



Exploring Solvent Stability against Nucleophilic Attack by Solvated LiO_2^- in an Aprotic Li-O₂ Battery

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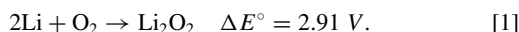
Solvent degradation due to reactivity with various oxygen species is one of the most important issues in aprotic Li-O₂ batteries. Recently, a more complete mechanism for discharge in an aprotic Li-air battery has been proposed, which accounts for the formation of solvated peroxides by disproportionation. In the present work, nucleophilic attacks by one of these solvated peroxides, LiO_2^- (solv) on some commonly used solvents in aprotic Li-air batteries, including acetonitrile (MeCN), 1-methyl-2-pyrrolidone (NMP), dimethoxy ethane (DME), and dimethyl sulfoxide (DMSO) have been explored by calculating the reaction and activation free energies using density functional theory (DFT) method. The results show that despite demonstrating strong stability against nucleophilic attacks by O_2^- (solv), these solvents are susceptible to nucleophilic attacks by LiO_2^- (solv). The results provide new insight for identifying stable solvents in aprotic Li-O₂ batteries.

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Manuscript submitted October 11, 2016; revised manuscript received December 14, 2016. Published December 28, 2016.

Active research¹⁻¹⁷ on the aprotic Li-air battery has been drawn by its high theoretical energy and power storage capacities of 11,000 Wh/kg and 3800 mAh/g, respectively.^{18,19} These values double those of the most advanced lithium ion batteries and close to those of gasoline. However, many challenges²⁰ must be overcome before a commercially viable battery can be produced. One critical issue is the degradation of solvents during the charge and discharge cycles of the battery. Common solvents in Li-air batteries such as propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC) have long been shown to degrade during discharge and fail to produce lithium peroxide (Li_2O_2), the desired discharge product in a two-electron process²¹⁻²³ described by



Bryantsev et al.²⁴⁻²⁶ and Freunberger et al.²⁷ attributed this failure to the reactions between these solvents and the superoxide radical ion (O_2^-) with the latter formed inevitably during discharge in the one-electron reduction of oxygen shown in Equation 2 as

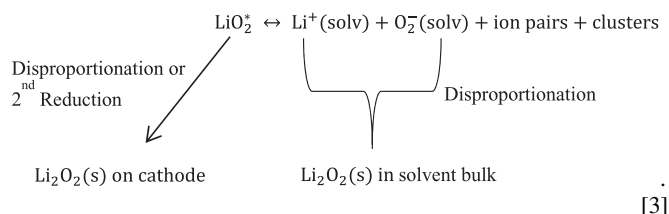


This hypothesis of degradation by superoxide is supported by the results of the computational studies carried out by Bryantsev et al.,²⁴⁻²⁶ the experiments carried out by Freunberger et al.²⁷ and Herranz et al.,²⁸ as well as many subsequent experiments showing the degradations of these solvents in the presence of O_2^- containing species such as potassium superoxide (KO_2). Bryantsev et al.^{24,25} screened a multitude of solvents computationally to identify acetonitrile (MeCN), lactams such as 1-methyl-2-pyrrolidone (NMP), and glymes such as dimethoxy ethane (DME), that can be used as stable solvents against degradation by superoxide. The computational results are supported by the presence of Li_2O_2 as the dominant discharge product in experiments that utilized MeCN,^{20,29} dimethyl sulfoxide (DMSO),^{20,29} NMP,^{30,31} and DME³² as solvents.

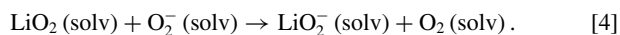
Despite their better stabilities, recent experiments have shown that, MeCN,^{29,33} DMSO,^{29,33-37} NMP,^{33,35,38,39} DME and glymes^{33,35,38,40-45} also experience degradations upon cycling. Younesi et al.,⁴³ Curioni et al.,^{46,47} Kumar et al.,⁴⁸ and Lau et al.^{49,50} theorize that solid Li_2O_2 deposited on the cathode and Li_2O_2 mini-clusters are responsible for the said degradations without the need of other oxygen species. Using X-ray photoelectron spectroscopy (XPS)⁴² Younesi et al. find that solid Li_2O_2 degrades tetraethylene glycol dimethyl ether (TEGDME). Curioni et al. use density functional theory based molecular dynamics

(DFTMD) simulations to show that reactions between these solvents and solid Li_2O_2 have low activation barriers.^{46,47} Kumar et al. utilize a variety of computation techniques, such as classical Monte Carlo and van der Waals-augmented DFT, to study the decomposition of DME on the surface of solid Li_2O_2 .⁴⁸ Lau et al. use DFT calculations^{49,50} and ab initio molecular dynamics (AIMD) simulations⁵⁰ to demonstrate the decomposition interactions of DME with Li_2O_2 clusters.

More recently, Johnson et al.⁵¹ and Laoire et al.⁵² report that LiO_2^- formed after the initial single-electron reduction of O_2 to O_2^- can equilibrate between precipitation on the cathode and dissolution in the solvent, as represented by Equation 3:⁵¹



The position of this equilibrium depends on the solubility of the species on the right hand side of Equation 3. Using a combination of cyclic voltammograms (CVs), in situ electrochemical surface-enhanced Raman spectroscopy (SERS), and rotating ring-disk electrode studies, Johnson et al.⁵¹ show that in solvents with small donor numbers (DN) like MeCN, LiO_2^- is mostly deposited on the surface of the cathode, and can then form Li_2O_2 via either disproportionation or a second one-electron reduction process, as illustrated in the left side reaction of Equation 3. On the other hand, in solvents with large DN's such as DMSO, LiO_2^- is mostly in solvated form, which can then form Li_2O_2 only through disproportionation. During this process, various peroxide-related species can be formed.²¹ Equation 4 shows the formation of LiO_2^- (solv) via disproportionation, while O_2^{2-} (solv) and Li_2O_2 (solv) are also formed in similar ways.



For O_2^- generated in Equation 2, alternative mechanisms of $\text{Li}_2\text{O}_2(\text{s})$ deposition via solution phase or surface phase have been reviewed by Aurbach et al.¹⁷ and correlated to DN. Based on the results, Johnson et al.⁵¹ propose a single mechanism of O_2 reduction to form Li_2O_2 , which is based on the donor number (DN) of the solvent used, with low DN solvents like MeCN favoring a surface pathway and high DN solvents such as DMSO favoring a solution pathway where an abundance of solvated peroxide-related species would be expected.

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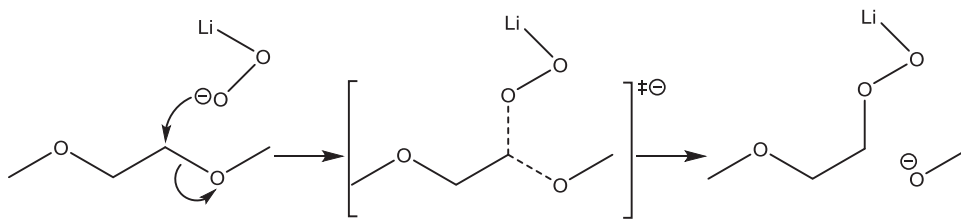


Figure 1. Schematic diagram of the nucleophilic attack by $\text{LiO}_2^-(\text{solv})$ on $-\text{CH}_2-$ of DME.

Based on these evidences to support the existence of $\text{LiO}_2^-(\text{solv})$, this contribution aims to investigate computationally the reactivity of $\text{LiO}_2^-(\text{solv})$ in nucleophilic reactions with the various functional groups appearing in the common solvents used in an aprotic Li-air battery, as depicted in Figure 1; and to discuss whether these reactions can lead to solvent degradations. In computational studies on solvent degradation involving O_2^- , most degradation pathways are on nucleophilic reactions, though other degradation pathways such as hydrogen abstraction have also been explored. As an initial study of reactivity, this work focuses on nucleophilic reaction due to solvated peroxides. Reactions with solvated species are studied instead of those deposited on the cathode surface because these reactions would take place in the bulk solvent and would not require a solid-solution interface. This also means that the direct effect of the discharge potential would be small. If the solvents are unstable against nucleophilic attacks by these solvated species, stability in presence of species deposited on the cathode surface becomes immaterial. It is our wish that this work can add to the current understanding of the chemistry inside the aprotic Li-air battery.

Computational Methods

All computations are carried out using the Gaussian09 software package.

The free energies of activation in solution phase are calculated using Equation 5:

$$\Delta_{act}G_{\text{soln}} = \Delta_{act}G_{\text{gas}} + \sum \Delta_{\text{solv}}G + RT \left[\sum \ln\left(\frac{RT}{P}\right)_{\text{TS}} - \sum \ln\left(\frac{RT}{P}\right)_{\text{reactants}} \right]. \quad [5]$$

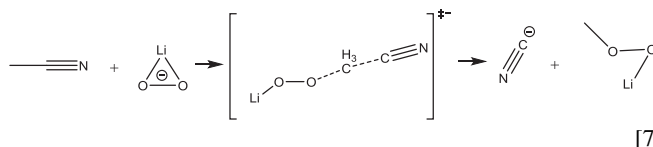
The free energies of reaction in solution phase are computed in a similar way. The solution-phase free energies of various species, $G_{\text{soln}}(\text{Species})$, are calculated by utilizing the dielectric continuum solvent model, SMD,⁵³ which has been parametrized to give accurate estimates of the free energies of solvation, $\Delta_{\text{solv}}G$. This can be combined with accurate estimates of gas phase free energies, G_{gas} , according to the recommendation by Ho et al.,⁵⁴ which can be then

rearranged to Equation 6, a formulation suggested by Ribeiro et al.:⁵⁵

$$G_{\text{soln}} = E_{\text{gas}} + \Delta_{\text{solv}}E + G_{\text{corr}} + RT \ln\left(\frac{RT}{P}\right). \quad [6]$$

The last term is included for the conversion from the standard state in gas phase to the solution-phase standard state that is 1 M.

All the solution-phase structures are optimized using the density functional theory (DFT) method of B3LYP with the 6-311++G(d,p) basis set. The optimized geometries are then used to compute the solution-phase thermal corrections to free energies, G_{corr} , also using B3LYP/6-311++G(d,p). Values of E_{gas} are obtained by calculating the electronic energies of the optimized solution-phase structures in the absence of the solvent continuum and at a higher level of theory. To facilitate choosing an accurate DFT method among numerous choices, a benchmark test is carried out for the nucleophilic reaction between LiO_2^- and MeCN, as described in Equation 7 and Figures 2a to 2c.



A series of different DFT methods are used to calculate the values of E_{gas} , using the 6-311+G(2d,2p) basis set, and the resulting enthalpies of reaction and activation are compared with those calculated with CCSD(T)/6-311+G(2d,2p). CCSD(T) involves a higher level of theory and in general gives more accurate results at the cost of greater computational cost, so it is frequently used as a benchmark against which other less costly methods are compared against. The results, as listed in Table I, show that the M06 method gives reaction and activation enthalpies that are closest to those obtained using CCSD(T). The M06 method was subsequently chosen to calculate values of E_{gas} throughout this study.

The enthalpies of solvation, ΔE_{solv} , are obtained by calculating the electronic energies of the optimized solution-phase structures in the presence and absence of the solvent continuum using B3LYP/6-31G(d), a method that has been demonstrated to give accurate values by Marenich et al.⁵³

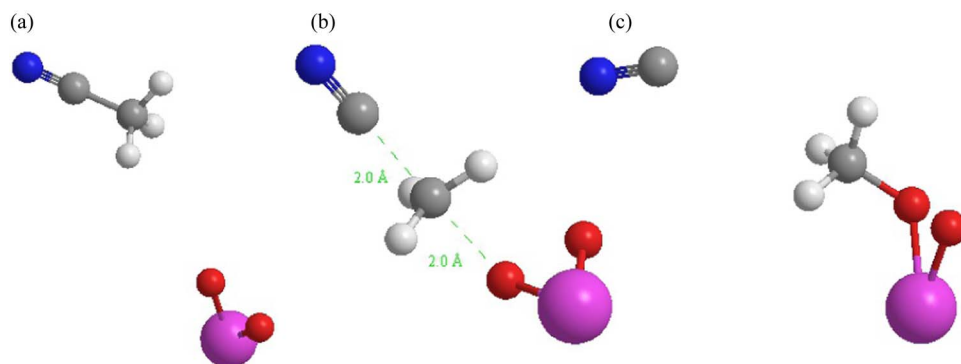


Figure 2. Structures of a) reactants, b) transition state complex, and c) products.

Table I. Reaction and activation enthalpies calculated with CCSD(T) and calculated deviation with seven different DFT methods, all using the 6-311+G(2d,2p) basis set.

	CCSD(T)	B3LYP	B97d	B3LYP-D3	X3LYP	M06	M062X	WB97XD
$\Delta_r H / \text{kcal mol}^{-1}$	-15.695	5.635	5.118	4.528	3.961	1.443	-2.805	-0.908
$\Delta_{\text{act}} H / \text{kcal mol}^{-1}$	16.622	2.878	-1.763	0.925	1.369	1.603	-0.787	1.622

To facilitate comparison, $\Delta_r G$ and $\Delta_{\text{act}} G$ values of nucleophilic reactions between O_2^- (solv) and the solvents are also calculated using the same method alongside those of O_2^{2-} (solv), Li_2O^- (solv) and Li_2O_2 (solv).

Results and Discussion

A series of common aprotic solvents that have been used in a Li-air battery is investigated in this study. These include carbonates such as PC, EC and DMC; lactones such as γ -butyrolactone (GBL); esters such as methyl acetate; nitriles such as MeCN and benzonitrile (BN); lactams such as NMP; glymes such as DME; and DMSO. Reaction free energies and activation energies between these solvents and nucleophiles O_2^- (solv), O_2^{2-} (solv), LiO_2^- (solv) and Li_2O_2 (solv) have been calculated according to the method described in the previous section. The computational results for the nucleophilic attacks by LiO_2^- (solv) on NMP, DME, DMSO, and MeCN are chosen for discussion and listed in Table II; whereas Table III gives the full results for other solvents and other nucleophiles. In addition, DN values of the solvents are listed to give a rough idea on the position of the equilibrium described by Equation 3.^{51,56,57}

NMP is chosen because the reaction on its carbonyl carbon, C2, is representative of similar reactions on solvents that contain the carbonyl group, namely PC, EC, DMC and GBL. Similarly, MeCN is chosen because the nucleophilic reaction on the nitrile carbon is repeatedly seen in other solvents containing the nitrile group. DME is chosen as a representative of the glyme family, which is a popular group of solvents among experimentalist working on the Li-air battery. DMSO is chosen because it is a common solvent used by experimentalist in Li-air battery. It is also very important to note that NMP, MeCN, DMSO, and DME are all solvents that have been proven computationally^{24,25} and experimentally^{20,28-32} to be stable against O_2^- (solv) and give Li_2O_2 as the main discharge product, but have been shown to degrade slowly over many charge-discharge cycles.^{29,33,35,38-45} In general, our results suggest that functional groups that contains C-X π -bonds, where X can be O of carbonyl groups or N of nitrile groups, are very susceptible to nucleophilic attacks by the solvated peroxides despite showing good stability against nucleophilic attacks by O_2^- (solv). The nucle-

ophilic reactions are computed to be almost always exergonic and frequently have small or no activation barriers. Nucleophilic attacks on ether groups of solvents such as DME by the solvated peroxides usually have higher activation barriers than those on C-X π -bonds, but the barriers are still small enough to be easily breached at room temperature. Similarly, the activation barriers of the nucleophilic attacks on the methyl group of DMSO by the solvated peroxides are also small enough to be breached at room temperature.

Table II lists the computed reaction and activation Gibbs free energies for the nucleophilic attacks by LiO_2^- (solv) on specific locations on NMP, MeCN, DME, and DMSO, as well as their respective dielectric constants, ϵ . The locations for nucleophilic attacks presented here have the lowest activation barriers among nucleophilic attacks on different sites on that particular solvent. The attack on -CH₂- of DME, as an example, is illustrated in Figure 1. The LiO_2^- (solv) species is chosen as it is a disproportionation product of the solvation pathway of Equation 4. The inclusion of Li containing species is also of relevance to the battery and the Li ion may have an influence on the attack on many functional groups.

Johnson et al.'s proposed relationship⁵¹ between solvents' DN and the solubility of LiO_2 is used here to correlate the relative position of the equilibrium described in Equation 3. The Gutmann's solvent DN^{56,57} of each solvent is listed in Table II. NMP has a very high DN of 27.3.^{56,57} Hence, it is expected that the solution pathway would dominate during discharge, and LiO_2^- (solv) would be present at a rather high concentration. It can be seen that the nucleophilic reaction between LiO_2^- (solv) and the carbonyl carbon is exergonic and has essentially no activation barrier. This suggests that NMP could be unstable in the presence of LiO_2^- (solv) and this nucleophilic reaction is likely to contribute to the degradation of NMP in the Li-air battery, as observed in some recent experiments.^{33,35,38,39} What is even more interesting is that the carbonyl carbon in an amide group is generally considered relatively protected toward nucleophilic attacks among functional groups that contain a carbonyl group. The fact that even this amide carbon is susceptible to nucleophilic attacks by LiO_2^- (solv) suggests that most of the solvents that have carbonyl groups would be expected to demonstrate similar vulnerability.

Table II. Computed reaction Gibbs free energies and free energy activation barriers for nucleophilic attacks by LiO_2^- (solv) with the implicit continuum solvent model. (All energies in kcal/mol).

Solvent	ϵ	DN ^{55,56}	LiO_2^- (solv)		
			Site ^a	$\Delta_r G$	$\Delta_{\text{act}} G$
NMP					
MeCN	32.2	27.3	C2	-9.70	-
	36.0	14.1	-CN	-11.42	-
DME	7.2	20.0	-CH ₂ -	-34.24	24.80
DMSO	48.0	29.8	-CH ₃	-18.58	22.07

^aSite of nucleophilic attack.

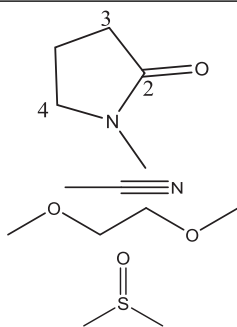
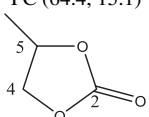
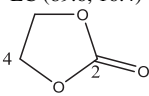
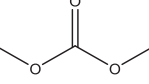
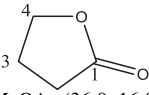
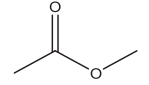
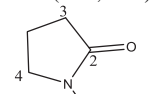
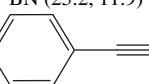
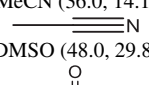
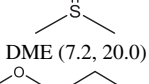
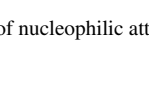


Table III. Computed reaction Gibbs free energies and free energy activation barriers for nucleophilic reactions with the implicit continuum solvent model. (All energies in kcal/mol).

Solvent (ϵ , DN)	Site ^a	O_2^- (solv)		O_2^{2-} (solv)		LiO_2^- (solv)		Li_2O_2 (solv)	
		Δ_rG	$\Delta_{act}G$	Δ_rG	$\Delta_{act}G$	Δ_rG	$\Delta_{act}G$	Δ_rG	$\Delta_{act}G$
PC (64.4, 15.1) 	C2	37.90	40.34	-27.95	-	-3.50	7.87	-5.48	-
	C4	-6.08	19.06	-66.90	-	-29.64	28.43	-19.99	23.26
	C5	-3.57	20.61	-60.77	4.33	-25.09	27.70	-23.29	22.32
EC (89.6, 16.4) 	C2	38.09	42.83	-29.54	-	-11.40	0.92	-3.87	-
	C4	-6.84	16.77	-64.10	0.04	-36.75	20.62	-18.07	19.51
DMC (3.09, 17.1) 	-CH3	-13.01	13.12	-116.49	-	-73.89	5.80	-32.23	26.27
GBL (39.1, 18.0) 	C1	32.41	36.36	-43.91	-	-21.32	-	-0.46	4.26
	C3	36.83	57.52	-26.88	32.40	-2.96	38.70	32.90	61.13
	C4	0.79	24.19	-63.85	4.28	-54.33	5.28	-22.31	24.21
MeOAc (36.0, 16.0) 	-CH3	-3.25	20.77	-86.12	2.75	-63.50	12.41	-38.16	27.48
NMP (32.2, 27.3) 	C2	27.84	30.59	-11.55	-	-9.70	-	18.44	18.48
	C3	47.10	71.52	-4.73	45.89	-0.52	56.27	35.68	69.98
	C5	22.99	43.29	-38.04	20.99	-12.23	28.95	5.06	47.74
BN (25.2, 11.9) 	-CN	17.72	20.46	-27.50	-	-10.12	-	4.76	6.37
MeCN (36.0, 14.1) 	-CH3	19.43	46.84	-46.53	23.69	-12.45	37.54	15.07	49.71
	-CN	56.05	10.37	-20.89	-	-11.42	-	8.08	12.81
DMSO (48.0, 29.8) 	-CH3	14.77	35.93	-43.91	16.27	-18.58	22.07	21.10	38.12
	-CH2-	27.97	40.22	-56.75	14.75	-34.24	24.80	-2.91	41.25
DME (7.2, 20.0) 	-CH3	24.57	36.84	-55.81	27.36	-37.46	28.41	-6.49	45.14

^aSite of nucleophilic attack.

DMSO also has a very high DN of 29.0,^{56,57} so it would be expected that the solution pathway would dominate and $LiO_2^-(solv)$ would be abundant during discharge. It can be seen from Table II that the nucleophilic reaction between DMSO and $LiO_2^-(solv)$ is exergonic with a low activation barrier that can be overcome easily even at room temperature. Thus, this nucleophilic reaction would be expected to contribute to the degradation of DMSO seen in recent experiments.^{29,33-37}

DME, a member of the glyme family, is currently one of the most popular solvents used in Li-air battery. It has a DN of 20.0, which puts it intermediate among solvents.^{56,57} Thus the expectation is that both the deposited LiO_2^- and solvated LiO_2^- shown in Equation 3 would be present during discharge and the relative position of the equilibrium depends on the particular environment, the potential, and the current. It seems safe to assume that a considerable amount of $LiO_2^-(solv)$ would be present during discharge. The computational results in Table II show that the nucleophilic reaction between $LiO_2^-(solv)$ and DME is exergonic with an activation barrier that is low enough to be easily overcome even at room temperature. As a result, the nu-

cleophilic reactions between the solvated $LiO_2^-(solv)$ and DME may contribute to slow degradation of DME in Li-air batteries shown in experiments.^{33,35,38,40-45}

This reaction can also be used to demonstrate the effect of the Li cation on activating the leaving group. The nucleophilic reaction between Li^+ -DME and solvated $LiO_2^-(solv)$ is more exergonic (Δ_rG goes from -34.24 kcal/mol to -37.52 kcal/mol) and has a lower activation barrier (from 24.80 kcal/mol to 22.97 kcal/mol). This means that Li^+ -DME is even more susceptible to nucleophilic attacks by the solvated peroxide species. However, it must be noted the rate of this reaction would depend on the concentration of Li^+ -DME, which would be quite low.

In light of these results, it has been speculated that the stability of DME toward nucleophilic attack by $LiO_2^-(solv)$ could be enhanced by making the O-CH₂- bond less polar. A subsequent calculation shows that by replacing one of the hydrogen atom with fluorine as shown in Figure 3, the activation barrier is elevated from 24.80 kcal/mol to 36.84 kcal/mol, while the reaction becomes more exergonic with a Δ_rG of -48.95 kcal/mol. This may help experimentalists to redesign

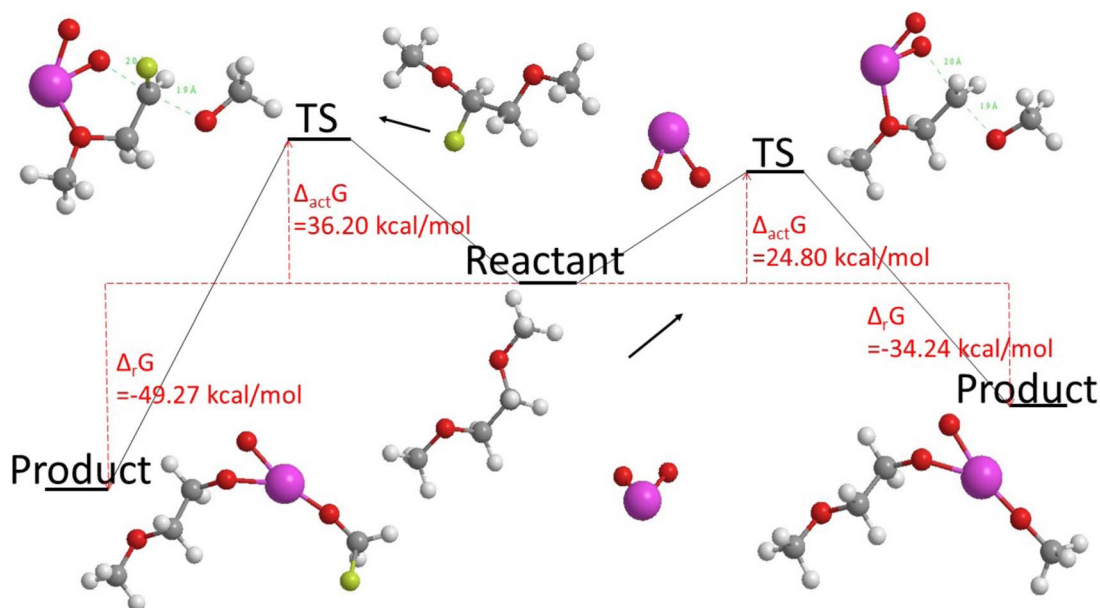


Figure 3. Schematic diagram of the reaction profile for the nucleophilic attack by $\text{LiO}_2^-(\text{solv})$ on $-\text{CH}_2-$ of DME (going right) and DME with one hydrogen replaced with fluorine (going left) together with the structures of the reaction complex, transition state complex and product.

the solvents used to give better stability over long cycling. However, it must be noted that by replacing the hydrogen atom with fluorine, the solvent becomes more susceptible to E2 elimination by $\text{LiO}_2^-(\text{solv})$. Our computation results show that the E2 elimination reaction is slightly exergonic and has a very low activation barrier of 2.52 kcal/mol. So one must bear this in mind when designing new solvents.

The nucleophilic attack on the nitrile carbon of MeCN shown in Table II is exergonic with no activation barrier. Therefore, this reaction will likely contribute to the degradation of MeCN in a Li-air battery as shown in recent experiments,^{29,33} if $\text{LiO}_2^-(\text{solv})$ were present during discharge. However, MeCN has a low DN of 14.1^{56,57}, thus most, if not all of the LiO_2 formed would deposit on the cathode surface (i.e. LiO_2^* in Equation 3) except at very high discharge potential and the concentration of $\text{LiO}_2^-(\text{solv})$ would likely be quite low. This suggests that $\text{LiO}_2^-(\text{solv})$ is unlikely to make substantial contribution to the degradation of MeCN. Instead, the degradation of MeCN will likely involve interactions with the cathode surface or deposited solid discharge intermediates or products. Note that the low DN of MeCN makes it a poor carrier of $\text{Li}^+(\text{solv})$ and leads to its relatively low popularity among experimentalists compared to the other two solvents. However, the suggestion here is that solvents with nitrile groups in general are unlikely to be stable against nucleophilic attacks by $\text{LiO}_2^-(\text{solv})$.

Figure 3 reveals that the Li in $\text{LiO}_2(\text{solv})$ is instrumental in bringing the DME and the nucleophile together, and stabilizing both the transition state and the products. This catalyst-like activity of the Li is also present in the nucleophilic attacks on NMP and MeCN, as can be seen in the orientation of Li in the transition state structures seen in Figure 4. This gives $\text{LiO}_2^-(\text{solv})$ greater reactivity toward these solvents that are stable in the presence of $\text{O}_2^-(\text{solv})$.

Conclusions

This study aims to investigate computationally and report the stabilities of four commonly used solvents in the Li-air batteries against nucleophilic attacks by solvated peroxide-related species $\text{LiO}_2^-(\text{solv})$, which is formed mainly from the disproportionation of dissolved $\text{O}_2^-/\text{LiO}_2$. The solvents studied have all shown strong stability against solvated superoxide radical ion, $\text{O}_2^-(\text{solv})$. Our computational results suggest that in all four cases solvated $\text{LiO}_2^-(\text{solv})$ displays stronger

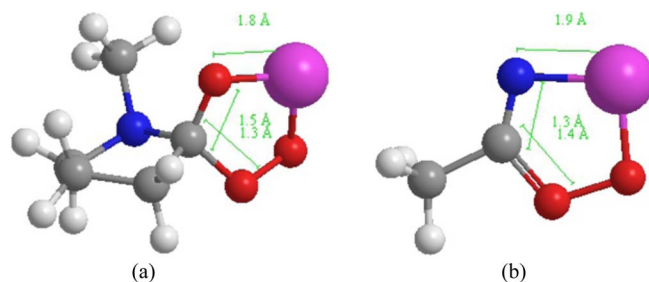


Figure 4. Transition state structures of the nucleophilic attacks by $\text{LiO}_2(\text{solv})$ on a) C2 of NMP, and b) nitrile carbon of MeCN.

nucleophilic reactivity when compared to $\text{O}_2^-(\text{solv})$. This is usually due to the fact that $\text{LiO}_2^-(\text{solv})$ has a lower oxidation state and the Li atom has been shown to assist the nucleophilic reactions. The nucleophilic reactions with $\text{LiO}_2^-(\text{solv})$, as well as its brethren $\text{O}_2^{2-}(\text{solv})$ and $\text{Li}_2\text{O}_2(\text{solv})$, may contribute to the degradations of some solvents that have been found to be stable against $\text{O}_2^-(\text{solv})$ and $\text{LiO}_2(\text{solv})$, and form Li_2O_2 as the dominant discharge product, but have been shown to degrade over many charge-discharge cycles. Only the nucleophilic attacks involving the solvated peroxide-related species were investigated in this study. Many other reaction pathways, such as hydrogen abstraction, may also play a part in the degradations of the solvents. These can be directions for future research efforts.

Acknowledgment

The authors acknowledge financial support received from the University of Hong Kong (Strategic Research Theme on Clean Energy and Seed Funding for Basic Research).

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