# Chemical Science

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# On the incompatibility of lithium-O<sub>2</sub> battery technology with $CO_2$ <sup>†</sup>

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Peroxide dianion, solubilized in a hexacarboxamide cryptand anion receptor, reacts rapidly with  $CO_2$  in polar aprotic organic media to furnish hydroperoxycarbonate (HOOCO<sub>2</sub><sup>-</sup>) and peroxydicarbonate ( $-O_2COOCO_2^-$ ). Peroxydicarbonate is subject to thermal fragmentation into two equivalents of the highly reactive carbonate radical anion, which is active for promoting hydrogen atom abstraction reactions responsible for the oxidative degradation of organic solvents. The activation and conversion of peroxide dianion by  $CO_2$  is general. Exposure of solid lithium peroxide ( $Li_2O_2$ ) to  $CO_2$  in polar aprotic organic media results in aggressive oxidation. These findings indicate that  $CO_2$  must not be introduced in conditions relevant to typical lithium- $O_2$  cell configurations, as production of  $HOOCO_2^-$  and  $-O_2COOCO_2^-$  during lithium- $O_2$  cell cycling will lead to cell degradation via oxidation of organic electrolytes and other vulnerable cell components.

#### Introduction

Two-electron reduction of molecular oxygen to peroxide dianion is an attractive cathode redox couple for developing rechargeable lithium-O<sub>2</sub> batteries.<sup>1</sup> Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) formation is deleterious to battery performance because it passivates electrodes and causes a drastic reduction in roundtrip efficiency of discharge-charge cycles.<sup>2,3</sup> Carbonate formation is typically ascribed to oxidative degradation of organic electrolytes<sup>4–6</sup> and carbon electrodes<sup>7</sup> by superoxide<sup>8,9</sup> and singlet oxygen.<sup>10</sup> Although peroxide is often considered to be a strong oxidant in aqueous media, salts of its dianion (O<sub>2</sub><sup>2–</sup>) are poor oxidizers in organic media due to their extremely low solubility and, for this reason, the possible role of peroxide in furnishing carbonate is underappreciated.<sup>11</sup> The presence of carbonate-derived CO<sub>2</sub> during the

Inderap-<br/>idants generated upon the facile and quantitative combination of<br/> $O_2^{2-}$  with CO2 via direct spectroscopic detection and exploratory<br/>reaction chemistry.Seachusetts<br/>mail: ccum-<br/>nue, Davis,**Results and Discussion**<br/>**Reaction of O**2<sup>2-</sup> with CO2 using an anion receptorAutonoma<br/>2209, Cuer-Despite the drastic and deleterious effect CO2 has upon the per-<br/>formance of a cycling lithium-oxygen battery, our understanding<br/>of the chemical entities responsible for this effect is poor and<br/>based primarily upon computational studies or observation of

terminal reaction products.<sup>2,8</sup> To examine the effect of CO<sub>2</sub> on the oxidative power of peroxide, an anion receptor complex<sup>13</sup> of peroxide dianion,  $[O_2 \subset mBDCA-5t-H_6]^{2-}$  (1, Fig. 1),<sup>12</sup> was employed as a soluble source of peroxide dianion. The anion receptor *mBDCA-5t-H*<sub>6</sub> encapsulates peroxide dianion via six N– H···O hydrogen bonds. Since its discovery, this cryptate has en-

recharge cycle of lithium-O2 batteries<sup>2</sup> prompted us to consider

the possibility that carbonate formation may be a consequence of peroxide combination with carbon dioxide; this would likely

confer increased solubility and yield powerful oxidizers. To ad-

dress this topic, we utilize an anion-receptor solubilized form of

peroxide dianion<sup>12</sup> to elucidate the molecular level details of its

reaction with carbon dioxide. As reported herein, we observe the

formation of strongly oxidizing peroxy(di)-carbonate intermedi-

ates and study their reaction with organic solvents to produce car-

bonate. In a complementary line of investigation, we show that carbon dioxide activation of insoluble Li<sub>2</sub>O<sub>2</sub> similarly engenders

solvent oxidation with the concomitant production of carbonate.

Our findings shed light on the identity and behavior of the hot ox-

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Fig. 1 Reaction scheme of peroxide cryptate 1 with CO<sub>2</sub> and line drawing of  $[O_2 \subset mBDCA$ -5t-H<sub>6</sub>]<sup>2-</sup> and  $[CO_3 \subset mBDCA$ -5t-H<sub>6</sub>]<sup>2-</sup>.



Fig. 3 Variable temperature  ${}^{13}$ C NMR (left) and  ${}^{17}$ O NMR (right) analysis of the reaction between  ${}^{13}$ CO<sub>2</sub> and 1.

abled exploration of the reactivity of peroxide dianion with small molecules in polar organic media without the complicating influence of acidic protons.<sup>12,14</sup> Despite being a simple molecule, peroxide dianion has yielded rich and previously unknown chemistry, including a metal-free oxidation of carbon monoxide (CO) generating carbonate, which is encapsulated by the anion receptor as  $[CO_3 \subset mBDCA-5t-H_6]^{2-}(2, Fig. 1)$ .<sup>14</sup>

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While the conversion of 1 to 2 under CO (1 atm, 40 °C) takes two hours to go to completion, exposing a dimethylformamided<sub>7</sub> (DMF-d<sub>7</sub>) solution of 1 to CO<sub>2</sub> (1 atm, 25 °C) resulted in essentially instantaneous formation of carbonate cryptate  $[CO_3 \subset mBDCA-5t-H_6]^{2-}$  as indicated by <sup>1</sup>H NMR spectroscopy. Formation of  $O_2$  gas was not observed by gas chromatography (GC) analysis of the reactor headspace gases, <sup>15</sup> suggesting the possibility of oxygen incorporation into the solvent molecules. To probe the fate of the "missing oxygen atom" according to the equation at the top of Figure 1, the reaction of  $CO_2$  and 1 was next performed in the presence of oxygen atom acceptors. While 1 on its own is unreactive towards PPh<sub>3</sub> and methoxythioanisole at 25 °C, exposing a mixture of 1 and organic oxygen-atom acceptor to CO2 (1 atm, 25 °C) resulted in rapid formation of triphenylphosphine oxide (90%, Fig. 2) or 1-(methylsulfinyl)-4methoxybenzene (61%, Fig. 2), respectively.



Fig. 2 Addition of CO<sub>2</sub> to 1 in the presence of an oxygen-atom acceptor.

Aiming to establish the chemical identity of the oxidant(s) generated upon exposure of peroxide cryptate 1 to CO<sub>2</sub>, we followed the reaction by variable temperature <sup>13</sup>C NMR spectroscopy. A strong new signal at  $\delta = 156.9$  ppm, together with one minor species resonating at  $\delta = 157.4$  ppm, was observed at -50 °C (Fig. 3). We first consider peroxycarbonate ( $-OOCO_2^{-}$ ) and hydroperoxycarbonate ( $HOOCO_2^{-}$ , Fig. 3) as candidates to correspond to the observed <sup>13</sup>C NMR signals, since hydroperoxycarbonate is known to be active for

sulfide oxidation.<sup>16,17</sup> The salt [PPN][HOO<sup>13</sup>CO<sub>2</sub>] (PPN = bis(triphenylphosphine)iminium) generated *in situ* from H<sub>2</sub>O<sub>2</sub> and bicarbonate [PPN][H<sup>13</sup>CO<sub>3</sub>] ( $\delta$  = 160.0 ppm)<sup>18–20</sup> showed a single <sup>13</sup>C resonance at  $\delta$  = 157.5 ppm, confirming the identity of the minor intermediate as HOOCO<sub>2</sub><sup>-</sup>.

Moreover, <sup>13</sup>C Gauge-Independent Atomic Orbital (GIAO) NMR calculations of chemical shifts for potential candidates were performed.<sup>15</sup> From a range of potential chemical species (Fig. 4), symmetric peroxydicarbonate  $(-O_2COOCO_2^-)$  emerged as the most plausible assignment for the major product at  $\delta = 156.9$ ppm, having the best match between observed and calculated <sup>13</sup>C NMR chemical shift. <sup>15</sup> In an effort to independently generate <sup>-</sup>O<sub>2</sub>COOCO<sub>2</sub><sup>-</sup>, an experiment was carried out in which excess <sup>13</sup>CO<sub>2</sub> was added to a frozen mixture of potassium *tert*-butoxide and bis(trimethylsilyl) peroxide giving rise to a single new <sup>13</sup>C NMR resonance at  $\delta$  = 155.5 ppm (-40 °C), tentatively supporting our assignment of the major  $1 + CO_2$  product as symmetric peroxydicarbonate; differences in the medium and reaction conditions may account for the observed chemical shift difference (155.5 ppm here versus 156.9 ppm, above). Similarly, superoxide  $(O_2^{\bullet-})$  has been documented to absorb two equivalents of  $CO_2$ , generating an unsymmetrical peroxydicarbonate (Fig. 4) as a precipitate.<sup>21</sup> In our hands, the low solubility of this unsymmetrical peroxydicarbonate material precluded its characterization by solution <sup>13</sup>C NMR studies under conditions we employed successfully for *in situ* characterization of  $-O_2COOCO_2^-$  and  $HOOCO_2^-$ ; this establishes that different oxidants are generated upon addition of CO<sub>2</sub> to superoxide as compared with peroxide dianion (Fig. 4).

Further support for the formation of HOOCO<sub>2</sub><sup>-</sup> and  $^{-}O_2COOCO_2^{-}$  upon interaction of CO<sub>2</sub> with peroxide sources was provided by variable temperature <sup>17</sup>O NMR spectroscopy. Due to the fast relaxation times of <sup>17</sup>O nuclei, observation of the <sup>17</sup>O resonance for mid-size molecules such as **1**-<sup>17</sup>O<sub>2</sub> and **2**-CO<sup>17</sup>O<sub>2</sub> is expected to be challenging in solution.<sup>22</sup> Indeed, <sup>17</sup>O NMR measurements of independently prepared peroxide cryptate **1**-<sup>17</sup>O<sub>2</sub> and carbonate cryptate **2**-CO<sup>17</sup>O<sub>2</sub> (70%, <sup>17</sup>O-enriched) show no resonances between  $\delta = -1100$  and +1800 ppm (H<sub>2</sub>O used as reference,  $\delta = 0$  ppm) in DMF. However, solid-state <sup>17</sup>O NMR measurements for **1**-<sup>17</sup>O<sub>2</sub> and **2**-CO<sup>17</sup>O<sub>2</sub> were success-

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Fig. 4 Possible intermediates during the conversion of 1 and  $CO_2$  to 2 (top) and formation of symmetric and unsymmetric peroxydicarbonate (bottom).

ful, as reported previously in the case of 2-CO<sup>17</sup>O<sub>2</sub>,<sup>14</sup> and in the present work for  $1-^{17}O_2$ , providing the benchmark  $^{17}O$  NMR chemical shifts ( $\delta = 260$  ppm for  $1^{-17}O_2$  and 170 ppm for 2-CO<sup>17</sup>O<sub>2</sub>) (Fig. 5). As seen in Fig. 3, 70% <sup>17</sup>O-enriched samples of  $HOOCO_2^-$  and  $^-O_2COOCO_2^-$  generated in DMF solution at -78 °C from the reaction of  $1-^{17}O_2$  and  $^{13}CO_2$  resulted in a broad <sup>17</sup>O NMR resonance at  $\delta$  = 275.3 ppm, assigned as overlapping signals of  $HOOCO_2^-$  and  $-O_2COOCO_2^-$ . Upon gradual warming of the sample to -10 °C, the intensity of the signal decayed; the signal ultimately resolved into two peaks with equal intensities at  $\delta$  = 278.7 and 264.0 ppm, distinct from those observed for  $1-^{17}O_2$  and  $2-CO^{17}O_2$ . The two peaks observed are attributed to  $HOOCO_2^{-}$  which contains two chemically inequivalent <sup>17</sup>O atoms ( $\delta$  = 278.7 ppm for HOOCO<sub>2</sub><sup>-</sup> and 264.0 ppm for HOOCO<sub>2</sub><sup>-</sup>), in contrast to the situation for <sup>-</sup>O<sub>2</sub>COOCO<sub>2</sub><sup>-</sup> in which the peroxy oxygen atoms are related by symmetry. The appearance of the relatively sharp <sup>17</sup>O NMR signals assigned to HOOCO<sub>2</sub><sup>-</sup> coupled with the concurrent observation of monodeprotonated cryptand  $([mBDCA-5t-H_5]^{1-})^{14}$  by <sup>1</sup>H NMR spectroscopy strongly suggests that HOOCO<sub>2</sub><sup>-</sup> is not strongly sequestered inside the anion receptor. The observed <sup>17</sup>O NMR chemical shifts are in accord with expectations arising from <sup>17</sup>O NMR absolute shielding calculations (Please see Table 1) and compare well with data for benchmark organic compounds containing the peroxy functional group.<sup>23</sup>

#### Mechanism of CO<sub>2</sub>/peroxide driven oxidation

Having thereby established the identity of the active oxidants generated from combination of  $O_2^{2-}$  and  $CO_2$  as  $HOOCO_2^-$  and  $^-O_2COOCO_2^-$ , we next turned our attention to the mechanism of  $CO_2$ /peroxide driven oxidation. The reaction of <sup>18</sup>O-labeled **1** and  $CO_2$  was performed in the presence of an oxidizable substrate. Exposure of a mixture of **1**-<sup>18</sup>O<sub>2</sub> and PPh<sub>3</sub> to  $CO_2$  furnished <sup>18</sup>OPPh<sub>3</sub> as the oxidized product based on GCMS analysis. <sup>15</sup> The obtained <sup>18</sup>O isotope labeling data preclude the possibility of O–O bond cleavage prior to the oxygen atom transfer (OAT) reaction, as such a process would yield isotopic scrambling and result in a mixture of <sup>16</sup>OPPh<sub>3</sub> and <sup>18</sup>OPPh<sub>3</sub>. Therefore, H<sup>18</sup>O<sub>2</sub>CO<sub>2</sub>–with its peroxy unit intact as it was derived from peroxide dianion–is implicated as the active species for the OAT conversion of PPh<sub>3</sub>



**Fig. 5** Experimental (black trace) and simulated (red trace) solid-state <sup>17</sup>O NMR spectra of (a)  $1^{-17}O_2$ , (b)  $2 \cdot CO^{17}O_2^{16}O$ , and (c) product resulting from treatment of solid  $1^{-17}O_2$  with CO<sub>2</sub>. All solid-state <sup>17</sup>O NMR experiments were performed on a Bruker Avance-600 (14.1 T) spectrometer under the static condition. A Hahn-echo sequence was used for recording the static spectra to eliminate the acoustic ringing from the probe. A 4-mm Bruker MAS probe was used without sample spinning. The effective 90° pulse was of duration 1.7  $\mu$ s. High power <sup>1</sup>H decoupling (70 kHz) was applied in all static experiments. A liquid H<sub>2</sub>O sample was used for both RF power calibration and <sup>17</sup>O chemical shift referencing ( $\delta = 0$  ppm).

to OPPh<sub>3</sub> (Fig. 6, OAT pathway). In contrast, addition of CO<sub>2</sub> to a solution of 1-<sup>18</sup>O<sub>2</sub> in the presence of the hydrogen atom donor 9,10-dihydroanthracene (DHA) led to a statistical mixture of anthraquinone products with <sup>16</sup>O and <sup>18</sup>O incorporation.<sup>15</sup> The observed isotope scrambling is likely due to a sequence of H-atom abstraction/radical recombination reactions. By analogy to the behavior of organic peroxydicarbonates,<sup>26</sup> symmetrical peroxydicarbonate would be expected to undergo O–O bond homolysis generating two equivalents of the reactive carbonate radical  $CO_3^{\bullet-}$  (Fig. 5, hydrogen atom transfer (HAT) pathway).<sup>27</sup> Quantum chemical calculations indicate that homolytic cleavage of the O–O bond in  $-O_2COOCO_2^-$  is only mildly endergonic (reaction free energy +14 kcal/mol); this species thus has an unusually weak O–O bond.

Homolytic cleavage of the O–O bond and generation of  $CO_3^{\bullet-}$  appears to be favorable for two reasons: (i) repulsion of the negative charge due to poor solvation in organic solvents resulting in Coulombic explosion<sup>28</sup> and (ii) resonance stabilization of the unpaired electron of carbonate radical anion over the carbonate  $\pi$  system. Carbonate radical has been generated previously via laser photolysis of aqueous persulfate in the presence of bicarbonate.<sup>29</sup> Carbonate radical has been implicated in guanine oxidation<sup>27</sup> and is also believed to be formed upon treatment of peroxynitrite (ONOO<sup>-</sup>) with CO<sub>2</sub>, in that case generating nitrogen dioxide as a byproduct.<sup>27,30,31</sup> Furthermore, in manganese-catalyzed oxidation of amino acids by H<sub>2</sub>O<sub>2</sub>, formation of reactive oxygen species occurred only when HCO<sub>3</sub><sup>-</sup> buffer was used.<sup>32,33</sup> Carbonate radicals generated in lithium-oxygen batteries can then engage in HAT reactions with solvents contain-

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**Table 1** Experimental solid-state <sup>17</sup>O NMR and ADF computational results on  $[K_2(DMF)_3][^{17}O_2 \subset mBDCA-5t-H_6]$ ,  $[K_2(DMF)_3][C^{17}O_3 \subset mBDCA-5t-H_6]$ , and related compounds.

Compound		$\delta_{iso}/{ m ppm}^a$	$\delta_{11}/{ m ppm}$	$\delta_{22}/{ m ppm}$	$\delta_{33}$ /ppm	C <sub>Q</sub> /MHz	$\eta_Q/MHz$
1	Exp	260	335	335	110	-16.6	0.0
	ADF	308	388	388	148	-17.5	0.000
2	Exp	170	266	194	50	7.5	0.7
	ADF	223	335	222	112	7.03	0.95
$O_2^{2-}$	Exp	221	398	398	-133	-18.66	0.000
$H_2O_2$	$Exp^b$	180	_		_	-16.31	0.687
	ADF	182	383	211	-48	-16.81	0.969
$Li_2O_2$	$Exp^{c}$	227	352	352	-23	-18.66	0.00
			2				24 5 1 6

[a] The uncertainties in experimental data are:  $\delta_{iso} \pm 2$  ppm;  $\delta_{ii} \pm 10$  ppm; C<sub>Q</sub>  $\pm 0.2$  MHz;  $\eta_Q \pm 0.1$ . [b] See reference.<sup>24</sup> [c] See reference.<sup>25</sup>

ing weak C-H bonds, driven by the high O-H bond strength (BDE  $\cong$  107 kcal/mol) of the bicarbonate that is formed. <sup>27</sup> Accordingly, we suggest that for stability under lithium-O<sub>2</sub> cell cycling conditions, an organic solvent/electrolyte should have no C-H bonds of BDE  $\cong$  107 kcal/mol or less.

To experimentally confirm the generation of  $CO_3^{\bullet-}$ , 1 was treated with CO<sub>2</sub> in the presence of the spin trap 5-tertbutoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) with reaction monitoring by EPR spectroscopy.<sup>34</sup> Upon addition of the CO<sub>2</sub>, signals for the hydroxyl adduct [BMPO–OH]<sup>•</sup> together with small quantities (ca. 5%) of an unidentified spin-trap adduct suspected to be  $[BMPO-OCO_2]^{\bullet-}$ , were observed within seconds (Fig. 7). Formation of [BMPO-OH]• is proposed to occur via rapid reaction between chemically generated CO3<sup>•-</sup> and BMPO yielding initially [BMPO–OCO<sub>2</sub>]<sup>•–</sup>, followed by decarboxylation and protonation; the proton source under these conditions could be the anion receptor mBDCA-5t-H<sub>6</sub> (Fig. 7C). This sequence is directly along the lines proposed for the related spin trap DMPO under exposure to carbonate radical.<sup>35,36</sup> On longer timescales, [BMPO-OH]• was further oxidized to [BMPO-O]• and other unidentified decomposition products.34



Fig. 6 Proposed mechanistic pathways for  $CO_2$ -mediated solvent decomposition in lithium- $O_2$  batteries. OER is an "oxygen evolving reaction", HAT is a "hydrogen atom transfer" oxidative process involving hydrogen atom abstraction by carbonate radical anion, and OAT is "oxygen atom transfer" to a substrate, S.



**Fig. 7** (a) X-band EPR spectra of: pristine BMPO in DMF (red), BMPO+1 without adding CO<sub>2</sub> in DMF (purple), and exposure of BMPO+1 to CO<sub>2</sub> in DMF (black). (b) Simulation of the EPR spectra of BMPO+1+CO<sub>2</sub> in DMF by linear combination of the contribution from:  $[BMPO-OCO_2]^{\bullet-}$  (green),  $[BMPO-OH]^{\bullet}$  (red), and  $[BMPO-O]^{\bullet}$  (yellow). (c) Formation of  $[BMPO-O]^{\bullet}$  from  $[BMPO-OH]^{\bullet}$  and an oxidant "[O]"

#### Activation of solid $Li_2O_2$ with $CO_2$ in aprotic organic media

To examine the effect of CO<sub>2</sub> on the oxidative power of Li<sub>2</sub>O<sub>2</sub> under conditions relevant to the charging of lithium-air cells, commercially available solid Li2O2 was exposed to CO2 (1 atm, 25 °C, 48 h) in 1,2-dimethoxyethane (DME). In contrast to the results from control experiments carried out similarly but in the absence of CO<sub>2</sub>, substantial amounts of methyl methoxyacetate were identified among the products of DME oxidation (Fig. 8). Approximately 51% of the Li<sub>2</sub>O<sub>2</sub> had been consumed, and quantitative conversion of consumed Li2O2 to Li2CO3 (based upon lithium) was observed by <sup>13</sup>C NMR spectroscopy and total inorganic carbonate (TIC) analysis.<sup>15</sup> The consumed peroxide must generate an oxidizing equivalent; 74% was identified as evolved O2 and 15% as methyl methoxyacetate (Fig. 8), with the balance unidentified. We also introduced solid  $Li_2O_2$  into neat DMSO under a CO<sub>2</sub> atmosphere (1 atm, 25 °C, 48 h), given the reported use of DMSO in lithium-O2 cells.  $^{\rm 37}$  More than 90%

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of the Li<sub>2</sub>O<sub>2</sub> consumed participated in the conversion of DMSO to DMSO<sub>2</sub> (Fig. 8). Viewed in the context of cycling lithium-O<sub>2</sub> cells, the rate of CO2-induced solvent decomposition in bona fide lithium-air cells is perhaps lower than that observed in the current study due to the difference in CO<sub>2</sub> partial pressures. Nonetheless, considering the low cycling rate and long cycling time of a typical lithium-air battery, 38 our findings underscore that extensive oxidative degradation of the electrolyte in a cell will occur during cell cycling even when a small amount of CO<sub>2</sub> is introduced or otherwise generated in the system.<sup>39</sup> During cell cycling, CO<sub>2</sub> is generated at the surface of lithium peroxide impregnated carbon electrodes, <sup>39</sup> leading us to speculate that the proposed chemistry (Fig. 8) should be expected to occur as well on a polarized electrode/electrolyte interface. It should be noted that while commercial Li<sub>2</sub>O<sub>2</sub> was used in the present study, it is conceivable that the varied morphologies of electrochemically generated Li<sub>2</sub>O<sub>2</sub> may react with CO<sub>2</sub> at different rates. Due to the preponderance of conditions which result in varied Li<sub>2</sub>O<sub>2</sub> crystallinity, size and surface structure, 40,41 commercial Li2O2 was chosen as an ideal benchmark reactant with CO<sub>2</sub>.

A recent publication reported that the secondary amine 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP), when present in a charging lithium-air cell (> 3.5 V vs. Li<sup>+</sup>/Li), was converted to the oxyl amine radical 4-oxo-TEMPO, as confirmed by EPR spectroscopy. 4-oxo-TEMP has been used in the past as a trap for singlet oxygen, leading the authors to propose that singlet oxygen was responsible for the observed conversion. <sup>10</sup> An alternative explanation for the production of 4-oxo-TEMPO involves the oxidants generated by activating Li<sub>2</sub>O<sub>2</sub> with CO<sub>2</sub>, considering that the onset potential of  $CO_2$  formation in a typical lithium-air cell is also 3.5 V.<sup>42</sup> Accordingly, we found that exposing  $Li_2O_2$  to  $CO_2$  (1 atm, 25 °C, 24 h) in the same solvent and electrolyte as described in the literature, but without the application of an electrode potential, also resulted in the formation of 4-oxo-TEMPO. Of the oxidizing equivalents generated during transformation of Li<sub>2</sub>O<sub>2</sub> to Li<sub>2</sub>CO<sub>3</sub>, ca. 15% were incorporated into the 4-oxo-TEMPO reaction product, based on EPR spin quantification. These exper-



Fig. 8 CO<sub>2</sub> mediated oxidation of organic solvents by Li<sub>2</sub>O<sub>2</sub>. Addition of excess CO<sub>2</sub> to solid Li<sub>2</sub>O<sub>2</sub> in the organic solvent 1,2-dimethoxyethane (DME) generates an oxidizing equivalent "O", which converts to O<sub>2</sub> (74%) and methyl methoxyacetate (15%) with the balance unidentified. A similar reaction performed in dimethylsulfoxide (DMSO) generated dimethylsulfone (DMSO<sub>2</sub>) in 90% yield.

iments suggest that the oxidation of 4-oxo-TEMP is most likely due to  $CO_2$ /peroxide-derived oxidants as opposed to singlet oxygen formation or at a minimum suggest that 4-oxo-TEMP is not a selective probe for singlet oxygen in Li-O<sub>2</sub> cells under conditions of  $CO_2$  availability.

#### Conclusions

While previous studies on lithium-O2 batteries have attributed the low cycling number and capacity fading to singlet oxygen<sup>10</sup> and superoxide, 4-7 it is now clear that CO<sub>2</sub>/peroxide-derived oxidants are responsible for carbonate formation by way of the active oxidants HOOCO<sub>2</sub><sup>-</sup> and CO<sub>3</sub><sup>•-</sup> via <sup>-</sup>O<sub>2</sub>COOCO<sub>2</sub><sup>-</sup>. Since prototypical lithium-air cells (ether electrolyte, carbon cathode) lose 5-7% of their capacity to parasitic CO<sub>2</sub> formation per complete cycle<sup>39</sup> and have a typical cycling number of *ca*. 50, the resulting CO<sub>2</sub>/peroxide dianion-derived oxidants are expected to cause organic electrolyte degradation. This oxidative degradation may occur both during discharge through reaction of peroxide dianion with CO<sub>2</sub> and during recharge through electrochemical oxidation of carbonate generating initially carbonate radical  $(CO_3^{\bullet-})$ . It has been established that recharge of a lithium-O2 battery regenerates CO<sub>2</sub> from Li<sub>2</sub>CO<sub>3</sub>; however, the mechanism and product(s) identification of electrochemical Li<sub>2</sub>CO<sub>3</sub> degradation have been unclear.<sup>2</sup> Our studies provide evidence for a mechanistic pathway by which carbonate radical anions when generated engage in C-H abstraction from the solvent (C-H bond  $\cong$  107 kcal/mol, or less)<sup>27</sup> and lead to solvent degradation and reformation of  $CO_2$  (Fig 6). The regenerated  $CO_2$  sets in motion a decomposition cycle; therefore if even a small percentage of the total Li<sub>2</sub>O<sub>2</sub> is converted to CO<sub>2</sub>, extensive oxidative degradation of the electrolyte in a cell will occur over the course of many cycles. If CO<sub>2</sub> cannot be excluded from these systems, then it is critical that the electrolyte and other cell components be invulnerable to reactive CO<sub>2</sub>/peroxide-derived oxidants if the full potential of rechargeable lithium-O<sub>2</sub> battery systems is to be realized.

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#### **Table of Contents Entry**



Peroxide dianion reacts with CO<sub>2</sub> in polar aprotic organic media to afford hydroperoxycarbonate and carbonate radical anion. These highly reactive species, if formed in lithium-O<sub>2</sub> cell, can lead to cell degradation via oxidation of electrolytes and electrode.