Reactivity of the Electrogenerated $O_2^{\cdot-}$/CO_2 System Towards Alcohols

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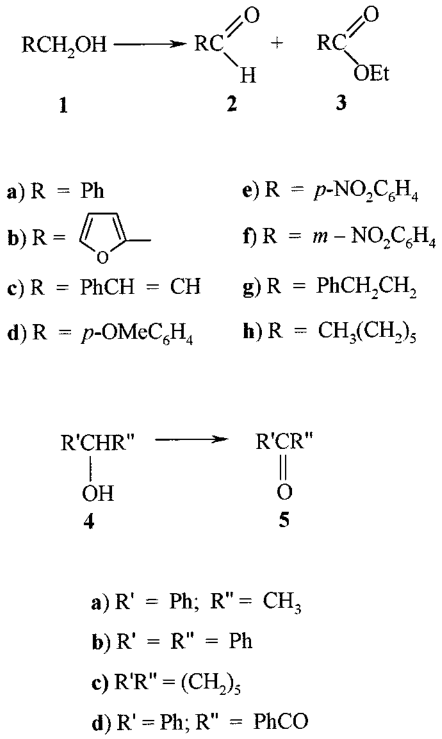
The reactivity towards alcohols of the system obtained from the reduction of dioxygen carried out in aprotic dipolar solvents and in the presence of carbon dioxide has been investigated. This reagent is able to convert primary and secondary alcohols into the corresponding aldehydes and ketones. The optimization of the experimental conditions as well as the advantages and the limitations of the method are reported.

Introduction

Previous studies from our group have shown that the system obtained by one-electron reduction of dioxygen performed in aprotic dipolar solvents and in the presence of carbon dioxide is able to carboxylate different types of substrates.[1] In particular, primary and secondary alcohols bearing a good leaving group at the α or β position are converted into cyclic carbonates, whereas unsubstituted primary and secondary alcohols are transformed into the corresponding linear carbonate after addition of an alkylating agent.[1b] In the course of experiments carried out on benzyl alcohol in order to optimize the reaction conditions, benzaldehyde was detected in the electrolyzed mixture in an amount roughly proportional to the concentration of carboxylating reagent and reaction time.[1b] In the literature[2] it has been reported that the chemical system KO_2/CO_2/18-crown-6 oxidizes olefins to oxiranes and sulfides to sulfoxides. Moreover, it is known that the electrochemically generated superoxide anion is able to convert primary and secondary alcohols into the corresponding carboxylic acids and ketones, respectively.[3] Therefore, the possibility to oxidize selectively primary alcohols to aldehydes by using a safe reagent such as the electrogenerated superoxide/carbon dioxide system seemed interesting, taking into account that the conversion of alcohols to aldehydes is usually performed with chromium complexes,[4] which cannot be considered an environmentally friendly reagent. On this basis, the reactivity of the electrogenerated $O_2^{\cdot-}/CO_2$ system towards representative primary alcohols was investigated. The reaction was then extended to a series of secondary alcohols to verify the limits and scopes of the method (Scheme 1).



Scheme 1

Results and Discussion

The nature and the yields of the products arising from the reaction between benzyl alcohol **1a** and $O_2^{\cdot-}/CO_2$ as a function of the elapsed time before the addition of EtI are reported in Table 1 (entries 1−5).

The maximum yield of benzyl ethyl carbonate is obtained for reaction times ≤1 h. At the same time, the yield of benzaldehyde **2a** undergoes a moderate increase (from 6 to 13%) and significant amounts of starting material remain in the mixture. Upon increasing the reaction time, the amounts of benzyl ethyl carbonate and **1a** decrease, and after 24 h these products are no longer detectable in the solution. In parallel, the yield of **2a** increases (up to 78%) and ethyl benzoate **3a** is also formed. These data suggest that the oxidation process is slower than the competitive carboxylation one, although the former becomes prevalent by increasing the time elapsed before the addition of EtI, possibly favoured by the decomposition of the initially formed carboxylate anion. Other experiments have been

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Table 1. Reactivity of the electrogenerated superoxide/carbon dioxide system towards the primary alcohols **1a−h** (CH_3CN/0.1 mol·L^{-1} TEAP; Hg cathode; Pt anode; E = −1.0 V; substrate = 2 mmol)

Entry	Substrate	n[a]	Time[b]	Products (yield %)[c]
1	**1a**	1.0	3 min.	**1a** (58), **2a** (6), $PhCH_2OCO_2Et$ (25)
2	**1a**	1.0	10 min.	**1a** (51), **2a** (6), $PhCH_2OCO_2Et$ (32)
3	**1a**	1.0	1 h	**1a** (52), **2a** (13), $PhCH_2OCO_2Et$ (33)
4	**1a**	1.0	6 h	**1a** (32), **2a** (38), $PhCH_2OCO_2Et$ (11), **3a** (5)
5	**1a**	1.0	24 h	**2a** (78), **3a** (8)
6	**1a**	0.5	24 h	**1a** (45), **2a** (40)
7	**1a**	1.5	24 h	**2a** (85), **3a** (10)
8	**1a**	2.0	24 h	**2a** (62), **3a** (22)
9	**1a**	1.5[d]	24 h	**1a** (54), **2a** (35), **3a** (2)
10	**1b**	1.5	24 h	**1b** (15), **2b** (61), **3b** (11)
11	**1c**	1.5	24 h	**1c** (21), **2c** (54), **3c** (17)
12	**1d**	1.5	24 h	**1d** (28), **2d** (61), **3d** (2)
13	**1e**	1.5	24 h	**1e** (28), **3e** (67)
14	**1f**	1.5	24 h	**1f** (2), **3f** (97)
15	**1f**	0.25	24 h	**1f** (66), **3f** (8)
16	**1f**	0.5	24 h	**1f** (55), **3f** (19)
17	**1f**	0.75	24 h	**1f** (48), **3f** (25)
18	**1f**	1.0	24 h	**1f** (17), **3f** (70)
19	**1g**	1.5	24 h	**1g** (97)
20	**1h**	1.5	24 h	**1h** (91)

[a] Number of Faraday/mol of substrate. − [b] Elapsed time between the current flow break and the addition of EtI. − [c] HPLC (entries 1−19) or GC (entry 20) analysis. − [d] DMF was employed as solvent.

performed in order to test the influence of both the current amount and the nature of the solvent on the oxidation reaction. The yield of **2a** increases by increasing the amount of current flowing through the cell and reaches a maximum value (85%) at 1.5F/mol of substrate (Table 1, entries 5−8). On the other hand, if *N,N*-dimethylformamide (DMF) is substituted for CH_3CN as solvent under otherwise identical conditions, the yield of **2a** sharply decreases (Table 1, entry 9).

Under optimized conditions of time, current and solvent, the primary alcohols **1b−h** were subjected to the oxidation process. Alcohols **1b−d** are converted into the corresponding aldehydes **2b−d** in good yield, even if the respective acids are also present in the reaction mixtures (Table 1, entries 10−12). Surprisingly, both 4-nitrobenzyl alcohol **1e** and 3-nitrobenzyl alcohol **1f** yield almost quantitatively carboxylates **3e** and **3f**, respectively (Table 1, entries 13,14). Aldehyde **2f** is never detectable in the reaction mixture, even after decreasing the current amount (Table 1, entries 15−18). Although the formation of aldehydic intermediates in the sequence from alcohols to acids can be easily put forward, separate experiments have been carried out to confirm this hypothesis.[5] Under reaction conditions identical to those used in the oxidation of the alcohols, $O_2^{\cdot-}/CO_2$ converts **2f** into **3f** quantitatively but converts **2a** into **3a** only to a limited extent (13%). In order to understand this behaviour, cyclic voltammetry measurements have been carried out for solutions of aldehydes **2a−f** in CH_3CN/0.1 M TEAP at a Hg cathode. The voltammograms of **2a−c** show only one reduction peak (at −1.84, −1.73 and −1.52 V, respectively), whereas that of **2d** presents two reduction peaks at −1.78 and −1.93 V. Finally, in the voltammograms of **2e** and **2f** three peaks are present at −0.70, −1.12, −2.25 V and −1.00, −1.78, −2.25 V, respectively. Under identical experimental conditions, the voltammogram of O_2 shows two reduction peaks, the first of which (at −0.74 V) is related to the one-electron reduction of O_2 to $O_2^{\cdot-}$. It is generally accepted that differences of the reduction potential values as small as those observed in the case of **2e,f** and O_2 allow a fast homogeneous electron transfer to occur.[6] Based on such a process, a mechanism has been proposed to explain the formation of carboxylates during the reduction of α-diketones in the presence of dioxygen in the catholyte.[7] On the assumption that superoxide anion can be released in the solution by the oxidizing agent,[8] a similar mechanism can be applied to the present case. It can explain the formation of the acids that always goes with the aldehydes and that become prevalent when the difference between the potential values allows a fast electron transfer.

Alcohols **1g,h** are stable towards the $O_2^{\cdot-}/CO_2$ system (Table 1, entries 19,20). It is likely that the acidity of the substrate plays a role in the oxidation process whose first step, according to the literature,[3] involves a deprotonation reaction. Previous studies report that electrogenerated superoxide anion oxidizes primary alcohols to the corresponding carboxylic acids independently of their nature.[3a] In order to compare the reactivity of the electrogenerated superoxide anion with the system under study in the same experimental conditions, O_2 was reduced at a mercury cathode and **1a** added to the solution. As expected, HPLC analysis showed that **3a** is the main oxidation product (see Experimental Section). If compared with the data reported in Table 1 (entry 9), these data indicate that the reactivity of the $O_2^{\cdot-}/CO_2$ system as an oxidant is quite different from that of $O_2^{\cdot-}$ alone. In contrast with the behaviour of this latter (see before), the system under study oxidizes only primary alcohols of the benzylic or allylic types. Assuming that their reduction potentials are not too close to that of dioxygen, the corresponding aldehydes are formed in good yields.

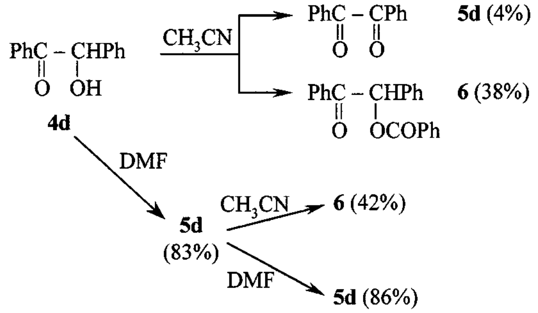
The reactivity of the secondary alcohols **4a−d** towards $O_2^{\cdot -}/CO_2$ has also been tested. At first, 1-phenylethanol (**4a**) was checked with solutions containing different concentrations of the reagent. The results of the analyses of the reaction mixtures are reported in Table 2 (entries 1−8) and show 1.5F/mol of alcohol as the optimum current amount. Once again, if DMF is employed as solvent instead of acetonitrile the ketone yield decreases (Table 2, entry 9). Under these conditions, alcohol **4b** yields the corresponding ketone **5b** in high yield (Table 2, entry 10), whereas the conversion of cyclohexanol **4c** into ketone **5c** takes place in lower yields, significant amounts of starting **4c** being recovered from the reaction mixture (Table 2, entry 11).

Table 2. Reactivity of the electrogenerated superoxide/carbon dioxide system towards the secondary alcohols **4a−c** (CH_3CN/0.1 mol·L^{-1} TEAP; Hg cathode; Pt anode; $E = -1.0$ V; reaction time = 24 h; substrate = 2 mmol)

Entry	Substrate	n[a]	Products (yield %)[b]
1	**4a**	0.2	**5a** (31)
2	**4a**	0.4	**5a** (63)
3	**4a**	0.6	**5a** (71)
4	**4a**	0.8	**5a** (84)
5	**4a**	1.0	**5a** (89)
6	**4a**	1.2	**5a** (95)
7	**4a**	1.5	**5a** (97)
8	**4a**	2.0	**5a** (97)
9	**4a**	1.5[c]	**5a** (41)
10	**4b**	1.5	**5b** (90)
11	**4c**	1.5	**5c** (31)[d]

[a] Number of Faraday/mol of substrate. − [b] HPLC (entries 1−10) or GC (entry 11) analysis. − [c] DMF was employed as solvent. − [d] **4c** (66%) is also present.

It should be pointed out that 2-hydroxy-1,2-diphenylethanone (**4d**) showed a different behaviour. From the workup of the reaction mixture, 1,2-diphenylethan-2-one-1-yl benzoate (**6**) and benzoic acid were isolated together with minor amounts of benzil (**5d**) (Scheme 2, Table 3, entry 1). However, if DMF is employed as solvent instead of acetonitrile the reaction of $O_2^{\cdot -}/CO_2$ with **4d** gives rise to **5d** and benzoic acid (Table 3, entry 2). The nature of the products obtained in acetonitrile suggest a reaction pathway involving a partial oxidation of **4d** to **5d** and a further transformation of this latter to an acylating species capable of converting **4d** into **6**. Benzoic acid is probably formed as a secondary product both from the ester synthesis and the acylating agent decomposition. To confirm this hypothesis, and with the aim of isolating the acylating species, **5d** and $O_2^{\cdot -}/CO_2$ were allowed to react under otherwise identical conditions: in this case compound **6** and ethyl benzoate were isolated (Table 3, entry 3). The formation of **6** from **5d** involves a reduction step to the hydroxy ketone **4d**, which can occur through an electron transfer in solution between $O_2^{\cdot -}/CO_2$ and **5d**.[5−7] The resulting radical anion evolves to **6**, probably through a complex, multistep sequence requiring protonation and acylation. To verify that a protonation step occurs (probably from the solvent), $O_2^{\cdot -}/CO_2$ was generated in DMF and **5d** added to the solution. After 24 h, only **5d** and ethyl benzoate were present in the reaction mixture (Table 3, entry 4). However, if a proton donor [10% CH_3CN or $CH_3CH(CO_2Et)_2$ in equimolar amounts with respect to the substrate] was added to $O_2^{\cdot -}/CO_2$ and **5d** in DMF, compound **6** was formed in concentrations proportional to the acid strength (Table 3, entries 5,6), in agreement with the hypothesis of the solvent involvement in the formation of **6**.



Scheme 2

Conclusion

The electrogenerated superoxide-carbon dioxide system behaves as a selective oxidizing agent. Starting from primary alcohols of the benzylic or allylic types this system allows the formation of aldehydes as the main products of the reaction, provided that the reduction potential of the aldehyde is not too close to that of dioxygen. Benzylic secondary alcohols are converted into the corresponding ketones in excellent yield. Other types of alcohols are stable or only partially oxidized. Within the limits of reactivity discussed above, the use of $O_2^{\cdot -}/CO_2$ as an oxidant presents some advantages: compared with the classical methods

Table 3. Reactivity of the electrogenerated superoxide/carbon dioxide system towards **4d** and **5d** (Hg cathode; Pt anode; supporting electrolyte = 0.1 mol·L^{-1} TEAP; $E = -1.0$ V; $n = 1.5$ F/mol of substrate; reaction time = 24 h; substrate = 2 mmol)

Entry	Substrate	Solvent	Products (yield %)[a][b]
1	**4d**	CH_3CN	**5d** (4), **6** (38), $PhCO_2H$ (58)
2	**4d**	DMF	**5d** (83), $PhCO_2H$ (16)
3	**5d**	CH_3CN	**6** (42), $PhCO_2Et$ (57)
4	**5d**	DMF	**5d** (86), $PhCO_2Et$ (27)
5	**5d**	DMF/CH_3CN[c]	**5d** (69), **6** (5), $PhCO_2Et$ (29)
6	**5d**	DMF/$CH_3CH(CO_2Et)_2$[d]	**5d** (17), **6** (35), $PhCO_2Et$ (67)

[a] (mol of product/mol of substrate) × 100. − [b] HPLC analysis. − [c] 10% (v/v). − [d] Equimolar with the substrate.

based on chromium complexes this procedure does not require toxic or polluting reagents, and shows a much greater selectivity, in terms of both substrate and product selectivity, when compared to superoxide anion only.

Experimental Section

General: The electrochemical apparatus, the cells, and the reference electrode have already been described.[9] The potential values are reported relative to SCE. Acetonitrile (Riedel-de Haën), *N*,*N*-dimethylformamide (DMF; Riedel-de Haën) and tetraethylammonium perchlorate (TEAP; Fluka) were purified as previously described.[10] IR, NMR, HPLC, GC and melting point apparatus were already described.[10] ^{1}H NMR spectra were recorded as solutions in $CDCl_3$, using Me_4Si as internal standard. HPLC analyses were carried out using a Merck Hibar LiChrocart (250−4, 5 μm) RP-18 column. A CH_3CN/H_2O mixture in a linear gradient from 35:65 to absolute CH_3CN over 20 min., followed by an isocratic step at this composition for 5 min., was used as eluent. A CH_3CN/H_3PO_4 0.01 mol L^{-1} mixture in a linear gradient from 0% to 100% of CH_3CN over 15 min., followed by an isocratic step at this composition for 5 min., was used for the analysis of benzoic acid. The flow rate was always 1 mL $min.^{-1}$. GC analyses were carried out using a Supelco Porapack PS 100 packed column (6 feet × 1/8 inch) in the temperature range 50−200 °C. All the quantitative analyses were performed with the internal standard method. In the HPLC analyses *N*-benzylpropanamide was used in the case of **1a**−**b** and **1d**, *N*-phenylpropanamide in the case of **1c**, **1f**, **2a**−**d**, **2f**, **3b**−**d**, **3f**, **4d**, **5b**, **5d** and **6**, *N*-phenylacetamide in the case of **1e**, **2e**, **3e** and **5a**, *N*-benzylacetamide in the case of **1g**, **2g**, **3g** and **4a**, and *N*-benzyl-2-methylacrylamide in the case of **3a** and **4b**. Dimethyl carbonate was used as internal standard for the GC analyses.

Electrochemistry: The controlled-potential electrolyses were carried out in CH_3CN/0.1 mol·L^{-1} TEAP (50 mL) where O_2 and CO_2 were simultaneously bubbling. After the flow of current was stopped, 40 mL of this solution were withdrawn and added to the substrate (2 mmol). The mixture was stirred at room temperature for 24 h.

Benzyl Alcohol (1a): After the flow of 240 C, five aliquots of 5 mL each were withdrawn and added to **1a** (0.25 mmol for each aliquot, in order to obtain 1.0F/mol of alcohol). At different times, a fivefold molar excess of EtI was added, the mixtures were stirred at room temperature for 24 h, and then analyzed. The results of HPLC analyses carried out on these solutions are reported in Table 1 (entries 1−5). Another set of experiments was planned in order to define the optimum current amount to employ. After the flow of 120 C, a sample (5 mL) was taken out and added to **1a** (0.25 mmol, in order to obtain 0.5F/mol of alcohol). Other samples were taken out at different current amounts and treated as above. The solutions were stirred at room temperature 24 h, a fivefold molar excess of EtI was added and after a further 24 h analyzed by HPLC. The current amount values together with the results of the analyses carried out on each solution are reported in Table 1 (entries 6−8). Under the best experimental conditions of current and reaction time, DMF was employed as solvent. The results of the HPLC analyses are reported in Table 1 (entry 9).

2-Furfuryl Alcohol (1b): The electrolysis was stopped after the flow of 360 C, corresponding to 1.5F/mol of alcohol. After 24 h, a fivefold molar excess of EtI was added to the mixture that was stirred at room temperature for a further 24 h and then analyzed. The results of the analysis are reported in Table 1 (entry 10).

Cinnamyl Alcohol (1c): The reaction was carried out as described for **1b**. The results of the HPLC analysis are reported in Table 1 (entry 11).

4-Methoxybenzyl Alcohol (1d): The reaction was carried out as described for **1b**. The results of the HPLC analysis are reported in Table 1 (entry 12).

4-Nitrobenzyl Alcohol (1e): The reaction was carried out as described for **1b**. The results of the HPLC analysis are reported in Table 1 (entry 13).

3-Nitrobenzyl Alcohol (1f): The reaction was carried out as described for **1b**. The results of the HPLC analysis are reported in Table 1 (entry 14). A set of experiments was carried out using different amount of current. The current amount values together with the results of the HPLC analyses performed on these solutions are reported in Table 1 (entries 15−18).

3-Phenyl-1-propanol (1g): The reaction was carried out as described for **1b**. The results of the HPLC analysis are reported in Table 1 (entry 19).

1-Heptanol (1h): The reaction was carried out as described for **1b**. The results of the GC analysis are reported in Table 1 (entry 20).

1-Phenyl-1-ethanol (4a): A set of experiments was carried out in order to define the optimum current amount to employ for the secondary alcohols. After the flow of 120 C a sample (5 mL) was taken out and added to **4a** (0.25 mmol). The mixture was stirred at room temperature for 24 h; 2 mL of 0.01 mol·L^{-1} H_3PO_4 were added to the solution, which was then analyzed. Other samples were taken out at different current amounts. The current amount values together with the results of the HPLC analyses carried out on these solutions are reported in Table 2 (entries 1−8). Under the best experimental conditions of current, DMF was employed as solvent. The results of the HPLC analyses are reported in Table 2 (entry 9).

Diphenylmethanol (4b): The electrolysis was stopped after the flow of 360 C, corresponding to 1.5F/mol of alcohol. After 24 h, 15 mL of 0.01 mol·L^{-1} H_3PO_4 were added to the solution, which was then analyzed. The results of the HPLC analyses are reported in Table 2 (entry 10).

Cyclohexanol (4c): The reaction was carried out as described for **4b**. The results of the GC analyses are reported in Table 2 (entries 11).

2-Hydroxy-1,2-diphenylethanone (4d): The electrolysis was stopped after the flow of 360 C, corresponding to 1.5F/mol of alcohol. After 24 h, a sample (2 mL) was taken out for the HPLC analysis. The remaining solution was diluted with water (150 mL) and extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. On the basis of IR and ^{1}H NMR spectra the residue (0.21 g) was identified as 1,2-diphenylethan-1-one-2-yl benzoate (**6**): m.p. 120−121 °C (ref.[11] m.p.119 °C). The aqueous solution was acidified (HCl) and extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue (0.12 g) was benzoic acid. The results of the HPLC analysis are reported in Table 3 (entry 1). Under otherwise identical conditions, the reaction was even carried out with DMF as solvent. The results of the analysis are reported in Table 3 (entry 2).

Benzil (5d): The reaction was carried out as described for **1b**. The results of the HPLC analysis are reported in Table 3 (entry 3). The reaction was also performed with DMF, a DMF/CH_3CN mixture (9:1, v/v), and DMF containing $CH_3CH(CO_2Et)_2$ (2 mmol) as proton donor. The results of the HPLC analyses are reported in Table 3 (entries 4−6).

Reaction Between $O_2^{\cdot -}$ and 1a: The controlled-potential electrolyses were carried out at −1.0 V in DMF/0.1 $mol \cdot L^{-1}$ TEAP (50 mL) where O_2 was bubbling. The electrolyses were stopped after the flow of 360 C, corresponding to 1.5F/mol of alcohol. At the end of the electrolysis 40 mL of the solution was withdrawn and added to **1a** (2 mmol). The mixture was stirred at room temperature for 24 h. EtI (10 mmol) was added to the solution, which was stirred for a further 24 h and then analyzed. The results of the HPLC analyses showed the presence of **1a** (60%) together with **2a** (5%) and **3a** (25%).

Reaction Between $O_2^{\cdot -}/CO_2$ and 2a,f: The reactions were carried out as described for **1b**. HPLC analyses showed for the reaction of **2a** the presence of starting **2a** (80%) and of **3a** (13%) and for **2f** the quantitative formation of **3f**.

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