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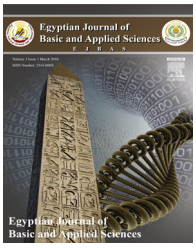

Full Length Article

Square wave voltammetric investigations on 2,2-Dimethyl-1,3-dioxan-5-phenylazo-4,6-dione

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ABSTRACT

The mostly advanced polarographic mode of measurement, square wave (SW), was applied for studying reduction of for 2,2-Dimethyl-1,3-dioxan-4,6-dione (Meldrum acid) and its 5-phenyl-azo substituent in 40% v/v ethanolic universal buffer (pH~ 2–12). At more negative potentials, a 2e pH-dependent wave ($dE_p/dpH = 31$ mv) was assigned to one carbonyl group, while at more positive potentials a 4e pH-dependent wave ($dE_p/dpH = 71$ mv) was assigned to the azomethine group. Based on the polarographic data and acid-base pK_a values were determined spectrophotometrically. The reduction mechanism pathway was suggested. The azomethine group proved to be in the azo form since the nitro group of the p-NO_2 derivative is reduced at a more negative potential than the azomethine linkage. Fair E_p-σ correlation was obtained with positive p values (~0.2–0.3), indicating that the substituents facilitate the reduction process at the dropping electrode.

1. Introduction

The growing interest on the chemistry of β-diketones was early compiled in a book dealing with different chemistry aspects of this class of compounds [1]. The considerable attention for these compounds lies, in view of its wide technical applications, particularly biochemical treatment of thrombosis [2], as anti-inflammatory agents [3] and miticidies [4]. Certain 1,3-indandione derivatives have been used as effective rodenticides [5]. In addition, these compounds are characterized by high conflicting tautomerizing structure. Early in 1908, Meldrum [6] reported that the condensation of malonic acid with acetone anhydride yielded a crystalline while solid which assigned the structure of a monobasic acid, β-dimethyl- β-propiolactone-α-carboxylic acid. This structure proved to be quite wrong, although forty years had elapsed before it was deduced that the condensation must involve only the carbonyl groups of the malonic acid. On this basis Davidson and Bernhard [7] correctly assigned the structure of Meldrum acid as 2,2-Dimethyl-1,3-dioxan-4,6-dione (I) whose properties therefore relate to those of other cyclic 1,3-diones such as dimedone barbituric acid, 1,3-indandione, etc. Although various organic synthesis routes were followed to prove the correct structure of Meldrum acid, physical investigations could emphasize further this view [8,9]. The present work was therefore undertaken with the following objectives:

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i. Emphasizing the β-diketo nature of Meldrum acid by coupling it with diazonium salts. Noteworthy, β-diketones are known to be ready coupling at the CH_2 group in position 2. Moreover, studying the competitive reactivities of the carbonyl and azomethine linkage in the presence of one another.
ii. To illustrate the nature of the possibly tautomeric forms according to the pH of the medium; also discrimination between the nature of the azomethine linkage: azo/hydrazone, via investigating substituent polarographic runs particularly that of the p-NO_2.
iii. Testing the fidelity of linear free energy relationship (LFER) through E_p-σ correlations.

2. Experimental

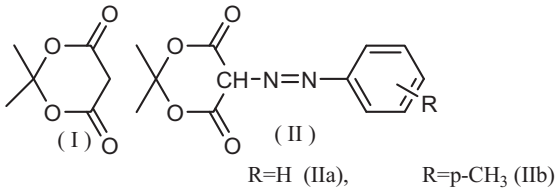
2.1. *Materials, reagents, solvents*

The materials used in this investigation were either Analar grade chemicals (AR) used as supplied, whereas the chemically pure quality reagents were used after proper purification.

2.2. *Organic syntheses*

2,2-Dimethyl-1,3-dioxan-5-phenylazo-4,6-dione(Meldrum acid I) (Fig. 1) was prepared following the "modified Meldrum method" reported by Davidson and Bernhard [7]. To a suspension of 52 g (0.5 mole) of powder Malonic acid in 60 ml (0.6 mole) of acetic acid, anhydride was added, while stirring, 1.5 ml of conc. Sulfuric acid. Largest of the malonic acid dissolved with spontaneous cool. To the resulting solution, 40 ml (0.55 mole) of acetone was added while cooling to maintain the temperature at 20–25 °C. The reaction mixture was allowed to stay overnight in the refrigerator and the resulting crystals filtered by suction and washed three times with sufficient ice water to cover the cake; yield of air-dried product: 35 g (49%). Recrystallization is conveniently effected without heating by dissolving 10 g of the product in 20 ml of acetone, filtering and addition 40 ml of water. The recovery is about 70%, m.p. 94–95 °C.

Compounds IIa–f (Fig. 1) were prepared by conventional coupling diazotized aniline or the corresponding aniline derivatives with Meldrum acid (I). Thus, aniline or the corresponding aromatic amine (20 mmol) was dissolved in 1 ml concentrated HCl and 5 ml of water cooled to 0 °C and then treated with a cold solution of 1.38 g $NaNO_2$ in 5 ml water. The diazotized amine was then added step by step to



R=H (IIa), R=p-CH_3 (IIb)
R=m-OCH_3 (IIc), R=p-Cl (IId)
R=m-NO_2 (IIe), R=p-NO_2 (IIf)

Fig. 1 – Structure of compounds I and II.

an ice cold solution of 20 mmole of Meldrum acid (I) in alcohol, containing sodium acetate (pH 7–9 after coupling), where the corresponding coupling products separates. The reaction mixture was left overnight in a refrigerator, filtered and recrystallized from ethanol. Purity credit was checked by TLC and m.p. and was found concordant with those reported.

2.3. *Polarographic square wave (SW) and cyclic voltammetric investigations*

2.3.1. *Apparatus*

Square wave measurements were recorded with 693 VA processor and 694 VA stand with multimode electrode (MME) (METROHM-SWITZERLAND) product. This relatively up-to-date assembly allows:

i. Three types of mercury electrodes combined in a single unit: HMDE, DME and SMDE.
ii. Program-controlled, automatic switching and mixing of these three electrode configurations during a single analysis via a software commands.
iii. The complete electrode is pneumatically controlled.

2.4. *Solution*

Stock solution 10^{-3} M of the compound to be investigated was freshly prepared by dissolving an accurately weighed amount of material in the appropriate volume of pure ethanol. From this solution the required concentration was prepared by appropriate dilution. For the relatively less soluble compounds (IIe,f; p-& m-NO_2), the least amount of DMF was used. The later does not exceed 0.4% (v/v) of the final solution. Britton-Robinson modified universal buffers [8] (prepared from Analar grade products) were used as supporting electrolyte. The pH value of each buffer was measured using digital pH meter (Hanna, Italy, ± 0.01 pH unit).

2.5. *Measurements*

Ethanol and the appropriate buffer solution were introduced into the polarographic cell. The solution was deoxygenated by bubbling purified nitrogen gas at the rate of 2–3 bubbles for 10 minutes. The calculated volume of depolarizer was then introduced into the cell. Purified nitrogen gas was further passed for 2 minutes.

Peak Potential (E_p) and peak current (i_p): These were read directly on the screen of the processor with ultimate accuracy. All values of E_p are expressed vs. Ag/AgCl electrode.

2.6. *Spectrophotometric determination of the apparent dissociation constant*

Spectrophotometric Measurement in the visible and UV ranges were carried out using processor NUICO 1200– UV/V. Spectrometer UV2.

For the determination of the acid dissociation constant of compound (I), (IIa–f), a fresh solution of the organic reagent