2688 © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***62,*** *2688—2692 (1989)* [Vol. 62, No. 8

Electrochemical Generation and Properties of the *p*-Dinitrobenzene Radical Anion in *N,N*-Dimethylformamide

Alexandra Sauer, Fritz Wasgestian,* and Ulrich Nickel†
Institute of Inorganic Chemistry, University of Cologne, 5000 Cologne 41, Federal Republic of Germany
†Institute of Physical and Theoretical Chemistry, University of Erlangen-Nuremberg,
Federal Republic of Germany

(Received October 17, 1988)

Potentiostatic reduction of *p*-dinitrobenzene in *N,N*-dimethylformamide yielded the anion radical. By careful exclusion of water and oxygen it was obtained free from by-products. It was stable for several hours at room temperature. Its UV-visible absorbance was determined in combination with polarographic analysis. The behavior towards water and oxygen is reported.

The electrochemical reduction of *p*-dinitrobenzene (pDNB) has been extensively studied. Polarography showed two reversible reduction waves, corresponding to the formation of the singly and doubly charged anions pDNB$^{\dot{-}}$ and pDNB^{2-}.[1-9] In aqueous solution *p*-nitrophenylhydroxylamine (Hy) was the first long-lived reduction product.[10] In aprotic solvents, however, pDNB$^{\dot{-}}$ was found to be stable. In DMF (*N,N*-dimethylformamide) it was obtained by potentiostatic reduction and characterized by ESR spectroscopy.[5,6]

The reaction of *p*-dinitrobenzene with OH$^-$ yielded *p*-nitrophenoxide (pNP$^-$).[11-13] In the absence of oxygen both pNP$^-$ and pDNP$^{\dot{-}}$ were observed spectrophotometrically in DMSO (dimethyl sulfoxide).[13]

Compared to the characterization by ESR and electrochemical methods the electronic absorption spectrum of pDNB$^-$ is not so well-known. In aqueous solution the radical spectrum was obtained after pulse radiolysis.[14,15] pDNB$^-$ decayed fast with a second order rate constant of 3.3×10^8 M^{-1} s^{-1} (1 M=1 mol dm^{-3}). In glassy solution in 2-methyltetrahydrofuran (MTHF) the radical was stable.[16] Its spectrum showed a pronounced vibrational fine structure. Recently a matrix molecule reorientation effect has been observed in the same solvent that blurred out the vibrational fine structure and caused a time dependent blue shift.[17] In aprotic solvents the *p*-dinitrobenzene radical (pDNB$^{\dot{-}}$) is sufficiently stable to be studied by conventional techniques at room temperature.

Preparation of the radical by reaction with OH$^-$ in aqueous DMSO was associated with the formation of pNP$^-$.[13] In the absorption spectrum pNP$^-$ superimposed the bands around 430 nm. The absorption coefficient which Abe and Ikegami[13] used in their kinetic treatment differed by more than one order of magnitude from that in glassy solution in MTHF. Brown et al.[18] obtained the radical by chemical reduction with sodium in 1,2-dimethoxyethane. They reported the absorption spectrum assuming quantitative conversion. However, the presence of pNP$^-$ could not be convincingly excluded. In our opinion another determination of the spectral characteristics, that is not disturbed by by-products or secondary reactions, is necessary.

Experimental

N,N-Dimethylformamide (DMF), Fluka ppa or Merck, Uvasol, was dried with anhydrous CuSO$_4$ and distilled. Solutions were deoxygenated by purging with dry

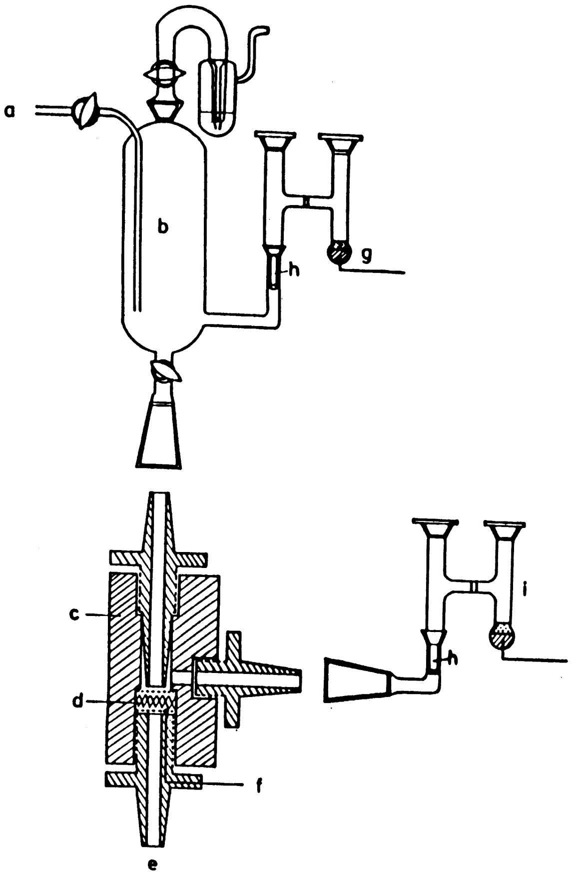

Fig. 1. Apparatus used for potentiostatic reduction of *p*-dinitrobenzene in DMF. a: argon entrance, b: vessel for stock solution, c: Teflon cell with working electrode, d: carbon fleece, e: exit to flow cell or ordinary spectrophotometric cell, f: Pt wire, g: counter electrode (SCE), h: agar-agar junction, i: reference electrode (SCE).

argon for 20 min. Supporting electrolytes were 0.1 M Bu_4NClO_4 (Fluka) or 0.1 M Et_4NClO_4 (Fluka). *p*-Dinitrobenzene (pDNB), Aldrich, was recrystallized from EtOH. For reasons of comparison the spectral data of *p*-nitrophenol (pNP) and *p*-nitrophenylhydroxylamine (Hy) were determined. pNP was obtained commercially (Merck), Hy was prepared according to literature.[19] Under our reaction conditions both were present in their base forms (pNP^- and Hy^-) with absorption maxima $\lambda(\varepsilon)$ [nm(1 mol^{-1} cm^{-1})] at 432 (3.7×10^4) and 465; 485 (1.7×10^4); 520 sh, respectively. In the presence of pDNB the base form of the hydroxylamine formed an adduct with absorption at 500 (2×10^4). Absorption spectra were recorded on a Cary 2300 and a Uvikon 810 (Kontron). Polarograms were obtained by use of a potentiostat (HEKAelectronic PG 284) in combination with an xy-recorder (Servogor xy). The cathode was a dropping mercury electrode, the counter electrode a saturated calomel electrode (SCE), and the reference electrode was a Pt-electrode.

The apparatus used for the quantitative reduction is depicted in Fig. 1. The cathode was a carbon fleece contacted with a perfoliated gold foil. Counter and reference electrodes were SCEs separated from the solution by an agar-agar salt bridge. The use of a calomel electrode as counter electrode was advantageous, because its large mercury pool acted as reductant. By this means oxidation of the solvent was avoided. Voltage was supplied from a potentiostat (Wenking LB75 or 70TS1). The reductions were performed at flow rates of 0.5—0.8 ml min^{-1} and currents of 0.6—1 mA. After passing the fleece, the solution was directed either to a spectrophotometric flow cell or to the polarographic cell. After having recorded the polarogram, a sample of the solution was transferred to a spectrophotometric cell by use of a syringe and a hypodermic needle. During this operation the cell was standing in a flask that was flushed with argon. By the latter method polarographic as well as spectrophotometric analysis could be performed in the same solution.

Tandem cells were applied to study the effects of additives. These cells contained two separated compartments containing the reactants. By shaking the solutions could be mixed.

The spectral changes during oxidation were observed in ordinary spectrophotometer cells. Immediately after reduction the cells were transfered to the spectrophotometer. Recording was started approximately 1 min after reduction. The slowly penetrating air caused reaction.

The following absorptivity coefficients were used for the spectrophotometric analysis.

[nm]	[M^{-1} cm^{-1}]		
	$pDNB^{\cdot-}$	Hy	pNP^-
800	1.1×10^4	$\leqslant1.0\times10^2$	$\leqslant1.0\times10^2$
500	7.6×10^2	2.0×10^4	$\leqslant1.0\times10^2$
430	7.7×10^3	1.1×10^4	3.6×10^4

At first the radical concentration was determined from the absorbance at 800 nm. Then at 500 nm the concentration of *p*-nitrophenylhydroxylamine (pDNB-adduct) was obtained by subtracting the contribution by $pDNB^{\cdot-}$. Finally the concentration of pNP^- was obtained from the absorbance at 430 nm.

Results and Discussion

a) Potentiostatic Reduction and Quantitative Analysis. In DMF the polarographic reduction showed two reversible steps at −580 and −915 mV. SCE in reasonable agreement with literature.[1,4,5,8] The first reduction step led to the radical anion $pDNB^-$ and the second to $pDNB^{2-}$. Potentiostatic reduction at potentials between −600 and −900 mV only produced the single charged anion. Reduced solutions had the same ESR spectrum as previously reported for $pDNB^{\cdot-}$.[5,6]

Figure 2 shows polarograms of pDNB and its radical ion. If both species were present in solution, the oxidation current of the radical superimposed the reduction current of pDNB at the position of the first half wave potential. Their relative heights were a measure of the concentrations. In the absence of side reactions and assuming equal diffusion coefficients of pDNB and $pDNB^{\cdot-}$:

$$c(\mathrm{pDNB}) = \frac{I_{\mathrm{red}}}{I^0_{\mathrm{red}}}\, c^0(\mathrm{pDNB});$$

$$c(\mathrm{pDNB}^{\cdot-}) = \frac{I_{\mathrm{ox}}}{I^0_{\mathrm{red}}}\, c^0(\mathrm{pDNB}) \qquad (1)$$

where I^0_{red} and c^0(pDNB) are the reduction current and the pDNB concentration of the initial solution.

Table 1 presents a selection of our reduction experiments. The first set gives some preliminary results,

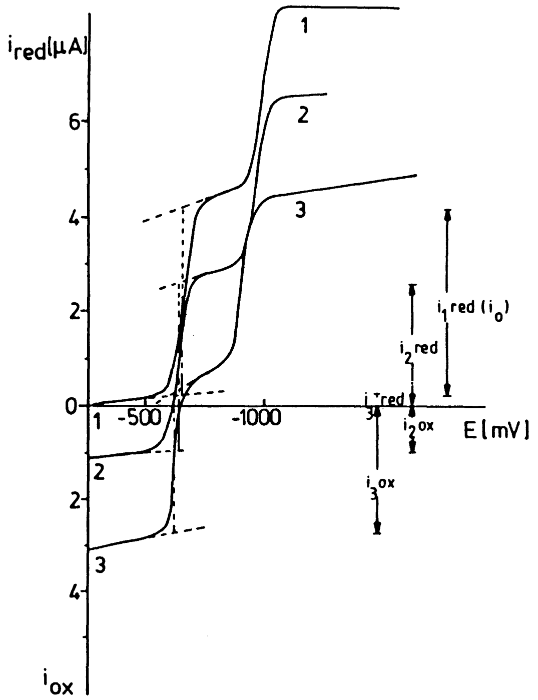

Fig. 2. Polarographic determination of pDNB and $pDNB^{\cdot-}$. 1: unreduced solution (1×10^{-3} M pDNB), 2: partly reduced solution (6×10^{-4} M pDNB. 3×10^{-4} M $pDNB^{\cdot-}$), 3: highly reduced solution (8×10^{-4} M $pDNB^{\cdot-}$).

Table 1. Survey on the Potentiostatic Reduction Experiments of *p*-Dinitrobenzene in DMF at Room Temperature by Means of the Apparatus Depicted in Fig. 1. Flow Rate 0.5—0.8 ml min^{-1}, Current 0.6—1 mA, Depending on the Potential E_{red}

$c_0\times10^4$ a)		E_{red}	$c\times10^4$/M			
M		mA	pDNB$^{\cdot-}$ a)		Hy	pNP$^-$
10.1	(8.7)	-800	0.55	(0.6)	0.31	0.09
9.7	(6.5)	-700	2.8	(2.4)	0.22	0.10
9.7	(5.9)	-950	2.9	(3.0)	0.12	0.18
4.9	(0.1)	-950	5.0	(4.9)	<0.02	<0.02
5.0	(0.1)	-950	4.8	(5.0)	<0.02	<0.02
2.4		-500	<0.02		<0.02	<0.02
		-600	<0.02		<0.02	<0.02
		-700	1.0		<0.02	0.08
		-800	2.5 b)		<0.02	0.02
		-1000	2.5 b)		0.01	0.05
		-1180	2.5 b)		0.09	0.08

a) In brackets concentrations determined polarographically after reduction. b) Radical concentrations determined at 750 nm.

where degassing was insufficient. The radical disappeared rather fast and pNP$^-$ was formed. Whereas in well-degassed and carefully dried solutions the radical was stable for several hours. In those solutions the radical concentrations were determined polarographically. Set 2 compared the data with those obtained spectrophotometrically.

Solutions containing 5×10^{-4} M or less could be completely reduced potentiostatically. Immediately after reduction the solutions were practically free from by-products. The effect of the reduction potential is demonstrated in the last set. Potentials of -0.5 and -0.6 V did not cause reaction. At -0.7 V the pDNB was reduced but less than 50%. In this solution pNP$^-$ was formed, whereas at -0.8 V the formation of pNP$^-$ was negligible. At potentials sufficiently negative to produce the pDNB^{2-} the hydroxylamine was found. In those solutions, where the pDNB was not completely reduced, the hydroxide ion, produced by electrolysis of traces of water or impurities of the electrolyte, led to substitution:[5]

$$RNO_2 + OH^- \longrightarrow ROH + NO_2^- \tag{2a}$$

$$ROH + OH^- \rightleftharpoons RO^- + H_2O \tag{2b}$$

$(R = O_2NC_6H_4)$

b) Spectral Characterization. From the electronic absorption spectrum recorded in combination with polarography (Fig. 3), the absorption coefficients were determined. By this procedure the spectrum was obtained without interference of pNP$^-$ that overlaps the band at 400 nm.[13] Compared with the low-temperature spectrum in 2-methyltetrahydrofuran the bands are broadened and the vibrational fine structure has disappeared.

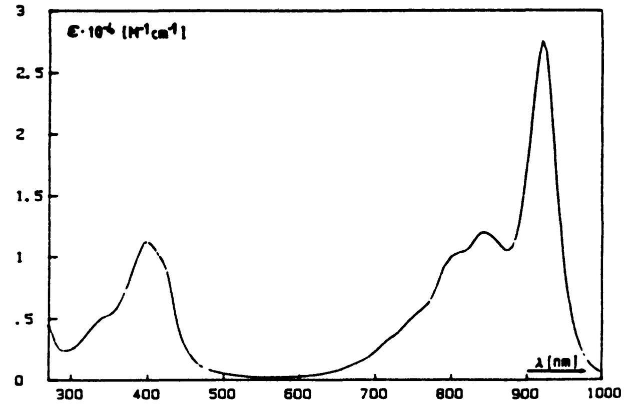

Fig. 3. UV-vis absorption spectrum of the *p*-dinitrobenzene radical anion. Avarage of 6 independent runs.

The absorbance is of the same order of magnitude as that in 2-methyltetrahydrofuran at low temperature. The spectral data estimated in Ref. 13 are obviously erroneous.

c) Reactivity of the Radical. The effect of additives was studied in the tandem cell. Dilution by DMF did not change the absorption spectrum. We regard this result as a proof that the system had no leakage. Addition of O_2 saturated DMF mainly reoxidized the radical. However, about 15% of the radical reacted to *p*-nitrophenoxide (pNP$^-$) probably with intermediate superoxide ions:

$$RNO_2^{\cdot-} + O_2 \longrightarrow RNO_2 + O_2^- \tag{3}$$

$$RNO_2^{\cdot-} + O_2^- \longrightarrow RO^- + NO_3^- \tag{4}$$

The reformed RNO_2 may also have reacted according to Eq. 2. The same percentage of pNP$^-$ was also obtained after shaking in air.

The spectral changes during oxidation are shown in

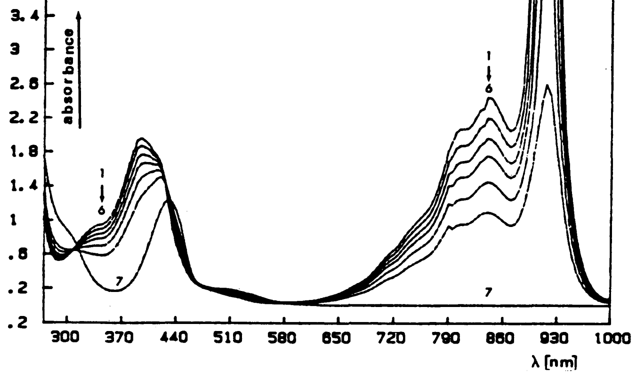

Fig. 4. Spectral changes during air oxidation of 1.7×10^{-4} M pDNB$^{\cdot-}$ 1: 0 min, 2: 5 min, 3: 15 min, 4: 26 min, 5: 47 min, 6: 83 min, 7: 18 h. Optical path length 1 cm, scan rate 5 nm s^{-1}, start at 1000 nm.

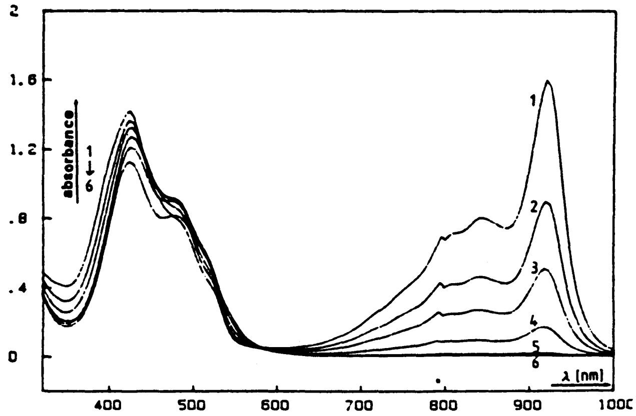

Fig. 5. Spectral changes during air oxidation of 1.2×10^{-4} M pDNB$^{\cdot-}$ in wet DMF (4 vol% H_2O). 1: 0 min, 2: 5 min, 3: 10 min, 4: 20 min, 5: 31 min, 6: 46 min. Pathlength 0.5 cm, other conditions as in Fig. 4.

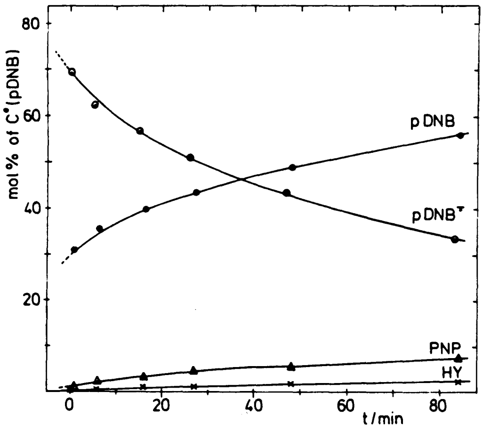

Fig. 6. Concentration changes during air oxidation of pDNB$^{\cdot-}$; analysis of data of Fig. 4; initial concentration of pDNB: 2.5×10^{-4} M.

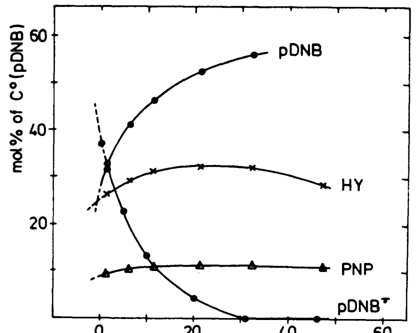

Fig. 7. Concentration changes during air oxidation of pDNB$^{\cdot-}$ in wet DMF; analysis of data of Fig. 5; initial concentration of pDNB 3.3×10^{-4} M.

Fig. 4. The disappearance of the radical caused the decrease of the band at 920 nm. In the 400 nm region the production of *p*-nitrophenoxide shifted the absorption maximum to 432 nm (absorption maximum of pNP$^-$). The curves pass through an isosbestic point at 310 nm although more than two components were present. However, the absorbance of pDNB, pNP$^-$, and pDNB$^{\cdot-}$ happens to be so similar at 310 nm that the minor contribution of pNP$^-$ did not become evident. The reappearing pDNB produced the increase in absorbance at $\lambda<300$ nm. The weak absorbance at 510 nm was caused by traces of *p*-nitrophenylhydroxylamine which was present as an adduct of its base form with pDNB.

In wet DMF (4 vol% H_2O) the pattern was more complex (Fig. 5). The radical disappeared much faster; pNP$^-$ and *p*-nitrophenylhydroxylamine (Hy) were produced in larger amounts. Initially, the hydroxylamine was formed as the base (absorption maximum at 480 nm), it reacted with pDNB forming the adduct with the absorption maximum at 500 nm.

Figures 6 and 7 show the kinetics in both systems. The remaining concentration of pDNB was determined from the sum of all the other known components. Figure 7 shows a decrease on hydroxylamine concentration that indicates the production of another compound. This could be *p*-nitronitrosobenzene which is formed by reaction of Hy with oxygen.[5] It does not absorb strongly in the visible region. Its intense absorption is found at 282 nm. For times longer than 30 min the sum analysis was not justified anymore. The radical decay was exponential in both solution.

We thank the "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie" for financial assistance.

References

1) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

2) R. Koopmann and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **70**, 127 (1966).

3) M. Svaan and V. D. Parker, *Acta Chem. Scand., Ser. B*, **40**, 36 (1986).

4) H. Bock and U. Lechner-Knoblauch, *Z. Naturforschung*, **40b**, 1463 (1985).

5) J. Q. Chambers III and R. N. Adams, *J. Electroanal. Chem.*, **9**, 400 (1965).

6) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

7) E. Ahlberg, B. Svensmark, and V. D. Parker, *Acta Chem. Scand., Ser. B*, **34**, 53 (1980).

8) Z. V. Todres, A. A. Pozdeeva, V. A. Chernova, and S. I. Zhdanov, *Tetrahedron Lett.*, **1972**, 3835.

9) A. Darchen and C. Moinet, *J. Electroanal. Chem.*, **78**, 81 (1977).

10) L. Holleck and H. Schmidt, *Z. Elektrochem.*, **59**, 56 (1955).

11) K. Bowden and R. S. Cook, *J. Chem. Soc. B*, **1971**, 1765.

12) I. I. Bilkis and S. M. Shein, *Tetrahedron*, **31**, 969 (1975).

13) T. Abe and Y. Ikegami, *Bull. Chem. Soc. Jpn.*, **51**, 196 (1978).

14) P. Neta, M. G. Simic, and M. Z. Hoffman, *J. Phys. Chem.*, **80**, 2018 (1976).

15) V. Jagannadham and S. Steenken, *J. Am. Chem. Soc.*, **106**, 6542 (1984).

16) T. Shida and S. Iwata, *J. Phys. Chem.*, **75**, 2591 (1971).

17) R. K. Huddleston and J. R. Miller, *J. Phys. Chem.*, **86**, 2410 (1982).

18) R. G. Brown, A. Harriman, and L. Harris, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1193 (1978).

19) R. Kuhn and F. Weygand, *Chem. Ber.*, **69**, 1969 (1936).