

SECONDARY REACTIONS IN CONTROLLED POTENTIAL COULOMETRY

PART V. REVERSAL COULOMETRIC STUDY OF THE REDUCTION OF *CIS*- AND *TRANS*-THIOINDIGO IN THE PRESENCE OF CARBON DIOXIDE, CINNAMONITRILE AND ACRYLONITRILE

LUN-SHU R. YEH and ALLEN J. BARD

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (U.S.A.)

(Received 20th September 1976)

ABSTRACT

Controlled potential reversal coulometry was applied to the following systems: (I) $C + ne = R$; $R + C \rightarrow RC$; $RC + ne \rightarrow$ products. (II) as in (I) except RC not electroactive. (III) $C + ne = R$; $R + X \rightarrow RX$; $RX + ne \rightarrow$ products. Equations for these e.c.e. and e.c. mechanisms were obtained and solved numerically. Working curves are presented for the calculation of the rate constants of the homogeneous reactions. This treatment was applied to studies of the reduction of thioindigo (TI) alone and in the presence of several reactants. For TI alone the reaction mechanism involves reaction of the radical anion ($TI^{\cdot-}$) with parent molecule followed by a second electron transfer. In the presence of excess dissolved CO_2 , acrylonitrile (AN), or cinnamionitrile (CN), reaction of $TI^{\cdot-}$ with these followed by a second electron transfer was proposed. Rate constants for the $TI-TI^{\cdot-}$ coupling reaction were 82 (*cis*-thioindigo), and 323 (*trans*-thioindigo) $l\ mol^{-1}\ s^{-1}$; pseudo-first-order reactions of $TI^{\cdot-}$ were 0.016 (*trans*-) and 0.047 (*cis*-) s^{-1} with CO_2 ; 0.023 (*trans*-) and 0.033 (*cis*-) s^{-1} with CN; 0.022 (*trans*-) and 0.032 (*cis*-) s^{-1} with AN.

INTRODUCTION

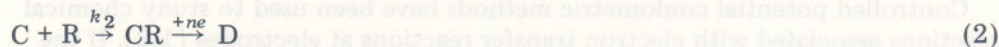
Controlled potential coulometric methods have been used to study chemical reactions associated with electron transfer reactions at electrodes [1,2]. If the products of the initial electron transfer undergo secondary reactions to generate or consume electroactive species by reaction with non-electroactive materials, the number of coulombs required for the electrolysis differs from that in the absence of such perturbing reactions and frequently leads to non-integral n_{app} values. However, reactions involving only products of electrolysis, such as electroreductive dimerization or electroreductive cross-coupling with non-electroactive materials, which do not affect the concentration of the original electroactive species or produce no new electroactive species, cause no deviations in the measured coulomb-time or current-time curves from those found with an unperturbed reaction system. For such cases controlled potential reversal coulometry [3], where the potential of the electrolysis is shifted after partial electrolysis to a potential at which the product of the original electrode reaction can undergo a further electrode reaction (most frequently the potential is shifted to cause the reverse electrode reaction), can be of value. Here a chemical reaction of the electrogenerated product will result in a smaller number of coulombs being con-

sumed in the reverse electrolysis than for the case with no kinetic perturbation. The type of following chemical reactions considered previously for reversal coulometry include a single first-order reaction, a single reversible first-order reaction, a single second-order reaction, parallel pseudo-first-order reactions and parallel first- and second-order reactions [3]. In a recent study of the electroreduction of thioindigo (TI) [4] we proposed a different reaction mechanism by which the electroreductive product was consumed; the radical anion (TI^-) coupled with the parent molecule to produce a dimeric anion which could accept another electron from the electrode. This reaction scheme was verified by rotating ring-disk electrode and cyclic voltammetry, exhaustive reductive coulometry and product analysis by mass spectrometry [4]. Because the coupling reaction was slow, especially for the *trans*-isomer, we reinvestigated it using controlled potential reversal coulometry. Moreover this technique allowed the investigation of the reactions of TI^- produced from both the *trans*- and *cis*-isomers with CO_2 , cinnamionitrile (CN) and acrylonitrile (AN).

MATHEMATICAL TREATMENT

The assumptions and conditions are the same as those previously described [1-3, 5-7]. The electrolysis of a species, C, is carried out under mass transfer-controlled conditions to produce R until a time t_1 , when the potential is shifted to one at which R is electrolyzed back to C. R and C react during and after R is generated by electrolysis. Two cases are considered in this category: case I, where the intermediate-parent product, CR, is electroactive at the potential where C is reduced and case II, where CR is electroinactive and the number of electrons transferred per molecule is usually non-integral. In addition to these, reversal coulometry for a pseudo-first-order e.c.e. reaction is also considered and discussed as case III.

Case I. Intermediate-parent coupling followed by further charge transfer is described by the equations:



The species CR is reduced at the reduction potential of C to D, and D is electroinactive. The system from $0 < t \leq t_1$ is described by the following equations:

$$d(\text{C})/dt = -p(\text{C}) - k_2(\text{C})(\text{R}) \quad (3)$$

$$d(\text{R})/dt = p(\text{C}) - k_2(\text{C})(\text{R}) \quad (4)$$

$$d(\text{CR})/dt = -p(\text{CR}) + k_2(\text{C})(\text{R}) \quad (5)$$

where the species in parentheses represents concentrations and the mass transfer constant, p , which depends upon prevailing mass transfer conditions, electrode area and solution volume, is assumed to be the same for C, R, and CR. (Several different symbols have been used for the mass transfer constant and the IUPAC recommendation for it is s . The symbol p is retained here, however, to maintain consistency with previous papers in this series.) The initial condition is $(\text{C}) = (\text{C})_i$, $(\text{CR}) = 0$, and $(\text{R}) = 0$ at $t = 0$; $(\text{C}) = (\text{C})_{t_1}$, $(\text{CR}) = (\text{CR})_{t_1}$ and $(\text{R}) = (\text{R})_{t_1}$ at $t = t_1$.

During the forward electrolysis the current, i_f , is given by:

$$i_f = nFVp[(C) + (CR)] \quad (6)$$

where F is Faraday's constant and V is the total volume of solution. The rate of electrolysis of C and CR is

$$d[(C) + (CR)]/dt = -p[(C) + (CR)] \quad (7)$$

so that

$$(C) + (CR) = (C)_i \exp(-pt) \quad (8)$$

The number of coulombs of electricity consumed in the forward electrolysis, Q_f , given by (9), is the same as that observed in an unperturbed electrolysis of C :

$$Q_f = \int_0^{t_1} i_f dt = nFV(C)_i [1 - \exp(-pt_1)] \quad (9)$$

At $t = t_1$ the potential is shifted to where the reverse electrolysis ($R \rightarrow C + ne$) occurs and the governing equations are:

$$d(C)/dt = p(R) - k_2(C)(R) \quad (10)$$

$$d(R)/dt = -p(R) - k_2(C)(R) \quad (11)$$

with the initial condition $(C) = (C)_{t_1}$, and $(R) = (R)_{t_1}$ at $t = t_1$. In the reverse electrolysis the number of coulombs of electricity consumed, Q_b , from $t = t_1$ to $t = t_2$ is given by

$$Q_b = \int_{t_1}^{t_2} i_b dt = \int_{t_1}^{t_2} nFVp(R) dt \quad (12)$$

where i_b is the current during the reverse electrolysis. Analytical solutions for these first-order non-linear differential equations could not be found and no closed form equation for Q_b/Q_f as a function of p , k_2 and $(C)_i$ could be obtained. However, they could be solved numerically for the instantaneous concentrations of C , R , and CR during the forward and back electrolysis by employing the computer subroutine DASCURU from IMSL (International Mathematical and Statistical Libraries, Inc.). DASCURU is an automatic step change differential equation solver written in the FORTRAN language. Q_f and Q_b could be found by numerical integration, using Simpson's rule, of the instantaneous concentrations calculated by DASCURU. More specifically, the time intervals 0 to t_1 , and t_1 to t_2 , were divided into a number of time intervals of equal length, Δt . For each Δt DASCURU was used to calculate the concentrations, using an external subroutine for eqns. (3), (4) and (5) during the forward electrolysis, and for eqns. (10) and (11) during the back electrolysis. Values of Q_b/Q_f (for $t_2 = 2 t_1$) were computed as functions of the dimensionless parameters $p/k_2(C)_i$ and pt_1 using the CDC 6400/6600 computer. Typical results of these calculations, shown in Fig. 1, can be used to determine k_2 .

When the back electrolysis is taken to completion, the number of coulombs of electricity consumed, Q_b^0 , can also be obtained with a similar procedure, where

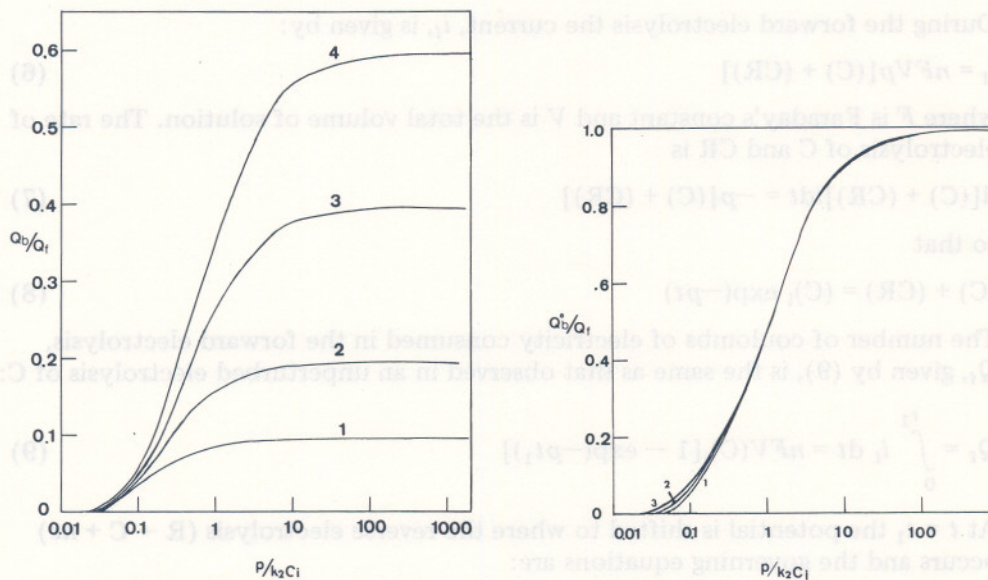


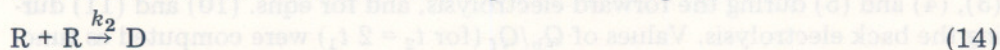
Fig. 1. Case I: variation of Q_b/Q_f with $p/k_2(C)_i$ for various values of pt_1 (or % electrolysis); $t_2 = 2t_1$. (1) 0.1 (9.5%), (2) 0.22 (20%), (3) 0.51 (40%), (4) 0.92 (60%).

Fig. 2. Case I: variation of Q_b^0/Q_f with $p/k_2(C)_i$ for various values of pt_1 (or % electrolysis): (1) 0.51 (40%), (2) 0.92 (60%), (3) 1.6 (80%).

the integration in (13) was stopped when the

$$Q_b^0 = \int_{t_1}^{\infty} i_b dt = \int_{t_1}^{\infty} nFVp(R)dt \quad (13)$$

increment of Q_b^0 dropped to a negligible value. Values of Q_b^0/Q_f as functions of $p/k_2(C)_i$ and pt_1 are shown in Fig. 2. The curves for different values of pt_1 are almost the same, so that the value of Q_b^0/Q_f obtained for a given $p/k_2(C)_i$ is essentially independent of the fraction of C reduced in the forward electrolysis for this mechanism. Since the reaction rate depends primarily upon the concentrations of the reactants, this mechanism can be easily distinguished from that involving a dimerization reaction of two R molecules. For a specific value of $p/k_2(C)_i$ in a dimerization, the consumption of R is greater for a high concentration of R (or high percentage of forward electrolysis) than a low concentration of R (or low percentage of forward electrolysis). Therefore, Q_b^0/Q_f is very sensitive to pt_1 [3]. To confirm the computer program and procedures employed here this dimerization reaction scheme, involving the following reaction:



was considered. The results of the computer treatment were identical to those obtained previously using a Bessel function approach [3].

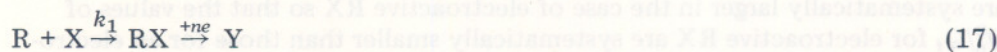
Case II. The intermediate species R is consumed by cross-coupling with parent molecule C but the product RC is electroinactive at the reduction potential of C. This scheme corresponds to eqns. (1) and (2) except for reduction of CR. During

the forward reaction, the system is described by eqns. (3) and (4). However, C is the only species which contributes to i_f , thus

$$Q_f = \int_0^{t_1} i_f dt = \int_0^{t_1} nFVp(C)dt \quad (15)$$

During the back electrolysis the system is described by eqns. (10) and (11). The results are shown in Fig. 3.

Case III. Pseudo-first-order e.c.e. reduction. When C is electrochemically reduced in the presence of a large excess of an electroinactive species X, the intermediate R is consumed by an irreversible first- or pseudo-first-order reaction to form RX, which is then reduced to an electroinactive species Y (e.c.e. mechanism):



Assuming the reduction of RX is mass transfer controlled at potentials where C is reduced, then during the forward electrolysis, the system is described by the simultaneous equations:

$$d(C)/dt = -p(C) \quad (18)$$

$$d(R)/dt = p(C) - k_1(R) \quad (19)$$

$$d(RX)/dt = k_1(R) - p(RX) \quad (20)$$

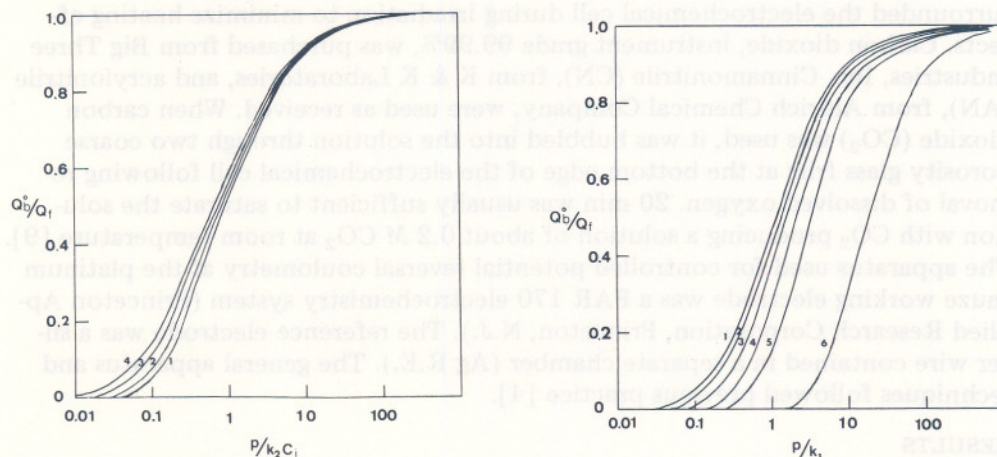


Fig. 3. Case II: variation of Q_b^0/Q_f with $p/k_2(C_i)$ for various values of pt_1 (or % electrolysis): (1) 0.51 (40%), (2) 0.92 (60%), (3) 1.6 (80%), (4) 6.9 (99.9%).

Fig. 4. Case III: variation of Q_b^0/Q_f with p/k_1 for various values of pt_1 (or % electrolysis): (1) 0.1 (9.5%), (2) 0.22 (20%), (3) 0.51 (40%), (4) 0.92 (60%), (5) 1.6 (80%), (6) 6.9 (99.9%).

Q_f is then

$$Q_f = \int_0^{t_1} i_f dt = \int_0^{t_1} nFVp[(C) + (RX)]dt \quad (21)$$

During the back electrolysis, only R is electroactive and

$$d(C)/dt = p(R) \quad (22)$$

$$d(R)/dt = -p(R) - k_1(R) \quad (23)$$

$$d(RX)/dt = k_1(R) \quad (24)$$

The computed values of Q_b^0/Q_f as a function of the dimensionless parameters p/k_1 and pt_1 , shown in Fig. 4, can be used to determine k_1 . Note that, these results are similar to those for a simple following first-order reaction (2) except that all curves are shifted to higher p/k_1 values for a given pt_1 , i.e., the Q_f values are systematically larger in the case of electroactive RX so that the values of Q_b^0/Q_f for electroactive RX are systematically smaller than those for an electroinactive product for a particular value of p/k_1 .

EXPERIMENTAL

Purified thioindigo (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 after drying under vacuum. N,N-dimethylformamide (DMF), purified as previously described [8], was used as a solvent in all experiments. Dissolved oxygen was removed by purging with extra dry nitrogen. A 275 W General Electric sunlamp equipped with a Corning 3-68 glass filter was used to irradiate the solution of TI to generate the *cis*-isomer [4]. A water bath surrounded the electrochemical cell during irradiation to minimize heating effects. Carbon dioxide, instrument grade 99.99%, was purchased from Big Three Industries, Inc. Cinnamionitrile (CN), from K & K Laboratories, and acrylonitrile (AN), from Aldrich Chemical Company, were used as received. When carbon dioxide (CO₂) was used, it was bubbled into the solution through two coarse porosity glass frits at the bottom edge of the electrochemical cell following removal of dissolved oxygen. 20 min was usually sufficient to saturate the solution with CO₂ producing a solution of about 0.2 M CO₂ at room temperature [9]. The apparatus used for controlled potential reversal coulometry at the platinum gauze working electrode was a PAR 170 electrochemistry system (Princeton Applied Research Corporation, Princeton, N.J.). The reference electrode was a silver wire contained in a separate chamber (Ag R.E.). The general apparatus and techniques followed previous practice [4].

RESULTS

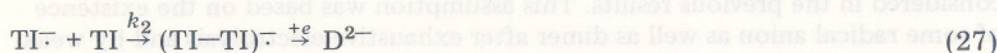
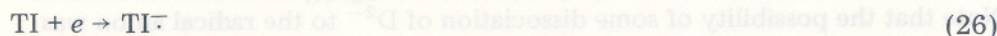
Thioindigo

Cyclic voltammetry of thioindigo (TI) shows one reduction peak at -0.30 V vs. a silver reference electrode and two oxidation peaks at -0.24 V and $+0.14$ V

on the reversal scan (Fig. 5). The *cis*- and *trans*-isomers showed no distinguishable difference in reduction peak heights or potentials when the *cis*-isomer was photogenerated from the same solution [4]. The oxidation peak at +0.14 V was very small for the *trans*-isomer, but was larger, at the expense of -0.24 V peak, for the *cis*-isomer. For reduction at -0.5 V followed by oxidation at +0.5 V, all of the reduced species and reaction products are oxidized back to the parent [4]. This allows TI to be used to calculate the p value of the system by determination of Q_b/Q_f , as previously described for a system with no complicating chemical reactions. Thus the forward electrolysis was carried out at -0.5 V for t_1 s to give Q_f , then the oxidation was carried out at +0.5 V for t_1 s to give Q_b , and the value of p was calculated using eqn. (25) [3].

$$Q_b/Q_f = 1 - \exp(-pt_1) \quad (25)$$

Values of p from these experiments in the absence of as well as in the presence of cinnamionitrile and carbon dioxide (which are reduced at much more negative potentials) are shown in Table 1. As shown previously [4], the reductive coulometric results for TI gave $n_{app} = 1$, and the isolated product after electrolysis showed higher molecular weight peaks by mass spectrometry. The results suggested that the oxidation peak at +0.14 V was due to the formation of the dimer. Furthermore, rotating ring-disk electrode techniques verified that the consumption of the radical anion was a second-order reaction resulting from the reaction of the radical anion with its parent molecule. Thus the reaction scheme given in eqns. (26) and (27) is an example of



case I described above. The second-order rate constants, k_2 , using reversal coulo-

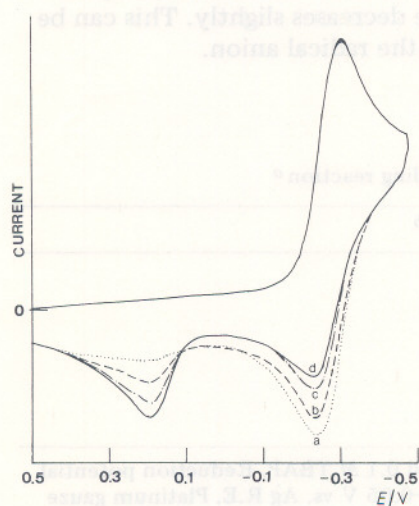


Fig. 5. Cyclic voltammograms of 0.16 mM thioindigo in 0.1 M TBAP-DMF solution. Scan rate, 100 mV s^{-1} . (a) *Trans*-isomer; (b) *trans*-isomer in the presence of 0.2 M dissolved CO_2 ; (c) *cis*-isomer; (d) *cis*-isomer in the presence of 0.2 M dissolved CO_2 .

TABLE 1
Reversal coulometry results of thioindigo systems in absence of side reactions^a

t_1/s	Trans		Cis	
	Q_b/Q_f	$10^2 \frac{b}{p/s^{-1}}$	Q_b/Q_f	$10^2 \frac{b}{p/s^{-1}}$
A. 0.16 mM thioindigo				
100	0.475	0.65	0.516	0.70
150	0.645	0.69	0.62	0.65
B. 0.10 mM thioindigo + 10.0 mM cinnamionitrile				
100	0.45	0.60	0.46	0.62
160	0.65	0.65	0.66	0.68
C. 0.16 mM thioindigo + 0.2 M CO ₂				
100	0.47	0.64	0.48	0.65
150	0.62	0.65	0.63	0.66
	Average	0.65	Average	0.66

^a Solutions (20 ml) of DMF containing 0.1 M TBAP; platinum gauze working electrode. Reduction potential was -0.5 V vs. Ag R.E.; oxidation potential was $+0.5$ V vs. Ag R.E. (Note that this oxidation potential regenerated all the reduced products back to parent molecules.)

^b Calculated from $Q_b/Q_f = 1 - \exp(-pt_1)$ [3].

metry and oxidation at -0.05 V, calculated from Q_b/Q_f , are shown in Table 2. Note that the possibility of some dissociation of D^{2-} to the radical anion was considered in the previous results. This assumption was based on the existence of some radical anion as well as dimer after exhaustive electrolysis and by weak electron spin resonance signals detected in the dimer solution. Therefore, in reversal coulometric experiments, the back electrolysis was not carried to completion, but rather for the same period of time, t_1 , as in the forward electrolysis. Note that as t_1 increases, the calculated k_2 value decreases slightly. This can be attributed to some dissociation of the dimer to the radical anion.

TABLE 2
Reversal coulometry of thioindigo with following coupling reaction^a

t_1/s	Q_b/Q_f	$k_2/l \text{ mol}^{-1} \text{ s}^{-1} \text{ }^b$
A. Trans-isomer		
150	0.24	90
300	0.32	74
B. Cis-isomer		
160	0.068	345
300	0.10	300

^a Solution (20 ml) was DMF containing 0.16 mM TI and 0.1 M TBAP. Reduction potential was at -0.5 V vs. Ag R.E.; oxidation potential was at -0.05 V vs. Ag R.E. Platinum gauze working electrode.

^b Values of rate constant k_2 were computed according to Case I, with $p = 0.0065$ used for all calculations.

Thioindigo with carbon dioxide, cinnamonnitrile and acrylonitrile

Cyclic voltammograms of TI in the presence of CO_2 are shown in Fig. 5. The presence of CO_2 causes a slight shift of the second reoxidation peak towards more positive potentials, so that it occurs at an E_{pa} of about +0.18 V, as well as a slight increase in the height of this peak at the expense of the first reoxidation peak. Similar cyclic voltammograms with a similar potential shift and peak height change were also obtained for TI in the presence of AN or CN, with the second reoxidation peak always occurring at +0.16 to +0.18 V vs. the silver reference electrode. Because of the slight instability of silver wire reference electrode in TBAP-DMF solution, exact reoxidation potentials of these peaks were not recorded. However, slight positive shifts of E_{pa} in the presence of these compounds were found compared to those where these compounds were absent. CO_2 , AN and CN were not electroactive at the potentials employed in these experiments and no reactions occurred between parent TI and any of these compounds. The height and location of the TI reduction wave was almost the same in the presence and absence of CO_2 , AN or CN.

When exhaustive reductive electrolysis of TI in the presence of CO_2 , AN or CN was carried out at -0.5 V, only one oxidation peak at about +0.18 V was seen after electrolysis for both the *cis*- and *trans*-isomers (Fig. 6). In these experiments the *cis*-isomer was produced from the more stable *trans*-form by irradiation with yellow light as described previously [4]. Although the cyclic voltammetric reduction of TI was not perturbed by the addition of CO_2 , AN or CN, the bulk reductive electrolysis of TI at -0.5 V gave n_{app} values of 2.0 per TI in the presence of CO_2 , AN or CN, compared to the n_{app} of 1 found in their absence. Reoxidation of the reduced products at +0.5 V regenerated the parent TI and also showed an $n_{app} = 2.0$. The actual n_{app} values obtained from controlled potential coulometry are shown in Table 3. The fact that complete regeneration of parent TI occurs by oxidation of the reduced products allows one to use these data to calculate the p values in the presence of CO_2 , AN or CN as shown in Table 1.

When TI was electrochemically reduced in the presence of a large excess of the electroinactive species CO_2 , AN or CN, the reaction apparently occurred by

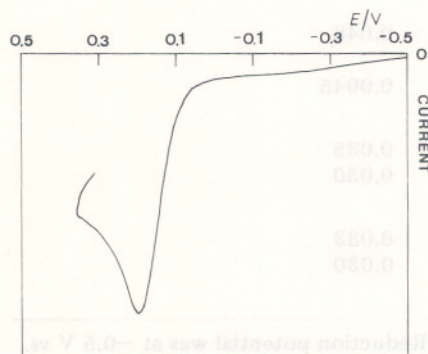


Fig. 6. Reoxidation curve at 100 mV s^{-1} for 0.16 mM thioindigo in the presence of 0.2 M dissolved CO_2 after exhaustive electrolytic reduction at -0.5 V vs. Ag R.E.

TABLE 3

Controlled potential coulometry n_{app} values for reduction of TI^a in presence of CO₂, AN, or CN

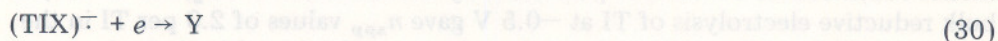
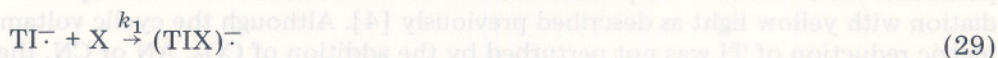
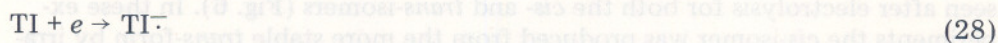
System	Reduction ^b		Oxidation ^c	
	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>
0.16 mM TI + 0.2 M CO ₂	1.96	1.95	1.92	1.94
0.20 mM TI + 20 mM AN	2.0	2.03	1.95	2.0
0.10 mM TI + 10 mM CN	1.98	1.92	1.97	1.88

^a Electrolysis was carried out in 0.1 M TBAP—DMF solutions; electrolysis time, about 20 min.

^b Reduction at -0.5 V vs. Ag R.E.

^c Oxidation at +0.5 V vs. Ag R.E. following reduction.

an e.c.e. mechanism in which TI⁻ was consumed by a pseudo-first-order reaction to form an intermediate which is reduced at the electrode in another one-electron reaction. Thus the total number of electrons transferred per TI molecule is 2 and the reaction mechanism follows Case III. The reaction sequence can be written as:



where X is CO₂, AN or CN and Y is the final product. Although eqn. (29) is a

TABLE 4

Reversal coulometric results and rate constants for reaction^a of thioindigo radical anion with CO₂, AN, or CN

t_1/s	<i>Trans</i>		<i>Cis</i>	
	Q_b/Q_f	k_1/s^{-1} ^b	Q_b/Q_f	k_1/s^{-1} ^b
A. 0.16 mM thioindigo + 0.2 M CO ₂				
100	0.085	0.018	0.0145	0.048
150	0.10	0.013		
160			0.0085	0.0045
B. 0.10 mM thioindigo + 10.0 mM cinnamionitrile				
100	0.057	0.025	0.029	0.035
160	0.036	0.021	0.019	0.030
C. 0.20 mM thioindigo + 20.0 mM acrylonitrile				
90	0.057	0.025	0.034	0.033
160	0.036	0.021	0.018	0.030
220	0.027	0.021		

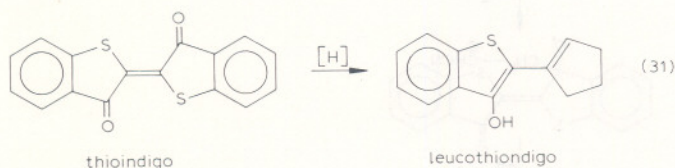
^a Solution (20 ml) was DMF containing 0.1 M TBAP. Reduction potential was at -0.5 V vs. Ag R.E.; oxidation potential was at -0.05 V vs. Ag R.E.

^b Values of rate constant k_1 were computed according to Case III, with $p = 0.0065$ used for all calculations.

second-order reaction, X is present in a large excess (100 times or more) compared to TI, so that it can be treated as a pseudo-first-order one. Controlled potential reversal coulometry was performed for these mixed systems at -0.5 V for reduction and -0.05 V for oxidation. The results and calculated pseudo-first-order rate constants based on the mechanism of Case III are shown in Table 4. Good agreement of the calculated k_1 values was found in duplicate experiments.

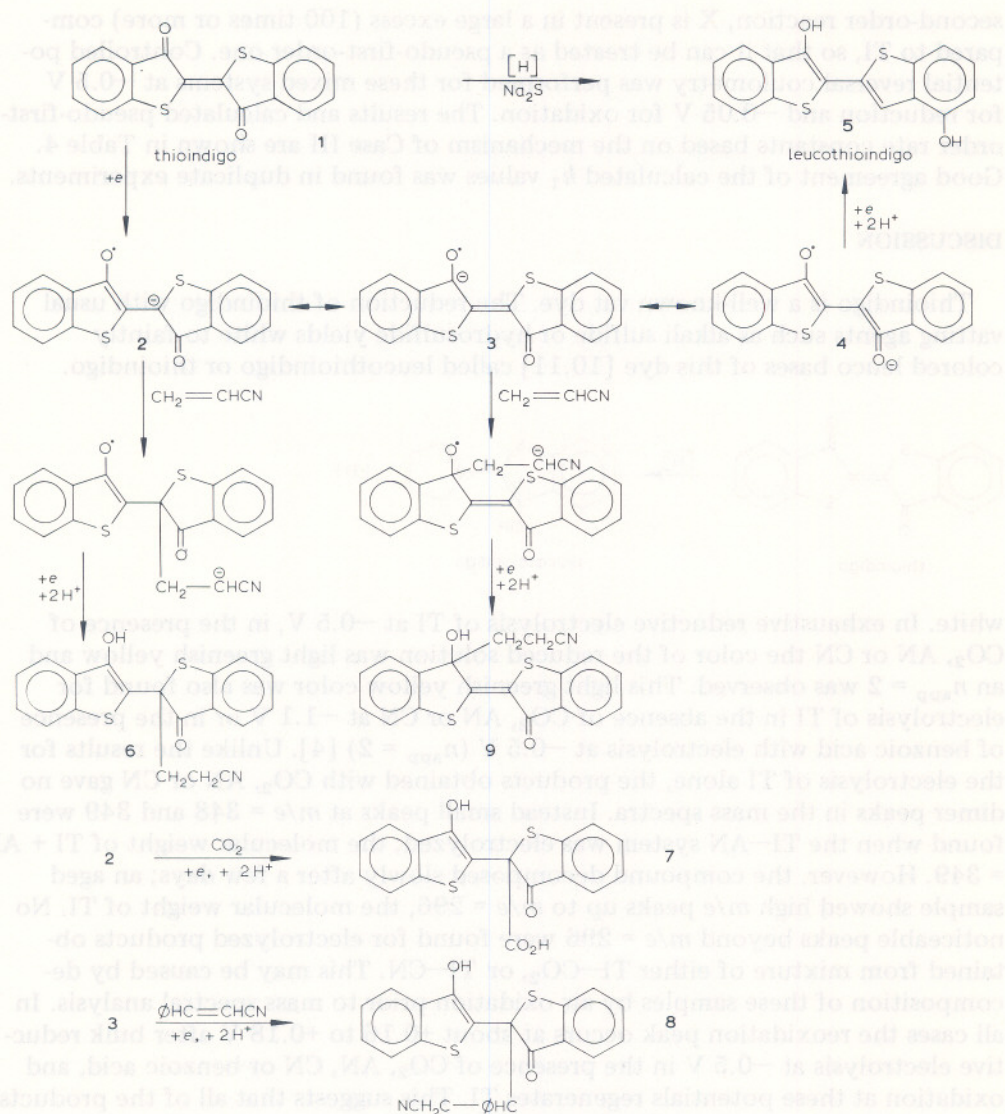
DISCUSSION

Thioindigo is a well-known vat dye. The reduction of thioindigo with usual vatting agents such as alkali sulfide or hydrosulfide yields white to faintly colored leuco bases of this dye [10,11] called leucothioindigo or thioindigo.

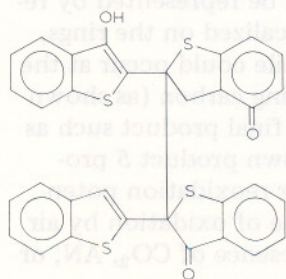


white. In exhaustive reductive electrolysis of TI at -0.5 V, in the presence of CO_2 , AN or CN the color of the reduced solution was light greenish yellow and an $n_{\text{app}} = 2$ was observed. This light greenish yellow color was also found for electrolysis of TI in the absence of CO_2 , AN or CN at -1.1 V or in the presence of benzoic acid with electrolysis at -0.5 V ($n_{\text{app}} = 2$) [4]. Unlike the results for the electrolysis of TI alone, the products obtained with CO_2 , AN or CN gave no dimer peaks in the mass spectra. Instead small peaks at $m/e = 348$ and 349 were found when the TI-AN system was electrolyzed; the molecular weight of TI + AN = 349 . However, the compound decomposed slowly after a few days; an aged sample showed high m/e peaks up to $m/e = 296$, the molecular weight of TI. No noticeable peaks beyond $m/e = 296$ were found for electrolyzed products obtained from mixture of either TI- CO_2 , or TI-CN. This may be caused by decomposition of these samples by air oxidation prior to mass spectral analysis. In all cases the reoxidation peak occurs at about $+0.16$ to $+0.18$ V after bulk reductive electrolysis at -0.5 V in the presence of CO_2 , AN, CN or benzoic acid, and oxidation at these potentials regenerates TI. This suggests that all of the products have similar or the same oxidizable functional groups. A reaction mechanism for these mixed system which accounts for this behavior is as follows. The one-electron reduction of TI produces the radical anion which can be represented by resonance forms 2, 3, and 4, structures with the charge delocalized on the rings, and equivalent *cis*-form structures. Attack by an electrophile could occur at the central ethylenic carbon (as shown below 2) at the O-bearing carbon (as shown below 3) or, less probably at the oxygen or on the ring. A final product such as structure 9 seems to be unlikely, and the fact that the known product 5 produced by the 2-electron reduction of TI shows very similar reoxidation potentials, the same light greenish yellow color and the same ease of oxidation by air (resulting in parent TI) as the products obtained in the presence of CO_2 , AN, or CN suggests 6, 7 and 8 as the most reasonable structures.

In the absence of CO_2 , AN, benzoic acid or CN the dimer formed can be as-



signed the structure 10, since the potential for oxidation of the dimer was about



the same as that for the other reduced electrolysis products. This suggests that the dimer and products 5, 6, 7 and 8 contain similar, or the same, functional groups, although knowledge of the actual structures of these compounds must await isolation of pure products and rigorous characterization.

The results obtained here do show, as has been previously observed with the dimerization of TI [4] and dialkyl maleates and fumarates [12,13], and the reaction of maleates and fumarates with AN and CO₂ [13,14], that the reactivity of the *cis*-anion radical is different from that of the *trans*-, and that electrochemical techniques are particularly useful in determining these reactivities. Controlled potential coulometric techniques are particularly suited for the reactions of interest here, which are too slow to study by voltammetric techniques.

ACKNOWLEDGMENTS

The support of this research by the Robert A. Welch Foundation and the National Science Foundation (GP-31414X) is gratefully acknowledged. We are indebted to Dr. George M. Wyman for the sample of TI and helpful comments.

REFERENCES

- 1 K.S.V. Santhanam and A.J. Bard in A.J. Bard (Ed.), *Electroanalytical Chemistry*, Marcel Dekker, New York, 4 (1970) 215.
- 2 L. Meites, in A. Weissberger and B.W. Rossiter (Eds.), *Techniques of Chemistry*, 1, Part IIA, Wiley-Interscience, New York, 1971 Ch. IX.
- 3 S.V. Tatwawadi and A.J. Bard, *J. Phys. Chem.*, 68 (1964) 2676.
- 4 L.S.R. Yeh and A.J. Bard, *J. Electroanal. Chem.*, 70 (1976) 157.
- 5 D.H. Geske and A.J. Bard, *J. Phys. Chem.*, 63 (1959) 1057.
- 6 J.S. Mayell and A.J. Bard, *J. Phys. Chem.*, 66 (1962) 2173.
- 7 L.N. Klatt, *J. Electroanal. Chem.*, 55 (1974) 161.
- 8 L.R. Faulkner and A.J. Bard, *J. Amer. Chem. Soc.*, 90 (1968) 6284.
- 9 H. Stephens and T. Stephens, *Solubility of Inorganic and Organic Compounds*, 1, Part 2 MacMillan, New York, 1963, 1063.
- 10 C.E. Dalglish and F.G. Mann, *J. Chem. Soc.*, 893 (1945) 910, 913.
- 11 J. Harley-Mason and F.G. Mann, *J. Chem. Soc.*, 404 (1942).
- 12 V.J. Puglisi, J.V. Kenkel, A. Lomax and A.J. Bard, *Faraday Discuss. Chem. Soc.*, 56 (1973) 353.
- 13 V.J. Puglisi and A.J. Bard, *J. Electrochem. Soc.*, 120 (1973) 748.
- 14 L.S.R. Yeh and A.J. Bard, *J. Electrochem. Soc.*, 81 (1977) 333 (this issue).