THE TEMPERATURE DEPENDENCE OF THE EFFICIENCY OF PHOTOINDUCED CHARGE SEPARATION IN AQUEOUS SOLUTION

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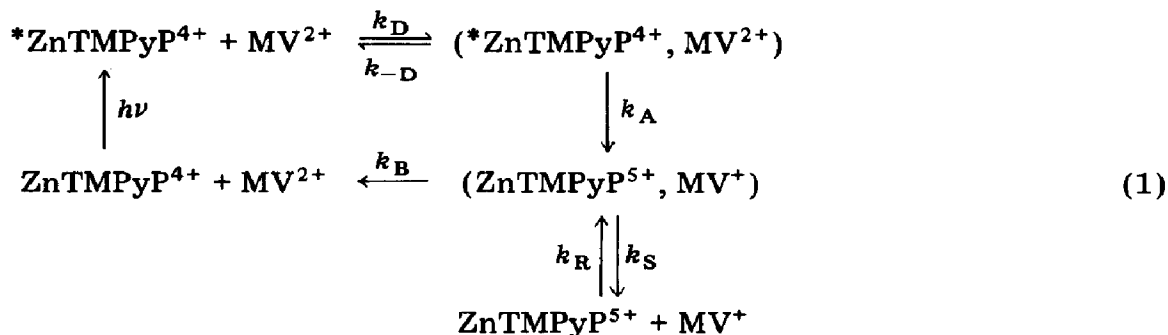
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Summary

The influence of temperature on the efficiency of charge separation in photosensitized reactions is described. The aim of this investigation is to determine whether the yield of products is increased on increasing the temperature which would be useful for the storage of solar energy. The system studied here consists of the electron transfer from a metalloporphyrin (zinc tetramethylpyridylporphyrin) to methyl viologen. This system has proved to be very efficient for sensitizing the photoreduction of water to hydrogen. Many factors affect the efficiency of the system but we find that increasing the temperature favours charge separation.

Porphyrins are very important compounds since they have been proved to be good sensitizers for photochemical reactions. They have been subjected to many studies during the past decade because of the possibility of using them as photosensitizers for the transformation of solar energy into chemically storable energy. The most active application in the field of solar energy, until now, has been the photodissociation of water into H_2 and O_2. Previous work has established that metalloporphyrins, in particular zinc porphyrins, can function as efficient sensitizers [1, 2]. It has also been found that positively charged compounds [3 - 5] are particularly good photosensitizers when methyl viologen (MV^{2+}) is used as an electron relay while, under identical conditions, negatively charged compounds were very poor sensitizers [6, 7]. Thus we have seen that the efficiency of electron transfer between the zinc porphyrin and the viologen, leading to separated ion products, is very much influenced by the nature of the water solubilizing groups. We have described this effect as being due to the electrostatic forces [8]. We have also seen that the efficiency of charge separation can be influenced by other factors such as ionic strength [9, 10]. We now look at the effect of temperature on the yield of ion products.

The system we have been studying can be summarized as ($ZnTMPyP^{4+}$ $\equiv$ zinc tetramethylpyridylporphyrin)

$$*\text{ZnTMPyP}^{4+} + \text{MV}^{2+} \xrightleftharpoons[k_{-\text{D}}]{k_{\text{D}}} (*\text{ZnTMPyP}^{4+}, \text{MV}^{2+})$$

$$\uparrow h\nu \qquad\qquad\qquad\qquad \downarrow k_{\text{A}}$$

$$\text{ZnTMPyP}^{4+} + \text{MV}^{2+} \xleftarrow{k_{\text{B}}} (\text{ZnTMPyP}^{5+}, \text{MV}^{+}) \qquad (1)$$

$$k_{\text{R}} \Updownarrow k_{\text{S}}$$

$$\text{ZnTMPyP}^{5+} + \text{MV}^{+}$$

One of the critical steps of this scheme is the formation of the ion pair $(\text{ZnTMPyP}^{5+}, \text{MV}^{+})$ since this complex can either dissociate to ground state reactants or separate into ion products. The final reaction (k_{S}) is the most useful since MV^{+} can be used later in the presence of a platinum catalyst for H_2 photogeneration from water [4] and ZnTMPyP^{5+} can be used to photogenerate O_2 from water in the presence of an RuO_2 catalyst for example [11]. In fact, it would be very useful to avoid the reaction leading back to the initial reactants (k_{B}). If we can minimize k_{B} and, in contrast, maximize k_{S}, then this would contribute to a maximization of the yield of redox products. We can actually express this yield as

$$\phi_{\text{ions}} = \phi_{\text{T}}\phi_{\text{Q}}\phi_{\text{S}} \qquad (2)$$

where the different terms have been described before [10], and the ϕ_{S} term itself refers to the probability of charge separation which is a function of k_{S} and k_{B}:

$$\phi_{\text{S}} = \frac{k_{\text{S}}}{k_{\text{S}} + k_{\text{B}}} \qquad (3)$$

From this last expression we see that a high k_{S} value compared with the k_{B} value will yield a ϕ_{S} value approaching 1.0. Since $\phi_{\text{T}} = 0.9$ [4] and $\phi_{\text{Q}} \approx 1.0$ [4], the ϕ_{ions} term will be maximum when ϕ_{S} is itself at its maximum value. In previous work [9, 10] we have seen that the Fuoss equation predicts that the rate of formation of the separated ion products should depend on the temperature. However, it is difficult to determine *a priori* from this equation whether an increase in temperature should favour or inhibit the reaction of separation, since the expression of k_{S} as a function of temperature is rather complex. Also, the mechanism involved in our system is complex owing to the reversibility of the various reactions.

A dependence of certain ionic reaction rates on temperature has been studied and an attempt was made to derive a temperature coefficient for the activation energy [12], but no clear relationship was found to express the activation energy of the ionic reactions in solution. In order to study the influence of temperature on the quantum efficiency ϕ_{ions} for formation of separated ion products we have used the ZnTMPyP^{4+}–MV^{2+} system as a model since at ambient temperature ϕ_{ions} is quite high and the products are observed easily by optical absorption. A solution of ZnTMPyP^{4+} (about
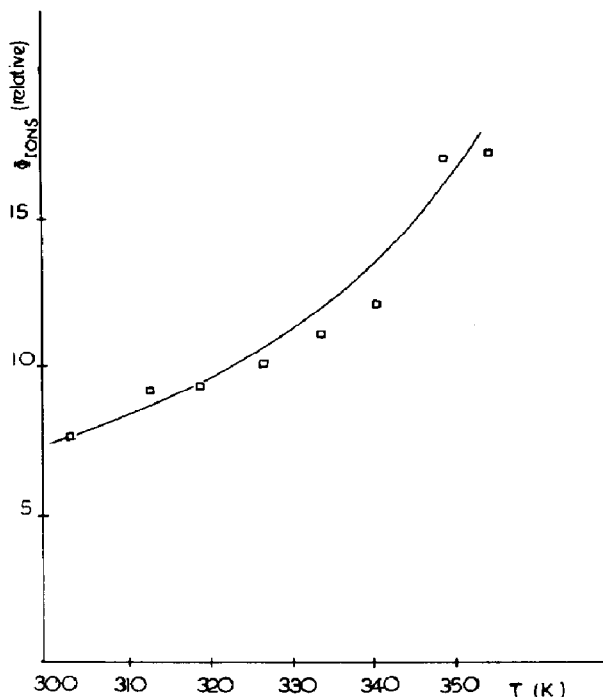
Fig. 1. Effect of temperature on the quantum yield for formation of redox ions.

2×10^{-5} M) in water at pH 4.7 (10^{-1} M acetate buffer) containing MV^{2+} (10×10^{-3} M) was purged thoroughly with argon. The cell used for the measurements was a 1 cm cuvette equipped with a water jacket through which thermostatted water was passed continuously. The cell was mounted in the sample holder of a frequency-doubled neodymium glass laser and the optical density changes observed at 605 and 750 nm were recorded after excitation using a 15 ns pulse. Monitoring at 605 nm allowed the transient concentration of MV^{+} to be measured ($\epsilon_{605\,nm} = 1.1 \times 10^{-4}$ cm^{-1} M^{-1}) whilst the $ZnTMPyP^{5+}$ species was observed at 750 nm ($\epsilon_{750\,nm} = 6000$ M^{-1} cm^{-1}). The ϕ_{ions} values were calculated as the average of the measurements made at the two wavelengths and several independent measurements were made at each temperature. The quoted values had a reproducibility of ±5%. Similarly, rate constants were obtained by monitoring the decay of MV^{+} and $ZnTMPyP^{5+}$ at their respective wavelengths and the quoted values refer to the average of the two measurements. The errors associated with the rate constant determinations are ±10%.

Figure 1 shows the influence of temperature on the quantum efficiency ϕ_{ions} for formation of the redox ion products. It is seen that ϕ_{ions} increases with increasing temperature throughout the range 20 °C $< T <$ 80 °C. The effect is small from 20 to 50 °C and then the slope of the curve increases from 50 to 80 °C. According to the general scheme given earlier, the temperature effect on ϕ_{ions} may be associated with the triplet quenching rate constant k_Q, where

$$k_Q = \frac{k_D k_A}{k_A + k_{-D}} \tag{4}$$

since

$$\phi_Q = \frac{k_Q(\text{MV}^{2+})}{k_Q(\text{MV}^{2+}) + \tau^{-1}} \tag{5}$$

and/or with k_S increasing more rapidly with temperature than does k_B. For the former case the most probable influence of temperature is concerned with the electron transfer step (k_A) since the standard free-energy change for this process is close to zero. If [13]

$$k_A = A \exp\left(-\frac{E_A}{RT}\right) \tag{6}$$

then increasing the temperature will favour electron transfer and hence k_Q will increase. Since under the experimental conditions employed ϕ_Q is less than unity, the overall value of ϕ_{ions} will be susceptible to slight changes in the ϕ_Q term. In the latter case ΔG^0 for geminate recombination (k_S) is extremely negative ($\Delta G^0 \approx -1.58$ eV [8]) so that this step most probably involves only a minimal activation energy. Thus k_B should possess only a small temperature coefficient. Consequently any increase in ϕ_S with increasing temperature must be associated with k_S having a substantial temperature coefficient. In previous work [8] we have described equations that allow direct calculation of k_S and using these we do in fact find that k_S should increase markedly with increasing temperature.

In separate experiments we measured the rate constant k_R for reverse electron transfer between the separated ions and found that it decreased with increasing temperature. This seems rather surprising since from the Arrhenius equation

$$k_R = A \exp\left(-\frac{E_A}{RT}\right) \tag{7}$$

we might expect to find the opposite effect. In fact, even when the full equation that describes intermolecular reaction between ions of charges Z_A and Z_B

$$k_R = Z_0 \exp\left(-\frac{E_A}{kT}\right) \exp\left(-\frac{Z_A Z_B e^2 L}{\epsilon k r_{AB}}\right) \exp\left(-\frac{Z_A Z_B e^2 K}{2\epsilon kT}\right)(1 - 3LT) \tag{8}$$

is used we would expect k_R to increase with increasing temperature (L is Abegg's constant and the other symbols have been defined fully in previous papers [8, 9]).

The observed k_R and the calculated value (from eqn. (7) taking $A = 29.56 \times 10^9$ cm^3 mol^{-1} s^{-1} and $E_A = 1200$ cal) are plotted *versus* temperature
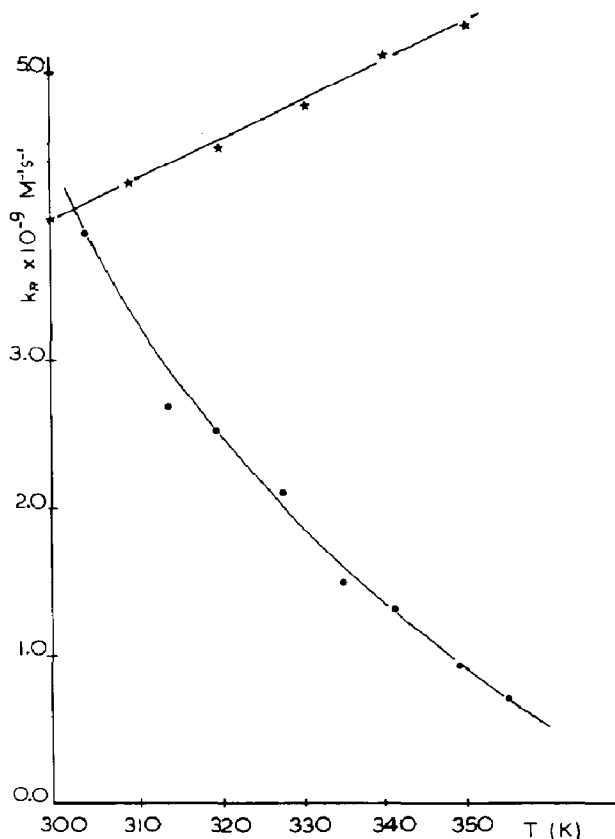
Fig. 2. Effect of temperature on the rate constant for deactivation of the ion pair complex: ●, experimental data; ★, theoretical data.

in Fig. 2. In its simplest form

$$k_R = \frac{k_{-S}k_B}{k_B + k_S} \qquad (9)$$

although spin statistical effects must be considered in a more thorough treatment. We have already argued that on increasing the temperature k_S increases much more than does k_B, and if this is true we might expect k_R to decrease with increasing temperature. Thus the dominant effect observed on increasing the temperature for the above system is that k_S increases whilst k_B remains much the same. This has the ideal effect in that ϕ_{ions} increases and k_R decreases. This is a very useful result since, if we are to use the reactions for the storage of solar energy, it seems likely that the ambient temperature of the solutions would be well in excess of that normally found in the laboratory.

Let us consider for a moment the sort of temperature that we might expect to be generated within the photolysis chamber of a practical solar energy storage device. In a crude experiment carried out on the roof of the Royal Institution on a sunny day, a beaker containing ZnTMPyP^{4+} in water reached a maximum temperature of 35 °C. Since this experiment was

performed in central London and no lenses, mirrors or optical concentrators were used, we might expect that in a practical solar energy storage device the temperature could be some 10 or 15 °C higher. In fact it would be beneficial to design a reactor in order to obtain the highest possible temperature since this would increase the yield of products as has been shown by the work described in this paper.

Acknowledgment

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