AZO-HYDRAZO TAUTOMERISM: FURTHER EVIDENCE BASED ON POLAROGRAPHIC REDUCTION AND ACIDITY FUNCTION OF SOME HETEROCYCLIC COMPOUNDS CONTAINING OXIMINO-GROUP

By

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تردد مجموعة آزو – هيدرازو : التثبت من الوجود في إحدى الصورتين من دراسات الإختزال البولاروجرافي والداله الحمضية لبعض المركبات اللاحلقيه الحاويه لمجموعة الأكزيم

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درس الإختزال البولاروجرافي وكذلك ثابت التأين الحمضي لـ ١، ٣ – إندان دايون – أحادي الأكزيم وكذا أربعة من مشتقاته الأستبداليه في محاليل منظمه ذات رقم هيدروجيني ٢ – ١١ . وقد أوضحت النتائج وجود المركبات في صوره الآزو نظراً لأختزال هذه المجموعات عند جهود أكثر إيجابية عن مجموعة الأكزيم . وقد أقترح نسخه للأختزال الكهربي للمركبات عند قطب الزئبق المتناقط . وعكست النتائج إنطباق علاقات الطاقة الحره الخطية لقيم جهود نصف الموجه وعدم إنطباقها لقيم ثابت التأمين الحمضي .

Key Words: Polarogrphy, Azo-hydrazo tautomerism, Heterocyclic compounds, Oximino-group.

ABSTRACT

Potentiometric pKa and polarographic behaviour of 1,3-indandione-monoxime-2-phenyl azo and four of its substituted derivatives were investigated in buffer solution of pH ~2-12. The results showed that the compounds are in the azo-form, where its reduction wave precedes that of the oxime. A mechanism for the electrodic processes was proposed. Half-wave potentials showed fair correlation with Hammett's s constants while pKa is practically independent.

INTRODUCTION

The conflict of azo-hydrazo tautomerism in aqueous media has been dealt polarographically. An uptake of 2e in a reversible wave, by compounds capable of existing in both tautomeric forms is taken as an azo form reducing according to the following reaction[1-6].

$$R_1-N=N-R_2 + 2H^+ \rightleftharpoons R_1-NH-NH-R_2$$
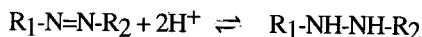
If the reduction of the molecule under investigation consumes 4e, one should be cautious since differentiation between azo/hydrazo tautomeric system on the basis of $E_{1/2}$ can be misleading[7-12]. In such cases the behaviour of the nitro substituent in any location of the molecule has been reported to discriminate both tautomeric forms. The importance of the nitro derivative lies in the fact that literature survey of an azo compound containing a nitro substituent the -N=N- group is reduced before the nitro [3,7,8] group, while if a hydrazone form, C=N-NH- prevails the opposite reduction sequence occurs[9-11]. In a previous work we aimed to approach this point through studying the effect of polarographically active group (namely oxime)[12]. The results showed that in case of acyclic compound the oxime group is reduced first followed by a hydrazone (and not azo) group. Going in this direction it seemed to us worthwhile to investigate the role of the oxime group in conjunction with an azo/hydrazo group in a cyclic compound(I).

I

R : a = H   b = p - CH₃
    c = p - O CH₃   d = p - Cl
    e = m - NO₂
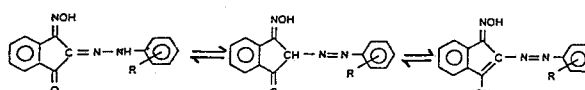
The role of substituent, particularly the nitro derivative on the ease of reduction and acid-base equilibrium was also examined to evaluate the fidelity of applying LFER to the compounds under consideration.

EXPERIMENTAL

Organic Syntheses

The parent compound Ia was prepared following procedures described by Gudriniece and Vanagas[13] by coupling diazotized aniline with 1,3-indandione whereby 2-phenylazo 1,3-indandione is formed which on recrystallization from alcohol separates in fine lustrous deep brown crystals, m.p. 192° C. The latter is then refluxed with hydroxylamine hydrochloride in alcohol for 2 hrs. After cooling Ia is separated, filtered and recrystallized from alcohol whereby Ia (2-phenyl azo-1,3-indandione monoxime) is obtained, m. p. 264-265°C. Following similar procedures compounds I_{b-e} were obtained by coupling the respective diazotized substituted aniline with 1,3-indanedione. Purity credit of the products was checked by microelemental analyses and TLC of the recrystallized products.

Polarographic Investigation
Apparatus

Polarograms were recorded with a pen type recording polarograph (E 506 Metrohm, Switzerland). The capillary possessed the following characteristics in H_2O open circuit:

$t = 4.6$ s drop^{-1}, m= 1.43 mg s^{-1} for h= 40 cm.

Solution

Stock solution (10^{-3} mol L^{-1}) was prepared by dissolving an accurately weighed quantity of material in the appropriate volume of absolute ethanol. Due to the limited solubility of the m-NO_2 derivative (Ie), the material was dissolved first in 5 ml of DMF. Britton-Robinson modified universal buffers[14,15] were used as supporting electrolyte.

Measurements

All experiments were carried out at 25±2°C. The $E_{1/2}$ was measured graphically and expressed vs SCE with an accuracy of ± 5 mV. The solution pH was measured directly after each polarogrpahic run using glass electrode. The later was previously calibrated in ethanolic solutions following the procedures outlined by van Uitert and Hass[16].

Procedure

Ethanol (6 ml) and the appropriate buffer solution (12 ml) were introduced in the polarographic cell and deaerated with a stream of purified nitrogen for 12 min. The calculated amount of stock solution (2 ml) was then introduced into the cell so that the final concentration of depolarizer was 10^{-4} M in 20 cm^3 of 40% (V/V) ethanolic buffer.

Determination of the number of electrons (n)

Controlled potential electrolysis (cpe) was carried out on 200 ml of 10^{-2} mol L^{-1} of Ia at pH 4.2 which is 40% (V/V) ethanolic buffer. The electrolysis cell was 250 ml conical flask with a working area of ~50 cm^2 in which the reference and auxilllary eletrodes and gas inlet were added through a cork. The potential was controlled at 0.060 V vs. SCE (i.e. on the limiting current plateau of wave a). Progress of electrolysis was followed by recording the decrease in current

with time and the number of electrons involved in the electrode process was computed from i-t curves following the method outlined by Lingane[17]. For wave (a) the number of electrons was calculated and found to be 3.87 (n=4). Comparison of the wave-heights of waves (a) and (b) showed that wave (b) is reduced in 4e wave. After complete electrolysis the cell was disconnected and aniline was detected in the electrolysed solution using the anthranilic acid spot test[18].

Determination of apparent dissociation constant by potentiometry

A freshly prepared stock solution of 10^{-3} mol L^{-1} (Ia-e) in 20 ml ethanol was placed in 100 ml beaker, diluted to 40 ml with distilled water so that the final concentration of the studied compound is 5×10^{-4} mol L^{-1} in 50% V/V ethanolic aqueous solution. The latter was then titrated against 10^{-2} mol L^{-1} free-carbonate sodium hydroxide solution with continuous stirring. The constant pH after each base addition was read on a digital pH meter (HANNA HI 9017 microprocessor) accurate to ± 0.01 pH unit. The pKa was then calculated using the well known Henderson-Hasselbach equation[14], by plotting log [A$^-$]/[HA] vs pH values. The intersection of the straight line with the pH axis at log [A$^-$]/[HA] = 0 gave the apparent pKa directly. All experiments were carried out at room temperature, 25±2°C.

RESULTS AND DISCUSSION

With the exception of compound Ie (m-NO_2 substituent) the polarograms of the other members of the series studied displayed two polarographic waves (a) and (b) with equal wave-height in the potential range 0 to -2.0 V (vs. SCE). Schematic polarograms of 10^{-4} mol L^{-1}, 40% V/V ethanolic buffers in the pH range ~2-11 of Ia taken as a representative example is shown in Fig. 1. The more-positive 4e wave a predominates throughout the whole pH range with approximate constant wave height. On the other hand the more negative wave (b) at pH > 5 splits

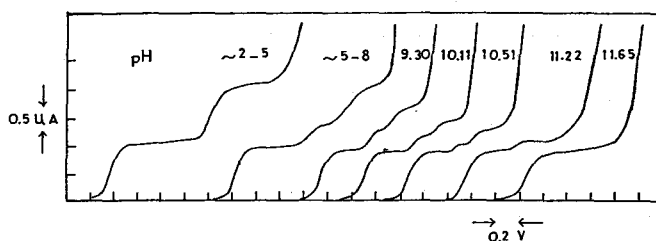Fig. 1. Schematic representation of the polarograms of 10^{-4}M 2-phenylazo-1,3-indandione-monozime 1_a in 40% v/v ethanolic Britton-Robinson buffers.

into two waves b_1 and (b_2) of equal heights and at still higher pH's (pH>8) decreases in height and practically disappears at pH ≥ 11. Effects of varying mercury pressure and depolarizer concentration, at selected pH values indicate that the waves are mainly controlled by diffusion in the region where i_l is practically pH independnt. Test of irreversibility of these waves through logarithmic analysis (log (i/i_l-i) vs f(E) indicated that these processes are irreversible in nature as shown by the values of transition
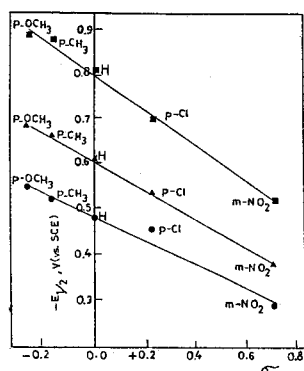
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Table 2
Results of the statistical treatment of the $E_{1/2}$-σ data (wave a) at different pH for compounds I_{a-e}.

pH	p^a	r^b	σd^c	n^d
4	0.256	0.970	±0.0156	5
4	0.312	0.998	±0.0037	5
4	0.387	0.995	±0.0097	5

a) reaction constant b) correlation coefficient
c) standard deviation calculated by[22]
$$S = \pm [\{Sy^2 - (Sxy)^2/Sx^2\}/n-2]^{1/2}$$

Fig. 4. $E_{1/2}$-σ relation for 2-phenylazo, 1-3-indandione-monoxime derivatives at different pH values; ● pH 4; ▲ pH 6; ■ pH 9.

As is clear good linearity was obtained with positive r values varying between 0.256 and 0.387. These values are in accordance with those reported in literature for compounds containing the azo -N=N group[23]. That the nitro-group is reduced after wave (a) is confirmed here by the fact that the point for m-NO$_2$ lies on the $E_{1/2}$-σ curve but not that for m-NHOH (reduced form of the nitro group), an indication that the reducible -N=N-centre is influenced by a nitro and not a hydroxylamine group.

On the other hand trials to correlate pKa values quoted in Table 1 to different σ sets (σ, σ^0, σ^+) showed no dependence. This is to be anticipated since ionization arises at the oxime group (step 1 scheme 2) which is sufficiently far from the substituent in the phenyl ring.

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