A Study of the Electronic Structure of Alkali Peroxides and Their Role in the Chemistry of Metal-Oxygen Batteries.

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Supporting information

S1 Active Orbitals in the C_{2v} symmetry

Symmetry of the 7 valence atomic orbitals to the Complete Active Space for each irreducible representation in the $C_{2v}$ group:
|   | \(a_1\) | \(b_1\) | \(b_2\) | \(a_2\) |
|---|------|------|------|------|
| O \(p_z\) (\(\rightarrow \pi_z\)) | O \(p_z\) (\(\rightarrow \pi_z^*\)) | O \(p_z\) (\(\rightarrow \pi_x\)) | O \(p_x\) (\(\rightarrow \pi_x^*\)) |
| O \(p_y\) (\(\rightarrow \sigma\)) | O \(p_y\) (\(\rightarrow \sigma^*\)) | \n| Li s | \n|   | \n
S2  Representative LiO$_2^-$ wavefunctions

The optimized CASSCF wavefunctions of the LiO$_2^-$ lowest electronic states (at selected geometries) are represented in terms of the CSFs active orbitals occupancy and their relative weights:

- **A$_1$** (b=1.60; h=1.50)

| $a_1$ | $b_1$ | $b_2$ | $a_2$ | coeff. | weight |
|---|---|---|---|---|---|
| 2  | 2  | 0  | 2  | 2  | -0.9417 | 0.8868 |
| 2  | 0  | 0  | 2  | 2  | 0.2309  | 0.0533 |
| 1  | 2  | 1  | 2  | 0  | 0.1906  | 0.0363 |
| 2  | 1  | 1  | 2  | 0  | -0.1210 | 0.0146 |

Leading configuration: (O $\pi_z$)$^2$(O $\pi_x$)$^2$(O $\sigma$)$^2$(O $\pi_z^*$)$^2$(O $\pi_x^*$)$^2$ (Li s)$^0$(O $\sigma^*$)$^0$

- **A$_2$** (b=1.35; h=1.75)

| $a_1$ | $b_1$ | $b_2$ | $a_2$ | coeff. | weight |
|---|---|---|---|---|---|
| 2  | 2  | 1  | 2  | 0  | 0.9986  | 0.9973 |

Leading configuration: (O $\pi_z$)$^2$(O $\pi_x$)$^2$(O $\sigma$)$^2$(O $\pi_z^*$)$^2$(O $\pi_x^*$)$^1$ (Li s)$^1$(O $\sigma^*$)$^0$

- **B$_1$** (b=1.35; h=1.85)

| $a_1$ | $b_1$ | $b_2$ | $a_2$ | coeff. | weight |
|---|---|---|---|---|---|
| 2  | 2  | 1  | 1  | 0  | 0.9997  | 0.9994 |

Leading configuration: (O $\pi_z$)$^2$(O $\pi_x$)$^2$(O $\sigma$)$^2$(O $\pi_z^*$)$^1$(O $\pi_x^*$)$^2$ (Li s)$^1$(O $\sigma^*$)$^0$
S3  Representative NaO\(_2^-\) wavefunctions

The optimized CASSCF wavefunctions of the NaO\(_2^-\) lowest electronic states (at selected geometries) are represented in terms of the CSFs active orbitals occupancy and their relative weights:

- **A\(_1\) (b=1.60; h=1.95)**

| \(a_1\) | \(b_1\) | \(b_2\) | \(a_2\) | coeff. | weight |
|---|---|---|---|---|---|
| 2 | 2 | 0 | 2 | 2 | -0.9556 | 0.9132 |
| 2 | 0 | 0 | 2 | 2 | 0.2339 | 0.0547 |
| 1 | 2 | 1 | 2 | 0 | 0.1521 | 0.0231 |

Leading configuration: \((O \pi_z)^2(O \pi_x)^2(O \sigma)^2(O \pi_z^*)^2(O \pi_x^*)^2\) (Na s)^0(O \sigma^*)^0

- **A\(_2\) (b=1.35; h=2.20)**

| \(a_1\) | \(b_1\) | \(b_2\) | \(a_2\) | coeff. | weight |
|---|---|---|---|---|---|
| 2 | 2 | 1 | 0 | 2 | 0.9978 | 0.9957 |

Leading configuration: \((O \pi_z)^2(O \pi_x)^2(O \sigma)^2(O \pi_z^*)^2(O \pi_x^*)^1\) (Li s)^1(O \sigma^*)^0

- **B\(_1\) (b=1.35; h=2.25)**

| \(a_1\) | \(b_1\) | \(b_2\) | \(a_2\) | coeff. | weight |
|---|---|---|---|---|---|
| 2 | 2 | 1 | 0 | 2 | 0.9978 | 0.9956 |

Leading configuration: \((O \pi_z)^2(O \pi_x)^2(O \sigma)^2(O \pi_z^*)^2(O \pi_x^*)^1\) (Li s)^1(O \sigma^*)^0
Higher spin multiplicities

For both the $A_2$ and $B_1$ singlet superoxide states, a corresponding triplet state is found to be very close in energy with respect to the open-shell singlet. Throughout the explored PES, the singlet-triplet splitting turned out to be within the range of 0.1 eV. In Figure S1 we report the energies of the singlet and triplet $A_2$ and $B_1$ PESs at the value $b=1.30$ Å.

Figure S1: LiO$_2^-$ system. PES cuts along $h$ showing the singlet-triplet energy splitting in two different electronic states.

Since the reactants of (R4) can be an overall singlet or triplet, the same spin multiplicities can emerge in the products. This can be obtained either by combining a singlet O$_2$ with both singlet and triplet MO$_2^-$, or triplet O$_2$ with a singlet MO$_2^-$. Hence, the triplet MO$_2^-$ product only
enters in the reactive pathway towards singlet oxygen, which is energetically disfavored by ca. 0.9 eV with respect to triplet oxygen.
The choice of the active space is rather arbitrary. It should include all possible orbitals that give rise to significant occupations in the electronic states of interest for the chemical problem at hand. For our purposes, the choice of 7 active valence orbitals fulfills this obligation. However, the $2p$ orbitals of Li are close in energy to the $2s$ one and their inclusion is worth to be explored. We have repeated some of the calculations using a larger [10,10] active space that includes the $2p$ orbitals of Li, to check whether their occupation gives rise to other electronic states which might be relevant for the reactions of superoxides. In Figure S3 we report three cuts of the resulting six lowest potential energy surfaces, at the same $b$ values as in Figure 3 of the main text ($b = 1.40$ Å, 1.50 Å, 1.65 Å).

When we include the $2p$ orbitals, three new electronic states appear at low energies, one for each of the $a_1$, $b_1$ and $a_2$ irreducible representation. They all correspond to superoxide states, with singly occupied $p_y$, $p_x$ and $p_z$ lithium orbitals. We will design them as $2A_1$, $2B_1$ and $2A_2$ and we have indicated them using dot-dashed lines in Figure S3.

The ground superoxide state $1A_2$ due to $2s$ occupancy (cyan, full line), is more than 0.5 eV lower in energy than the $2A_2$ state due to the $2p$ occupancy (cyan, dashed line) which is characterized by a PES that appears to be simply shifted upwards in energy with respect to the former. The same happens to the $2A_1$ state (violet, dashed line) that lies at higher energies, but has a PES that is almost parallel to the $1A_2$ one.

Interestingly, the two $B_1$ states arising from either the $2s$ or $2p$ occupancy (green) are close to each other, and they clearly interact in the range of $b = 1.45 \div 1.65$. However, the $B_1$ states represent electronically excited superoxide which we have included for sake of completeness but should play a minor role in the reactive behavior of (su)peroxides.
Overall, the chemistry of the low-lying electronic configurations are mainly dominated by the Li 2s orbital, in agreement with the conclusions of ref. [27]. The little relevance of Li 2p orbitals in the active space of neutral LiO₂ was also noticed in ref. [20].

As the low-lying superoxide state 1A₂ seems unaffected by an expansion of the active space, the discussion in the main text on the nature of the ground state of LiO₂⁻ when varying the b and h parameters remains substantially unaltered and it is possible to limit the discussion to the electronic states arising from the 2s occupancy.
**Figure S2**: $\text{LiO}_2^-$ system. PES cuts at $b = 1.40$ Å, 1.50 Å, 1.65 Å (from top to bottom) obtained using a [10,10] active space. Solid lines: electronic states with $2s$ occupancy. Dashed lines: electronic states with $2p$ occupancy.
Figure S3: LiO$_2^-$ system, $|E(A_1) - E(B_1)|$ energy difference as a function of coordinates. The white line is the crossing seam of the two states. Above the line $E(A_1) > E(B_1)$. The colormap scale is in eV.