

**METHYLENE-BLUE-SENSITIZED PHOTO-OXIDATION OF TERPENES**

MARCO G. CASAROTTO and GERALD J. SMITH

*Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052 (Australia)*

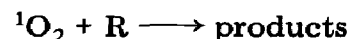
(Received February 25, 1987)

**Summary**

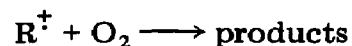
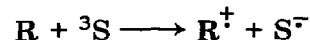
Electron transfer reactions occur between the triplet state of methylene blue and some terpenes, *e.g.* citronellol,  $\alpha$ -pinene and  $\beta$ -pinene. The rate constants  $k_{ET}$  for these reactions were determined but no linear correlation between  $\ln k_{ET}$  and the ionization potentials of the terpenes was found. This finding was explained in terms of stereoelectronic effects associated with the terpenes.

**1. Introduction**

Dye-sensitized photo-oxidation reactions have received a good deal of attention [1 - 4]. Two mechanisms for these reactions have been proposed, one of which involves the formation of singlet oxygen and subsequent reaction with the substrate:



where S is the sensitizing molecule and R is the substrate. The other mechanism involves direct electron transfer:



The relative importance of these two competing reaction mechanisms in different systems has been the subject of much discussion.

Some photo-oxygenations of terpenes sensitized by methylene blue are used in the synthesis of valuable chemicals for the perfume industry, *e.g.* rose oxide from citronellol [5]. These products result from the reaction of singlet oxygen with the terpene. However, when a powerful electron acceptor such as 9,10-dicyanoanthracene is used as a photosensitizer in the oxidation of  $\alpha$ -pinene,  $\beta$ -pinene or citronellol [6], the appearance of charge-transfer-stabilized exciplexes and the nature of some of the products suggest that electron transfer may occur in addition to the singlet-oxygen-mediated

oxidation. No direct observation has been made of electron transfer between these terpenes and methylene blue, which is the dye widely used to sensitize the singlet oxygen reactions. However, the relative importance of electron transfer reactions which may accompany the singlet oxygen reaction is of interest because of the commercial importance of these oxidations.

## 2. Experimental details

Dry ethanol was purified by distillation. Methylene blue (Fluka, puriss grade) was purified by the method described by Bergman and O'Konski [7]. D,L-Citronellol supplied by Sigma,  $\alpha$ -pinene (L. R. grade) supplied by Hopkins and Williams and  $\beta$ -pinene (practical grade) supplied by Fluka were used as received.  $1 \times 10^{-5}$  M solutions of methylene blue in alcohol were prepared with various concentrations of terpene present and all solutions were acidified slightly by brief exposure to hydrogen chloride vapour. Such treatment was found to be necessary to ensure that the triplet state of methylene blue formed on irradiation existed in the protonated form (in water,  $pK_a(^3\text{MB}) \approx 7$  [8]).

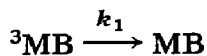
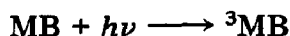
The solutions were placed in a 10 mm square fused silica fluorescence cell where they were deoxygenated by bubbling gently with oxygen-free nitrogen gas. The solutions were subjected to 30 ns pulses of 532 nm radiation from a Q-switched neodymium laser. The resulting transient absorption at 420 nm is associated with both the triplet state of methylene blue and the methylene blue free radical [9]. The absorption at 420 nm originating from the methylene blue free radical was measured at various concentrations of terpene and the data was analysed in a manner similar to that described by Kayser and Young [9] to derive the rate constant for the electron transfer reaction from the terpene to methylene blue.

## 3. Results and discussion

We found that the lifetime of the triplet state of methylene blue, in the deoxygenated, spectroscopic grade alcohol from several suppliers and in ethanol distilled in this laboratory which had not been acidified prior to photolysis was about an order of magnitude greater than the 6 - 7  $\mu\text{s}$  reported previously [9, 10]. We believe that these solvents must contain trace amounts of basic impurities which result in the triplet state of methylene blue existing, at least partly, in a deprotonated form. After acidification, in the manner described in Section 2, the decay was exponential with a lifetime of 5.9  $\mu\text{s}$  and we believe that under these conditions the triplet state of methylene blue exists in a protonated form [11].

The transient absorbance at 420 nm in the presence of terpene displayed a rapid initial decay associated with the triplet state of methylene blue followed by a very much slower decay lasting longer than 100  $\mu\text{s}$  associated with the methylene blue free radical,  $\text{MB}^\cdot$  [12].

The reaction steps occurring in this system are given in the following scheme:



where MB is methylene blue and T is the terpene.

With such a set of reactions

$$[\text{MB}^-]_i = \frac{k_{\text{ET}}[\text{T}]}{k_{\text{ET}}[\text{T}] + k_1} [{}^3\text{MB}]_0$$

where  $[\text{MB}^-]_i$  is the initial concentration of the semireduced methylene blue free radical following the laser flash and  $[{}^3\text{MB}]_0$  is the concentration of the triplet state of methylene blue produced in the absence of terpene.  $[\text{MB}^-]_i$  was determined by extrapolating the slowly decaying part of the transient absorption to the time of the laser flash and using the extinction coefficient for  $\text{MB}^-$  of  $1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  reported by Kayser and Young [9]. From the ratio of the intercept to the gradient of a plot of  $[\text{MB}^-]_i^{-1}$  against  $[\text{T}]^{-1}$  and the rate constant  $k_1$  in the absence of terpene, the rate constant  $k_{\text{ET}}$  of the electron transfer reaction can be obtained. The value of  $k_1$  was determined to be  $1.7 \times 10^5 \text{ s}^{-1}$  and the values of  $k_{\text{ET}}$  obtained for  $\alpha$ -pinene,  $\beta$ -pinene and citronellol are given in Table 1.

TABLE 1

Rate constants  $k_{\text{ET}}$  for the electron transfer from terpenes to the triplet state of methylene blue, and the ionization potentials of the terpenes

Terpene	$k_{\text{ET}}$ ( $\text{M}^{-1} \text{ s}^{-1}$ ) ( $\pm 10\%$ )	Ionization potential (eV) [13]
$\alpha$ -Pinene	$1.5 \times 10^4$	8.31
$\beta$ -Pinene	$5.2 \times 10^3$	8.7
Citronellol	$6.9 \times 10^6$	8.63

The comparatively high rate constant for electron transfer from citronellol to the triplet state of methylene blue is commercially undesirable because this reaction is in competition with the reaction producing the singlet oxygen needed for the conversion of citronellol to rose oxide. In the solutions used in the commercial photo-oxidation process (i.e. 5 vol.% citronellol in alcohol), if the solution is saturated with oxygen, about 10% of  ${}^3\text{MB}$  will react via electron transfer. This is calculated by taking the rate constant for the  ${}^3\text{MB}$  sensitized formation of singlet oxygen as  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [9]. By comparison, with the same concentration of the pinenes, it would be expected that only about 0.01% of  ${}^3\text{MB}$  reacts via electron transfer.

The large difference observed between the rate constants for electron transfer from the pinenes to <sup>3</sup>MB and that from citronellol to <sup>3</sup>MB cannot be predicted from their relative ionization potentials (see Table 1) [13]. Generally, in photoinduced electron transfer reactions there is a simple relationship between the ionization potential (or oxidation potential) of the electron donor and the rate constant. This is because the free energy change  $\Delta G_{ET}$  accompanying an electron transfer involving an excited state, electron-accepting species is given by

$$\Delta G_{ET} \approx IP_D - E(A^-/A) - E(A^*) - C \quad (1)$$

where  $IP_D$  is the ionization potential of the electron donor,  $E(A^-/A)$  is the reduction potential of the acceptor,  $E(A^*)$  is the energy of the excited state of the acceptor (in this case the triplet state energy of methylene blue) and  $C$  is a constant which includes the stabilization energy experienced on forming the ion pair. Rehm and Weller [14] found that when  $\Delta G_{ET} > 20 \text{ kJ mol}^{-1}$

$$\ln k_{ET} \propto -\Delta G_{ET}$$

Therefore, for a given electron acceptor, there should be a linear relationship between  $\ln k_{ET}$  and the  $IP_D$ . However, for the terpenes studied in this work, no such dependence of  $\ln k_{ET}$  on  $IP_D$  was found and therefore some additional factor must be important in determining the rates of these reactions. Stereoelectronic constraints associated with the reaction between <sup>3</sup>MB and  $\alpha$ - or  $\beta$ -pinene can explain this finding. When an electron is transferred from the double bond in the pinene to methylene blue, the resulting radical cation of pinene will not be stabilized by hyperconjugation of the lone electron with allylic C—H bonds to the extent experienced in a more flexible olefin such as citronellol, *i.e.* the constant  $C$  in eqn. (1) is smaller. This is because of configurational constraints on some of the allylic hydrogen atoms imposed by the ring and dimethylmethylene bridge structures in the  $\alpha$ - and  $\beta$ -pinenes.

A similar explanation has been proposed previously for the finding that the rate constants for the reactions of singlet oxygen with cyclic alkenes are lower than that for non-cyclic alkenes with the same ionization potentials [13].

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