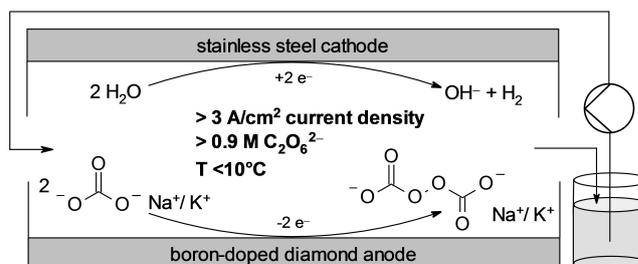**Electrochemistry** | Hot Paper |

Concentrated Aqueous Peroxodicarbonate: Efficient Electrosynthesis and Use as Oxidizer in Epoxidations, *S*-, and *N*-Oxidations

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Dedicated to Professor Manfred T. Reetz

Abstract: Peroxodicarbonates are of substantial interest as potentially powerful and sustainable oxidizers but have so far been accessible only in low concentrations with unsatisfactory energy efficiency. Concentrated ($>$ 0.9 mol L^{-1}) peroxodicarbonate solutions have now been made accessible by the electrolysis of aqueous K$_2$CO$_3$/ Na$_2$CO$_3$/KHCO$_3$ solutions at high current density of 3.33 A cm^{-2} in an efficiently cooled circular flow reactor equipped with a boron-doped diamond anode and a stainless-steel cathode. Their synthetic potential as platform oxidizers was clearly demonstrated in transformations including sulfoxidation, *N*-oxidation, and epoxidation.

Scheme 1. Circular flow electrosynthesis of concentrated peroxodicarbonate.

*I*n electrochemical water splitting, valuable hydrogen gas is generated along with commercially insignificant dioxygen.[1] Only in some cases, industrial scale cathodic hydrogen generation has been combined with value creation at the anode. Examples include the chloroalkaline electrolysis[2] and the electrosynthesis of ammonium peroxodisulfate[3] or sodium periodate.[4] It would be highly desirable to combine industrial scale hydrogen generation with the formation of a sustainable platform oxidizer, but only few substrates are sufficiently stable to survive the extremely high current densities and very positive potential ranges of such processes. We have now evaluated the anodic oxidation of non-toxic, inexpensive carbonate salts and found an efficient process for the generation of concentrated peroxodicarbonates (C$_2$O$_6^{2-}$) solutions at high current densities (Scheme 1).

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Potassium peroxodicarbonate (K$_2$C$_2$O$_6$) was discovered by von Hansen and Constam in 1896 when they electrolyzed K$_2$CO$_3$ solutions at Pt electrodes. They referred to the product, which they isolated as blue crystals, as a "percarbonate".[5] This name is nowadays used for an adduct of sodium carbonate and hydrogen peroxide (Na$_2$CO$_3$·1.5 H$_2$O$_2$), synthesized by Tanatar in 1899 from Na$_2$CO$_3$ and H$_2$O$_2$.[6] The structure of potassium peroxodicarbonate with its central peroxide moiety was clarified by Jansen et al. in 2002.[7] Von Hansen's peroxodicarbonate and Tanatar's percarbonate clearly are different species with distinct reactivities, but the names are still inconsistently used.

The potential of peroxodicarbonates as "green" oxidizers has been recognized early on.[5a] However, more than a hundred years after its discovery, only few preparative applications of this attractive oxidizer have been reported, e.g. by Chardon et al. as an agent for bleaching or removal of organic pollutants,[8] by Einaga et al. as oxidizer in a Ru(bpy)$_3^{2+}$ based electroluminescence system,[9] and by Bulman Page et al. in an asymmetric epoxidation of alkenes via oxaziridinium intermediates.[10]

The main reason for this lack of applications is that peroxodicarbonate is hard to access chemically and has a limited thermal stability. The published half-life of peroxodicarbonate at 20 °C is only 69 minutes.[8] The pioneering electrochemical syntheses were performed with Pt electrodes. However, the corrosion of Pt electrodes under similar conditions, e.g. in the Löwenstein–Riedel process, is a well-documented and costly problem.[11] A breakthrough with regard to electrode stability was achieved in 2003, when Nishiki and Saha introduced the use of boron-doped diamond (BDD) anodes. These anodes are considered as

sustainable carbon electrodes with utmost stability.[12] However, only 45 mM sodium peroxodicarbonate concentrations could be reached initially.[13] Rodrigo et al. observed that at lower current densities (<0.1 A cm^{-2}), hydrogen peroxide is formed as a byproduct.[14] Based on these results, several groups reported electrochemical formation of H_2O_2 during the electrolysis of aqueous carbonate solutions, though it is not entirely clear, if H_2O_2 or peroxodicarbonate was the primary product.[15] High Faradaic efficiencies up to 98 % have been reported for the electrochemical oxidation of aqueous carbonate solutions at concentrations well below 0.1 mM.[16] Chardon et al. recently developed a circular flow system that enabled the generation of sodium peroxodicarbonate in up to a concentration of 0.28 M, albeit at a low efficiency of 2.6 kWh mol^{-1}.[8,17]

When testing the oxidation power of such dilute solutions against various substrates, we did not reach preparatively useful reactivity levels (Figure S9). Clearly, the potential of peroxodicarbonate as sustainable oxidizer can only be unleashed if concentrated solutions are made accessible.

In order to tackle this key challenge, we set up a circular flow cell with a 10.8 cm^2 Si-supported BDD anode at a distance of 1 mm, and a stainless steel cooling jacket that also serves as cathode.[18] This layout ensures a low electrical resistance, a homogeneous current density over the electrode surface, and an efficient mass and heat transfer.[19] 35 mL electrolyte were continuously pumped through the flow-cell and the 100 mL reservoir (Figure S2).[17] After administering 1.5 F relative to the total amount of carbonate, the total oxidizer content was determined by converting all peroxodicarbonate species into hydrogen peroxide by addition of excess H_2SO_4, and then performing an iodometric titration. It should be noted that this established method[8] does not permit to distinguish between the original nature of the oxidizer.

When electrolyzing a 1.5 M solution of Na_2CO_3 under literature conditions[8] with this state-of-the-art cell, a peroxodicarbonate concentration of only 266 mM was reached, (Table 1, Entry 1). We thus thoroughly optimized the reaction conditions. With sodium/potassium double salts, higher concentrations were obtained (Entry 3 *vs.* 1, 2). The addition of bicarbonate also proved beneficial (Entry 4), presumably, since it balances the hydroxide ions released over the course of the electrolysis. The optimal salt composition was found to be 1.125 M K_2CO_3, 0.90 M Na_2CO_3 and 0.225 M $KHCO_3$. When reducing the coolant temperature below 0 °C, the flow became sluggish due to precipitation inside the flow electrolyzer. However, when increasing the cooling efficiency by cooling the anode with a copper block and adding a heat exchanger to the electrolyte loop, a step-up in the peroxodicarbonate concentration was observed (Entry 5).

Realizing the crucial influence of the electrolyte temperature on the peroxodicarbonate concentration, we constructed an electrolysis cell with an elaborate heat-transfer system (Figure 1). A $60\times20\times3$ mm BDD/Si-anode and a 0.5 mm thin steel cathode are embedded in liquid-cooled copper bodies, which act as heat sinks. The high heat

Table 1: Development of an efficient electrosynthesis of peroxodicarbonate.

$$2\ \ ^-O-\overset{O}{\underset{O}{C}}-O^-\ \ \xrightarrow[\text{0°C, H}_2\text{O}]{\substack{-2\text{ e}^- \\ \text{BDD(+)}}}\ \ ^-O-\overset{O}{\underset{O}{C}}-O-O-\overset{O}{\underset{O}{C}}-O^-$$

Entry	carbonate M_2CO_3	d [mm]	A [cm^2]	j [A cm^{-2}]	FE [%]	$c(C_2O_6^{2-})$ [mM]
1	Na	1	10.8	0.8	24	266
2	K	"	"	"	23	258
3	Na/K	"	"	"	20	337
4	Na/K/H	"	"	"	24	406
5[a]	"	"	"	"	35	588
6[a]	"	"	6	1.6	30	503
7[b]	"	"	"	1.44	41	687
8[b]	"	0.3	"	"	39	666
9[b]	"	"	3	2.88	42	709
10[b]	"	"	1.5	5.76	21	354
11[b,c]	"	"	3	2.88	28	791
12[b,c]	"	"	"	3.33	30	838
13[b,c]	"	"	"	3.5	29	823
14[b,c]	"	"	"	4	28	795
15[b,d]	"	"	"	3.33	8	919
16[b,d,e]	"	"	"	"	9	1018

d: interelectrode gap; A: geometric electrode surface area; j: current density; FE: Faradaic efficiency. *Conditions:* circular flow cell with internally cooled (0 °C) stainless steel cathode, BDD anode, flow rate 3 L h^{-1}, 1.5 F relative to total amount of carbonate. Carbonate electrolyte M_2CO_3: $M=$Na, $c=$1.5 M; $M=$K, $c=$1.5 M, $M=$Na/K 1:1.25, $c=$2.25 M, $M=$Na/K/H 0.9:1.125:0.225, $c=$2.25 M. [a] additional in-line heat exchanger; [b] Cell design as detailed in Figure 1; [c] 2.5 F rel. to carbonate; [d] 10.0 F rel. to carbonate, [e] D$_2$O as solvent.
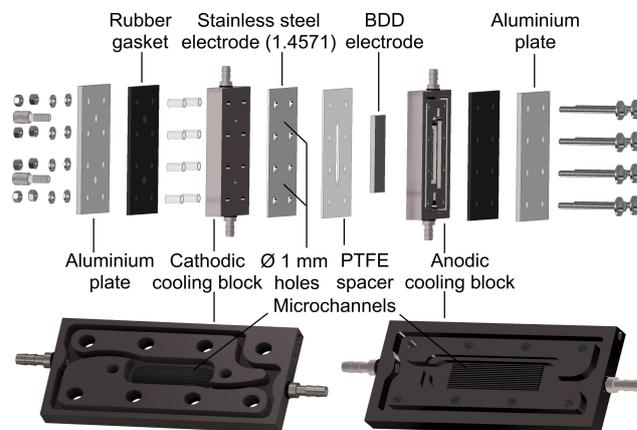

Figure 1. Exploded view of the newly designed copper-based cooling cell.

conductivity of the copper in combination with a microchannel structure of the internal cooling system ensures a rapid heat transfer from the electrodes to the coolant. The new cell design decisively enhances the efficiency of peroxodicarbonate formation. At a coolant temperature of 0 °C, it allows keeping the electrolyte below 10 °C even at extreme current densities, preventing thermal decomposi-

tion of the $C_2O_6^{2-}$ while avoiding precipitation of product within the cell (Entry 7).

Lowering the interelectrode gap minimizes energy consumption and in particular heat evolution, with the best result being obtained at 0.3 mm (Entry 8). The current density in relation to the cooling power was further increased by reducing the area of the cutout in the PTFE spacer (Entries 9 and 10). The highest peroxodicarbonate concentrations (>0.8 M at 2.5 F rel. to carbonate) were obtained at a current density of 3.33 A cm^{-2}. Comparative evaluation of various BDD coated 2–3 mm thick electrodes revealed an efficiency order of BDD on Si > BDD on Ta > BDD on Nb > BDD on glassy carbon substrates[20] (see Supporting Information for details). This suggests that the thermal dissipation rather than the electric conductivity of the bulk material is decisive.

The plot in Figure 2 shows how the concentration of the peroxodicarbonate steadily increases with the amount of transferred charge, reaching concentrations above 0.9 M at a tenfold excess of electrons. The efficiency of the process is remarkably high, particularly at moderate electrolysis duration. A concentration of 337 mmol L^{-1} was reached with a Faradaic efficiency of 60 % at 0.5 F rel. to carbonate and an energy consumption of 0.65 kWh mol^{-1} of $C_2O_6^{2-}$. Expectedly, the efficiency decreases when aiming at record concentrations. The solution can be stored at 0 °C for several hours. Upon heating to room temperature, evolution of dioxygen is observed.

When replacing the water by D$_2$O, peroxodicarbonate, concentrations beyond 1 mol L^{-1} were finally reached, more than three times as high as the previous record.[8] Such a solvent isotope effect has also been reported in the electrolysis of chloride salts and was postulated to result from weaker hydrogen bonds between anions and D$_2$O compared to H$_2$O.[21]

The ^{13}C NMR spectrum of the reaction solution shows a new signal downfield of the carbonate signal at $\delta = 162$ ppm, which increases with the oxidizer concentration (Figure S8). Addition of NaOH or H$_2$SO$_4$ revealed that the species is stable between pH 8 and 13.5. In contrast, mixtures of H$_2$O$_2$ and bicarbonate show a peroxomonocarbonate signal at $\delta = 158$, which disappears above pH 12.[22] These investigations point towards peroxodicarbonate as the predominant peroxo species in solution. The IR spectrum of the electrolyzed carbonate solution features a signal at 1300 cm^{-1}, which is not observed is a control experiment in which 35 % aqueous hydrogen peroxide is added to the same carbonate solution.
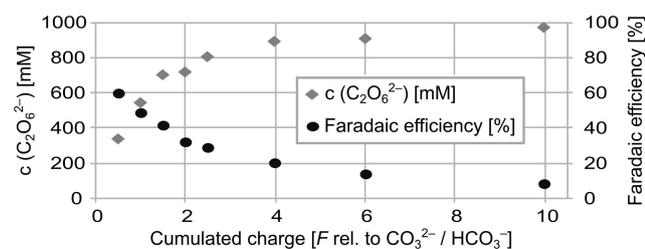
The latter solution shows a signal at 2800 cm^{-1} that is not visible in the electrolyzed solution. The total amount of oxidant as determined by iodometry is larger than calculated from the integral of the peroxodicarbonate NMR signal (see the Supporting Information). This is in line with literature reports in which hydrogen peroxide and peroxomonocarbonates are proposed as additional species in solution.[14]

The oxygen-transfer reactivity of concentrated peroxodicarbonate solutions was probed using the water-soluble reagent methyl(methylthio)methyl sulfoxide. The oxygen-transfer parameter χ_{SO} (Figure 3, Table S2) quantifies the ratio between nucleophilic (sulfoxide oxidation) and electrophilic (sulfide oxidation) reactivity. It ranges from $\chi_{SO} \approx 0.01$ for electrophilic oxidizers like oxone or acidic hydrogen peroxide to $\chi_{SO} = 1.0$ for nucleophilic permanganate. On this scale, H$_2$O$_2$/KHCO$_3$ solutions have an χ_{SO} of 0.28. The electrogenerated peroxodicarbonate solutions show an χ_{SO} of 0.35. This value can be tuned over a wide range by adjusting their pH: At pH 13.5, the χ_{SO} increases to 0.74, at pH 11—which is still well within the stability range of peroxodicarbonate—the χ_{SO} decreases to 0.14.

The synthetic utility of peroxodicarbonate for the oxidation of sulfides and sulfoxides is demonstrated by the examples in Table 2. By stirring sulfides with aqueous solutions of peroxodicarbonate, with the carbonate buffer acidified to pH 11 by sulfuric acid, various sulfides were selectively converted into the corresponding sulfoxides (**2a**–**2c**). When using an excess of basic peroxodicarbonate (pH 12.5), a series of sulfoxides was cleanly oxidized to the corresponding sulfones (**4a**–**4c**).

We next probed the reactivity of the peroxodicarbonate against tertiary amines. The anodic oxidation of tertiary amines generates iminium cations, which leads to dealkylation and other non-selective follow-up reactions.[23] Hence, the industrially relevant *N*-oxidation of tertiary amines is only possible with chemical oxygen-transfer reagents such as peroxoacids,[24] dioxiranes,[25] or hydrogen peroxide in the presence of catalysts or mediators.[26] We were pleased to find that our electrogenerated >0.9 M peroxodicarbonate solutions led to selective *N*-oxidation of water-soluble amines in near quantitative yields without organic solvent, mediator or catalyst (Table 2, **6a**–**6d**, **6f**). For water-insoluble, lipophilic amine substrates, ethanol was added as a cosolvent (**6e**). Remarkably, almost no con-
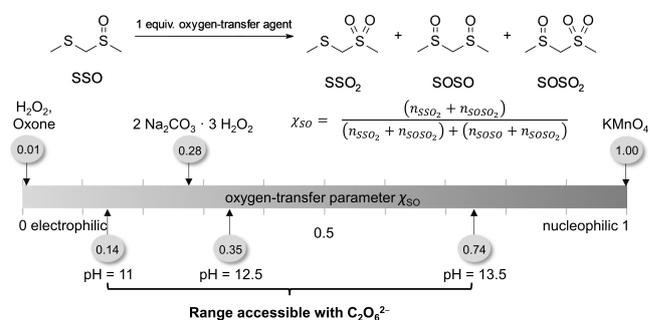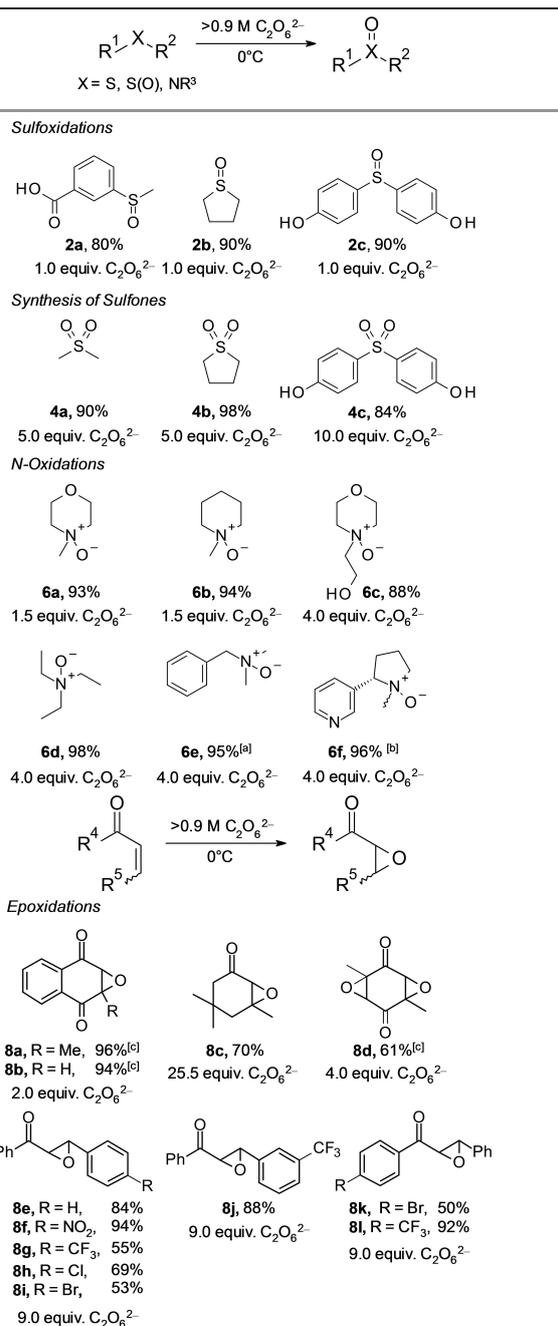
Figure 2. Effect of the amount of applied charge (electrolysis time).

Figure 3. Probing nucleophilic vs. electrophilic oxygen transfer reactivity.

Table 2: Oxidation of substrates with electro-generated peroxodicarbonate.

$$R^1 \overset{X}{\diagdown} R^2 \xrightarrow[0°C]{>0.9\ M\ C_2O_6^{2-}} \overset{O}{\underset{R^1 \diagdown X \diagdown R^2}{}}$$

X = S, S(O), NR³

Sulfoxidations

2a, 80%
1.0 equiv. C₂O₆²⁻

2b, 90%
1.0 equiv. C₂O₆²⁻

2c, 90%
1.0 equiv. C₂O₆²⁻

Synthesis of Sulfones

4a, 90%
5.0 equiv. C₂O₆²⁻

4b, 98%
5.0 equiv. C₂O₆²⁻

4c, 84%
10.0 equiv. C₂O₆²⁻

N-Oxidations

6a, 93%
1.5 equiv. C₂O₆²⁻

6b, 94%
1.5 equiv. C₂O₆²⁻

6c, 88%
4.0 equiv. C₂O₆²⁻

6d, 98%
4.0 equiv. C₂O₆²⁻

6e, 95%[a]
4.0 equiv. C₂O₆²⁻

6f, 96% [b]
4.0 equiv. C₂O₆²⁻

$$R^4 \diagdown \underset{R^5}{\diagup} \xrightarrow[0°C]{>0.9\ M\ C_2O_6^{2-}} R^4 \diagdown \underset{R^5}{\overset{O}{\diagup O}}$$

Epoxidations

8a, R = Me, 96%[c]
8b, R = H, 94%[c]
2.0 equiv. C₂O₆²⁻

8c, 70%
25.5 equiv. C₂O₆²⁻

8d, 61%[c]
4.0 equiv. C₂O₆²⁻

8e, R = H, 84%
8f, R = NO₂, 94%
8g, R = CF₃, 55%
8h, R = Cl, 69%
8i, R = Br, 53%
9.0 equiv. C₂O₆²⁻

8j, 88%
9.0 equiv. C₂O₆²⁻

8k, R = Br, 50%
8l, R = CF₃, 92%
9.0 equiv. C₂O₆²⁻

S-oxidation: 1.00 mmol of the substrate were stirred with the indicated amount of >0.9 M C₂O₆²⁻ solution prepared according to Table 1, Entry 15 and 1.00 mmol with H₂SO₄ (pH 11) at 0°C for 16 h. *S(O)- and N-oxidation*: 1.00 mmol of the substrate were stirred with the indicated amount of >0.9 M C₂O₆²⁻ solution prepared according to Table 1, Entry 15 at 0°C, 16 h. *Epoxidation*: 1.00 mmol of the substrate were stirred with the indicated amount of C₂O₆²⁻ solution in 20 mL EtOH at 0°C for 1–3 h. [a] 5 mL aqueous EtOH as cosolvent. [b] 1 mL H₂O as cosolvent. Mixture of diastereomers. [c] 20 mL of a 2:1:1 CH₂Cl₂/EtOH/H₂O mixture as cosolvent. All yields refer to isolated amounts.

version was achieved in comparative experiments with 0.25 M peroxodicarbonate solutions, as they had previously been accessible by state-of-the-art electrosynthesis. This demonstrates the enabling character of the new electrochemical process.

We went on to investigate the epoxidation of α,β-unsaturated carbonyl compounds. Bulman Page et al. had shown that 0.04 M peroxodicarbonate solutions oxidize chiral oxaziridines to iminium-salts. These promote the enantioselective epoxidation of alkenes.[10] In contrast, concentrated peroxodicarbonate solution directly converts enones into the respective epoxides. The reactions were conducted without any catalyst in aqueous ethanol solutions. Products arising from sensitive quinone substrates (**8a**, **8b** and **8d**) required a biphasic process with dichloromethane as a co-solvent to retard base-promoted epoxide ring-opening. The epoxidation of menadione (**7a**) was successfully performed on multi-gram scale demonstrating the scalability of the procedure. These examples further illustrate the potential of concentrated peroxodicarbonate as electrochemically accessible "green" oxidizer for ex-cell oxidation processes.

In conclusion, a flow cell designed to maximize the heat transfer from the BDD anode and the steel cathode to the coolant, a ternary K₂CO₃/Na₂CO₃/KHCO₃ electrolyte, and the use of high current densities of above 3 A cm⁻² are the decisive factors enabling the electrochemical synthesis of concentrated peroxodicarbonate solutions. These were shown to be powerful and green oxidizers, permitting *N*- and *S*-oxidations as well as epoxidations. This sets the stage for the development of sustainable ex-cell electrochemical oxidations based on peroxodicarbonate, provided that thermal stability can be further improved. This finding will contribute to the electrification of organic synthesis and generation of value-added chemicals by this future technology.[27]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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