Supporting Information for
Oxidation Induced Decomposition of Ethylene Carbonate from DFT Calculations – Importance of Explicitly Treating Surrounding Solvent

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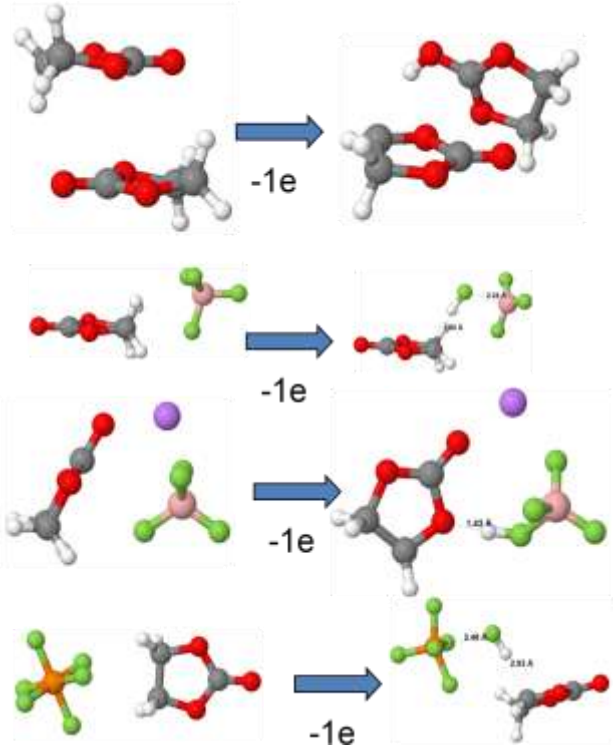

Figure S1. Optimized geometries of complexes and their oxidized analogs from M05-2X/cc-pvTz calculations.

Table S1. Oxidation potential of EC containing complexes from M05-2X/cc-pvTz, MP4/6-311++G(d) and G4MP2 calculations.

	Method	ε=20.5	ε=78.4
EC_2	M05-2X/cc-pvTz	5.9	5.9
	G4MP2		5.7
	MP4/6-311++G(d)		6.0
EC/BF_4^-	M05-2X/cc-pvTz	6.3	6.3
$EC/LiBF_4$	M05-2X/cc-pvTz	6.6	
EC/PF_6^-	M05-2X/cc-pvTz	6.6	6.6

Charges from the electrostatic potential fit for EC_2 and EC_2-e shown in Figure S2 are given in Table S2.

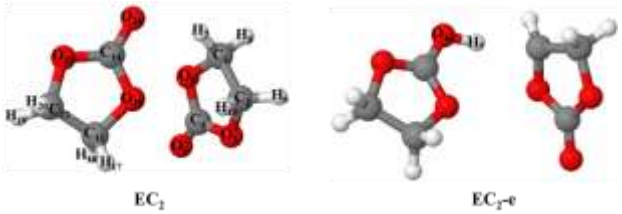

Figure S2. Geometry of EC_2 and oxidized (EC_2-e) optimized at B3LYP/6-311++G(d) level.

Table S2 ChelpG charge distribution of EC_2 before and after oxidation from B3LYP/6-311++G(d) shown in Figure S2.

Atoms	EC_2	EC_2-e
C_1	0.085	0.093
C_2	0.275	0.163
O_3	-0.489	-0.433
C_4	1.030	0.991
O_5	-0.466	-0.388
O_6	-0.696	-0.621
H_7	0.097	0.348
H_8	0.079	0.154
H_9	0.050	0.099
H_{10}	-0.006	0.087
C_{11}	0.147	0.102
C_{12}	0.153	0.157
O_{13}	-0.458	-0.350
C_{14}	0.939	1.011
O_{15}	-0.360	-0.343
O_{16}	-0.661	-0.519
H_{17}	0.062	0.119
H_{18}	0.070	0.120
H_{19}	0.077	0.103
H_{20}	0.069	0.108

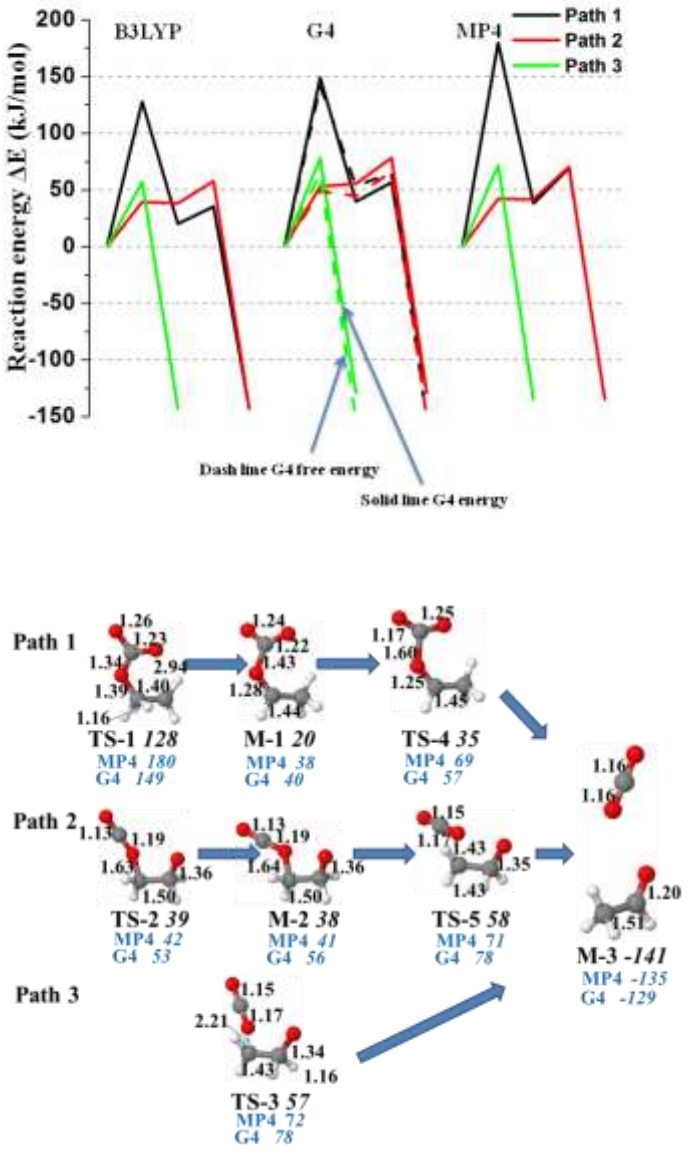

Figure S3. Reaction energy profile of oxidation decomposition of EC-e in implicit solvent from B3LYP/6-311++G(d), MP4/6-311++G(d)//B3LYP/6-311++G(d) and G4.

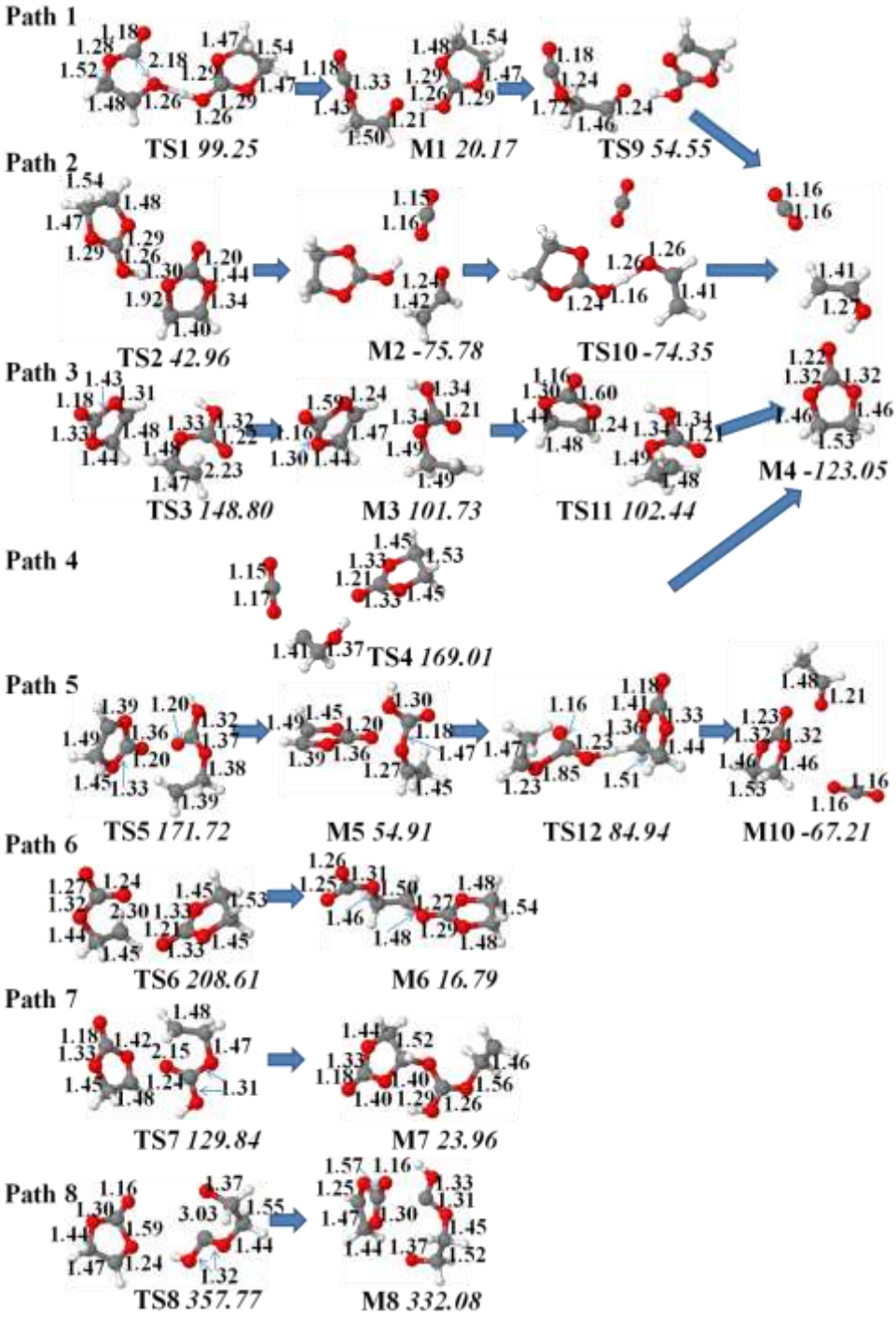

Figure S4. The oxidized EC_2 decomposition reactions with energies shown in kJ/mol.

Termination reactions of the initial oxidation products of EC_2-e are also investigated. At room temperature, the most probable oxidation products are CO_2 and ethanol radical cation (R1). The possible reaction paths of R1 are presented in Figure S5. It is more energetically favorable for R1 to gain one electron generating vinyl alcohol, rather than passing high activation energy (226.14kJ/mol) to form aldehyde radical (R2). With the high energy released from the reduction,

vinyl alcohol is easily to pass TS(2) to form a more stable product aldehyde. CO_2, aldehyde and small amount of vinyl alcohol have been detected as overcharge/thermal decomposition products of EC based electrolyte[1,2].

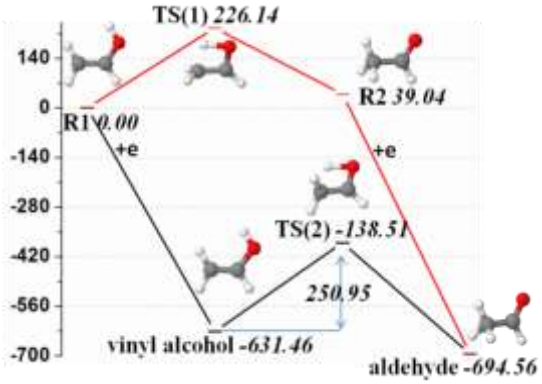

Figure S5. Possible reaction paths and energy (relative to R1) of R1 in implicit solvent.

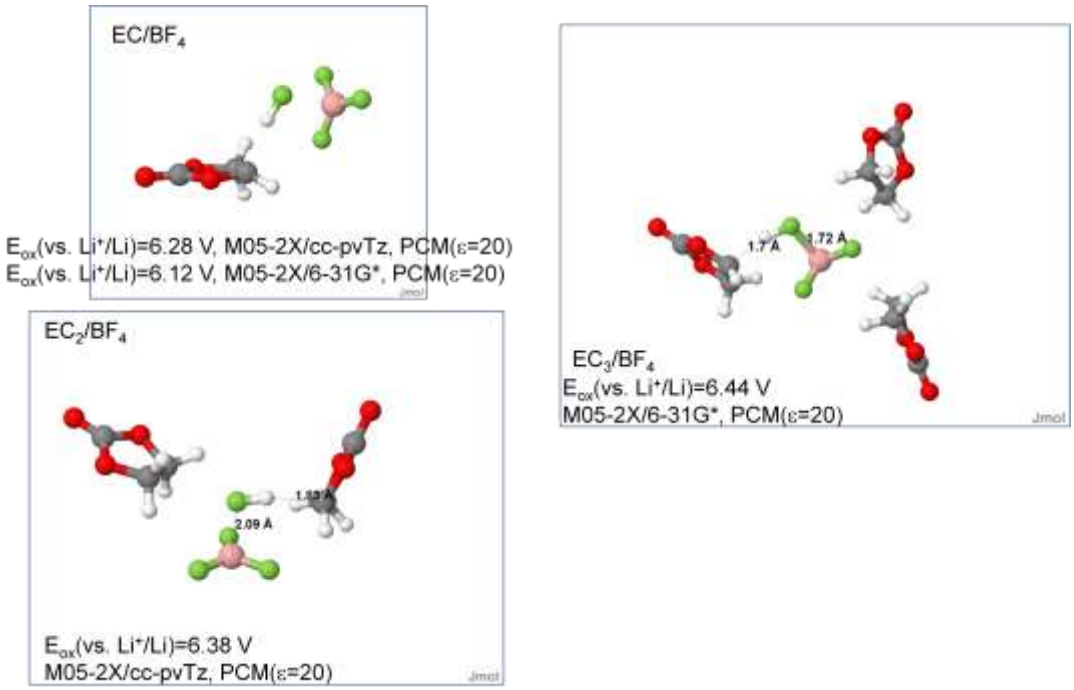

Figure S6. Initial oxidation of EC/BF_4^-, EC_2/BF_4^-, EC_3/BF_4^- complexes studied at M05-2X/cc-pvTz level with PCM(acetone).

References

(1) Mogi, R.; Inaba, M.; Iriyama, Y.; Abe, T.; Ogumi, Z. Study on the decomposition mechanism of alkyl carbonate on lithium metal by pyrolysis-gas chromatography-mass spectroscopy. J. Power Sources, 2003,119-121, 597-603
(2) Aurbach, D.; Gamolsky, K.; Markovsky, B.; Salitra, G.; Gofer,Y.; Heider, U.; Oesten, R.; Schmidt, M. The Study of Surface Phenomena Related to Electrochemical Lithium Intercalation into Li_xMO_y Host Materials (M = Ni, Mn). J. Electrochem. Soc. 2000, 147, 1322:1331.