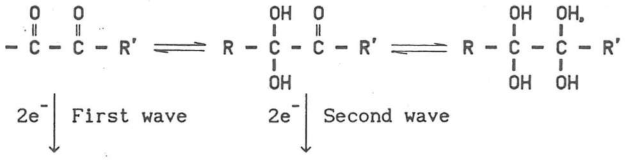
EFFECT OF PROTON-DONORS ON THE ELECTROREDUCTION OF 3,4-HEXANEDIONE

M. Ruiz Montoya and J. M. Rodríguez Mellado

Departamento de Química Física y Termodinámica Aplicada, Facultad de Ciencias, Universidad de Córdoba, 14004-Córdoba (Spain)

The α-dicarbonyl compounds are generally hydrated in aqueous solution, its degree of hydration depending on the nature of the groups adjacent to the dicarbonyl arrangement. Proton-donors are usually involved in the electroreduction processes of these compounds on mercury electrodes [1]. The two polarographic waves observed in most cases, are due to the reduction of both the free and the monohydrated forms:



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R' \rightleftharpoons R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-\overset{\overset{O}{\|}}{C}-R' \rightleftharpoons R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-R'$$

$2e^-\downarrow$ First wave $\qquad 2e^-\downarrow$ Second wave

The reduction of this last species occurs at more negative potentials than that of the first one, and in most cases is overlapped with the discharge of the supporting electrolyte.

The general mechanism of these reduction processes can be described as ECE or CECE, where the rate-determining step at the potentials corresponding to the rising portion of the wave is a protonation reaction involving any proton-donor present in the solution, including the H_3O^+ ion.

This communication deals with the effect of the nature and concentration of proton-donors on the electrochemical reduction of 3,4-hexanedione (I), from which no references have been found in the literature.

I shows in dc polarography a reduction wave below pH 6 and above pH 8, whereas in the pH range 6-8 the polarograms show two very close waves. In the same zone of pH the width of the DP polarograms is greater than those obtained at pH<6 and pH>8. The limiting current of this wave is pH-dependent, as found for other α-dicarbonyl compounds [2], showing the acid-base catalysis of the preceding dehydration reaction.

The half-wave potential of this wave is dependent on both the nature and the concentration of the proton-donors used as background electrolyte.

Portugaliæ Electrochimica Acta, 9 (1991) 211-214

Buffered solutions of citric, acetic + phosphoric, nicotinic and malic acids were used as supporting electrolytes. In all cases the $E_{1/2}$ shifted towards negative values when the pH increases, but the shape of this variation (and the value of the $E_{1/2}$ itself) depends on the supporting electrolyte used. The variations approach roughly to -60 mV/decade, indicating that one H^+ ion is involved in the process, before or in the rate-determining step.

Logarithmic analyses of the wave, made in the form of E vs. $\log[i/(i_L-i)]$ plots, were linear at pH<6 and pH>8, having slopes close to -65 and -40 mV/decade, respectively. The above values were also obtained from the DP polarograms, which were symmetrical. Moreover, the experimental DP polarograms fit acceptably the equation corresponding to first-order processes [3]. The logarithmic analyses show strong deviations from linearity in the pH range 6-8.

From the above data it can be inferred that below pH 6 the rate-determining step must be a chemical reaction placed between the two one-electron transfers. The Tafel slopes (close to -60 mV/decade) together the reaction order with respect to I concentration (close to the unity) support this conclusion.

The influence of the concentration of proton-donors on the reduction process has been investigated. At constant pH and ionic strength the limiting current of the wave remains unchanged when the concentration of proton-donor is increased, indicating that its influence on the rate of the dehydration reaction is low. On the contrary, the half-wave potentials were shifted to less negative values, as is shown in figure 1, indicating that the proton-donors are involved in the reduction process. The reaction orders with respect to the proton-donors vary from zero, at low values of concentration of proton donors, to the unity, at high values of concentration. Moreover, the plots of current vs. proton-donor concentration at potentials corresponding to the foot of the wave, were linear with positive intercepts (figure 2).

Based upon the abovementioned results, it can be concluded that the rds of the process must be a protonation reaction having a rate constant as follows [1]:

$$k = k_0 + k_H c_H + \Sigma k_{HT_i} c_{HT_i} \qquad (1)$$

where k_0, k_H and k_{HT_i} are the rate constants corresponding to the protonation

by water, H^+ ion and proton-donor "i", respectively.

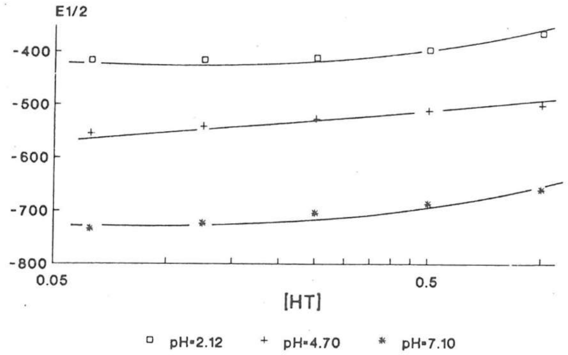


Figure 1. Variation of the half-wave potential with the logarithm of the concentration of proton-donor.

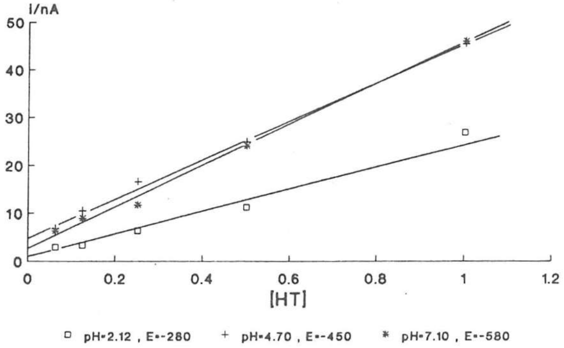


Figure 2. Variation of the current at the foot of the wave with the concentration of proton-donor.

In both cases HT is acetic (pH 4.7) or phosphoric acid.

At potentials corresponding to the foot of the polarographic wave, the cathodic current can be expressed as:

$$i = 2FKK' \, (k_0 + k_H c_H + \Sigma k_{HT_i} c_{HT_i}) c_I c_H \exp(-FE/RT) \qquad (2)$$

where K accounts for the equilibrium constants of both the reactions preceding the rds and the dissociation of the proton-donors in solution, K'accounts for the potential of the reference electrode, and c_I is the concentration of I.

From the above equation it can be easily shown that the results obtained at the foot of the wave agree with the theoretical predictions. In the same way are explained the logarithmic analyses and the variation of the half-wave potential with both the pH and the concentration of proton-donor.

Above pH 8 the polarographic and kinetic parameters show that the reduction process is irreversible, being the rds the second one-electron transfer. The reaction orders with respect to I and to the H^+ ion were 1 and zero, respectively. In the pH range 6-8, both the logarithmic analyses and the shape of the variation of the half-width of DP polarograms with the pH indicate the occurrence of the reduction of two species at very close potentials, and related by a protonation equilibrium. Since the reduction potential of the monohydrated species is much more negative, we can conclude that above pH 8 the electroactive species is the unprotonated form of I.

In this case, the i-E relationship at potentials corresponding to the foot of the wave reads:

$$i = 2FKK'\, c_I \exp[-(1+\beta)FE/RT] \qquad (3)$$

and the proton-donors are not involved in the process, as is experimentally found.

References

1. J. M. Rodríguez Mellado, M. Blázquez and J. J. Ruiz, Electrochim. Acta **31** (1986) 1473 and references cited therein.

2. a) J.M. Rodríguez Mellado, L. Camacho and J.J. Ruiz, J. Electroanal. Chem. **177** (1984) 39; b) J. M. Rodríguez Mellado, J. L. Avila and J. J. Ruiz, Can. J. Chem. **63** (1985) 891

3. J. M. Rodríguez Mellado, M. Blázquez, M. Domínguez and J. J. Ruiz, J. Electroanal. Chem. **195** (1985) 263

Acknowledgements

Financial supports of CICYT (Project PB88-0284) and Junta de Andalucía are gratefully acknowledged.

REDOX PROPERTIES AND LIGAND EFFECTS OF SOME PHOSPHONIUM-FUNCTIONALIZED ISOCYANIDE COMPLEXES OF GROUP VI TRANSITION METAL CARBONYLS

M.T.A. RIBEIRO and A.J.L. POMBEIRO*

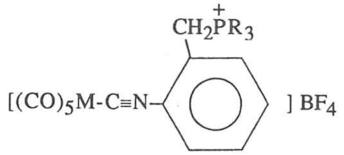
Centro de Química Estrutural, Complexo I
Instituto Superior Técnico, Av. Rovisco Pais,
1096 Lisboa Codex, Portugal

G. FACCHIN, R.A. MICHELIN* and M. MOZZON

Istituto di Chimica Industriale, Facoltà di Ingegneria,
Università di Padova, 35131 Padova, Italy

INTRODUCTION

Within our interest on the electrochemical investigation of the electron-donor/acceptor properties of isocyanide ligands C≡NR (R=H, alkyl, aryl or ferrocenyl-functionalized species) [1], we now report the anodic behaviour of the following complexes presenting phosphonium-functionalized isocyanides, which, to our knowledge, provides the first example of an electrochemical study of coordination compounds with such a type of ligands:



[M=Cr; R_3=Me_3 (1) or Ph_2Bz (2). M=Mo; R_3=Ph_2Bz (3) or Ph_3 (4). M=W; R_3=Ph_2Bz (5) or Ph_3 (6)].

Portugaliæ Electrochimica Acta, 9 (1991) 215-220