

PHOTOGALVANIC CELLS VII: THE KINETICS OF PHOTBLEACHING

W. JOHN ALBERY, PATRICK R. BENSON and ANDREW W. FOULDS

Department of Chemistry, Imperial College, London, SW7 2AY (Gt. Britain)

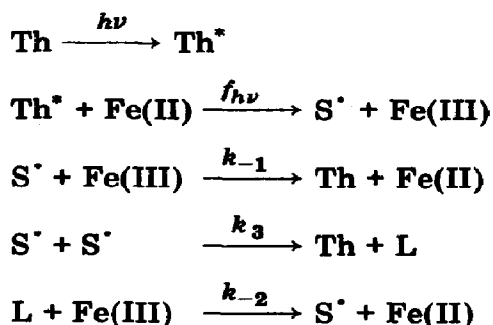
(Received September 17, 1979)

Summary

The efficiency of a photo-redox system for a photogalvanic cell can be tested by measuring the kinetics of the bleaching process. A wave separating the bleached and unbleached system is observed to pass through a 10 cm cell. A theory is developed to describe how the velocity of this wave depends upon the kinetics of both the bleaching reaction and the back reaction. For the iron-thionine system theory and experiment are shown to be in good agreement in 1 cm and 10 cm cells.

1. Introduction

In this work we describe theory and experiments for the kinetics of the processes leading to the photostationary state when the irradiance is sufficiently large for the photogalvanic solution to become bleached. The particular system we studied is the iron-thionine system [1 - 4]:



where Th, S[·] and L are given in Fig. 1. The notation for the rate constants has been given previously [5, 6]. With sufficiently intense irradiance the thionine can be almost completely converted to leucothionine and the solution becomes bleached. This photostationary state is unusual in that the concentration of leucothionine is then nearly equal to the concentration of thionine in the dark; the much smaller concentration of thionine has to be

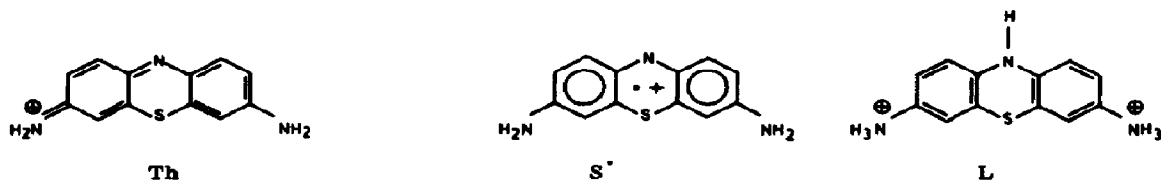
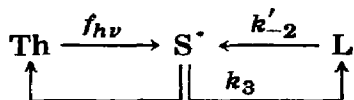


Fig. 1. The forms of thionine in the iron-thionine system.

sufficient to absorb the photons necessary to maintain the photostationary state. Another unusual feature of the transient behaviour on the way to the photostationary state is that the bleaching starts at the front of the cell and travels through the cell as a wave. Our theoretical treatment describes the concentrations with respect to both time and distance.

2. Theory

Under conditions of high irradiance (and low [Fe(III)]) the iron-thionine system reacts by the A2 B2 C1 mechanism [4 - 6]. This mechanism can be conveniently written as



where $k'_{-2} = k_{-2}[\text{Fe(III)}]$.

We write

$$a = [\text{Th}]/[\text{Th}]_D$$

$$b = [\text{S}^{\bullet+}]/[\text{Th}]_D$$

$$c = [\text{L}]/[\text{Th}]_D$$

where $[\text{Th}]_D$ is the concentration of thionine in the dark. Then for monochromatic light of irradiance I

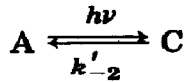
$$f_{h\nu} = \varphi_1 I \epsilon [\text{Th}]_D a \quad (1)$$

$$\frac{\partial c}{\partial t} = -\frac{\partial a}{\partial t} = \frac{1}{2} \varphi_1 I \epsilon a - \frac{1}{2} k'_{-2} c \quad (2)$$

and

$$a + c = 1 \quad (3)$$

Here b is assumed to be negligible compared with a or c , the factors of $\frac{1}{2}$ arise from the dismutation reaction and φ_1 is the quantum efficiency for the formation of $\text{S}^{\bullet+}$. It should be noted that eqn. (2) would also apply (without the factors of $\frac{1}{2}$) for the following simpler system:



The variation of I with distance x through the cell is given by

$$\frac{\partial I}{\partial x} = -I\epsilon[\text{Th}]_D a \quad (4)$$

By introducing the dimensionless variables

$$\chi = x\epsilon[\text{Th}]_D = x/X_e \quad (5)$$

$$\tau = t\frac{1}{2}\phi_1 I_0 \epsilon \quad (6)$$

$$\kappa = k'_{-2}/\phi_1 I_0 \epsilon \quad (7)$$

$$\theta = I/I_0 \quad (8)$$

we obtain

$$\frac{\partial a}{\partial \tau} = -\theta a + \kappa(1 - a) \quad (9)$$

and

$$\frac{\partial \theta}{\partial \chi} = -\theta a \quad (10)$$

with the boundary conditions that

$$\text{at } \tau = 0 \quad a = 1 \quad (11)$$

and

$$\text{at } \chi = 0 \quad \theta = 1 \quad (12)$$

If we assume that κ is so small that the term in κ can be ignored in eqn. (9), then the solution of eqns. (9) and (10) with the boundary conditions is given by

$$a = \{1 + \exp(\tau - \chi) - \exp(-\chi)\}^{-1} \quad (13)$$

and

$$\theta = \{1 + \exp(\chi - \tau) - \exp(-\tau)\}^{-1} \quad (14)$$

where

$$\frac{\partial a}{\partial \tau} = \frac{-\exp(\tau - \chi)}{\{1 + \exp(\tau - \chi) - \exp(-\chi)\}^2} = -\theta a$$

$$\frac{\partial \theta}{\partial \chi} = \frac{-\exp(\chi - \tau)}{\{1 + \exp(\chi - \tau) - \exp(-\tau)\}^2} = -\theta a$$

For a cell of length l , where

$$\chi_l = l\epsilon[\text{Th}]_D \gg 1$$

the terms $\exp(-\chi)$ and $\exp(-\tau)$ in eqns. (13) and (14) are negligible for most of the cell. Hence we find

$$a \approx \{1 + \exp(\tau - \chi)\}^{-1} \quad (15)$$

and

$$\theta \approx \{1 + \exp(\chi - \tau)\}^{-1} \quad (16)$$

These equations describe the progress of the bleaching wave through the cell. In particular

$$a = \theta = \frac{1}{2}$$

when

$$\tau = \chi$$

and the velocity of the wave is given from eqns. (5) and (6) by

$$v_0 = x/t = \frac{1}{2} \varphi_1 I_0 / [\text{Th}]_D \quad (17)$$

The velocity is determined from the number of photons per unit area per unit time I_0 which with a quantum efficiency of $\frac{1}{2}\varphi_1$ are required to bleach all the thionine $[\text{Th}]_D$. The variations of concentration and irradiance with time and distance described by eqns. (15) and (16) are shown in Fig. 2.

In the treatment so far we have ignored any back reaction described by κ . For the solution to become bleached, $\kappa \ll 1$. Low values of κ do not affect the bleaching process at the wave front. However, the back reaction in the bleached part of the solution behind the wave front has to be balanced in the steady state by the forward reaction which therefore consumes photons.

From eqn. (9), $\partial a / \partial \tau = 0$ after the wave front has passed and

$$a = (1 + \theta / \kappa)^{-1} \quad (18)$$

Substitution into eqn. (10) and integration gives

$$\kappa \ln \theta + \theta = 1 - \kappa \chi$$

Expansion of the logarithmic term shows that, for small values of κ

$$\theta \approx 1 - \kappa \chi \quad (19)$$

Hence there is a linear decrease of the irradiance with distance in the bleached part of the cell. This decrease in irradiance means that the velocity of the wave slows down as it travels through the cell. In describing the wave front we replace τ as defined by eqn. (6) with

$$\begin{aligned} \tau_{\chi_*} &= (t - t_{1/2}) \frac{1}{2} \varphi_1 I_0 \epsilon \theta \\ &= (t - t_{1/2}) \frac{1}{2} \varphi_1 I_0 \epsilon (1 - \kappa \chi_*) \end{aligned} \quad (20)$$

where $t_{1/2}$ is the time at which the solution at χ_* becomes half bleached. Then, for χ close to χ_* and t close to $t_{1/2}$, we can follow the previous argument and hence obtain for the irradiance

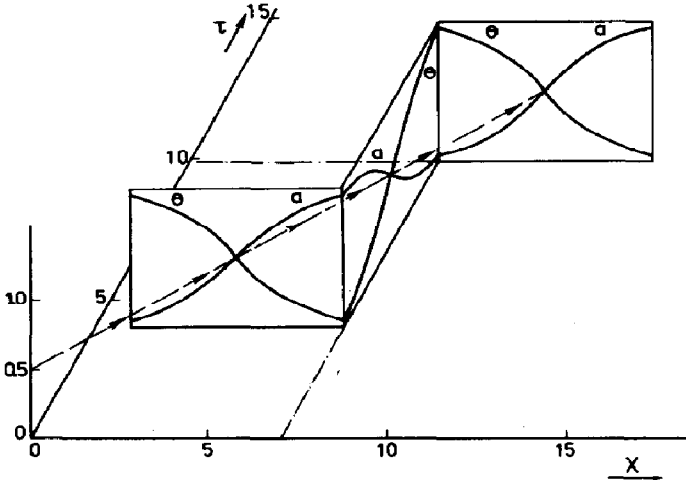


Fig. 2. A plot of eqns. (15) and (16) describing the bleaching wave moving through the cell. The curves labelled θ refer to the irradiance and the curves labelled α refer to the thionine concentration. The two slices across the diagram show "photographs" of the irradiance and thionine concentration at particular times. The slice into the diagram shows the transient behaviour at a particular point down the cell. The broken line through the midpoints shows the velocity of the wave as it moves through the cell.

$$\theta \approx \frac{(1 - \kappa \chi_*)}{1 + \exp(\chi - \chi_* - \tau \chi_*)} \quad (21)$$

This equation does not hold at the front of the cell for $\chi < 5$ since we have ignored the terms $\exp(-\chi)$ and $\exp(-\tau)$. For the velocity we find

$$v_{\chi_*} = v_0(1 - \kappa \chi) \quad (22)$$

where v_0 is given by eqn. (17).

The velocity is measured by observing the time $t_{1/2}$ taken for the solution at the end of the cell of thickness l to become half bleached. Then from eqn. (22)

$$\begin{aligned} t_{1/2} &= \int_0^l \frac{dx}{v_x} = - \frac{\ln(1 - Bl)}{v_0 B} \\ &= - \frac{l \ln \theta_l}{v_0(1 - \theta_l)} \end{aligned} \quad (23)$$

where

$$\begin{aligned} B &= \kappa \epsilon [\text{Th}]_D \\ &= k'_{-2} [\text{Th}]_D / \phi_1 I_0 \end{aligned} \quad (24)$$

and from eqn. (21) the irradiance in the steady state of the light passing through the cell is

$$\theta_l = 1 - Bl \quad (25)$$

From eqns. (16) and (20) the shape of the transient as the wave front reaches the end of the cell may be written as

$$\begin{aligned} \ln(\theta_l/\theta - 1) &= -\tau\chi_* = l \\ &= -\frac{1}{2}\varphi_1 I_0 \epsilon \theta_l (t - t_{1/2}) \end{aligned} \quad (26)$$

We studied this system in a 1 cm cell and in a 10 cm cell. In the 10 cm cell χ was approximately 55 at the end of the cell and, on opening the camera shutter, a well-developed wave was seen to pass down the cell. For this experiment we could therefore measure the time $t_{1/2}$ for the wave to reach the end of the cell and the transmittance θ_l of the solution in the cell, and we were able to analyse the shape of the transient when it reached the end of the cell according to eqn. (26). For the 1 cm cell the distance was too short for the wave to be fully developed and θ_l was very close to unity. Hence for this cell the back reaction is negligible and we analysed the transient according to a rearranged form of eqn. (16):

$$\ln(\theta^{-1} - 1) = \ln\{\exp(\chi) - 1\} - \frac{1}{2}\varphi_1 I_0 \epsilon t \quad (27)$$

We also obtained a value for v_0 (when $\chi = \tau$) by finding the time t_* when

$$\theta = \{2 - \exp(-l\epsilon[\text{Th}]_D)\}^{-1} \quad (28)$$

and

$$v_0 = l/t_* \quad (29)$$

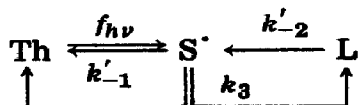
From these experiments we obtain information about the rate of photo-generation of leucothionine from $\varphi_1 I_0 \epsilon$, from analysis of the transient or from v_0 . The measurement of B using the 10 cm cell gives information about the ratio of the generation rate to the rate of the back reaction; because the solution is bleached a 10 cm cell is needed to measure the small fraction of unbleached thionine. The rate of the back reaction can be very simply obtained by combining B and v_0 :

$$k'_{-2} = 2Bv_0 \quad (30)$$

This quantity can be measured directly from $t_{1/2}$ measurements on the 10 cm cell (eqn. (23)) together with θ_l from eqn. (25).

The iron-thionine system will react by three different mechanisms depending on the irradiance of the light and the concentrations of Fe(II) and Fe(III) [5, 6]. So far we have assumed that with high irradiance (and low [Fe(III)]) the mechanism is A2 B2 C1. In practice it is difficult to make this mechanism completely dominant in the steady state. There is some significant back reaction of S^\cdot with Fe(III) with rate constant k_{-1} — the A1 B2 C1 mechanism. However, whilst this route contributes significantly in the steady state, it is insignificant in the transient behaviour at the wave front. This is because at the wave front the high flux of photons acting on the unbleached concentration of thionine produces sufficient semi-thionine for the dismutation reaction of S^\cdot to be completely dominant (A2 B2 C1). Thus it is possible

for a system at a particular value of χ to start with mechanism A1 B2 C1, to change to A2 B2 C1 as the wave front passes and then to return to A1 B2 C1 in the bleached steady state, where the photogenerating flux has been reduced because of the bleaching. In our case the analysis assuming the A2 B2 C1 mechanism is correct for the transient behaviour. However, we have to modify the treatment for the steady state in the bleached solution. The reaction scheme becomes



where $k'_{-1} = k_{-1} [\text{Fe(III)}]$. Because the solution is bleached $[\text{L}] \approx [\text{Th}]_{\text{D}}$. Hence in the steady state

$$k_3[\text{S}^{\bullet}]^2 = k'_{-2}[\text{Th}]_{\text{D}} \quad (31)$$

We define a quantum efficiency φ_2 for the fraction of S^{\bullet} that form L compared with those that form Th [7]:

$$\begin{aligned} \varphi_2 &= \frac{k_3[\text{S}^{\bullet}]^2}{2k_3[\text{S}^{\bullet}]^2 + k'_{-1}[\text{S}^{\bullet}]} \\ &= \{2 + k'_{-1}/(k_3k'_{-2}[\text{Th}]_{\text{D}})^{1/2}\}^{-1} \end{aligned} \quad (32)$$

Then for the steady state we must redefine κ in eqn. (7) to give

$$\kappa = \frac{k'_{-2}(1 - \varphi_2)}{\varphi_1\varphi_2 I_0\epsilon} \quad (33)$$

where $(1 - \varphi_2)$ and φ_2 describe the partitioning of S^{\bullet} for the back reaction and the forward reaction respectively. Substitution of eqn. (32) into eqn. (33) gives

$$\kappa = \frac{k'_{-2} + k'_{-1}(k'_{-2}/k_3[\text{Th}]_{\text{D}})^{1/2}}{\varphi_1 I_0\epsilon} \quad (34)$$

In this expression the k'_{-2} term derived earlier is associated with the A2 B2 C1 mechanism and the extra k'_{-1} term is associated with the A1 B2 C1 mechanism. It is interesting that the analysis of the bleached photostationary state is much simplified by the fact that the flux through transition state 2 is independent of the light intensity; this then fixes the concentration of the semi-thionine intermediate (see eqn. (31)) and hence φ_2 .

Finally in order to bleach the solution we have to irradiate the system with polychromatic light. A detailed analysis comparing the equations for polychromatic radiation with those for monochromatic light shows that the corrections are of the order of 10%. Hence we write

$$\bar{\epsilon} = \epsilon_{\text{max}}/1.10 \quad (35)$$

where $\bar{\epsilon}$ is the effective extinction coefficient and ϵ_{max} is the extinction coefficient at the maximum absorbance. Similarly we replace I_0 by

$$\bar{I}_0 = \bar{\epsilon}^{-1} \int_0^{\infty} I' \epsilon d\lambda \quad (36)$$

where I' is the irradiance per unit wavelength.

3. Experimental

The apparatus has been described previously [6]. Moderately parallel light from a 250 W quartz-halogen projector lamp was passed through either a 1 cm or a 10 cm cell, then through a monochromator and finally to a photodiode. The monochromator was set at 600 nm, which is λ_{\max} for the thionine absorption band. The irradiance of the light was varied using a set of neutral density filters. The transients were measured using an Edwardian Camera shutter with a time constant of 2 ms and were recorded on either a Gould OS 4000 digital storage oscilloscope or directly on to a Bryans 29000 A4 XYt recorder. The preparation of chemicals and solutions has been described previously [6]. The 1 cm cell was thermostatted at 25 °C; experiments in the 10 cm cell had to be carried out at room temperature, 23 ± 2 °C.

4. Results and discussion

We carried out two sets of experiments as given in Table 1. The irradiance was decreased by up to a factor of 4 for the 1 cm cell and by up to a factor of 2 for the 10 cm cell through the use of four and five neutral density filters respectively. Photodiode readings were taken with distilled water in the cell and throughout θ is the photodiode reading divided by the value with distilled water.

Typical photodiode transients are shown in Fig. 3. The long "induction" period in the 10 cm cell while the wave is travelling through the cell should be noted. The movement of the wave front along the cell can also be observed directly. The transients were analysed using eqns. (27) and (26), and the results are shown in Figs. 4 and 5 respectively. Good straight lines are found. For the 10 cm cell results for θ_1 as a function of the transmittance Φ of the neutral density filter are given in Table 2. For the 1 cm cell $\theta_1 = 1$ throughout. The gradients of plots such as those in Figs. 4 and 5 are plotted against Φ in Fig. 6. As required by eqn. (26) the gradients for the 10 cm cell experi-

TABLE 1
Experimental conditions

Cell length l (cm)	$[Th]_D$ (μM)	$[Fe(II)]$ (mM)	$[Fe(III)]_D$ (μM)	$[H_2SO_4]$ (mM)
1	10	50	91	50
10	42.5	50	100	50

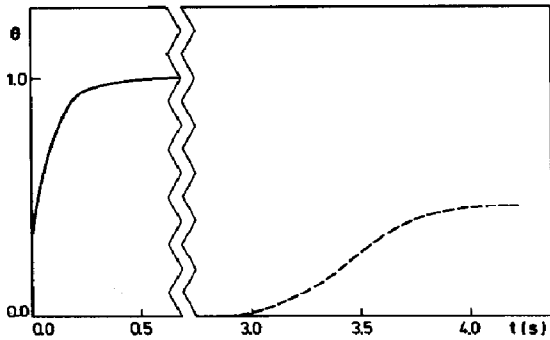


Fig. 3. Typical photodiode transients: —, 1 cm cell; ---, 10 cm cell. The discontinuity in the time scale should be noted.

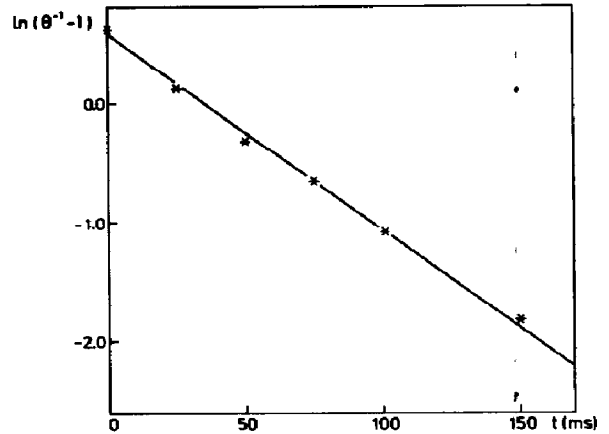


Fig. 4. An analysis of a typical transient in the 1 cm cell according to eqn. (27).

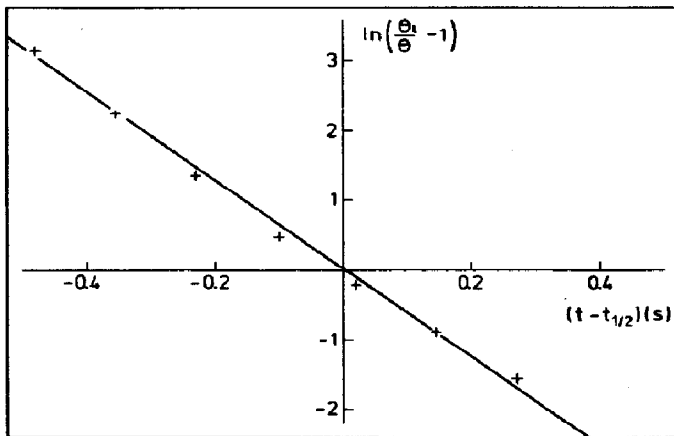


Fig. 5. An analysis of a typical transient in the 10 cm cell according to eqn. (26). It should be noted that, as required by eqn. (26), the straight line passes through the origin.

TABLE 2

Φ	θ_1
1	0.484
0.71	0.409
0.60	0.373
0.47	0.268

ments have been divided by the values of θ_1 in Table 2. A good straight line is found for the 1 cm cell experiments; the results from the 10 cm cell experiments are in reasonable agreement but there is more scatter. From the gradient for the 1 cm cell experiments we obtain

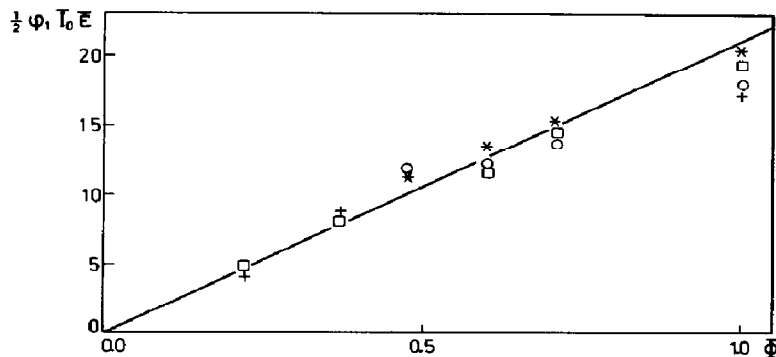


Fig. 6. A plot of $\frac{1}{2}\varphi_1\bar{I}_0\bar{\epsilon}$ against the transmittance Φ of the filter for four different types of analysis: +, 1 cm transient analysis, eqn. (27), Fig. 4; o, 10 cm transient analysis, eqn. (26), Fig. 5; □, values of $\frac{1}{2}\varphi_1\bar{I}_0\bar{\epsilon}$ calculated from ν_0 for the 1 cm cell using eqns. (29) and (17); *, similar values calculated from eqns. (41) and (17) for the 10 cm cell.

$$\frac{1}{2}\varphi_1(\bar{I}_0)_{\Phi=1}\bar{\epsilon} = 21 \text{ s}^{-1} \quad (37)$$

This may be compared with a value calculated by convoluting the lamp output with the thionine absorption spectrum and using $\varphi_1 = 0.56$ [7, 8] to give

$$\frac{1}{2}\varphi_1(\bar{I}_0)_{\Phi=1}\bar{\epsilon} = 16 \text{ s}^{-1} \quad (38)$$

Reasonable agreement is found. These results from the 1 cm cell transients are an interesting way of measuring the effective forward reaction for a photogalvanic system driven by polychromatic light.

Figure 6 also shows the values of ν_0 for the 1 cm cell calculated from eqn. (29). The values have been multiplied by $\bar{\epsilon}[\text{Th}]_D$ since from eqn. (17) $\frac{1}{2}\varphi_1 I_0 \epsilon = \nu_0 \epsilon [\text{Th}]_D$. As required by eqn. (17) the values of ν_0 vary linearly with Φ , and it is satisfactory that these points lie on the same line.

Next we consider the values of B which can be obtained from the analysis of θ_t for the 10 cm cell experiments using eqn. (25). In these experiments the long path length allows us to measure the small amount of thionine present in the bleached solution. Unfortunately we have to make a correction for other species which also absorb significantly when the thionine solution is bleached. This absorption is small and the Beer-Lambert law may be expanded to give a term that is linear with distance. Hence from eqns. (24) and (25) we obtain

$$1 - \theta_t = \Sigma \epsilon c l + B_{\Phi=1} / \Phi \quad (39)$$

where $\Sigma \epsilon c l$ describes the absorption due to the other species and B/Φ describes the absorbance caused by the photostationary concentration of thionine; this is inversely proportional to the irradiance described by Φ . Two plots of eqn. (39) are shown in Fig. 7. One plot is for the conditions given in Table 1 and the other is for the same conditions except that there was no added Fe(III) ($[\text{Fe(III)}]_D = 0$). The concentration of Fe(III) in the bleached photostationary state is given by

$$[\text{Fe(III)}]_{h\nu} = [\text{Fe(III)}]_D + 2[\text{Th}]_D \quad (40)$$

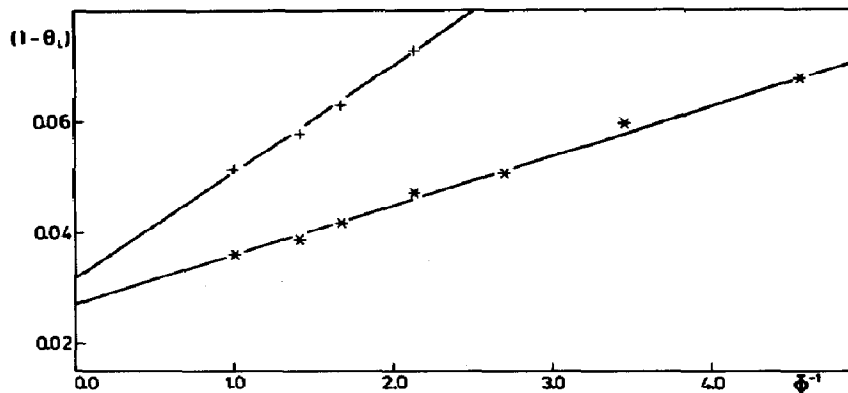


Fig. 7. Plots of eqn. (39) showing that the residual optical density in the 10 cm cell is partly caused by an impurity: +, conditions given in Table 1; *, experiments with no added Fe(III).

Both plots are good straight lines and have a common intercept caused by the other absorbing species. Because of the bleaching and the long path length these species are observed at concentrations of less than $1 \mu\text{M}$. From the gradients we obtain the values of $B_{\Phi=1}$ given in Table 3, together with values calculated from eqns. (24) and (34) using the values of the rate constants which we have previously measured [7]. Again reasonable agreement is found.

We now turn to the measurement of ν_0 in the 10 cm cell from the time $t_{1/2}$ taken for the wave to reach the end of the cell. Allowing for the residual absorption we obtain a modified form of eqn. (23):

$$\nu_0 = \frac{l}{t_{1/2}} \left(\frac{1 - \theta_I}{\theta_I - \theta_l} \right) \left(\frac{\ln \theta_I}{\ln \theta_l} - 1 \right) \quad (41)$$

where $\theta_l = \exp(-\Sigma \epsilon c l) \approx 0.70$.

The values of $\nu_0 \epsilon [\text{Th}]_D$ are plotted in Fig. 6 as a function of the irradiance. Reasonable agreement is found with the values obtained from the 1 cm cell and from the transient analysis for the 10 cm cell. Hence the passage of the wave down the 10 cm cell is well described by the theory.

TABLE 3

Values of $B_{\Phi=1}$

$[\text{Fe(III)}]_{h\nu}^a$ (μM)	$B_{\Phi=1}^b$	$B_{\Phi=1}^c$
85	9×10^{-3}	8×10^{-3}
185	1.9×10^{-2}	1.8×10^{-2}

^a Calculated from eqn. (40).

^b From gradients in Fig. 7.

^c Calculated from eqns. (24) and (34).

In this work we have therefore described how measurements of the bleached photostationary state in the 10 cm cell together with transient measurements in either cell allow the rate of photogeneration (eqn. (37)) and the rate constant for the back reaction (eqn. (30)) to be calculated. While there are other techniques for measuring the back reaction, such as stopped flow, flash photolysis, flash electrolysis [7, 9] or the transparent rotating disc electrode [7], it is particularly useful to have a technique that measures the photogeneration rate for polychromatic light directly since the convolution of lamp intensity with the absorption band of the dye is tedious and somewhat inaccurate.

Acknowledgment

We thank the Science Research Council for support for this work and we regret that Shell employed P.R.B. This is a contribution from the Oxford Imperial Energy Group.

References

- 1 E. Rabinowitch, *J. Chem. Phys.*, **8** (1940) 551.
- 2 C. G. Hatchard and C. A. Parker, *Trans. Faraday Soc.*, **57** (1961) 1093.
- 3 N. N. Lichtin, in J. R. Bolton (ed.), *Solar Power and Fuels*, Academic Press, New York, 1977, p. 119 ff.
- 4 M. I. C. Ferreira and A. Harriman, *J. Chem. Soc., Faraday Trans. I*, **73** (1977) 1085.
- 5 W. J. Albery, W. R. Bowen and M. D. Archer, *J. Photochem.*, **11** (1979) 15.
- 6 W. J. Albery, W. R. Bowen, M. D. Archer and M. I. Ferreira, *J. Photochem.*, **11** (1979) 27.
- 7 W. J. Albery, P. N. Bartlett, W. R. Bowen, F. S. Fisher and A. W. Foulds, *J. Electroanal. Chem.*, accepted for publication.
- 8 W. J. Albery, W. R. Bowen, F. S. Fisher and A. D. Turner, *J. Electroanal. Chem.*, accepted for publication.
- 9 Y. Ohsawa and S. Aoyagui, *J. Electroanal. Chem.*, **90** (1978) 143.