

THE ELECTROREDUCTION OF *CIS*- AND *TRANS*-THIOINDIGO IN N,N-DIMETHYLFORMAMIDE SOLUTIONS

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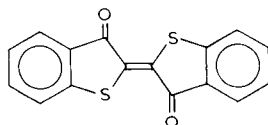
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ABSTRACT

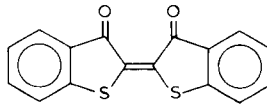
The reduction of the *cis*- and *trans*-isomers of thioindigo (TI) at a platinum electrode was studied by cyclic voltammetry, controlled potential coulometry, rotating ring-disk electrode voltammetry, and e.s.r. spectroscopy. The *trans*-isomer produces predominantly the radical anion upon one-electron reduction while the *cis* radical anion isomerizes to the *trans* form and dimerizes much more rapidly than *trans*-TI. Reduction of both forms at the second reduction wave or in the presence of benzoic acid proceeds by a two-electron reaction probably to a protonated dianion species. Both the dimeric dianion and the protonated dianion can be oxidized back to *trans*-TI.

INTRODUCTION

Recent reports from this laboratory [1,2] were concerned with differences in behavior of electrogenerated radical anions derived from the *cis*- and *trans*-isomers diethyl maleate and diethyl fumarate, in which the *trans* radical anion was found to undergo a slow dimerization reaction and did not react with an added large excess of acrylonitrile while the *cis* radical anion isomerized to the *trans* form, dimerized more rapidly than that of the *trans*, and reacted with acrylonitrile. To examine further these reactivity differences in *cis*- and *trans* radical ion species, we undertook an investigation of the electroreduction of thioindigo (TI). TI can exist in a *trans* (T) or *cis* (C) form and the photochemical aspects of the system have been studied in depth by Wyman et al. [3–6]. Thus solutions containing either the T or C forms as the major components can be prepared by irradiation at selected wavelengths and the quantitative determination of both forms is readily accomplished since they



trans-TI or T



cis-TI or C

show different absorption spectra and only the *trans* form fluoresces [7]. In this paper we describe cyclic voltammetric, rotating ring-disk electrode (RRDE) and coulometric studies of *cis*- and *trans*-TI and demonstrate differences in the reactivity of the respective radical anions.

EXPERIMENTAL

Purified TI was kindly furnished by Dr. G.M. Wyman (Army Research Office, Durham). Tetrabutylammonium perchlorate (TBAP), polarographic grade, obtained from Southwestern Analytical Chemical Company, was used as the supporting electrolyte. The *N,N*-dimethylformamide (DMF), purified as previously described [8], was used as a solvent in all experiments. A 140 watt Hanovia medium pressure mercury lamp equipped with a Corning 3-68 glass filter was used to irradiate the solution in a small cell designed for spec-

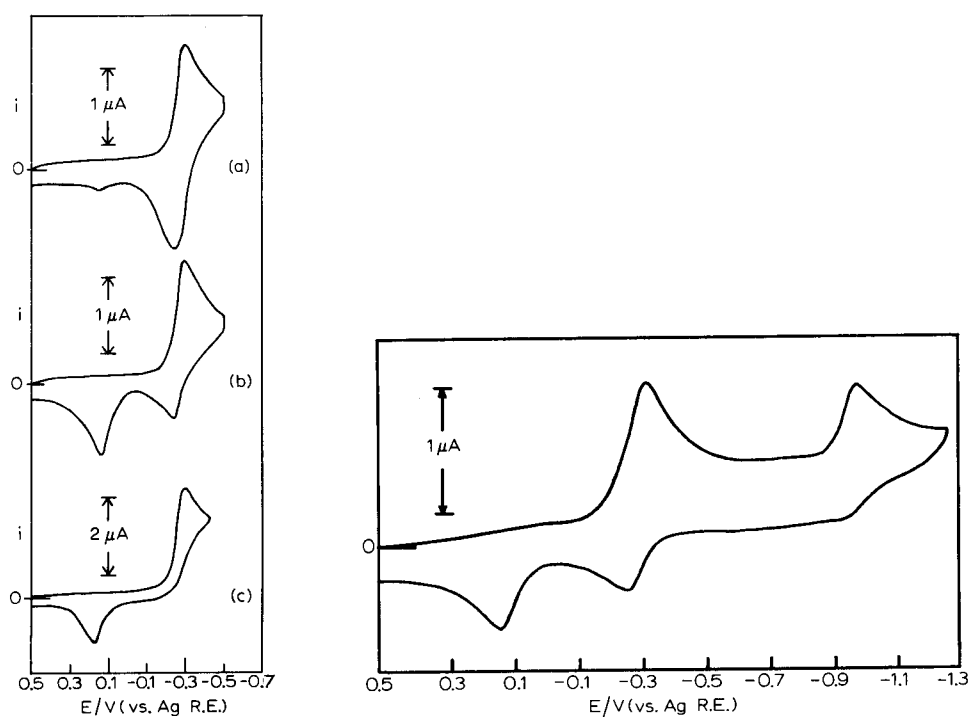


Fig. 1. Cyclic voltammograms of 0.25 mM thioindigo in 0.1 M TBAP-DMF solution. Scan rate, 100 mV s^{-1} . (a) *Trans*-isomer; (b) *cis*-isomer; (c) *trans*-isomer in the presence of 25 mM benzoic acid.

Fig. 2. Cyclic voltammogram of 0.22 mM thioindigo in 0.1 M TBAP-DMF solution scanned to -1.3 V . Scan rate, 100 mV s^{-1} . The *trans*- and *cis*-isomers showed indistinguishable curves.

trometric and cyclic voltammetric measurements. A 275 watt General Electric sunlamp, with the same glass filter, was used to irradiate the solution contained in the large cell for RRDE and coulometric studies. A water bath surrounding the cells during irradiation was used to minimize heating effects. A transparent Dewar flask filled with carbon tetrachloride and dry ice (-22°C) was also used in some irradiation experiments to stabilize the *cis*-isomer produced. The small cell contained a silver wire pseudo-reference electrode in a separate compartment and platinum wire working (0.05 cm^2) and counter electrodes. The small electrochemical cell was designed to fit the Cary Model 14 spectrophotometer sample chamber so that the solution composition in the cell could be analyzed optically. The cell used for RRDE and coulometric studies was previously described [9]. However, a cap was made to seal the cell so that electrochemical studies could be carried out outside the dry box. A large area platinum gauze working electrode and an isolated Ag reference electrode were used for coulometric studies. A small platinum wire electrode, placed in the coulometric cell, was used for cyclic voltammetric monitoring of the solution before and after every stage of the electrolysis. The RRDE, also described previously [9], with $r_1 = 0.187\text{ cm}$, $r_2 = 0.200\text{ cm}$, $r_3 = 0.332\text{ cm}$ had a theoretical collection efficiency, N , of 0.555. A Princeton Applied Research Model 170 instrument was used for all cyclic voltammetric and coulometric measurements. For RRDE studies, a Tacussel Bipad bipotentiostat, programmed through a simple summing operational amplifier circuit with a Wavetek Model 114 Function Generator and a d.c. power supply, was employed. A Moseley Model 7100B dual pen strip chart recorder was used to record the disk and ring electrode currents simultaneously. All the solutions were prepared in a Vacuum Atmospheres Corp. glove box equipped with a Model MO-40-1 Dri-Train. RRDE and most of the coulometric studies were carried out inside the dry box, while the small cell was sealed before removal for electrochemical experiments.

RESULTS

Cyclic voltammetry

Solid TI dissolved in DMF containing 0.1 M TBAP produces a pink solution with essentially the same absorption spectrum as that reported for the *trans*-isomer in benzene [7]. The cyclic voltammogram (c.v.) of this solution at a platinum electrode shows a reduction peak with a peak potential (E_{pc}) of -0.305 V vs. Ag with an oxidation peak on scan reversal with $E_{pa} = -0.245\text{ V}$ and a very small second oxidation wave at $+0.14\text{ V}$ (Fig. 1a). The ratio of the anodic peak current (i_{pa}) to the cathodic one (i_{pc}) is near one, especially at lower TI concentrations where the second oxidation wave is absent. Typical results at different scan rates (ν) are given in Table 1. When the solution is irradiated with light filtered through a Corning 3-68 filter (i.e. yellow light) the solution color changes to orange and the absorbance spectrum shows high

conversion to the *cis*-isomer. Total conversion to the *cis* form could not be obtained, however. The *cis*-isomer rapidly converts to a mixture in which the *trans* form predominates when exposed to daylight; even in the dark slow

TABLE 1

Cyclic voltammetry results for *cis*- and *trans*-thioindigo in 0.1 M TBAP—DMF in absence and presence of benzoic acid

Concn. (c)/mM	Scan rate (ν)/mV s ⁻¹	$i_p \nu^{-1/2} / \mu\text{A s}^{1/2} \text{mV}^{-1/2} \text{ }^a$							
		<i>cis</i>			<i>trans</i>			<i>trans</i> with 100- fold excess ben- zoic acid	
		Redn.	1st reox.	2nd reox.	Redn.	1st reox.	2nd reox.	Redn.	2nd reox.
0.25	50	0.159	0.058	0.096	0.160	0.156	0.002	0.280	0.121
	100	0.158	0.060	0.094	0.160	0.156	0.002	0.261	0.120
	200	0.158	0.063	0.092	0.159	0.157	0.001	0.250	0.118
	500	0.160	0.066	0.090	0.159	0.157	0.001	0.230	0.114
	1,000	0.159	0.079	0.078	0.158	0.157	0	0.218	0.106
	2,000	0.160	0.086	0.073	0.160	0.159	0	0.194	0.095
	5,000	0.157	0.091	0.066	0.158	0.158	0	0.175	0.079
	10,000	0.156	0.097	0.059	0.158	0.158	0	0.160	0.064
0.125	50	0.079	0.050	0.026	0.079	0.076	0.001	0.141	0.057
	100	0.078	0.051	0.025	0.079	0.076	0.001	0.132	0.052
	200	0.078	0.052	0.024	0.079	0.078	0	0.124	0.047
	500	0.079	0.054	0.023	0.078	0.077	0	0.116	0.042
	1,000	0.079	0.056	0.021	0.078	0.077	0	0.108	0.036
	2,000	0.078	0.058	0.019	0.078	0.078	0	0.098	0.029
	5,000	0.079	0.062	0.017	0.079	0.079	0	0.088	0.024
	10,000	0.079	0.064	0.015	0.079	0.079	0	0.080	0.016
0.062	50	0.040	0.031	0.0067	0.040	0.039	0	0.072	0.027
	100	0.040	0.031	0.0065	0.039	0.038	0	0.067	0.025
	200	0.040	0.032	0.0062	0.040	0.039	0	0.061	0.023
	500	0.039	0.033	0.0060	0.040	0.039	0	0.057	0.021
	1,000	0.040	0.034	0.0054	0.040	0.040	0	0.054	0.017
	2,000	0.040	0.034	0.0050	0.040	0.040	0	0.049	0.013
	5,000	0.040	0.035	0.0045	0.040	0.040	0	0.044	0.008
	10,000	0.040	0.036	0.0040	0.040	0.040	0	0.041	0.004
E_p^b /V vs. Ag wire, RE		-0.30	-0.24	0.14	-0.305	-0.245	0.14	-0.29	0.16

^a i_p = peak current; ν = scan rate. First reoxidation wave measured from projected decaying current portion of reduction wave, 2nd reoxidation measured from decaying current of first reoxidation wave.

^b Averaged values.

conversion to *trans* was found. A c.v. of *cis*-TI obtained under irradiation (Fig. 1b) shows a reduction peak with virtually the same E_{pc} and $i_{pc}/v^{1/2}$ as the *trans*-isomer. On the reverse scan, however, the peak at -0.24 V is much smaller while that at $+0.14$ V is much larger than that for the *trans* form, with the relative peak heights a function of concentration and scan rate (Table 1). If the scan is continued past the first reduction wave, a second wave is observed at -0.97 V, with the two oxidation waves present on scan reversal (Fig. 2). Under these conditions the behavior of the *cis* and *trans* forms are indistinguishable.

Controlled potential coulometry

Bulk exhaustive electrolytic reduction of the *trans*-isomer at the first reduction wave (-0.5 V) gave n_{app} (number of electrons per molecule of TI) of one (Table 2). The resulting blue solution when transferred to an electron spin resonance (e.s.r.) cell under nitrogen or in the glove box showed an intense e.s.r. signal which could be fitted to the coupling constants previously reported for the radical anion prepared by dissolving TI in alkaline oxygen-free acetone [10] or by reaction of TI in ethereal solutions with potassium metal [11] (Fig. 3). An oxidative c.v. of this solution (Fig. 4a) shows two oxidation waves; the ratio of peak currents for the first to the second wave is 4/1, independent of scan rate. Controlled potential oxidation at these waves shows a similar n_{app} ratio (Table 2). The solution reoxidized at -0.05 V is orange-red while that following oxidation at $+0.5$ V is the original TI pink color and shows essentially the same c.v. as the original *trans*-TI solution. Exposure of the blue reduced solution to air or addition of a small amount of sulfuric acid similarly regenerates the pink *trans*-TI solution. Reduction of *trans*-TI at the second reduction peak shows an n_{app} of two and yields a green-yellow solu-

TABLE 2

Controlled potential coulometry results ^a

Electrolysis	Potential/V vs. Ag	n_{app}		
		<i>trans</i>	<i>cis</i>	<i>trans</i> with benzoic acid
First reduction	-0.5	1.0	1.0	2.0 ^b
First reoxidation	-0.05	0.8	0.4	—
Second reoxidation	$+0.5$	0.2	0.57	1.9
Second reduction	-1.2	2.0	2.0	

^a Solution contained 0.25 mM thioindigo and 0.1 M TBAP in DMF. Electrolysis time was about 25 min.

^b Solution contained 25 mM benzoic acid. Electrolysis at -0.4 V.

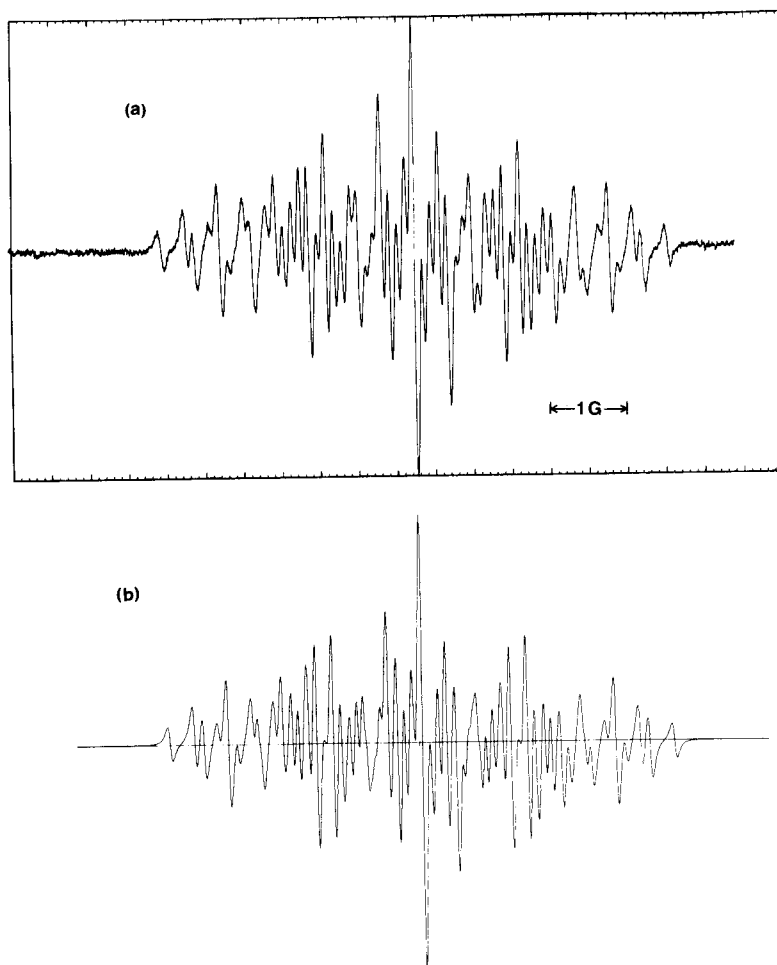


Fig. 3. (a) E.s.r. spectrum of the anion radical of thioindigo generated from reductive bulk exhaustive electrolysis of 0.2 mM thioindigo in 0.1 M TBAP-DMF solution. (b) Simulated e.s.r. spectrum using four sets of two equivalent protons with coupling constants of 1.375, 1.163, 0.450, and 0.330 gauss, line width of 0.065 gauss, and total width of 6.635 gauss.

tion. In a c.v. of this solution the oxidation peak at -0.24 V is absent and a strong peak at $+0.14$ V is found. This solution is also oxidized at $+0.5$ V back to the original pink TI solution. The solution resulting from reduction at the second wave as well as that from reduction at the first wave followed by re-oxidation at -0.1 V both exhibit weak e.s.r. signals of the TI radical anion, which tend to increase with time after removal of the sample from the electrolysis cell.

Bulk electrolysis of the *cis*-isomer was carried out by irradiation of the electrolysis cell containing the TI solution (immersed in a cooling bath to prevent

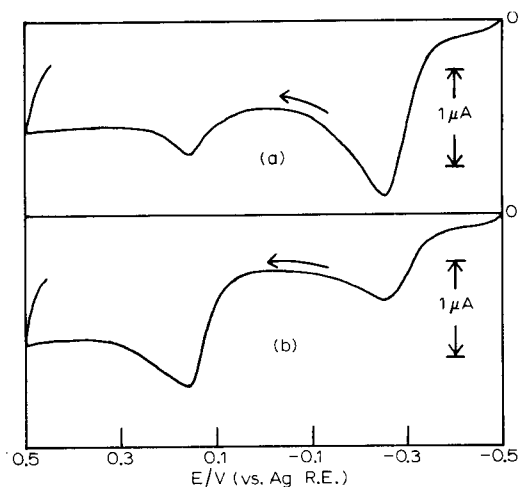


Fig. 4. Reoxidation curves at 200 mV s^{-1} for 0.25 mM thioindigo after bulk exhaustive reduction at $-0.5 \text{ V vs. Ag - R.E.}$ for (a) *trans*-isomer and (b) *cis*-isomer.

solution heating) before and during the electrolysis. Reduction at the first wave also showed a one-electron reaction (Table 2) and the production of a purple solution. The c.v. obtained for this solution (Fig. 4b) showed two oxidation waves, but in this case the ratio of peak currents of the first and second waves was $2/3$, independent of scan rate. Similarly the n_{app} values for the coulometric reoxidations (Table 2) showed a larger contribution from the second oxidation wave. The strong e.s.r. signal observed upon reduction and the weak signal found after oxidation at the first wave were the same as those observed for the *trans*-TI.

Rotating ring-disk electrode studies

The previous results are consistent with a mechanism involving an initial one-electron transfer reaction to produce a radical anion which then reacts, very slowly for the *trans*-isomer but rapidly for the *cis* form to produce a product which can be oxidized to form TI. To obtain more information about the nature of the reaction of the radical anion, RRDE studies were performed. A typical RRDE voltammogram for a solution containing mostly *cis*-TI (obtained by irradiation of the *trans*-isomer solution before and during the experiment, with the cell contained in the glove box) is shown in Fig. 5. Given in this Figure are: (a) the disk current, i_d , (b) the ring current, i_r , for a ring electrode potential, E_r , of -0.05 V (detection of radical anion), and (c) the ring current, i_R , for $E_r = +0.5 \text{ V}$ (detection of both the oxidizable reaction product and radical anion), for the disk potential, E_d , scanned between 0 and -1.2 V . A *trans*-TI solution shows qualitatively similar behavior, but with larger values of i_r/i_d for i_d values on the first reduction wave at the same ro-

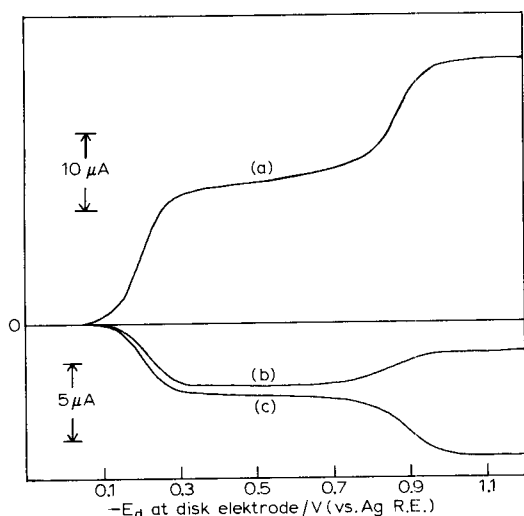


Fig. 5. RRDE voltammograms of 0.175 mM thioindigo (mainly *cis* form) in 0.1 M TBAP-DMF solution at a rotation rate of 1350 rpm. (a) Disk electrode current; (b) ring electrode current at $E_r = -0.05$ V; (c) ring electrode current at $E_r = +0.5$ V.

tation rate. Values of the collection efficiency for the radical anion, $N_K = |i_r/i_d|$, as a function of $\text{CONI} = i_d/i_{d,l}$ where $i_{d,l}$ is the limiting disk current for the first reduction wave, are given in Fig. 6. Note that N_K for *trans*-TI is near that for theoretical collection of all disk-generated species (0.555), while that for the *cis*-isomer is significantly smaller and varies with the rotation rate (ω) and the magnitude of the disk current. The collection efficiency for the reaction product, $N'_K = |(i_R - i_r)/i_d|$, for the *cis*-isomer, and $N''_K = |i_R/i_d|$

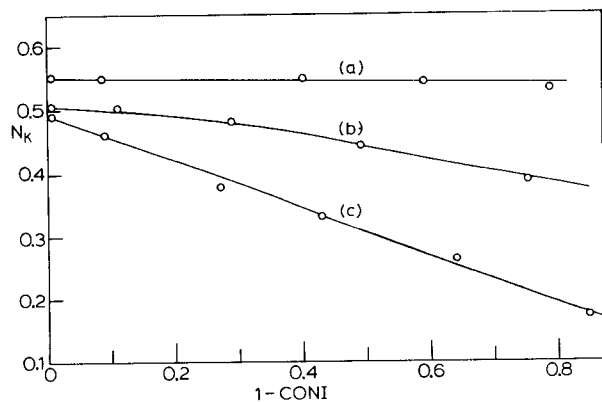


Fig. 6. Collection efficiency for the anion radical of 0.175 mM thioindigo in 0.1 M TBAP-DMF solution. (a) *Trans*-isomer at 1540 rpm; (b) *cis*-isomer at 2250 rpm; (c) *cis*-isomer at 430 rpm.

TABLE 3

Typical rotating ring-disk electrode results for *cis*-thioindigo ^a

i_d = disk current; i_r = ring current at $E_r = -0.05$ V (first oxidation wave); i_R = ring current at $E_r = +0.5$ V (second oxidation wave); $\text{CONI} = i_d/i_{d,0}$; $N_K = |i_r/i_d|$; $N'_K = |(i_R - i_r)/i_d|$; $N''_K = |i_R/i_d|$.

Rotation rate/rpm	E_d/V	$i_d/\mu A$	$i_R/\mu A$	$i_r/\mu A$	N_K	N'_K	CONI	N''_K
430	-0.15	-0.7	0.27	0.12	0.17	0.214	0.16	0.39
	-0.18	-1.63	0.69	0.43	0.264	0.159	0.36	0.423
	-0.20	-2.55	1.15	0.85	0.335	0.118	0.57	0.451
	-0.25	-3.30	1.54	1.25	0.38	0.087	0.73	0.497
	-0.28	-4.10	2.20	1.90	0.465	0.073	0.91	0.537
	-0.40	-4.50	2.50	2.20	0.49	0.067	1.00	0.555
1350	-0.15	-1.18	0.50	0.26	0.22	0.203	0.15	0.424
	-0.18	-2.58	1.25	0.90	0.35	0.136	0.33	0.484
	-0.20	-3.95	2.05	1.70	0.43	0.089	0.51	0.519
	-0.25	-5.50	2.94	2.60	0.47	0.068	0.71	0.534
	-0.28	-6.95	3.86	3.43	0.495	0.062	0.89	0.555
	-0.40	-7.80	4.35	3.94	0.505	0.059	1.00	0.555
2250	-0.15	-1.60	0.76	0.45	0.28	0.194	0.16	0.475
	-0.18	-3.50	1.80	1.35	0.385	0.128	0.35	0.514
	-0.20	-5.40	2.85	2.40	0.445	0.084	0.54	0.528
	-0.25	-7.10	3.90	3.40	0.48	0.070	0.71	0.549
	-0.28	-8.95	5.00	4.50	0.504	0.056	0.89	0.558
	-0.40	-10.00	5.55	5.05	0.505	0.050	1.00	0.555

^a The solution resulted from irradiation of a 0.175 mM thioindigo, 0.1 M TBAP, DMF solution and contained predominantly *cis* form.

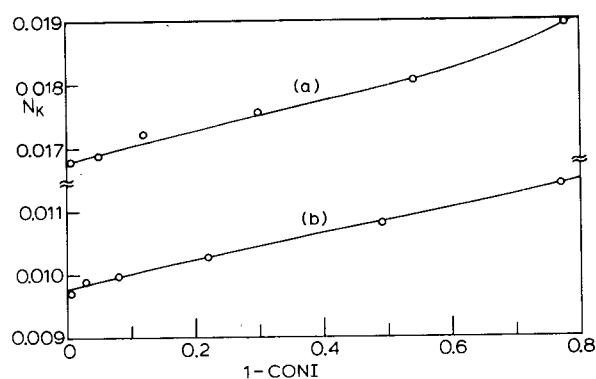


Fig. 7. Collection efficiency for the anion radical of thioindigo (0.25 mM) in the presence of 25 mM benzoic acid, in a 0.1 M TBAP-DMF solution, at $E_r = -0.05$ V and rotation rate of (a) 2250 rpm and (b) 1350 rpm.

as functions of CONI and ω are given in Table 3. Note that relative production of reaction product is smallest where CONI = 1.0, at the plateau of the reduction wave, and increases for values of i_d on the rising portion of the wave. The variation of N_K and N'_K with CONI indicates that the following reaction is at least second order in radical anion, and the direction of variation suggests coupling with the parent molecule [1,9].

Effect of addition of acid

When excess benzoic acid is added to a solution of *trans*-TI, the cyclic voltammetric results (Fig. 1c) show a large increase in the reduction wave, with a disappearance of the radical anion oxidation wave and an increase of the second oxidation wave on reversal (Table 1). Controlled potential coulometry under these conditions results in an $n_{app} = 2$ for reduction at -0.4 V and a similar value for reoxidation at $+0.5$ V (Table 2). A c.v. after reduction and reoxidation closely resembles that of the original solution (Fig. 1c). An RRDE voltammogram of a 0.25 mM TI– 0.1 M TBAP solution containing 25 mM benzoic acid shows N_K values of about 0.01 to 0.02 for rotation rates of 1350 to 2250 rpm (Fig. 7), so that detection of a small amount of surviving radical anion is possible.

DISCUSSION

The electrochemical results show that although the *trans* and *cis* forms of thioindigo undergo reduction at the same potential to form a radical anion, the rates of the chemical reactions following this electron transfer are very different for the two species. For the *trans*-TI on the cyclic voltammetric time scale the reaction is mainly

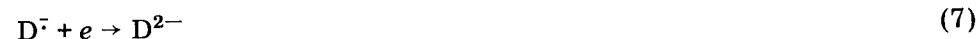


For the *cis*-isomer the following reaction mechanism is proposed (where D represents a dimer of TI)

Reduction (first wave)



and/or



Reoxidation (first wave)



(second wave)



Evidence for the isomerization of $C^{\cdot-}$ to the *trans* form is the fact that the same e.s.r. spectrum is observed on reduction of either form and the previously reported fact that generation of a small amount of radical anion shifts a mixture of *cis*- and *trans*-TI completely to the *trans* form [11] presumably via the occurrence of reaction (12) along with reaction (3). Several factors point to formation

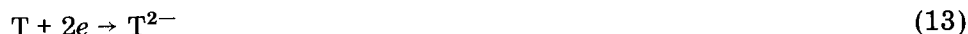


of dimer. The relative height of the second (dimer dianion) reoxidation wave increases with increasing concentration of parent (Table 1); in fact doubling the TI concentration increases this relative wave height by a factor of four. Moreover, coulometric oxidation at the second wave regenerates parent TI with n_{app} essentially equal to one. Mass spectroscopy of the reduction product also provides evidence of dimerization. After coulometric reduction of the *cis* form, benzoic acid was added to protonate any dimer dianion and the DMF removed by vacuum evaporation. The solid was washed several times with distilled water to remove TBAP and benzoic acid and the resulting solid was dried under vacuum. Mass spectra were obtained for the parent TI and the reduced product. The mass spectrum of the TI shows a strong parent peak at $m/e = 296$ as previously noted [12]. The reduction product shows this peak, but also peaks at the higher m/e values of 307, 308, 321, 354, 391, 392, 406, 407, 414, and 446. Small peaks at m/e values up to 600 were also found, as well as a doubly charged peak at 330.5 corresponding to a mass number of 661. Thus dimer formation is likely, and some polymer production may also occur, giving rise to the higher peaks and the small deviation between n_{app} for reduction and reoxidation of the *cis*-isomer. We did not attempt to elucidate the structure or properties of the dimeric species. Chang et al. [11] also found evidence for the reversible formation of diamagnetic dimer from the radical anion at low temperatures following potassium reduction in ethereal solvents. A slow dimerization of the *trans* form is suggested by the appearance of the dimer oxidation wave following controlled potential reduction. This reaction is slow, however, since the c.v. of a pure *trans*-TI solution shows only a very small second oxidation wave. The rapid isomerization of $C^{\cdot-}$ to $T^{\cdot-}$ and dimerization to D^{2-} accounts for the relatively small sensitivity of the ratio of first and second reoxidation peaks in cyclic voltammetry to scan rate, i.e., the first reoxidation peak represents mostly $T^{\cdot-}$, rather than $C^{\cdot-}$, oxidation.

Evidence for the e.c.e. reaction sequence (reactions 5–8) rather than radi-

cal anion coupling (reaction 4) as the major path to dimer in this case comes from the RRDE experiments (Fig. 6). Radical anion coupling would show an increasing N_K with $1 - \text{CONI}$, while the e.c.e. path shows the observed decreasing N_K behavior [1,9]. Unfortunately, because both *cis*- and *trans*-TI reduce at the same potentials and their radical anions oxidize at the same potentials, it was not possible to use the RRDE techniques employed in the fumarate—maleate work [2,13] to estimate the individual rate constants for isomerization and dimerization unambiguously. Based on the proposed mechanism, one would expect that the collection efficiency $N_K'' = |i_R/i_d|$ would be the theoretical value (0.55), since all disk generated species ($C^{\cdot-}$, $T^{\cdot-}$, and D^{2-}) would be oxidized to parent at the ring potential of +0.5 V. While this is true for *cis*-TI at large values of CONI (i.e., for i_d values near the limiting values), at smaller values N_K'' is somewhat smaller, particularly at the lower rotation rates (Table 3). This deviation may be attributed to the previously mentioned polymerization reaction or perhaps to a scavenging of a small amount of $C^{\cdot-}$ by an impurity in the solution.

The second reduction step of TI, based on the voltammetry and coulometry results, is a two-electron process. The dianion that is produced reacts to produce a small amount of radical anion (since some ring current is observed for $E_r = -0.05$ V when the disk is at potentials of the second wave; Fig. 5b) and probably protonated product (reactions 14 and 15); the mechanism



for the *cis*- and *trans*-isomers at the second reduction wave is apparently quite similar. Appreciable formation of dimer dianion by reaction of T^{2-} with T apparently does not occur to an appreciable extent, since this would result in n_{app} values smaller than 2.0. The observation of weak e.s.r. signals in solutions prepared by coulometric reduction of TI at the second wave or reduction at the first wave followed by oxidation at -0.05 V can probably be ascribed to a small amount of dissociation of the dimer dianion (reaction 4). In fact, during the electrolytic oxidation of the radical anion at -0.05 V the current does not decay to the background level, but rather to a slightly higher value, attributable to this small amount of dissociation.

In the presence of proton donor the first reduction wave involves a two-electron transfer probably leading to the protonated species via an e.c.e. reaction (or a nuance thereof) and perhaps to a small amount of dimer (Fig. 1c). Details of this process were not investigated further. The results from the two-electron reduction of TI or the reduction in the presence of acid suggest that the protonated species oxidizes at the same potential as the dimer to regenerate parent TI.

In general the behavior of the *cis*- and *trans*-isomers of TI parallel those observed for diethyl maleate and fumarate, i.e., the *cis*-isomer radical anion

tends to isomerize and is the more reactive species. However, while the maleate and fumarate reduce at different potentials, both TI isomers have the same E_p values. This can probably be attributed to the relative distance between the oxygen atoms (which probably have the highest electron density in the radical anion) in *cis*-TI compared to diethyl maleate.

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