ANALYTICAL SCIENCES JUNE 2005, VOL. 21

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Electrochemical Investigation of 1,3,5-Triphenylformazan and Its Nitro Derivatives in Dimethyl Sulfoxide

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Cyclic voltammetric (CV) and chronoamperometric (CA) behaviors of 1,3,5-triphenylformazan (TPF), 3-(*p*-nitrophenyl)-1,5-diphenylformazan (PNF) and 3-(*m*-nitrophenyl)-1,5-diphenylformazan (MNF) were studied in dimethyl sulfoxide medium. TPF was found to give a single sharp cathodic CV peak corresponding to a gain of one-electron per molecule. The diffusion coefficient and the number of electrons transferred were calculated using the Baranski equation with the CV-data obtained by an ultramicroelectrode. Standard rate constants for the reduction were calculated by the Klingler–Kochi technique. The electrochemical data obtained support the mechanism proposed by Umemoto.

(Received July 20, 2004; Accepted December 6, 2004)

Introduction

The increasing interest in the chemistry of formazans is primarily due to their biological activity[1] and their use for analytical purposes, especially in trace element determinations.[2] It was found that formazans, together with metals could act as dyes.[3,4] Although formazans have been extensively studied,[5] little has been reported about their electrochemical behavior. Umemoto reports that 2,3,5-triphenyltetrazolium ion, the oxidation product of triphenylformazan, is reduced to the anion of formazan by a two-electron reaction in dimethyl sulfoxide. The same anion also results when 1,3,5-triphenylformazan is reduced electrochemically by a one-electron mechanism.[6,7] Elenien suggested that *p*-Cl and *o*-CH_3 diphenylformazans are oxidized in a single step two-electron transfer, followed by a deprotonation reaction that forms the corresponding tetrazolium cation in ethanol/buffer media.[8] To our knowledge, there has been no systematic study concerning the electrochemical kinetics and diffusion coefficient of this reaction and whether or not adsorption plays a role in the electrochemistry of these compounds.

This paper mainly concerns the electrochemical behavior and redox mechanism of 1,3,5-triphenylformazan (TPF), 3-(*m*-nitrophenyl)-1,5-diphenylformazan (MNF) and 3-(*p*-nitrophenyl)-1,5-diphenylformazan (PNF) in dimethyl sulfoxide. The diffusion coefficient, the number of electrons transferred and the standard heterogeneous electrochemical rate constants (k_s) were determined by using cyclic voltammetry and chronoamperometry.

An electrochemical investigation of the formazan-tetrazolium system has already been carried out by Umemoto and Elenien.[6-8] Here, we expand these studies with two nitro derivatives and also present some kinetic features.

The structures of 1,3,5-triphenylformazan and its nitro derivatives are given in Fig. 1.

Experimental

Chemicals

1,3,5-Triphenylformazan and its derivatives were prepared as described in the literature.[9] The compounds were purified by recrystallization from ethanol until a sharp melting point (173°C for TPF, 180°C for MNF, 196°C for PNF) was reached and no impurities on TLC plates were observed. The structures of the purified compounds were elucidated by using IR, ^{1}H-NMR and elemental analysis. Dimethyl sulfoxide (DMSO) used was an absolute dry (water ≤ 0.01%) batch of Fluka (41648) kept on beads of a molecular sieve (4 Å).

The supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBATFB) was purchased from Fluka (21796-4) and was used without purification. All of the other chemicals were of reagent grade and were used without further purification.

Apparatus

Voltammetric measurements were made with the aid of a BAS100 B/W electrochemical analyzer. A platinum electrode (PE) (BAS MF-2013) and a 100 μm-platinum ultramicroelectrode (BAS MF-2150) were used as a working electrode. The electrodes were polished before each use with alumina polishing powder. A platinum wire was used as the auxiliary electrode (BAS MW-1034). The reference electrode was a silver wire in contact with 0.1 M $AgNO_3$ in dimethyl

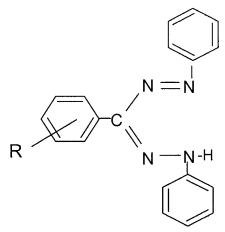

Fig. 1 The structure of formazans (R = H, *m*-NO_2, *p*-NO_2).

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Table 1 Diffusion coefficients, number of electrons, standard rate constants for heterogeneous electron transfer (k_s) in dimethylsulfoxide ($c = 1.03 \times 10^{-3}$ M TPF, MNF and PNF containing 0.10 M tetrabutylammonium tetrafluoroborate)[a]

Compound	Diffusion coefficient (D)/cm^2 s^{-1} $D \pm ts/\sqrt{N}$	Number of electrons transferred		Standard rate constants (k_s)/cm s^{-1} $k_s \pm ts/\sqrt{N}$
		Peak A	Peak F + G	
TPF	$2.48 \times 10^{-6} \pm 2.10 \times 10^{-7}$	1.11 ± 0.24	—	$1.25 \times 10^{-2} \pm 2.40 \times 10^{-4}$
MNF	$1.17 \times 10^{-6} \pm 4.29 \times 10^{-7}$	0.97 ± 0.17	2.12 ± 0.16	$1.26 \times 10^{-2} \pm 7.18 \times 10^{-4}$
PNF	$3.66 \times 10^{-6} \pm 3.15 \times 10^{-7}$	0.85 ± 0.21	2.21 ± 0.26	$1.23 \times 10^{-2} \pm 3.67 \times 10^{-4}$

a. 95% confidence level, $N = 6$.

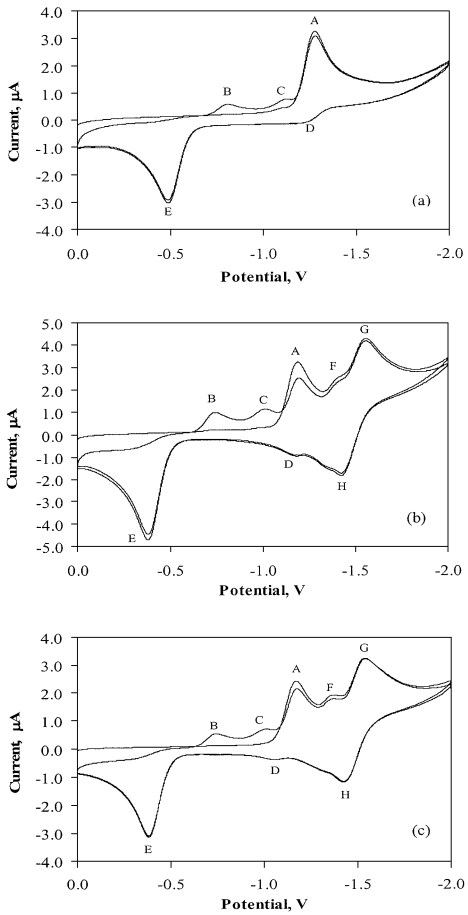

Fig. 2 Cyclic voltammograms of 1.03×10^{-3} M (a) TPF, (b) MNF, and (c) PNF in dimethyl sulfoxide containing 0.10 M tetrabutylammonium tetrafluoroborate at 100 mV/s scan rate.

sulfoxide. All solutions were deaerated for 10 min with pure argon. All the measurements were taken at room temperature, 25 ± 1°C.

Method

The number of electrons transferred and the diffusion coefficients were determined by the ultramicroelectrode CV technique of Baranski.[12] The heterogenous rate constants were calculated according to the Klingler-Kochi method.[15]

Results and Discussion

Characterization of the electrode reactions

Cylic voltammograms (CV) of the three compounds obtained

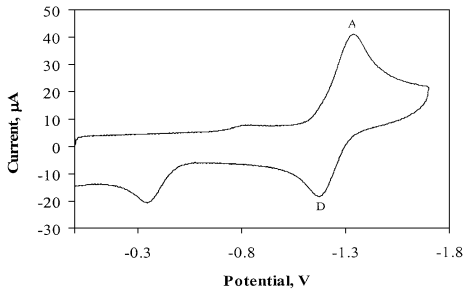

Fig. 3 Cyclic voltammogram of 1.20×10^{-3} M TPF in dimethyl sulfoxide containing 0.10 M tetrabutylammonium tetrafluoroborate at a scan rate of 10 V/s.

at a scan rate of 100 mV s^{-1} are shown in Fig. 2. On the CV of TPF (Fig. 2a), a distinct reduction peak (A) at –1276 mV, an oxidation shoulder (D) at around –1246 mV and a sharp oxidation peak (E) at –487 mV are discernable. The peaks denoted as B and C do not appear in the first run and become more pronounced in the successive runs, indicating that they are related to the oxidation product formed during the development of peak E. The same phenomenon is reported by Umemoto.[7]

With the *p*-NO_2 and *m*-NO_2 derivatives, the cathodic peaks corresponding to the parent formazan structure appear at –1176 and –1190 mV, respectively (Figs. 2b, c). These peaks apparently shifted to less negative potentials, reflecting the mesomeric effect of the nitro group. The shifts are strikingly close to each other; this is not surprising, because the Hammett constant contributions of *m*-NO_2 and *p*-NO_2 are almost the same.[16]

The CV's of PNF and MNF also display two additional cathodic peaks one ill-resolved and one distinct. These peaks are characteristic of aromatic nitro groups.[10,11]

The number of electrons per molecule transferred during the reduction of TPF, PNF and MNF is calculated by ultramicroelectrode CV runs.[12] Diffusion coefficient calculations were also based on this technique. The number of electrons transferred and the diffusion coefficient values are tabulated in Table 1.

The reduction of TPF and its nitro derivatives appear to be quasi-reversible, because ΔE_p ($E_p^a - E_p^c$) is larger than 59/n mV; also, as the scan rate increases, the anodic peak D becomes more pronounced (Fig. 3), the cathodic peak potential becomes more negative and ΔE_p increases. Furthermore, as can be seen from Figs. 4 and 5, the cathodic peak current increases with an increase in $v^{1/2}$ and the i_p^a/i_p^c ratio tends to approach to unity. The same phenomenon was observed with PNF and MNF in this regard. All these results are consistent with a quasi-reversible behavior.[13,14]

To throw light on whether adsorption is operative in the electrochemical process in question, we made use of cyclic

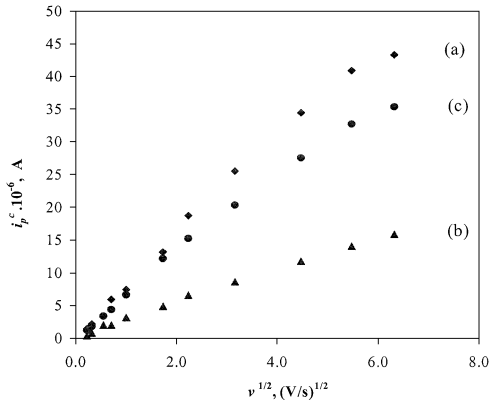

Fig. 4 Variation of cathodic peak currents with $v^{1/2}$ of 1.03×10^{-3} M (a) TPF, (b) MNF, and (c) PNF in dimethyl sulfoxide containing 0.10 M tetrabutylammonium tetrafluoroborate.

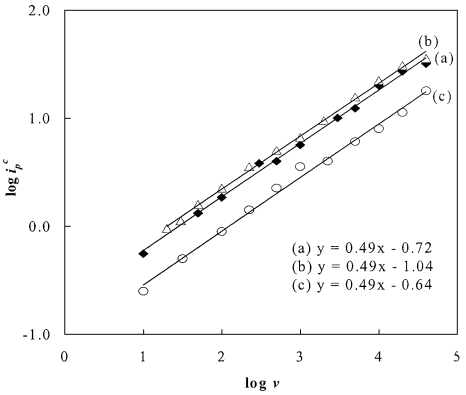

Fig. 6 log i_p^c–log v plots of 1.03×10^{-3} M (a) TPF, (b) MNF and (c) PNF in dimethyl sulfoxide containing 0.10 M tetrabutylammonium tetrafluoroborate.

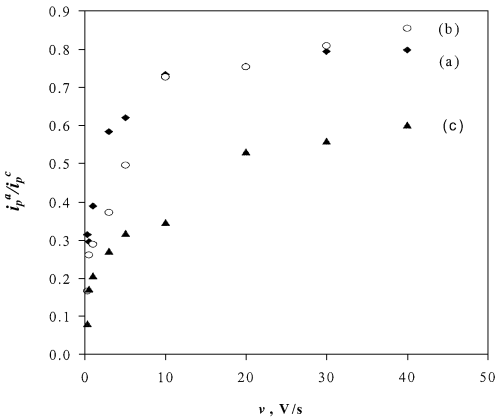

Fig. 5 Variation of i_p^a/i_p^c ratio with v of 1.03×10^{-3} M (a) TPF, (b) MNF, and (c) PNF in dimethyl sulfoxide containing 0.10 M tetrabutylammonium tetrafluoroborate.

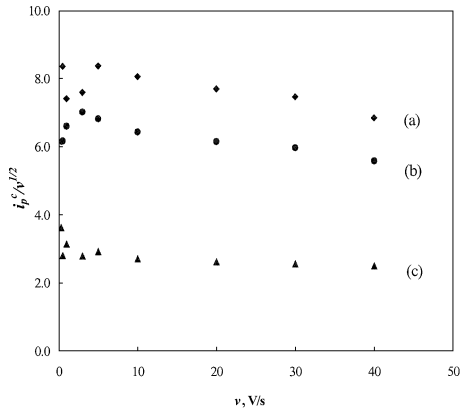

Fig. 7 Variation of $i_p^c/v^{1/2}$ ratio with v of 1.03×10^{-3} M (a) TPF, (b) MNF, and (c) PNF in dimethyl sulfoxide containing 0.10 M tetrabutylammonium tetrafluoroborate.

voltammetry.[14] The log i_p *vs.* log v plots are given in Fig. 6 for each compound. The slopes of these graphs fall in the range: 0.49 ± 0.01 for all the three compounds. Such results indicate that the adsorption phenomenon is not dominant. The fact that no pre- or post-peaks are observed in the CV's of the three compounds at high scan rates is another indication that adsorption does not occur, to any considerable extent, on the electrode surface.[14]

Klingler-Kochi method for the determination of the heterogeneous electron-transfer standard rate constants

As the scan rate is increased, E_p^a, E_p^c and $E_{p/2}$ values change and so does the value of k_s. The k_s *vs.* $v^{1/2}$ plot tends to take the form of a plateau at high scan rates. In our case, this happened after the ΔE_p exceeded ~30000 mV.[15] The average k_s values that are independent of v at 25°C are tabulated in Table 1. These k_s values are another indication that the system is quasi-reversible, because the condition $2 \times 10^{-5}\ v^{1/2} < k_s < 0.3\ v^{1/2}$ is met here.[14]

Studies on the reaction mechanism

The anodic peak corresponding to the reduction of the parent formazan structure (peak D) becomes more distinct at high scan rates (Fig. 3); $i_p^c/v^{1/2}$ *vs.* v graphs are virtually parallel (slightly ascending) to *horizontal* axis (Fig. 7); and i_p^a/i_p^c increases so as to approach unity (Fig. 5). All these results indicate that the mechanism is EC. To verify this, we measured E_p^c and E_p^a values at various scan rates. The results are given in Table 2. Table 2 shows that E_p^c shifts to more negative values with higher scan rates and that a tenfold increase in v brings about a shift of 30/n mV in E_p^c. These findings support the idea that an EC mechanism is involved.

Based on the ESR studies on the reaction mixture, Umemoto[7] suggests the following mechanism for the reduction of TPF:

Table 2 CV voltammetric data of compounds in dimethylsulfoxide (c = 1.03×10^{-3} M TPF, MNF and PNF containing 0.10 M tetrabutylammonium tetrafluoroborate) at 100 mV/s scan rate (mV)

Comp.	E_p^c(A)	E_p^c(B)	E_p^c(C)	E_p^c(F)	E_p^c(G)	E_p^a(D)	E_p^a(E)	E_p^a(H)
TPF	–1276 –1310[a]	–806	–1126	—	—	–1246	–487	—
MNF	–1190 –1217[a]	–744	–1018	–1398	–1562	–1163	–381	–1432
PNF	–1173 –1203[a]	–746	–1016	–1377	–1543	–1161	–384	–1435

a. Scan rate 1000 mV/s.

$TPF + e \longrightarrow (TPF\cdot)^{-}$ (electrode reaction)
$TPF\cdot \longrightarrow (TPF\cdot)^{-} + H$ (chemical reaction)

The reduction of NO_2 group in PNF and MNF proceeds in two steps; as the peaks are not resolvable, only the total number of electrons transferred in two steps were calculated, which is 2 in this case (Table 1). Our electrochemical data support this mechanism for PNF and MNF as well as for TPF.

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