Tetrahedron Letters No. 12, pp 1063 - 1066.
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0040-4039/79/0315-1063$02.00/0

ON THE ELECTROCHEMICAL REDUCTION OF α-DIKETONES IN THE PRESENCE OF OXYGEN

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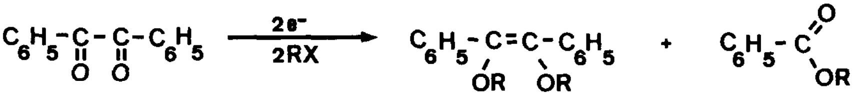
It is known(1) that during the electrolysis of benzil, in the presence of an electrophile such as methyl chloride, some benzoic esters are isolated in addition to the vinyl ethers that one expects :



cis + trans

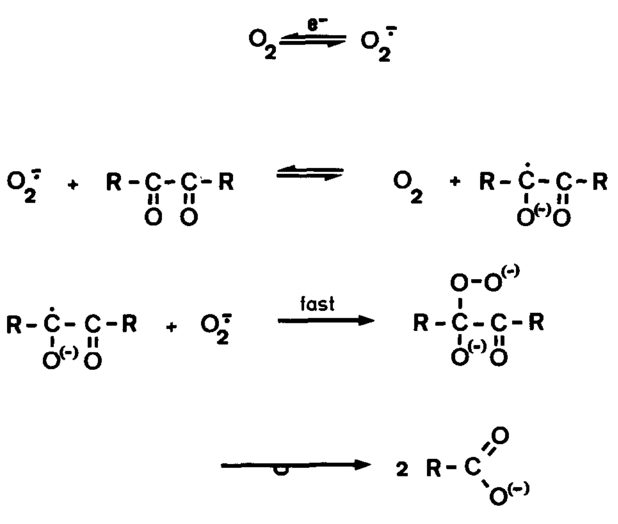
Very recently(2), during an attempt at cyclization with bifunctional electrophiles (1,3 and 1,4-dihalogeno propane and butane), the presence of benzoic esters was confirmed, It was expected that the formation of such esters would be brought about, by the presence, in situ, of oxygen in the catholyte solution readily reduced at the electrolysis potential. Very recent papers(3-6) devoted to the chemical properties of superoxide ion seem to confirm our point of view and prompt us to study more carefully the behaviour of some organic compounds that are easily reducible and lead to a rather stable anion radical. This paper describes the electrochemical reduction of α-diketones. Other works, devoted to the behaviour of activated olefines and aromatics hydrocarbons, will be submitted later.

Experimental results :

Diketones [I] - [VI] were reduced in the dimethylformamide chosen as a typical aprotic dipolar solvent. The redox potentials of these diketones can be compared to the redox potential of O_2 in the same experimental conditions. The potential difference ΔE between the couples diketone/ diketone$^{\bar{\cdot}}$ and $O_2/O_2^{\bar{\cdot}}$ was selected in order to be either very small or rather large. Figure I shows the behaviour of ketones [IV] and [V] according to the value of ΔE. For $\Delta E < 0.3$ volt, the addition of [IV] to the oxygen solution may induce a twofold increase of the current peak corresponding to the reduction of O_2 ; for sufficiently large concentrations the specific step for [IV] appears : it must be stressed that the current is significantly smaller in the presence than in the absence of O_2. For $\Delta E \geqslant 0.5$

volt, it may be noted that the addition of the diketone (for example [V]), does not modify the oxygen reduction current. However, when the potential of the working electrode reaches the zone where the diketone is reduced, the reverse sweep shows for the oxygen step a certain irreversibility.

In the table, it is demonstrated that the electrochemical reduction of α-diketones in an air saturated solution in dipolar aprotic solvents is in fact oxidative, with a cleavage of the -CO-CO- bond. This result was previously obtained with alkali metal superoxides(5,6) for diketones [I] [IV] and [V] in benzene. Let us note that diketones [I] and [IV] have redox potential very close to that of oxygen. For $\Delta E \geqslant 0.5$ volt, electrolyses at the potential of reduction of O_2 are less efficient. The oxidative reduction is only observed in a good yield when the fixed potential of the cathode allows the reduction of the diketone, i.e. when $O_2^{\dot{-}}$ and diketone$^{\dot{-}}$ are simultaneously present at the interface (and later in solution). The work presented here shows clearly that with such carbonyl compounds as [IV] the superoxide ion may act as a reducing reagent, the homogeneous electron transfer being followed by a fast chemical reaction assumed to be a radical coupling.



$$O_2 \overset{e^-}{\rightleftharpoons} O_2^{\dot{-}} \qquad (1)$$

$$O_2^{\dot{-}} + R-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-R \rightleftharpoons O_2 + R-\underset{\displaystyle O^{(-)}}{\underset{|}{\dot{C}}}-\underset{\displaystyle O}{\underset{\|}{C}}-R \qquad (2)$$

$$R-\underset{\displaystyle O^{(-)}}{\underset{|}{\dot{C}}}-\underset{\displaystyle O}{\underset{\|}{C}}-R + O_2^{\dot{-}} \xrightarrow{\text{fast}} R-\overset{\displaystyle O-O^{(-)}}{\overset{|}{\underset{\displaystyle O^{(-)}}{\underset{|}{C}}}}-\underset{\displaystyle O}{\underset{\|}{C}}-R \qquad (3)$$

$$\longrightarrow 2\ R-C\overset{\nearrow O}{\underset{\searrow O^{(-)}}{}} \qquad (4)$$

For $\Delta E \geqslant 0{,}5$ volt, the electron transfer according to the reaction (2) is very slow. The electrochemical methods however allow the fast formation of diketone by means of fixed potential electrolyses and in these conditions reaction (3) may be faster. The mechanism presented here is more probable than the one previously hypothesized(4,5) assuming a nucleophilic attack of substrate$^{\dot{-}}$ on O_2. Electrochemically speaking, it seems very improbable that one would observe at the reduction potential of O_2 or the diketone a further electron transfer to the complex anion radical that has been produced. Concerning diketones [I] [II] or [III] of which redox potentials are more positive than that of O_2 the equilibrium (2) is displaced from right to left. However, the displacement (according to cyclic voltammetries data) appears to be slower than previously. It is assumed that the proposed mechanism is still valid with a slower radical coupling which may have been caused by the rigid structure of the anion radical of these diketones.

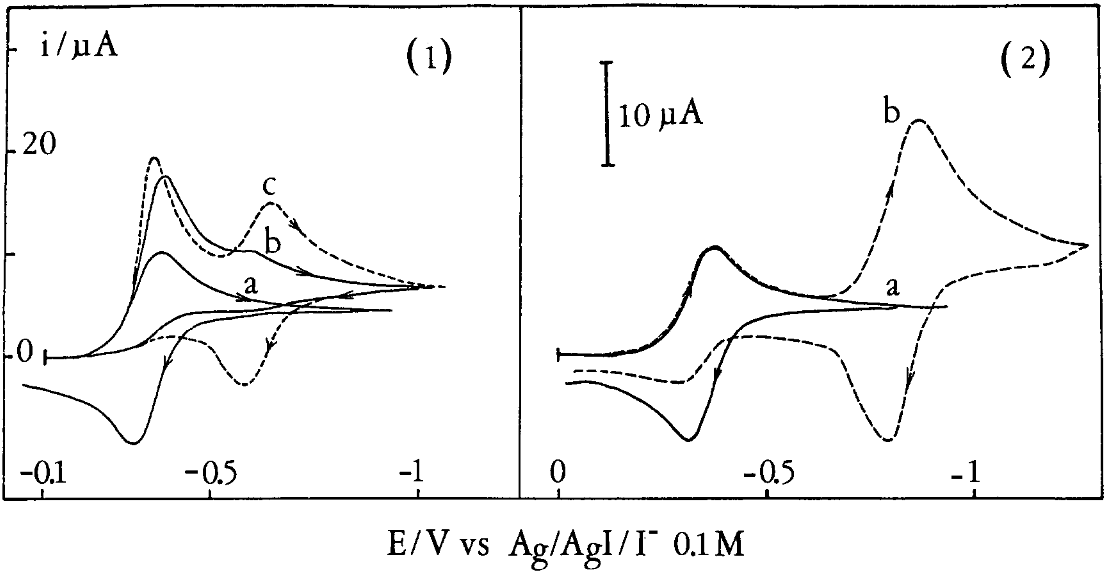


FIGURE : Cyclic voltammetric curve of a saturated solution of oxygen in DMF/Bu_4NClO_4 0.1M. (t° = 25°C). Stationary mercury electrode. Potential sweep rate : 100 mV/s (curves a).

(1) : With [IV] at the concentration of 1.6 mM. (curve b) and 3.2 mM. (curve c).

(2) : With [V] at the concentration of 5 mM. (curve b).

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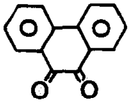
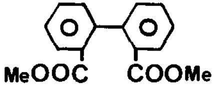
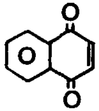
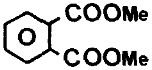
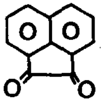
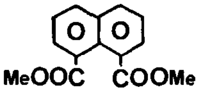
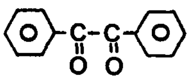
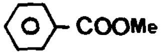
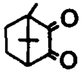
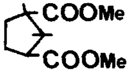
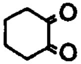
(Received in UK 15 January 1979)

TABLE : Mixed electrolyses of some diketones with oxygen. Volume of the catholyte 60 ml. The solution was saturated with oxygen (t° = 25°C). Working electrode : mercury pool (area 19 cm^2). Reference : Ag/AgI/I$^-$ 0.1M. Supporting electrolyte $Bu_4N^+ClO_4^-$ 0.2 M in aprotic DMF. Concentration of the substrate : 5.10^{-2}M.

a) : Redox potential E° of the first peak

b) : $\Delta E = E°\,(substrate) - E°(O_2)$

c) : After the methylation of the catholyte during the work up.

α-diketones		E°(V) (a)	Cathode potential (V)	ΔE(V) (b)	Coulometry (F.mol^{-1})	PRODUCTS (c)	(yields)
	[I]	- 0.07	- 0.45	+ 0.27	2.0		(73)
	[II]	- 0.12	- 0.45	+ 0.22	2.0		(62)
	[III]	- 0.31	- 0.45	+ 0.03	2.0		(57)
	[IV]	- 0.61	- 0.45	- 0.27 O	2.0		(100)
	[V]	- 0.84	- 0.45 - 0.90	- 0.50	2.0		(54) (82)
	[VI]	- 1.39	- 0.45 - 1.60	- 1.05	2.4	$MeOOC-(CH_2)_4-C$ Me	(22) (33)