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THE POLAROGRAPHIC INVESTIGATION OF 4-NITRO-2'-HYDROXY-5'-TERT-BUTYLAZOBENZENE

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ABSTRACT

The polarographic reduction of the azo dye 4-nitro-2'-hydroxy-5'-tert-butylazobenzene in Britton Robinson Buffer with pH range of 2 and 12 at room temperature has been investigated in aqueous-ethanol solution of ratio 1:1. Two straight lines were obtained from the $E_{1/2}$ -pH plots for the compound. Diffusion controlled reduction behaviour was observed in acid and alkaline media. In addition, a polarographic determination method for the analysis of 4-nitro-2'-hydroxy-5'-tert-butylazobenzene has been developed. The detection limit was 50 pbb for this medium.

INTRODUCTION

Azo dyes are the largest group of organic dyes and constitute more than 35% of the global production of all dyes and thus are used widely by human beings in their living and natural environments. However, azo dyes have toxicological properties and therefore require sensitive, selective methods to determine their physicochemical characteristics (1-3).

Carcinogenic azo dyes have been used for many years in producing liver tumors in rats (4). Because of the suspect that the derivatives of azobenzenes are chemical

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carcinogens even in trace amounts, they may have determinant effects on biological processes.

The studies were mainly concerned with aromatic azo compounds because of (i) the importance of this group in the dyestuff industry, (ii) the interest in carcinogenic properties and (iii) the use of azo compounds for the indirect determination of non-electroactive metals (1).

Early investigation on the polarographic reduction of azobenzene and substituted azobenzenes have been discussed briefly (3-6). The polarographic behaviour of some azo compounds have been studied in aqueous buffer solutions in order to clarify the mechanism of the electrode processes by gathering values for the kinetic parameters. Polarography has also been used to determine azo dyes and their metal complexes and the diffusion coefficients (7-9). In the present work the polarographic reduction of newly synthesized 5-nitro-2'-hydroxy-5'tert-butylazobenzene has been studied and the mechanism of reduction and optimal conditions for analytical determinations have been discussed. This compound has not been investigated so far by polarographic techniques.

EXPERIMENTAL

The synthesis and spectroscopic properties of 4-nitro-2'-hydroxy-5'-tert-butylazobenzene were reported elsewhere (10,11). 500 ppm stock solution of the azo compound in ethanol has been prepared. Britton Robinson Buffer and absolute ethanol (1:1) solution with different pH values was used as supporting electrolyte. 100 µl of the stock solution was added to 10 ml of electrolyte at different pH values. Differential Pulse Polarograms (DPP) of the samples were obtained on a EG&G Princeton Applied Research (PAR) Model 384 B Polarographic analyzer. Scan rate, purge time and pulse height were chosen as 4 mV/s, 240 s and 0.050 V, respectively.

RESULTS AND DISCUSSION

Two peaks are clearly seen on the differential pulse polarograms (DPP) at the pH range between 2 and 12 which belong to the two electroactive groups, $-NO_2$ and -N=N-. At the pH value of 4.65 the first peak (-N=N-) has an $E_{1/2}$ value of -0.384 V (vs Ag/AgCl) and the second peak has an $E_{1/2}$ value of -0.716 V (vs Ag/AgCl), respectively (Figure 1).

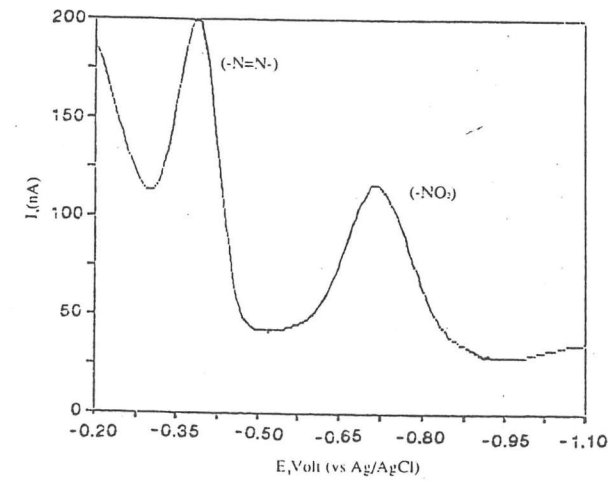

Figure 1. Polarograms of the azo compound in Britton-Robinson 1:1 ethanolic aqueous buffered solutions of pH 4.65.

The I/pH Relation

The reduction current of azo gruop (-N=N-) in acid media (pH=2.00-7.00) exihibited similar behaviour in alkaline solutions (pH=7.00-12.00). The Limiting current was approximately the same.

$E_{1/2}$ - pH Curve

The DPP data obtained for the azo compound (20 °C) are shown on Table 1. The

Table (1). DPP data obtained for the azo group (-N=N-) determined for the azo compound (20°C).

pH	$E_{1/2}$	nF/RT	n	Z_H'
4.00	-0.344	82.21	2.08	2.10
5.20	-0.416	82.79	2.09	2.11
6.30	-0.484	79.85	2.02	2.04
7.10	-0.536	82.07	2.07	2.09
8.30	-0.600	82.86	2.09	2.11
9.00	-0.640	81.77	2.06	2.08
9.95	-0.688	83.72	2.11	2.13
10.60	-0.724	84.69	2.14	1.36
11.20	-0.748	80.53	2.03	1.29
11.75	-0.772	81.54	2.06	1.31
12.10	-0.780	82.64	2.09	1.32

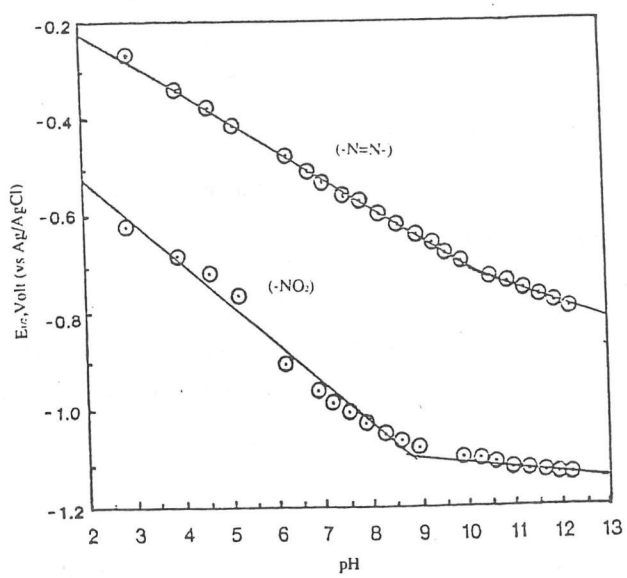

Figure 2. pH dependence of the $E_{1/2}$ for the azo compound.

$E_{1/2}$ values of reduction waves belonging to -N=N- and $-NO_2$ groups shift to more negative potentials with increasing pH, denoting that electrode reaction involves H^+ ions (Figure 2) (3-5). The slopes of the $E_{1/2}$ / pH plots show slight change near pH 10.5 for -N=N- and near pH=8.8 for $-NO_2$ groups.

These facts are indicating that electrode reactions change on passing from these pH values. The slope of curves are 0.059 and 0.037 for -N=N- group and 0.083 and 0.012 for $-NO_2$ group. From the relation given below (12);

$$E_{1/2} / pH = 0.059\ Z_H' / n$$

it can be concluded that the number of electrons consumed equals to that of the protons contributing to elecrode reaction of -N=N- group in pH=2.0-10.5. The observed shift of the 4-nitro-2'- hydroxy- 5'-tert-butylazobenzene peaks to more negative potentials with increasing acidity is in agreement with the following relationship given for -N=N- group in the pH range 2.00-10.50 ;

$$E_{1/2} = -0.108(\pm0.006) - 0.059(\pm0.0006)\ pH$$

(correlation coefficient, r= 0.999) and in the pH range 10.50-12.00 by

$$E_{1/2} = -0.369(\pm0.0026) - 0.037(\pm0.003)\ pH$$

(correlation coefficient, r=0.991) for -N=N- group. The relationship for the reduction of $-NO_2$ group may be given similarly,

$$E_{1/2} = -0.362(\pm0.028) - 0.083(\pm0.004)\ pH \quad (pH\ 2.0\text{-}9.5)$$

(correlation coefficient, r=0.986) and

$$E_{1/2} = -0.983\ (\pm0.004) - 0.012(\pm0.002)\ pH \quad (pH\ 9.0\text{-}12.0)$$

(correlation coefficient, r=0.920).

The characteristics of this dependence may be explained in terms of preprotanation of the azo group (3,4). This leads to a decrease in the electron density around the -N=N- bond facilitating the reduction process.

Reversibility of the waves

The fundamental equation for testing thermodynamic reversibility of the waves is (13);

$E_{dme} / \log (I/I_d-I) = 0.0591/n$ at 25 °C

The E_{dme} versus log (I/I_d - I) plots for -N=N- group were linear with correlation ceofficients around 0.99. The slopes of the lines, number of electrons and protons consumed were calculated and displayed in Table 1.

The slopes of the E_{dme} vs log (I/I_d-I) plots indicate that the electroreduction of the azo grup is reversible. The number of electrons consumed is 2 in acidic and alkaline media.

The graph of $E_{1/2}$ vs. pH shows linear character. The number of protons (Z_H') participating in the rate determining step was computed from the slopes of $E_{1/2}$ vs pH as well as the slopes of E vs. Log ($I/(I_d-I)$ according to equation (13);

$Z_H' = (E_{1/2} / pH) / (0.0591/n)$ at 25 ^oC

The values of Z_H' were found to be similar to the number of electrons in the first part of the curves (Figure 2) but after inflection point (pH=10.5), the Z_H' values were around 1.3 denoting the number of electrons consumed higher than the number protons. The results are given in Table 1.

Cyclic Voltammetry

Cyclic voltammograms of 4-nitro-2'-hydroxy-5'-tert-butylazobenzene on hanging mercury drop electode are shown in Figure 3, indicating the reversible course of reduction of azo group in this azo compound. The reduction of nitro group is irreversible as seen in Figure 3. Anodic peak was observed on the cyclic voltammograms for the azo group but not observed for nitro group.

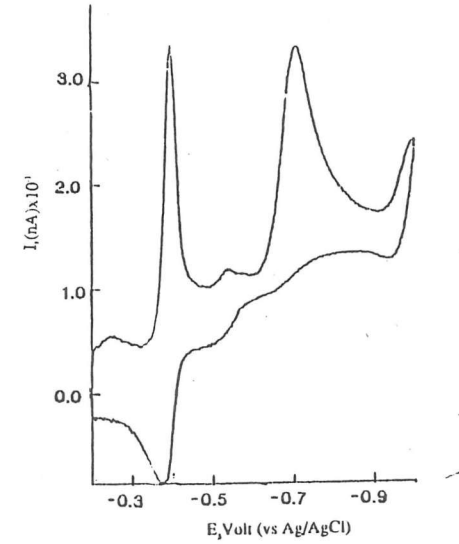

Figure 3. Cylic voltammograms pH at 4.5.

Reduction Mechanism

Reduction mechanisms of aromatic azo compounds are usually as follows (1);

$R_1 - N = N - R_2 + 2H^+ + 2e \longrightarrow R_1 - NH - NH - R_2$

In our study the constancy of n values and limit current values for pH intervals during the study show that the azo compound has been turned into a hydrazo compound. Therefore the reduction process takes place through the hydrogenation of -N=N- centre of the azo compound and two electons were consumed in this process.

Analytical Applications

To test the validity of Ilkovic eqution (12,13) and the applicability of the polarographic method for the determination of the azo compound, the values of the total limiting current are plotted versus the concentration of the organic compounds at the pH 9.00 (Figure 4).

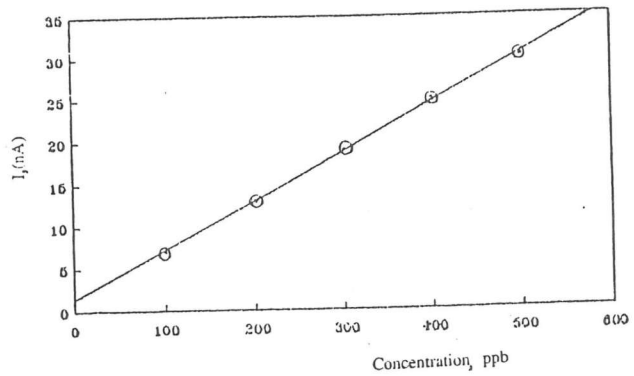

Figure 4. Current concentration dependence for the azo compound.

Satisfactory linear relations are obtained at different pH's. The straight line equation which obtained by the regression analysis is as follows;

$$Y = (1.4 \pm 0.4) + 0.116\ (\pm 0.002)\ X$$

(correlation coefficient r= 0.998). As a result it has been found that differential puls polarographic analysis is a rapid and reliable method for both qualitative and quantitative analysis of 4-nitro-2'-hyroxy-5'-tert-butylazobenzene.

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