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## Control of the electrochemical reduction of horminone by pH imposition in acetonitrile

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### Abstract

An electrochemical study using transient techniques of a quinone-type natural product, horminone, has been performed in acetonitrile in the presence of two buffer solutions of pH = 17.2 and pH = 15.5. Using linear sweep voltammetry, it was found that at both pH values the reduction mechanism of horminone involves a monoelectronic charge-transfer step, followed by a protonation step and homogeneous charge-transfer step due to disproportionation of the protonated intermediate. At pH = 15.5 the mechanism for the homogeneous charge-transfer step was found to be of the DISP1 type (first order disproportionation) from the results of double step chronoamperometry experiments. At pH = 17.2 the latter mechanism was found to be of the DISP2 type (second order disproportionation) since at this pH value the protonation step is minimized, thus causing the disproportionation reaction to be the controlling step of the mechanism.

**Keywords:** Horminone; Electrochemical reduction; Disproportionation; pH control

### 1. Introduction

Horminone (**I**) is a quinone-type natural product. Some derivatives of horminone possess pharmacological properties [1–3]. These properties might be related to the electrochemical behavior of this compound known to occur with this kind of quinone [4]. In addition, the latter behavior is closely related to their acid–base properties, since electro-generated species possess a basic character whose strength depends on their structure and on the acidity level of the solution. In order to understand such a phenomenon, it is necessary to undertake a study of the electrochemical behavior of the horminone in a pH-controlled reaction media. However, to the best of our knowledge, there are no electrochemical studies of this system in acetonitrile (AN) or other solvent of this sort in these or other conditions.

The electrochemical behavior of quinones is compatible with the scheme of a series of consecutive reactions involving proton and electron exchange in order to produce the corresponding hydroquinone. Depending on the medium and the nature of the quinone, the reduction mechanism can be either of the ECE type [5–7] or a disproportionation reaction of the type DISP1 or DISP2 [8]. These mechanisms have been reported in aprotic solvents in the presence of weak acids as proton donors, but nothing has been reported as to the acidity levels in such reaction media in order to inhibit or to enhance a desired mechanism, i.e. to control the path of the electroreduction. In this work, a study of the reduction mechanism of horminone was performed in AN as aprotic medium, in the presence of two different buffer solutions in order to show that acidity levels determine the type of reduction mechanism of the horminone. Linear sweep voltammetry and double potential step chronoamperometry were employed in order to distinguish between these three kinetic situations [8–11], two of first order (ECE, and first order disproportionation (DISP1)) and one of the second order (second order disproportionation (DISP2)).

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