Electrochemical Behaviour of 2, 4-Dinitro and 2, 4, 6-Trinitro Diphenylamines in Dipolar Aprotic Media

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The electrochemical behaviour of 2,4-dinitro and 2,4,6-trinitrodiphenylamines (DPA's) in dimethylformamide (DMF) and acetonitrile (AN) in the presence of tetraethylammonium iodide (TEAI) and sodium nitrate has been investigated by polarographic, cyclic voltammetric and micro-coulometric techniques. Dinitro DPA gave two irreversible, diffusion-controlled waves in the ratio 1:2 in DMF and AN solutions containing TEAI while it gave three waves in the ratio 1:1:6 in sodium nitrate supporting electrolyte. Cyclic voltammograms of the compound showed three cathodic peaks (one reversible two irreversible) in both the solvents in the presence of TEAI and sodium nitrate supporting electrolytes. 2,4,6 - trinitro DPA in DMF and AN solutions in the presence of TEAI gave three irreversible diffusion controlled waves of equal height. Cyclic voltammograms of this compound showed three cathodic peaks corresponding to the three dc steps. Based on the results obtained, suitable mechanisms were proposed for the electroreduction of these DPA's in the two solvents.

Nitrosubstituted diphenylamines (DPA's) with the nitro groups in different positions of the phenyl rings yield compounds of widely varying pK_a and have been extensively used for the generation of H - acidity scales in amphiprotic and dipolar aprotic media[1-3]. In our earlier work from this laboratory, the polarographic reduction of nitro substituted DPA's in buffered methanol-water mixtures has been reported[4-5]. However, their reduction in dipolar aprotic solvents has not received any attention in spite of the interesting possibility that it provides for generating radical anions[6]. This prompted us to study the electrochemical behaviour of the title DPA's at mercury cathode in N,N-dimethylformamide (DMF) and acetonitrile (AN) in the presence of tetraethylammonium iodide (TEAI) and sodium nitrate supporting electrolytes.

EXPERIMENTAL

DMF and AN (Pfizer) were purified according to the methods described in litrature[7,8] TEAI (Fluka) specified for polarographic work was used as such. Sodium nitrate (AR,BDH) was dried in an air oven at 80 C and stored in a desiccator. The dme used in these studies had the following characteristics: 'm' = 1.743 mg./ s; and 't' = 6.0 s in 0.1M aqueous KCl at a mercury pressure (uncorrected for back pressure) of 53.0 cm. All measurements were made using a silver wire as reference electrode , but these data were converted to SCE reference scale. A multipurpose cyclic voltammetric module[9] in conjunction with a three electrode assembly hmde., mercury pool electrode and silver wire electrode) was employed in the present work and the cyclic voltammograms were either recorded on an X-Y recorder or stored and traced from an oscilloscope depending upon the sweep rate.

All experiments were carried out at 30 + 0.1°C

RESULTS AND DISCUSSION

a. 2,4-DINITRO DPA REDUCTION IN DMF AND AN SOLUTIONS:

Table 1 gives the dc, ac polarographic and microcoulometric data for the reduction of 2,4-dinitro DPA (5.0×10^{-4}M) in DMF and AN solutions in the presence of 0.1M TEAI supporting electrolyte. The relevant dc and ac polarograms are shown in Fig.1. 2,4-dinitro DPA gives two well-defined waves both in DMF and AN and the wave heights are approximately in the ratio 1:2. ($n_{app} = 4$ for the first wave as obtained from microcoulometric experiment, Table 1. $n_{app} = 8$ by comparison of the wave heights. Both the waves are found to be diffusion controlled on the basis of limiting currents, i_l vs h plots[10]. The logarithmic plots for both the waves in the two solvents are linear, but the slope values for the first wave (Table 1) are very much higher when compared to a reversible four electron process. The ac summit potentials (E_s) are more negative when compared to the dc $E_{\frac{1}{2}}$ values. It is therefore concluded that both the waves of 2,4 -dinitro DPA

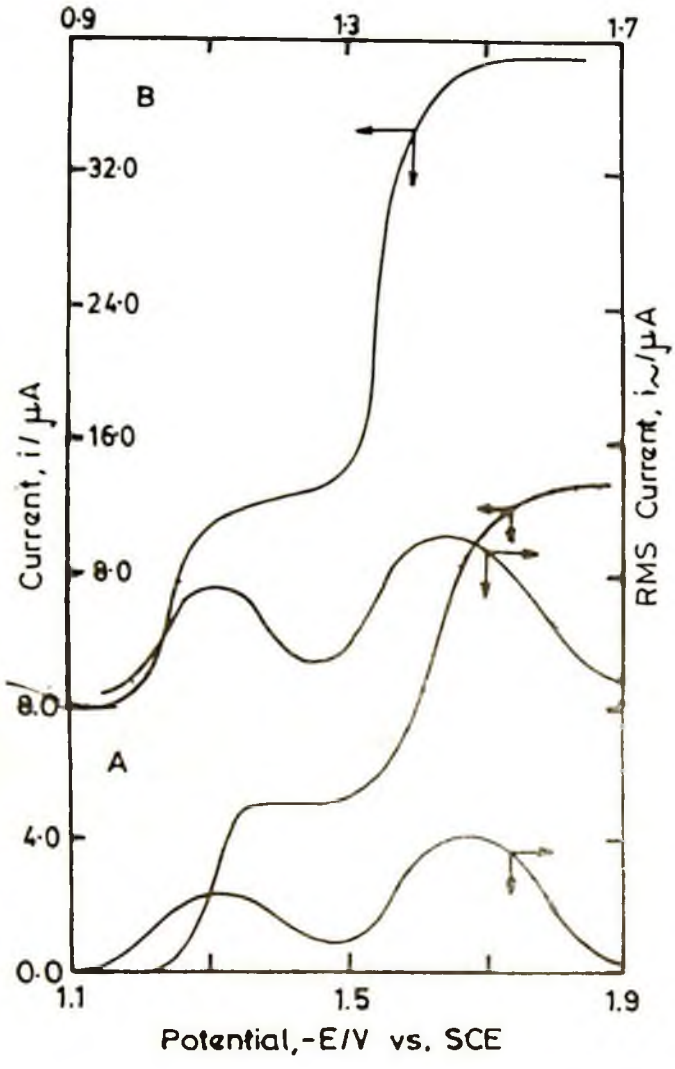


Fig. 1 Dc and Ac polarograms of 2,4-dinitro DPA in DMF(A) and AN(B) with 0.1M TEAI supporting electrolyte.

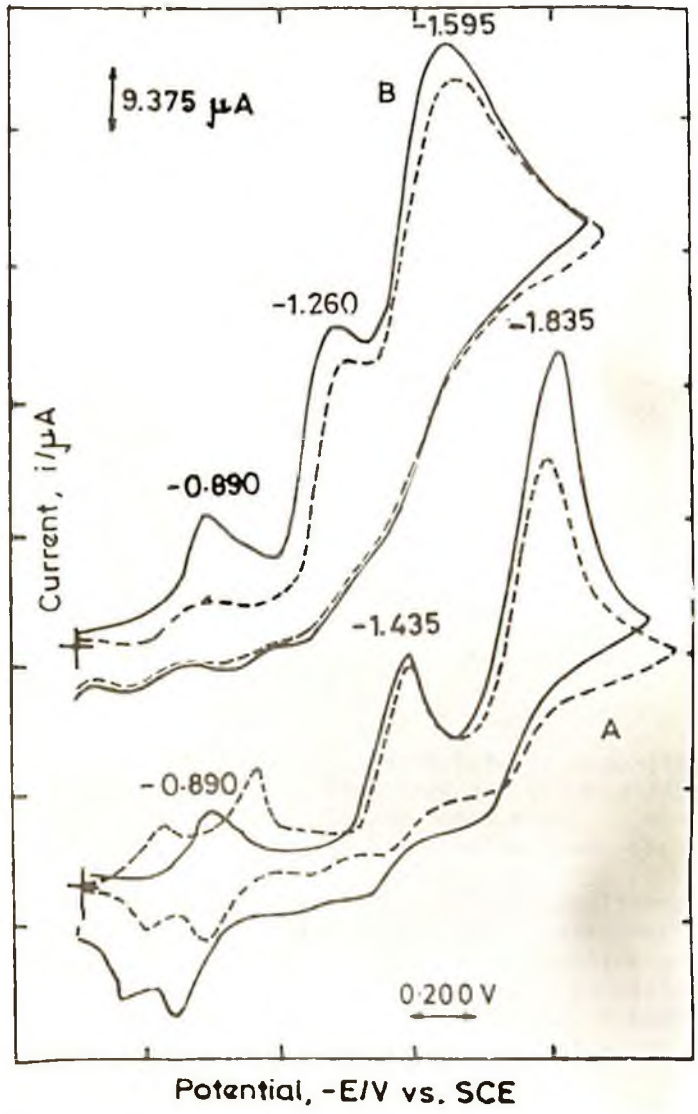


Fig. 2 Cyclic voltammograms of 2,4-dinitro DPA in DMF(A) and AN(B) with 0.1M TEAI supporting electrolyte at 0.1650 V/sec sweep rate (dashed line represents repeated sweep).

in DMF and AN solutions in the presence of 0.1M TEAI supporting electrolyte are irreversible in nature[11].

However, in the presence of 0.1M $NaNO_3$ supporting electrolyte in DMF solutions, it was found that 2,4-dinitro DPA gave three well defined waves in the ratio 1:1:6 (wave I : wave II : wave III). It may be pointed out that Rogers and Watson[12] reported three waves in the polarographic reduction of 2,2-dinitrobiphenyl, of which the first two waves corresponded to one electron reversible reduction whereas in the present work two one-electron waves are observed only in the presence of sodium nitrate as stated above. n_{app} = 1 for each of the first two waves was confirmed by microcoulometry. The analysis of the waves in DMF solutions in the presence of 0.1M $NaNO_3$ supporting electrolyte showed the diffusion-controlled nature of the waves. Log plots for the three waves are found to be non-linear. The wave slopes ($E_{\frac{1}{4}} - E_{\frac{1}{2}}$) for the first two waves are large for one-electron reversible reduction step and the ac summit potentials are more negative compared to the dc $E_{\frac{1}{2}}$ values. In a similar way, the wave slope for the third wave is found to be very large for six electron reversible process (n_{app} = 6 obtained for the third wave by comparison of wave heights).

The cyclic voltammetric data obtained on 2,4-dinitro DPA in DMF and AN solutions in the prese-

TABLE 1

POLAROGRAPHIC AND MICROCOULOMETRIC DATA FOR THE REDUCTIONS OF 2,4-DINTITRO DPA (5.0×10^{-4}M) AND 2,4,6-TRINITRO DPA (3.0×10^{-4}M) IN DMF AND AN SOLUTIONS; ALL POTENTIALS ARE w.r.t.SCE.

Compound	Medium	Wave	$-E_{\frac{1}{2}}$ (V)*	$-E_p$ (V)+	$-(E_{\frac{3}{4}} - E_{\frac{1}{4}})$ (V)	$-dE/d \log \left(\frac{i_d - i}{i}\right)$	Microcoulometric data: Applied potential (V)	n_{app}
	DMF/TEAI	I	1.300	1.345	0.048	0.063	1.400	4.08
		II	1.620	1.650	0.070	0.092	--	8.16#
2,4-dini-	DMF/$NaNO_3$	I	0.746	0.815	0.150	--	0.950	0.96
tro DPA		II	1.130	1.215	0.065	--	1.280	1.92
		III	1.560	1.650	0.130	--	--	7.68#
	AN/TEAI	I	1.050	1.105	0.050	0.057	1.200	4.06
		II	1.360	1.445	0.043	0.042	--	8.12#
	DMF/TEAI	I	1.286	1.295	0.088	--	1.365	6.02
		II	1.446	1.530	0.036	--	--	12.04#
		III	1.648	1.760	0.052	--	--	18.06#
2,4,6-tri-	AN/TEAI	I	1.216	1.230	0.050	--	1.265	5.88#
nitro DPA		II	1.300	1.310	0.034	--	--	11.76#
		III	1.446	1.500	0.072	--	--	17.64#

*Half-Wave Potential, accuracy ± 2 mV + Summit Potential, accuracy ± 5 mV

Calculated values based on wave heights.

nce of 0.1M TEAI supporting electrolyte are summarised in Table 2 and the cyclic voltammograms are shown in Fig.2. It is seen that this compound gives rise to three cathodic peaks in the forward scan. This is similar to the case of ortho-and para-dinitrobenzenes in DMF [13]. The peak potentials of all the three peaks become more negative with increasing sweep rate. When the potential sweep is reversed at the end of the first cathodic peak, corresponding anodic peak is observed at about 60 mV more positive to the cathodic peak potential at low sweep rates, indicating the presence of a single-electron reversible process under cyclic voltammetric conditions. However, it may be pointed out that the cathodic and anodic peaks pertaining to this process are shifted to more negative and positive potentials, repectively, with increasing sweep rate thus indicating a slow charge-transfer step[14]. The reversal of the potential sweep at the end of the second cathodic peak does not show any anodic peak in the vicinity of the cathodic peak but an anodic peak occurs at a much more positive potential (at -1.110V vs SCE in DMF and at -0.945V vs SCE in AN) which gives rise to a barely observable new cathodic peak on the first reverse sweep. This indicates the presence of a new redox couple arising from the reduction product at the second cathodic peak which seems to involve the participation of at least two or more electrons on the basis of peak separation (ΔE_p) values. Similarly, a reversal of the potential sweep at the end of the third cathodic peak does not show any anodic peak in the vicinity of this

TABLE 2

CYCLIC VOLTAMMETRIC DATA FOR 2,4-DINITRO (5.0×10^{-4} M) AND 2,4,6-TRINITRO (3.0×10^{-4} M) DPA'S IN DMF AND AN IN THE PRESENCE OF 0.1M TEAI SUPPORTING ELECTROLYTE; ALL POTENTIALS ARE w.r.t SCE.

Compound/ Solvent	Sweep rate, V (Vs^{-1})	$-(E_p^c)_I$ (V)	$(i_p^c)_I$ (μA)	$-(E_p^a)_I$* (V)	$(i_p^a)_I$ (μA)	$-(E_p^c)_{II}$ (V)	$(i_p^c)_{II}$ (μA)	$-(E_p^c)_{III}$ (V)	$(i_p^c)_{III}$ (μA)
2,4-dinitro DPA/DMF	0.0743	0.885	7.50	0.825	3.75	1.415	19.22	1.785	42.66
	0.1650	0.890	11.25	0.825	7.26	1.435	27.19	1.835	55.31
	0.2534	0.895	13.59	0.820	10.31	1.455	30.70	1.845	58.36
	0.4417	0.905	18.28	0.820	15.94	1.475	38.44	1.880	72.19
2,4-dinitro DPA/AN	0.0743	0.885	11.72	0.830	3.28	1.235	25.78	1.575	37.50
	0.1650	0.890	17.81	0.825	6.56	1.260	35.16	1.595	46.88
	0.4100	0.895	28.13	0.820	11.25	1.275	49.22	1.605	53.28
	0.7640	0.900	38.67	0.815	15.94	1.290	58.13	1.630	77.34
2,4,6-trinitro DPA/DMF;AN	0.0743	1.425	17.34	--	--	1.595	17.81	broad peak	
		1.295#	23.44#	--	--	1.435#	34.69#	1.615#	+
	0.1650	1.445	23.91	--	--	1.615	21.56	broad peak	
		1.325#	30.23#	--	--	1.465#	43.13#	1.645#	+
	0.4100	1.455	31.95	--	--	1.635	32.81	broad peak	
		1.335#	43.13#	--	--	1.475#	52.97#	1.665#	+
	0.7640	ill-defined		--	--	ill-defined		broad peak	
		1.355#	57.19#	--	--	1.485#	64.22#	1.685#	+

* Anodic peak is observed when the voltage sweep is reversed after the apperarance of the first cathodic peak

\+ Peaks are ill-defined and hence peak current values are not quoted

\# Values in AN solutions

cathodic peak but two new redox couples are indicated at more positive potentials involving multielectron irreversible steps (Fig.2.) . The absence of the anodic peaks corresponding to second and third cathodic peaks of this compound proves the total irreversibility[15-17] of the electrode reactions corresponding to these peaks.

The cyclic voltammetric results of 2,4-dinitro DPA in DMF solutions in the presence of 0.1M $NaNO_3$ supporting electrolyte, are comparable with those obtained in 0.1M TEAI supporting electrolyte. It is found that the reversal of the potential at the end of the second cathodic peak does not show any anodic peak corresponding to this cathodic peak, but an anodic peak is observed at a much more positive potential (-0.37 V Vs SCE) , which gives rise to a new cathodic peak on the first reverse sweep. The same observation holds good when the potential is reversed at the end of the third cathodic peak.

The first wave of reduction of 2,4-dinitro DPA in DMF and AN solutions in the presence of 0.1M TEAI supporting electrolyte coresponds to a four electron process while the second wave most presumably is an eight electron reduction. The overall reduction, corresponds to a twelve electron reduction under microcoulometric (polarographic) conditions (Table 1).

b. 2,4,6-TRINITRO DPA REDUCTION IN DMF AND AN SOLUTIONS:

The dc, ac polarographic and microcoulometric results on the reduction of 2,4,6-trinitro DPA (3.0×10^{-4} M) in DMF and AN Solutions in the presence of 0.1M TEAI supporting electrolyte are presented in Table 1 and polorograms are shown in Fig.3. The first two waves are not as well separated in AN as in DMF. While three ac peaks are noted corresponding to the three dc waves in DMF, only two ac peaks are seen in AN presumably because the peaks for the first two waves are merged as seen from the small kink in the ac polarogram (Fig 3B).

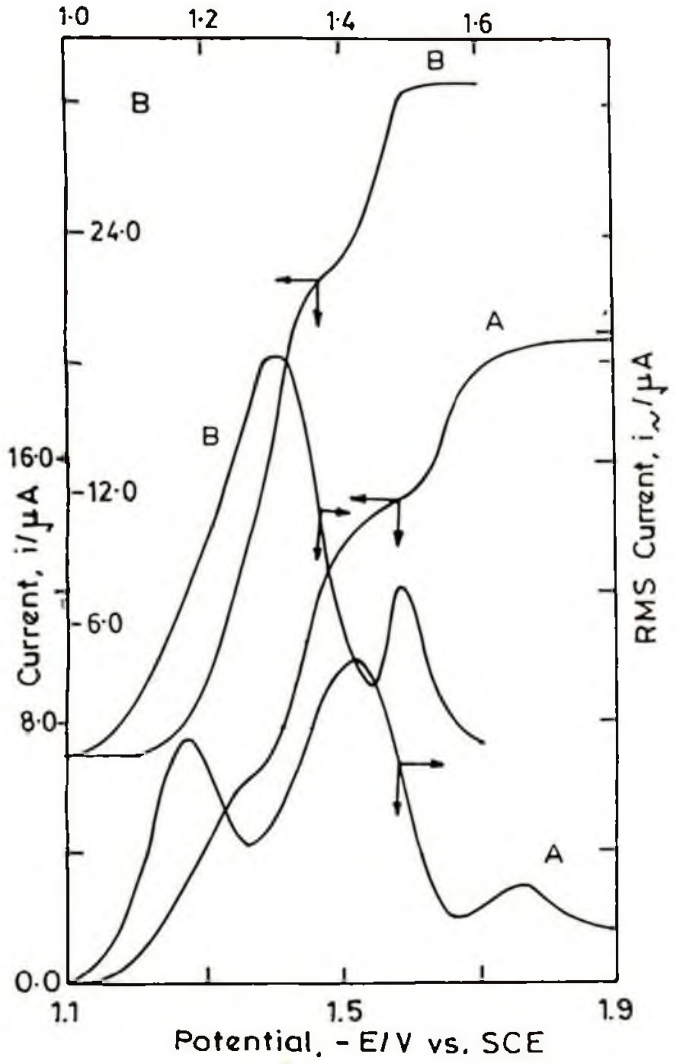


Fig. 3 Dc and Ac polarograms of 2,4,6-trinitro DPA in DMF(A) and AN(B) with 0.1M TEAI supporting electrolyte.

The polarographic data on the reduction of 2,4,6-trinitro DPA in DMF and AN solutions containing 0.1M TEAI supporting electrolyte (Table 1) indicate clearly the electrode reactions pertaining to the three diffusion-controlled waves are irreversible in nature and each wave corresponds to 6 electron reduction.

The cyclic voltammetric results on this compound are presented in Table 2 and the voltammograms are shown in Fig.4. It is seen that three cathodic peaks are observed in this case also and the peak potentials are shifted to more negative values with increasing sweep rate. When the potential sweep is reversed at the end of the first, second and third cathodic peaks, respectively, no anodic peaks are observed in the region of the corresponding cathodic peaks

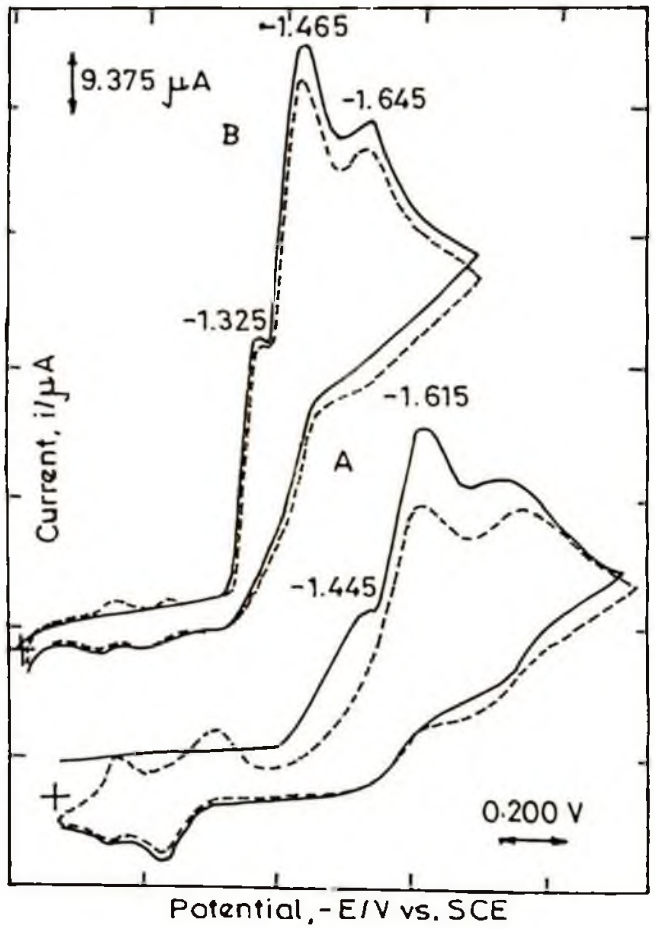


Fig. 4 Cyclic voltammograms of 2,4,6-trinitro DPA in DMF(A) and AN(B) with 0.1M TEAI supporting electrolyte at 0.1650 V/sec. sweep rate(dashed line represents repeated sweep).

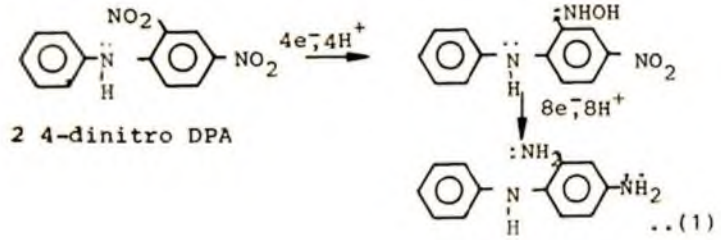
indicating irreversibility of the respective electrode reactions. However on the basis of the same arguments given earlier, the two anodic

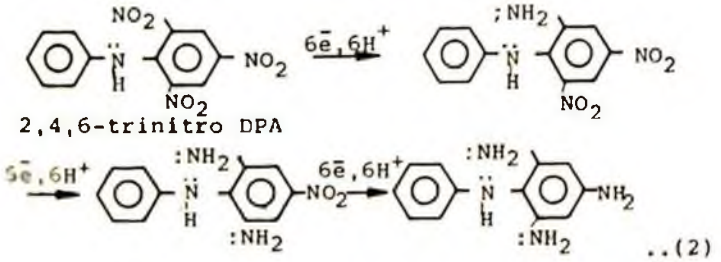
peaks observed at more positive potentials (Fig.4) may be attributed to multielectron oxidations.

Microcoulometric experiments on 2,4,6-trinitro DPA in DMF and AN solutions in the presence of 0.1M TEAI supporting electrolyte with the potential fixed at the limiting region of the first wave gave a value, $n_{app} = 6$ (Table 1). Considering that the three reduction waves obtained on this compound are approximately of equal height (Fig.3), it is concluded that the total number of electrons involved in the reduction in DMF and AN solutions is equal to 18. This compound, did not give well-defined waves in the presence of sodium nitrate supporting electrolyte.

c. MECHANISM OF REDUCTION FOR 2,4-DINITRO AND 2,4,6-TRINITRO DPA'S IN DMF AND AN SOLUTIONS:

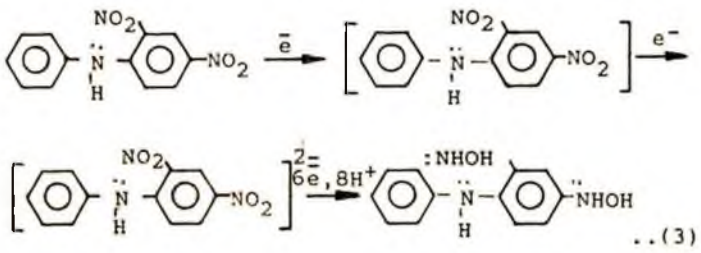
Based on the polarographic, cyclic voltammetric and coulometric results obtained on the reductions of 2,4-dinitro and 2,4,6-trinitro DPA's in DMF and AN solutions, the following mechanistic schemes are proposed:





The overall reduction of 2,4-dinitro DPA corresponds to twelve electrons. The first four electrons and four pro-tons step gives the corresponding 2-hydroxylamino-4-nitro DPA and subsequent participation of eight electrons and eight protons leads to 2,4-diamino DPA product. It may be stated that controlled-potential electrolysis of 2,4-dinitro DPA in dMF or AN solutions in the presence of 0.1M TEAI supporting electrolyte carried out in the cavity of the EPR spectrometer[22] gave evidence for the formation of 2,4-dintitro DPA anion radical and hence it is concluded that the first stage of reduction is occurring through the radical anion intermediate and subsequent uptake of three more electrons resulted in the formation of the hydroxylamine derivative.[23-27]

The overall reduction of 2,4-dinitro DPA in DMF solutions in the presence of sodium nitrate supporting electrolyte requires, eight electrons (one electron each for the first two waves and six electrons for the third wave, Table 1). Since the possibility of two electrons being added to the same nitro group is improbable on the basis of electrostatic considerations, it may be expected that each electron is added to each of the two nitro groups and subsequently the addition of six electrons takes place according to the following scheme:



In this case also, controlled - potential electrolysis in the cavity of EPR cell gave an EPR signal[22], thus confirming the presence of a radical anion intermediate in the first step of reduction. In the above scheme (Scheme 3), it is presumed that six electrons and eight protons are equally utilised by the two nitro radical groups. There is yet another poissibility in which one of the nitro radical anion functions is reduced to-NO with the uptake of one-electron and two protons while the other nitro radical anion function gets reduced to $-NH_2$ with the uptake of five electrons and six electrons. This possibility is not considered[28] in the absence of any definite evidence for the formation of nitroso derivative. The formation of 2,4-dihydroxylamine DPA in DMF in the presence of sodium nitrate supporting electrolyte is in good agreement with our earlier work on mono nitro DPAs in dipolar aprotic solvents[29]

It may be mentioned that the protons required for the above mentioned reductions (Schemes 1, 2 and 3) are supplied presumably by the trace amounts of water present in the solvents[31] or by the solvent itself[31] as in the case of acetonitrile.

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