

# Correlation of Open-Circuit Voltage and Short-Circuit Current of the Totally Illuminated, Thin-Layer Iron-Thionine Photogalvanic Cell with Photostationary Composition<sup>1</sup>

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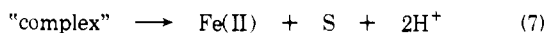
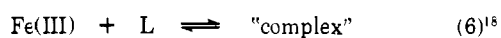
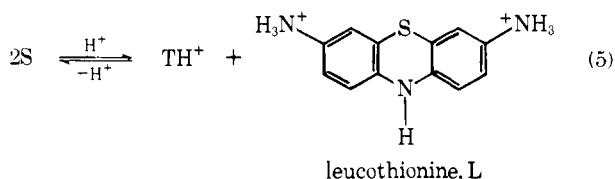
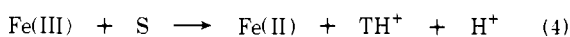
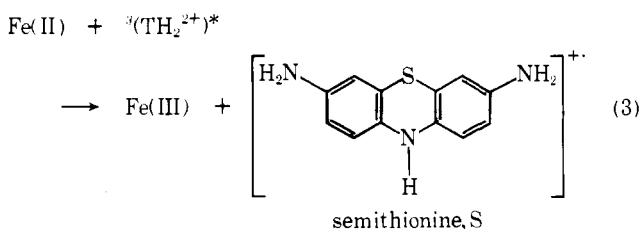
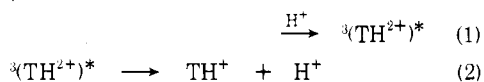
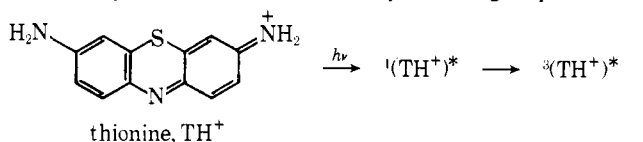
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**Abstract:** Single-electrode potentials measured relative to an SCE reference for totally illuminated, thin-layer (TI-TL) iron-thionine photogalvanic cells with SnO<sub>2</sub> anodes and InSnO<sub>2</sub> cathodes were correlated with the measured extent of photobleaching of the solutions at the photostationary state. The measured electrode potentials were compared with calculated values obtained using a simplified mixed-potential model for electrodes in contact with two or more redox systems not at equilibrium. The comparison indicates that rate constants for electron exchange are greater for the dye couple than for the iron couple at both electrodes but that the difference is much larger at SnO<sub>2</sub> than at InSnO<sub>2</sub>. Present results together with previously reported data correlating short-circuit current of the TI-TL iron-thionine cell with photostationary composition are consistent with the assumption that leucothionine is the principal form of reduced thionine active at the electrode under the conditions employed. These conditions include use of sulfate as anion, 1 × 10<sup>-2</sup> M acid and ferrous iron, 10<sup>-3</sup>-10<sup>-5</sup> M initial concentration of thionine, and 35-95% photobleaching.

## Introduction

Since the earliest study of the iron-thionine photogalvanic system by Rabinowitch in 1940,<sup>2</sup> it has been recognized that it should be possible to correlate the potential of an electrode immersed in an illuminated iron-thionine solution with the photostationary-state solution composition. Several authors have presented theoretical calculations of photogalvanic potentials.<sup>1-7</sup> In some cases the calculated potentials were compared with measured voltages in iron-thionine photogalvanic cells.<sup>2,3,6,7</sup> Theoretical calculations have also been used to predict optimum cell performance<sup>4,5</sup> and in discussions of the probable mechanisms of iron-thionine photogalvanic cells.<sup>2,6,7</sup>

Extensive investigation of the photochemistry of the iron-thionine system in acidic solution by several groups<sup>8-18</sup> has



established the sequence of reactions described in eq 1-7. Unfortunately, previous theoretical discussions of iron-thionine photogalvanic cell potentials have not been based on consideration of the entire reaction sequence. Gomer<sup>4</sup> ignored reactions 5-7 and assumed that all reduced thionine is present as S. Shigehara and Tsuchida<sup>7</sup> estimated the photostationary-state concentration of S by considering only the equilibrium constant for eq 5 and Rabinowitch<sup>2b</sup> did not attempt to calculate the photostationary-state concentration of S.

We have previously presented measurements and calculations of photostationary-state compositions for specific iron-thionine solutions at various light intensities and initial concentrations of thionine<sup>19,20</sup> and a correlation of the current output of totally illuminated, thin-layer (TI-TL) iron-thionine photogalvanic cells<sup>21</sup> (SnO<sub>2</sub> anode, Pt cathode) with the concentration of reduced dye present at photostationary state.<sup>19</sup>

In the present paper, a method of correlating open-circuit voltage with photostationary-state solution composition is presented. This discussion, together with the previously presented data regarding short-circuit current, indicates that the principal anodic process in the cell is the two-electron oxidation of leucothionine rather than the one-electron oxidation of semithionine as postulated by several previous workers.<sup>2,6,7,21</sup>

The correlation of the potential of an electrode in contact with an illuminated iron-thionine solution with the photostationary-state solution composition may be approached in several ways. The method described below is essentially that used by Miller<sup>3</sup> and by Rabinowitch<sup>2b</sup> and is based on the principles of mixed potential for an electrode in contact with two or more redox systems which are not at equilibrium. Each redox system produces a current at the electrode which can be resolved into a cathodic and an anodic component. If no current is flowing through the external circuit of the cell, i.e., under open-circuit conditions, the sum of the cathodic current components is equal to the sum of the anodic components. For each redox system the cathodic current component,  $i_c$ , and the anodic component,  $i_a$ , are defined by eq 8 and 9 in which  $n$  is the number of electrons transferred in the redox equation,  $F$  is the faraday,  $A$  is the electrode area,  $C_o$  and  $C_r$  are the concentrations of the oxidized and reduced forms of the couple, respectively,  $k_c$  and  $k_a$  are rate constants for the electron-exchange reactions at the electrode when  $E = 0$ ,  $\alpha$  is a transfer

coefficient,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $E$  is the electrode potential.

$$i_c = nFAC_0k_c \exp(-\alpha nFE/RT) \quad (8)$$

$$i_a = nFAC_rk_a \exp[(1 - \alpha)nFE/RT] \quad (9)$$

For the iron-thionine system, the species which can participate in the cathodic process are Fe(III), S, and TH<sup>+</sup> (as either a one- or two-electron acceptor); the species which can be involved in the anodic process are Fe(II), S, and L (as either a one- or two-electron donor). Thus the general equation for the illuminated electrode at open circuit is eq 10, where  $f = F/RT$  and  $n$  may be either 1 or 2 depending on the number of electrons involved in the rate-determining step of the electrode reactions of thionine and leucothionine.

$$k_{c,1}[\text{Fe(III)}] \exp(-\alpha_1 fE) + 2k_{c,2}[\text{TH}^+] \exp(-\alpha_2 n fE) + k_{c,3}[\text{S}] \exp(-\alpha_3 fE) = k_{a,1}[\text{Fe(II)}] \exp((1 - \alpha_1) fE) + 2k_{a,2}[\text{L}] \exp((1 - \alpha_2) n fE) + k_{a,3}[\text{S}] \exp((1 - \alpha_3) fE) \quad (10)$$

The exact expression in eq 10 can be reduced to a more useful form with suitable simplifying assumptions. Rabinowitch<sup>2b</sup> explained his results using a model which arbitrarily assumed that the cathodic electron-exchange rate constants,  $k_{c,n}$ , were all equal while the anodic rate constants,  $k_{a,n}$ , differed in a manner which reflected differences in the standard oxidation potentials of the species involved. The electron-transfer rate constants  $k_{c,n}$  and  $k_{a,n}$  reflect the free energy of activation for the process of transferring an electron from the electrode to a species in solution or the reverse, i.e.,  $k_c = (k_b T/h) \exp(-\Delta G_{et}^\circ/RT)$ , where  $k_b$  is the Boltzmann constant and  $h$  is Planck's constant. An estimate for the free energy of activation for the electron transfer can be obtained from the standard oxidation potentials of the species involved. Thus we have  $k_c = k'_c \exp(\alpha n f E^\circ)$  and  $k_a = k'_a \exp[-(1 - \alpha) n f E^\circ]$  in which  $E^\circ$  is the standard oxidation potential for the couple under the conditions of the measurement (i.e., the measured equilibrium potential when  $C_o = C_r$  in the particular solvent used).<sup>22</sup> We shall further assume that there is an intrinsic difference in the reactivity of the dye species when compared with the iron species which can be expressed by a difference in the  $k'$  values. Referring to eq 10, we set  $k'_{c,1} = k'_{a,1} \equiv k_1$  and  $k'_{c,2} = k'_{c,3} = k'_{a,2} = k'_{a,3} \equiv k_2$ . Using these approximations and setting  $\alpha_1 = \alpha_2 = \alpha_3 = 1/2$  and  $n = 1$  gives

$$\exp(fE) = \{k_1[\text{Fe(III)}] \exp(fE^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})/2) + 2k_2[\text{TH}^+] \exp(fE^\circ(\text{TH}^+/\text{S})/2) + k_2[\text{S}] \exp(fE^\circ(\text{S}/\text{L})/2)\} / \{k_1[\text{Fe(II)}] \times \exp(-fE^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})/2) + 2k_2[\text{L}] \exp(-fE^\circ(\text{S}/\text{L})/2) + k_2[\text{S}] \exp(-fE^\circ(\text{TH}^+/\text{S})/2)\} \quad (11)$$

Most studies of the iron-thionine photogalvanic system have employed cells with two identical inert electrodes, usually platinum, with the solution surrounding one electrode kept in the dark while the solution surrounding the other electrode was illuminated. In the dark, the concentrations of L and S are negligibly small. Therefore, the potential of the dark electrode is established entirely by the iron redox couple and eq 11 reduces to the familiar Nernst expression,  $E = E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + (1/f) \ln([\text{Fe(III)}]/[\text{Fe(II)}])$ . The photogalvanic potential in such cells depends on the shift in potential of the electrode in the illuminated solution as other terms in eq 11 become important.

A significant advance in the design of iron-thionine photogalvanic cells was the recent invention of the TI-TL cell.<sup>21,23,24</sup> In this cell both electrodes are in contact with the

same, approximately homogeneous, solution at photostationary state. A potential difference between the electrodes is observed when the cell is illuminated because of large differences in the electron-exchange rate constants,  $k_1$  and  $k_2$  of eq 11, at the different electrodes. The dye couple TH<sup>+</sup>/L or TH<sup>+</sup>/S is much more reactive at SnO<sub>2</sub> than is the iron couple Fe<sup>3+</sup>/Fe<sup>2+</sup> while at the Pt or InSnO<sub>2</sub><sup>25</sup> electrode the reactivities of the couples are more nearly equal. The reason for the selectivity of response of the SnO<sub>2</sub> anode is discussed in detail elsewhere.<sup>26</sup>

We can determine the standard potentials  $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$ ,  $E^\circ(\text{TH}^+/\text{S})$ , and  $E^\circ(\text{S}/\text{L})$  for various solvent mixtures and pH values (see below). We can then use eq 11 to calculate the extent of the difference in reactivity of the electrodes to the dye couple and the iron couple by simultaneously determining the electrode potential,  $E$ , and the photostationary-state reactant concentrations. We have investigated two solvent systems: 0.01 M sulfuric acid dissolved in water and in 50% (v/v) acetonitrile/water.

## Experimental Section

**A. Materials.** Thionine was MCB thionine acetate certified 99% pure and was used without further purification.

Deionized, distilled water was redistilled from alkaline permanganate in an aged Pyrex still.

Acetonitrile was "UV grade, Distilled in Glass" from Burdick & Jackson Laboratories, Inc.

Magnesium trifluoromethylsulfonate was prepared by the reaction of trifluoromethylsulfonic acid with magnesium carbonate.

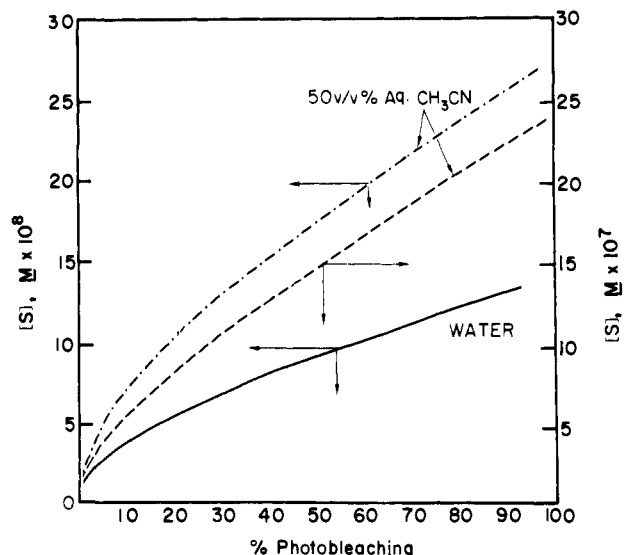
All other materials were reagent grade used as received.

**B. Apparatus.** Simultaneous monitoring of electrode potentials relative to an SCE reference electrode and the extent of photo-bleaching at photostationary state was accomplished using a cross-illumination apparatus which has been previously described.<sup>19,20</sup> The iron-thionine solutions were contained in TI-TL cells with two transparent electrodes, an SnO<sub>2</sub>-coated glass anode, and an InSnO<sub>2</sub>-coated glass cathode. The electrodes were separated by 80- $\mu\text{m}$  Teflon or 25- $\mu\text{m}$  Celgard 2400 spacers and were filled with photogalvanic solution by capillary action. The cell was dipped into a reservoir of iron-thionine solution, and the reservoir was connected through a sintered glass disk with another reservoir containing a similar electrolyte solution without the dye into which was dipped a commercial saturated calomel reference electrode. The cell was positioned in the cross-illumination apparatus oriented at a 45° angle to the photolyzing light beam from a 150-W xenon lamp and also at a 45° angle to a weak probing light beam fixed at a 90° angle to the photolyzing light. The probe beam was first passed through an Oriel filter monochromator to produce a narrow wavelength band centered at 600 nm and then through the sample cell. The transmitted probe beam was then passed through a Schoeffel Model C100 miniature grating monochromator and was detected with an RCA 1P28A photomultiplier tube connected to a Tektronix Model 569 storage oscilloscope. The photolyzing light beam was filtered with a Corning 0-53 glass filter to remove UV wavelengths, and the intensity of the beam was adjusted using neutral-density filters to produce different extents of bleaching at the photostationary state. Changes in absorbance of the cell solution at 600 nm were recorded while the potential differences between the SnO<sub>2</sub> electrode and the SCE reference and between the InSnO<sub>2</sub> electrode and the SCE were simultaneously monitored using a Keithley 610C electrometer.

The tin oxide thin-film electrodes on low-alkali glass substrates were obtained from Corning Glass Works. These were cut to approximately 2.5 × 3.5 cm. The active electrode area (~3 cm<sup>2</sup>) was obtained by masking the remainder of the SnO<sub>2</sub> film with pressure-fit Teflon or Celgard 2400 masks. The indium tin oxide coated glass cathodes were obtained from PPG. Electrical connections were made to the masked portion of the electrodes.

## Results

**A. Standard Potentials for the Thionine and Iron Systems.** The equilibrium potential of the thionine/leucothionine (TH<sup>+</sup>/L) couple depends on solution pH. In acid media, the two-step reduction of thionine to leucothionine proceeds through the one-electron intermediate, S, and hydrogen ions



**Figure 1.** Calculated concentration of semithionine present in photobleached iron–thionine solutions. Dark solution composition:  $1 \times 10^{-4}$  M  $\text{TH}^+$ , 0.05 M  $\text{FeSO}_4$ ,  $4 \times 10^{-4}$  M  $\text{Fe}^{3+}$ , 0.01 M  $\text{H}_2\text{SO}_4$  in water (—);  $1 \times 10^{-4}$  M  $\text{TH}^+$ , 0.01 M  $\text{FeSO}_4$ ,  $7 \times 10^{-5}$  M  $\text{Fe}^{3+}$ , 0.01 M  $\text{H}_2\text{SO}_4$  in 50% (v/v) acetonitrile/water (---);  $1 \times 10^{-3}$  M  $\text{TH}^+$ , 0.017 M  $\text{FeSO}_4$ ,  $7.6 \times 10^{-5}$  M  $\text{Fe}^{3+}$ , 0.01 M  $\text{H}_2\text{SO}_4$  in 50% (v/v) acetonitrile/water (---).

are incorporated into the molecule. In neat water as solvent the equilibrium electrode potential in volts vs. SCE fits eq 12 in the approximate pH range 1–4.<sup>27</sup>

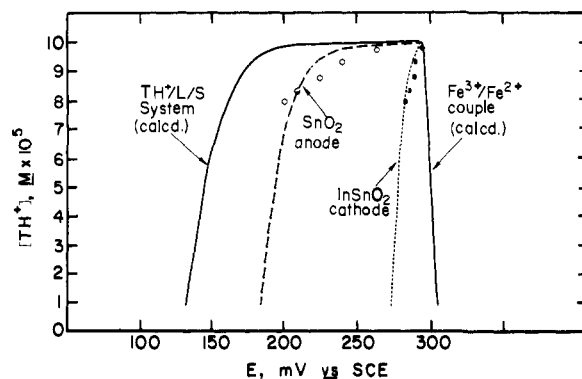
$$E(\text{TH}^+/\text{L}) = 0.321 - 0.09 \text{ pH} + 0.03 \log \left( \frac{[\text{TH}^+]}{[\text{L}]} \right) \quad (12)$$

By measuring the potential relative to SCE of a platinum probe electrode dipped into various thionine/leucothionine solutions as described below, we have verified eq 12 and have found that in 50% (v/v) acetonitrile/water in the pH range 1–3,  $E^\circ = 0.321$  is replaced in eq 12 by  $E^\circ = 0.29$ .

Leucothionine was prepared by the photoreduction of thionine with ferrous acetate.<sup>28</sup> A measured volume of  $\sim 1 \times 10^{-4}$  M thionine solution in the appropriate solvent (water or 50% (v/v) acetonitrile/water) was deaerated by purging with prepurified nitrogen. Sufficient ferrous sulfate and sodium acetate were added to make the solution  $\sim 3 \times 10^{-4}$  M in  $\text{Fe}^{2+}$  and  $\sim 1.5 \times 10^{-3}$  M in acetate. The solution was illuminated with a 150-W tungsten lamp until the solution bleached to a pale yellow. Filtering through a fine sintered glass disk under nitrogen to remove precipitated ferric acetate left a colorless leucothionine solution. Measured amounts of a deaerated thionine solution of known concentration were added to the leucothionine solution with constant nitrogen purging in a vessel fitted with a platinum probe electrode and connected by a siphon to an SCE reference electrode. Ionic strength of the solution was fixed at  $\mu \approx 0.5$  M by addition of magnesium trifluoromethylsulfonate or tetramethylammonium bromide. The pH was adjusted by addition of sulfuric acid.

The standard potential for the  $\text{Fe(III)}/\text{Fe(II)}$  couple in 0.01 M aqueous  $\text{H}_2\text{SO}_4$  and in 50% (v/v) acetonitrile/water 0.01 M in  $\text{H}_2\text{SO}_4$  was similarly measured by mixing solutions of ferrous and ferric sulfate at known concentration and measuring the potential relative to the SCE of a platinum electrode dipped into the solution. Values obtained relative to SCE were  $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.42$  V in water and 0.43 V in 50% (v/v) acetonitrile/water.

The standard electrode potentials for the two one-electron steps  $E^\circ(\text{TH}^+/\text{S})$  and  $E^\circ(\text{S}/\text{L})$  can be calculated from  $E^\circ(\text{TH}^+/\text{L})$  and the equilibrium constant for reaction 5,  $K_5$ . In discussions of the potential of iron–thionine photogalvanic



**Figure 2.** Electrode potentials measured for  $\text{SnO}_2$  (O) and  $\text{InSnO}_2$  (●) electrodes of an illuminated TI–TL iron–thionine cell containing a solution with dark composition  $1 \times 10^{-4}$  M  $\text{TH}^+$ , 0.05 M  $\text{FeSO}_4$ ,  $4 \times 10^{-4}$  M  $\text{Fe}^{3+}$ , and 0.01 M  $\text{H}_2\text{SO}_4$  in water. Calculated curves (see text) are shown for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple, the  $\text{TH}^+/\text{L}/\text{S}$  system, and mixed potentials with  $k_2/k_1 = 50$  (···) and  $k_2/k_1 = 2500$  (---).

cells, several authors<sup>2,7,13</sup> have assumed  $K_5 = 0.01$ – $0.05$ , the value reported by Michaelis, Schubert, and Granick in 1940.<sup>29</sup> More recent studies<sup>14,30</sup> have shown, however, that  $K_5 \ll 0.01$ . We have recently evaluated  $K_5$  by a kinetic method and found it to be  $(0.4$ – $0.8) \times 10^{-6}$  in 0.01 M aqueous  $\text{H}_2\text{SO}_4$  and  $(0.9$ – $1.8) \times 10^{-6}$  in 50% (v/v) acetonitrile/water 0.01 M in  $\text{H}_2\text{SO}_4$ .<sup>30</sup> We obtain the following standard potentials in volts vs. SCE at pH 2 and room temperature:  $E^\circ(\text{TH}^+/\text{L}) = 0.142$ ,  $E^\circ(\text{TH}^+/\text{S}) = -0.04$ ,  $E^\circ(\text{S}/\text{L}) = 0.33$  in water and  $E^\circ(\text{TH}^+/\text{L}) = 0.11$ ,  $E^\circ(\text{TH}^+/\text{S}) = -0.06$ ,  $E^\circ(\text{S}/\text{L}) = 0.28$  in 50% (v/v) acetonitrile/water.

**B. Photostationary-State Composition of Illuminated Iron–Thionine Solutions.** Using the cross-illumination technique, we can monitor the change in absorbance at 600 nm,  $\Delta A$ , of iron–thionine solutions under illumination at various intensities. Since leucothionine does not absorb at 600 nm,<sup>31</sup> if the concentration of S at photostationary state is small,  $\Delta A$  is a measure of the extent of conversion of  $\text{TH}^+$  to L.

At photostationary state  $d[\text{L}]/dt = 0$ . From reactions 5–7 we obtain eq 13 in which the concentrations are those present

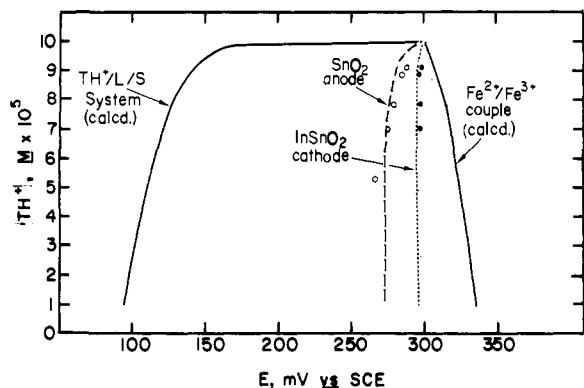
$$d[\text{L}]/dt = k_5[\text{S}]^2 - K_6k_7[\text{L}][\text{Fe(III)}] - \frac{1}{2}k_{-5}[\text{TH}^+][\text{L}] = 0 \quad (13)$$

at photostationary state. These concentrations can be expressed as  $[\text{Fe(III)}] = [\text{Fe(III)}]_d + 2[\text{L}] + [\text{S}]$  and  $[\text{TH}^+] + [\text{S}] + [\text{L}] = [\text{TH}^+]_d$ , using the subscript d to indicate the concentrations present in the dark. If [S] is very small  $[\text{Fe(III)}] \approx [\text{Fe(III)}]_d + 2[\text{L}]$  and  $[\text{TH}^+] + [\text{L}] \approx [\text{TH}^+]_d$ . Substituting these values for [Fe(III)] and [TH<sup>+</sup>] in eq 13 and rearranging gives eq 14 for the photostationary-state concentration of [S].

$$[\text{S}]^2 = \{K_6k_7[\text{L}][[\text{Fe(III)}]_d + 2[\text{L}]] + \frac{1}{2}k_{-5}([\text{TH}^+]_d - [\text{L}])[\text{L}]\} / k_5 \quad (14)$$

Rate constants  $k_5$ ,  $k_{-5}$ , and  $K_6k_7$  for the two solvents 0.01 M aqueous sulfuric acid and 0.01 M sulfuric acid in 50% (v/v) acetonitrile/water have been published.<sup>18,30</sup> Plots of [S] at photostationary state vs. extent of photobleaching, calculated from these constants using eq 14, are shown in Figure 1. The concentration of S increases with increasing photobleaching but even in very strongly bleached solutions  $[\text{S}] < 0.3\%$  of  $[\text{TH}^+]_d$ .

**C. TI–TL  $\text{SnO}_2/\text{InSnO}_2$  Electrode Potentials.** Using the cross-illumination technique with the iron–thionine solutions in TI–TL cells with two transparent electrodes, the extent of photobleaching and the electrode potentials relative to an SCE reference were monitored simultaneously. In Figures 2–4 the electrode potentials are plotted vs. the concentration of  $[\text{TH}^+]$  remaining at photostationary state. The open-circuit voltage

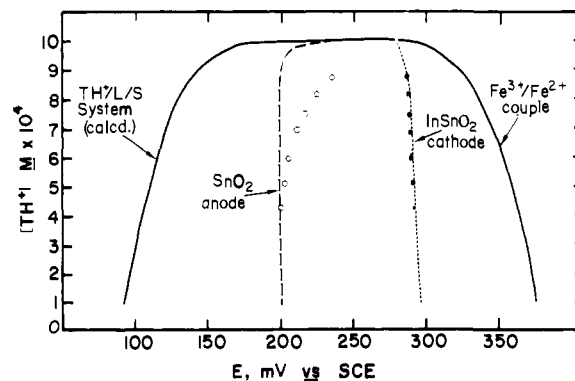


**Figure 3.** Electrode potentials measured for SnO<sub>2</sub> (○) and InSnO<sub>2</sub> (●) electrodes of an illuminated TI-TL iron-thionine cell containing a solution with dark composition  $1 \times 10^{-4}$  M TH<sup>+</sup>, 0.01 M FeSO<sub>4</sub>,  $7 \times 10^{-5}$  M Fe<sup>3+</sup>, and 0.01 M H<sub>2</sub>SO<sub>4</sub> in 50% (v/v) acetonitrile/water. Calculated curves (see text) are shown for the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple, the TH<sup>+</sup>/L/S system, and mixed potentials with  $k_2/k_1 = 5$  (···) and  $k_2/k_1 = 15$  (-·-·-).

of the cell is the difference between the potential of the SnO<sub>2</sub> electrode and that of the InSnO<sub>2</sub> electrode. The experiments with  $1 \times 10^{-4}$  M total dye concentration using water (Figure 2) and 50% (v/v) acetonitrile/water (Figure 3) as solvent were done with the same electrodes. A different set of electrodes were used for the experiment employing  $1 \times 10^{-3}$  M total dye concentration (Figure 4). Different SnO<sub>2</sub> electrodes produce different open-circuit voltages in TI-TL cells with the same solution and counterelectrode. The electrodes used in obtaining the data of Figures 2 and 3 give cell voltages much smaller than the best obtained in TI-TL cells with SnO<sub>2</sub> anodes.

The ideal TI-TL cell would have one electrode which was totally unresponsive to the dye system but which would readily allow electron exchange with the iron couple and a second electrode with the opposite response, allowing rapid exchange with the dye system but no exchange with the iron system. These extremes are illustrated by the solid lines in Figures 2-4. The potential for the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple was calculated by setting  $k_2 = 0$  and  $k_1 = 1$  in eq 11. The potential of the dye system was calculated by setting  $k_1 = 0$  and  $k_2 = 1$  in eq 11. Treated in this manner, the semithionine terms in eq 11 have little effect on the calculated potentials, and neglecting those terms does not appreciably shift the calculated curve for the thionine system. Calculating the potential curve for the thionine system using eq 12 produces substantially the same results.

Figures 2-4 show that the SnO<sub>2</sub> and InSnO<sub>2</sub> electrodes do not respond perfectly selectively but rather attain a mixed potential at photostationary state in which both the iron and thionine systems participate. The dashed and dotted lines in Figures 2-4 are calculated mixed-potential curves obtained using eq 11. Calculated curves very closely approximating the experimental values for the InSnO<sub>2</sub> electrode potentials were obtained by setting  $k_2/k_1 = 5$  for the two cell solutions in 50% (v/v) acetonitrile/water and  $k_2/k_1 = 50$  for the cell solution using water as solvent. Correlation of the potential of the SnO<sub>2</sub> electrode with curves calculated in this manner is less satisfactory. Reasonable agreement is obtained for the solutions with  $1 \times 10^{-4}$  M total thionine (Figures 2 and 3) using  $k_2/k_1 = 15$  for the solution with 50% (v/v) acetonitrile/water as solvent (Figure 3) and  $k_2/k_1 = 2500$  for the solution with water as solvent (Figure 2). The calculated greater selectivity of SnO<sub>2</sub> with water as the solvent agrees with cyclic voltammetric data<sup>26</sup> which show that SnO<sub>2</sub> is more reversible to the TH<sup>+</sup>/L couple in water than in 50% (v/v) aqueous acetonitrile while the reverse is true for the Fe(III)/Fe(II) couple. For the cell with  $1 \times 10^{-3}$  M total dye (Figure 4) the calculated line



**Figure 4.** Electrode potentials measured for SnO<sub>2</sub> (○) and InSnO<sub>2</sub> (●) electrodes of an illuminated TI-TL cell containing a solution with dark composition  $1 \times 10^{-3}$  M TH<sup>+</sup>, 0.017 M FeSO<sub>4</sub>,  $7.6 \times 10^{-5}$  M Fe<sup>3+</sup>, and 0.01 M H<sub>2</sub>SO<sub>4</sub> in 50% (v/v) acetonitrile/water. Calculated curves (see text) are shown for the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple, the TH<sup>+</sup>/L/S system, and mixed potentials with  $k_2/k_1 = 5$  (···) and  $k_2/k_1 = 200$  (-·-·-).

for  $k_2/k_1 = 200$  is shown, but the measured SnO<sub>2</sub> electrode potential at <40% photobleaching is considerably more positive than the calculated potential.

Adsorption of thionine and leucothionine on the electrode surfaces probably plays a part in diminishing the reactivity of the iron couple and/or increasing the reactivity of the dye couple at both electrodes.<sup>3,26</sup> In addition, at the SnO<sub>2</sub> electrode surface the rate constants for electron transfer between species in solution and the electrode are expected to be related to the extent of overlap of the energy levels of the solute species with available energy levels in the semiconductor.<sup>26</sup>

In any case, the data in Figures 2-4 show that (1) both electrodes are more reactive to the thionine system than to the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple, (2) the difference in relative reactivity is greater at the SnO<sub>2</sub> electrode than at the InSnO<sub>2</sub> electrode, and (3) the difference in relative reactivity is diminished at both electrodes when the solvent is changed from water to 50% (v/v) acetonitrile/water.

## Discussion

We have previously shown<sup>19</sup> that the short-circuit current in TI-TL iron-thionine photogalvanic cells is directly proportional to the extent of photobleaching at photostationary state. Since most of the reduced thionine is present as L, the short-circuit current is directly proportional to [L]. However, Figure 1 shows that [S] increases approximately linearly with increasing photobleaching when the solution is more than about 10% photobleached. Furthermore, the energy diagram for the SnO<sub>2</sub> semiconductor anode<sup>26</sup> suggests that S should be a more efficient electron donor than L at SnO<sub>2</sub>. However, observed quantum efficiencies for conversion of absorbed light into current rule out the possibility of S as the only anodically active form of reduced thionine as has been postulated.<sup>6,7,21</sup> Less than 0.3% of the reduced thionine in the photobleached solution is present as S. Therefore, if S were the only form of reduced thionine which acted as an electron donor, the quantum efficiency of conversion of absorbed light to current would be less than 0.003. In some cells it is at least 0.1. Cyclic voltammetric evidence and interfacial energies<sup>26</sup> indicate that if conditions could be found to allow S to be present in high concentration at the photostationary state, it might well be a more efficient charge carrier than L. Under all conditions which we have investigated to date, however, S is present in such low concentrations that L is almost certainly the principal electrode-active form of reduced thionine.

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## Does a Methyl Substituent Stabilize or Destabilize Anions?

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**Abstract.** Ab initio molecular orbital calculations show that whereas methanol is a stronger acid than water, propyne is a weaker acid than acetylene, and acetic acid is a weaker acid than formic acid, in agreement with gas-phase experimental data. A rationalization for this capability of a methyl substituent to sometimes stabilize and sometimes destabilize anions relative to their parent acids is provided within the framework of perturbation molecular orbital theory.

### Introduction

Although the methyl-substituent effect is of fundamental importance in the understanding of organic reactions in general and substituent effects in particular, the subject remains poorly understood even today. Traditionally, a methyl group has been thought to be solely electron releasing, resulting in the stabilization of cations and the destabilization of anions.<sup>2</sup> This supposition was based in part on the increasing stabilities of successively methyl-substituted carbocations and the decreased acidities in solution of acetic acid compared with that of formic acid and methanol compared with that of water.

More recently, both experimental and theoretical studies have shown that the experimentally observed lower acidity of methanol compared to that of water is a solvent effect: in the gas phase the reverse order is found, i.e., methanol is *more* acidic than water.<sup>3</sup> This observation has been attributed to the ability of alkyl groups to both donate and accept electrons as the charge site demands, resulting in the stabilization of both positive and negative charge through a polarization-type process.<sup>3</sup>

However, there are glaring exceptions to this generalization. Notably, acetic acid has recently been found to be less acidic than formic acid<sup>4</sup> and propyne, a weaker acid than acetylene,<sup>5</sup> even in the gas phase. Clearly, in these two instances the methyl substituent appears to have a destabilizing effect on the corresponding anions highlighting the inadequacy of the present picture of the methyl-substituent effect. Surprisingly, these exceptions have gone relatively unnoticed and have not yet been satisfactorily explained.

In this paper, we utilize ab initio molecular orbital theory to provide a quantitative confirmation of these results and then present a qualitative rationalization within the framework of perturbation molecular orbital (PMO) theory. Our model enables a more general prediction of the effect of a methyl substituent on the stability of anions.

### Method and Results

Standard ab initio molecular orbital calculations were carried out using a modified version of the Gaussian 70 system of programs<sup>6</sup> and the 4-31G basis set.<sup>7</sup> Subject to certain symmetry constraints, all structures were fully optimized at the 4-31G level using a gradient optimization procedure.<sup>8</sup> Theoretical geometries are compared with corresponding experimental parameters<sup>9,10</sup> in Table I while calculated total energies, including relevant previously reported values,<sup>11–15</sup> are shown in Table II. Theoretical and experimental heats of proton-transfer reactions are compared in Table III.

### Discussion

Although the calculated structures are not of primary concern in this paper, we note several points. First, the 4-31G C≡C and C—C bond lengths for propyne are in substantially better agreement with experimental values (cf. Table I) than are previously reported<sup>16</sup> STO-3G lengths (1.170 and 1.484 Å, respectively). In a similar manner, the 4-31G values of the C—O and C=O lengths in formic acid show considerable improvement over the STO-3G results<sup>17</sup> (1.385 and 1.214 Å, respectively). For acetic acid, no complete experimental