the reductive decomposition of the solvents [ethylene carbonate (EC) and propylene carbonate (PC)], and the additives [vinylene carbonate (VC), ethylene sulfite (ES), and glycol sulfate (GS)] in the lithium-ion battery electrolyte. The molecular structures of the above are depicted in Fig. 1. It has been proposed that the initial reaction is an electron transfer from the electrode to the solvent (or additive) molecules that are coor-

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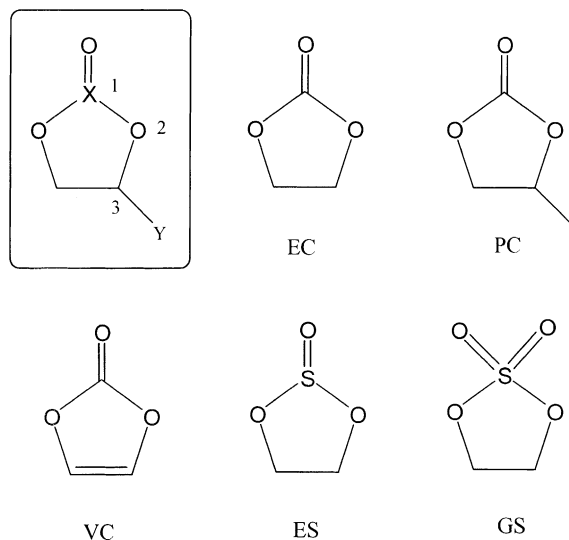


Fig. 1. Molecular structures of EC, PC, VC, ES, and GS.

minated with lithium ions [12]. We have performed calculations on the $M-Li_n$ complexes (where $M = EC, PC, VC, ES$, and GS , and $n = 0, 1$, and 2) to gain an insight into the initial reactions at the microscopic level. Details of the calculations are given in Section 2. Results and discussion are presented in Section 3. The Letter ends with the conclusions in Section 4.

2. Calculation details

Kohn–Sham DFT calculations were performed for geometry optimization with a hybrid functional (B3LYP) [17–19], which is a three-parameter mixture of density functional and ‘exact’ Hartree–Fock exchange. Single-point energies were also calculated at the ab initio MP2 level of theory using the B3LYP optimized geometries. Occupied and virtual orbitals are fully correlated at the MP2 calculations. Spherical 6-311+G* basis set [20–22] was used for the DFT and MP2 calculations. All the calculations were carried out with the program package GAUSSIAN 98 [23]. Spin-unrestricted scheme was employed for the even and odd numbered electron systems to permit any possible bond cleavage in the calculations for geometry optimization. The stationary point wave

functions were also checked for spin contamination by evaluation of the $\langle S^2 \rangle$ values. For the DFT calculations, $\langle S^2 \rangle$ before annihilation was generally between 0.75 and 0.77 for the doublet states, indicating that the spin-contamination problem would little affect the results and discussion.

3. Results and discussion

In Fig. 2, we present the optimized structures and binding energies (ΔE_1 and ΔE_2) of the lithium atoms in the $M-Li_n$ complexes (where $M = EC, PC, VC, ES$, and GS , and $n = 0, 1$, and 2). The ΔE_1 and ΔE_2 values are defined as the energy changes in the stepwise addition reactions, $M + Li \rightarrow M-Li$ and $M-Li + Li \rightarrow M-Li_2$, respectively. The reactions between M and a lithium atom are found to be exothermic by 1.3–2.8 eV for the molecules at the B3LYP level of theory. The most stable form of the $EC-Li$ complex is an open-chain radical structure, with the bond cleavage of the O_2-C_3 bond having a ΔE_1 value of -1.82 eV. The structures of the $PC-Li$ and $VC-Li$ complexes are very similar to that of the $EC-Li$ structure, having ΔE_1 values of -1.79 and -1.27 eV, respectively. The higher ΔE_1 value for the $VC-Li$ complex originates from the stabilization of VC by the presence of a conjugation unit, $O-C=C-O$. For the same reason, there is another stable structure for the $VC-Li$ complex, i.e., the C_1-O_2 broken-bond form, whereas this is not the case for the $EC-Li$ and $PC-Li$ complexes. From our results, one is able to design a carbonate having a lower ΔE_1 value than that of EC , if required for a particular purpose. For example, the ΔE_1 value of 4-ethenyl-1,3-dioxolan-2-one is -2.54 eV at the B3LYP level of theory, because the molecule contains a functional group that stabilizes the open-chain radical (see Fig. 3). The most stable $ES-Li$ complex has an $S-O$ broken-bond structure with a ΔE_1 value of -2.79 eV. The ΔE_1 value is smaller than those of the carbonates by more than 1 eV. It is noteworthy that the complex has a Li-bridged structure, and not an open-chain form, as shown in Fig. 2. The $O-C$ broken-bond structure is less stable than the $S-O$ broken-bond form by about 0.87 eV. Similarly, the most stable $GS-Li$ complex has an $S-O$

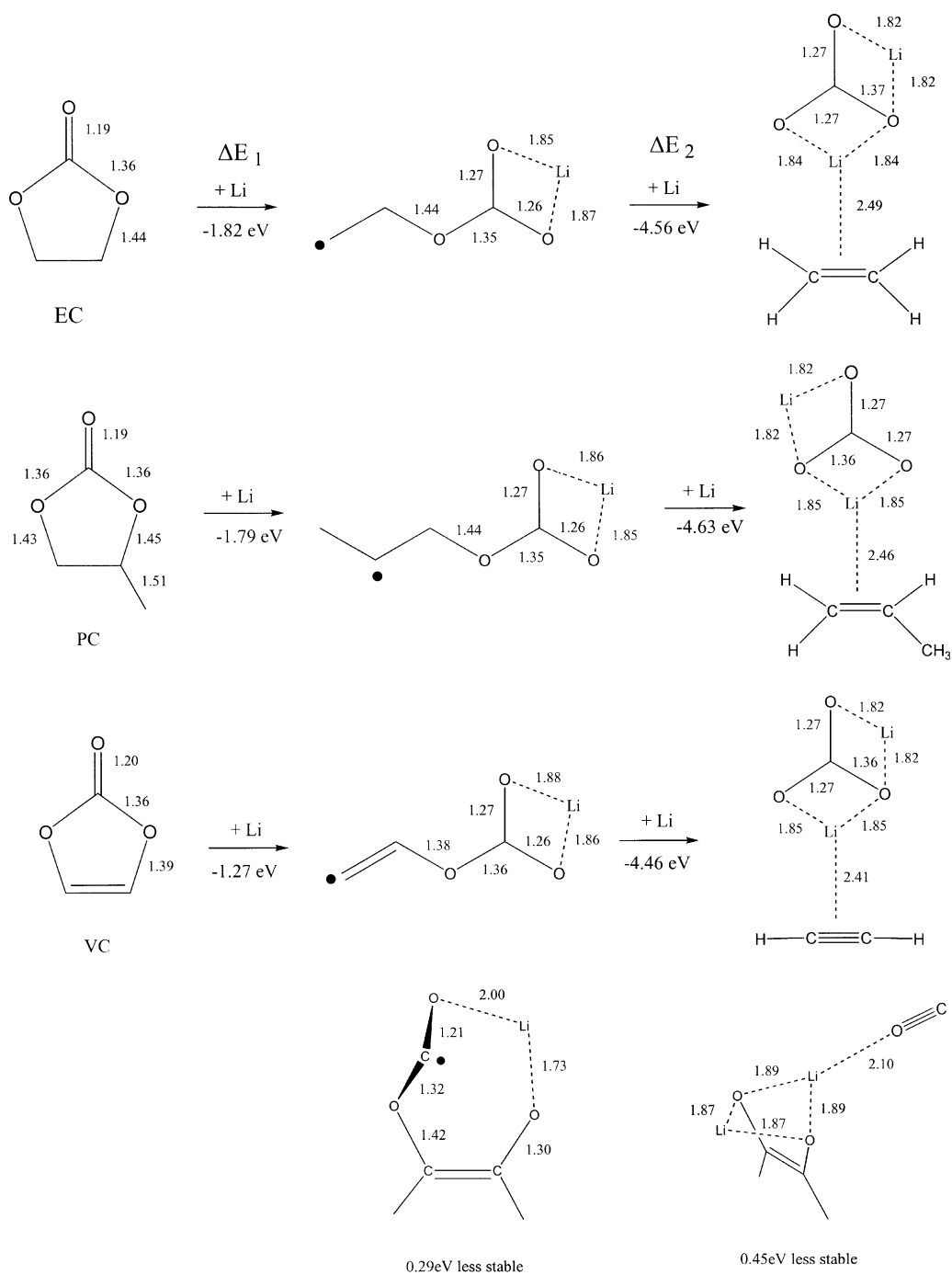


Fig. 2. The B3LYP optimized geometries and $\Delta E_1, \Delta E_2$ values for the $M-Li_n$ complexes ($M = EC, PC, VC, ES$, and GS , and $n = 0, 1$, and 2). Units are in Å.

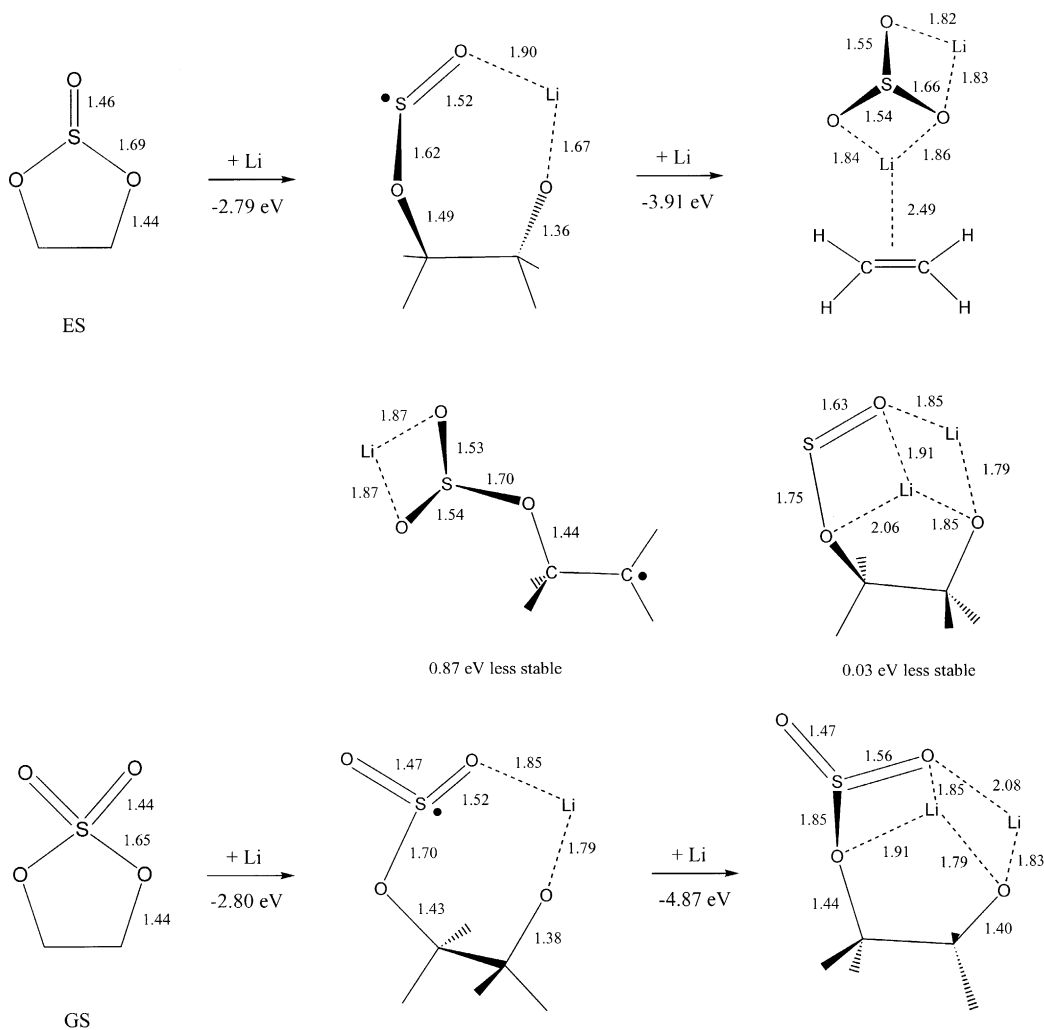


Fig. 2. (continued).

broken-bond structure, where the binding energy with the lithium atom is very similar to that for the ES–Li complex.

Let us now turn to the results for the $M\text{--Li} + \text{Li} \rightarrow M\text{--Li}_2$ reactions. It should be mentioned that the $M\text{--Li}$ complexes may be decomposed via other possible pathways before undergoing the second electron reduction [7], although these were not considered in this work.

The second Li addition reactions are highly exothermic by 3.9–4.9 eV for the complexes at the B3LYP level of theory (see Fig. 2). The most stable products for the $\text{ECLi} + \text{Li}$ and $\text{PCLi} + \text{Li}$ reac-

tions are weakly-bonded complexes of $\text{Li}_2\text{CO}_3\text{--C}_2\text{H}_4$ and $\text{Li}_2\text{CO}_3\text{--C}_3\text{H}_8$, respectively, where the binding energies between the two fragments were 0.34 and 0.40 eV, respectively. It should be noted that Li_2CO_3 was found experimentally in most solid–electrolyte interface films of lithium-ion batteries [24,25].

There was no noticeable difference in the solvent decomposition between the EC and the PC in this work. Experimentally however, solvent co-intercalation, decomposition, and subsequent exfoliation were observed when graphite anodes were cycled in a PC-based electrolyte, while these were

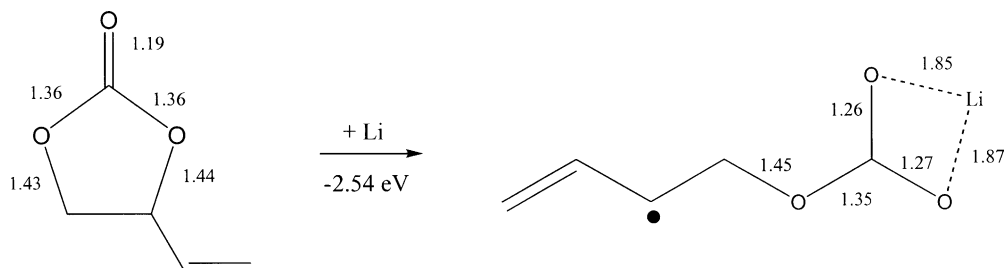


Fig. 3. The B3LYP optimized geometries and ΔE_1 value for the $M-Li_n$ complexes (M = 4-ethenyl-1,3-dioxolan-2-one, and ($n=0$ and 1). Units are in Å.

not observed with an EC-based electrolyte [26–28]. It may be concluded from our results that the graphite exfoliation could not be explained by the electronic structures of EC and PC alone [29].

Similarly to EC and PC, the most stable form of the $VCLi + Li$ reaction product was the $Li_2CO_3-C_2H_2$ complex, with a ΔE_2 value of -4.46 eV. In addition, there is another stable decomposition product for the reaction, i.e., a $CO-Li_2C_2O_2$ complex having a similar stability ($\Delta E_2 = -4.01$ eV), implying that the conjugation unit, $O-C=C-O$, may be maintained even after the two-electron reduction reaction. The $ES(Li)_2$ complex is decomposed into the $Li_2SO_3-C_2H_4$ complex with a ΔE_2 value of -3.91 eV. In contrast to the carbonate cases, a structure with two Li-bridges ($\Delta E_2 = -3.88$ eV) was found to be as stable as the $Li_2SO_3-C_2H_4$ complex, as shown in Fig. 2. We could obtain a similar structure for $EC(Li)_2$ as a local minimum, but it was much less stable than the fragmentation reaction product, i.e., the $Li_2CO_3-C_2H_4$ complex. For the $GS(Li)_2$ complex, such a structure with two Li-bridges is more stable than the possible fragmentation products, Li_2SO_4 and C_2H_4 , or Li_2SO_3 and C_2H_4O

fragments, by 0.62 and 0.96 eV, respectively, at the B3LYP level of theory. The ΔE_2 value for GS is smaller than that for ES by about 1 eV, because the second electron is mainly transferred to the $-SO_3$ in GS, which has a higher electron affinity than the $-SO_2$ unit in ES. In contrast to this, the first electron is transferred mainly to the O_2 position in ES and GS, which leads to similar ΔE_1 values for ES and GS. The existence of such stable Li-bridged structures may indicate that there is less gas generation in the reduction reactions for ES and particularly for GS, than in the carbonate cases.

We have also calculated all the systems shown in Fig. 2 at the ab initio MP2 level of theory using the B3LYP optimized geometries to assess the quality of the B3LYP energies. The ΔE_1 and ΔE_2 values are listed in Table 1. The B3LYP method gives somewhat higher molecular stabilities, by about 0.3 eV, for the radical structures with respect to the MP2 method, but both methods provide qualitatively similar results for all cases.

Aurbach et al. [11] calculated the open-chain radicals for the EC-Li and PC-Li complexes at the unrestricted HF/3-21G level of theory, and the

Table 1
The ΔE_1 and ΔE_2 values (in eV) computed at the DFT and MP2 levels of theory

M	ΔE_1^a		ΔE_2^a	
	B3LYP	MP2	B3LYP	MP2
EC	-1.82	-1.57	-4.56	-4.58
PC	-1.79	-1.43	-4.63	-4.71
VC	-1.27	-0.97	-4.46	-4.76
ES	-2.79	-2.41	-3.91	-4.08
GS	-2.80	-2.37	-4.87	-4.99

^a ΔE_1 and ΔE_2 refer to the binding energies for $M + Li \rightarrow M-Li$ and $M-Li + Li \rightarrow M-(Li)_2$ reactions, respectively.

authors reported a higher binding energy with a lithium atom for EC compared to PC, where the reaction energy difference was 0.19 eV. Endo et al. [12] also calculated the EC–Li and PC–Li complexes with the restricted open-shell HF/6-31G* method, but the authors did not consider an open-chain radical structure in their work, and hence provided somewhat different results from ours. Zhang et al. [13] reported the order of solvent re-

duction as EC > PC > VC based on calculations of the reduction potentials, which is in line with our results. To the best of our knowledge, there has been no attempt to examine the reductive decomposition of ES and GS.

Finally, we have investigated the transition states for the bond-cleavage reactions of EC, VC, and ES. The transition-state geometries were optimized at the unrestricted HF level of theory,

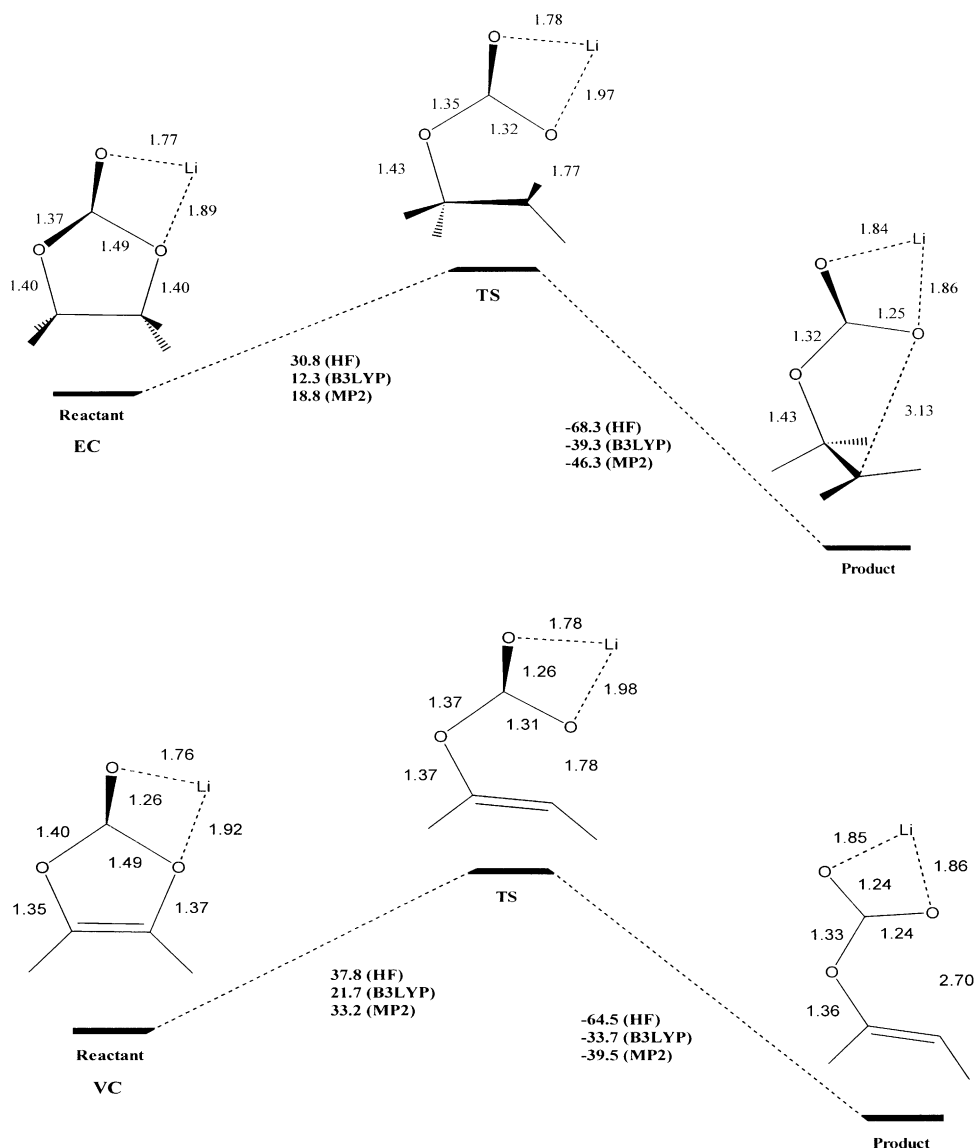


Fig. 4. Potential energy profiles for the reductive bond-cleavage reactions of EC, VC, and ES.

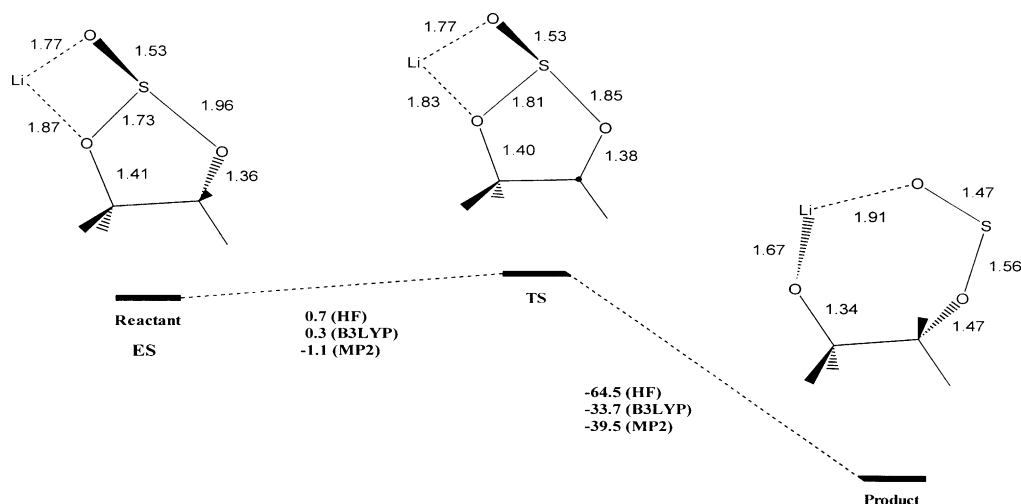


Fig. 4. (continued).

followed by single-point energy evaluations at the B3LYP and MP2 levels. Potential energy profiles for the reductive dissociations are shown in Fig. 4. The transition states were confirmed by the sole imaginary frequency and primary intrinsic reaction coordinate (IRC) [30,31] calculation. The imaginary frequencies are 1881, 1979, and 313 cm^{-1} for EC, VC, and ES, respectively. The activation energies from the calculations are the smallest for ES, followed by EC and VC, which are in line with the trends in the ΔE_1 values. It is noteworthy that the activation energy is close to zero for ES, implying that the reductive decomposition by a lithium atom may occur without barrier. Recently, Wang et al. [15] reported that the activation energy is 13.4 kcal/mol for the bond-cleavage reaction of EC at the B3PW91 level of theory, which is in good agreement with our B3LYP result of 12.3 kcal/mol.

4. Conclusions

Unrestricted KS-DFT and ab initio MP2 calculations for the structure and stability of M-Li_n complexes (where $\text{M} = \text{EC}, \text{PC}, \text{VC}, \text{ES}, \text{and GS}$, and $n = 0, 1$, and 2) were performed to gain an insight into the reductive decomposition of the solvents and additives in a lithium-ion battery

electrolyte. The bonding between the molecules and lithium atoms takes place by exothermic reactions, particularly for the second lithium addition reactions. Although the calculated molecules are geometrically similar, it is found that the reactions with lithium atoms may lead to various reaction products depending upon their structures and stabilities. From the methodological point of view, employing an unrestricted scheme is necessary for investigating the reductive decompositions.

There was no noticeable difference in solvent decomposition between the EC and the PC complexes. It is rather difficult to break the ring structure of VC because of the presence of a conjugation unit, O-C=C-O , which may be maintained even after the two-electron reductive decomposition. For ES and GS, the reductive ring opening is more energetically favorable by one-electron transfer than for the carbonates considered here. The S-O broken-bond structure is more stable than the O-C broken-bond form for the ES-Li and the GS-Li complexes. Reductive decomposition to form two fragments seems to be less favorable for ES and particularly for GS, relative to the carbonates. A second lithium atom addition is more favorable for GS than for ES, which arises from a higher electron affinity of the $-\text{SO}_3$ unit than that of $-\text{SO}_2$ unit. Reductive decomposition by lithium atoms appears to be in

order of the most energetically favorable, $ES \sim GS > EC \sim PC > VC$, and $GS > PC \sim EC \sim VC > ES$ for the first and second lithium atom addition reactions to the molecules, respectively. The transition states were also determined for EC, VC, and ES. The activation energy is the lowest for ES, nearly zero, followed by EC and VC, which is in line with the trends in ΔE_1 values.

Although further works are required to conclude a general rule for designing solvent or additive molecules, we believe that the present approach is a feasible and reasonable way to explore the mechanism of the initial reaction of solvent (or additive) reductive decomposition in a lithium-ion battery electrolyte.

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