Flash Photolysis Study of Phenosafranine-EDTA System

K K ROHATGI-MUKHERJEE* & MANASHI BAGCHI
Physical Chemistry Laboratories, Jadavpur University, Calcutta 700 032

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The photogalvanic system phenosafranine (PSFH $^\cdot = $ DH$^-$) ($C = 1 \times 10^{-5}$ M) in the presence of EDTA (0.1 M) has been subjected to flash photolysis studies to identify the photoelectroactive species. The spectra of the transient species produced by 200 J flash is recorded at a delay time of 0.4 ms between 300 nm and 700 nm for solutions of pH 4.55, 6.2 and 7.00, in the absence and presence of the electron donor EDTA. At low pH values in the absence of EDTA, $\lambda_{\text{max}}$ at 640 nm is assigned to semidye radical anion of PSFH $^\cdot$ generated by D-D mechanism

$$3\text{DH}^- + 3\text{DH}^- \rightarrow \text{DH}^- + \text{DH}^-$$

where $3\text{DH}^-$ results from the shift in the protolytic equilibrium in the triplet state: $3\text{DH}^- + \text{H}^+ \rightarrow 3\text{DH}^-$. System exhibits second order decay constant, $k_2 = 2.6 \times 10^8 M^{-1} s^{-1}$. At higher pH values $\lambda_{\text{max}}$ is blue shifted to 620 nm and first order decay kinetics is observed: $k_1 = 4.4 \times 10^2$; $t_{1/2} = 1.5$ ms. In presence of EDTA at low pH, $\lambda_{\text{max}}$ appears at 620 nm and decay constant obeys first order kinetics. But at higher pH, $\lambda_{\text{max}}$ shifts to 640 nm and absorbance increases with pH reaching a maximum at pH 6.2 and decreasing again at pH 7, simulating the pH dependence of photovoltage ($V_{\text{em}}$) generation in a PSF + EDTA photogalvanic cell. The appearance of maximum at pH 6.2 in both the cases is due to $pK$ values of EDTA, dissociated species $\text{HY}^-$ and $\text{Y}^-$ only being good electron donors. The species responsible for photoelectroeffect is identified as the semi-radical ion, $\text{DH}^-$. 

The dye phenosafranine (3,7-diamino-5-phenylphenazinium chloride, PSF) has been observed$^1$ to produce high photopotential in a photogalvanic (PG) cell with platinum electrodes in both, light and dark compartments, in the presence of reducing agents such as ethylenediaminetetraacetic acid (EDTA). Since the observation of PG effect by Eisenberg & Silverman$^2$, in recent times Kaneko & Yamada$^3$ have demonstrated high photopotential ($-844$ mV) for Safranine-O (tolylSafranine)-EDTA system. Photochemistry of dyes, an essential step in understanding the mechanism of PG effect, is very sensitive to substituents as demonstrated by Bonneau et al.$^4$ - $^6$ for thionine, azure blue and methylene blue. Therefore, a study of the triplet state photochemistry of PSF and its interaction with EDTA was taken up using flash photolysis technique although the transient photochemistry of Safranine-O has been reported by Baumgartner et al.$^7$.

The cationic dyes are known to have different acid-base properties in the triplet state as compared to the ground, as well as the singlet states. For thiazine dyes Fischer$^8$, has observed three protonated species $^3\text{D}$, $^3\text{DH}^+$ and $^3\text{DH}_2^+$. These conjugate forms show different reactivity towards reducing agents. For the phenazine dye Safranine-O also, stages of protonation observed by Baumgartner et al.$^7$ with $pK$s at 7.5 and 9.2 respectively are

$$^3\text{DH}_2^+ + \text{H}^+ \rightleftharpoons ^3\text{DH}^+ \rightleftharpoons ^3\text{D} + \text{H}^+$$

where $^3\text{DH}_2^+$, $^3\text{DH}^+$ and $^3\text{D}$ are respectively doubly protonated, singly protonated and basic triplets of the dye, expressed in general notations. Besides these three triplets, two radical ions are also reported$^7$:

$$\text{DH}^+ + \text{H}^+ \rightleftharpoons \text{DH}^-$$

Materials and Methods

Phenosafranine (George T. Gurr Ltd, London) was crystallised from water. EDTA (disodium salt dihydrate) was of AR (BDH) grade. The pH was adjusted to 4.55, 6.2 and 7.0 by adding HCl or NaOH as required. No buffer was used since it was found to give reduced value for photovoltage and reduced probability for photobleaching. In fact Bonneau et al.$^5$ have observed definite complex formation with phosphate ions of the buffer.

The Applied Photophysics Flash Kinetics Spectrophotometer model K-2, consisted of two xenon flash lamps of 200 J energy each with a flash duration of 0.1 ms. The dimensions of the tubular photolysis cell were: internal diameter, 1.6 cm; and optical path length, 10.3 cm (internal dimensions). The volume of photolyte solution ($C = 1.0 \times 10^{-5}$ M) used was 23 ml. The solutions were deoxygenated by bubbling purified N$_2$-gas through a syringe introduced through a rubber septum. The spectra were obtained by flash kinetic spectrophotometric technique. After each flash, the maximum growth point of the signal trace on the storage oscilloscope, at any given wavelength,
produced by transmitted monitoring beam, was noted. This signal was proportional to the changes in transmittance (ΔT) of the sample at the given wavelength and hence was proportional to the absorption by the transient species produced by the flash energy (200 J). Prior to measurement, the base line was adjusted to 100% transmission and the zero was adjusted with the shutter of the monitoring beam closed. Hence the changes in transmittance (ΔT) in terms of changes in optical density was given by Eq. (1)

$$\text{ΔOD} = -\log \frac{\Delta T}{T_0} = -\log \frac{\Delta I}{I_0} \quad ... \ (1)$$

where ΔI is the change in the transmitted intensity. The time base was in millisecond. Since the duration of the flash is 0.1 ms, ΔOD could not be observed at a shorter time period.

**Results**

The dye PSF absorbs maximally at 520 nm in dilute aqueous solution with a broad absorption band lying between 400 nm and 600 nm. At concentrations greater than C = 2 x 10^{-5} M it tends to aggregate and spectrum shifts to 503 nm establishing a definite monomer⇒dimer equilibrium. In ethanol and glycerol the maximum shifts to the red, λ_{max} = 535 nm. The spectrum is insensitive to pH in the range 3 and 10, indicating that in the ground state, only one species is present throughout this pH range. This species is the singly protonated dye, the site of protonation being the amino nitrogen. The dye is weakly fluorescent and the fluorescence spectrum is the mirror image of the absorption band. The fluorescence spectrum is also invariant in the pH range 3 and 10. The EDTA quenches the fluorescence of PSF very weakly. In all probability EDTA deactivates the singlet excited dye to the ground state as observed by Bonneau\(^9\) for the dye oxonine.

In the present study the transient absorption spectra of the dye phenoasafranine have been obtained at three pH values: 4.5, 6.2 and 7.00, adjusted by adding appropriate acid or alkali to maintain conditions similar to that obtained in the photogalvanic set up. Buffers were avoided because a detailed study of the effect of buffer salts has not been made as yet for PSF + EDTA system.

The triplet state is generated by flash photolysis of dilute solution (C = 1 x 10^{-5} M) of the dye at appropriate pH. The singlet excited state cannot be observed as the time period of the flash is too large to compete with the fast decay of the singlet. It is assumed that triplet dye is formed with unit efficiency (ϕ = 1). The transient spectra do not appear unless the solutions are completely deoxygenated. This establishes that the spectra are due to the triplet forms of the dye or its reaction products. The transient spectra between the wavelengths 300 nm and 700 nm are presented in Fig. 1. The sensitivity of the photomultiplier-detector system does not permit observations beyond 700 nm. The spectra are recorded at 0.4 ms delay time after the flash at each wavelength.

In region between 400 nm and 590 nm lies the absorption due to ground state dye. The negative values obviously are due to disappearance of the ground state species by light absorption and one would have expected strong negative differential absorption at 520 nm, the absorption maximum of the dye in the ground state. But the nature of the curve suggests that the triplet species also have strong absorption in this region. The negative peak at 460 nm is smaller at pH 4.55 and increases at pH 7.00. It is difficult to identify at this stage, the species responsible for absorbance change in this region. Baumgartner et al.\(^7\) have not considered this region of the spectrum at all, neither they have mentioned such observations. To avoid complications for the time being, awaiting further detailed studies, we also will not discuss the absorption characteristics in this wavelength region.

Interesting changes in the shapes and intensities of the transient absorption spectra are observed between 590 nm and 700 nm when the pH of the solutions are varied. At pH 4.55 the only transient species expected to be present is the doubly protonated triplet dye \(3DH_2^+\) (\(3PSFH_2^+\)). One can calculate approximate number of photons emitted from two flash lamps of 200 J intensity per flash assuming that nearly 15% of the radiation emitted from a blackbody at a given colour temperature are within 100 nm of wavelength centred at 500 nm. The calculations show that the number of photons available are three orders of magnitude greater than the number of photons emitted from each flash lamp.
magnitude greater than the number of molecules present in the given volume of solution of concentration $1 \times 10^{-5} M$ under study. Therefore one can assume that all the ground state molecules are promoted to the singlet state and they populate the triplet state with unit efficiency. This may be presumptuous but we start with this assumption. The evolution of the doubly protonated triplet species can be represented as shown in Scheme I.

$$\text{DH}^{+} + \text{hv} \rightarrow \text{DH}^{++}$$

$$\text{DH}^{+} \rightarrow \text{DH}^{+} + H^+ \rightleftharpoons \text{DH}^{2+}$$

Scheme I

For Saf-O system, Baumgartner et al.\(^7\) have calculated a $pK = 7.5$ for this acid-base equilibrium. Such calculations could not be made in the case of PSF because the nature of the spectrum at higher pH shows considerable variation in shape and intensity. The spectra have been noted at 0.4 ms delay whereas Baumgartner et al.\(^7\) had observed the spectra for Saf-O at 50 $\mu$s delay. The absorption maximum is fairly broad and is identified at 640 nm. This peak apparently overlaps the ground state absorption. A second peak appearing at 380 nm is also attributed to the same species as suggested for Saf-O. At higher pH values of 6.25 and 7.00, the maximum shifts to 620 nm with the change in the shape of the absorption band. The experiments repeated after 4 months with the same flash lamp are recorded as the second line [repeat (R) experiments] in each spectrum.

In Fig. 2 are presented difference spectra in the presence of EDTA, ($C = 0.1 M$). There is a sharp decrease in $\Delta OD$ at pH 4.55 with concomitant change in the shape of the differential absorption band. The maximum shifts to 610 nm from 640 nm. There is considerable positive absorbance in the region of ground state absorption. Surprisingly the spectrum resembles that at pH 6.25 in the absence of EDTA. At higher pH values and in the presence of EDTA, the maxima again occur at 640 nm with concomitant increase in $\Delta OD$. The intensity reaches a maximum value at pH 6.25 and decreases without any change in the band shape at pH 7.00. In many ways these spectra resemble the spectrum of the dye at pH 4.55 in the absence of EDTA suggesting that the two may be due to the same species of the dye.

**Decay kinetics of the transient species**

The kinetics of decay of the transient species have been studied at 600 nm and pH 4.55. For pH 6.25 and 7.00, decay curves were monitored at 630 nm. Since a photographic arrangement for recording the oscilloscope has not been developed as yet, the decay curves have been reconstructed from the recorded $\Delta T$ as a function of time for the given wavelength. The curves are presented in Fig. 3a at the three pH values. The decay curves in the presence of EDTA are presented in Fig. 3b. The plots of $\Delta OD$ as a function of time according to the first order as well as the second order kinetic expression in the absence and presence of

![Fig. 2](image2)

**Fig. 2**—Differential absorption spectra of transient produced by flash photolysis of dye PSF ($C = 1.0 \times 10^{-4} M$) + EDTA ($C = 0.1 M$) [(A) pH, 4.55; (B) pH, 5.51; (C) pH, 6.25; and (D) pH, 7.00]

![Fig. 3](image3)

**Fig. 3**—Decay curves for transient species produced at different pH [(a) PSF + water, (b) PSF + EDTA]
EDTA at pH 4.55, 6.25 and 7.00 respectively are presented in Figs 4-6.

At pH 4.55 the plot is linear for second order decay kinetics in the absence of EDTA but not for the first order. The second order decay law for like molecules only, is expressed by Eq. (2)

\[
\frac{1}{C} - \frac{1}{C_0} = k_2 t
\]

or, \[
\frac{1}{ed} \left( \frac{1}{C} - \frac{1}{C_0} \right) = \frac{k_2 t}{ed}
\]

or, \[
\frac{1}{OD} = \frac{1}{OD_0} + \frac{k_2 t}{ed} \quad \ldots \ldots \quad (2)
\]

where \( \varepsilon \) is the molar extinction coefficient of the transient species and \( d \) is the length of the absorption cell \( (d=10.3 \text{ cm}) \). From the plot one obtains the slope and the intercept extrapolated to zero time.

Slope = \( \frac{k_2}{ed} = 10.7 \times 10^3 \text{ s}^{-1} \)

Intercept = \( \frac{1}{\varepsilon C_0 d} = 4 \)

Assuming 100\% transformation to \( ^3 \text{DH}_2^+ \) on light absorption, and \( C_0 = 1.0 \times 10^{-5} \text{ M} \)

\[
\varepsilon_{600} = \frac{1}{4 \times 1 \times 10^{-5} \text{ M} \times 10.3 \text{ cm}} = 2.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}
\]

\[
k_2 = 10.7 \times 10^3 \text{ s}^{-1} \times \varepsilon \times d = 2.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}
\]

\[
\tau_{1/2} = \frac{1}{k_2 C_0} = 0.38 \times 10^{-3} \text{ s} = 380 \mu s
\]

Since spectrum is recorded at 0.4 ms delay time which is nearly equal to the half-life of the species, the concentration of initial triplet must be nearly half that at zero time. Therefore, \( C \) after 0.4 ms delay \( \approx 4.9 \times 10^{-6} \text{ M} \).

The experiment was repeated after 4 months with freshly prepared solution. \(^3 \text{DH}_2^+ \) species formed in repeat experiment after 4 months, i.e. \( C_0(R) \) is observed to decrease by nearly seven-fold (Fig. 4a), although the slope is the same. A likely explanation is that the intensity of the flash lamp has decreased due to constant use, so that there are not enough photons to excite all the molecules to higher energy state. A

![Fig. 4—Decay kinetics at pH 4.55 of (a) PSF + water and (b) PSF + EDTA, according to first order and second order rate expressions](image)

![Fig. 5—Decay kinetics at pH 6.25 of (a) PSF + water and (b) PSF + EDTA, according to first order and second order rate expressions](image)

![Fig. 6—Decay kinetics at pH 7.00 of (a) PSF + water and (b) PSF + EDTA, according to first order and second order rate expressions](image)
fraction of molecules therefore will remain in the ground state even at zero time.

At pH 6.25 the decay curve at 630 nm is more complex (Fig. 5a). It may be suggested that a first order decay is taken over by a second order decay after 4 ms, i.e. three half-lives. The first order rate constants for two sets, the second one repeated after 4 months, are

\[
\text{Set (I) } k_1 = 4.4 \times 10^2; \quad \tau_{1/2} = 1.5 \text{ ms} \\
\text{Set (R) } k_1 = 3.9 \times 10^2; \quad \tau_{1/2} = 1.8 \text{ ms}
\]

The slopes of the second order plots as well as the intercepts vary slightly for the two sets (I) slope = 10 \times 10^3 s^{-1}; (I) intercept = 4 \((R)\) slope = 13 \times 10^3 s^{-1}; (R) intercept = 20

From (I) we have; \(k_2 = 1.2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}\)

At pH 7 the decay at 630 nm is very fast and first order for more than two half-lives (Fig. 6a). This pH is very near the \(pK\) value for protolytic equilibrium between \(3\text{DH}_2^+\) and \(3\text{DH}^+\). From the slope of the plot, unimolecular decay constant \(k_1 = 2.7 \times 10^3 \text{s}^{-1}\) with a half-life \(\tau_{1/2}\) of 0.36 ms is calculated. The decay curve does not show complete recovery of absorbance (Fig. 3) indicating the presence of a very long lived species or a permanent change on flashing.

**Discussion**

Although the events immediately following the light absorption cannot be monitored efficiently in this model of the flash unit, some interesting correlations could be established from the absorption spectra of the transient as a function of \(pH\) in the absence and presence of the electron donor, EDTA. The decay kinetics are helpful in establishing the mechanism. All relevant data are presented in the Table 1.

From a rough calculations of absorbances at different \(pH\) values in the absence of EDTA, the protolytic equilibrium: \(3\text{DH}_2^+ \rightleftharpoons 3\text{DH}^+\), works out to have a \(pK \approx 7\). Therefore the only species likely to be present at \(pH\) 4.55 is the doubly protonated dye in the triplet state, i.e. \(3\text{DH}_2^{+2}\) if all the dye molecules are electronically excited by the flash energy. The observed second order decay at this \(pH\) in the absence of any reducing agent can be explained by two mechanisms: (i) quenching by T-T mechanism, i.e. interaction between two triplets; and (ii) quenching by T-S mechanism i.e. quenching by ground state (S) dye, giving the rate expression (3) for quenching

\[
-\frac{d[T]}{dt} = k_1[T] + k_2[T][T] + k_3[T][S]
\]

where \([T]\) = concentration of triplet dye species \(3\text{DH}_2^{+2}\). This type of expression has been suggested for chlorophyll triplets. But for PSF, quenching by ground state triplets does not seem to be important from following considerations. The slope I (I = initial set; R = repeat set) of the second order plot (Fig. 4a) is well reproduced on repetition after 4 months (fresh solution but old flash lamp). Since the intercepts are different, the concentration of the excited species initially generated must have decreased because of the decrease in the number of photons available from the old lamp. The percentage decrease can be evaluated by comparing the ratios (slope/intercept) for two sets or comparing the two intercepts. Both calculations show a reduction by a factor or 0.14 in the apparent initial concentration of the triplet dye, suggesting that the ground state is not completely emptied. In spite of the presence of a large concentration of the dye in the ground state the decay rate remains the same. This suggests that ground state dye molecules are not effective quenchers of the triplet dye. One of the reasons could be that T-T quenching is a spin-allowed process whereas T-S quenching is spin-restricted according to Wigner’s spin conservation rule,

\[
T + T \rightarrow S + S; \quad T + S \rightarrow S + S
\]

The appearance of a first order term in the repeat experiment \((k = 4.6 \times 10^2 \text{s}^{-1}; \quad \tau_{1/2} = 1.5 \text{ ms})\) where

| Table 1—Rate and Spectroscopic Parameters from Flash Study |
|-----------------------------|-----------------------------|-----------------------------|
| \(pH\) | 4.55 \(\lambda = 600 \text{ nm}\) | 6.25 \(\lambda = 630 \text{ nm}\) | 7.0 \(\lambda = 630 \text{ nm}\) |
| \(k_1\) | \(2.6 \times 10^8 \text{ M}^{-1} \text{s}^{-1}\) | \(1.2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}\) | \(2 \times 10^3 \text{s}^{-1}\) |
| \(k_{\text{600}}\) | \(2.4 \times 10^3 \text{ cm}^{-1}\) | \(4.6 \times 10^2 \text{ cm}^{-1}\) | \(9 \times 10^2 \text{ cm}^{-1}\) |
| \(\tau\) | \(2.2 \times 10^{-3} \text{s}\) | \(2.3 \times 10^{-3} \text{s}\) | \(0.5 \times 10^{-3} \text{s}\) |
| \(\tau_{1/2}\) | \(1.5 \text{ ms}\) | \(1.5 \text{ ms}\) | \(0.35 \text{ ms}\) |
| \(C_0\) | \(\text{370} \mu\text{s}\) | \(\text{1 m}\) | \(\text{1 m}\) |
decay rate also agrees within an order of magnitude.

due to 3DH~. At pH 7, only first order decay is
probability is reduced and spectrum is preponderantly
are the same as observed at pH 4.55 and must be due to
conditions.

discrepancy from

shape as that at pH 6.25 but the absorbance is lowered.

The recorded spectrum at pH 7 has nearly the same
in the absence of EDTA should also be assigned to

The last step is important. The triplet-triplet
mechanism in dyes is known to involve electron
transfer between each other producing the two radical
ions, reduced semidye and oxidised dye radical. We
suggest that the spectrum recorded at 0.4 ms delay
period at pH 4.55 is due to semidye radical ion -DH~.
This is substantiated by the discussion in the sequel.

The spectrum recorded at pH 6.25 is primarily due to
absorption by 3DH~ as a shift in absorption maximum to 620 nm is observed. Due to shift in the
photoredox reaction is carried out in a photogalvanic

donor Hy3 - is low. As the

of 3DH~ is high but the concentration of the electron
acceptor Hy3 - only have free lone pair electrons on N-atom
available for donation to suitable acceptors. Therefore
EDTA will act as an efficient donor at high pH only.
The species available as electron acceptors at low pH is
predominantly 3DH~. At low pH the concentration of 3DH~ is high but the concentration of the electron
donor Hy3 - is low. As the pH increases, [3DH~] decreases but [HY3] increases. The electron transfer
produces a radical ion semidye. The semidye

is surprising because one expects electron transfer quenching and formation of radical ion in the presence
of EDTA. One may be tempted to assign this spectrum to the semidye radical ions generated by the step:
3DH~ +e-→3DH~. In that case, the spectra at higher
pH in the absence of EDTA should also be assigned to the radical ion.

But the observations are that as the pH of the
solution is increased at constant [EDTA], the nature of the spectra again change, maximum shifts to longer
wavelength (λmax = 640 nm) with concomitant increase in absorbance. The absorbance increases to a
maximum value at pH 6.25 and starts decreasing with further increase in pH. This behaviour is reminiscent of variation of photovoltage (Voc) with pH when the photoredox reaction is carried out in a photogalvanic

It has been well documented in the literature that the tetrabasic acid EDTA has pK values of 2.0, 2.69, 6.16 and 10.26. Bonneau et al. have shown that the triply ionised and fully ionised species HY3 and Y4 only have free lone pair electrons on N-atom available for donation to suitable acceptors. Therefore EDTA will act as an efficient donor at high pH only. The species available as electron acceptors at low pH is predominantly 3DH~. At low pH the concentration of 3DH~ is high but the concentration of the electron donor HY3 is low. As the pH increases, [3DH~] decreases but [HY3] increases. The electron transfer produces a radical ion semidye. The semidye

\[ \text{[3DH}^2+] \text{ is much reduced may be due to the direct decay to the ground state} \]
\[ 3\text{DH}^2+ \rightarrow \text{DH}^+ + \text{H}^+ \]

which becomes competitive at low concentrations of
dye triplets. The rate law can than be expressed by Eq.

\[ \frac{d[3\text{DH}^2+]}{dt} = k_1[3\text{DH}^2+] \]
\[ + k_2[3\text{DH}^2+]^2 \]

with the involvement of the steps shown in Scheme 2.

\[
\begin{align*}
\text{DH}^+ & \xrightarrow[hv]{\text{hv}} \text{1DH}^+ \rightarrow 3\text{DH}^+ \\
3\text{DH}^+ & + \text{H}^+ \rightarrow 3\text{DH}^2+ \\
3\text{DH}_2^2+ & \rightarrow \text{DH}^+ + \text{H}^+ \\
3\text{DH}_2^2+ & + 3\text{DH}_2^2+ \rightarrow \text{H}^+ \text{3DH}_2^2+ + \text{DH}_2 \\
3\text{DH}_2^2+ & \rightarrow \text{oxidised reduced} \\
\text{Scheme 2}
\end{align*}
\]

The recorded spectrum at pH 7 resembles closely the spectrum recorded at 0.4 ms delay when the solution is
flashed in the presence of EDTA (C = 0.1 M) at pH 4.55, although with reduced absorbance (Fig. 2). This

Fig. 7—Plot of photovoltage Voc versus ODmax of transient species produced on flashing (PSF + EDTA) system at different pH values [(A) pH, 4.55; (B) pH, 5.51; (C) pH, 6.25; and (D) pH, 7.00]
Table 2—Observed Values of OD\textsubscript{max} at 640 nm in Flash Study and \( V_{oc} \) in Photogalvanic Study for a Solution of PSF (\( C = 1 \times 10^{-5} \) M) and EDTA (\( C = 0.1 \) M) as a Function of \( pH \)

\[
\begin{array}{lcccc}
\text{pH} & 4.55 & 5.5 & 6.25 & 7.0 \\
\text{OD\textsubscript{max} at 640 nm} & 0.0365 & 0.070 & 0.088 & 0.058 \\
\text{\( V_{oc} \) in mV at 30°C} & 675 & 712 & 735 & 710 \\
\text{\([3DH^+]\) in M} & 9.96 \times 10^{-6} & 8.4 \times 10^{-6} & 5 \times 10^{-6} & 5 \times 10^{-6} \\
\text{\([3DH^+]\) in M} & 0.003 \times 10^{-6} & 1.5 \times 10^{-6} & 5 \times 10^{-6} & 5 \times 10^{-6} \\
\end{array}
\]

\( \text{(a) Ref. 1.} \)

concentration will increase with initial increase in \( pH \), reach a maximum and decrease again for further increase in \( pH \) since the concentration of the acceptor molecule, \( 3\text{DH}_2^+ \) will gradually decrease. This also indicates that \( 3\text{DH}_2^+ \) is more easily reduced than the basic triplet \( 3\text{DH}^+ \) in agreement with the observation of other workers\(^7\).

From these observations one is forced to conclude that the spectra with absorption maximum at 640 nm at higher \( pH \) values in the presence of EDTA are due to protonated semidye \( \cdot\text{DH}_2^+ \). If that is so then the spectra at \( pH 4.55 \) in the absence of EDTA (\( \lambda_{\text{max}} = 640 \) nm) are also due to protonate semidye, produced by T-T interaction which is an important mode of decay of \( 3\text{DH}_2^+ \) of PSF. The spectra showing absorption maximum at 620 nm observed at high \( pH \) values in the absence of EDTA and at low \( pH \) values in the presence of EDTA must be due to \( 3\text{DH}_2^+ \). At low \( pH \) in the presence of EDTA appearance of 620 nm maximum is evidently due to low concentration of donor ions \( \text{HY}^3^- \). The direct dependence of light intensity and \( V_{oc} \) with unit slope as reported earlier\(^1\), indicates that photovoltage generation is a one-photon process. This further confirms the active participation of the semidye radical ion, \( \cdot\text{DH}_2^+ \) (PSFH\(^+\)) in the electrode process.

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References