On the incompatibility of lithium–O₂ battery technology with CO₂†

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When solubilized in a hexacarboxamide cryptand anion receptor, the peroxide dianion reacts rapidly with CO₂ in polar aprotic organic media to produce hydroperoxycarbonate (HOOCO₂⁻) and peroxydicarbonate (O₂COOCO₂⁻). Peroxydicarbonate is subject to thermal fragmentation into two equivalents of the highly reactive carbonate radical anion, which promotes hydrogen atom abstraction reactions responsible for the oxidative degradation of organic solvents. The activation and conversion of the peroxide dianion by CO₂ is general. Exposure of solid lithium peroxide (Li₂O₂) to CO₂ in polar aprotic organic media results in aggressive oxidation. These findings indicate that CO₂ must not be introduced in conditions relevant to typical lithium–O₂ cell configurations, as production of HOOCO₂⁻ and O₂COOCO₂⁻ during lithium–O₂ cell cycling will lead to cell degradation via oxidation of organic electrolytes and other vulnerable cell components.

Introduction

The two-electron reduction of molecular oxygen to the peroxide dianion is an attractive cathode redox couple for developing rechargeable lithium–O₂ batteries. Lithium carbonate (Li₂CO₃) formation is deleterious to battery performance because it passivates electrodes and causes a drastic reduction in the round trip efficiency of discharge–charge cycles. Carbonate formation is typically ascribed to oxidative degradation of organic electrolytes and carbon electrodes by superoxide and singlet oxygen. Although peroxide is considered to be a strong oxidant in aqueous media, salts of its dianion (O₂⁻²) are poor oxidizers in organic media due to their extremely low solubility and so, for this reason, the possible role of peroxide in furnishing carbonate is underappreciated. The presence of carbonate-derived CO₂ during the recharge cycle of lithium–O₂ batteries 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 address this topic, we utilized an anion-receptor solubilized form of the peroxide dianion to elucidate the molecular level details of its reaction with carbon dioxide. As reported herein, we observed the formation of strongly oxidizing peroxy(di)-carbonate intermediates and studied their reaction with organic solvents to produce carbonate. In a complementary line of investigation, we showed that carbon dioxide activation of insoluble Li₂O₂ similarly engenders solvent oxidation with the concomitant production of carbonate. Our findings shed light on the identity and behavior of the hot oxidants generated upon the facile and quantitative combination of O₂⁻² with CO₂ via direct spectroscopic detection and exploratory reaction chemistry.

Results and discussion

Reaction of O₂⁻² with CO₂ using an anion receptor

Despite the drastic and deleterious effect that CO₂ has upon the performance of a cycling lithium–oxygen battery, our understanding of the chemical entities responsible for this effect is poor and based primarily upon computational studies or observation of terminal reaction products. To examine the effect of CO₂ on the oxidative power of peroxide, an anion receptor complex of the peroxide dianion, [O₂⁺mBDCA-5t-H₄]⁺⁻ (1, Fig. 1), was employed as a soluble source of peroxide dianion. The anion receptor mBDCA-5t-H₄ encapsulates the peroxide dianion via six N–H···O hydrogen bonds. Since its
discovery, this cryptate has enabled exploration of the reactivity of the peroxide dianion with small molecules in polar organic media without the complicating influence of acidic protons.\textsuperscript{12,14} Despite being a simple molecule, the peroxide dianion has yielded rich and previously unknown chemistry, including metal-free oxidation of carbon monoxide (CO) generating carbonate, which is encapsulated by the anion receptor as \( [\text{CO}_3\text{C}MnBDCA-5t\text{-H}_6]^2^- \) (Fig. 1).\textsuperscript{14}

While the conversion of 1 to 2 under CO (1 atm, 40 °C) takes two hours to go to completion, exposing a dimethylformamide-peroxide cryptate \( [\text{CO}_3\text{C}MnBDCA-5t\text{-H}_6]^2^- \) (DMF-d\textsubscript{7}) solution of 1 to CO\textsubscript{2} (1 atm, 25 °C) resulted in the essentially instantaneous formation of carbonate cryptate \( [\text{CO}_3\text{PH}_3\text{C}MnBDCA-5t\text{-H}_6]^2^- \) as indicated by \(^1\text{H} NMR spectroscopy. Formation of \( \text{O}_2 \) gas was not observed by gas chromatography (GC) analysis of the reactor headspace gases,\textsuperscript{15} 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 Fig. 1, the reaction of \( \text{CO}_2 \) and 1 was next performed in the presence of oxygen atom acceptors. While 1 on its own is unreactive towards \( \text{PH}_3 \) and methoxythioanisole at 25 °C, exposing a mixture of 1 and an organic oxygen-atom acceptor to \( \text{CO}_2 \) (1 atm, 25 °C) resulted in the rapid formation of triphenylphosphine oxide (90%, Fig. 2) or 1-(methylsulfonyl)-4-methoxybenzene (61%, Fig. 2), respectively.

Aiming to establish the chemical identity of the oxidant(s) generated upon exposure of peroxide cryptate 1 to \( \text{CO}_2 \), we followed the reaction by variable temperature \(^{13}\text{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 considered peroxyxcarbonate \( (\text{O}_2\text{COOCO}_2^-) \) (Fig. 3) and hydroperoxycarbonate \( (\text{HOOCO}_2^-) \) (Fig. 3) as candidates to correspond to the observed \(^{13}\text{C} NMR signals, since hydroperoxycarbonate is known to be active for sulfide oxidation.\textsuperscript{16,17} The salt \([\text{PPN}][\text{HOOC}\text{O}_2\text{CO}_2]^- \) (PPN = bis(triphenylphosphine)iminium), which was generated \textit{in situ} from \( \text{H}_2\text{O}_2 \) and bicarbonate \([\text{PPN}][\text{H}_2\text{CO}_3]^- \) (\( \delta = 160.0 \) ppm),\textsuperscript{18-20} showed a single \(^{13}\text{C} NMR-resonance at \( \delta = 157.5 \) ppm, confirming the identity of the minor intermediate as \( \text{HOOCO}_2^- \).

Moreover, \(^{13}\text{C} \) Gauge-Independent Atomic Orbital (GIAO) NMR calculations of the chemical shifts of potential candidates were performed.\textsuperscript{19} From a range of potential chemical species (Fig. 4), symmetric peroxydicarbonate \( (\text{O}_2\text{COOCO}_2^-) \) emerged as the most plausible assignment for the major product at \( \delta = 156.9 \) ppm, having the best match between the observed and calculated \(^{13}\text{C} NMR chemical shift.\textsuperscript{15} In an effort to independently generate \( \text{O}_2\text{COOCO}_2^- \), an experiment was carried out in which excess \(^{13}\text{CO}_2 \) was added to a frozen mixture of potassium tert-butoxide and bis(trimethylsilyl) peroxide giving rise to a single new \(^{13}\text{C} NMR-resonance at \( \delta = 155.5 \) ppm (\( -40 \) °C), tentatively supporting our identification of the major 1 + \( \text{CO}_2 \) product as symmetric peroxydicarbonate. Differences in the medium and reaction conditions may account for the observed chemical shift difference (155.5 ppm here \textit{versus} 156.9 ppm, above). Similarly, superoxide \( (\text{O}_2^-) \) has been documented to absorb two equivalents of \( \text{CO}_2 \), generating unsymmetrical peroxydicarbonate (Fig. 4) as a precipitate.\textsuperscript{21} In our hands, the low

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**Fig. 1** The reaction scheme of peroxide cryptate 1 with \( \text{CO}_2 \) and a line drawing of \( [\text{O}_2\text{C}MnBDCA-5t\text{-H}_6]^2^- \) and \( [\text{CO}_3\text{C}MnBDCA-5t\text{-H}_6]^2^- \).

**Fig. 2** Addition of \( \text{CO}_2 \) to 1 in the presence of an oxygen-atom acceptor.

**Fig. 3** Variable temperature \(^{13}\text{C} NMR (left) and \(^{17}\text{O} NMR (right) analysis of the reaction between \(^{13}\text{CO}_2 \) and 1.

**Fig. 4** Possible intermediates during the conversion of 1 and \( \text{CO}_2 \) to 2 (top) and formation of symmetric and unsymmetric peroxydicarbonate (bottom).
solubility of this unsymmetrical peroxycarbonate material precluded its characterization by solution $^{13}$C NMR studies under conditions we employed successfully for in situ characterization of $\text{O}_2\text{COOCO}_2^-$ and HOOCO$_2^-$. This establishes that such oxidants are generated upon addition of CO$_2$ to superoxide as compared with the peroxy dianion (Fig. 4).

Further support for the formation of HOOCO$_2^-$ and $\text{O}_2\text{COOCO}_2^-$ upon interaction of CO$_2$ with peroxydase sources was provided by variable temperature $^{17}$O NMR spectroscopy. Due to the fast relaxation times of $^{17}$O nuclei, observation of the $^{17}$O resonance for mid-size molecules such as $^{1}$H$_2$O$_2$ and 2-CO$_2$O$_2$ was expected to be challenging in solution. Indeed, $^{17}$O NMR measurements of independently prepared peroxy cryptate 1-$^{17}$O$_2$ and carbonate cryptate 2-CO$_2$O$_2^-$ (70%, $^{17}$O-enriched) showed no resonances between $\delta = -1100$ and +1800 ppm ($\text{H}_2\text{O}$ used as a reference, $\delta = 0$ ppm) in DMF. However, solid-state $^{17}$O NMR measurements for 1-$^{17}$O$_2$ and 2-CO$_2$O$_2^-$ were successful, as reported previously in the case of 2-CO$_2$O$_2^-$ 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$_2$O$_2^-$) (Fig. 5, Table 1). As seen in Fig. 3, 70% $^{17}$O-enriched samples of HOOCO$_2^-$ and $\text{O}_2\text{COOCO}_2^-$ generated in DMF solution at $-78$ °C from the reaction of 1-$^{17}$O$_2$ and $^{13}$CO$_2$ in a broad $^{17}$O NMR resonance at $\delta = 275.3$ ppm, assigned as overlapping signals of HOOCO$_2^-$ and $\text{O}_2\text{COOCO}_2^-$. 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$_2$O$_2^-$. The two peaks observed are attributed to HOOCO$_2^-$ which contains two chemically inequivalent $^{17}$O atoms ($\delta = 278.7$ ppm for HOOCO$_2^-$ and 264.0 ppm for HOOCO$_2^-$), in contrast to the situation for $\text{O}_2\text{COOCO}_2^-$ in which the peroxy oxygen atoms are related by symmetry. The appearance of the relatively sharp $^{17}$O NMR signals assigned to HOOCO$_2^-$ coupled with the concurrent observation of monodeprotonated cryptand ([mBDCA-5t-H$_2$])$^{14}$ by $^1$H NMR spectroscopy strongly suggests that HOOCO$_2^-$ is not strongly sequestered inside the anion receptor. The observed $^{17}$O NMR chemical shifts are in accordance with expectations arising from $^{17}$O NMR absolute shielding calculations and compare well with data for benchmark organic compounds containing the peroxy functional group.21

**The mechanism of CO$_2$/peroxide driven oxidation**

Having thereby established the identity of the active oxidants generated from the combination of $\text{O}_2^{2-}$ and CO$_2$ as HOOCO$_2^-$ and $\text{O}_2\text{COOCO}_2^-$, we next turned our attention to the mechanism of CO$_2$/peroxide driven oxidation. The reaction of $^{18}$O-labeled 1 and CO$_2$ was performed in the presence of an oxidizable substrate. Exposure of a mixture of 1-$^{18}$O$_2$ and PPh$_3$ to CO$_2$ furnished $^{18}$OPPh$_3$ as the oxidized product based on GCMS analysis.23 The obtained $^{18}$O isotope labeling data precluded 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 $^{16}$OPPh$_3$ and $^{18}$OPPh$_3$. Therefore, $^{18}$O$_2$CO$_2^-$ with its peroxy unit intact as it was derived from the peroxy dianion – is implicated as the active species for the OAT conversion of PPh$_3$ to OPPh$_3$ (Fig. 6, OAT pathway). In contrast, addition of CO$_2$ to a solution of 1-$^{18}$O$_2$ in the presence of the hydrogen atom donor 9,10-dihydroanthracene (DHA) led to a statistical mixture of anthraquinone products with $^{16}$O and $^{18}$O incorporation.27 The observed isotope scrambling was likely due to a sequence of H-atom abstraction/radical recombination reactions. By analogy to the behavior of organic peroxycarbonates,26 symmetrical peroxycarbonate would be expected to undergo O-O bond homolysis generating two equivalents of the reactive carbonate radical $\text{CO}_2^{1-}$ (Fig. 6, hydrogen atom transfer (HAT) pathway).25 Quantum chemical calculations indicate that homolytic cleavage of the O-O bond in $\text{O}_2\text{COOCO}_2^-$ is only mildly endergonic (reaction free energy +14 kcal mol$^{-1}$). This species thus has an unusually weak O-O bond.

Homolytic cleavage of the O-O bond and generation of CO$_2^{1-}$ appears to be favorable for two reasons: (i) repulsion of the negative charge due to poor solvation in organic solvents resulting in coulombic explosion28 and (ii) resonance stabilization of the unpaired electron of the carbonate radical anion over the carbonate $\pi$ system. Carbonate radicals have been generated previously via laser photolysis of aqueous persulfate in the presence of bicarbonate.29 Carbonate radicals have been implicated in guanine oxidation30 and are also believed to be formed upon treatment of peroxydinitrite (ONOO$^-\text{O}$) with CO$_2$, and in that case generate nitrogen dioxide as a byproduct.27,28,31 Furthermore, in the manganese-catalyzed oxidation of amino acids by H$_2$O$_2$, the formation of reactive oxygen species only
occurred when HCO$_3^-$ buffer was used.$^{12,13}$ Carbonate radicals generated in lithium–oxygen batteries can then engage in HAT reactions with solvents containing weak C–H bonds, driven by the high O–H bond strength (BDE $\equiv 107$ kcal mol$^{-1}$) of the bicarbonate that is formed.$^{27}$ Accordingly, we suggest that for stability under lithium–O$_2$ cell cycling conditions, an organic solvent/electrolyte should have no C–H bonds of BDE $\equiv 107$ kcal mol$^{-1}$ or less.

To experimentally confirm the generation of CO$_3^{2-}$, 1 was treated with CO$_2$ in the presence of the spin trap 5-tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO), and the reaction was monitored by EPR spectroscopy.$^{34}$ Upon addition of the CO$_2$, signals for the hydroxyl adduct [BMPO–OH]$^-$ together with small quantities (ca. 5%) of an unidentified spin-trap adduct suspected to be [BMPO–O$\cdot$CO$_2$]$^{2-}$ were observed within seconds (Fig. 7). Formation of [BMPO–OH]$^-$ is proposed to occur via a rapid reaction between the chemically generated CO$_3^{2-}$ and BMPO, initially yielding [BMPO–O$\cdot$CO$_2$]$^{2-}$, followed by decarboxylation and protonation. The proton source under these conditions could be the anion receptor mBDCA-5t-H$_6$ (Fig. 7C). This sequence is directly along the lines proposed for the related spin trap DMPO under exposure to carbonate radicals.$^{15,16}$ On longer timescales, [BMPO–OH]$^-$ was further oxidized to [BMPO–O]$^-$ and other unidentified decomposition products.$^{34}$

### Activation of solid Li$_2$O$_2$ with CO$_2$ in aprotic organic media

To examine the effect of CO$_2$ on the oxidative power of Li$_2$O$_2$ under conditions relevant to the charging of lithium–air cells, commercially available solid Li$_2$O$_2$ was exposed to CO$_2$ (1 atm, 25 °C, 48 h) in 1,2-dimethoxyethane (DME). In contrast to the results from the control experiments carried out similarly but in the absence of CO$_2$, substantial amounts of methyl methoxacetate were identified among the products of DME oxidation (Fig. 8). Approximately 51% of the Li$_2$O$_2$ was consumed, and quantitative conversion of the consumed Li$_2$O$_2$ to Li$_2$CO$_3$ (based upon lithium) was observed by $^{13}$C NMR spectroscopy and total inorganic carbonate (TIC) analysis.$^{15}$ The consumed peroxide must generate an oxidizing equivalent; 74% was identified as

### Table 1: Experimental solid-state $^{17}$O NMR and ADF computational results on [K$_2$(DMF)$_3$][C$^{17}$O$_3$⊂mBDCA-5t-H$_6$], [K$_2$(DMF)$_3$][C$^{17}$O$_3$⊂mBDCA-5t-H$_6$], and related compounds

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$^a$ The uncertainties in the experimental data are: $\delta_{17O} \pm 2$ ppm; $\delta_{17O} \pm 10$ ppm; $C_Q \pm 0.2$ MHz; $\eta_Q \pm 0.1$. $^b$ See ref. 24. $^c$ See ref. 25.
evolved O₂ and 15% as methyl methoxyacetate (Fig. 8), with the remainder unidentified. We also introduced solid Li₂O₂ into neat DMSO under a CO₂ atmosphere (1 atm, 25 °C, 48 h), given the reported use of DMSO in lithium–O₂ cells. More than 90% of the Li₂O₂ consumed participated in the conversion of DMSO to DMSO₂ (Fig. 8). Viewed in the context of cycling lithium–O₂ 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 CO₂ partial pressures. Nonetheless, considering the low cycling rate and long cycling time of a typical lithium–air battery, our findings highlight that extensive oxidative degradation of the electrolyte in a cell will occur during cell cycling even when a small amount of CO₂ is introduced or otherwise generated in the system. During cell cycling, CO₂ is generated at the surface of lithium peroxide-impregnated carbon electrodes, leading us to speculate that the proposed chemistry (Fig. 8) should be expected to occur on a polarized electrode/electrolyte interface as well. It should be noted that while commercial Li₂O₂ was used in the present study, it is conceivable that the varied morphologies of electrochemically generated Li₂O₂ may react with CO₂ at different rates. Due to the preponderance of conditions which result in varied Li₂O₂ crystallinity, size and surface structure, commercial Li₂O₂ was chosen as an ideal benchmark reactant with CO₂.

A recent publication reported that when present in a charging lithium–air cell (>3.5 V vs. Li⁺/Li), the secondary amine 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP) 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 4-oxo-TEMP is most likely due to CO₂/ peroxide-derived oxidants as opposed to singlet oxygen formation or at the very least that 4-oxo-TEMP is not a selective probe for singlet oxygen in Li–O₂ cells under conditions of CO₂ availability.

Conclusions

While previous studies on lithium–O₂ batteries have attributed the low cycling number and capacity fading to singlet oxygen and superoxide, it is now clear that CO₂/peroxide-derived oxidants are responsible for carbonate formation by way of the active oxidants HOOCO₂⁻ and CO₂⁻ via –O₂COOCO₂⁻. Since prototypical lithium–air cells (ether electrolyte, carbon cathode) lose 5–7% of their capacity to parasitic CO₂ formation per complete cycle and have a typical cycling number of ca. 50, the resulting CO₂/peroxide dianion-derived oxidants were expected to cause organic electrolyte degradation. This oxidative degradation may occur both during discharge through reaction of the peroxide dianion with CO₂ and during recharge through electrochemical oxidation of carbonate initially generating the carbonate radical (CO₂⁻). It has been established that recharging a lithium–O₂ battery regenerates CO₂ from Li₂CO₃, however identification of the mechanism and product(s) of electrochemical Li₂CO₃ degradation have been unclear. 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 ≈ 107 kcal mol⁻¹, or less) and lead to solvent degradation and reformation of CO₂. The regenerated CO₂ sets in motion a decomposition cycle, therefore if even a small percentage of the total Li₂O₂ is converted to CO₂, extensive oxidative degradation of the electrolyte in a cell will occur over the course of many cycles. If CO₂ cannot be excluded from these systems then it is critical that the electrolyte and other cell components are invulnerable to reactive CO₂/peroxide-derived oxidants if the full potential of rechargeable lithium–O₂ battery systems is to be realized.

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