Computational Study of the Mechanisms of Superoxide-Induced Decomposition of Organic Carbonate-Based Electrolytes

2 AUTHORS:

Vyacheslav S Bryantsev

Oak Ridge National Laboratory

78 PUBLICATIONS **2,246** CITATIONS

SEE PROFILE

Mario Blanco

King Abdullah University of Science and Tec…

64 PUBLICATIONS **1,717** CITATIONS

SEE PROFILE

Computational Study of the Mechanisms of Superoxide-Induced Decomposition of Organic Carbonate-Based Electrolytes

Vyacheslav S. Bryantsev* and Mario Blanco

Liox Power, Inc., 129 North Hill Avenue, Suite 103, Pasadena, California 91106, United States

S *Supporting Information*

ABSTRACT: There is increasing experimental evidence that organic carbonate-based electrolytes are incompatible with the discharge products of the nonaqueous lithium—air (oxygen) battery. Theoretically, the lithium—air battery offers the highest gravimetric density for energy storage applications, promising to revolutionize electric vehicle transportation. Calculations suggest that propylene carbonate, ethylene carbonate, and dimethyl carbonate, commonly used electrolytes in Li-ion batteries, are easily decomposed by the superoxide ion via nucleophilic attack at the ethereal carbon atom. In the case of propylene carbonate, base-mediated proton abstraction from the methyl group has to be considered as an additional solvent decomposition pathway. The present study provides a mechanistic understanding of solvent instability to assist the design of stable electrolytes for Li—air energy storage systems.

SECTION: Molecular Structure, Quantum Chemistry, General Theory
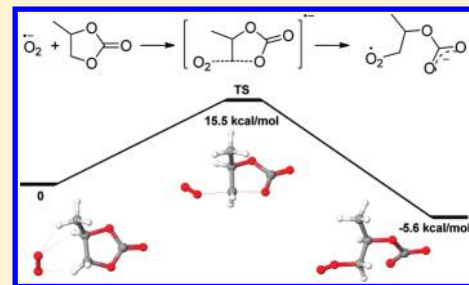
The lithium—air battery[1−10] has attracted a great deal of interest recently due to the fact that its high theoretical gravimetric energy density holds promise for all-electric vehicle applications (for the latest reviews, see refs 11 and 12). Recent studies at the University of St. Andrews,[13,14] Toyota,[15−17] and IBM[11,18] have shown that the most commonly used propylene carbonate (PC)-based electrolytes are not stable against oxygen reduction products. The evidence comes from FT-IR and Raman spectroscopy data[13−17] indicating that the primary discharge product in carbonate-based electrolytes is not lithium peroxide, Li_2O_2, but carbonate species, such as RO—(C=O)—OLi and Li_2CO_3 products, rendering recharging nearly impossible because the electrolyte is consumed in the reaction. Furthermore, in situ differential electrochemical mass spectrometry (DEMS) experiments[13−18] reveal that during charging of the discharged battery, CO_2 is evolved as a predominant oxidation product, most probably from the oxidative decomposition (during recharge) of lithium carbonates and alkyl carbonates.

Although there is a lack of fundamental understanding of the mechanism of decomposition of carbonate solvents by oxygen reduction products, the superoxide ion, O_2^- is believed to be the responsible species.[13−17] The most direct evidence comes from the irreversibility of the O_2/O_2^- redox couple in the PC solvent containing large organic cations.[13,14,17] Detailed mechanistic knowledge would greatly aid in the identification of appropriate stable electrolytes for the normal operation of Li—air cells. In this work, we employ quantum chemical calculations to unravel the initial mechanism of superoxide-ion-induced decomposition of PC.

Extensive research on the organic chemistry of O_2^- in aprotic media has established that this anion radical reacts with organic substrates via nucleophilic attack, proton/hydrogen abstraction, and electron transfer.[19,20] Due to a relatively wide electrochemical

stability window of PC (more than 4 V at the glassy carbon electrode),[21] the direct electron transfer from/to superoxide is not expected. In what follows, we report the computed free-energy barriers (ΔG_{act}) and reaction free energies (ΔG_r) for nucleophilic substitution and proton/hydrogen abstraction reactions.

Electronic structure calculations were carried out using the Jaguar 7.5[22] and the NWChem 5.1[23] programs. Geometries were optimized at the B3LYP/6-311++G** level,[24,25] except for molecular complexes with explicit solvent molecules, for which the B3LYP/6-31G** method was used. In addition, single-point energy calculations were performed using the cc-pVTZ basis set on Li and the aug-cc-pVTZ basis set on other elements. Transition-state search was performed using a standard quasi-Newton method in Jaguar,[22] starting from the partially optimized geometry along the chosen reaction coordinate and the precalculated Hessian. The nature of all transition states was confirmed by the presence of a single imaginary frequency in the vibrational spectrum, corresponding to the motion along the reaction coordinate. We checked the accuracy of the B3LYP functional by comparing with the second-order Möller—Plesset perturbation theory (UMP2)[23,26] and coupled-cluster calculations with singles, doubles, and perturbative triples excitations (UCCSD(T))[23,27−29] for unrestricted reference wave functions, as well as with experiment. Test calculations for the reaction of O_2^- with ethylene carbonate showed that the use of the B3LYP/aug-cc-pVTZ method does not lead to significant differences in activation (~2.1 kcal/mol) and reaction (~0.6 kcal/mol) energies when compared to benchmark calculations at the extrapolated

CCSD(T)/aug-cc-pV5Z level (Table 1). Similarly, B3LYP/aug-cc-pVTZ performs satisfactory (the mean absolute error of 2.0 kcal/mol, relative to experiment[30]) for electron affinities of O_2 and HOO and proton affinities of O_2^- and HOO^- (Table 2). The overall good agreement thus justifies the use of the B3LYP method to probe the reactivity of organic carbonates with superoxide.

Solvation calculations were carried out using the Poisson–Boltzmann continuum model in Jaguar,[22] with the default values of solute atomic radii. The dielectric constants for propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonates (DMC) are given in Table 3, and probe radii are defined from their molecular weights and liquid densities at room temperature as follows: 2.566 (PC), 2.354 (EC), and 2.556 (DMC). The treatment of solvation effects is extended beyond the dielectric continuum description by explicitly including several additional solvent molecules in the vicinity of the reaction center.

We first consider O_2^- acting as a nucleophile. Figure 1 represents reaction free-energy profiles of nucleophilic attack by O_2^- on three different carbon atoms of the PC molecule. Superoxide addition to one of the ethereal carbon atoms yields a

peroxyalkyl carbonate, which is thermodynamically more stable than the initial complex by 5.5–5.6 kcal/mol. A very low activation barrier for this reaction (15.5–16.7 kcal/mol) suggests that PC easily decomposes during the electrochemical reduction of oxygen by an S_N2 mechanism. It should be noted that the initial nucleophilic displacement reaction involving superoxide is typically the rate-determining step.[31,32] A subsequent one-electron reduction of organic peroxy radicals (ROO) by O_2^- to peroxy anions (ROO$^-$) is highly exergonic and occurs near the diffusion-controlled limit.[32−34] A peroxy anion is normally expected to be more reactive than the starting superoxide.[32−34] This is confirmed by our calculations for the nucleophilic attack of the methylperoxy anion (CH_3OO^-) on PC, which is strongly favorable thermodynamically ($\Delta G_r = -21.2$ kcal/mol) and requires little activation energy ($\Delta G_{act} = 11.2$ kcal/mol).

It is generally assumed that liquid-phase reactions of O_2^- with aliphatic esters, which are most closely related by chemical structure to alkyl carbonates, proceed via attack at the carbonyl carbon.[20,35−37] However, we find that O_2^- addition to the carbonyl carbon of PC leads to an adduct that is 36.9 kcal/mol less stable than the reactant complex and requires an activation energy of 41.9 kcal/mol (Figure 1). Thus, nucleophilic substitution at the carbonyl carbon of PC is not supported by our calculations.

To investigate whether our conclusions can be generalized to other carbonates, we calculated activation energies and thermodynamic parameters for nucleophilic attack of O_2^- on ethereal carbon atoms of ethylene carbonate and dimethyl carbonate. The

Table 1. Changes in Reaction (ΔE_r) and Activation (ΔE_{act}) Energies for Superoxide Addition to the Ethereal Carbon Atom of Ethylene Carbonate in the Gas Phase Calculated by Various Methods (kcal/mol)[a]

method	ΔE_r	ΔE_{act}
UMP2/aug-cc-pVDZ	−1.63	14.18
UMP2/aug-cc-pVTZ	−1.31	15.12
UMP2/aug-cc-pVQZ	−1.57	15.02
UMP2/aug-cc-pV5Z	−1.53	15.07
UCCSD(T)/aug-cc-PVDZ	−6.05	11.40
UCCSD(T)/aug-cc-pV5Z[b]	−5.95	12.30
B3LYP/6-311++G**	−7.14	9.76
B3LYP/aug-cc-pVTZ	−6.53	10.21

[a] Structures of the complexes used in DFT and post-Hartree–Fock UMP2 and UCCSD(T) calculations are obtained at the B3LYP/6-311++G** and UMP2/aug-cc-pVDZ levels, respectively. [b] Estimated by combining the UMP2/aug-cc-pV5Z energies with UCCSD(T)/aug-cc-pVDZ corrections.

Table 3. Computed Free-Energy Barriers (ΔG_{act}) and Reaction Free Energies (ΔG_r) for Nucleophilic Attack by the Superoxide Ion on Ethereal Carbon Atoms of Propylene Carbonate (PC), Ethylene Carbonate (EC), and Dimethyl Carbonate (DMC) Calculated in the Field of the Continuum Solvent (kcal/mol)[a]

solvent	ε	ΔG_{act}	ΔG_r
PC	64.4	15.47	−5.64
EC	89.6	14.22	−6.94
DMC	3.09	12.42	−11.39

[a] Structures of the transition-state complexes for EC and DMC are similar to that shown for PC in Figure 1.

Table 2. Calculated and Measured Gas-Phase Electron Affinities (EA) of O_2 and HOO and Proton Affinities (PA) of O_2^- and HOO^- (kcal/mol)[a]

	EA		PA		
method	O_2	HOO	O_2^-	HOO^-	MAE[b]
experiment	10.33 ± 0.14	24.86 ± 0.14	353.00 ± 0.70	376.50 ± 0.50	
UCCSD(T)/aug-cc-pV5Z[c]	10.56	25.21	353.14	376.27	0.24
UCCSD(T)/aug-cc-PVTZ	8.93	23.81	353.08	376.31	0.68
B3LYP/aug-cc-pVTZ	13.00	23.86	351.10	374.08	2.00
B3LYP/6-311++G**	14.02	24.15	349.41	373.51	2.75
UMP2/aug-cc-pVQZ	8.44	30.67	346.21	375.07	3.98
UMP2/aug-cc-pV5Z	9.08	31.21	346.01	374.89	4.05
UMP2/aug-cc-pVTZ	7.46	29.81	345.95	374.92	4.11

[a] Structures of the complexes used in DFT and post-Hartree–Fock UMP2 and UCCSD(T) calculations are obtained at the B3LYP/6-311++G** and UMP2/aug-cc-pVTZ levels, respectively. [b] Computational methods are listed in order of increasing mean absolute error (MAE), relative to experiment.[30] [c] Estimated by combining the UMP2/aug-cc-pV5Z energies with UCCSD(T)/aug-cc-pVTZ corrections.
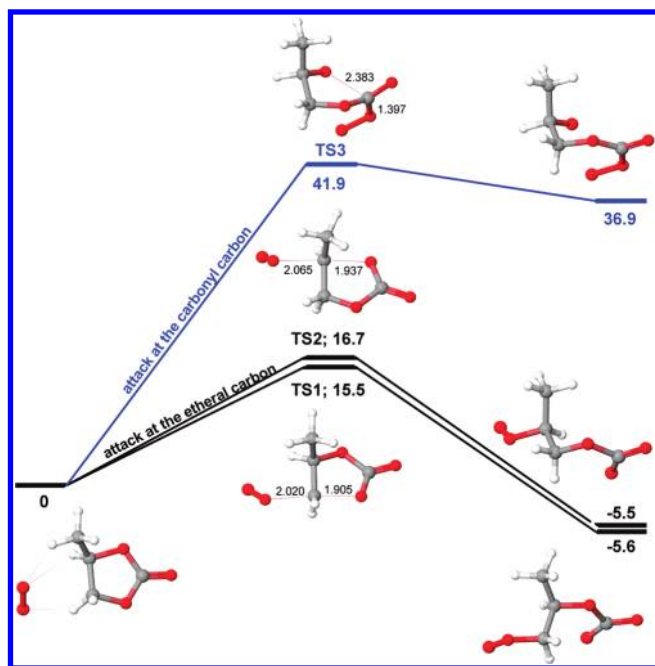
Figure 1. Reaction free-energy profile (T = 298.15 K) for nucleophilic attack of O_2^- at the carbonyl and ethereal carbon atoms of PC calculated in the field of the continuum solvent (kcal/mol). DFT-optimized C—O bond lengths in the transition states are shown.
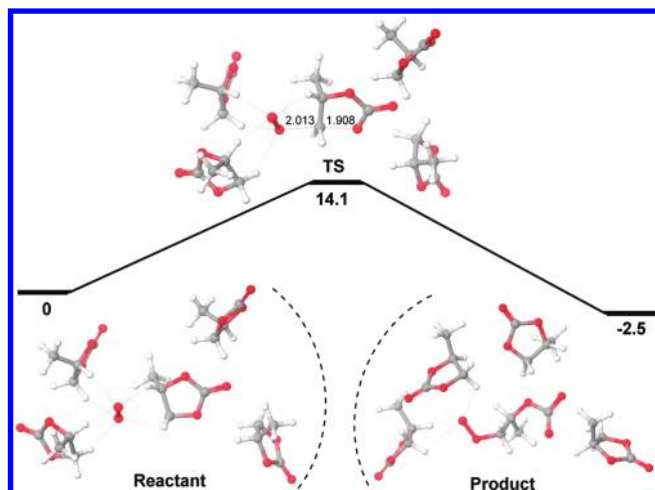

Figure 2. Reaction energy profile for nucleophilic attack of O_2^- at the ethereal CH_2 carbon of PC calculated in the presence of four additional solvent molecules and the dielectric field of a solvent continuum (kcal/mol). DFT-optimized C—O bond lengths in the transition states are shown.

results, Table 3, confirm that ethereal carbon addition reactions can readily occur in all cases. Activation barriers for EC and DMC are even smaller than those for PC, and their variation is inversely correlated with the change in the reaction free energy.

In modeling solvation effects, an important question arises as to whether computational results are sensitive to the presence of explicit solvent molecules surrounding the reaction system. Figures 2 and 3 provide illustrative examples of such mixed cluster/continuum models, where additional PC molecules serve to effectively solvate the charged species involved in the nucleophilic displacement at the ethereal and carbonyl carbons, respectively.
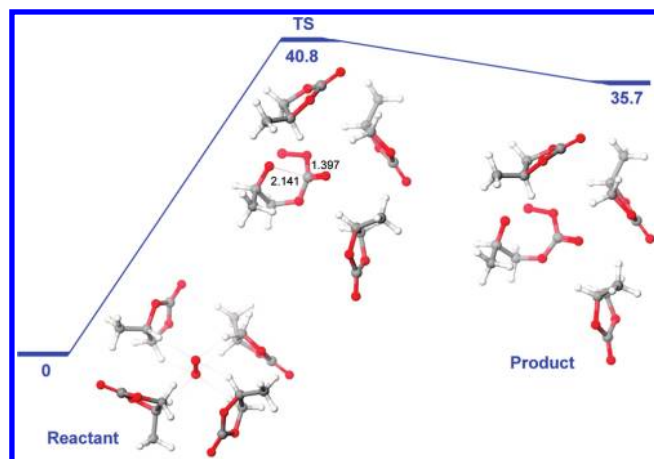

Figure 3. Reaction energy profile for nucleophilic attack of O_2^- at the carbonyl carbon of PC calculated in the presence of three additional solvent molecules and the dielectric field of a solvent continuum (kcal/mol). DFT-optimized C—O bond lengths in the transition states are shown.

Comparison of free energy-profiles shown in Figures 1–3 suggests that using the mixed cluster/continuum approach instead of the implicit representation of a solvent does not significantly alter any of the results based on the simpler implicit solvation model. Thus, our calculation results, independent of the solvation model used, strongly support the S_N2 mechanism whereby O_2^- preferentially attacks the less-hindered ethereal carbon atom of PC. This is in agreement with the mechanism of nucleophilic addition of O_2^- to alkyl esters in the gas phase, as evidenced by mass spectrometric studies.[38,39]

The described mechanism of superoxide-induced decomposition of organic carbonate solvents in the absence of explicit counterions is expected to be observed in the case wherein the electrolyte salt comprises a large organic cation that does not strongly interact with superoxide. Having ΔG_{act} = 15.5 kcal/mol (Figure 1 and Table 3), the estimated half-life of O_2^- in PC using the classical transition-state theory is on the order of 0.5 min. This is in agreement with observation[17] that oxygen reduction in a 0.1 M TEA^+TFSA^-/PC electrolyte is irreversible on the time scale of cyclic voltammetry (100 mV/s scan rate).

For the Li—air battery, an important question arises as to whether the decomposition reaction of O_2^- with carbonate solvents would also occur in the presence of Li^+ ions. To address this question, we considered a structural model of a reaction center for nucleophilic attack of lithium superoxide LiO_2 on the EC substrate depicted in Figure 4. In this model, the second Li^+ ion was used to allow the formation of organic lithium carbonate species, and five additional EC molecules were placed into the system to ensure adequate solvation of ionic and charged species. Although the presence of Li^+ ions causes some increase in the activation energy for the nucleophilic attack, the barrier height of 20.2 kcal/mol is not sufficiently high to prevent the occurrence of solvent decomposition reactions. It is also possible that some Li_2O_2 will be formed during the discharge of a battery. However, Li_2O_2 might be at least partially converted to Li_2CO_3 via a base-mediated proton transfer from PC, as discussed below.

Finally, in the presence of water or weak acids, we expect O_2^- to undergo a commonly accepted mechanism of proton abstraction[34] to initially form HOO, which is reduced by another O_2^- to give HOO^-, which in turn abstracts the second proton to yield the final product, H_2O_2. The possibility of a nucleophilic

381

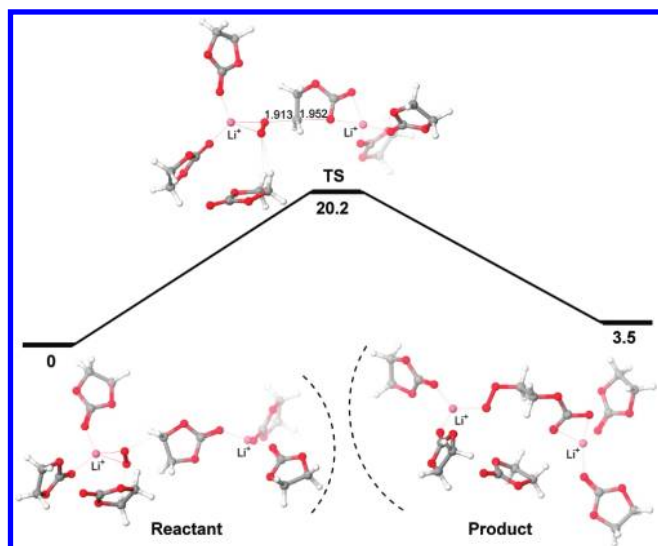dx.doi.org/10.1021/jz1016526 |*J. Phys. Chem. Lett.* 2011, 2, 379–383

Figure 4. Reaction energy profile for nucleophilic attack of LiO_2 at the ethereal CH_2 carbon of EC. Electrolyte effects were modeled by explicit inclusion of five additional EC molecules and one Li^+ ion in the vicinity of the reaction center and implicit treatment of the rest of the solvent with a dielectric continuum model (kcal/mol). DFT-optimized C—O bond lengths in the transition states are shown.
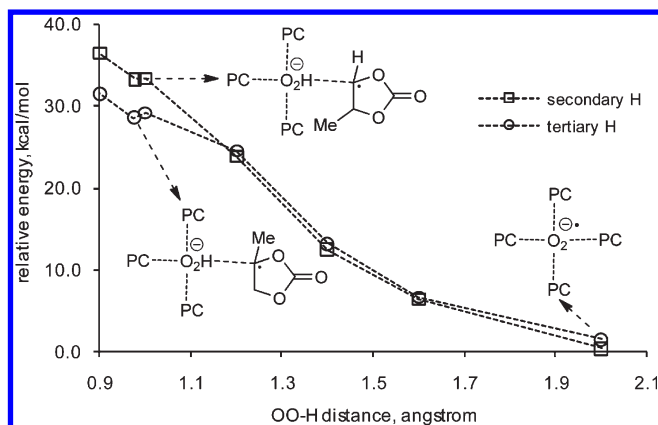

Figure 5. Potential energy curves for secondary and tertiary proton/H-atom abstraction from PC by the superoxide (kcal/mol) calculated in the presence of three additional solvent molecules and the field of continuum solvent. A schematic drawing of the reactants and products is shown.

substitution reaction between HOO and PC can be ruled out as the initial step. It is predicted to be strongly unfavorable under standard conditions (ΔG_{act} = 42.4 kcal/mol; ΔG_r = 20.4 kcal/mol).

It has been speculated that PC decomposition by superoxide might occur through a proton-abstraction mechanism.[16] To test this hypothesis, we constructed potential energy curves for proton/H-atom abstraction from PC to the superoxide (Figure 5). The results indicate that proton/H-atom abstraction for hydrogen atoms attached to the ring carbons is unlikely as it requires at least ∼30.0 kcal/mol of energy to reach the local minimum corresponding to hydroperoxyl anion HOO^-.

However, to our surprise, superoxide-mediated proton transfer can occur more readily from the methyl group of PC. We found that proton abstraction from the methyl group of PC is associated with ring opening (CH_2—O bond cleavage), yielding initially the propylenyl carbonate anion and HOO^* radical, which
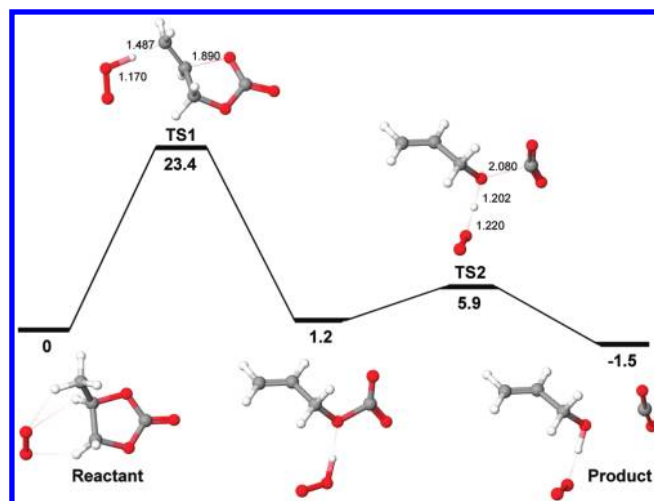

Figure 6. Reaction free-energy profile (T = 298.15 K) for O_2^--mediated proton transfer from the methyl group of PC to yield allyl alcohol (CH_2=$CHCH_2OH$) and carbon dioxide calculated in the field of the continuum solvent (kcal/mol). DFT-optimized C—O bond lengths in the transition states are shown.

in the next step generate allyl alcohol and CO_2 to give back the original superoxide. As seen from Figure 6, the overall process is thermodynamically favorable (ΔG_r = −1.5 kcal/mol) and does not require significant activation energy (ΔG_{act} = 23.4 kcal/mol for the initial rate-limiting step). Although the calculated activation barrier is distinctly higher than that obtained in the S_N2-type reaction, O_2^--mediated proton transfer from the methyl group of PC can be considered as a secondary mechanism of PC decomposition. Because superoxide is functioning as a base and it is being regenerated, other bases in the absence of superoxide can also cause PC decomposition through the same mechanism. For example, the desirable discharge products in Li—air cells, Li_2O_2 and Li_2O, perhaps in the presence of a slight amount of water, may facilitate proton abstraction. This is consistent with several reports suggesting that the chemical and electrochemical stability of PC in contact with Li_2O_2 could be significantly reduced.[11,15]

Furthermore, the generated HOO^* radical (Figure 6) in the presence of excess O_2^- can easily undergo further reduction to HOO^-. The latter anion is known to be a much stronger proton acceptor than the initial superoxide.[34] Similarly, in separate calculations involving Li^+ ions, we found that lithium peroxide anion LiO_2^- is a stronger base than O_2^-.

At present, formulation of electrolytes for commercial lithium-ion batteries indispensably involves the use of organic carbonate solvents. A combination of useful properties of diesters of the carbonic acid has prompted researchers over the last several years to consider them as potential electrolyte solvents for the non-aqueous lithium—air battery. However, there is strong experimental evidence,[11,13−18] now supported by our theoretical calculations, that cyclic and linear carbonates are unstable against superoxide. We find that the nucleophilic attack of O_2^- at the ethereal carbon atom of carbonate solvents is an important decomposition mechanism of carbonate-based electrolytes during the electrochemical reduction of oxygen. Base-mediated proton transfer from the methyl group of PC can also be considered as a special case of PC decomposition. The mechanisms presented here may assist the design of stable electrolytes that withstand the specific chemical environment in Li—air systems.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Complete ref 23, Cartesian coordinates, and absolute energies at the B3LYP/aug-cc-pVTZ level of theory for all structures discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: slava@liox.com.

■ REFERENCES

(1) Abraham, K. M.; Jiang, Z. A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery. *J. Electrochem. Soc.* **1996**, *143*, 1–5.

(2) Read, J. Characterization of the Lithium/Oxygen Organic Electrolyte Battery. *J. Electrochem. Soc.* **2002**, *149*, A1190–A1195.

(3) Read, J.; Mutolo, K.; Ervin, M.; Behl, W.; Wolfenstine, J.; Driedger, A.; Foster, D. Oxygen Transport Properties of Organic Electrolytes and Performance of Lithium/Oxygen Battery. *J. Electrochem. Soc.* **2003**, *150*, A1351–A1356.

(4) Kuboki, T.; Okuyama, T.; Ohsaki, T.; Takami, N. Lithium−Air Batteries Using Hydrophobic Room Temperature Ionic Liquid Electrolytes. *J. Power Sources* **2005**, *146*, 766–769.

(5) Ogasawara, T.; Débart, A.; Holzapfel, M.; Novák, P.; Bruce, P. G. Rechargeable Li_2O_2 Electrode for Lithium Batteries. *J. Am. Chem. Soc.* **2006**, *128*, 1390–1393.

(6) Read, J. Ether-Based Electrolytes for the Lithium/Oxygen Organic Electrolyte Battery. *J. Electrochem. Soc.* **2006**, *153*, A96–A100.

(7) Kowalczk, I.; Read, J.; Salomon, M. Li−Air Batteries: A Classical Example of Limitations Owing to Solubilities. *Pure Appl. Chem.* **2007**, *79*, 851–860.

(8) Mirzaeian, M.; Hall, P. J. High Capacity Carbon Based Electrodes for Lithium/Oxygen Batteries. *Power System Tech.* **2007**, *31*, 90–96.

(9) Débart, A.; Bao, J.; Armstrong, G.; Bruce, P. G. An O_2 Cathode for Rechargeable Lithium Batteries: The Effect of a Catalyst. *J. Power Sources* **2007**, *174*, 1177–1182.

(10) Débart, A.; Paterson, A. J.; Bao, J.; Bruce, P. G. α-MnO_2 Nanowires: A Catalyst for the O_2 Electrode in Rechargeable Lithium Batteries. *Angew. Chem., Int. Ed.* **2008**, *47*, 4521–4524.

(11) Girishkumar, G.; McCloskey, B.; Luntz, A. C.; Swanson, S.; Wilcke, W. Lithium−Air Battery: Promise and Challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2193–2203.

(12) Kraytsberg, A.; Ein-Eli, Y. Review on Li−Air Batteries — Opportunities, Limitations and Perspective. *J. Power Sources* **2011**, *196*, 886–893.

(13) Freunberger, S. A.; Hardwick, L. J.; Peng, Z.; Giordani, V.; Chen, Y.; Maire, P.; Novák, P.; Tarascon, J.-M.; Bruce, P. Fundamental Mechanism of the Lithium−Air Battery. The 15th International Meeting on Lithium Batteries, Montréal, Canada, June 27−July 2, 2010.

(14) Freunberger, S. A.; Peng, Z.; Hardwick, L. J.; Chen, Y.; Barde, F.; Bruce, P. Understanding the Chemical Reactions in the Lithium−Oxygen Battery. 218th ECS Meeting, Las Vegas, NV, October 10−15, 2010; Abstract 340.

(15) Mizuno, F.; Nakanishi, S.; Kotani, Y.; Yokoishi, S.; Iba, H. Rechargeable Li−Air Batteries with Carbonate-Based Liquid Electrolytes. *Electrochemistry* **2010**, *78*, 403–405.

(16) Takechi, K.; Sudo, E.; Inaba, T.; Mizuno, F.; Nishikoori, H.; Shiga, T. Solvent Screening of the Electrolyte for Nonaqueous Li−Air Batteries. 218th ECS Meeting, Las Vegas, NV, October 10−15, 2010; Abstract 586.

(17) Mizuno, F. Fundamental Study on Rechargeable Reaction of Lithium−Oxygen Battery. Symposium on Energy Storage beyond Lithium Ion: Materials Perspectives, Oak Ridge, TN, October 7−8, 2010; https://www.ornl.gov/ccsd_registrations/battery/agenda.shtm.

(18) Girishkumar, G.; McCloskey, B. Investigating the Electrochemistry of Li−O_2 Battery Using DEMS and Surface Characterization Techniques. Symposium on Energy Storage beyond Lithium Ion: Materials Perspectives, Oak Ridge, TN, October 7−8, 2010.

(19) Frimer, A. A.; Rosenthal, I. Chemical Reactions of Superoxide Anion Radical in Aprotic Solvents. *Photochem. Photobiol.* **1978**, *28*, 711–719.

(20) Sawyer, D. T.; Valentine, J. S. How Super Is Superoxide? *Acc. Chem. Res.* **1981**, *14*, 393–400.

(21) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303–4417.

(22) *Jaguar*, version 7.5; Schrödinger, LLC: New York, 2008.

(23) Straatsma, T. P.; Aprà, E.; Windus, T. L.; Bylaska, E. J.; de Jong, W.; Hirata, S.; Hackler, M.; Pollack, L.; Harrison, R. et al. NWChem, A Computational Chemistry Package for Parallel Computers, version 5.1; Pacific Northwest National Laboratory: Richland, WA, 2007.

(24) Becke, A. D. Density Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(25) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle−Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988**, *37*, 785–789.

(26) Möller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618–622.

(27) Purvis, G. D., III; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model — The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.

(28) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A 5th-Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

(29) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J.* Coupled-Cluster Methods with Noniterative Triple Excitation for Restricted Open-Shell Hartree−Fock and Other General Single Determinant Reference Functions − Energies and Analytical Gradients. *Chem. Phys.* **1993**, *98*, 8718–8733.

(30) *Chemistry WebBook*, NIST Standard Reference Database Number 69; http://webbook.nist.gov/chemistry/ (June 2005).

(31) Roberts, J. L., Jr.; Sawyer, D. T. Facile Degradation by Superoxide Ion of Carbon Tetrachloride, Chloroform, Methylene Chloride, and *p,p*′-DDT in Aprotic Media. *J. Am. Chem. Soc.* **1981**, *103*, 712–714.

(32) Daasbjerg, K.; Lund, H. The Nucleophilicity of Superoxide towards Different Alkyl Halides Estimated from Kinetic Measurements. *Acta Chem. Scand.* **1993**, *47*, 597–604.

(33) Chin, D. H.; Chiericato, G., Jr.; Nanni, E. J., Jr.; Sawyer, D. T. Proton-Induced Disproportionation of Superoxide Ion in Aprotic Media. *J. Am. Chem. Soc.* **1982**, *104*, 1296–1299.

(34) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. Mechanism of Superoxide Ion Disproportionation in Aprotic Solvents. *J. Am. Chem. Soc.* **1987**, *109*, 3768–3775.

(35) San Filippo, J., Jr.; Romano, L. J.; Chern, C.-I. Cleavage of Esters by Superoxide. *J. Org. Chem.* **1976**, *41*, 586–588.

(36) Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. Reactivity of Superoxide Ion with Carbonyl Compounds in Aprotic Solvents. *J. Am. Chem. Soc.* **1979**, *101*, 640–644.

(37) Webster, R. D.; Bond, A. M. Different Mechanisms for the Reaction of Disubstituted Aromatic Esters and Thioic S-Esters with electrochemically generated superoxide. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1075–1079.

(38) McDonald, R. N.; Chowdhury, A. K. Gas-Phase Ion−Molecule Reactions of Dioxygen Anion Radical ($O_2^{-\bullet}$). *J. Am. Chem. Soc.* **1985**, *107*, 4123–4128.

(39) Stemmler, E. A.; Diener, J. L.; Swift, J. A. Gas-Phase Reactions of $O_2^{-\bullet}$ with Alkyl and Aryl Esters of Benzenedicarboxylic Acids. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 990–1000.

383

dx.doi.org/10.1021/jz1016526 |*J. Phys. Chem. Lett.* 2011, 2, 379–383