

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-acenaphthylen-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 benzoine¹ or in aprotic media, but in the presence of electrophiles to get dialkylated² or diacylated³ 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 described⁷ 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 $E^{0'}$ (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 $E^{0'}$ 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 $\text{CH}_2\text{Cl}_2/\text{Et}_4\text{NCl}$ 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_4NCl 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 authors⁸ assumed that, under open-air

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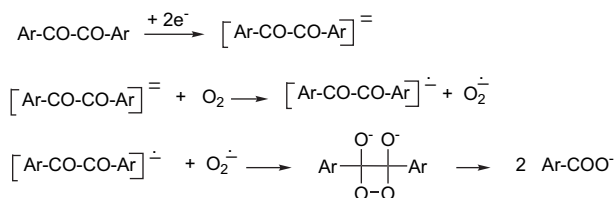
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Table 1

Peak potentials E (V vs Ag/Ag^+) of α -dicarbonyl compounds **1(a–d)** in dichloromethane/ Et_4NCl 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 $\text{O}_2^{\cdot-}$, 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 V¹⁰ 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 suggested¹¹ 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 $\text{O}_2^{\cdot-}$, 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.

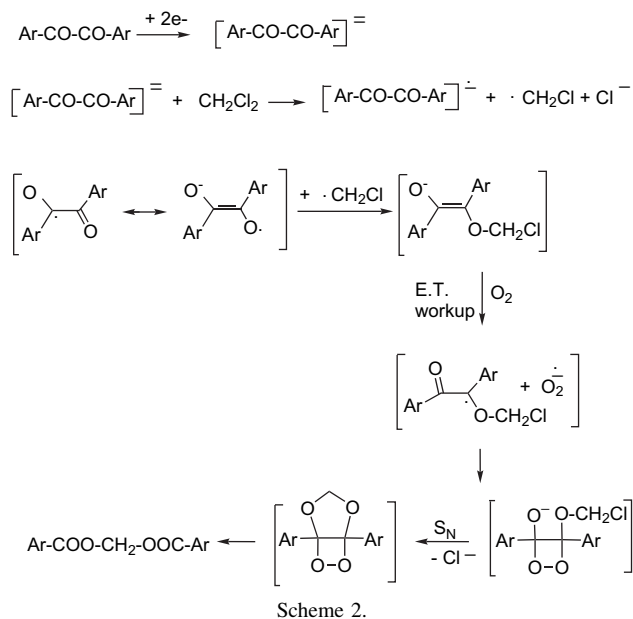
Concerning the formation of the methylene diesters, the following way, as shown in Scheme 2, is proposed.

This proposal is supported by the fact that formal potentials $E^{0'}$ (taken as the average of the cathodic and the anodic peak potentials, E_{pc} and E_{pa}) of benzil 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 $\text{Ag}/$



Scheme 2.

Ag^+) as E_{pc1} and E_{pc2} , respectively (see Table 1). The corresponding formal potentials $E^{0'}$ 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 $E^{0'}_1 = -0.75$ V. In a previous work⁷ we described that $E^{0'}$ 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 expected⁷ 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).

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