Activation of Carbon Dioxide by Electrogenerated Superoxide Ion: A New Carboxylating Reagent

Maria Antonietta Casadei, Stefania Cesa, and Franco Micheletti Moracci*

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma "La Sapienza", P.le Aldo Moro 5, I-00185 Roma, Italy

Achille Inesi*

Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università dell'Aquila, I-67040 Monteluco di Roio, L'Aquila, Italy

Marta Feroci

Dipartimento di ICMMPM, Università di Roma "La Sapienza", Via del Castro Laurenziano 7, I-00161 Roma, Italy

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CO_2 has a long history of use in organic synthesis because it is an inexpensive reagent that is available on a large scale. The thermodynamic stability and relative kinetic inertness of CO_2 require its preliminary activation, and electrochemical techniques provide some solutions to the problem.[1] CO_2 has been activated either by direct (at the electrode) or indirect (through heterogeneous or homogeneous catalysis) reduction. Furthermore, examples of both redox[2,3] and chemical[2,4] homogeneous catalysis have been described. Most of the latter employed transition metals complexes, which can also promote the insertion of CO_2 into suitable organic substrates.[5]

Among the possible activators of CO_2, very little attention has been paid to the superoxide ion, although superoxide-activated CO_2 was suggested to be responsible for the vitamin K-dependent carboxylation of glutamic acid residues of prothrombin.[6] To our knowledge, only two subsequent reports dealing with the system $O_2^{\bullet-}$ + CO_2 are present in the literature. Sawyer *et al.*[7] investigated the reactivity of electrogenerated superoxide ion toward CO_2 in aprotic solvents. Evidence supporting the formation of peroxydicarbonate ion $C_2O_6^{2-}$ as the ultimate reaction product was gained; its tetramethylammonium salt was isolated from a nonelectrochemical reaction between $(Me_4N)O_2$ and CO_2, which allowed its structural characterization. The overall stoichiometry of the process was established (eq 1),

$$2CO_2 + 2O_2^{\bullet-} \rightarrow C_2O_6^{2-} + O_2 \qquad (1)$$

and a reaction mechanism was suggested (eqs 2−4), involving nucleophilic addition of $O_2^{\bullet-}$ to CO_2 as the primary step.

$$O_2^{\bullet-} + CO_2 \rightarrow CO_4^{\bullet-} \qquad (2)$$

$$CO_4^{\bullet-} + CO_2 \rightarrow C_2O_6^{\bullet-} \qquad (3)$$

$$C_2O_6^{\bullet-} + O_2^{\bullet-} \rightarrow C_2O_6^{2-} + O_2 \qquad (4)$$

The formation of $CO_2^{\bullet-}$ as an intermediate by electron transfer from $O_2^{\bullet-}$ to CO_2 was ruled out,[7] owing to the large difference (about 1V) between the reduction potentials of O_2 and CO_2 in aprotic solvents.[8] Hirobe *et al.*[9] investigated the reactivity of the nonelectrochemical KO_2−CO_2 system and evidenced its oxidizing power toward olefins and sulfides which were converted into oxiranes and sulfoxides, respectively. On the basis of isotope incorporation using $K^{18}O_2$ as the reagent, a reaction mechanism involving the $[O_2^{\bullet-}CO_2]$ complex and $CO_2^{\bullet-}$ as intermediates in the formation of a peroxycarbonate radical anion was suggest.

$$O_2^{\bullet-} + CO_2 \rightarrow [O_2^{\bullet-}CO_2] \rightarrow O_2 + CO_2^{\bullet-} \qquad (5)$$

$$CO_2^{\bullet-} + O_2 \rightarrow CO_4^{\bullet-} \qquad (6)$$

This would then evolve to HCO_4^- and/or $HC_2O_6^-$ ions, which were believed to be the oxidizing species.

We have found that the superoxide ion, generated by electroreduction of O_2 in dipolar aprotic solvents, activates CO_2 to give a carboxylating reagent, which is able to convert NH-protic acetamides or propanamides bearing a leaving group at the ω position into oxazole or 1,3-oxazine derivatives, respectively. Carboxamides were selected as the substrate because we previously showed[10] that acetamides of type **1**−**3** (Scheme 1) on treatment with an electrogenerated base in the presence of CO_2 yield oxazolidine-2,4-diones, a class of biologically active substances.[11] The process was supposed to involve an intermediate carbamate ion cyclizing to the product *via* intramolecular S_N2. According to the first of the established procedures (method A), the carboxylation process can be accomplished by reducing a DMF (or MeCN) solution of O_2, CO_2, and the substrate (**1** or **2**) at a potential value ($E = -1.0$ V *vs* SCE) corresponding to the first reduction peak of O_2. At this potential, neither

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Scheme 1

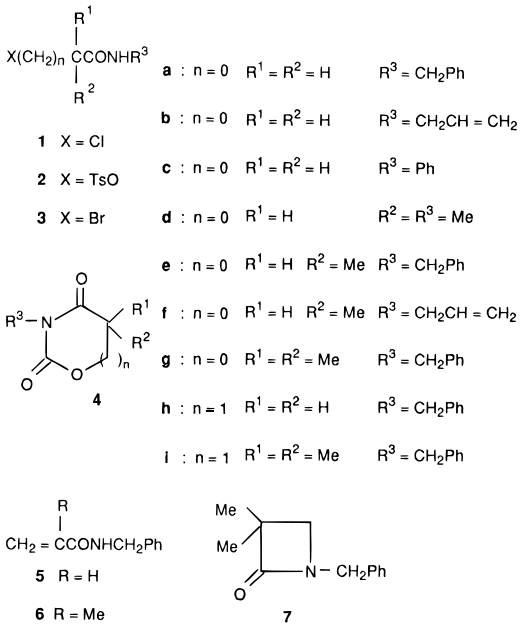

Table 1. Carboxylation of Amides 1 and 2 by Electroreduction of O_2 in the Presence of CO_2 and the Substrate

entry	substrate	SSE[a]/ cathode	*E* or *I*	*n*[b]	products (yield, %)[c]
1	**1a**	A/Hg	−1.0 V	1.0	**4a** (85)
2	**1a**	B/Hg	−1.0 V	1.0	**4a** (86)
3	**1a**	A/C	−1.0 V	1.0	**4a** (87)
4	**1a**	A/C	10 mA cm^{-2}	0.5	**4a** (22), **1a** (68)
5	**1a**	A/C	10 mA cm^{-2}	1.0	**4a** (60), **1a** (32)
6	**1a**	A/C	10 mA cm^{-2}	1.5	**4a** (70), **1a** (17)
7	**1a**	A/C	10 mA cm^{-2}	2.0	**4a** (80)
8	**1a**	A/Hg	10 mA cm^{-2}	0.5	**4a** (48), **1a** (46)
9	**1a**	A/Hg	10 mA cm^{-2}	1.0	**4a** (82), **1a** (12)
10	**1a**	A/Hg	10 mA cm^{-2}	1.5	**4a** (80)
11	**1a**	A/Hg	10 mA cm^{-2}	2.0	**4a** (71)
12	**1b**	A/Hg	−1.0 V	1.0	**4b** (88)
13	**1e**	A/Hg	−1.0 V	1.2	**4e** (64), **1e** (29)
14	**2a**	A/Hg	−1.0 V	1.0	**4a** (94)
15	**2c**	A/Hg	−1.0 V	1.0	**4c** (71)
16	**2d**	A/Hg	−1.0 V	1.2	**4d** (96)
17	**2e**	A/Hg	−1.0 V	1.2	**4e** (98)
18	**2f**	A/Hg	−1.0 V	1.0	**4f** (93)

[a] Solvent-supporting electrolyte system: A = DMF−0.1 M TEAP; B = MeCN−0.1 M TEAP. [b] Faraday/mol of substrate. [c] HPLC or GC analysis.

CO_2 nor the substrate undergoes reduction, thus assuring that the overall process is initiated exclusively by $O_2^{\bullet-}$. The influence of various experimental parameters has been checked by using chloroacetamide **1a** (Table 1, entries 1−11). Under potentiostatic control, high yields of oxazolidinedione **4a** are obtained independent of the nature of the cathode and the solvent (entries 1−3). The nature of the electrode appears to play a role in the electrolyses carried out under galvanostatic control. In fact, when reticulated carbon is used as the cathode, the attainment of high yields of **4a** involves the halving of the current yield (entries 4−7), whereas on a Hg cathode both chemical and current yields are high (entries 8−11). As expected, the nature of both the N-substituent and the nucleofugal influences the yield of **4**. The first being the same, the substitution of chlorine for a tosyloxy group causes an increase in the yield of **4**, which is very sharp when the cyclization involves a secondary carbon (*cf.* entries 14 and 17 *vs* 1 and 13). On the other hand, by

Table 2. Carboxylation of Amides 1−3 by Electroreduction of O_2 in the Presence of CO_2 Followed by Addition of the Substrate[a]

entry	substrate	*n*[b]	products (yield, %)[c]
1	**1a**	1.0	**4a** (65), **1a** (13)
2	**1a**	1.5	**4a** (82)
3	**2a**	1.0	**4a** (94)
4	**2c**	1.2	**4c** (57)
5	**3a**	1.0	**4a** (97)
6	**3c**	1.2	**4c** (36)
7	**2i**	1.0	**7** (89)
8	**3g**	1.0	**6** (27), **3g** (54)
9	**3h**	1.0	**4h** (43), **5** (40)

[a] DMF−0.1 M TEAP, Hg cathode, $E = -1.0$ V. [b] Faraday/mol of substrate. [c] HPLC analysis.

increasing the electron-withdrawing ability of the N-substituent, the yield of **4** sharply decreases, also in the case where the better leaving group is present (entries 14 and 15). These results are consistent with a reaction pathway involving a preliminary deprotonation of the amide NH, followed by carboxylation and cyclization of the resulting carbamate ion. The question arises whether the superoxide itself or basic species arising from its reaction with CO_2 are responsible for the deprotonation of the NH group. Information about the reactivity of the system $O_2^{\bullet-} + CO_2 +$ substrate can be gained by cyclic voltammetry experiments (Hg cathode, $\nu = 0.2$ V s^{-1}). The addition of **1a** to a saturated DMF solution of O_2 ($c = 4.8 \times 10^{-3}$ M) causes an increase of the current value pertinent to the first reduction peak of O_2 which is 40% of the initial value when [**1a**] $= 5 \times 10^{-3}$ M and 50% when [**1a**] $= 1 \times 10^{-2}$ M. Under these condition, the second reduction and the oxidation peaks of O_2 as well as the reduction peak of **1a** disappear. Subsequent addition of **1a** does not further modify the voltammogram. These results indicate that $O_2^{\bullet-}$ is able to deprotonate **1a** according to the known[7] overall eq 7.

$$2O^{\bullet-} + 2\ HA \rightarrow H_2O_2 + O_2 + 2A^- \qquad (7)$$

As reported,[7] the addition of CO_2 to a DMF solution of O_2 modifies the voltammogram of the latter; under our conditions, when $[CO_2]/[O_2] = 4$ the current value of the first reduction peak of O_2 is 5-fold the initial value. Finally, if both **1a** and CO_2 are simultaneously added to the solution of O_2 and the molar ratio [**1a**]/$[CO_2]$ is of the same order of that used during the electrolyses (1:4), the current value is 4- to 5-fold the initial value. As a whole, the voltammetric data suggest that the superoxide preferentially reacts with CO_2 also in the presence of the substrate. To support this conclusion, the electrolytic procedure has been modified in that the substrate is added after the current is switched off and the solution is bubbled with N_2 (method B). Before adding the substrate, the absence of O_2, $O_2^{\bullet-}$, CO_2, and, more generally, any species reducible between 0.0 V and the discharge of the supporting electrolyte was ascertained by voltammetry. According to this procedure, the oxazolidine-2,4-diones are formed in yields comparable with those obtained according to procedure A (Table 2, entries 1−6), thus supporting the starting hypothesis. It should be noted that by using procedure B, substrates bearing an electrophore more easily reducible than O_2 can also be carboxylated, greatly increasing the usefulness of the method.

According to Sawyer,[7] the activation of CO_2 by superoxide would result in the formation of the $C_2O_6^{2-}$ ion as

the final product which, therefore, would be regarded as the reagent responsible for the carboxylation carried out according to procedure B. However, it cannot be excluded that, when proceeding according to method A, other intermediates of the reaction between $O_2^{\bullet-}$ and CO_2, as those described by Sawyer[7] and Hirobe,[9] may be involved in the carboxylation process leading to **4**. Indeed, additional reaction pathways must be operative during carboxylation by procedure A since only in this case was H_2O_2 detected in the electrolyzed solutions (20−25% with respect to the number of Faraday consumed, as ascertained by routine titrimetric analyses).[12] The simplest explanation for the formation of H_2O_2 during procedure A is that competitive deprotonation of the substrate by the superoxide can also occur, although the intervention of other basic species cannot be *a priori* discarded.

To test the effectiveness and generality of the electrochemical procedure of carboxamides carboxylation, a few other experiments were carried out. **1a** was submitted to carboxylation in a nonelectrochemical system containing KO_2, CO_2, and 18-crown-6 ether. If an equimolar amount of KO_2 was used, oxazolidinedione **4a** was obtained in 20% yield; values comparable with those observed in the electrochemical procedures are only attained when using a molar excess of KO_2. Finally, the electrochemical procedure was extended to other NH-protic carboxamides. In principle, any of such substrates bearing a leaving group at the appropriate position should undergo the carboxylation−cyclization process. However, the steric hindrance and the length of the chain (and hence the size of the cycle to be formed) play an essential role in the course of the reaction (Table 2, entries 7−9). Apparently, when the cyclization rate of the intermediate carbamate ion is lowered, competitive reaction patterns become important, owing to the reversibility of the first carboxylation step.

Further studies using different classes of substrates to establish the scope and generality of this new carboxylating procedure are in progress.

Conclusions

A new mild, safe carboxylating reagent is available from the electrochemical reduction of O_2 in the presence of CO_2. When applied to NH-protic carboxamides bearing a leaving group at the carbon atom adjacent to the carbonyl, the procedure affords oxazolidine-2,4-diones in high to excellent yields. The substrate can be added to the solution at the beginning of the electrolysis or, taking advantage of the stability of the reagent, after the current is switched off, thus making the carboxylation process independent of the presence of electrophores in the substrate, which are even more easily reducible than O_2.

Experimental Section

General. The electrochemical apparatus, the cells, and the reference electrode as well as the IR, HPLC and GC instruments were described elsewhere.[13] The values of the working potential are given relative to SCE. Column chromatography (cc) was performed on Merck silica gel 70−230 mesh; ^{1}H NMR spectra were acquired using an AC 200 Bruker spectrometer and Me_4-Si as the internal standard. HPLC analyses were carried out using a Merck Hibar LiChrocart (250-4; 5 μm) RP-18 column; a CH_3CN-H_2O (35:65) mixture was used as the eluent in the analysis of the solutions containing **4a** and **4e**. In all the other analyses, a CH_3CN-H_2O mixture in a linear gradient from 1:9 to 9:1 in 25 min was employed. The flow of the eluent was always 1 mL min^{-1}. GC analyses were carried out using a J and W fused silica megabore DB-WAX (30 m) column in the temperature range 130−150 °C, depending on the nature of the oxazolidinedione. Quantitative HPLC and GC analyses were carried out with the internal standard method using authentic samples of every compounds. *N*,*N*-Dimethylformamide (DMF, Aldrich), acetonitrile (MeCN, Carlo Erba), and tetraethylammonium perchlorate (TEAP, Fluka) were purified as already described.[13] The solution of the supporting electrolyte (0.1 M) in the chosen solvent was percolated on activated alumina just before using.

Reagents. *N*-Benzylchloroacetamide (**1a**),[14] *N*-allylchloroacetamide (**1b**),[15] *N*-benzyl-2-chloropropanamide (**1e**),[16] *N*-benzylbromoacetamide (**3a**),[17] bromoacetanilide (**3c**),[18] *N*-benzyl-2-bromo-2-methylpropanamide (**3g**),[19] and *N*-benzyl-3-bromopropanamide (**3h**)[20] were obtained through the reaction between the opportune chloro(bromo)acyl chloride(bromide) and amine. *N*-Benzyl-*O*-tosylglycolamide (**2a**),[21] *N*-phenyl-*O*-tosylglycolamide (**2c**),[21] *N*-methyl-*O*-tosyllactamide (**2d**),[10] *N*-benzyl-*O*-tosyllactamide (**2e**),[10] and *N*-allyl-*O*-tosyllactamide (**2f**)[10] were synthesized by reacting the corresponding bromo amide with silver toluene-4-sulfonate as previously described.[21]

N-Benzyl-2,2-dimethyl-3-(tosyloxy)propanamide (**2i**) was obtained with the same procedure as an oil: IR (neat) 3330, 1640, 1600, 1530 cm^{-1}; ^{1}H NMR δ 1.22 (s, 6H), 2.44 (s, 3H), 4.01 (s, 2H), 4.40 (d, 2H), 6.05 (s, 1H), 7.2−7.4 (m, 7H), 7.73 (d, 2H). Anal. Calcd for $C_{19}H_{23}NO_4S$: C, 63.17; H, 6.42; N, 3.88. Found: C, 63.37; H, 6.50; N, 3.70.

Electrocarboxylation of 1,2 by reduction of O_2 in the Presence of Both CO_2 and the Substrate (Method A). The controlled-potential electrolyses were carried out at −1.0 V on solutions of the substrate (2 mmol) in DMF(MeCN)−0.1 M TEAP (50 mL), where O_2 and CO_2 were simultaneously bubbling. Under galvanostatic conditions, the electrolyses were carried out at a current density of 10 mA cm^{-2}. At the end of the electrolysis, the solution was stirred overnight at room temperature.[22] A sample of the electrolyzed solution (2 mL) was taken off for HPLC or GC analyses, and the solvent was removed under reduced pressure from the remaining solution. The residue was extracted with Et_2O (5 × 30 mL), H_2O (100 mL) was added to the insoluble portion in ether, and the mixture was extracted with $CHCl_3$ (3 × 50 mL). The extracts were dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The residues were analyzed by IR, ^{1}H NMR, and TLC and were combined if they had the same composition. Column chromatography of the mixtures allowed the isolation of oxazolidinediones **4a**−**f**, which were identified by comparison with authentic samples.[10] The results of the HPLC and GC analyses carried out on the electrolyzed solutions are reported in Table 1.

Electrocarboxylation of 1−3 by Reduction of O_2 in the Presence of CO_2, Followed by Addition of the Substrate (Method B). The controlled-potential electrolyses were carried out at −1.0 V on DMF−0.1 M TEAP solutions (50 mL), where O_2 and CO_2 were simultaneously bubbling. At the end of the electrolysis, N_2 was flowing through the solution for 5 min, the substrate (2 mmol) was added, and the solution was stirred overnight at room temperature.[22] The mixture was worked up as described above. The residue from the reaction of **2i** was

(12) Permanganate and iodimetric titrations have been also used in ref 7 to establish the peroxide content of $(Me_4N)_2C_2O_6$.

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(22) The solutions were analyzed after a 12 h delay to ensure that, independent of the nature of the substrate, the reaction goes to completion.

1-benzyl-3,3-dimethyl-2-azetidinone (**7**).[23] The mixture from **3g** was resolved by cc (petroleum ether−acetone (7:3) as eluent) into the starting amide and *N*-benzylmethacrylamide (**6**).[24] Column chromatography of the mixture from **3h** (chloroform−acetone (9:1) as eluent) gave 3-benzyl-3,4,5,6-tetrahydro-2*H*-1,3-oxazine-2,4-dione (**4h**)[25] and *N*-benzylacrylamide (**5**).[26] The results of the HPLC analyses carried out on the electrolyzed solutions are reported in Table 2.

Carboxylation of 1a with KO_2−CO_2. To a mixture of KO_2 (30 mg, 0.42 mmol) and 18-crown-6 (100 mg, 0.39 mmol) in DMF (10 mL) in which CO_2 was bubbling was added **1a** (71 mg, 0.39 mmol). After the mixture was stirred overnight at room temperature, HPLC showed the presence of **4a** (20%) and unreacted **1a** (68%). Upon an increase in the amount of KO_2 (120 mg, 1.7 mmol) and 18-crown-6 (200 mg, 0.78 mmol), **4a** was formed in 80% yield.

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