

## ELECTROCHEMICAL STUDIES AND PHOTOCONVERSION OF *CIS*- AND *TRANS*-6,6'-DIETHOXYTHIOINDIGO

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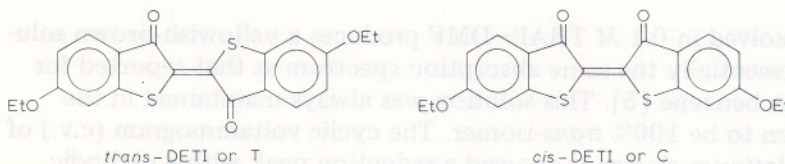
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### ABSTRACT

The reduction of *cis*- and *trans*-6,6'-diethoxythioindigo (DETI) at a platinum electrode in *N,N*-dimethylformamide (DMF) solution was studied by cyclic voltammetry and controlled potential coulometry. The *cis*-form, produced by photoisomerization of the *trans*-form, is reduced at less negative potentials than the *trans*-. The *trans*-isomer produces a fairly stable radical anion upon one-electron reduction; the *cis*-radical anion isomerizes rapidly to the *trans*-form and also dimerizes much more rapidly than the *trans*-isomer. A photogalvanic cell based on this system was devised but showed low efficiency for conversion of radiant energy to electricity.

### INTRODUCTION

In a previous report from this laboratory [1] we discussed the electrochemical reduction of *trans*- and *cis*-thioindigo (TI) in DMF solution. The proposed mechanism involved reduction of both forms to the radical anions, which then undergo dimerization reactions, with the *cis*-radical anion reacting much more rapidly than the *trans*-. In a later study [2] we showed that the *cis*-radical anion reacted more rapidly than the *trans*- with CO<sub>2</sub>, acrylonitrile and cinnamionitrile. Since *trans*-TI can be converted to *cis*-TI by irradiation with yellow light [3-5], systems such as this are of interest in electrochemical studies of photoeffects and the possible conversion of radiant energy to electrical energy. However two features of the TI system make such applications difficult. The reduction of both *cis*- and *trans*-TI occur at virtually the same potential and *cis*-TI very rapidly converts to the *trans*-form so that solutions of the pure *cis*-form could not be obtained. Wyman suggested [6] that 6,6'-diethoxythioindigo (DETI) might be of more use, since both



isomers are fairly stable and solutions of pure *cis*- and pure *trans*- can be obtained by irradiation at suitable wavelengths. As with TI, it is possible to distinguish between the *cis*- and *trans*-forms of DETI, by their different absorption



spectra. In this paper we report cyclic voltammetric and controlled potential coulometric studies of DETI and demonstrate generation of a photocurrent using this system.

## EXPERIMENTAL

Purified DETI was kindly furnished by Dr. G.M. Wyman (Army Research Office, Durham). N,N-dimethylformamide (DMF), obtained from American Drug and Chemical Co., was purified [7] and used as a solvent in all experiments. Tetra-n-butylammonium perchlorate (TBAP), polarographic grade, obtained from Southwestern Analytical Chemical Company, was vacuum dried and used as the supporting electrolyte.

A 275 W General Electric sunlamp equipped with a Corning 3-68 glass filter (yellow) was used to irradiate the solution. A small electrochemical cell [1] was used so that the solution composition in the cell could be analyzed spectrophotometrically. A large cell [1] containing a silver wire pseudo-reference electrode (Ag R.E.), a platinum wire working ( $0.05 \text{ cm}^2$ ) and counter electrodes, all in different compartments, was used for voltammetric, coulometric and photochemical studies. A large area platinum gauze working electrode, placed in the working electrode compartment, was used for coulometric studies and bulk electrolysis. A small platinum wire electrode, placed in the coulometric cell, was used for cyclic voltammetric monitoring of the solution before and after the electrolysis. For photochemical studies, a platinum foil (ca.  $2 \text{ cm}^2$ ), placed close to the wall of the coulometric cell, and a platinum gauze electrode, used as the counter electrode, were connected through a sensitive galvanometer (Model 2430C, Leeds and Northrup Co., Philadelphia, Pa). Only the platinum foil electrode and the solution between the electrode and the wall of the coulometric cell were irradiated in these experiments.

A water bath surrounded the cells during irradiation to minimize heating effects. Dissolved oxygen was removed from the solution by bubbling extra-dry nitrogen into the solution for about 30 min before the experiments. The solution surface was continually flushed with nitrogen during the experiments. A Model 170 Electrochemistry System (Princeton Applied Research Corporation, Princeton, N.J.) was employed for all electrochemical studies. General procedures and instrumentation followed previous practice [1].

## RESULTS AND DISCUSSION

### *Cyclic voltammetry*

Solid DETI dissolved in 0.1 M TBAP-DMF produces a yellowish-brown solution which gives essentially the same absorption spectrum as that reported for the *trans*-isomer in benzene [5]. This solution was always maintained in the dark and was taken to be 100% *trans*-isomer. The cyclic voltammogram (c.v.) of *trans*-DETI at a platinum electrode showed a reduction peak with a cathodic peak potential ( $E_{pc}$ ) of  $-0.54 \text{ V}$  vs. Ag R.E. with an oxidation peak on the reverse scan with  $E_{pa} = -0.48 \text{ V}$  and a very small second oxidation peak at  $-0.03 \text{ V}$  (Fig. 1a). The ratio of the first anodic peak current ( $i_{pa}$ ) to the cathodic one



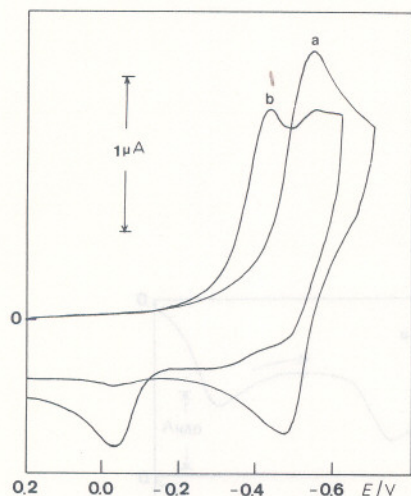


Fig. 1. Cyclic voltammograms of 0.2 mM 6,6'-diethoxythioindigo in 0.1 M TBAP-DMF solution. Scan rate,  $100 \text{ mV s}^{-1}$ . (a) *Trans*-isomer and (b) *cis*-isomer.

( $i_{pc}$ ) was near one. When the solution was irradiated with yellow light (i.e., filtered through a Corning 3-68 filter) the solution turned yellow and showed the same absorption spectrum as that reported for the *cis*-isomer in benzene [5]. The spectrum was reproducible for a period of at least 10 min, indicating that the *cis*-isomer was fairly stable in DMF solution. The *cis*-isomer slowly converts to a mixture in which the *trans*-isomer predominates when exposed to daylight; the rate of conversion was slow in the dark.

A c.v. of *cis*-DETI obtained under irradiation shows a reduction peak with  $E_{pc} = -0.43 \text{ V}$  (Fig. 1b). Immediately following the reduction peak at  $E_{pc} = -0.43 \text{ V}$ , a second reduction peak at  $E_{pc} = -0.54 \text{ V}$ , the reduction potential of the *trans*-isomer, was also observed. On the reverse scan, the anodic peak at  $-0.48 \text{ V}$  was much smaller, while that at  $-0.03 \text{ V}$  was much larger, than that for the *trans*-isomer. In addition, a small bump at  $E_{pa} = -0.37 \text{ V}$ , corresponding to the reoxidation of the reduction product at  $E_{pc} = -0.43 \text{ V}$ , was observed. On continuous scanning of the *cis*-isomer, the c.v. reduction peak height at  $E_{pc} = -0.43 \text{ V}$  decreased and that at  $E_{pc} = -0.54 \text{ V}$  increased, while the oxidation peak heights at  $E_{pa} = -0.37 \text{ V}$  and  $-0.03 \text{ V}$  decreased and that at  $-0.48 \text{ V}$  increased.

For *trans*-DETI (or T) on this timescale the reaction is apparently reduction to the radical anion



The potential for reduction of *trans*-DETI is negative of that for TI ( $-0.30 \text{ V}$  vs. Ag R.E.) because of the electron donating properties of the ethoxy groups. The *cis*-DETI (or C) reduces more easily than the *trans*-isomer (unlike *cis*-TI). To elucidate the mechanism of the reduction of C, c.v. was performed at several scan rates (Fig. 2). At scan rates above  $500 \text{ mV s}^{-1}$ , only one reduction peak at  $-0.43 \text{ V}$  was observed in the first scan; in the second and successive scans the peak at  $-0.54 \text{ V}$ , which occurs at the same potential as that for T reduction ap-



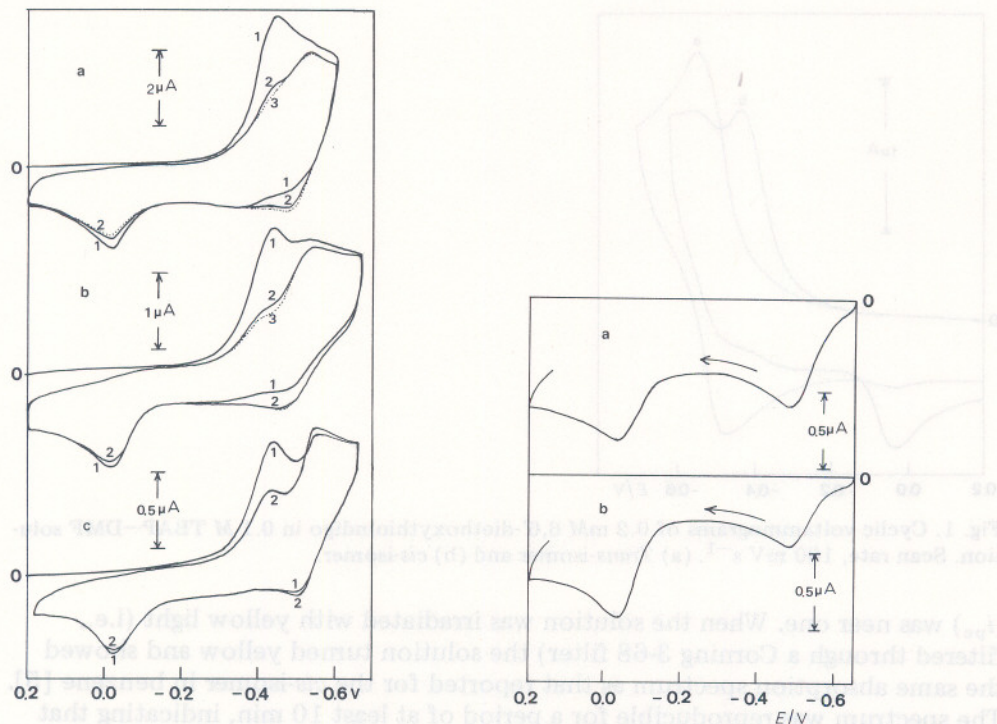


Fig. 2. Cyclic voltammograms of 0.2 mM *cis*-6,6'-diethoxythioindigo in 0.1 M TBAP-DMF solution. (1) First scan; (2) second scan; (3) third scan. Scan rates: (a) 500; (b) 200; (c) 50  $\text{mV s}^{-1}$ .

Fig. 3. Cyclic voltammograms of 0.2 mM 6,6'-diethoxythioindigo after exhaustive electrolytic reduction at  $-0.65$  V vs. Ag R.E. for (a) *trans*-isomer and (b) *cis*-isomer. Scan rate, 200  $\text{mV s}^{-1}$ .

peared and increased in height at the expense of  $-0.43$  V peak. Moreover the oxidation peak at  $-0.48$  V is smaller and the peak at  $-0.03$  V is larger for the first scan than in the second and subsequent scans. At slower scan rates the  $-0.54$  peak is more prominent, even on the first scan.

#### Controlled potential coulometry

Bulk exhaustive electrolytic reduction of the *trans*-isomer at  $-0.65$  V produced a brownish-red solution and showed an  $n_{\text{app}}$  value (number of electrons per molecule of DETI) of one. An oxidative c.v. of this reduced solution showed two oxidation peaks (Fig. 3a); the ratio of the peak currents for the first peak ( $E_{\text{pa}} = -0.48$  V) to the second ( $E_{\text{pa}} = -0.03$  V) was about 3/2, independent of the scan rate. Bulk electrolysis of this solution at  $+0.2$  V restored the original yellowish-brown color and gave an  $n_{\text{app}}$  value of one.

Bulk electrolysis of the *cis*-isomer was carried out under irradiation of the coulometric cell containing the DETI solution before and during the electrolysis. Reduction at  $-0.65$  V again showed a one-electron reaction and the production of a brownish-red solution. An oxidative c.v. of this reduced solution showed



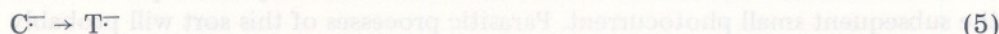
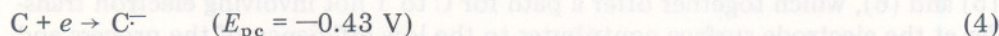
the same two oxidation peaks as the reduced solution of the *trans*-isomer (Fig. 3b). The ratio of peak currents for the first peak to the second was about 1/2, independent of scan rate. The original DETI color could also be regenerated by oxidation at +0.2 V.

#### Proposed mechanism

These results, taken together with previous work on the electrochemistry of TI [1], suggest the following mechanism. The  $T^{\cdot-}$  species, while stable on the cyclic voltammetric time, apparently undergoes a slow reversible dimerization (as *trans*-TI does) to form the species oxidized at  $-0.03$  V:



The *cis*-DETI forms an anion radical,  $C^{\cdot-}$ , which apparently is not stable even at short times, since only a small reversal peak is seen in the c.v. for the first wave. The build-up of the *trans*-peak can be accounted for by the isomerization of  $C^{\cdot-}$  followed by electron transfer:



The dimerization rate of  $C^{\cdot-}$  is also much faster than that of  $T^{\cdot-}$ , since the dimer oxidation wave is prominent on the c.v. of the *cis*-isomer



The difference in the c.v.  $E_{pc}$  values of the two isomers may be attributed, at least partially, to the more rapid reaction of  $C^{\cdot-}$ , shifting the reduction wave towards positive potentials. However some difference in the thermodynamic  $E^0$  values for the two forms is also possible, although this is not observed for TI.

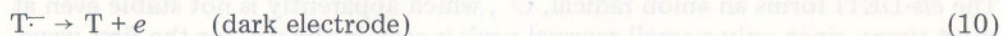
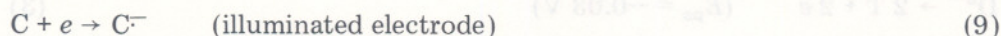
#### Photoelectrochemical experiment

The difference in  $E_{pc}$  values for C and T and the fact that T can be converted to C by irradiation suggested that a photogalvanic cell could be produced based on the DETI system. The coulometric cell containing two Pt electrodes immersed in the DETI-TBAP-DMF solution was employed. The coulometric cell was completely covered with black electrical tape, except for a small window facing the Pt foil electrode (area, ca.  $2 \text{ cm}^2$ ). No light penetrated the solution behind the Pt foil electrode to the Pt gauze counter electrode immersed in the same solution. The cell was immersed in a water bath to prevent solution heating and extra-dry nitrogen was passed over the surface of the solution before and during the experiments. The solution containing *trans*-DETI was first subjected to coulometric reduction (employing the Pt gauze electrode as cathode and a Pt electrode in a separate compartment as anode) until about half of the T-form was reduced, thus producing a solution containing T,  $T^{\cdot-}$  and  $D^{2-}$ . All connec-



tions to the potentiostat were disconnected and a sensitive galvanometer was connected between the Pt foil and the Pt gauze. In the dark, no current flow was detected. When the Pt foil was illuminated, a current of about  $0.3 \mu\text{A}$  appeared. This current decayed slowly when the irradiating light was blocked and increased again when the block was removed. The action spectrum of the photocurrent, obtained by irradiating the electrode through a circular graded interference filter (Barr and Stroud, Ltd.) showed that the response followed the absorption spectrum of *trans*-DETI with a maximum at about 510 nm.

The current flow under irradiation can be ascribed to conversion of T to C near the illuminated electrodes followed by reduction of C at this electrode and oxidation of  $\text{T}^-$  at the dark electrode, i.e.



The product  $\text{C}^-$  then can isomerize to  $\text{T}^-$  and diffuse into the bulk solution, restoring the cell solution to the original condition. The occurrence of reactions (5) and (6), which together offer a path for C to T not involving electron transfer at the electrode surface contributes to the low efficiency of the process and the subsequent small photocurrent. Parasitic processes of this sort will probably occur with most homogeneous systems utilizing such photoisomerizations in electrochemical cells [8]. Moreover the dark color of the solution decreases the amount of light penetrating to the electrode surface. Light absorbed well away from the electrode will not be useful in the current producing processes because of the parasitic reactions. Because the efficiency of the process appeared low, quantitative measurement of the efficiency and optimization of cell design was not attempted.

#### ACKNOWLEDGEMENTS

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