

## The electrochemical reduction of o-nitrotoluene to o-tolidine. II. Voltammetry and reaction mechanism

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# THE ELECTROCHEMICAL REDUCTION OF *O*-NITROTOLUENE TO *O*-TOLIDINE—II. VOLTAMMETRY AND REACTION MECHANISM

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**Abstract**—*O*-tolidine obtained by reduction of *o*-nitrotoluene is used in the production of dyestuffs. Various steps in this reduction have been investigated by means of controlled-potential electrolysis and measuring voltammograms at rotating disc electrodes. Results of the first types of experiments are already published and those of the latter type are presented in the recent paper. Voltammograms are measured for the reduction of nitrotoluene, azoxytoluene and azotoluene with various electrode materials in alkaline ethanol-water solution and in alkaline aqueous solutions containing McKee salt and for the reduction of azoxytoluene and azotoluene in acidic ethanol-water solutions as well as in acidic aqueous solution containing McKee salt and acid. The reduction wave of nitrotoluene does not correspond to a single product reaction, whereas those of azoxytoluene and azotoluene correspond to a single-product process, respectively. It has been found likely that dimerization of the intermediate nitrosotoluene radical anion occurs on formation of azoxytoluene. This conclusion strongly deviates from the Haber scheme mostly proposed for the reduction mechanism of aromatic nitro-compounds and supports that of Fry.

## NOMENCLATURE

$A$	Surface area of electrode
$c^*$	Concentration of species in bulk solution
$D$	Diffusion coefficient
$E$	Cathode potential vs sce
$F$	Faraday constant
$i$	Current
$i_l$	Limiting current
$n$	Number of electrons involved in electrode reaction
$\nu$	Kinematic viscosity
$\omega$	Angular velocity of rotating-disc electrode

## 1. INTRODUCTION

The electrochemical reduction of *o*-nitrotoluene (nitrotoluene) to *o*-tolidine (tolidine) has been studied extensively. Results of controlled-potential electrolysis of nitrotoluene and its reduction compound 2,2'-dimethylazoxybenzene (azoxytoluene) are already published [1, 2]. Results of voltammetric experiments are presented in this paper.

In contrast to nitrobenzene, there is a lack of data on voltammetric reduction of nitrotoluene and azoxytoluene in alkaline solutions; they are presented here.

## 2. EXPERIMENTAL

The experiments were carried out in a thermostatted glass cell with an air-tight test compartment of 150 cm<sup>3</sup>, separated from the other compartment by an ion-exchange membrane (Naphion 425). All potentials are given vs the saturated calomel electrode, used as reference electrode. The test electrodes were of the rotating-disc type (diameter 0.60 cm) in a Kel-F holder; rotation speed between 5 and 33 rev/s. The counter-electrode was a 1 cm<sup>2</sup> platinum sheet.

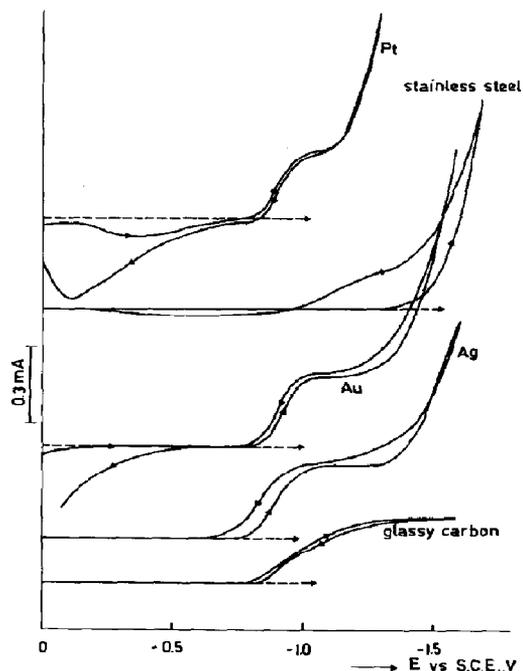


Fig. 1. Voltammograms of nitrotoluene on rotating-disc electrodes, made of Pt, stainless steel, Ag, Au or glassy carbon, in an ethanol-water solution (volumetric ratio 98:2) containing 1 mM nitrotoluene and 0.4 M NaOH. Electrode surface: 0.283 cm<sup>2</sup>, temperature: 50°C, rotation speed: 5 rev/s, sweep rate: 20 mV/s, starting potential: 0 V and the other limits of potential sweep: -1500 mV for Pt, -1700 mV for stainless steel and -1600 mV for Au, Ag and glassy carbon. The horizontal arrow indicates the zero current for the corresponding voltammogram.

The solution of the test compartment was made oxygen-free by bubbling argon through it for 20 mins. Argon was saturated by being passed through the same solution without substrate.

The voltammograms were obtained with a Wenking potentiostat, type 68 Fr 0.5, in combination with a Wenking linear voltage scan generator, type VSG 72; the curves were recorded with a Philips X-Y recorder, type PM 8120.

### 3. RESULTS

#### 3.1. Nitrotoluene

3.1.1. *Alkaline ethanol-water solution.* Voltammograms of nitrotoluene in alkaline ethanol-water solution were determined for various electrode materials, as Ag, Au, Pt, glassy carbon and stainless steel. Results are given in Fig. 1. The shape of the voltammogram depends strongly on the nature of the electrode material. The cathodic wave is well defined and of about the same height for Pt, Au, and Ag. The cathodic wave at glassy carbon appears to be split up, its total height being, however, practically the same as that of the properly shaped waves. No clearly-shaped wave has been obtained for stainless steel; moreover, the direction of potential sweep strongly affects the voltammogram.

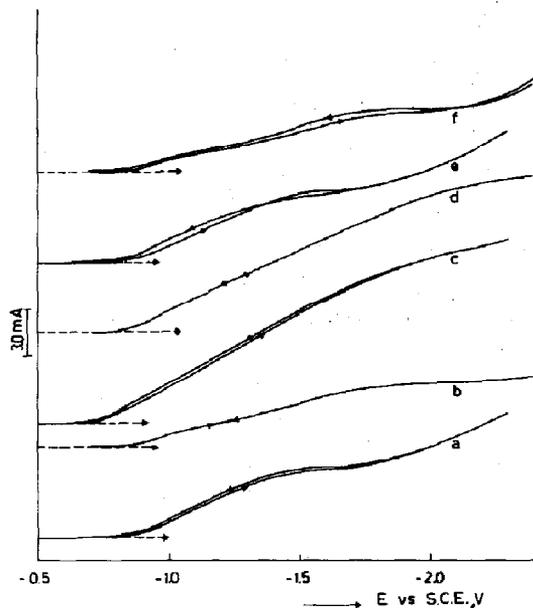


Fig. 2. Voltammograms of nitrotoluene on rotating-disc electrodes of gold [(a), (c) and (e)] and of glassy carbon [(b), (d) and (f)] in an ethanol-water solution (volumetric ratio 98:2) containing 10 mM [(a), (b), (e) and (f)] or 25 mM [(c) and (d)] nitrotoluene and 0.4 M NaOH. Electrode surface: 0.283 cm<sup>2</sup>, temperature: 50°C, rotation speed: 5 rev/s, sweep rate: 20 mV/s [(a), (b), (c) and (d)] and 200 mV/s [(e) and (f)], starting potentials: -500 mV [(a), (c)] and -700 mV [(b), (d) and (f)] and the other limits of potential sweep: -2300 mV [(a), (c) and (e)] and -2500 mV [(b), (d) and (e)]. The horizontal arrow indicates the zero current for the corresponding voltammogram.

The effect of nitrotoluene concentration and of sweep rate on shape and height of the voltammogram for gold and glassy carbon electrodes is shown in Fig. 2. The waves on a glassy carbon electrode show a clearer splitting up than those represented in Fig. 1.

From the voltammograms for various nitrotoluene concentrations (1–25 mM; Figs 1 and 2) it follows that the limiting current,  $i_l$ , of nitrotoluene reduction, increases linearly with increasing nitrotoluene concentration. The limiting currents at both sweep rates, viz. 20 and 200 mV/s, are equal (Fig. 2). Moreover, it has been found that the limiting current of nitrotoluene reduction is proportional to the square root of angular velocity of the disc electrode and decreases with increasing NaOH concentration (0.1–1.0 M), corresponding to the increase in kinematic viscosity.

The effect of temperature on voltammograms for a gold electrode is shown in Fig. 3. This figure shows that the limiting current increases strongly with increasing temperature.

Voltammograms of nitrosotoluene and of toluene hydroxylamine should be valuable for elucidating the mechanism of nitrotoluene reduction. It was impossible to measure these voltammograms since both compounds were destroyed within a few minutes in an ethanol-water solution having a volumetric ratio of 98:2 containing 0.4 M NaOH.

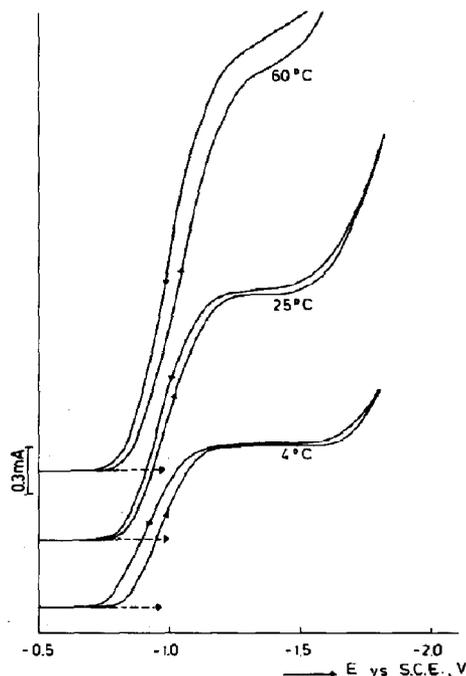


Fig. 3. Voltammograms of nitrotoluene on a rotating-disc electrode of gold at various temperatures and in an ethanol-water solution (volumetric ratio 98:2) containing 5 mM nitrotoluene and 0.4 M NaOH. Electrode surface: 0.283 cm<sup>2</sup>, rotation speed: 5 rev/s, sweep rate: 20 mV/s, starting potential: -500 mV and the other limit of potential sweep: -1800 mV. The horizontal arrow indicates the zero current for the corresponding voltammogram.

3.1.2. *Alkaline aqueous solution containing McKee salts.* Voltammograms of nitrotoluene in alkaline aqueous solution containing 2.5 M sodium toluenesulphonate for a gold and a glassy carbon electrode, at various angular velocities of the disc electrode and sweep rates, are given in Figs 4 and 5, respectively. These figures show that the voltammograms for both electrode materials differ greatly; in both cases hysteresis occurs.

The wave of nitrotoluene reduction on glassy carbon electrode is found to split-up very clearly during the cathodic sweep but this does not occur during the anodic sweep at a sweep rate of 20 mV/s; at 200 mV/s the phenomenon is even more pronounced. No splitting-up of waves has been found for a gold electrode.

The limiting current of nitrotoluene reduction at a sweep rate of 20 mV/s for a gold as well as a glassy carbon electrode increases linearly with the square root of angular velocity of the disc electrode (Figs 4 and 5). The limiting current for a gold electrode is about 10% higher than for a glassy carbon electrode. The maximum in the reduction wave during the cathodic sweep at a high sweep rate, *viz.* 200 mV/s, is caused by too low a rate of diffusion of nitrotoluene.

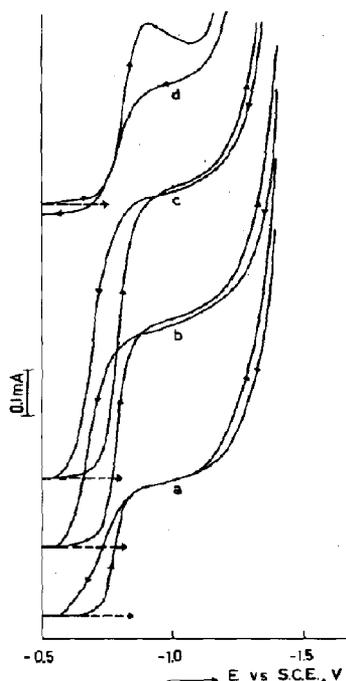


Fig. 4. Voltammograms of nitrotoluene on a rotating-disc electrode of gold at various rotation speeds and sweep rates and in an aqueous solution containing 1.8 mM nitrotoluene, 0.1 M NaOH and 2.5 M Na-toluenesulphonate. Electrode surface: 0.283 cm<sup>2</sup>, temperature: 60°C, rotation speed: 5 rev/s [(a) and (d)], 15 rev/s (b) and 25 rev/s (c), sweep rates: 20 mV/s [(a), (b) and (c)] and 200 mV/s (d), starting potential: -500 mV and the other limit of potential sweep: -1400 mV. The horizontal arrow indicates the zero current for the corresponding voltammogram.

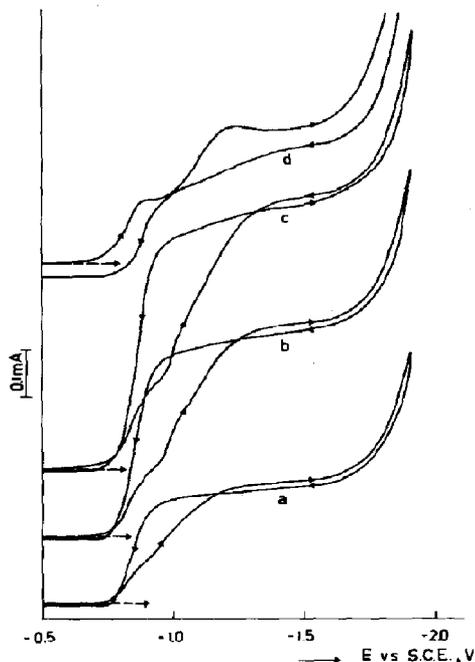


Fig. 5. Voltammograms of nitrotoluene on a rotating-disc electrode of glassy carbon at various rotation speeds and sweep rates and in an aqueous solution containing 1.8 mM nitrotoluene, 0.1 M NaOH and 2.5 M Na-toluenesulphonate. Electrode surface: 0.283 cm<sup>2</sup>, temperature: 60°C, rotation speed: 5 rev/s [(a) and (d)], 15 rev/s (b) and 25 rev/s (c), sweep rates: 20 mV/s [(a), (b) and (c)] and 200 mV/s (d), starting potential: -500 mV and the other limit of potential sweep: -1900 mV. The horizontal arrow indicates the zero current for the corresponding voltammogram.

### 3.2. Azoxytoluene and azotoluene

3.2.1. *Alkaline solution.* Voltammograms of azoxytoluene in alkaline ethanol-water solution (volumetric ratio of 90:10) for various electrode materials are given in Fig. 6. Reduction waves are only distinguishable, but different for silver and glassy carbon electrodes; they are, however, practically equal in height.

In Fig. 7 voltammograms of azoxytoluene in alkaline ethanol-water solution (volumetric ratio of 98:2) are shown for a silver and a glassy carbon electrode at different sweep rates; the other electrode materials investigated, *viz.* gold and stainless steel, gave no, or badly-shaped, reduction waves. Figure 7 shows that the sweep rate influences the voltammograms for silver: the reduction wave during the anodic sweep appears to be split-up clearly at a sweep rate of 200 mV/s. This phenomenon also occurs to a slight extent at lower sweep rates, *viz.* 20 mV/s.

Figure 8 shows voltammograms of azoxytoluene and azotoluene at a glassy carbon electrode in alkaline ethanol-water solutions and in aqueous solutions containing a large quantity of McKee salt. From this figure it follows that the limiting current of azotoluene reduction is practically half that for the azoxytoluene reduction.

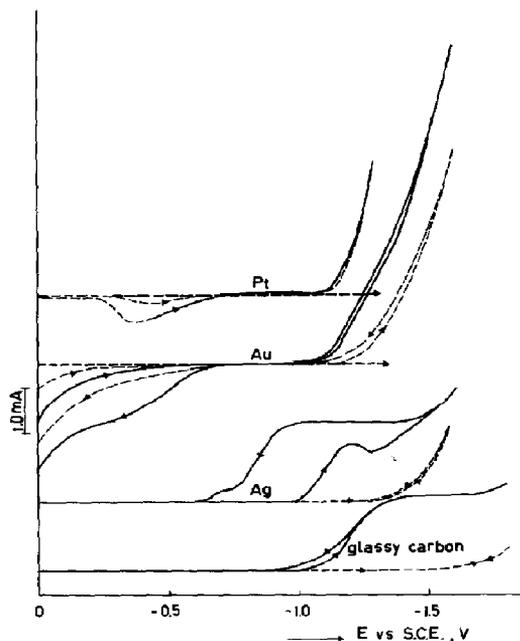


Fig. 6. Voltammograms of azoxytoluene on rotating-disc electrodes of Ag, Au, Pt or glassy carbon in an ethanol-water solution (volumetric ratio 90:10) containing 5 mM azoxytoluene and 0.4 M NaOH (solid lines). Voltammograms of blanks, dotted lines. Temperature: 60°C, rotation speed: 5 rev/s, sweep rate: 20 mV/s, starting potential: 0 mV and the other limits of potential sweep -1800 mV for glassy carbon, -1600 mV for silver and gold and -1300 mV platinum. The horizontal arrow indicates the zero current for the corresponding voltammogram.

It has been found that the limiting current of azoxytoluene as well as that of azotoluene increases with square root of angular velocity of the disc electrode in both ethanol-water solutions and aqueous solutions, containing McKee salt.

**3.2.2. Acid solution.** Voltammograms of azoxytoluene and azotoluene at a glassy carbon electrode are given in Fig. 9 for an ethanol-water solution containing 0.2 M  $H_2SO_4$  and an aqueous solution containing 2.5 M sodium toluenesulphonate and 0.1 M toluenesulphonic acid. This figure shows that the azotoluene waves are well shaped in both solutions and that the azoxytoluene wave is hardly distinguishable in the alcohol-water solution. In an aqueous solution containing McKee salt the limiting current of azotoluene is about half that of the azoxytoluene reduction wave.

#### 4. DISCUSSION

##### 4.1. Values of $n$ from voltammograms and preparative electrolysis and of diffusion coefficients

Voltammograms of nitrotoluene on Pt, Au, Ag and glassy carbon (Figs 1, 3, 4 and 5), of azoxytoluene on Ag and glassy carbon (Figs 6-9) and of azotoluene on glassy carbon (Figs 8 and 9) show well-shaped re-

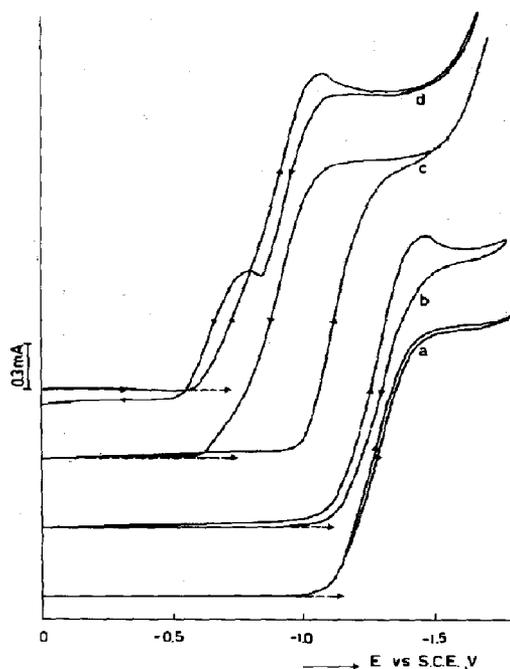


Fig. 7. Voltammograms of azoxytoluene on rotating-disc electrodes of glassy carbon [(a), (b)] and silver [(c), (d)] at various sweep rates and in an ethanol-water solution (volumetric ratio 98:2) containing 5 mM azoxytoluene and 0.4 M NaOH. Temperature: 60°C, rotation speed: 5 rev/s, sweep rate: 20 mV/s [(a) and (c)] and 200 mV/s [(b) and (d)], starting potential: 0 V and the other limit of potential sweep: -1800 mV. The horizontal arrow indicates the zero current for the corresponding voltammogram.

duction waves: the limiting current has been determined as a function of several parameters (*viz.* angular velocity of disc electrode, potential scan rate, concentration of substrate, composition of supporting electrolyte and type of solvent).

The limiting current for a reaction controlled by mass transfer at a rotating-disc electrode is given by Levich's relation[3]

$$i_l = 0.62 n F A c^s D^{2/3} \nu^{-1/6} \omega^{1/2}$$

From the results given in Section 3, it follows that the limiting reduction currents of nitrotoluene, azoxytoluene and azotoluene satisfy this relation. Since the kinematic viscosity was determined separately,  $n$  and  $D$  are the unknown parameters.

The effects of the potential of a Pt electrode on the chemical yield of azoxytoluene formation by reduction of nitrotoluene in an alkaline ethanol-water solution at low concentrations of nitrotoluene and at 50°C are given in Fig. 4 of [1]. It was found that at a nitrotoluene conversion of 75% the number of electrons involved at reduction of 1 molecule of nitrotoluene were 5.0, 4.8, 5.2, 5.2 and 5.5 at respectively -1050, -1100, -1150, -1200 and -1270 mV. These values of  $n$  can be explained since in addition to azoxytoluene a number of unknown by-products are formed [1]. Taking into consideration that the limiting current is attained at potentials lower than -1000 mV, the increase in  $n$  with increasing cathodic polarization is

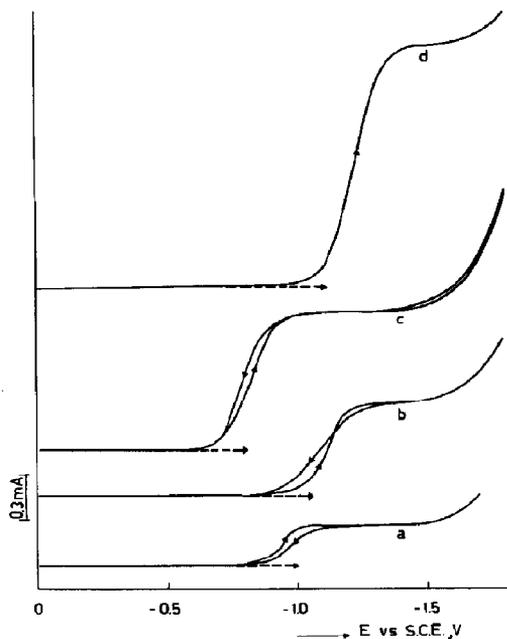


Fig. 8. Voltammograms of azoxytoluene [(a) and (c)] and azotoluene [(b) and (d)] on rotating-disc electrode of glassy carbon in two different alkaline solutions, viz. an aqueous solution containing 5 mM azoxytoluene or azotoluene, 2.5 M Na-toluenesulphonate and 0.1 M NaOH [(a) and (b)] and an ethanol-water solution (volumetric ratio 90:10) containing 5 mM azoxytoluene or azotoluene and 0.4 M NaOH [(c) and (d)]. Temperature: 60°C, rotation speed: 5 rev/s, sweep rate: 20 mV/s, starting potential: 0 V and the other limit of potential sweep: -1700 mV. The horizontal arrow indicates the zero current for the corresponding voltammogram.

caused by the increasing rate of hydrogen evolution.

Coulometric measurements of nitrobenzene reduction in alkaline ethanol-water solutions[4] give only minimum values of  $n$ ; they varied strongly, *ie* from 4.3 to 7.0.

On the other hand, preparative electrolyses of azoxytoluene in alkaline ethanol-water solutions give more useful results. Practically, azoxytoluene is quantitatively reduced to hydrazotoluene on a stainless steel electrode at -2000 mV and 60°C in an alkaline ethanol-water solution[1].

Consequently, the height of the total reduction wave of azoxytoluene to hydrazotoluene is determined by a four-electron step; this agrees with[5].

Substitution of  $i_1 = 1.60$  mA (Fig. 9 for the glassy carbon electrode),  $n = 4$  and of  $\nu = 1.32 \times 10^{-2}$  cm<sup>2</sup>/s into Levich's relation gives a diffusion coefficient of  $8.9 \times 10^{-6}$  cm<sup>2</sup>/s for azoxytoluene in an ethanol-water solution (volumetric ratio 90:10), containing 0.4 M NaOH, at 60°C.

Analogously, we calculated at 60°C:  $D_{\text{azoxytoluene}} = 10.1 \times 10^{-6}$  and  $1.85 \times 10^{-6}$  cm<sup>2</sup>/s for, respectively, and ethanol-water solution (volumetric ratio 98:2) containing 0.4 M NaOH, and an aqueous solution containing 2.5 M Na-toluenesulphonate and 0.1 M NaOH.

From Fig. 9 it follows that the diffusion coefficient of azotoluene is practically equal to that of azox-

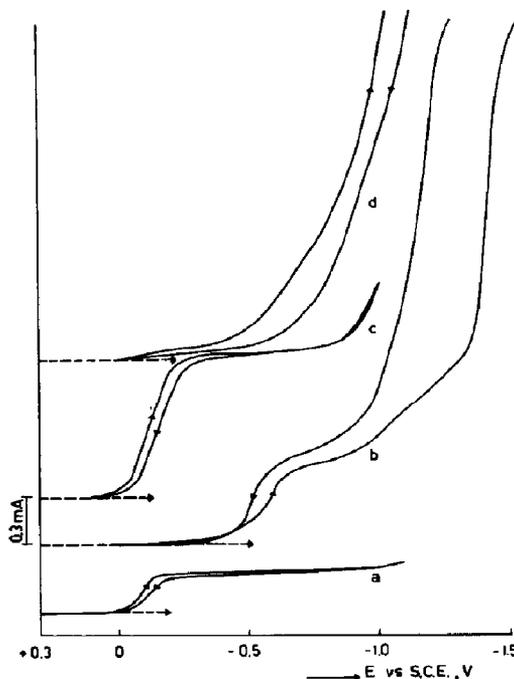


Fig. 9. Voltammograms of azoxytoluene [(b) and (d)] and azotoluene [(a) and (c)] on a rotating-disc electrode of glassy carbon in two different acid solutions, viz. an aqueous solution containing 5 mM azoxytoluene or azotoluene, 0.1 M toluene sulphonic acid and 2.5 M Na-toluenesulphonate [(a) and (b)] and an ethanol-water solution (volumetric ratio 90:10) containing 5 mM azoxytoluene or azotoluene and 0.2 M H<sub>2</sub>SO<sub>4</sub> [(c) and (d)]. Temperature: 60°C, rotation speed: 5 rev/s, sweep rate: 20 mV/s, starting potentials: 300 mV [(a) and (c)] and 0 mV [(b) and (d)] and the other limits of potential sweep: -1000 mV [(a) and (c)] or -1500 mV [(b) and (d)]. The horizontal arrow indicates the zero current for the corresponding voltammogram.

ytoluene since the reduction of azotoluene proceeds according to a single two-electron step[5]. With the Stokes-Einstein equation, it was calculated that the diffusion coefficient of nitrotoluene is about 20% higher than that of azoxytoluene. From the limiting currents (Figs 3 and 4) it follows that at 60°C  $n = 5.8$  for the reduction of nitrotoluene on a gold electrode in an ethanol-water solution (volumetric ratio 98:2) containing 0.4 M NaOH and  $n = 5.0$  for that in an aqueous solution containing 2.5 M Na-toluenesulphonate and 0.1 M NaOH.

In general, the polarographic wave of nitrobenzene in alkaline solution is considered as an irreversible 4-electron wave[6]. This conclusion was based on questionable assumptions and/or results. For instance, Pearson[7] assumes that the diffusion coefficient of nitrobenzene is the same as that of the benzoate ion. For the first reduction wave of nitrotoluene in acid solution Vyayalakshamma and Subrahmanya[4] have found that  $n = 4$  whereas, according to Heyrowsky and Vavkrika[8]  $n$  is greater than 4. It is assumed that the diffusion coefficient obtained for acid solution is the same as for alkaline solution[4].

In both investigations[4, 8] no product analysis was carried out. Certainly, we also made assumptions in the determination of the diffusion coefficient of



lamine is improbable. Moreover, in alkaline solution, nitrotoluene can be reduced nearly quantitatively to azoxytoluene using different types of electrode materials[1]. From this result it follows that it is likely that a dimerization step occurs in the formation of azoxytoluene, since it is very unlikely that the ratio between nitrosotoluene and toluenehydroxylamine at the electrode surface is such that a reaction of both species gives a quantitative yield of azoxytoluene for all the electrode materials investigated. Consequently, our results evidently support the mechanism proposed by Fry[6].

No different opinions are given in literature as to the mechanism of the reduction of azoxytoluene to hydrazotoluene. That part of the Haber scheme has been accepted unanimously and is also supported by the results given in this paper.

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