

## FORMATION OF $e_{aq}^-$ FROM EXCITED THIONINE AND METHYLENE BLUE IN AQUEOUS SOLUTIONS

WALTRAUT VONACH and NIKOLA GETOFF

*Institut für Theoretische Chemie und Strahlenchemie der Universität Wien and Ludwig Boltzmann Institut für Strahlenchemie, Währingerstrasse 38, A-1090 Vienna (Austria)*

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### Summary

Electron ejection is observed when aqueous thionine or methylene blue is excited using light of wavelength 253.7 nm. The quantum yields  $Q(e_{aq}^-)$  are  $5.5 \times 10^{-3}$  for protonated thionine (pH 7),  $9.5 \times 10^{-3}$  for unprotonated thionine (pH  $\geq 13.5$ ) and  $5.0 \times 10^{-3}$  for methylene blue (pH 7). Further, excited  $OH_{aq}^-$  ions produce  $e_{aq}^-$  with a quantum yield of 0.05. The  $pK_2$  value of thionine was redetermined and was found to be  $11.5 \pm 0.1$ .

### 1. Introduction

The manifold applications of thiazine dyes include use as sensitizer redox components in photogalvanic cells for solar energy utilization [1 - 3]. It has been shown that the fluorescence of thionine ( $TH^+$ ) [4, 5] and methylene blue ( $MB^+$ ) [6 - 8] is quenched by metal ions. For example, in the presence of  $Fe^{2+}$  ions the singlet state  $^1MB^+$  of  $MB^+$  can, in addition to luminescing, decay by charge or energy transfer to semiquinone or excited ferrous ions  $Fe^{2+*}$  respectively, which result in the production of solvated electrons  $e_{aq}^-$  [8]. In acid solutions the  $e_{aq}^-$  are converted into hydrogen atoms ( $k(e_{aq}^- + H_{aq}^+) = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [9]) which can attack the dye molecule on various sites by forming semiquinone (86%) and hydrogen adducts (5.4%) or by splitting the S—C bond (8.6%) [10, 11]. The last two processes result in decomposition of the dye. Similar observations have been reported for thionine [11, 12].

Aromatic compounds containing certain substituents (e.g.  $-OH$ ,  $-O^-$ ,  $-NH_2$  and  $-N(CH_3)_2$ ) are able to eject electrons [13 - 16] when excited in the singlet state. This effect is accompanied by a corresponding decrease in  $Q_F$  [16 - 24] and is dependent on temperature [25] as well as on the nature of the solvent [23]. Photoejection of electrons has also been observed from a number of flavines in water-methanol solutions [26].

Laser flash photolysis (694.3 nm) of  $MB^+$  in alkaline water (pH 8.2) and neutral acetonitrile revealed, in addition to the formation of the triplet

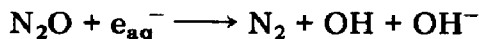
dye  ${}^3\text{MB}^+$ , a small absorption at 520 nm which was assigned to semioxidized methylene blue (radical cation  $\text{MB}^{2+}$ ) [27]. Hence it was concluded that  $\text{MB}^{2+}$  is the result of an electron ejection process from the excited dye molecule. A radical cation, however, can also be formed by electron transfer from the singlet excited dye molecule.

The present investigations are therefore focused on a direct determination of the  $e_{\text{aq}}^-$  yield from electronically excited thionine and methylene blue in neutral and alkaline aqueous solutions.

## 2. Experimental details

### 2.1. Preparation of the solutions

Thionine hydrochloride (molecular weight, 267.76) and methylene blue trihydrate (molecular weight, 373.8; EGA Chemie, F.R.G.) were recrystallized from *n*-butanol or 50 vol.% water-ethanol solutions as previously described [11]. The purity was checked by absorption spectroscopy (Coleman 575, Perkin-Elmer). The solutions were prepared using fresh quadruply distilled water. Experiments at pH 7 and pH 13.7 (adjusted by the addition of  $1.5 \text{ mol dm}^{-3}$  NaOH) were carried out with thionine and experiments at pH 7 were carried out with methylene blue. The solutions were saturated with high purity  $\text{N}_2\text{O}$  (Messer-Griesheim, Austria) which served as an appropriate scavenger for the solvated electrons as it undergoes the reaction



with  $k = 0.91 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [28].  $\text{N}_2\text{O}$  is transparent to light of wavelength 253.7 nm. The resulting OH species were scavenged by *tert*- $\text{C}_4\text{H}_9\text{OH}$  present in the solutions at a concentration of  $1 \text{ mol dm}^{-3}$  ( $k(\text{OH} + \text{tert-C}_4\text{H}_9\text{OH}) = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [29]). The concentrations of both dyes were varied.

### 2.2. Light source and actinometry

All solutions were irradiated in a double-walled vessel ( $4\pi$  irradiation geometry) which was connected to a thermostat to maintain a constant temperature of  $30 \pm 0.5 \text{ }^\circ\text{C}$  as described previously [30, 31]. A low pressure mercury lamp (Osram HNS 10 W) with a Vycor filter providing monochromatic UV radiation of wavelength 253.7 nm was used as the light source. The actinometry was performed using a deoxygenated aqueous solution of  $\text{ClCH}_2\text{COOH}$  of concentration  $0.5 \text{ mol dm}^{-3}$  which gave  $Q(\text{Cl}^-) = 0.34$  at  $30 \text{ }^\circ\text{C}$  [32]. Irradiation of a total solution volume of 150 ml gave a light intensity  $I_0$  of  $6.2 \times 10^{17} \text{ quanta ml}^{-1} \text{ min}^{-1}$ .

### 2.3. Analysis

The quantum yields of the ejected electrons  $e_{\text{aq}}^-$  obtained under various experimental conditions were determined by measuring the nitrogen yield. The mixture of gases evolved (nitrogen and hydrogen) was collected using a

vacuum line and was analysed by gas chromatography (Perkin-Elmer, Fraktometer 116 E column containing molecular sieve). In this case  $Q(N_2) = Q(e_{aq}^-)$ . The following corrections were applied to the measured nitrogen and hydrogen yields.

(a) Solutions with the corresponding pH values were irradiated at 30 °C in the absence of dye (thus they contained 1 mol *tert*-C<sub>4</sub>H<sub>9</sub>OH dm<sup>-3</sup> and 2 × 10<sup>-2</sup> mol N<sub>2</sub>O dm<sup>-3</sup>). The nitrogen and hydrogen yields obtained were referred to the number of quanta absorbed (data for matrix correction). The matrix data were then subtracted from the nitrogen and hydrogen yields obtained in the presence of the dyes.

(b) Corrections for partial light absorption at low dye concentrations (less than 1 × 10<sup>-4</sup> mol dm<sup>-3</sup>), where the matrix can also absorb, are also required. It should be noted that small hydrogen yields were observed on prolonged UV irradiation of the systems under investigation. Hence to keep the dye photolysis process at as low a level as possible a relatively small UV dose was applied.

### 3. Results and discussion

#### 3.1. Formation of $e_{aq}^-$ from $OH^-$ at 253.7 nm

It was first necessary to determine  $Q(e_{aq}^-)$  for the electronically excited  $OH_{aq}^-$ . Solutions containing 10<sup>-2</sup> - 1 mol NaOH dm<sup>-3</sup> saturated with N<sub>2</sub>O in the presence of 1 mol *tert*-C<sub>4</sub>H<sub>9</sub>OH dm<sup>-3</sup> were irradiated with light of wavelength 253.7 nm for 10 min at 30 °C. The main reactions taking place were



with  $k_2 = 0.91 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [28] and



with  $k_3 = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [29]. The mean value of numerous determinations of  $Q(N_2) = Q(e_{aq}^-)$  was 0.05. It should be noted for comparison that an earlier experiment in which  $OH_{aq}^-$  was illuminated at 184.9 nm gave a value of 0.11 for  $Q(e_{aq}^-)$  [33].

#### 3.2. The thionine system

The absorption spectrum of unbuffered aqueous thionine changes at pH ≥ 9.5 such that the absorption maxima show a blue shift as can be seen in Fig. 1. The corresponding molar extinction coefficients  $\epsilon$  were determined and are included in the figure. In this pH range thionine exists in two forms:



Measurement of the optical density (OD) at 288 and 592 nm as a function of pH in the range 7 - 14 enabled the pK value to be determined from

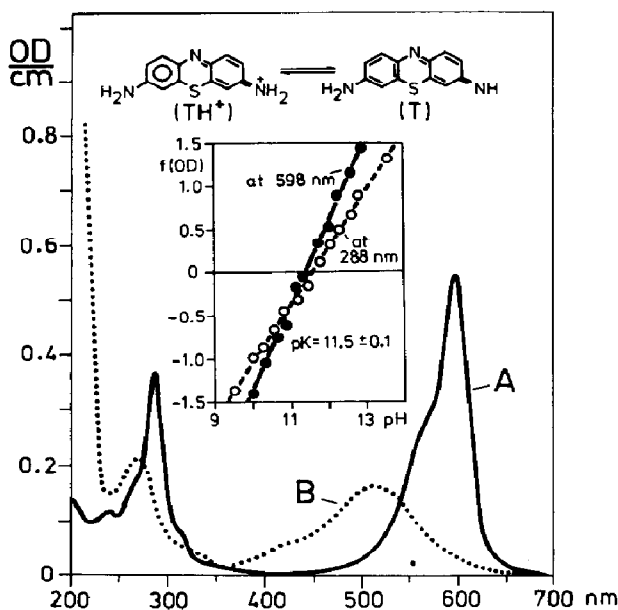


Fig. 1. Absorption spectra of aqueous thionine solutions with a concentration of  $1 \times 10^{-5}$  mol dm $^{-3}$  at pH 7 (curve A) and pH 14 (curve B);  $\epsilon_{598} = 54\,800$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ;  $\epsilon_{288} = 38\,000$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ;  $\epsilon_{518} = 18\,500$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ;  $\epsilon_{270} = 23\,000$  dm $^3$  mol $^{-1}$  cm $^{-1}$ . The inset shows  $f(\text{OD})$  vs. pH at 288 and 598 nm (see text).

#### Hammett's relation [34]

$$pK = \text{pH} - \log\left(\frac{\text{OD}_b - \text{OD}}{\text{OD} - \text{OD}_a}\right) = \text{pH} - f(\text{OD}) \quad (5)$$

where  $\text{OD}_a$  and  $\text{OD}_b$  are the optical densities of the pure acid and basic forms of the dye. By plotting the logarithmic expression  $f(\text{OD})$  from eqn. (5) as a function of pH a mean value of  $11.5 \pm 0.1$  was obtained for  $pK$  (Fig. 1, inset).

The electron ejection process from aqueous thionine excited at its second absorption band was studied at pH 7 (100%  $\text{TH}^+$ ), and pH 13.7 (100% T). The strong alkaline dye solutions were unstable and therefore they were freshly prepared, immediately saturated with  $\text{N}_2\text{O}$  for about 45 min and then irradiated. The inset to Fig. 2 shows the nitrogen yield as a function of the quanta absorbed by thionine solutions of concentration  $5 \times 10^{-5}$  mol dm $^{-3}$  containing 1 mol  $\text{tert-C}_4\text{H}_9\text{OH}$  dm $^{-3}$  and  $2 \times 10^{-2}$  mol  $\text{N}_2\text{O}$  dm $^{-3}$  at pH 7 and pH 13.7. The nitrogen yields are corrected as described above. The quantum yields of  $e_{\text{aq}}^-$  for the protonated and unprotonated dye forms can be derived from curves A and B in the inset to Fig. 2 and are found to be  $5.1 \times 10^{-3}$  and  $9.8 \times 10^{-3}$  respectively.

To avoid absorption corrections higher dye concentrations sufficient for complete light absorption were used in a second series of experiments. However, it is well known that dimer formation occurs at  $\text{TH}^+$  and  $\text{MB}^+$

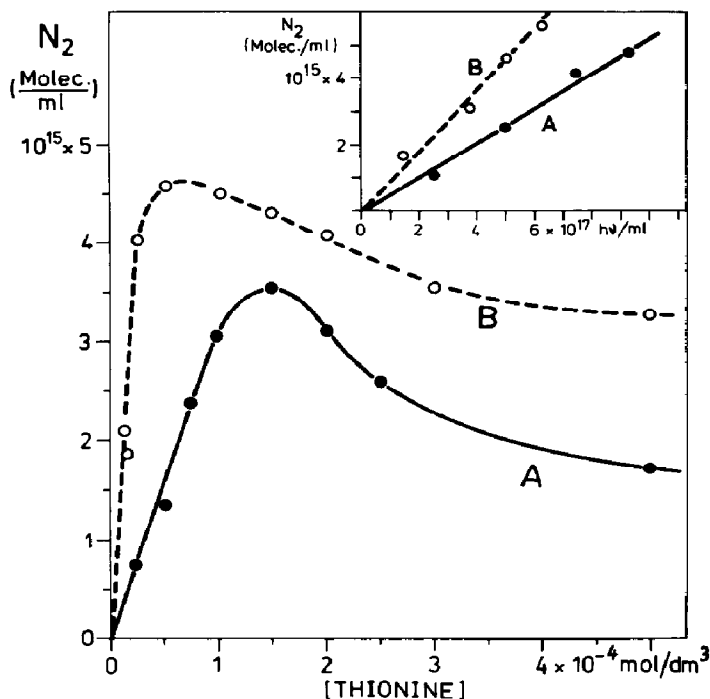


Fig. 2. Nitrogen yield ( $e_{\text{aq}}^-$ ) as a function of the thionine concentration from  $1 \times 10^{-5}$  to  $5 \times 10^{-4}$  mol  $\text{dm}^{-3}$  in the presence of 1 mol *tert*- $\text{C}_4\text{H}_9\text{OH}$   $\text{dm}^{-3}$  and  $2 \times 10^{-2}$  mol  $\text{N}_2\text{O}$   $\text{dm}^{-3}$  at pH 7 (curve A) and pH 13.7 (curve B). The applied UV dose was  $18.6 \times 10^{17}$  quanta  $\text{ml}^{-1}$ . The inset shows the dependence of the nitrogen yield ( $e_{\text{aq}}^-$ ) on the absorbed UV dose at pH 7 (curve A) and pH 13.7 (curve B) for a solution containing  $5 \times 10^{-5}$  mol thionine  $\text{dm}^{-3}$ , 1 mol *tert*- $\text{C}_4\text{H}_9\text{OH}$   $\text{dm}^{-3}$  and  $2 \times 10^{-2}$  mol  $\text{N}_2\text{O}$   $\text{dm}^{-3}$ .

concentrations in excess of  $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  [35, 36], although the presence of *tert*- $\text{C}_4\text{H}_9\text{OH}$  mitigates this effect to some extent.

Figure 2 shows the nitrogen yield as a function of thionine concentration at pH 7 (curve A) and pH 13.7 (curve B). It is obvious from the shapes of the curves that dye dimers are formed at pH 7 and thionine concentrations in excess of  $10^{-4}$  mol  $\text{dm}^{-3}$  so that the electron ejection process is gradually quenched probably by intramolecular energy transfer processes. A  $Q(\text{N}_2) = Q(e_{\text{aq}}^-)$  value of  $5.8 \times 10^{-3}$  was calculated from the tangent to curve A (pH 7) at a  $\text{TH}^+$  concentration of  $1.5 \times 10^{-4}$  mol  $\text{dm}^{-3}$  where the light absorption is 100%. The corresponding value for unprotonated thionine T (curve B) was  $Q(e_{\text{aq}}^-) = 9.2 \times 10^{-3}$ . These quantum yields are in very good agreement with those obtained as a function of the UV dose (Fig. 2, inset). It is interesting that the electronically excited unprotonated thionine T ejects about twice as many electrons as the protonated form does.

### 3.3. The methylene blue system

Although methylene blue is present in its single protonated form  $\text{MB}^+$  at  $\text{pH} > 4$  [37], in alkaline solutions a decrease in the OD values occurs in both the first ( $\lambda_{\text{max}} = 665$  nm) and the second ( $\lambda_{\text{max}} = 296$  nm) absorption bands. In

strong alkaline aqueous solutions ( $\text{pH} \geq 13$ ) methylene blue is rather unstable and a fine dye precipitation takes place after storage for longer than 1.5 h. Therefore the electron ejection process was studied in neutral  $\text{MB}^+$  solutions with concentrations in the range  $10^{-5} - 10^{-3} \text{ mol dm}^{-3}$  in the presence of  $1 \text{ mol tert-C}_4\text{H}_9\text{OH dm}^{-3}$  and  $2 \times 10^{-2} \text{ mol N}_2\text{O dm}^{-3}$  at  $30^\circ\text{C}$ . The nitrogen yield (equivalent to  $e_{\text{aq}}^-$ ) showed a similar dependence on the dye concentration to that of  $\text{TH}^+$  (Fig. 2). A quantum yield  $Q(\text{N}_2) = Q(e_{\text{aq}}^-)$  of  $5 \times 10^{-3}$  was derived from the tangent to this curve.

No  $e_{\text{aq}}^-$  formation could be established for either dye on excitation in the first absorption band. The quantum yield is probably very low in this case. It should also be noted that the hydrogen yield observed was generally about two orders of magnitude lower than the corresponding nitrogen yield.

It is obvious from the experimental results that the ejection of electrons from aqueous thionine and methylene blue excited in their second absorption bands is a monophotonic process. The  $Q(e_{\text{aq}}^-)$  values are very low compared with those of aqueous aniline, for example, where  $Q(e_{\text{aq}}^-)$  values of 0.06 and 0.34 are obtained for excitation in the  $S_1$  and  $S_2$  states respectively [21, 24]. This could be explained by the fact that the main decay path of the electronically excited thiazine dyes is intersystem crossing (triplet formation) and fluorescence [5, 38].

The previously reported formation of semioxidized methylene blue by laser flash excitation in the first absorption band [27] is probably a bi-photonic process.

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