

Polarographic behaviour of 2,4-dinitrodiphenylamine in amphiprotic media

V JOHN KOSHY, C S VENKATACHALAM and C KALIDAS

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

MS received 1 March 1980 ; revised 20 May 1980

Abstract. Two six-electron diffusion-controlled irreversible waves are obtained for the polarographic reduction of 2,4-dinitrodiphenylamine (DPA) in buffered and unbuffered media in all compositions of methanol-water mixtures. Based on the polarographic and coulometric data, it is suggested that each of the nitro groups is reduced to the corresponding amine in a single step *via* the diimine intermediate to give 2,4-diamino DPA as the final product. The influence of various factors such as structure of the depolariser, pH and composition of methanol on the reduction of the compound is also discussed.

Keywords. Polarography ; controlled-potential electrolysis ; 2,4-dinitro DPA.

1. Introduction

Aromatic nitro compounds follow two clear-cut pathways of reduction depending on the nature of the substituents in the phenyl ring (Stocesova 1949; Shreve and Markham 1949; Heyrovsky and Vavricka 1970)—(i) a two-step reduction process wherein the hydroxylamine first formed in a four-electron reduction step is further reduced at a more negative potential to the corresponding amine and (ii) a single-step reduction process wherein the hydroxylamine formed as in (i) undergoes dehydration to form the quinone-imine intermediate which undergoes subsequent reduction at more positive potential to give the corresponding amine.

Nitrosubstituted diphenylamines (DPAS) are known to have considerable application as H- and redox indicators (Stewart and O'Donnell 1964; Gandikota and Rao 1974). These compounds and their reduction products are used in the synthesis of number of dyes (Asquith and Campbell 1963) and phenazine derivatives (Cross *et al* 1971). In view of their importance in analytical and industrial chemistry, the polarographic behaviour of these compounds was undertaken and in continuation of our earlier work on this subject (John Koshy *et al* 1974, 1978), we present here the results on the polarographic reduction of 2,4-dinitro DPA in methanol-water mixtures of varying composition in the range 30-80% v/v methanol.

2. Experimental

The experimental cell and the instruments used in various electrochemical measurements are similar to those described earlier (John Koshy *et al* 1974, 1978). The d.m.e. had the following capillary characteristics: $m = 1.743 \text{ mg s}^{-1}$ and $t = 6.0 \text{ sec}$ at 56 cm height (uncorrected for back pressure) of mercury column in 0.1 M KCl under open circuit conditions. The drop-time was controlled by a hammer arrangement to 5.3 sec throughout the polarographic measurements.

2,4-dinitro DPA was prepared and purified according to the procedures reported earlier (Stewart and O'Donnell 1964). Doubly-distilled methanol (AR BDH) was used for preparing different compositions of methanol-water mixtures. The pH of the solutions was controlled by Britton-Robinson (BR) and Clark and Lubs (CL) buffers in the range 30–60% v/v methanol and 60–80% v/v methanol, respectively. KCl (AR BDH) was used as the supporting electrolyte without further purification. The ionic strength of the experimental solutions was maintained throughout at 0.2. The details of the coulometric cell used in controlled potential electrolysis (CPE) and the method of evaluating the total number of electrons (n) in an electrode reaction have been described previously (John Koshy *et al* 1974). The UV-visible spectra of the reduction product of the compound were obtained through Carl Zeiss DMR 21 spectrophotometer.

3. Results and discussion

The polarographic reduction of 2,4-dinitro DPA was found to give two diffusion-controlled (Meites 1965) waves of nearly the same wave height both in buffered and unbuffered media in all compositions of methanol-water mixtures. In buffered media, the waves were observed to be closely spaced at low pH values, but their separation increased as the experimental solution is made more alkaline. The relevant polarographic data in one solvent composition 40% v/v methanol are presented in table 1. Plots of $\log(i_d - i)/i$ versus $-E$ for both the waves are found to be nonlinear, the a.c. summit potentials (E_s) are more negative than the corresponding d.c. $E_{1/2}$ values of the waves and further, the $(E_{3/4} - E_{1/4})$ values are seen to be much higher (table 1) than $0.056/n$ ($n = 6$ for each wave from coulometry, see later for details). All these results indicate the irreversible nature of the electrode process corresponding to the two waves.

Controlled-potential coulometry carried out on 2,4-dinitro DPA at the limiting regions of the first and second waves in acidic and neutral media gave $n = 6$ and 12, respectively (table 2). The n values for both the wave in alkaline solutions were evaluated from Ilkovic equation as CPE did not yield reproducible results, possibly due to side reactions (Vijayalakshamma and Subramanya 1971).

The product at the limiting region of the first wave is 2-amino 4-nitro DPA. The presence of the amino group brings about a red shift in the absorption maximum of the second nitro group (Fieser and Fieser 1958) which is confirmed by UV-visible spectra. Controlled potential electrolysis at the limiting region of the second wave gave a colourless solution which presumably corresponds to 2,4-diamino DPA. The solution turns violet on exposure to air due to the aerial oxidation of the diamino DPA (Jolles 1956).

Table 1. D.C. and A.C. polarographic data for the reduction of 2,4 dinitro DPA (4.0×10^{-5} M) in buffered 40% (v/v) methanol solutions at $30 \pm 0.1^\circ$ C.

pH ^a	Wave	Half wave potential $-E_{1/2}/v$ ^b vs SCE	$-(E_{3/4} - E_{1/4})/v$	A.C. Summit potential $-E_s/v$ ^c vs SCE	$-\Delta E_{1/2}/v$	$-\frac{dE_{1/2}/v}{dpH}$
2.38	I	0.096	0.058	
	II	0.236	0.024	0.266	0.140	
3.97	I	0.190	0.044	
	II	0.346	0.034	0.366	0.156	
5.07	I	0.246	0.042	0.258	..	0.057 (I)
	II	0.406	0.034	0.396	0.160	
5.57	I	0.278	0.044	0.302	..	0.059 (II)
	II	0.444	0.038	0.446	0.166	
7.16	I	0.362	0.038	0.386	..	
	II	0.524	0.038	0.532	0.162	
8.69	I	0.448	0.034	0.468	..	
	II	0.616	0.048	0.624	0.168	
9.90	I	0.526	0.032	0.555	..	
	II	0.709	0.046	0.718	0.183	

^a pH values pertain to the particular solvent composition as the standard state.

^b Accuracy ± 2 mV

^c Accuracy ± 4 mV

Considering the ease of reduction of the two nitro groups, it is plausible to expect that the reduction of the nitro group in the second position will be facilitated compared to that in the fourth position because of the possibility of an internal H-bonding between this nitro group and the NH group which reduces the electron density on the nitro group in second position. Similar arguments were suggested earlier for the reduction of other aromatic nitro compounds (Aistle and McConnel 1943; Astle and Cropper 1943) and also to explain the ease of reduction of 2-nitro DPA compared to 4-nitro DPA (our unpublished work).

The $E_{1/2}$'s of both waves become more negative (table 1) with increasing pH of the solution indicating the participation of protons in the electrode processes (Heyrovsky and Vavricka 1972). A similar trend for the variation of $E_{1/2}$'s is observed with increasing composition of methanol at a given pH.

The difference in $E_{1/2}$'s of the two waves ($\Delta E_{1/2} = E_{1/2}^I - E_{1/2}^{II}$) increases with increasing pH of the solution which is in agreement with the observations reported on other aromatic nitro compounds (Pearson 1948, Boyd and Reidlinger 1960).

Table. 2 Macroculometric data for the reduction of 2,4 dinitro DPA in buffered methanol-water mixtures. Temperature = $30 \pm 0.1^\circ \text{C}$.

Solvent comp. % methanol (v/v)	pH	First wave		Second wave	
		Potential of electrolysis - E/V vs SCE	n^b	Potential of electrolysis - E/V vs SCE	n^b
40	2.15	0.175	5.92	0.600	12.11
	7.08	0.400	5.94	0.700	12.08
	9.01	0.850	11.87 ^c
60	2.38	0.200	6.03	0.600	11.93
	7.23	0.400	6.07	0.750	11.98
	9.31	0.950	11.74
80	3.17	0.200	5.93	0.600	11.89
	7.21	0.400	5.90	0.800	11.89
	9.50	1.050	11.85 ^c

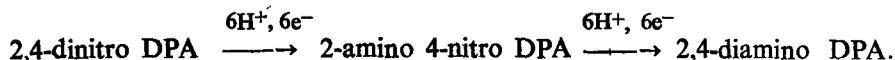
^a pH values pertain to the particular solvent composition as the standard state.

^b Accurate to ± 0.05

^c Calculated n value, taking i_d at the potential indicated.

This is ascribed to the formation of the anilinium salt of 2-amino 4-nitro DPA (acidic region) in the first stage of reduction and at higher pH's the salt formation is less favoured. Thus the $E_{1/2}$ of the nitro group in the fourth position is shifted to more negative values leading to increasing magnitudes of $\Delta E_{1/2}$.

On the basis of these results, the following mechanism may be suggested for the reduction of 2,4-dinitro DPA in buffered solutions of methanol :



Since each of the nitro groups is reduced to the corresponding amine in a single step, it is reasonable to expect that the reduction proceeds *via* the diimine intermediate as postulated in the case of mononitrodiphenylamines (John Koshy *et al* 1978). The formation of the diimine intermediate was suggested earlier by Farsang *et al* (1973) in the cyclic voltammetric study on the oxidation of 2,4-diamino DPA in aqueous solutions employing a carbon paste electrode. Cyclic voltammetric studies on 2,4-dinitro DPA in unbuffered solutions (our unpublished work) of methanol-water mixtures also confirm the above observations.

References

- Asquith R S and Campbell B 1963 *Anal. Chim. Acta* 79 678
 Astle M J and Cropper N P 1943 *J. Am. Chem. Soc.* 65 2395

- Astle M J and McConnel W P 1943 *J. Am. Chem. Soc.* **65** 35
Boyd R N and Reidlinger A A 1960 *J. Electrochem. Soc.* (C) 2085
Cross B, Williams P J and Woodall R E 1971 *J. Chem. Soc.* (C) 2085
Farsang G, Vass, V, Ladanyi L and Saber T M H 1973 *J. Electroanal. Chem.* **43** 397
Fieser L F and Fieser M 1958 *Organic chemistry* 3rd edition (New York : Reinhold) p. 883
Gandikota M and Rao G G 1974 *Anal. Chim. Acta* **72** 163
Heyrovsky M and Vavricka S 1970 *J. Electroanal. Chem.* **28** 409
Heyrovsky M and Vavricka S 1972 *J. Electroanal. Chem.* **36** 203, 207
John Koshy V, Venkatachalam C S and Kalidas C 1974 *Trans. Soc. Adv. Electrochem. Sci. Technol.* **9** 162
John Koshy V, Venkatachalam C S and Kalidas C 1978 *J. Electroanal Chem.* **89** 191.
Jolles Z E 1956 *Chemistry of carbon compounds* (Amsterdam : Elsevier) Part B **3** 722
Meites L 1965 *Polarographic techniques* 2nd edition (New York : Interscience) p. 132
Pearson J 1948 *Trans. Faraday Soc.* **44** 683
Shreve O D and Markham E C 1949 *J. Am. Chem. Soc.* **71** 2993
Stewart P and O'Donnell J P 1964 *Can. J. Chem.* **42** 1681
Stocesova D 1949 *Coll. Czech. Chem. Commun.* **14** 615
Vijayalakshamma S K and Subramanya R S 1971 *Indian J. Chem.* **9** 1265