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Electrochemical monitoring of the thermal decomposition of arenediazonium ions with time in acidic MeOH/H₂O mixtures: dediazotization rate constant

Abstract The rate of the spontaneous decomposition of 4-methylbenzenediazonium tetrafluoroborate, 4MBD, was determined. The effects of solvent composition (MeOH/H₂O) on its electrochemical processes and on those of the derivatized 2-naphthol-6-sulfonate-4-toluene (6S2NPT) azo dye were investigated by Differential Pulse Polarography (DPP). This electrochemical technique shows an effective sensitivity for detecting arenediazonium ions and derivatized azo dyes.

1 Introduction

Arenediazonium compounds, ArN_2^+, are strong oxidizing agents that undergo homolytic fragmentation upon reacting with certain electron donors to produce arenediazenyl radicals [1–3], which dissociate rapidly into an aryl radical and N_2 (Scheme 1). Evidences of the involvement of aryl radicals between arenediazonium ions and relevant physiological compounds have primarily been obtained by ESR. The use of radical trapping reagents have been exploited to probe the involvement of radicals during com-
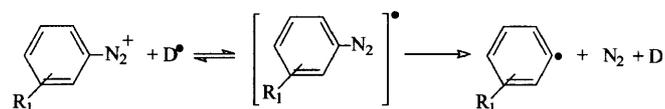
Scheme 1 Homolytic dediazotization in presence of electron donors with the final formation of aryl radical

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petitive homolytic and heterolytic dediazotizations. Interest in homolytic fragmentation of arenediazonium ions or its derivatives has notably increased in recent years because it is believed that the ability of arenediazonium ions to generate radicals may be responsible, to some extent, for the mutagenic and carcinogenic properties of aromatic diazonium compounds [4, 5].

Arenediazonium ions can acquire electrons by means of two different mechanisms [6]. The first one involves the electrochemically generation of an electron by γ-irradiation or by photolytic dissociation; the second one involves the transfer of an electron from inorganic or organic compounds. A large number of reducing agents can be used to generate aryl radicals [6, 7], but probably the most convenient source of free aryl radicals is the electrochemical reduction of arenediazonium salts [1, 3, 6, 8] because they have been shown to be easily reducible species. Furthermore, from a mechanistic point of view, the simplest way of transferring electrons to arenediazonium ion is the reduction at an electrode.

Elofson et al. [9, 10] and Atkinson et al. [11] reported independently, that arenediazonium ions can be reduced at a dropping mercury electrode. Some confusing features were shown in aqueous media: two polarographic waves have been observed and tabulated, but they have only qualitative significance since their shapes are irregular. Polarographic half-wave reduction potentials, $E_{1/2}$, for a number of arenediazonium salts have been measured in a variety of solvents [9, 10]. Thus, $E_{1/2}$ for benzenediazonium tetrafluoroborate in sulfolane was found to be +0.295 V vs SCE (saturated calomel electrode), increasing to +0.450 V with a p-NO₂ substituent or decreasing to +0.140 V measured for the p-methoxy benzenediazonium salt.

The reduction of a number of 4-substituted benzenediazonium tetrafluoroborates has also been studied in aqueous solution [3], using a dropping mercury electrode (DME). Two polarographic waves are observed in potential regions of + 0.05 V to –0.02 V (vs Ag/AgCl), a potential where few organic compounds are electroactive [12], and around –0.97 V to –1.03 V. Microcoulometry [1] at the DME shows that the two waves correspond to the uptake of one elec-
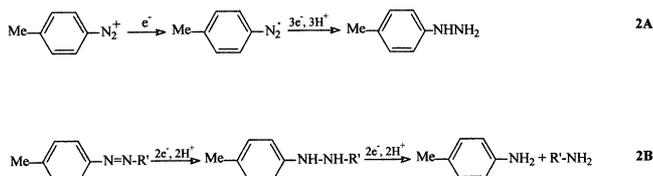
Scheme 2 Electrochemical reduction processes: *A*. arenediazonium ion, 4MBD, in acidic solution and *B*. azo group, after coupling arenediazonium ion, 4MBD, with 2N6S at basic pH to give 6S2NPT azo dye

Fig. 1 Polarograms of 4MBD (8.7×10^{-5} M) at different solvent compositions. The electrodic processes are indicated in the figure. [HCl] = 0.01 M, T = 25 °C

tron for the first wave, yielding a diazenyl radical, and four (overall processes) electrons, respectively, yielding phenylhydrazine [8] (Scheme 2A and inset of Fig. 1). At a selected pH [11, 13–15] the diffusion currents are proportional to the arenediazonium salt concentration. Therefore, a DME electrode can be used to determine arenediazonium salts [10] both qualitatively and quantitatively by comparing the measured diffusion current with a calibration curve obtained from diffusion current-salt concentration profile.

Although a large number of methods for the electrochemical detection of organic compounds like phenols, haloarenes and azo dyes are well established and continuously improving, little attention has been paid to the use of electrochemical methods for the detection of arenediazonium ions or to monitor dediazotizations [14, 15]. In previous work [15] we have shown how electrochemical methods can provide valuable information about the thermal decompositions of arenediazonium ions in aqueous systems. In order to expand the applicability of the electrochemical methods to monitor dediazotizations in nonaqueous solvents, we have studied the thermal decomposition of 4-methylbenzenediazonium tetrafluoroborate salt in methanol-water mixtures. As we will show, the results are in perfect agreement with those reported in the literature obtained with different techniques.

2 Experimental

2.1 Reagents and Solutions

4MBD was synthetized following a standard nonaqueous procedure [16]. To minimize its possible decomposition via the Schieman reaction or with water vapor, 4MBD was stored in dark desiccator at 0 °C and recrystallized periodically with cold diethyl ether. Stock standard solutions (usually 4.5×10^{-2} M) of diazonium salt were prepared daily in aqueous 0.1 M HCl and stored at low temperature (< 0 °C) in the dark to minimize diazotate formation and spontaneous hydrolysis.

The reagents used in the synthesis of 4MBD were purchased from Aldrich, while 2-naphthol-6-sulfonic acid, sodium salt (2N6S), was received from Pflatz & Baüer. Other reagents employed were from Riedel-de-Haën. All solutions were prepared from analytical grade chemicals, without further purification, and distilled-deionized water from a Millipore Milli-Q system of 18 MΩ cm resistivity was used throughout.

The azo dye 6-sulfonate-2-naphthol-1-azo-p-toluene (6S2NPT) was prepared by coupling 4MBD with an aliquot of a buffered (TRIS, pH 8.3) solution containing a large excess of 2N6S (see procedures). Auxiliary experiments performed by monitoring azo dye formation spectrophotometrically demonstrated that, under such experimental conditions, the coupling reaction was at least 100 times faster than dediazotization. Once the coupling reaction was complete, the solutions were purged with N_2 gas (99.999%) at least during 20 min and kept under a nitrogen atmosphere during the electrochemical experiments.

2.2 Instrumentation

Differential pulse polarograms (DPP) were obtained on a Metrohm Polarecord E506, attached to a 663 VA-Stand equipped with water jacketed voltammetric cell. A three-electrode system composed of a mercury multimode [DME, static mercury drop electrode (SMDE) or hanging mercury drop electrode (HMDE)] type electrode as working electrode, an Ag/AgCl electrode as reference and a glassy carbon rod (2×65 mm) as auxiliary electrode was used. The output signal was displayed on a Linseis (LY 16100-II) X-Y/T recorder.

All experiments were carried out at constant temperature by using a Pselecta (Ultrasonic-320) thermostat, which guarantees a precision in temperature of ± 0.1 °C. pH measurements were obtained with a Metrohm-model 744 pH-meter.

2.3 Procedures

Coupling reaction method. This special protocol was such as described by García-Meijide et al. [16]. Typically, 15–20 volumetric

flasks (10 mL) containing 2.9 mL of the reaction medium (99.6% MeOH in 0.01 M HCl) were thermostated, for about 40 min, at T = 60 °C. The dediazotization was initiated by rapidly adding an aliquot (0.1 mL) of the 4MBD stock solution to each volumetric flask (giving 1.6×10^{-4} M in the reaction media). To quench the reactions, an aliquot of the 2N6S quenching solution (1 mL), which was prepared by dissolving 2N6S in a solution containing TRIS buffer ([TRIS] = 0.05 M) to give final 2N6S concentrations about 10-fold excess over that of arenediazonium salt at pH 8.3, was added to each volumetric flask at selected, increasingly longer intervals of time. This pH was chosen to maximize the rate of 6S2NPT azo dye formation [16, 17, 18] because naphthoxide ions couple much more rapidly than their protonated forms [19, 20]. We have found that the methodology still works at pH 12.2, thus the competing diazotate formation with OH⁻ is still insignificant [17]. In each set of experiments, one sample was quenched immediately and, a second one, was allowed to go to completion, whithout adding the quenching solution. The unquenched sample was used to estimate the 4MBD concentration at infinite time. The immediately quenched sample (i.e., t = 0) was used to check the possible hydrolysis and decomposition of the solid 4MBD substrate.

After the reaction was completed, the test solutions were cooled to room temperature and diluted up to the mark with the TRIS buffer solution; so the MeOH composition decreases to 65% after dilution. All series of test solutions were transferred to the polarographic cell, purged with nitrogen during 10 min and the DP polarograms were recorded in 65% MeOH. The azo dye compound formed (6S2NPT) in the coupling reaction was investigated at pH 8.3, following the reduction peak of the azo group (Scheme 2B) at –600 mV (*vs.* Ag/AgCl reference electrode). The residual current in DPP experiments was obtained with 3 mL of reaction media and 1 mL of quenching solution diluted up to 10 mL with TRIS buffer.

DP polarographic methods. 10 mL of different MeOH/H₂O composition, containing the supporting electrolyte solution (usually 0.01 M HCl), was added to the cell, degassed with nitrogen, and thermostated at 35 °C.

The electronically-controlled drop time was 0.4 s and a pulse-amplitude of –80 mV was applied. The polarograms were recorded using a potential scan of 7.5 mVs⁻¹. After recording the polarogram corresponding to the blank, 20 μL of a 4.35×10^{-2} M of 4MBD stock standard solution (giving 8.7×10^{-5} M in the cell) was added to 10 mL of the degassed supporting electrolyte solution and then the polarogram was recorded at t = 0. The subsequent polarograms were repeated under the same conditions, recording the elapsed time between polarograms.

Kinetic data were obtained from these polarograms, following the first reduction peak of the diazonium group (Fig. 1) at a peak potential between –40 mV and –160 mV (*vs* Ag/AgCl reference electrode), depending on MeOH/H₂O compositions in cell.

2.4 Methods

Kinetic data were obtained by employing the DPP technique. Observed rate constants were calculated by fitting the peak current, ip, to the integrated first order Eq. (1) using a nonlinear least-square method provided by a commercial computer program, where M is the peak current of the solution component that is monitored, 4MBD or 6S2NPT.

$$Ln\frac{(M_\infty - M_t)}{(M_\infty - M_O)} = -k_{obs}t \tag{1}$$

Dediazotization experiments were carried out at 60 °C at different MeOH/H₂O compositions, with 4MBD as limiting reagent.

3 Results

3.1 Effects of solvent composition on the reduction processes of 4MBD

Figure 1 shows typical polarograms for 4MBD at different MeOH/H₂O compositions. At any solvent composition, two polarographic peaks are observed; the first one is associated with a one-electron transfer to yield the diazenyl radical. Following this reduction process, a second reduction peak involving three electrons and three protons is observed, to give the corresponding phenylhydrazine, in agreement with reported results for other arenediazonium salts [14, 15].

It is worth to note that the peak potentials of both reduction processes are shifted to more negative values
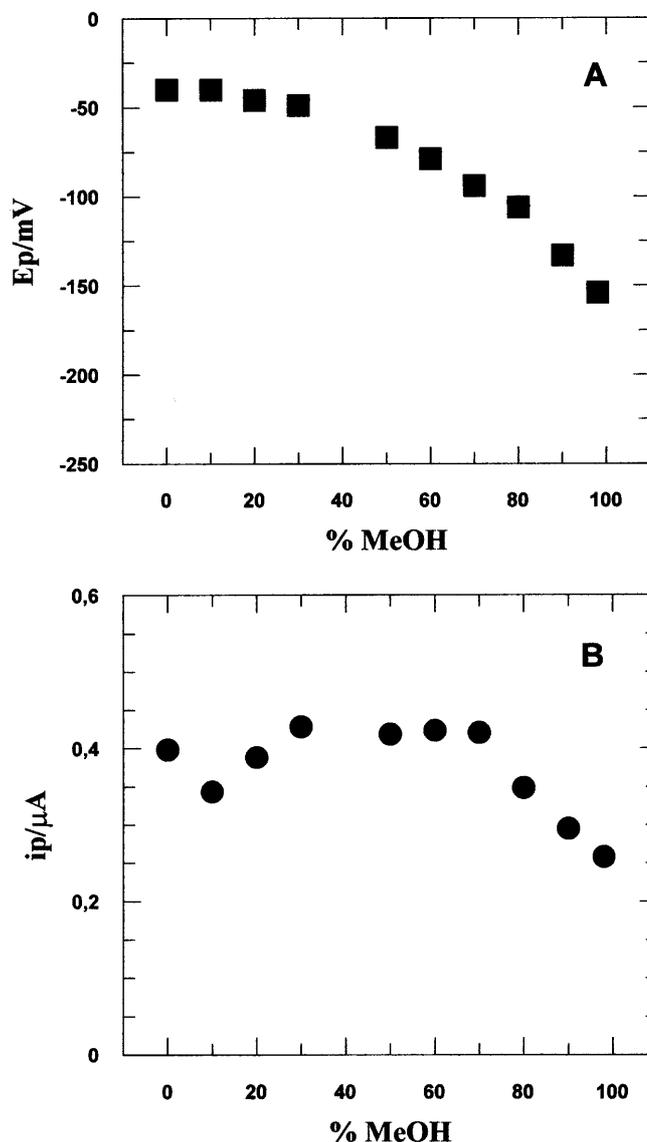
Fig. 2 Effects of solvent composition on the peak potential (*A*) and peak current (*B*) for 4MBD. 4MBD = 8.7×10^{-5} M, [HCl] = 0.01 M, T = 25 °C

upon increasing the MeOH content, suggesting that the reduction of 4MBD is more difficult at high percentages of MeOH than in pure water. MeOH favors, however, the chemical process by increasing the activation entropy [21]. On the other hand, peak potential shifts (shown in Fig. 2A) are negligible with MeOH contents below to 30% and modest with MeOH contents up to 40%, δV = ca. 0.1 V, thus no significant changes in the dediazotization product distribution are expected, in agreement with reported product distribution analysis (HPLC) for this arenediazonium ion [21]. The effect of solvent composition on peak current (first reduction process) of 4MBD was also investigated. Figure 2B shows that negligible peak heights shifts were obtained for MeOH contents in the voltammetric cell below to 70%.

3.2 Effects of solvent composition on the 6S2NPT reduction process and relationship between peak current and azo dye concentration

Dediazotization of 4MBD at T = 25 °C is too slow [16, 21] for practical kinetic experiments; thus in order to obtain reasonable half-life times, the temperature was increased up to T = 60 °C ($\tau_{1/2}$ = ca. 1 h). At this temperature, the volatility of Hg and convection currents in the electrode made impossible to obtain reliable results. Consequently, we employed a derivatization method to quench the dediazotization reaction at convenient times. The method, which is described in the experimental section, is based on the use of the competitive coupling reaction between 4MBD and 2N6S which yields the 6S2NPT azo dye. To perform the experiment, solid 6S2NPT was synthesized [16].

The effect of solvent composition on peak potentials and peak currents for the reduction process of 6S2NPT was investigated by changing the solvent composition. The polarograms (not shown) indicate that negligible peak potential and peak heights shifts were obtained. Similar results were obtained when the measurements were obtained 48 h after carrying out the coupling reaction, indicating that the formed azo compound is stable for some time.

The relationship between peak currents and azo dye concentration was obtained from the polarograms in hydroalcoholic solutions (65% in MeOH) of the synthesized 6S2NPT and from mixtures containing a large excess of the coupling agent 2N6S and different amounts of 4MBD. As expected, both methods gave the same results. A linear relationship (cc > 0.9996) exists between peak heights and azo dye concentration within the concentration range investigated. The equation obtained was: ip (μA) = (-2.8 ± 0.3) $\times 10^{-3}$ + (9.8 ± 0.1) $\times 10^{-3}$ 6S2NPT (μM). Therefore, peak currents provide a direct measurement of azo dye concentration and consequently an indirect measurement of the amount of unreacted arenediazonium ion.

3.3 Kinetic results

Figure 3, chosen as representative, shows a typical kinetic plot for diazonium ion loss at 99.6% MeOH obtained by
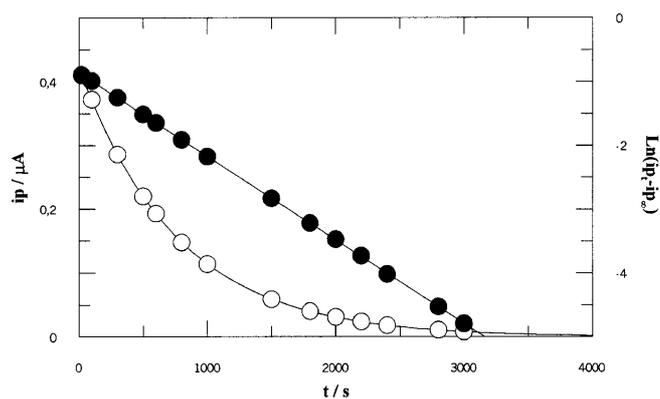
Fig. 3 Typical kinetic plot for the disappearance of 6S2NPT azo dye. Experimental dediazotization conditions: 4MBD = 1.6×10^{-4} M, 99.6% MeOH, [HCl] = 0.01 M, T = 60 °C. The reaction was quenched with an aliquot of 4.2×10^{-2} M 2N6S (dissolved in 5×10^{-2} M TRIS buffer to give final pH 8.3). Polarographic measurements were obtained at T = 25 °C in 68% MeOH

measuring the decrease in the reduction peak of the 6S2NPT azo dye at 65% MeOH and the corresponding first order plot, from where the observed rate constant k_{obs} was obtained (see Eq. 1), yielding a value of k_{obs} = 13.12 $\times$ 10^{-4} s^{-1}, in perfect agreement with those reported in the literature obtained by different techniques like N_2 evolution [22] UV-VIS spectroscopy (k_{obs} = 13.25 $\times 10^{-4}$ s^{-1}) [16] and by HPLC [21].

4 Discussion

The thermal stability of arenediazonium ions is strongly dependent on both the position and nature of the substituents on the aromatic ring [6, 23]. Most *para* substituents, including electron-withdrawing ($-NO_2$) and electron-donating groups (like $-CH_3$) show a marked stabilizing effect. Consequently, all dediazotization experiments were carried out at T = 60 °C to speed up the reaction [24]. Direct DPP monitoring of 4MBD loss by using any of its reduction peaks was not possible at T = 60 °C because large variations in the dropping time were observed, probably due to high Hg volatility and convection currents close to the electrode surface. Lower temperatures allow direct monitoring of arenediazonium ion loss by DPP [14], but slows 4MBD dediazotization significantly [22]. Thus, although we have not been able to monitor the loss of arenediazonium ion directly, we have obtained a similar information by employing an indirect method. The obtained rate constant values are close to those reported in the literature.

A number of methods have been developed to monitor the dediazotizations [16, 21–24]: measuring of N_2 evolution, changes of activation volume, and derivatization of unreacted arenediazonium ions with phenols or amines to give azo dyes. The most recent ones use gas chromatography-mass spectroscopy (GC-MS) and liquid chromatography (LC) to determine the products of the reactions (usu-

586

ally phenols, ArOH, haloarenes, ArCl, and in some reactions, benzene, ArH, and biaryls, Ar-Ar). UV-VIS spectroscopy cannot usually be used to monitor the reaction because both diazonium salts and dediazotization products absorb in the same UV regions and even their spectra may be masked by those of added electrolytes like chlorocuprate(I) and chlorocuprate(II) complexes. Therefore, new methods of investigation are needed to obtain a complete scope of the kinetics and mechanisms of the reactions of one of the most useful and versatile kind of compounds, the arenediazonium ions.

Electrochemical measurements have been proved to be a powerful tool to study the mechanisms of this reactions since they allow the determination of rate constants and, depending on the nature of the arenediazonium ion, estimation of product yields [15]. They also provide useful information on the presence of transient intermediates formed in the course of dediazotizations, where other techniques fail. Furthermore, since polarograms reflect all reduction steps of the diazonium ion, the electrochemical technique provides valuable information on the effects of chemical compounds on such reduction processes, allowing to discern between, for example, inner or outer sphere mechanisms [25].

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