Light-induced Electron-transfer Reactions. Part 1. Kinetics of Formation of Hydrogen Peroxide by Irradiation with Visible Light of Aqueous Solutions containing Tris(2,2′-bipyridine)ruthenium(II), Oxalic Acid, Manganese(II), and Oxygen

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Hydrogen peroxide is formed by the light-catalyzed reaction of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) in an aqueous dilute sulphuric acid solution containing oxalic acid, manganese(II) sulphate, and oxygen. The amount of H_2O_2 formed increases greatly with increasing intensity of visible light, with increasing concentration of $[Ru(bipy)_3]^{2+}$ or oxygen, and with increasing concentration of manganese(II), and increases linearly with increasing hydrogen-ion concentration up to about 0.3 mol dm^{-3} but then decreases with further increase. On the other hand, the rate of formation of H_2O_2 is almost independent of the concentration of oxalic acid when $[H_2C_2O_4] < [Mn^{II}]$ and slightly decreases when $[H_2C_2O_4] \geqslant [Mn^{II}]$. No formation of H_2O_2 is found in the dark or in the absence of any one of $[Ru(bipy)_3]^{2+}$, manganese(II), and oxalic acid. The formation of H_2O_2 is greatly retarded by the presence of copper(II) sulphate or methylviologen. A chain mechanism of reaction is proposed to account for these facts.

In previous studies [1-3] considerable amounts of hydrogen peroxide were found to be formed upon the slow addition of various oxidants to oxalic acid solutions of dilute sulphuric acid containing manganese(II) sulphate and oxygen. The oxidants included Mn^{VII}, Cr^{VI}, Ce^{IV}, and Co^{III} (refs. 1 and 3) as well as oxygen itself over longer periods.[2] In the present work no oxidizing agents were added and instead tris(2,2′-bipyridine)ruthenium(II) ion irradiated with visible light was used as a catalytic initiator for the formation of H_2O_2 in solutions of similar composition to those employed previously.[1-3] It was found that large amounts of hydrogen peroxide were formed continuously with time. The overall reaction is as in equation (1). It is of interest in the context of

$$C_2O_4^{2-} + 2\,H^+ + O_2 \longrightarrow H_2O_2 + 2\,CO_2 \qquad (1)$$

model solar-energy conversion systems.

Experimental

Chemicals.—The $[Ru(bipy)_3]Cl_2\cdot6H_2O$ (bipy = 2,2′-bipyridine) was prepared as described in the literature [4] and recrystallized twice. The purified product had an absorption coefficient of 1.4×10^4 dm^3 mol^{-1} cm^{-1} at 452 nm which is identical with that reported previously.[5] Manganese(II) sulphate of reagent grade was recrystallized twice from aqueous dilute sulphuric acid containing some methanol and dried at about 80 °C. The concentration of manganese(II) ion in the stock solution was determined by titration with a standard solution of disodium dihydrogenethylenediaminetetra-acetate. All other chemicals used were of guaranteed-reagent grade. Deionized water was further distilled with and without addition of permanganate ion in a glass still. The concentration of oxygen dissolved in solutions was adjusted by the saturation of air, pure oxygen, or a mixture of air and oxygen with nitrogen gas and bubbling them through the reaction solution.

Procedure.—The reaction vessel was a colourless glass bottle (5 dl; diameter 70 mm, thickness 1 mm, with 10 mm neck) placed in thermostatted water in a cubic bath of colourless glass (2 × 3 × 3 dm, thickness 6 mm). Unless otherwise stated, the sample was irradiated with light from two 100-W tungsten lamps which were placed 3 dm to the right- and left-hand sides of the centre of the reaction vessel. The irradiation continued throughout the reaction. Aliquot samples were withdrawn at appropriate times and mixed with cation-exchange resin [Dowex 50W-X8, 200—400 mesh, hydrogen form (Wako Pure Chemicals Co.), washed with distilled water] in order to remove the $[Ru(bipy)_3]^{2+}$ ion from the reacting solution and to stop the reaction. After filtration, the concentration of hydrogen peroxide formed was measured by polarography at −1.30 V *vs.* s.c.e. (saturated calomel electrode) at 25 °C in an acetate buffer (0.05 mol dm^{-3} each of acetic acid and sodium acetate), and 0.01% gelatine. The sum of the H_2O_2 formed and of the oxalic acid remaining was determined by titration with permanganate, thus yielding the concentration of the oxalic acid remaining. The concentration of $[Ru(bipy)_3]^{2+}$ ion was determined spectrophotometrically using the molar absorption coefficient of 1.4×10^4 dm^3 mol^{-1} cm^{-1} at 452 nm. The luminescence of $[Ru(bipy)_3]^{2+}$ was measured by using a Shimazu RF-500 spectrofluorometer at an excitation energy of 450 nm; when necessary, the oxygen dissolved in the $[Ru(bipy)_3]^{2+}$ solution was removed by bubbling of pure argon gas through it.

Results

Under all the experimental conditions employed the molar concentration of hydrogen peroxide formed was, within experimental error, equal to that of the oxalic acid which disappeared. Typical results are given in Table 1. It was confirmed that the concentration of $[Ru(bipy)_3]^{2+}$ did not change over 13 h and decreased only by about 2% on standing the solution for 38 h under the conditions given in Table 1. This fact indicates that the tris(2,2′-bipyridine)ruthenium(II) ion acts as a catalyst in the chain reaction. It was also confirmed, under the conditions in Table 1, that there was no appreciable formation of hydrogen peroxide over 5 h in the absence of $[Ru(bipy)_3]^{2+}$, but that its concentration was 5×10^{-4} mol dm^{-3} after 9 h and 2.7×10^{-3} mol dm^{-3} after 24 h, and that no H_2O_2 was observed in the absence of manganese(II) or oxygen, and in the dark under any conditions employed.

Effect of Light Intensity.—The irradiation with visible light of a solution containing oxalic acid, manganese(II) sulphate,

Table 1. Hydrogen peroxide formation by the light-induced electron-transfer reactions

t/h	$10^3[H_2O_2]$ formed / mol dm^{-3}	$10^3[H_2C_2O_4]$ disappeared / mol dm^{-3}
1	0.34	0.4
2	0.77	0.8
3	1.11	1.1
4	1.53	1.6
5	1.87	1.9

Conditions: 5 × 10^{-5} mol dm^{-3} $[Ru(bipy)_3]Cl_2$, 0.01 mol dm^{-3} oxalic acid, 0.05 mol dm^{-3} manganese(II) sulphate, and 0.1 mol dm^{-3} H_2SO_4; air-saturated; 25 °C; irradiation with two tungsten lamps.

Table 2. Effect of light intensity [a]

	$10^3[H_2O_2]_{formed}$/mol dm^{-3}			
t/h	Dark [b]	Room light	Two W lamps	Four W lamps
1	0.01	0.13	0.34	0.45
2	0.00	0.40	0.77	0.99
3	0.00	0.74	1.11	1.49
4	0.01	0.97	1.53	1.92
5	0.00	1.24	1.87	2.29
6	0.00	1.34	2.17	2.62

[a] Conditions as in Table 1, except for light intensity. [b] The reaction vessel was covered with black plastic adhesive tape.

sulphuric acid, and tris(2,2′-bipyridine)ruthenium(II) chloride resulted in the formation of hydrogen peroxide and its amount increased with increasing light intensity. Results obtained at various intensities of light are given in Table 2.

Temperature Dependence.—The effect of temperature on the rate of formation of hydrogen peroxide was examined over the range 5—40 °C. Plots of $[H_2O_2]_{formed}$ *vs*. t under the given conditions were rectilinear from $t = 0$ to $t = 5$ h, in accordance with equation (2). Arrhenius plots of log $k_{obs.}$

$$[H_2O_2]_{formed} = k_{obs.}\, t \qquad (2)$$

vs. T^{-1} were also rectilinear over the range 5—25 °C (see Figure 1) and the activation energy corresponding to the overall reaction is estimated to be 49 kJ mol^{-1} from these plots, excluding one plot at 40 °C which deviates from a straight line.

Effect of Oxalic Acid.—Unless oxalic acid was present in the reacting solution no hydrogen peroxide was formed. However, the presence of a small amount of oxalic acid led to a large amount of H_2O_2, and the values of $[H_2O_2]_{formed}$ at a given time were almost independent of the concentration of oxalic acid over the range 0.001—0.01 mol dm^{-3}; oxalic acid concentrations greater than 0.05 mol dm^{-3} led to a slightly reduced formation of H_2O_2 (see Figure 2). In Figure 2 are also shown the calculated concentrations of mono(oxalato)manganese(II) as a percentage of that of the total manganese(II). When the concentration of oxalic acid is 0.01 mol dm^{-3}, only 5% of the manganese(II) added is mono(oxalato)manganese(II) under these conditions. When $[H_2C_2O_4]_{added} \geqslant [Mn^{II}]_{added}$, some di(oxalato)manganate(II) may be present. The rate of formation of hydrogen peroxide was also almost independent of the oxalic acid concentration. When the initial concentration of oxalic acid was 1.0 × 10^{-3} mol dm^{-3}, all the oxalic acid had become hydrogen peroxide after 4 h, and the peroxide formed did not decompose over 10 h under continuous irradiation (see Figure 3). From results in Figure 3, it is also confirmed that the molar concentration of hydrogen peroxide formed is equal to that of the oxalic acid which disappears.

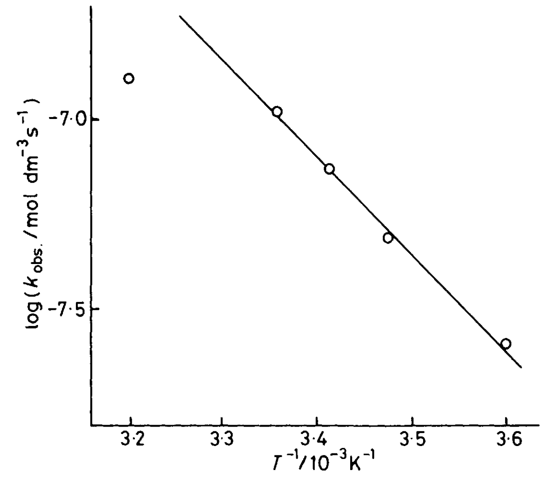

Figure 1. Arrhenius plot for the overall rate constant $k_{obs.}$ in equation (2). Conditions as in Table 1

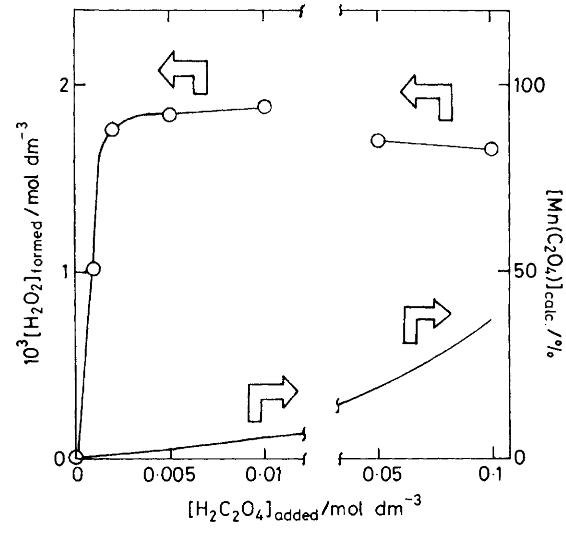

Figure 2. Effect of concentration of the oxalic acid added; $[H_2O_2]_{formed}$ indicates the concentration of hydrogen peroxide formed at a reaction time of 5 h. The other conditions are as in Table 1; $[Mn(C_2O_4)]_{calc.}$ is the concentration of mono(oxalato)manganese(II) calculated by using equilibrium constants (see text)

Effect of Hydrogen-ion Concentration.—When the concentration of sulphuric acid was varied, that of the hydrogen peroxide formed increased linearly with increasing hydrogen-ion concentration for $[H^+] < 0.28$ mol dm^{-3}, but for $[H^+] > 0.28$ mol dm^{-3} it tended to zero (see Figure 4). Under the conditions of Figure 4, the equilibria $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$, $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ (pK_1 = 1.99), $H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$ (pK_2 = 1.1), $HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$ (pK_1 = 3.6), and $Mn^{2+} + C_2O_4^{2-} \rightleftharpoons Mn(C_2O_4)$ (log K = 3.75) will be predominant. We calculated the variation of concentration of mono(oxalato)manganese(II) *i.e.* $Mn(C_2O_4)$, with that of sulphuric acid. The results are also

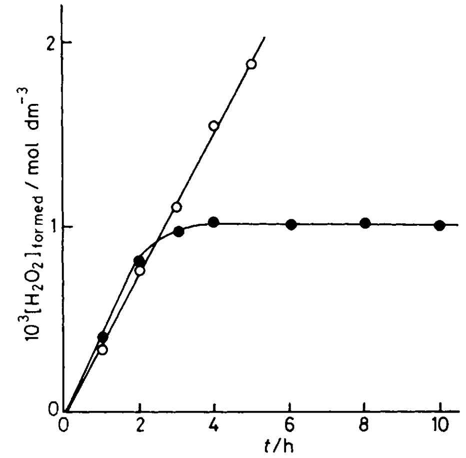

Figure 3. Effect of concentration of oxalic acid on the rate of formation of hydrogen peroxide, and the stability of the hydrogen peroxide formed. The initial concentrations of oxalic acid are 1.0 × 10^{-3} (●) and 0.01 mol dm^{-3} (○). Other conditions as in Table 1

shown in Figure 4. The concentration of $Mn(C_2O_4)$ decreases with increasing $[H^+]$; when the hydrogen peroxide formed is at a maximum, the concentration of $Mn(C_2O_4)$ is only 6 × 10^{-4} mol dm^{-3} which corresponds to 1.3% of the total manganese(II) added, and after the maximum it tends to zero (see Figure 4). Preliminary experiments showed that no appreciable decomposition of $[Ru(bipy)_3]^{2+}$ due to the photochemical reaction occurred at 1 mol dm^{-3} in sulphuric acid for 5 h under the conditions of Figure 4.

Effect of Manganese(II) *Concentration.*—The effect of manganese(II) was examined under the conditions given in Table 1. Plots of log $[H_2O_2]_{formed}$ *vs.* log $[Mn^{II}]_{added}$ are given in Figure 5, from which it is found that the rate of formation of hydrogen peroxide is approximately 0.3 order with respect to the manganese(II) concentration.

Effect of the Concentration of $[Ru(bipy)_3]^{2+}$.—The concentration of $[Ru(bipy)_3]^{2+}$ was unchanged during the reaction; that of the hydrogen peroxide formed was, within experimental error, proportional to the square root of the concentration of $[Ru(bipy)_3]^{2+}$ in the range 0—1 × 10^{-5} mol dm^{-3} and then, independent of it at concentrations larger than 3 × 10^{-5} mol dm^{-3} (see Figure 6).

Effect of Oxygen Concentration.—In Figure 7 are shown the results obtained with different pressures of oxygen gas in solution. It was thought that the $[H_2O_2]_{formed}$ or $k_{obs.}$ was approximately proportional to the square root of the oxygen pressure. In the case of the N_2-saturated run, commercially available nitrogen gas, which had been passed once through alkaline pyrogallol solution, was bubbled through the reaction mixture. However, a small amount of hydrogen peroxide was formed after 2 h, indicating that the reaction is very sensitive to oxygen. Incidentally, by using polarography we noticed that the removal of the oxygen dissolved in a solution containing $[Ru(bipy)_3]^{2+}$ ion was much harder than that in the absence of the complex ion.

Effect of Methylviologen and Copper(II) *Ions.*—Under the same conditions as in Table 1, hydrogen peroxide formation was retarded by the presence of methylviologen (1,1′-dimethyl-4,4′-bipyridinium dichloride) or copper(II) ion, the latter being a powerful inhibitor (see Figure 8).

Luminescence of $[Ru(bipy)_3]^{2+}$.—For clarification of the electron-transfer step in the initial stage of the reaction, the luminescence of $[Ru(bipy)_3]^{2+}$ was measured in pure water and in solutions of various constituents in the presence or in the absence of oxygen. The luminescence was not appreciably affected by the presence of manganese(II) sulphate, oxalic acid, and/or sulphuric acid in the absence as well as in the presence of oxygen, but was somewhat quenched by the presence of oxygen, methylviologen, or copper(II) sulphate. Some luminescence spectra are illustrated in Figure 9.

The characteristics of the formation of hydrogen peroxide are summarized in Table 3.

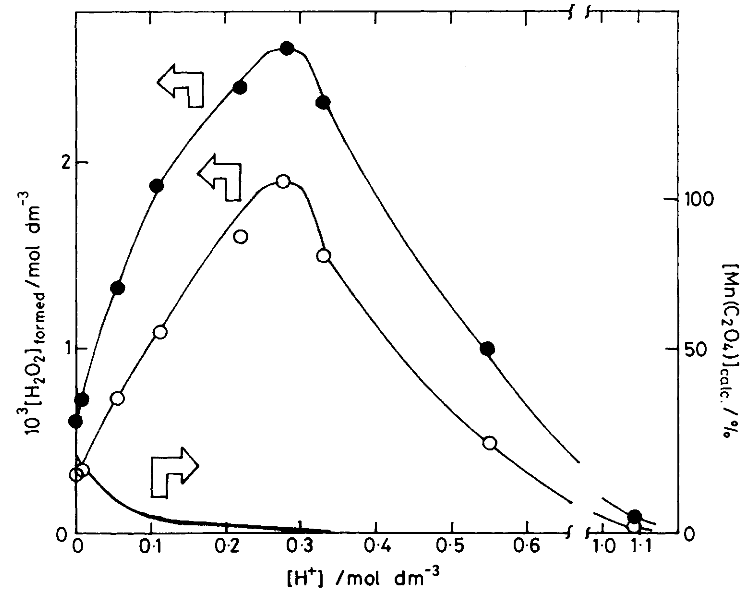

Figure 4. Relationships between $[H_2O_2]_{formed}$, $[H^+]$, and $[Mn(C_2O_4)]_{calc.}$ for results at t = 3 (○) and 5 h (●). Other conditions as those in Table 1; $[Mn(C_2O_4)]_{calc.}$ was obtained as in Figure 2

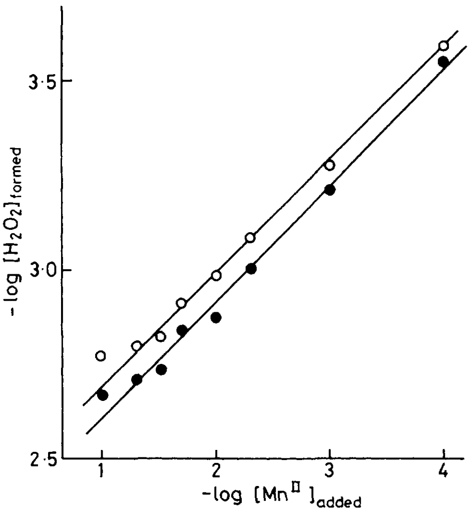

Figure 5. Plots of $-\log [Mn^{II}]_{added}$ *vs.* $-\log [H_2O_2]_{formed}$ at $t = 4$ (○) and 5 h (●). Other conditions as in Table 1

Discussion

Manganese(III) ion can form mono-, di-, and tri-oxalato-complexes with oxalate, and we will use the notation $Mn^{III}(ox)$ for these complexes. Manganese(II) ion can also form one or more complexes with oxalate, and we use the symbol Mn^{II} for all forms of manganese(II) involving the aquated manganese(II) ion. As with $Mn^{III}(ox)$, the equilibria are dependent on the concentrations of manganese, oxalate, and acid, and on temperature. As can be seen in Figures 2 and 4, most Mn^{II} under the conditions employed in this study is in the aquated form.

From results of the luminescence measurements, the photo-excited species $[Ru(bipy)_3]^{2+*}$ does not react, at least apparently, with Mn^{II} under the conditions, and reaction (4) will be negligible. On the other hand, the well known reactions (5)—(7) could occur to some extent, where k_q represents the

$$[Ru(bipy)_3]^{2+} \xrightarrow{h\nu} [Ru(bipy)_3]^{2+*} \quad (3)$$

$$[Ru(bipy)_3]^{2+*} + Mn^{II} \longrightarrow [Ru(bipy)_3]^{+} + Mn^{III}(ox) \quad (4)$$

$$O_2 + [Ru(bipy)_3]^{2+*} \longrightarrow O_2^- + [Ru(bipy)_3]^{3+};$$
$$k_q = 5.5 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ (ref.\ 6) \quad (5)$$

$$MV^{2+} + [Ru(bipy)_3]^{2+*} \longrightarrow MV^{+} + [Ru(bipy)_3]^{3+};$$
$$k_q = 4.6 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}\ (ref.\ 6) \quad (6)$$

$$Cu^{2+} + [Ru(bipy)_3]^{2+*} \longrightarrow Cu^{+} + [Ru(bipy)_3]^{3+};$$
$$k_q = 6.2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}\ (ref.\ 7) \quad (7)$$

rate constant for the corresponding quenching reaction and MV^{2+} is methylviologen ion. The $[Ru(bipy)_3]^{3+}$ generated by these reactions is thermodynamically a powerful oxidant with $E_{\frac{1}{2}} = 1.29$ V,[8] and is fully capable of oxidizing the oxalate ion in acidic solution to produce $C_2O_4^{\cdot -}$ (or $CO_2^{\cdot -}$) radical. This leads to the expectation that hydrogen peroxide will be formed even in the absence of manganese(II), according to reactions (8)—(12).

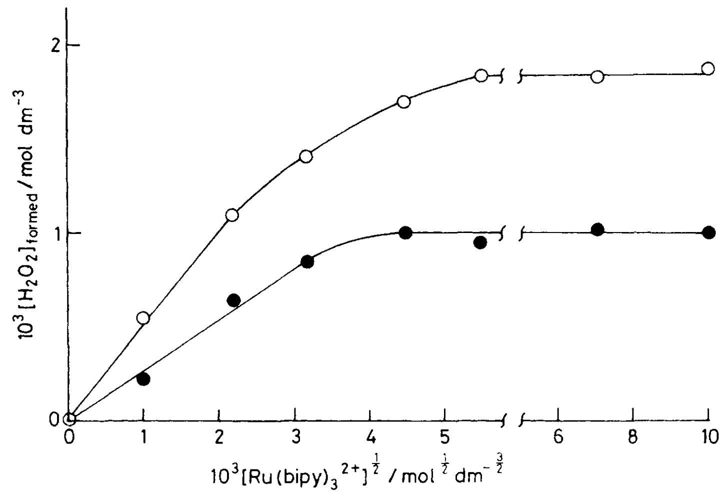

Figure 6. Plots of $[H_2O_2]_{formed}$ *vs.* $[Ru(bipy)_3{}^{2+}]^{\frac{1}{2}}$ at $t = 3$ (●) and 5 h (○). Other conditions as in Table 1

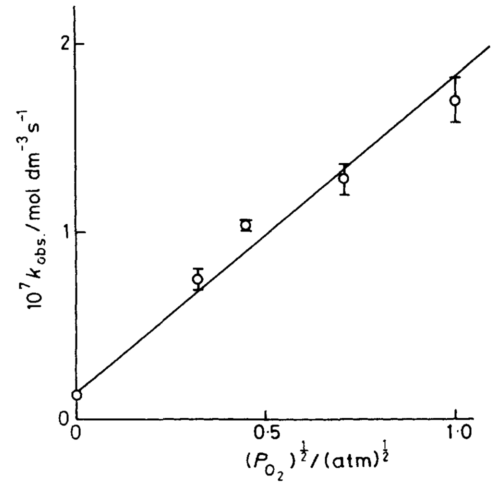

Figure 7. Plots of $k_{obs.}$ in equation (2) against the square root of the oxygen pressure (1 atm = 101 325 Pa). Conditions as in Table 1

Table 3. Characteristics of the formation of hydrogen peroxide [a]

Series no.	Reaction time (t)	$[Ru(bipy)_3^{2+}]$	$[O_2]$	$[Mn(SO_4)]$	$[H_2C_2O_4]$	$[H^+]$	Light intensity	Temperature	$[H_2O_2]_{formed}$
1	Various	zero	———	———	———	———	———	———	none
2	Various	———	zero	———	———	———	———	———	none
3	Various	———	———	zero	———	———	———	———	none
4	Various	———	———	———	zero	———	———	———	none
5	Various	———	———	———	———	———	zero	———	none
6	Various	———	———	———	———	———	———	———	proportional to t
7	———	Various	———	———	———	———	———	———	*b*
8	———	———	Various	———	———	———	———	———	proportional to $[O_2]^{\frac{1}{2}}$
9	———	———	———	Various	———	———	———	———	proportional to $[Mn^{II}]^{0.3}$
10	———	———	———	———	Various	———	———	———	independent of $[H_2C_2O_4]$
11	———	———	———	———	———	Various	———	———	increases linearly to a maximum, then decreases
12	———	———	———	———	———	———	Various	———	increases with increasing light intensity
13	———	———	———	———	———	———	———	Various	increases with increasing temperature
14	———	———	———	———	———	———	———	———	decreases in presence of MV^{2+} or Cu^{2+}

[a] Short lines indicate constant values. [b] $[H_2O_2]_{formed}$ is, within experimental error, proportional to $[Ru(bipy)_3^{2+}]^{\frac{1}{2}}$ at low concentration and then reaches a constant value at the high concentration (see Figure 6).

$$[Ru(bipy)_3]^{3+} + C_2O_4^{2-} \longrightarrow [Ru(bipy)_3]^{2+} + C_2O_4^{\cdot -} \text{ (or } CO_2^{\cdot -} + CO_2) \quad (8)$$

$$CO_2^{\cdot -} + O_2 \longrightarrow CO_2 + O_2^-; \quad k = 2.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 9)} \quad (9)$$

$$O_2^- + H^+ \rightleftharpoons HO_2; \; pK_a = 4.75 \text{ (ref. 10)} \quad (10)$$

$$2\,HO_2 \longrightarrow O_2 + H_2O_2; \quad k = 7.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 10)} \quad (11)$$

$$[Ru(bipy)_3]^{2+} + HO_2 + H^+ \longrightarrow [Ru(bipy)_3]^{3+} + H_2O_2 \quad (12)$$

However, no appreciable formation of H_2O_2 was found in the absence of manganese(II) in a solution containing oxalic acid, sulphuric acid, and oxygen, methylviologen, or copper(II) sulphate. This fact is probably attributable to the much faster back reactions in equations (5)—(7) than the forward reaction of (8). Consequently we assume the mechanism in equations (13)—(18) to account for the reaction characteristics given in Table 3. The overall reaction is then written as in equation (19), which is essentially the same as reaction (1). Reactions (13)—(18) constitute a chain reaction in which (13) is the initiating reaction and (18) a probable terminating reaction. The assumption of steady-state concentrations for HO_2, [Ru-

$$[Ru(bipy)_3]^{2+} + O_2 + H^+ + h\nu \xrightarrow{k_1} [Ru(bipy)_3]^{3+} + HO_2 \quad (13)$$

$$Mn^{II} + [Ru(bipy)_3]^{3+} \xrightarrow{k_2} Mn^{III}(ox) + [Ru(bipy)_3]^{2+} \quad (14)$$

$$Mn^{II} + HO_2 + H^+ \xrightarrow[(ox^{2-})]{k_3} Mn^{III}(ox) + H_2O_2 \quad (15)$$

$$Mn^{III}(ox) \xrightarrow{k_4} Mn^{II} + CO_2 + CO_2^{\cdot -} \quad (16)$$

$$CO_2^{\cdot -} + O_2 + H^+ \xrightarrow{k_5} HO_2 + CO_2 \quad (17)$$

$$Mn^{III}(ox) + HO_2 \xrightarrow{k_6} Mn^{II} + H^+ + O_2 \quad (18)$$

$$O_2 + 2\,H^+ + h\nu \xrightarrow{(ox^{2-})} H_2O_2 + 2\,CO_2 \quad (19)$$

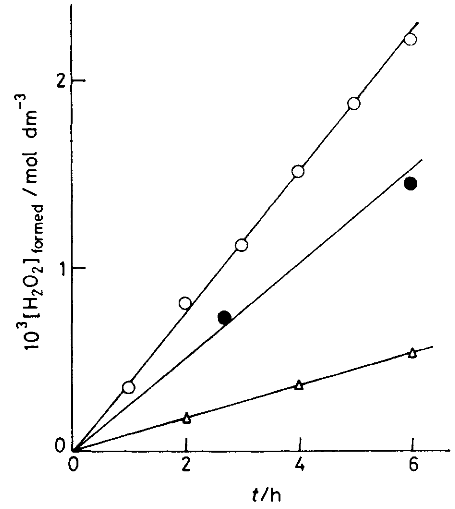

Figure 8. Effect of methylviologen and copper(II) ions: ○, conditions as in Table 1; ●, as above but containing 1×10^{-3} mol dm^{-3} methylviologen; △, as in ○ but containing 1×10^{-4} mol dm^{-3} copper(II) sulphate

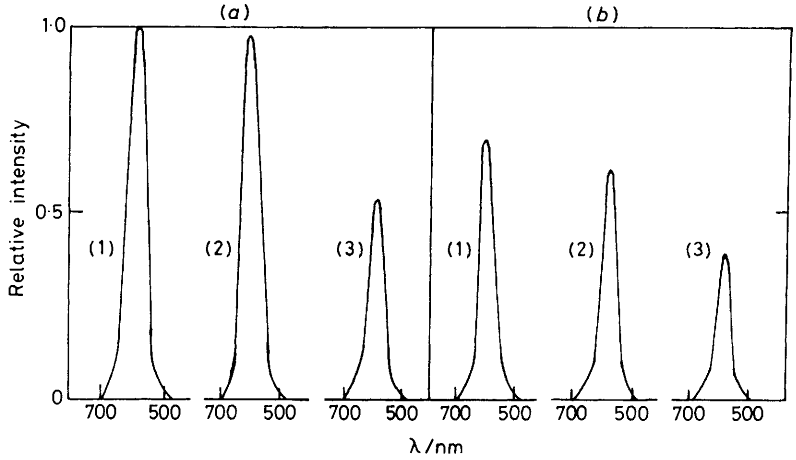

Figure 9. Luminescence spectra of $[Ru(bipy)_3]^{2+}$ ion in the absence of oxygen (*a*) and in the presence of air dissolved in solution (*b*). Compositions: (1) as in Table 1; (2) same as in (1) but also containing 1×10^{-4} mol dm^{-3} copper(II) sulphate; (3) same as in (1) but also containing 1×10^{-3} mol dm^{-3} methylviologen

$$d[H_2O_2]/dt = k_3[Mn^{II}][HO_2][H^+] = \sqrt{\{k_1k_3k_4[Ru(bipy)_3{}^{2+}][Mn^{II}][O_2](hv)/k_6\}}\ [H^+] \qquad (20)$$

$$[H_2O_2]_{formed} = \sqrt{\{k_1k_3k_4[Ru(bipy)_3{}^{2+}][Mn^{II}][O_2](hv)/k_6\}}\ [H^+]t \qquad (21)$$

$(bipy)_3]^{3+}$, $Mn^{III}(ox)$, and $CO_2{}^{\cdot -}$ leads to equations (20) and (21). Equation (21) appears to be in agreement with the observed facts in respect of (1) the linear plots of $[H_2O_2]_{formed}$ *vs.* *t*, (2) the linear plots of $[H_2O_2]_{formed}$ *vs.* $[H^+]$ at $[H^+] < 0.28$ mol dm^{-3} (Figure 4), (3) the linear plots of $[H_2O_2]_{formed}$ *vs.* $[Ru(bipy)_3{}^{2+}]^{\frac{1}{2}}$ at $[Ru(bipy)_3{}^{2+}] < 1 \times 10^{-5}$ mol dm^{-3} (Figure 6), (4) the linear plots of $k_{obs.}$ of equation (2) *vs.* $(P_{O_2})^{\frac{1}{2}}$ (Figure 7), and (5) the increase of $[H_2O_2]_{formed}$ with increasing light intensity (Table 2). The deviation of the observed order of 0.3 in respect of $[Mn^{II}]$ from the 0.5 to be expected from equation (21) is not clearly understood, but might be due to the complexing equilibria between manganese(II) and oxalate ions, and to the occurrence of some competitive reactions dependent on the concentration of manganese(II). The specific dependence of the oxalic acid concentration on the $[H_2O_2]_{formed}$ might be also important in this context. When $[H_2C_2O_4]_{added} \geqslant [Mn^{II}]_{added}$, the rate of formation of hydrogen peroxide slows down slightly (Figure 2) due to the formation of di- and/or tri-(oxalato)manganese(III) which decompose at a slower rate than mono(oxalato)manganese(III). As can be seen from Figure 3, the rate of formation of hydrogen peroxide is almost independent of the concentration of oxalic acid, indicating that the rates of the reactions (14)—(16) are not greatly influenced by the oxalic acid concentration, although they cannot occur in the absence of oxalic acid. The value of $[H_2O_2]_{formed}$ became almost constant, independent of the concentration of $[Ru(bipy)_3]^{2+}$, at $>3 \times 10^{-5}$ mol dm^{-3} (Figure 6). This fact could be accounted for by the occurrence of the back reactions in equations (13) and (14) under such conditions. The back reaction in equation (13) may compete with the forward reaction in (15) and thus unless manganese(II) is present the back reaction in equation (13) could predominate. The deviation from the observed facts might also be due to the occurrence of probable competitive reactions such as the back reactions in equations (13) and (14). The retardation by MV^{2+} and Cu^{2+} of the formation of hydrogen peroxide could be attributable to the competitive quenching [equations (6) and (7)] of $[Ru(bipy)_3]^{2+}$ by these ions, and to the subsequent occurrence of reactions (22) and (23) which will compete with reactions (14) and (16), respectively.

$$[Ru(bipy)_3]^{3+} + MV^+ \text{ (or } Cu^+) \longrightarrow [Ru(bipy)_3]^{2+} + MV^{2+} \text{ (or } Cu^{2+}) \qquad (22)$$

$$Mn^{III}(ox) + MV^+ \text{ (or } Cu^+) \longrightarrow Mn^{II} + MV^{2+} \text{ (or } Cu^{2+}) \qquad (23)$$

From equations (2) and (21), $k_{obs.}$ may be expressed as in equation (24). Therefore, the activation energy $E_{obs.}$ which is

$$k_{obs.} = \{k_1k_3k_4[Ru(bipy)_3{}^{2+}][Mn^{II}][O_2](hv)/k_6\}^{\frac{1}{2}}\ [H^+] \qquad (24)$$

obtained from Arrhenius plots of log $k_{obs.}$ *vs.* T^{-1} (Figure 1) is a composite function of the activation energies of the separate steps in the reaction, *i.e.* $2E_{obs.} = E_1 + E_3 + E_4 - E_6$. If the activation energy for the terminating reaction E_6 is assumed to be negligibly small, that for the initiation and for the propagation steps is estimated to be $E_1 + E_3 + E_4 = 98$ kJ mol^{-1}. (The subscripts of E_n refer to k_n rather than the equation numbers.) Finally, it is noted that the photo-oxidation of manganese(II) by molecular oxygen, *i.e.* $Mn^{II} + O_2 + H^+ + hv \longrightarrow Mn^{III}(ox) + HO_2$, is much slower than reactions (13) and (14), being fully negligible under the conditions employed in the present work.

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