Electron transfer in the cathodic reduction of α-dicarbonyl compounds

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Abstract

Electron transfer processes take place during the cathodic reduction, under an argon atmosphere, of different α-dicarbonyl substrates. Carboxylic acids or methylene diesters are obtained from benzil or furil after electron transfer to the oxygen in the air, during the workup, or after electron transfer to the solvent. Involving an electron transfer to dichloromethane, 2-hydroxy-2-hydroxymethyl-2H-acenaphtylen-1-one or benzo[1,3]dioxin-8-one are formed when acenaphthenequinone or 1,2-cyclohexanedione are, respectively, reduced.
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1. Introduction

The electrochemical reduction of α-dicarbonyl substrates has already been studied, from the synthetic point of view, in diaryl-1,2-diketones such as benzil, both, under protic conditions to prepare benzoine[1] or in aprotic media, but in the presence of electrophiles to get dialkylated[2] or diacylated[3] compounds, as well as enediol iminocarbonates.[4]

However, the preparative scaled cathodic reduction of other α-dicarbonyl compounds has been poorly studied. An example is the acylation of 1,2-acenaphthenedione that affords, depending on the employed acylating reagent, the diacylated derivative or a diketopinacol diester.[5] The enediol diester formation from 9,10-phenanthrenequinone or 1,2-acenaphthenequinone has also been performed.[6]

Recently, an easy conversion of *ortho*-quinones into 1,3-dioxoles has been described[7] as a single-step process by cathodic reduction in dichloromethane. In this paper it was demonstrated that the formation of the dioxole did not occur through a nucleophilic substitution in the solvent by the electrogenerated dianion, but through an electron transfer. The yield of the formed 1,3-dioxole did not depend on the use of stronger or weaker nucleophiles, but rather it depends on the formal potential $E^{0\prime}$ (taken as the average of the cathodic and the anodic peak potentials E_{pc} and E_{pa}) of the second reduction peak of the quinone. The more negative $E^{0\prime}$ value of the quinone, the higher yield of dioxole was obtained.

In the present work 1,2-dicarbonyl substrates: benzil (**1a**), α-furil (**1b**), acenaphthenequinone (**1c**), and 1,2-cyclohexanedione (**1d**) have been electrolyzed under aprotic CH_2Cl_2/Et$_4$NCl and potentiostatic conditions to afford, in some cases, non-dioxole products whose formation is rationalized through anion radical species.

2. Results and discussion

2.1. Benzil and α-furil

Cyclic voltammetry of benzil (**1a**) and α-furil (**1b**) in dichloromethane/Et$_4$NCl shows a reversible two-electron reduction peak (see Table 1) with E_{pc} and E_{pa} values of −1.07 and −0.87 V (vs Ag/Ag^+), respectively.

Preparative electrolysis of **1a** afforded, after a charge consumption corresponding to a 2e⁻/substrate molecule process, benzoic acid (**3a**) (30% yield) together with the corresponding methylene diester (60% yield). Similar results were obtained with **1b**.

The electroreduction of benzil to benzoic acid has been, under different experimental conditions, already described in the literature. Some authors[8] assumed that, under open-air

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Table 1
Peak potentials E (V vs Ag/Ag^+) of α-dicarbonyl compounds **1(a–d)** in dichloromethane/Et$_4$NCl as SSE (solvent-supporting-electrolyte system)

1	Substrate	E_{pc1}	E_{pc2}	E_{pa1}	E_{pa2}
a	Benzil	−1.07		−0.96	
b	α-Furil	−0.87		−0.77	
c	Acenaphthenequinone	−0.77	−1.49	−0.74	−1.36
d	1,2-Cyclohexanedione	−1.67			

Scan rate: 50 mV/s, cathode: Pt, anode: Pt.
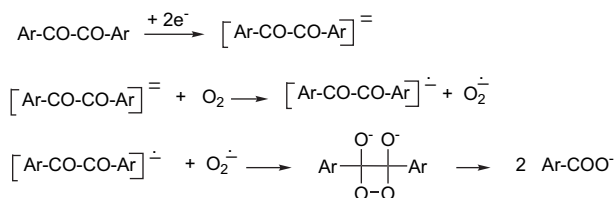
Scheme 1.

atmosphere, the O_2 is cathodically reduced to superoxide anion $O_2^{-\bullet}$, which reacts further with benzil. However, this postulate is ruled out in our process because we have carried out the electrolysis under an argon atmosphere.

Once the reduction was finished, the cathodic solution was elaborated, under open-air atmosphere. Under these conditions, the oxygen transforms the electrogenerated dianion into the corresponding anion radical by electron transfer (the reduction potential of O_2 is −0.85 V versus SCE,[9] less negative than −1.7 V[10] of CH_2Cl_2), at the same time superoxide anion is evolved. Both immediately react to give a dioxetane intermediate that decomposes to the dicarboxylate, as it is indicated in Scheme 1.

The formation of non-isolable dioxetane intermediate has already been suggested[11] in the literature by reduction of the diketone to the corresponding anion radical, at the same time O_2 is electrochemically reduced to superoxide anion $O_2^{-\bullet}$, leading to the dioxetane after coupling of both anion radicals. This possibility is also discarded in our case because we are working under argon atmosphere.

Concerning the formation of the methylene diesters, the following way, as shown in Scheme 2, is proposed.

This proposal is supported by the fact that formal potentials $E^{0\prime}$ (taken as the average of the cathodic and the anodic peak potentials, E_{pc} and E_{pa}) of benzyl and α-furil are −1.01 and −0.82 V (vs Ag/Ag^+), respectively, in both cases higher than −0.8 V and subsequently an electron transfer to the solvent, dichloromethane, can take place.[7] On the other hand, the enolate will acquire the more stable trans-disposition, hindering the formation of the expected 1,3-dioxole.

The mentioned methylene diesters have been chemically obtained by reaction of tetraethylammonium carboxylates with dichloromethane after 4-days refluxing conditions,[12] or by using PEG-600 as catalyst.[13]

2.2. Acenaphthenequinone

Cyclic voltammetry of acenaphthenequinone (**1c**) shows, under anhydrous dichloromethane/tetraethylammonium chloride as SSE, two reversible peaks at −0.77 and −1.49 V (vs $Ag/$
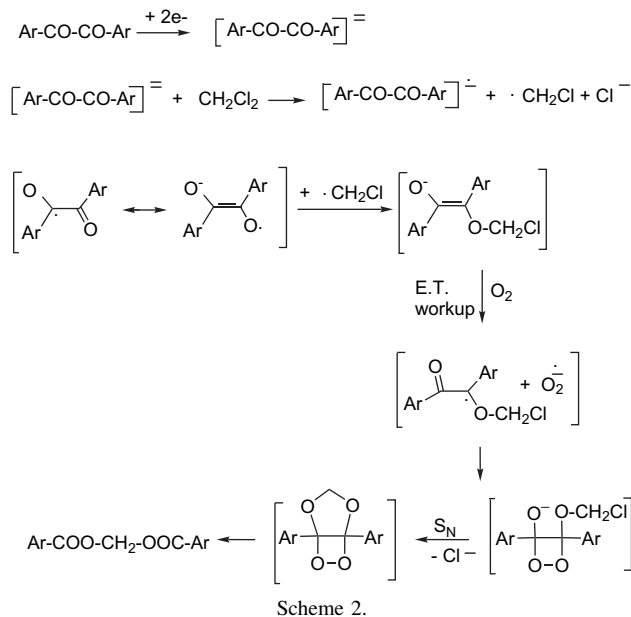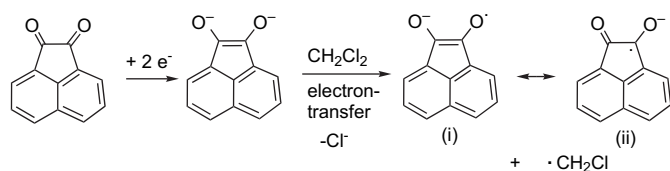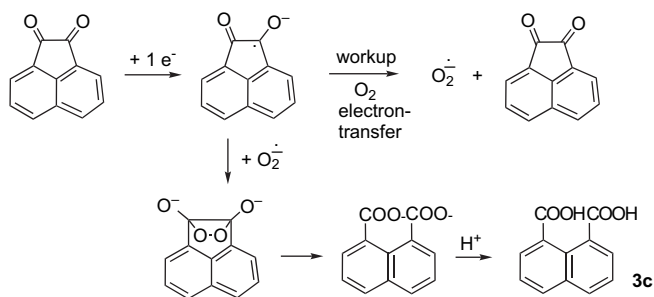

Scheme 2.

Ag^+) as E_{pc1} and E_{pc2}, respectively (see Table 1). The corresponding formal potentials $E^{0\prime}$ are −0.75 and −1.42 V, respectively.

When preparative electrolysis of **1c** was carried out at the constant potential value of the first voltammetric peak, a charge consumption corresponding to a 1 Faraday/mol process is achieved by coulometry. The main obtained product, after treatment of the catholyte, was the starting material, however, some amount (10%) of naphthalene-1,8-dicarboxylic acid (**3c**) was also formed.

Electrolysis of **1c**, carried out at the constant potential value of the second reduction peak, afforded, after a charge consumption corresponding to a 2 Faraday/mol process, 2-hydroxy-2-hydroxymethyl-2H-acenaphthylen-1-one (**2c**, 44% yield) and naphthalene-1,8-dicarboxylic acid (**3c**, 47% yield).

These results can be explained taking into account that the reduction of **1c** at the first voltammetric peak potential affords an anion radical that was not able to transfer one electron to the solvent, CH_2Cl_2. The reason is the formal potential value $E^{0\prime}_1 = -0.75$ V. In a previous work[7] we described that $E^{0\prime}$ values less negative than −0.8 V (vs SCE) do not mediate in the reduction of dichloromethane. However, when this cathodic solution is elaborated, under open-air atmosphere, the main anion radical molecules transfer an electron to the oxygen with a reduction potential considerably less negative than that of CH_2Cl_2. At this time superoxide anion is formed and further coupled with some acenaphthenequinone anion radical molecules, still present in solution, to afford the dicarboxylic acid **3c** (Scheme 3), similar to the previously described procedure for benzil and α-furil.

Preparative electrolysis of **1c** at the second voltammetric peak potential affords the corresponding dianion which evolves to 2-hydroxy-2-hydroxymethyl-2H-acenaphthylen-1-one (**2c**), instead of the expected[7] 1,3-dioxole. The explanation of this result (Scheme 4) is based on the different contribution to the resonance hybrid of the radical anion forms, (i) and (ii).

Scheme 3.

Scheme 4.

The contribution of resonance forms in *o*-quinone anion radicals, as 9,10-phenanthrenequinone (Scheme 5) is well defined. The form (ii) contributes considerably less than **i** to the resonance hybrid, because the aromatization of the ring is not modified in the first one.

However, in acenaphthenequinone the resonance keto-form (ii) contributes higher to the stability of the anion radical than the keto-form in *o*-quinones, due to the fact that now an aromatic ring is not destroyed. The coupling reaction between the anion radical and the chloromethyl radical ˙CH₂Cl, with subsequent nucleophilic attack and further ring opening of the spiro epoxide, affords **2c**, as indicated in Scheme 6.

The formation of naphthalene-1,8-dicarboxylic acid takes place because the electron transfer of the dianion to the solvent is very slow, and some dianion molecules, still present in the workup, transfer the electron to the oxygen of the air. It is supported by the fact that, whether the catholyte is immediately elaborated under open-air atmosphere, or it is allowed to stay for 2–3 h under stirring and argon atmosphere, the yield of **2c** is considerably improved with time, to **3c** expense. The given yields correspond to crudes elaborated after stirring.
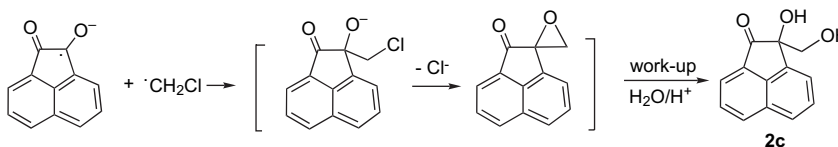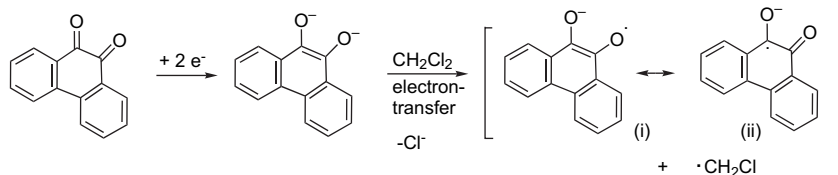
2.3. 1,2-Cyclohexanedione

Cyclic voltammetry of 1,2-ciclohexanedione (**1d**) shows, under anhydrous dichloromethane/tetraethylammonium chloride, an irreversible peak at -1.67 V (vs Ag/Ag^+). This voltammogram is in agreement with the hydrogen evolution experimentally observed in the cathodic compartment when preparative electrolysis of **1d** was carried out at the potential of -1.7 V.

The first electron transfer to **1d** affords an anion radical that evolves to hydrogen and the enolate as shown in Scheme 7. This anion reacts with another substrate molecule, adsorbed at the electrode surface, to give after condensation a new anion, which can be immediately reduced to the dianion
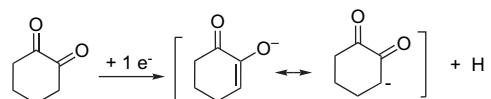
Scheme 7.

(Scheme 8) or can be desorbed, due to its negative charge, from the cathode to the solution, as a tetraethylammonium salt, subsequently protonated during the workup to give 1′-hydroxy-bicyclohexyl-2,3,2′-trione (**3d**), obtained from the aqueous phase as a secondary product (32%). In solution, **3d** is stabilized as the 1,3-diol tautomer form.

An electron transfer from the dianion to the solvent, CH₂Cl₂, allows the formation of the anion radical, chloromethyl radical ˙CH₂Cl, and chloride anion, as shown in Scheme 9. Final coupling of radicals with further intramole-

Scheme 8.
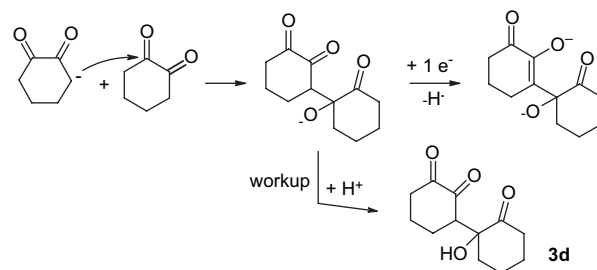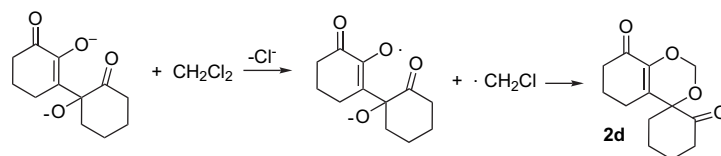
Scheme 5.

Scheme 6.

Scheme 9.

cular nucleophilic substitution afforded a benzo[1,3]dioxin-8-one (**2d**) in 42% yield.

In this case, the electrolysis was finished (the current decreased from 120 to 30 mA) after a charge consumption corresponding to 0.8 Faraday/mol was circulated through the cell, which is in agreement with the yields of the obtained products **2d** and **3d** and with the mechanism proposed to explain their formation.

3. Experimental section

Compounds **1a**–**e** are commercially available and have been used without purification.

3.1. General electrochemical procedure

The electrochemical reductions were performed under potentiostatic conditions in a concentric cell with two compartments separated by a porous (D4) glass frit diaphragm and equipped with a magnetic stirrer. A platinum plate was used as the cathode (9 cm^2) and as the anode (4 cm^2), and a Ag/AgCl electrode as the reference. The SSE was nominally anhydrous dichloromethane containing 0.05 M tetraethylammonium chloride.

A solution of the electroactive α-dicarbonyl compound (3.0 mmol in 60 ml of SSE) was electrolyzed under argon atmosphere (the solution was deaerated by Argon bubbling for 15 min) at a constant potential corresponding to the single reduction peak (**1a**, **1b**, **1d**) or second reduction peak (**1c**). Once the reduction was finished the solvent in the cathodic solution was removed under reduced pressure. The residue was extracted with ether/water and the organic phase dried over Na$_2$SO$_4$ and concentrated by evaporation. The resulting solids were chromatographed on silica gel (22×3 cm) column, using CH$_2$Cl$_2$, CH$_2$Cl$_2$/hex or CH$_2$Cl$_2$/EtOH as eluents. Spectroscopic description of the new compounds is given below. Compound **2c** was characterized as 2-hydroxyketone and **2d** as benzo[1,3]dioxin-8-one. The aqueous phase was acidulated with HCl (5%) and further extracted with ether, dried over Na$_2$SO$_4$, and concentrated by evaporation. From the aqueous solutions were isolated the dicarboxylic acids (**3a**, **3b**, and **3c**) and the 1′-hydroxy-bicyclohexyl-2,3,2′-trione (**3d**).

3.1.1. 2-Hydroxy-2-hydroxymethyl-2H-acenaphthylen-1-one (2c)

(283 mg, 44% yield). Mp 153–155 °C. IR (KBr) ν=3414, 3030, 2923, 1720, 1604, 1493, 1180, 1059, 835, 782 cm^{-1}. ^{1}H

NMR (300 MHz, CDCl$_3$) δ: 2.6 (br s, 2H), 3.92 (s, 2H), 7.65–7.76 (m, 3H), 7.87–7.92 (m, 1H), 7.95 (d, 1H, J=7.0 Hz), 8.13 (d, 1H, J=8.2 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$) δ: 66.7, 79.2, 121.1, 122.5, 125.9, 128.4, 128.8, 130.5, 130.6, 132.3, 137.0, 141.9, 205.1. MS *m/e* (relative intensity) EI: 196 (M$^+$−18, 100), 183 (53), 168 (11), 155 (19), 139 (23), 127 (79), 115 (7), 101 (9), 74 (20), 63 (24), 51 (15). MS *m/e* (relative intensity) IQ: 215 (M$^+$+1, 8), 197 (M$^+$+1−18, 57), 196 (100), 184 (49), 169 (26), 155 (27), 139 (12), 127 (31). Anal. Calcd for C$_{13}$H$_{10}$O$_3$: C, 72.90; H, 4.67. Found: C, 73.07; H, 4.60.

3.1.2. Benzo[1,3]dioxin-8-one (2d)

(297 mg, 42% yield), oil. IR (KBr) ν=3416, 2922, 1714, 1693, 1454 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.62–2.58 (m, 13H), 2.8 (td, 1H, J$_1$=13.6 Hz, J$_2$=6.1 Hz), 4.8 (d, 1H J=6.1 Hz), 5.2 (d, 1H J=6.1 Hz). ^{13}C NMR (75.4 MHz, CDCl$_3$) δ: 20.1, 22.1, 25.7, 27.1, 36.4, 38.1, 38.2, 80.9, 87.4, 132.6, 145.2, 192.4, 207.6. MS *m/e* (relative intensity) EI: 237 (M$^+$+1, 9), 236 (M$^+$, 67), 208 (8), 192 (9), 180 (12), 179 (35), 150 (100), 121 (20), 107 (15), 84 (35), 79 (53), 66 (41), 55 (66). MS *m/e* (relative intensity) IQ: 277 (M$^+$+41, 5), 265 (M$^+$+29, 15), 237 (M$^+$+1, 59), 207 (100), 179 (17). Anal. Calcd for C$_{13}$H$_{16}$O$_4$: C, 66.10; H, 6.78. Found: C, 65.87; H, 6.88.

3.1.3. 1′-Hydroxy-bicyclohexyl-2,3,2′-trione (3d)

(216 mg, 32% yield), oil. IR (KBr) ν=3392, 2927, 1674, 1408, 1310, 1110 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.1–2.60 (m, 14H), 15.0 (br s, 1H). ^{13}C NMR (75.4 MHz, CDCl$_3$) δ: 178.2, 174.0, 164.1, 122.5, 80.1, 34.4, 33.0, 26.4, 26.2, 23.1, 22.7, 22.2. MS *m/e* (relative intensity) EI: 224 (M$^+$, 5), 206 (38), 178 (37), 150 (100), 122 (31), 79 (44), 55 (62). Anal. Calcd for C$_{12}$H$_{16}$O$_4$: C, 64.29; H, 7.14. Found: C, 64.11; H, 6.97.

Acknowledgements

References and notes

1. Stapelfeldt, H. E.; Perone, S. P. *Anal. Chem.* **1968**, *40*, 815; Stapelfeldt, H. E.; Perone, S. P. *Anal. Chem.* **1969**, *41*, 623; Johnson, D. C.; Gaines, P. R. *Anal. Chem.* **1973**, *45*, 1670.

2. Simonet, J.; Lund, H. *Bull. Soc. Chim. Fr.* **1975**, 2547; Boujlel, K.; Simonet, J. *Tetrahedron Lett.* **1979**, *20*, 1497.

3. Adams, C.; Kamkar, N. M.; Utley, J. H. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1767; Guirado, A.; Barba, F.; Manzanera, C.; Velasco, M. D. *J. Org. Chem.* **1982**, *47*, 142.

4. Guirado, A.; Zapata, A.; Galvez, J. *Tetrahedron Lett.* **1994**, *35*, 2365; Guirado, A.; Zapata, A.; Jones, P. G. *Tetrahedron* **1995**, *51*, 3641; Guirado, A.; Zapata, A.; Jones, P. G. *Tetrahedron* **1995**, *51*, 10375; Guirado, A.; Zapata, A.; Andreu, R.; Martiz, B. *Tetrahedron Lett.* **2002**, *43*, 1405.

5. Guirado, A.; Barba, F.; Hursthouse, M. B.; Arcas, A. *J. Org. Chem.* **1989**, *54*, 3205.

6. Guirado, A.; Barba, F.; Tevar, A. *Synth. Commun.* **1984**, *14*, 333.

7. Batanero, B.; Barba, F. *Org. Lett.* **2005**, *7*, 2567.

8. Boujlel, K.; Simonet, J. *Tetrahedron Lett.* **1979**, *20*, 1063.

9. *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Eds.; Marcel Dekker: 2001; p 1205.

10. *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Eds.; Marcel Dekker: 2001; p 254.

11. Feriani, L.; Kossai, R.; Boujlel, K. *Electrochim. Acta* **1991**, *36*, 783.

12. Holmberg, K.; Hansel, B. *Tetrahedron Lett.* **1975**, *27*, 2307.

13. Bhanudas, P. K.; Manikrao, M. S.; Prakash, P. W. *Synth. Commun.* **1997**, *27*, 1703.