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Combined Experimental and Computational Efforts to Establish Ion Mobility, Solubility and Stability of Functional liquids for Electrochemical Energy Storage

January 2023

Avni P. Singhal Shi Jun Ang Livia Giordano Rafael Gomez-Bombarelli Yang Shao-Horn



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Summary

This work provides a computation-driven investigation of the stability of organic electrolytes for lithium-air batteries. Electrolyte instability is currently a key challenge that limits practical use of aprotic Li-air batteries, and the chemical processes that cause this instability are often kinetically-driven. Computational screening for kinetic stability involves the determination of reaction barriers for the numerous potential reaction mechanisms, barriers that are challenging to calculate due to the difficulty of locating transition state structures.

Here we screen a broad set of substituted electrolytes for susceptibility to nucleophilic attack by superoxide. We find that carbonates are not typically expected to be stable and that sulfones are generally stable, validating literature trends. We study the effects of chemical functionalization with electron-donating and withdrawing groups and their interplay with steric factors, identifying functional groups and other chemical modifications that increase stability in these groups.

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1.0 Introduction



Figure 1 Electrolyte compound classes analyzed in this study. X and Y denote substitution by side chains such as methyl or fluoride.

Lithium-air batteries have been proposed as a promising solution for applications requiring high gravimetric energy density such as fully electric vehicles. However, common organic electrolytes with wide electrochemical window used in traditional lithium-ion batteries, such as unsubstituted and alkyl-substituted carbonates, in which Li-ion has high solubility, degrade readily in the presence of reduced O2 radical species such as superoxide anions [1] [2] [3]. On the other hand, sulfones are known to be more chemically robust but suffer in terms of electrochemical stability [3] [4]. Feng et al. suggested that the primary chemical processes responsible for these degradations are hydrogen removals, proton removals, nucleophilic attacks, oxidations and reductions [5]. The authors have developed a "BANE" computational approach based on ground state organic electrolyte properties aiming to provide a comprehensive prediction on whether a candidate is chemically and electrochemically stable [5].



Figure 2 **a** Possible mechanisms of alkyl cleavage nucleophilic attack of superoxide on electrophilic electrolytes. Carbonates can react on the carbon atoms adjacent to the ester oxygen, while sulfones react through the α carbon. **b** acyl cleavage of carbonate

However, the chemical processes that cause electrolyte instability are often kinetically driven and thus thermodynamics and kinetics must both be investigated in order to fully evaluate candidate stability [1]. Computational screening for kinetic stability requires determining reaction barriers for the numerous potential reaction mechanisms.

Calculation of reaction barriers in complex molecules with electronic structure methods is a challenging task. It is necessary to estimate the Gibbs free energies of reactants, products, and corresponding transition state (TS) structures. The former two straightforward to automate in a high-throughput fashion but the latter requires complex calculations that typically rely heavily on user input and chemical intuition and do not lend themselves to automation [6]. Existing automated approaches are limited in scope; single-ended string methods require good initial guesses and double-ended string methods frequently fail for complex molecules [7] [8].

Here, we quantify the reaction free-energy barriers for kinetically-controlled electrolyte decomposition processes, in particular nucleophilic attack by superoxide, which is formed during electrochemical cycling in Li-air batteries. Previous barrier studies only focused on a few commonly available carbonates and sulfones [3] and thus we aim to provide a comprehensive analysis of substituted carbonates and sulfones in order to understand the role of chemical functionalization of electron-donating groups (EDGs) and electron-withdrawing groups (EWGs) and their interplay with steric factors in the reaction kinetics of electrolytes with radical oxygen nucleophiles. We aim to predict the electrochemical stability of substituted sulfones and see if there is a sulfone with oxidative stability as high as common carbonates.

We initially conduct this analysis with user-driven identification of transition states and subsequently present a pipeline for automated calculation to enable evaluation across a broader range of chemistries. This pipeline integrates cheminformatics-based reaction

encoding, relaxed potential energy scans, and nudged elastic band calculations to enable determination of free-energy barriers for reactions of interest of candidate electrolytes at scale. In particular, cheminformatics tools are used to programmatically generate products from reactants and track reactive atoms [9], relaxed potential energy scans to obtain initial reaction paths, and climbing-image nudged elastic band calculations to obtain transition state guesses from these starting paths [10]. The pipeline is preliminarily evaluated on carbonate and sulfone chemistries.

2.0 Methodology and Computational Details

a. User-Driven Transition State Search

Minima and transition states were user-generated for all reaction mechanisms of substituted carbonate and sulfones of interest. Geometry optimizations of stable minima and transition states were carried out using (U)B3LYP-D4/def2-SVP level of theory. Frequency calculations were performed at the same level of theory to confirm the nature of the stationary points (i.e. no imaginary frequencies for minima and one imaginary frequency for transition states); and to obtain the Gibbs free energy corrections to the corresponding electronic energies. The highly accurate DLPNO-(U)CCSD(T)/def2-TZVPD level of theory was used to obtain reliable electronic energies of the DFT optimized structures. The SMD implicit solvation model was used in all computations with dimethyl sulfoxide (DMSO) as the solvent to mimic the electrolyte environment.

b. High-Throughput Transition State Search

Cheminformatics-based enumeration of reaction space:



Mono- and di- substituted carbonates and sulfones of interest were represented and enumerated through the simplified molecular-input line-entry system (SMILES). The SMILES arbitrary target specification (SMARTS) language was used to produce atom-mapped eactions and products for each reactive site on each molecule.

Automated pipeline for transition state geometry and barrier calculation:



A high-throughput density functional theory (DFT) pipeline was used to calculate DFT free energies for the reactions with superoxide. Geometry optimizations of stable minima were carried out using (U)B3LYP-D4/def2-SVP level of theory; initial conformers were generated

using RDKit forcefield methods, optimized upon with GFN-xTB, and the top two conformers optimized with DFT. The SMD implicit solvation model was used in all DFT computations with DMSO as the solvent.

Reactant poses were generated in order to place the reactive atoms for electrolyte and superoxide reactions nearby, and at the correct angles for SN1 and SN2 mechanisms respectively. Small random translations were applied in the case of collisions.

A relaxed potential energy scan (PES) was then performed starting from the reactant pose over the superoxide-carbon bond of interest. Reactive-atom based angle and bond constraints were applied in order to drive the reaction to the correct mechanism and prevent undesired interactions. The nudged-elastic band method (NEB) was then performed from the starting images from the potential energy scan. The Zoom climbing-image (Zoom-CI) variation was run in order to relax the images and climb to the transition state. From here, single-ended transition state search methods were applied, specifically eigenvector-following (EF).

Frequency calculations were performed to confirm the nature of the stationary points and to obtain Gibbs free energy corrections to the corresponding electronic energies. Lastly, intrinsic reaction coordinate (IRC) calculations were performed to confirm the transition state found through generation of the weighted minimum energy path (MEP) from the transition state geometry.

3.0 Results and Discussion

(a) Sulfone and Carbonate Barrier Analysis

Electrophilic ester and carbonate centers can, in principle, react with nucleophiles through the carbonyl carbon (resulting in so-called acyl cleavage) or through the carbon adjacent. We evaluate these mechanisms separately and also distinguish between singly and doubly substituted electrolytes.



Figure 3 Top colored arrows point to the reactive sites in cyclic carbonates and sulfone studies. Second Activation free energy (barrier) for attack of oxygen radical on respective sites. Third reaction free energy for the unimolecular attack, downstream reactions maybe be further up or downhill Fourth correlation between reaction and activation free energies follows the Hammond postulate

3.1 $S_N 2$ attack on monosubstituted cyclic carbonates and sulfones

We obtained the activation free energies (Figure 3b) and the reaction free energies (Figure 3c) of monosubstituted (X=H, Me, OMe, N(Me)2, F and CF3) carbonates and sulfones. The chosen substituents are commonly found in organic electrolyte molecules. F and CF₃ are electron withdrawing and Me, OMe, N(Me)₂ are electron donating. All of the S_N2 barriers are 26 kcal/mol or less, which corresponds to an estimated reaction half-life of hours to days at room temperature. Thus, single-substituted carbonates are not expected to be chemically stable in the presence of superoxide species.

No significant difference between activation free energies of attack sites for Me and OMe, with reaction free energies differing by less than 4 kcal/mol. Adjacent sites for F and CF₃ are more susceptible to S_N2 due to the presence of electron withdrawing inductive effect and less steric hindrance as compared to the substitution site.

The corresponding activation free energies are 5.33 and 5.22 kcal/mol lower for the adjacent sites as compared to the substitution sites. For $X=N(Me)_2$, the substitution site becomes much more vulnerable due the bulky methyl groups of $N(Me)_2$, destabilizing the 5-membered ring structure. The difference between their activation free energies is 13.80 kcal/mol. Overall, the most stable cyclic carbonate studied is X=OMe, with a barrier of 24.05 and 23.24 kcal/mol, for substitution and adjacent sites respectively.

There are four possible S_N2 sites for cyclic sulfones illustrated in Figure 2. However, the attack of beta carbons (relative to S) lead to the formation of highly unstable primary carbanions. Their associated barriers are more than 40 kcal/mol for all six sulfones considered (Fig. SX). Hence, it is less chemically relevant to consider these reactions. The attack of alpha carbons, on the other hand, gives rise to activation free energies between 32 - 38 kcal/mol, thus the preferred sites of attack. These magnitudes translate to an extremely long reaction half-life of more than 5500 years suggesting that sulfones are kinetically stable against superoxide. The most stable cyclic sulfone studied is the one substituted by OMe with activation free energy of 38.11 kcal/mol.

In Figure 3d, we show a scatter plot of reaction free energies against activation free energies. The calculated R2 and spearman rank (ρ) correlation coefficients are 0.81 and 0.84 respectively, which indicates good correlations between the two quantities for the 22 reactions involving monosubstituted carbonates and sulfones studied. This suggests that we can have reasonable estimations of reaction kinetics from reaction thermodynamics, which may allow us to bypass the need to locate relevant transition states that are more demanding in terms of computational requirements and complexity.

	σ_p versus ΔG^{\ddagger}		σ_m versus ΔG^{\ddagger}		σ_p versus ΔG		σ_m versus ΔG	
	R^2	ρ	R ²	ρ	R ²	ρ	R ²	ρ
Carb'	0.32	0.77	0.39	0.94	0.19	-0.49	0.00	-0.03
Carb	0.78	-0.94	0.64	-0.77	0.58	-0.77	0.35	-0.49
Sulf a'	0.48	-0.26	0.14	-0.03	0.43	-0.94	0.10	-0.66
Sulf α	0.35	-0.31	0.04	0.03	0.97	-0.94	0.78	-0.77

Table 1. Regression parameters for Hammett equation of the activation and reaction free energies for the studied compounds. (C for

To rationalize how electronic effects affect the calculated reaction free energy barriers, we evaluated the fit of our results to Hammett's equation (log $k \sim \rho \sigma$). While Hammett's equation is less applicable to aliphatic compounds, it may provide insight into the role of electronic effects in these reactions. The substituent-specific Hammett's constants (σ) that parametrize the equation have been fitted for many functional groups to relate meta (σ_m) and para (σ_p) substitution effects for the rate of deprotonation of benzoic acid. These parameters provide a quantitative estimate of the resonance and inductive effects for a particular functional group. Although originally parametrized for the abovementioned narrow class of reactions, they have been shown to be widely applicable for many reactions involving substituted aromatic systems. We evaluated whether the para or meta parameter are better correlated. It was found that only the S_N2 activation free energy at adjacent sites of monosubstituted cyclic carbonates has reasonable correlation with σ_p , with R₂ and ρ values of 0.74 and -0.94 (Table 1).



Figure 4 *Top* relaxed energy scans for addition of superoxide on the carbonyl carbon in monosubstituted cyclic carbonates. No stable tetrahedral intermediate is observed. *Bottom* The only identified transition states correspond to ring-opened acyl-cleave compounds and relative free energy with respect to reactants in kcal/mol. Cyclic carbonates undergo unimolecular acyl ring opening as a rate limiting step

Hammett's equation does not take into account steric effects, and thus it is expected that do better for S_N2 attacks at sites adjacent to the substituents. Interestingly, the rank correlations between the Hammett's constants and ΔG is significantly better as compared to ΔG_{\pm} for the monosubstituted sulfones suggesting that the thermodynamics of these reactions are better described than the kinetics by Hammett's equation. In general, our calculations suggest better correlations between σ_p and ΔG or ΔG_{\pm} than the corresponding σ_m quantities.

3.2 Nucleophilic attack at carbonyl carbon of monosubstituted cyclic carbonates

While nucleophilic substitutions at carbonyl carbons typically involve stable reaction intermediates with tetrahedral coordination in the carbonyl carbon (Figure 2) that can be identified with electronic structure methods, the addition step of superoxide to monosubstituted cyclic carbonates is energetically uphill and no local minima is identified except for the more electron withdrawing groups, where a very flat minima, or inflection point, can be seen at around 1.70.

From the relaxed potential energy surface scans presented in Figure 4a, the structures are 5-12 kcal/mol higher with forming C-O bond length at 1.4 Å (typical equilibrium C-O bond length expected for the tetrahedral intermediate) as compared to the corresponding reactant complexes at 3.0 Å. The transition states for all six cyclic carbonates are located for the second step (loss of leaving group) with activation free energy of more than 40 kcal/mol relative to individual reactants. Our results suggests that nucleophilic substitutions at carbonyl carbons of monosubstituted cyclic carbonates are not energetically feasible regardless of the nature of the substituent. Similar conclusion was reached by Bryantsev *et al.* for ethylene, propylene and dimethyl carbonates.

3.3 S_N2 attack on disubstituted cyclic carbonates and sulfones

Given the tunability of organic electrolytes, it may be possible to identify stable carbonates by further chemical modifications, or to further improve the properties of sulfone compounds. For this, we evaluated the reactivity of double-substituted carbonates and sulfones.

We name the disubstituted cyclic carbonates X-Y; where substituent X is attached to the same carbon atom as S_N2 attack site, while substituent Y is attached to the adjacent carbon atom orientated trans to X. The activation and reaction and free energies are reported in Figure 5. For every molecule there are two entries, depending on where the addition takes place (the matrices in Figure 5 are not symmetrical). We found that even double substituted carbonates remate poorly stable. We also found that energies per site can differ significantly with respect to S_N2 attack sites, especially when the two substituents have opposite electronic effects. For example, the S_N2 attack on the F-bearing carbon in F-N(Me)₂ is 30.50 kcal/mol (relatively stable), while attack on the N-bearing carbon of N(Me)₂-F is 10.95 kcal/mol. Thus, the molecule will not be stable since the reaction will proceed through the lowest free energy channel.



Figure 5 *Left* Activation and free energy for alkyl ring opening of di-substituted carbonates (top) and sulfones (bottom). *Right* correlation between activation and reaction free energies

Comparing the more susceptible site in each molecule across the 15 disubstituted cyclic carbonate molecules considered, the one that has the highest barrier is OMe-OMe (25.31 kcal/mol), the lowest barrier is N(Me)₂-F (10.95 kcal/mol). The activation free energy of the most kinetically stable OMe-OMe translates to a reaction half-life of about 6.5 days at 300 K. In addition, the ring-opened product is about 12 kcal/mol higher in free energy as compared to the free reactants suggesting that the first step in the decomposition reaction is not thermodynamically favorable and only very small amounts of product will be formed. The calculated equilibrium constant at 300K is $6.26 \times 10_8$ and the half-live of the reverse reaction is about 0.1 ms. Comparing the reaction free energies of all 15 disubstituted cyclic carbonates, the most thermodynamically stable molecule against S_N2 attack of superoxide is again OMe-

OMe. It is interesting to note that all but two (F-OMe and F-N(Me)₂) ring-opened products are higher in free energy as compared their constituent reactants. This is in contrary to the S_N2 reactions between monosubstituted cyclic carbonates and superoxide where the majority are exergonic. There seems to be no good correlation between Δ Gs and the corresponding Δ G_‡s in terms their magnitudes (R₂=0.37), while the rank correlation is reasonably good with ρ =0.78.

All S_N2 reactions between disubstituted cyclic sulfones and superoxide have activation free energies greater than 29 kcal/mol. The highest barrier is the superoxide attack of N(Me)₂-N(Me)₂ which has a barrier of 36.73 kcal/mol. Similar to the monosubstituted sulfones, all reactions involving disubstituted sulfones are endergonic. No good correlations for values (R₂=0.41) and fair correlations for rank (ρ =0.62) between Δ Gs and Δ G_ts.

3.4 Nucleophilic attack on carbonyl carbon of disubstituted cyclic carbonates

In section 4.2, we have concluded that regardless of electronic effects of the functional group, nucleophilic attack on the carbonyl carbon of monosubstituted carbonates is monotonically increasing in energy for the addition step and no tetrahedral intermediate, while the rate-limiting unimolecular 2nd elimination step is 40 kcal/mol or more for all the substituents studied.

Surprisingly, for disubstituted cyclic carbonates, if both substituents are electron withdrawing (i.e. X and Y = F, F₃C), the first addition step can become energetically favorable and the bond distance between superoxide oxygen and carbonyl carbon starts resembling that of typical tetrahedral intermediates. From the relaxed potential energy surface scans (Figure 6), the minima are 8.20, 5.69 and 2.75 kcal/mol more stable relative to a C(carbonyl carbon)-O(closer superoxide oxygen) distance of 3.0Å for F-F, F-F₃C and F₃C-F₃C respectively. Still, no barrier for the addition is appreciable, and the rate limiting step in the decomposition is the ring opening.



Figure 6 *Top* relaxed energy scans for addition of superoxide on the carbonyl carbon in disubstituted cyclic carbonates

3.5 Susceptibility of tetrasubstituted cyclic carbonates against superoxide

To eliminate the possibilities of hydrogen and proton abstractions by superoxide in cyclic carbonates, an avenue to look into would be tetrasubstitution by substituents that we found to inhibit reactivity, such as F or OMe. However, we found that they make attack at the carbonyl carbon more favorable (Figure 7) for 4F and 4OMe systems and the S_N2 attack at ethereal carbons facile, with activation free energies of 23.9 and 21.2 kcal/mol respectively. This is due to the fact that the substituents at adjacent carbons are eclipsed with one another which destabilize the ring structure.



Figure 7 *Top* relaxed energy scans for addition of superoxide on the carbonyl carbon in disubstituted cyclic carbonates

(b) Evaluation and Discussion of automated platform

As described above, an automated platform was developed to extend the previous findings to additional chemistries in a scalable manner. Establishing this pipeline required decisions to mitigate a number of challenges with the relaxed scan which will be discussed here. Typically, relaxed scans of combination reactions are performed in the direction of bond breaking, which, in this case, would be the ring-closing and breaking of the superoxide - carbon bond. This avoids pose-generation or collision issues. However, ring-opened products have high RMSD (root mean squared distance) from the reactants; that is, significant geometric modification would be required for ring closure, so it does not occur in single-dimensional scans. Multi-dimensional scans were considered, but are highly inefficient and computationally expensive.

For this reason, scans were performed in the formation of superoxide - carbon bond direction with the superoxide - carbon bond distance collective variable. However, due to the small size of the superoxide, enforcing the distance between one of the oxygen atoms and carbon was inadequate to prevent interaction with the other oxygen atom. Moreover, the superoxide frequently approached the carbonate/sulfone at an incorrect angle, resulting in a superoxide-catalyzed reaction rather than an SN2 reaction with superoxide. To mitigate these issues, poses were generated that placed the superoxide at the correct angle relative to its reactive site (i.e. 180 degrees to the bond that was to be broken for an SN2 reaction). Simply enforcing such a requirement in the scan without an adequate pose would result in collision and thus explosion of the molecule. However it could be maintained with two angle requirements that were implemented in the scan to keep the superoxide and ring atoms at the correct angle. Additional requirements such as freezing of the superoxide bond positions was also considered, but ultimately unnecessary when the angle requirements were included. This resulted in generation of sensible scan trajectories, which were subsequently refined through eigenvector following (and in some cases, NEB).

This approach was tested on the SN2 mechanism for superoxide attack of carbonates and attack of sulfones at the alpha site.

As shown with a few examples here, the relaxed surface scans produced sensible trajectories and highest energy images with transition states (the left and right images correspond to the highest energy images of the blue and orange trajectories respectively) that were relatively accurate for SN2 reactions, as well as energies in the right magnitude range. However, these geometries remained too far from the transition state to perform a single-ended search like eigenvector-following.



In order to assist the single-ended search, it was provided the transition state mode and active atoms. This helped generate geometries with a single imaginary frequency, yet in general, and in the examples above, invalid transition states were still produced, with energies that were too low.



Overall, of the 55 reactions from which scans and subsequent transition state geometries were produced, 39 reactions had transition state geometries with a single imaginary frequency, and all except 2-3 of these displayed an incorrect reaction mechanism, most often as shown below wherein the superoxide rotates to be parallel to the broken bond, producing barriers largely <10kcal/mol.

The need for mechanism-enforcing initial poses and requirements in the scan, and inability to produce accurate barriers from these scans suggests a need for alternate approaches. Thus additional high-throughput methods are being explored that can use the data produced from these scans to enable more scalable approaches to barrier-finding. One such approach is using the trajectories from these scans, alongside additional off-equilibrium geometries, to produce interatomic neural network potentials [11].



A preliminary potential trained on 1000+ geometries using PaiNN (polarizable atom interaction neural network) shown here has acceptable performance on a held-out test set of geometries. Such a potential would enable use of otherwise unfeasibly expensive methods like reactive molecular dynamics to identify transition states in a more robust manner [12].

4.0 Conclusion

We have evaluated the reaction kinetics of substituted cyclic carbonates and sulfones against superoxide ions that may be formed in lithium air batteries. It was found that monosubstituted carbonates are kinetically not stable. Disubstitution with two groups in trans broadens the range of reaction and activation free energies and some promising combinations are seen, in particular dimethoxy-substituted carbonates have higher barriers and are not thermodynamically favored to undergo the initial reaction. However, further reactivity analysis of the intermediates formed is necessary, as stable decomposition products may be formed that make the full pathway thermodynamically favored.

We observe that sulfones are generally very stable against nucleophilic attack by superoxide, and identify many chemical modifications that retain such stability. This will be advantageous to fine-tune other desired properties of sulfone electrolytes, such as electrochemical stability window, by modifying the substituents without loss of stability against nucleophilic superoxide. We additionally establish a high-throughput pipeline that can be used to extend the findings of these reactions of carbonates/sulfones with superoxide to additional molecules. Such a

pipeline could enable a broader study of the susceptibility of substituted carbonate/sulfones to superoxide attack with little additional labor. Moreover, the neural network potential trained on the trajectories generated by this pipeline could enable an even broader evaluation of the stability of other organic electrolytes.

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