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Reduction of two isomeric oximes of aryl alkyl 1,2-diketones: Difference in products formed in polarography and controlled potential electrolysis

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Abstract

At pH lower than 5 under conditions of d.c. polarography and cyclic voltammetry the oxime $PhCOC(=NOH)CH_3$ does not yield the expected reducible α-aminoketone, but rather a non-reducible olefin derivative. Its formation is attributed to a reduction of a diprotonated form of a ketoimine intermediate. In the same pH-range under conditions of controlled potential electrolysis the olefin derivative is slowly converted in a homogeneous reaction into a reducible α-aminoketone.

Keywords: Polarography; Cyclic voltammetry; Controlled potential electrolysis, Oximes; Reaction intermediates; Tautomers

1. Introduction

If consecutive electroreductions – either of the same electroactive group or of two such groupings – are interposed by a chemical reaction (I), its effects depend both on the rate of such reaction (υ) and on the time-windows of the technique used.

$$A \xrightarrow{\text{el}} B \underset{\upsilon}{\overset{\text{ch.r.}}{\rightarrow}} C \xrightarrow{\text{el}} D \qquad \text{(I)}$$

In the linear sweep voltammetry (LSV) or cyclic voltammetry (CV) this time-window can be variable by controlling the scan rate, but is typically a fraction of a second. In d.c. polarography (DCP) the time-window is given by the drop-time used and is usually between 2 and 5 s. In controlled potential electrolysis (CPE) the chemical reactions involved have usually half-times of the order of minutes.

If the rate of the chemical reaction (υ) is fast when compared to the available time-window, the current of the second reaction step remains unaffected by the rate of the interposed reaction, but the characteristic potential ($E_{1/2}$ or E_p) depends on the rate of the chemical process. If the rate of the chemical reaction is comparable with the available time-window, both the potential and the current of the second reaction step depend on the rate of the chemical reaction. Finally, if the reaction is too slow to result in a significant conversion of the species generated in the first step of the electroreduction, a single wave, corresponding to the reduction in the first step, is observed.

In this communication attention will be paid to systems, where the rate of the chemical reaction is too slow to affect the i–E curves obtained by CV or DCP. In such cases only one wave corresponding to a conversion of A to B is observed. Under conditions of CPE the chemical reaction is, nevertheless, sufficiently fast to produce the reducible product C. In such cases, i–E curves recorded with a small electrode used for analysis during the CPE on a large electrode show a reduction wave of the species C increasing with the time of electrolysis.

Reductions of two groups of compounds bearing two identical electroactive centers belonging to this category

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were reported: one is the reduction of benzil at pH < 8, which occurs in a single two-electron step, corresponding to a reduction to 1,2-dihydroxystilbene. This compound is not reducible in the available potential range, but during the CPE is slowly chemically converted in the bulk of the solution into the reducible benzoin [1–5]. The second group is represented by 1,4-dicarbonylbenzenes, where the diprotonated forms are reduced first to substituted quinonemethides. These species are not further reduced within the available potential range, but are chemically slowly converted into reducible ketols [3,6,7]. In both these cases, the non-reducible species B can undergo electrooxidation. The pH-dependence of its stability can be followed by changes of anodic oxidation waves. Monoprotonated forms of parent compounds follow, on the other hand, the conventional reduction pattern, observed with other aromatic carbonyl compounds. We report a similar reduction sequence involving the reduction of a monoxime of an unsymmetrical 1,2-diketone, the 1-phenyl-1,2-propanedione-2-oxime, $PhCOC(=NOH)CH_3$ **1**.

2. Experimental

The polarographic current–voltage curves were recorded on an IBM EC/225 Voltammetric Analyzer combined with an IBM 7424 MT X-Y-T Recorder. The capillary electrode used had the following characteristics: $m = 2.5\ \text{mg s}^{-1}$, $t_1 = 3.0$ s at $h = 70$ cm. A Kalousek cell with a saturated calomel reference electrode (SCE) separated by a liquid junction was used. A Denver Instrument Model UB-10 pH-meter was used with a glass electrode to determine the pH. 1-phenyl-1,2-propanedione-2-oxime (**1**) was supplied by Aldrich. 1-Phenyl-1,2-propanedione-1-oxime (**2**) was prepared at the Department of Electrochemistry at J. Heyrovský Institute of Physical Chemistry of the Academy of Science of the Czech Republic in Prague. They have been used without further purifications. The 0.01 M stock solutions of investigated oximes were prepared freshly for all compounds in acetonitrile. A 0.01 M stock solution of investigated oximes was added to the buffered supporting electrolyte after deaeration. Gelatin was added to prevent formation of streaming maxima. The final concentration of the investigated oxime in the buffered supporting electrolyte was 0.1 mM, and after brief final purging by nitrogen the current–voltage curves were recorded.

3. Results and discussion

The 1-phenyl-1,2-propanedione-2-oxime **1** is reduced in acidic media in a single four-electron step (i_1). At pH higher than about 4 this wave is accompanied by another wave (i_2) at more negative potential. The limiting current of wave i_2 gradually increases with increasing pH, until at pH about 7 it reaches a value corresponding to a two-electron reduction. This process in wave i_2 corresponds to a reduction of an α-aminoketone, which – in protonated form – is reduced to the corresponding ketone, which can be further reduced at still more negative potentials in waves i_{3a} and i_{3b} (Fig. 1).

In the first two-electron process (1) the oxime **1** is reduced to an imine. The imine, resulting in the first two-electron uptake (1), is in the vicinity of the electrode surface diprotonated (2) and (3). The diprotonated form is reduced (4) into a 1-hydroxy-2-aminoolefin, which is not further reducible within the available potential range in the supporting electrolyte used (5). The presence of an anodic peak on CV proved the formation of 1-hydroxy-2-aminoolefin, which is oxidized most probably to the ketoimine (6).

The monoprotonated form of the ketoimine is reduced, as in the reduction of other oximes [8], to an α-aminoketone (7). This species is further reduced at more negative potentials to an aryl alkyl ketone (8) in a process resembling reduction of other α-aminoketones [9].

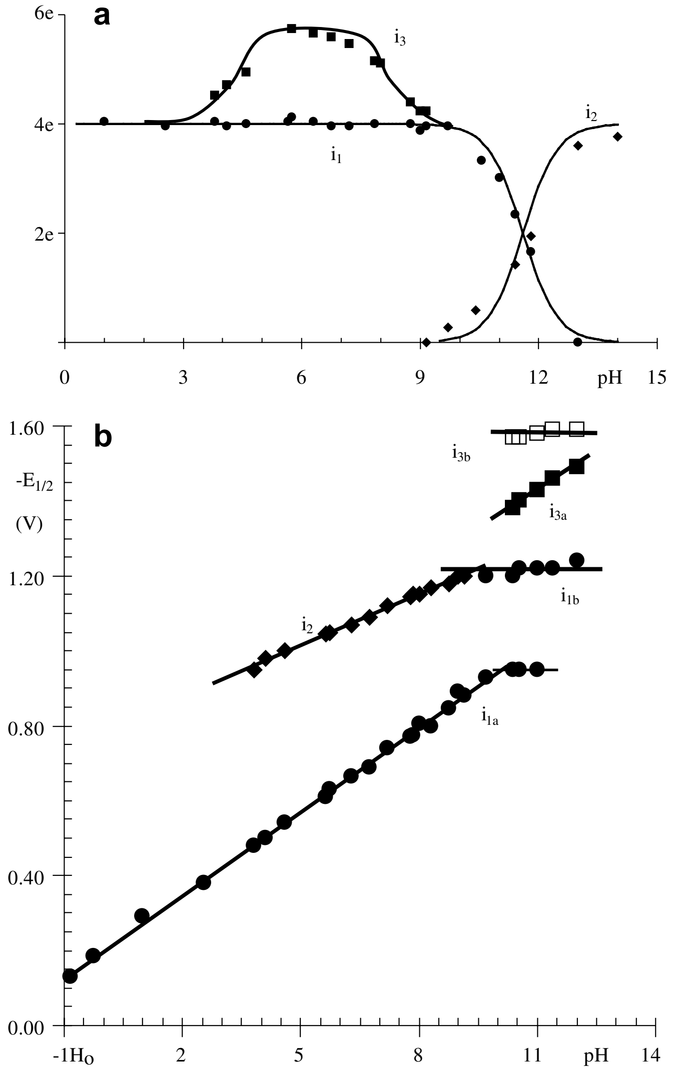

Fig. 1. Dependence of limiting currents (a) and that of haf-wave potentials (b) in solution of 0.1 mM oxime **1** on pH. The current axis indicates corresponding number of electron transferred at the sum of limiting current. Symbols: (a) ● wave i_1, ◆ wave i_2, and ■ wave i_3 (b) ● wave i_1, ▲ wave i_2, and ■ wave i_{3a} and □ wave i_{3b}.