(vi) In concentrated solutions also the decay rate is faster and non-exponential (Fig. 4).

(vii) The decay curve for phosphorescence is completely exponential even though a faster rate is observed in concentrated frozen glass.

(viii) The DF decay time is greater than the phosphorescence decay time of the same sample (for a 5×10^{-5} M solution $\tau_{DF} = 2 \cdot 6$ sec, $\tau_P = 2 \cdot 2$ sec).

E-type DF which represents a thermal activation of triplets to the lowest excited singlet state cannot be involved since the DF is observed at 80 K at which temperature thermal activation is energetically not probable.

If the triplet-triplet annihilation process was involved, DF would show a biphotonic nature with $I_{DF} \alpha I_p^2$ and $\tau_{DF} = \frac{1}{2} \tau_P$. As mentioned earlier in a series of experiments with increasing solute concentration, the phosphorescence intensity increases whereas DF shows a decrease. This observation along with $\tau_{DF} > \tau_P$ and monophotonic nature of DF rules out the triplet-triplet annihilation as well as any other mechanism which includes the participation of triplet state.

The results obtained here, however, suggest that the excited singlet state giving rise to DF is generated by the recombination of radical ions and trapped electrons originally produced by the one photon ionization of the dye, as also observed in some other acridine dyes[5,6,10]. This recombination will give rise to a simple exponential decay as observed. The initial faster decay is due to the reversal of the CT state.

The decrease in intensity and decay time of DF with increasing concentration can be explained to be due to increase in columbic attraction between the charged cation and the trapped electron, which abbreviates the storage time of the electrons in the traps. Similarly, with increasing temperature the thermal motion decreases the storage time of electrons and a faster decay is observed. The increase in I_{DF} with 365 nm excitation is obviously due to enhanced photoionization of the molecule with more energetic radiation.

The slight anomaly in the intensity distribution of DF cannot be explained in a normal way. It is possible that the molecule formed on recombination in the excited state may slightly be perturbed, compared to a relaxed molecule emitting prompt fluorescence.

May 1, 1981.

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PHOTOELECTROCHEMICAL CONVERSION OF LIGHT USING ELECTRODES COATED WITH POLYMER FILM CONTAINING THIAZINE DYE

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THIONINE condensed with poly(N-methylolacrylamide) produces a water insoluble film which can be coated on to a platinum electrode. Irradiation of the coated platinum electrode using a tungsten lamp produces an open circuit photopotential of 32 mV and short circuit current of $3 \cdot 7 \mu A$. The direction of current flow in this type of cell is reversed compared with the well-known thionine-Fe(II) photogalvanic cell which shows that the irradiated platinum electrode functions as a photocathode. The cathode reaction is suggested to be
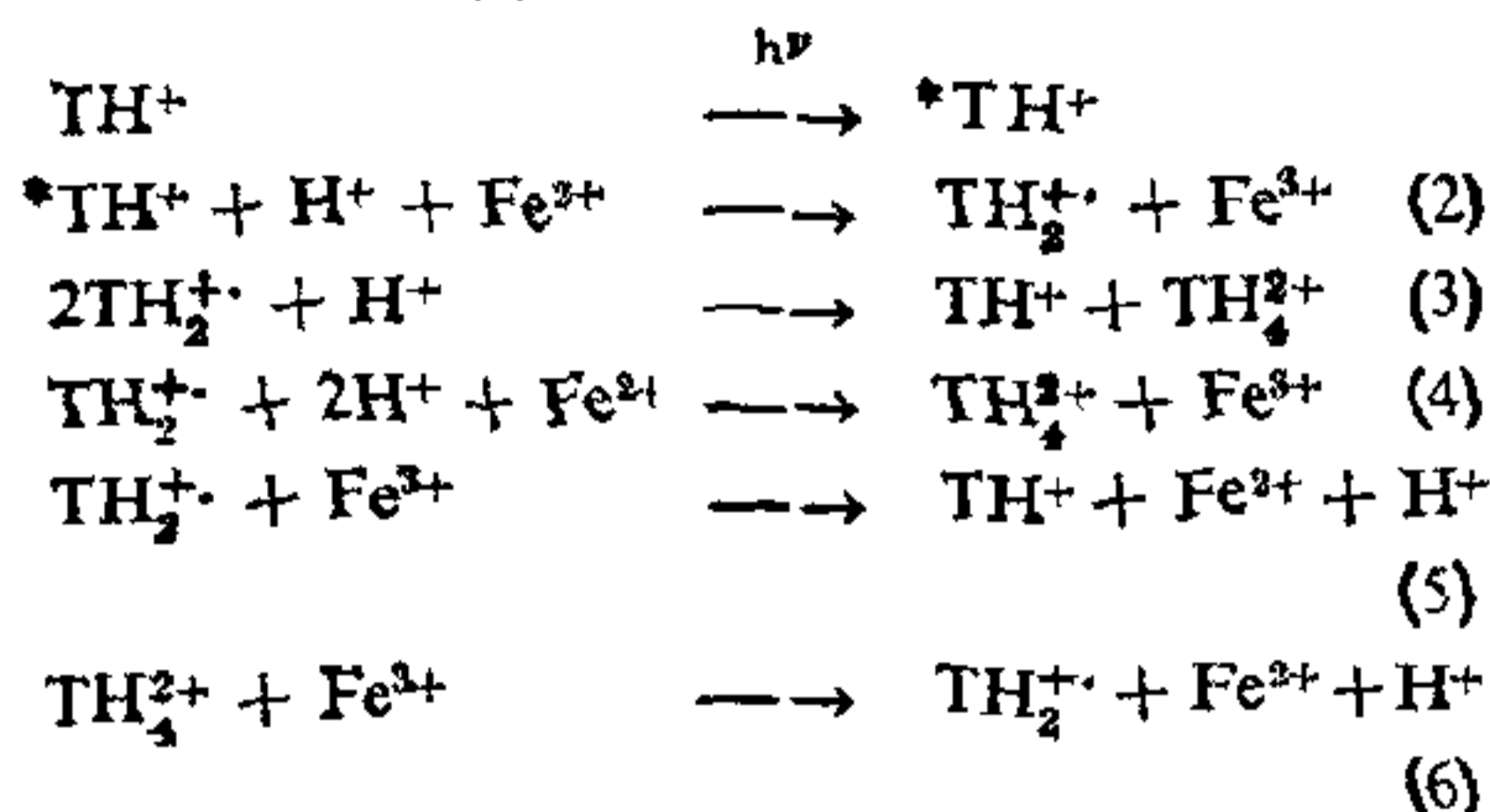
$$[\text{Semithionine} - \text{Fe}]^{++} + e \rightarrow \text{Semithionine} + \text{Fe}^{2+}$$
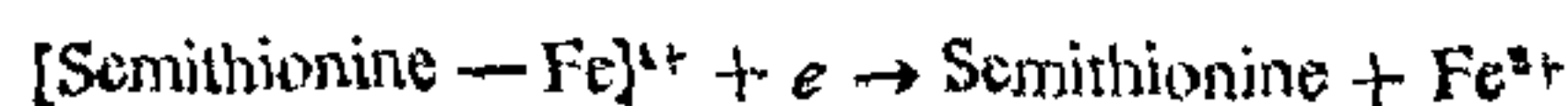
Fe^{2+} ions produced at the anode combines with semithionine to give thionine and ferrous ion back.

The power output of the cell is comparable to that of the Totally Illuminated Thin Layer cell using SnO_2 as the anode. The advantage in this cell is that light is absorbed by the film only without any thionine in the solution. The coating procedure is simple with no need for electro-deposition or vacuum coating.
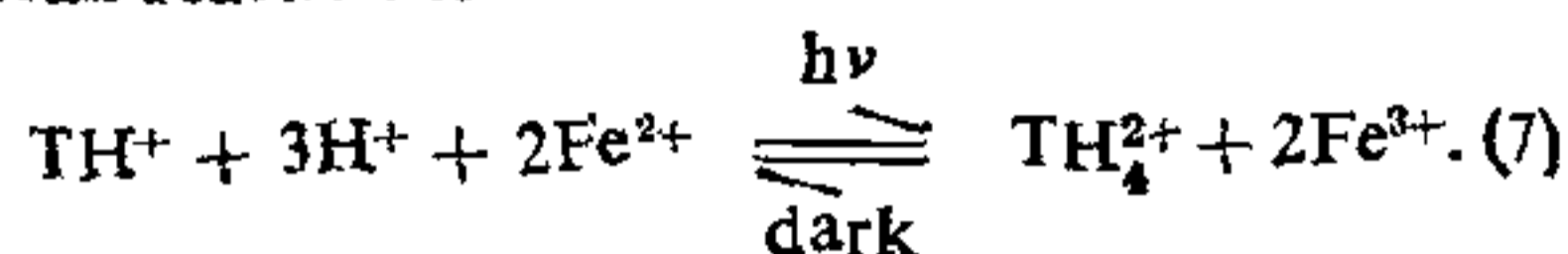
Introduction

The photoredox property of Iron(II)-Thionine (TH) system is widely studied due to its utilization in photo-

galvanic cells to convert solar energy into electrical energy[1]. The proposed sequence of reactions are shown in equations (1) to (6).

$$TH^+ \xrightarrow{h\nu} {}^*TH^+ \quad (1)$$

$${}^*TH^+ + H^+ + Fe^{2+} \longrightarrow TH_2^+ \cdot + Fe^{3+} \quad (2)$$

$$2TH_2^+ \cdot + H^+ \longrightarrow TH^+ + TH_4^{2+} \quad (3)$$

$$TH_2^+ \cdot + 2H^+ + Fe^{2+} \longrightarrow TH_4^{2+} + Fe^{3+} \quad (4)$$

$$TH_2^+ \cdot + Fe^{3+} \longrightarrow TH^+ + Fe^{2+} + H^+ \quad (5)$$

$$TH_4^{2+} + Fe^{3+} \longrightarrow TH_2^+ \cdot + Fe^{2+} + H^+ \quad (6)$$

the overall reaction is

$$TH^+ + 3H^+ + 2Fe^{2+} \underset{dark}{\overset{h\nu}{\rightleftharpoons}} TH_4^{2+} + 2Fe^{3+}. \quad (7)$$

In spite of considerable work in this system, the power conversion efficiency is very low ($\sim 0.1\%$). This is primarily due to the energy wasted in rapid back reactions occurring in the bulk of the solution. In the present work thionine is condensed with a macromolecule to increase the life-time of the reduced dye. The polymer-bound thionine is coated onto a platinum electrode so that light can be absorbed close to the electrode to allow the photo-generated product to react at the electrode more effectively.

Experimental

N-methylolacrylamide is prepared by the reaction of paraformaldehyde on acrylamide in dichloromethane following the procedure of Feur and Hart[2] and is polymerized in aqueous medium to get poly (N-methylolacrylamide). Purified thionine is condensed with poly(N-methylolacrylamide) to obtain poly (acrylamidomethylthionine) according to the procedure of Kamogawa, Kato and Sugiyama[3]. The polymer-bound thionine coated electrode is prepared by evaporating an aqueous solution of poly (acrylamidomethylthionine) on a platinum plate.

Photogenerated potential is measured using a cell consisting of an electrode of polymer-bound thionine coated platinum plate (1 cm²) and the other of clean platinum plate (1 cm²) with an electrode separation of less than 1 mm.

Results and Discussion

The polymer-bound thionine is coated onto platinum electrode and the open circuit photopotential is measured by connecting it to a clean platinum electrode in a single compartment cell containing the reductant (10^{-2} M) and sulphuric acid (10^{-2} N). The open circuit photopotentials for different reductants are shown in Table I. Using this cell the direction of electron flow is found to be opposite to that in photogalvanic cells consisting of Iron(II)-Thionine

TABLE I

[Reductant] = 1×10^{-2} M	pH = 2
Reductant	ΔE_{oc} (mv)
FeSO₄	32[a]
FeSO₄	10[b]
K₄[Fe(CN)₆]	2[a]
Hydroquinone	20[a]

a—in aqueous solution.
b—in 50% water—acetonitrile solution.

system. In contrast to the homogeneous Thionine-Fe(II) photogalvanic cells[4,5] in the present cell the polymer-bound thionine coated electrode acts as a photocathode[6].

The electrode reaction at the illuminated electrode is ascertained from applied voltage vs photocurrent curves. The photocurrent vs applied voltage wave for the coated platinum electrode is shown in Fig. 1. The curve shows that even at a positive potential of $+0.4$ V, where the tendency of the polymer-bound dye is to be in the oxidised state, the direction of photocurrent is opposite to that for Iron(II)-Thionine system. When the applied voltage is changed from negative to positive value the photocurrent passes through a maximum. As the applied voltage becomes more negative the fraction of the adsorbed dye in reduced form by electrolytic reduction increases and hence the low photocurrent. As the applied potential is changed to positive value the fraction of the adsorbed dye as leucothionine is decreased and the photocurrent increases.
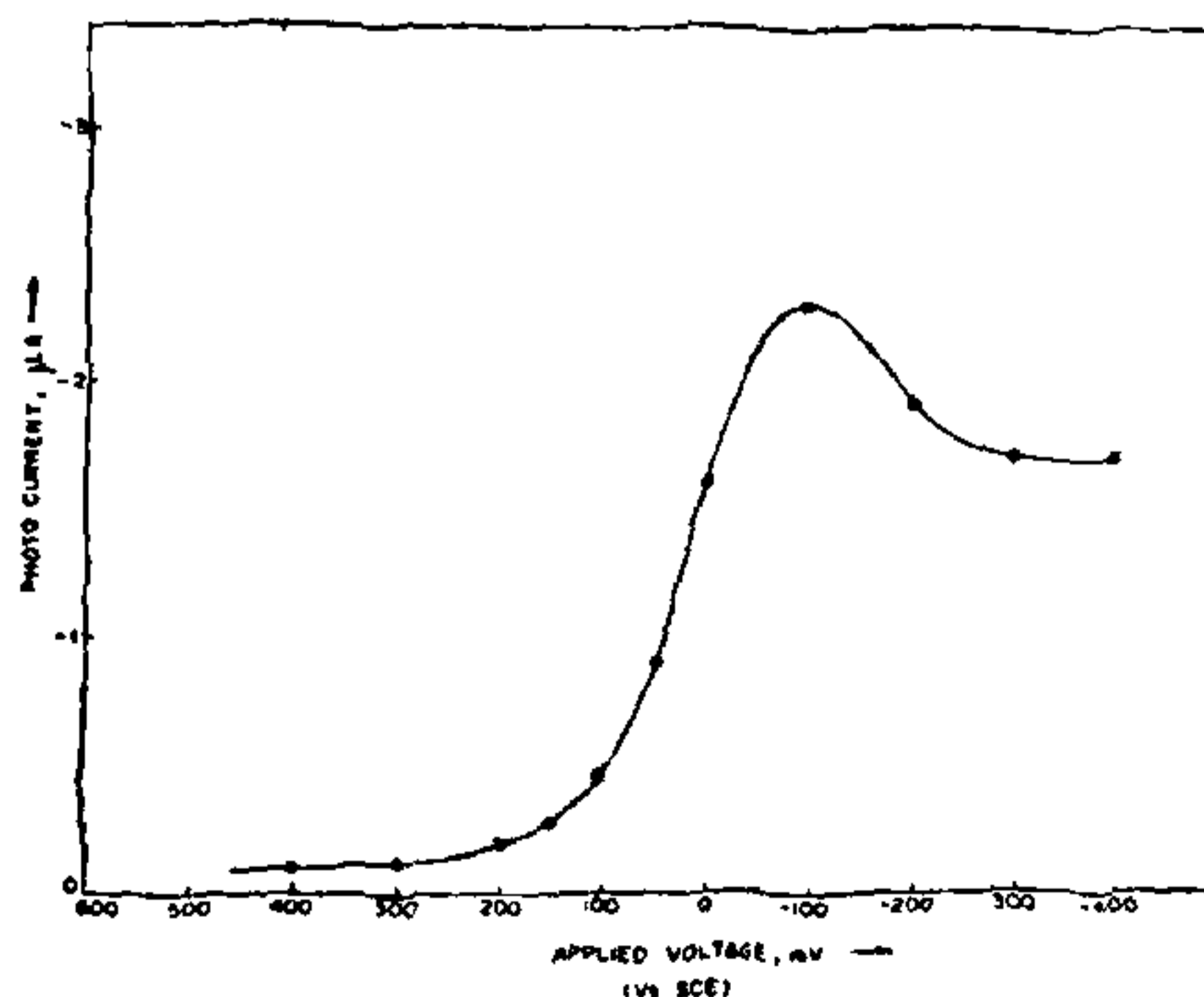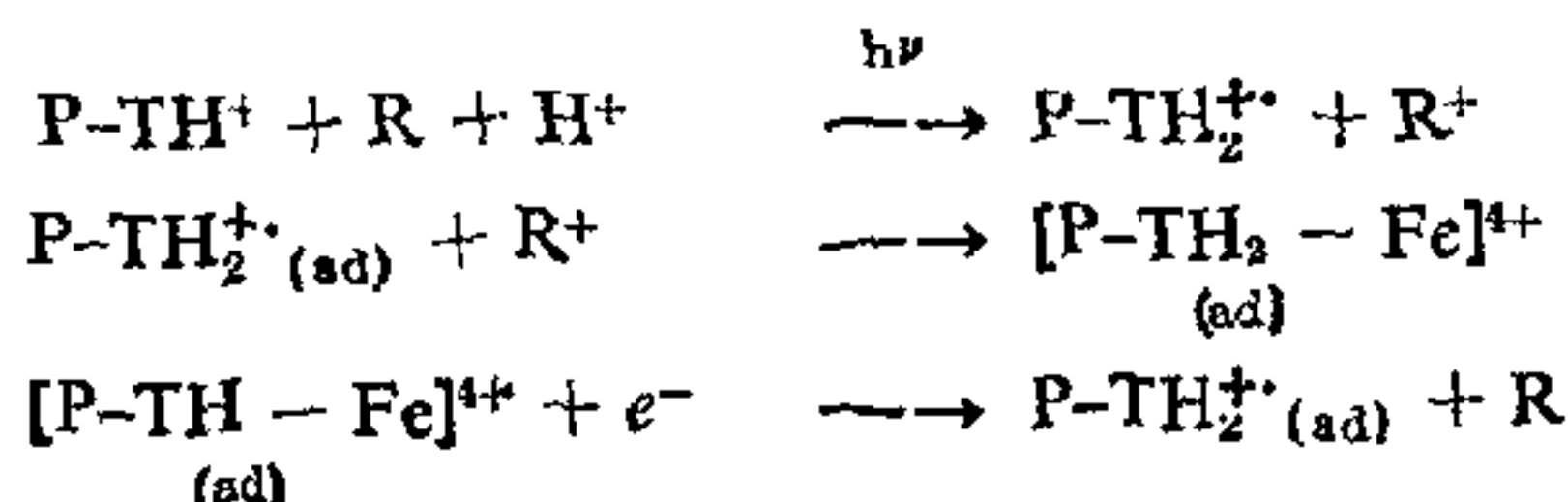

Fig. 1. Photocurrent vs applied potential curve for the polymer-dye coated electrode.

The reaction scheme at the illuminated polymer-bound thionine coated platinum electrode is proposed to be as shown below:

$$P\text{-}TH^+ + R + H^+ \xrightarrow{h\nu} P\text{-}TH_2^{+\cdot} + R^+$$

$$P\text{-}TH_2^{+\cdot}{}_{(ad)} + R^+ \longrightarrow [P\text{-}TH_2 - Fe]^{4+}_{(ad)}$$

$$[P\text{-}TH - Fe]^{4+}_{(ad)} + e^- \longrightarrow P\text{-}TH_2^{+\cdot}{}_{(ad)} + R$$

where R represents Fe(II), hydroquinone or $Fe(CN)_6^{4-}$

Polymer-bound semithionine and Fe^{3+} are produced photochemically and Fe^{3+} ion forms a complex with the polymer-bound semithionine adsorbed at the surface. This complex undergoes reduction at the platinum electrode. *The reaction at the other* electrode is proposed to be

$$R \rightarrow R^+ + e \ .$$
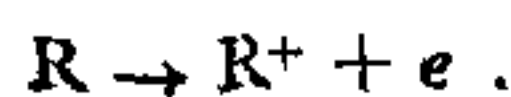
Among the various reductants used in the Totally Illuminated Thin Layer Cell with one of the platinum electrodes coated with polymer-bound thionine, ferrous sulphate gives the maximum power output which is ~ 10 times higher than the power output of polymer-bound thionine-Iron(II) system in this cell with one clean platinum electrode and another SnO_2 electrode.

January 2, 1981.

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REACTION OF N-BROMOSUCCINIMIDE ON (+)-3-CARENE

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THE reaction of N-bromosuccinimide on (+)-3-carene(I) has been reported[1] to give the *trans*-bromohydrin(II). The latter was also converted into the carane-β-epoxide (III). In this communication we report the
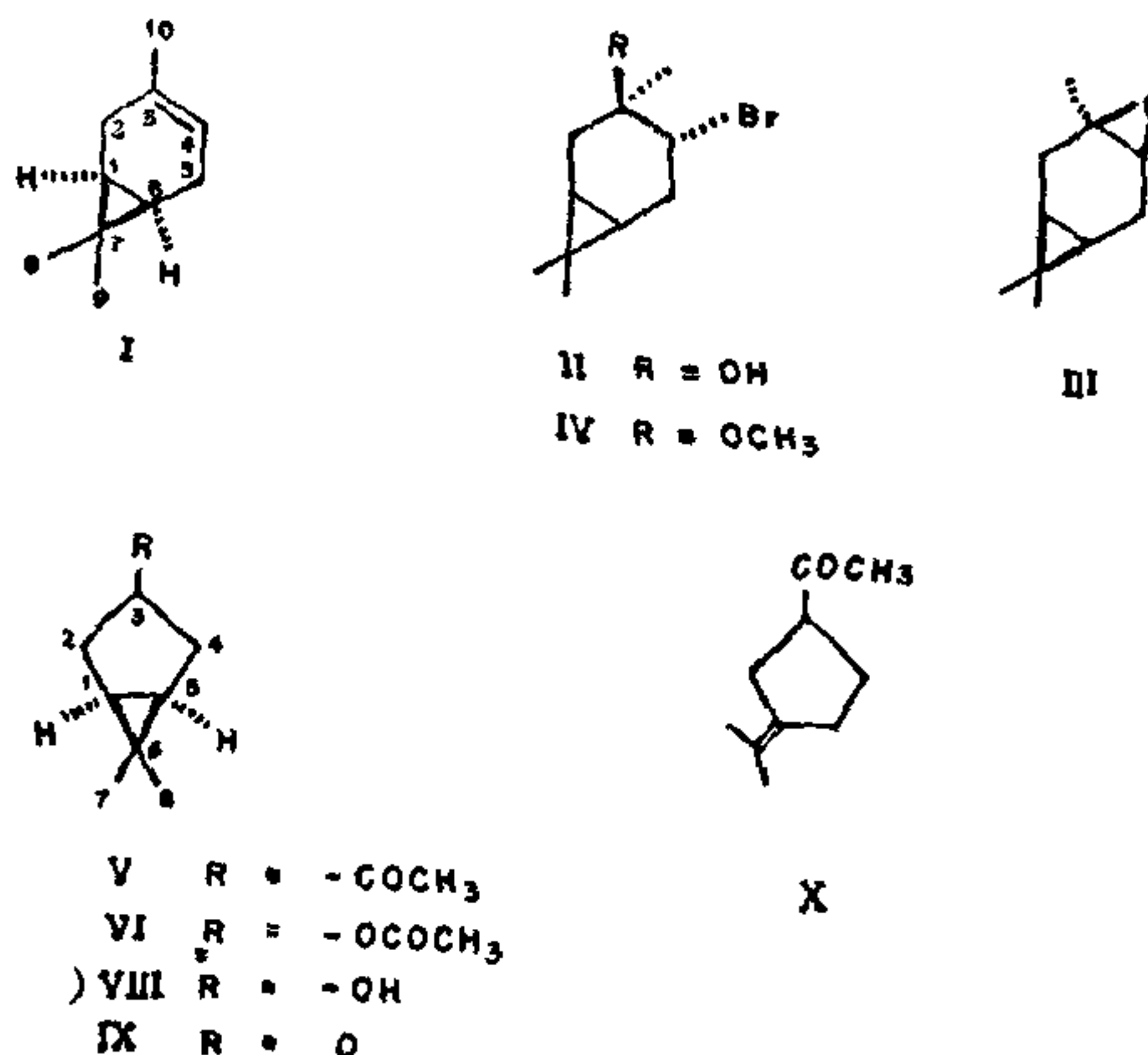
reaction of N-bromo-succinimide on (I) in different solvents and also report some interesting transformations of (II), leading to some useful intermediates.

Treatment of (I) with aqueous N-bromosuccinimide in tertiary butanol, afforded as the major product the bromohydrin (II), $C_{10}H_{17}OBr$, m.p. 60–62°; identified by spectral data; IR* bands at 3,390, 1,100 (tertiary--OH); PMR* (CCl₄) signals at: 9·3 (2H, *m*, C_1 and C_6-H), 8·98, 8·95 (3H each, *s*, C_7-methyls), 8·68 3H, *s*, C_8-CH_3), 7·6 (4H, *m*, C_2 and C_5-H) and 6·07 (1H, *t*, J = 9 Hz, C_4-H). However, when (I) is treated with aqueous *N*-bromosuccinimide in methanol, a different bromocompound, $C_{11}H_{19}OBr$ was obtained as a liquid to which structure (IV) has been assigned on the basis of spectral data; PMR (CCl₄); 9·28 (2H, *m*, C_1 and C_6-H), 9·0, 8·97 (3H each, *s*, C_7-methyls), 8·73 (3H, *s*, C_8-CH_3), 7·83 (4H, *m*, methylene protons at C_2 and C_5), 6·87 (3H, *s*, —OCH_3 at C_3) and 6·10 (1H, *t*, J = 9 Hz, C_4-H).

Treatment of the compound(II) with aq. silver nitrate in acetone solution gave a mixture of three compounds (TLC), from which the major product was isolated by fractional distillation, followed by chromatography to give the ketone (V), $C_{10}H_{14}O$, M^+ 152, b.p. 85–90°/4 mm, $(\alpha)_D^{28}$ ± 0 (*c*, 3), identified by spectral data; IR: 1,709 ($>C=O$); PMR (CCl₄): 9·05 (6H, *s*, *gem*-dimethyl), 8·77 (2H, *m*, cyclopropane protons), 8·27 (4H, *m*, methylene protons), 7·97 (3H, *s*, —$COCH_3$) and 7·43 (1H, *m*, CH, α to $>C=O$).

It gave a semicarbazone, $C_{11}H_{19}ON_3$, m.p. 162–163°.