

PHOTOLYSIS OF $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ IN DIMETHYLFORMAMIDE

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Summary

The photolysis of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in dimethylformamide solutions on irradiation at $\lambda = 313$ nm in the ligand-metal charge transfer band of the complex was studied. A marked influence of O_2 on the reaction quantum yield at a complex concentration of about 10^{-4} M and 25°C was observed, as well as H_2O_2 generation during the photolysis. The reaction mechanism proposed involved two intermediates which were detected using electron paramagnetic resonance spectrometry and flash photolysis measurements.

1. Introduction

The photolysis of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in aqueous solutions and in solvent mixtures at low temperatures has been extensively studied [1 - 3]. These studies [1] have resulted in quantum yield values of about unity, independent of the complex and O_2 concentrations, when the complex was irradiated in the ligand-metal charge transfer (LMCT) band. Low temperature studies [2, 3] have revealed the generation of two reaction intermediates, assigned by Posnyak and coworkers to $[\text{Mn}(\text{C}_2\text{O}_4)_2(\text{C}_2\text{O}_4^{\cdot-})]^{3-}$ and $\text{C}_2\text{O}_4^{\cdot-}$. These intermediates in the photolysis mechanism are both O_2 sensitive. This does not agree with the quantum yield values which are O_2 independent [1]. However, our studies of the photolysis of $[\text{Mn}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{K}$ in dimethylformamide (DMF) solutions [4, 5] have revealed a marked dependence of the quantum yield on both O_2 and complex concentration in the range $1 \times 10^{-4} - 2 \times 10^{-3}$ M. At a complex concentration of 1×10^{-3} M the quantum yield reaches its upper limit and is then almost independent of both the O_2 and complex concentrations.

The aim of this work was to obtain some information about the oxygen effect and the intermediates involved in the photolysis of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in DMF solutions so that a consistent reaction mechanism could be proposed.

2. Experimental

The complex $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 3\text{H}_2\text{O}$ was prepared using the method described elsewhere [6]. Carlo Erba reagent grade DMF was used as solvent. Its water content of 0.1% was determined by Karl Fischer titration. The complex concentration range of 1×10^{-4} - 5×10^{-5} M was limited because of the low solubility of the complex in DMF.

In order to perform irradiations in the absence or presence of O_2 , argon or O_2 were bubbled through the solutions of the complex for longer than $\frac{1}{2}$ h before each experiment. Traces of H_2O_2 which appeared during the photolysis were detected spectrophotometrically using $\text{Ti}(\text{SO}_4)_2$ reagent.

The irradiations at $\lambda = 313$ nm, in the LMCT band of the complex, were carried out using a photochemical set-up and an irradiation procedure which have been described elsewhere [5]. The UV spectra were recorded on an SP-800 Pye-Unicam instrument. Quantum yield calculations were performed using an equation derived from that proposed by Kling *et al.* [7] so that the internal light filtering effect could be taken into account:

$$\phi = V/\epsilon\bar{Q}_0 t \quad (1)$$

$$V = (\epsilon_A - \epsilon_B)(c_0 - c) + 2.303\epsilon_B c_0 \log\left(\frac{c_0}{c}\right) + \frac{1}{l} \log\left(\frac{1 - T_0}{1 - T}\right) + \epsilon_B c_0 \bar{R}_1 \quad (2)$$

In these equations ϕ is the reaction quantum yield, \bar{Q}_0 is the mean incident light intensity (M min^{-1}), l is the optical depth of the reaction system (cm), c_0 and c are the initial concentration and the concentration after an irradiation interval t respectively (M), T_0 and T are the initial transmittance of the system and the transmittance after an irradiation interval t respectively, ϵ_A ($= 3.20 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and ϵ_B ($= 5.47 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$) are the molar absorptivities of the complex and the reaction products respectively at $\lambda = 313$ nm, and \bar{R}_1 is the average of the error which affects the value of V by neglecting an infinite expansion series in eqn. (2).

Electron paramagnetic resonance (EPR) spectra were recorded at liquid nitrogen temperature using an ART 1 spectrometer; the flash photolysis measurements were performed on a D-10 Applied Photophysics apparatus.

3. Results and discussion

Spectra of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in DMF at various times during the photolysis are shown in Fig. 1. The quantum yield data derived from these spectra for oxygen-saturated and deoxygenated solutions are given in Tables 1 and 2 respectively. The quantum yield values obtained in this work agree with those previously reported [1]. For deoxygenated solutions of the complex a value of 1.23 ± 0.12 was obtained which is slightly different from that of 1.00 reported by Porter *et al.* [1]. This small difference can be explained in terms of the change of solvent.

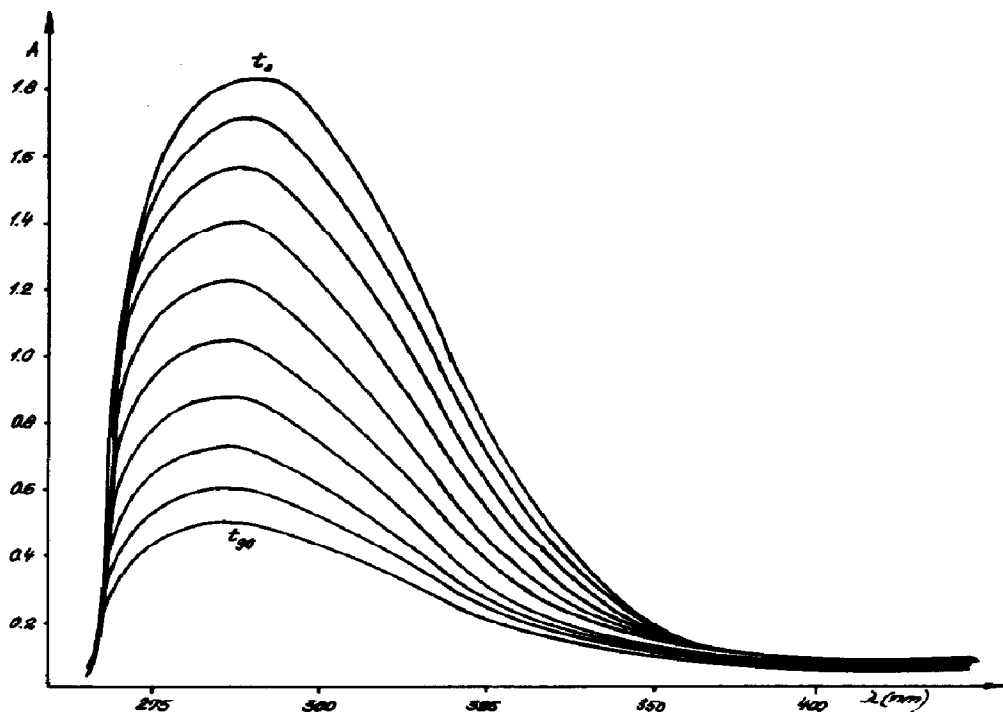


Fig. 1. Absorption spectra of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ at 25 °C in DMF at various times during the photolysis: $c_0 = 1.31 \times 10^{-4} \text{ M}$; $\lambda = 313 \text{ nm}$; $\bar{Q}_0 = 1.42 \times 10^{-6} \text{ M min}^{-1}$; $\Delta t = 10 \text{ min}$.

TABLE 1

Quantum yield data for the photolysis of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in oxygen-saturated DMF^a

t (min)	V (cm^{-1})	$\epsilon_A \bar{Q}_0 t \times 10^3$ (cm^{-1})	α (%)	ϕ^b
0	0.0	0.0	0.0	—
5	15.7	23.0	4.0	0.68
10	26.0	46.1	7.0	0.56
20	56.2	92.2	15.0	0.61
30	87.8	138.2	23.0	0.63
42	133.6	193.5	34.0	0.69
51	165.0	235.0	41.0	0.71

^a $c_0 = 1.01 \times 10^{-4} \text{ M}$; $\bar{Q}_0 = 1.55 \times 10^{-6} \text{ M min}^{-1}$.

^b $\phi_{\text{av}} = 0.65 \pm 0.07$.

It can be seen that the quantum yield value for a deoxygenated solution is about twice that for an oxygen-saturated solution. Additional data were obtained for aerated solutions and the quantum yield value was almost the same as that determined in oxygen-saturated solutions, e.g. 0.73 ± 0.06 (air)

TABLE 2

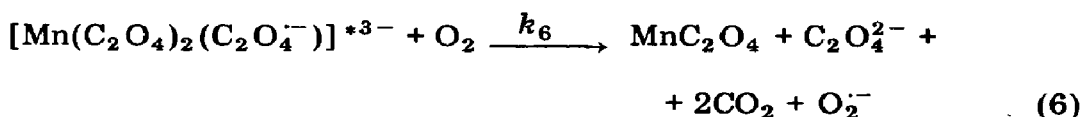
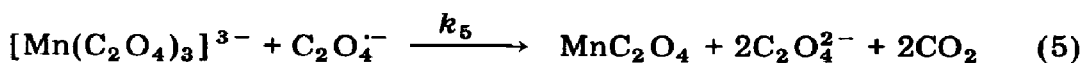
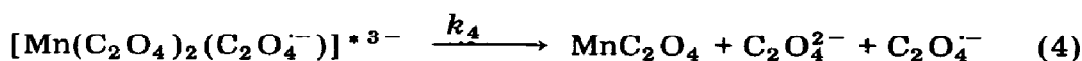
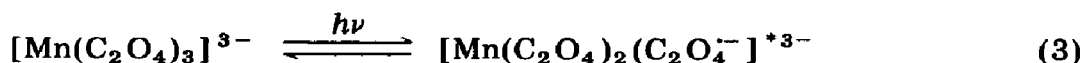
Quantum yield data for the photolysis of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in deoxygenated DMF^a

t (min)	V (cm^{-1})	$\epsilon_A \bar{Q}_0 t \times 10^3$ (cm^{-1})	α (%)	ϕ^b
0	0.0	0.0	0.0	—
15	92.5	68.2	35.6	1.36
33	177.0	150.0	53.3	1.18
51	278.9	231.7	66.7	1.20
75	398.0	340.8	75.6	1.17

^a $c_0 = 4.5 \times 10^{-5}$ M; $\bar{Q}_0 = 1.42 \times 10^{-6}$ M min⁻¹.^b $\phi_{av} = 1.23 \pm 0.12$.

and 0.65 ± 0.07 (oxygen). Our results regarding the effect of O_2 on the quantum yield data are similar to those obtained by Rowan *et al.* [8] for the photolysis of $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$.

This O_2 effect and the quantum yield values for deoxygenated solutions, as well as the photolysis data [1] for aqueous solutions or mixtures of solvents [2, 3], of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ led us to consider the following reaction sequence:



Reactions (3) - (5) take place in the absence of O_2 , whereas in the presence of O_2 processes (6) and (7) have to be taken into account.

The quantum yield values in oxygenated and deoxygenated solutions respectively show that reactions (6) and (7) compete efficiently with reaction (5), *i.e.*

$$k_5 [[\text{Mn}(\text{C}_2\text{O}_4)_3]^{3-}] \ll (k_6 + k_7)[\text{O}_2]$$

For $[\text{O}_2] \approx 10^{-3}$ M and, in our experiments, for $[[\text{Mn}(\text{C}_2\text{O}_4)_3]^{3-}] \leq 10^{-4}$ M this condition is fulfilled [9].

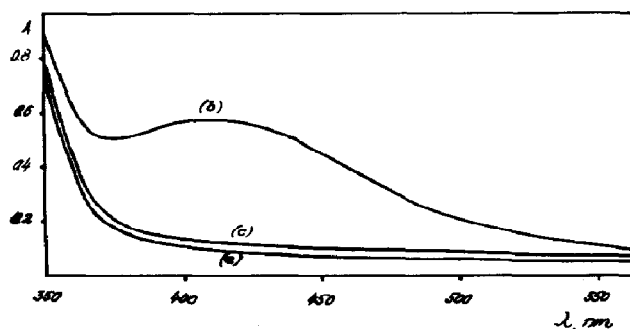
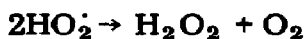
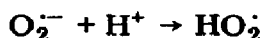
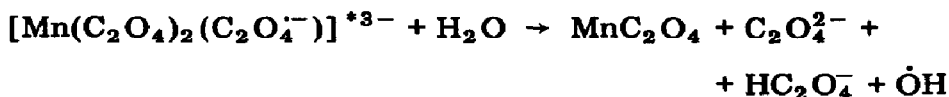


Fig. 2. H_2O_2 generation in: curve (a), a deoxygenated solution in the dark; curve (b), an oxygenated irradiated solution; curve (c) a deoxygenated irradiated solution.

However, the O_2^- intermediate generated in processes (6) and (7) produces H_2O_2 according to the scheme of Kolthoff *et al.* [10]:



The generation of H_2O_2 in irradiated oxygenated solutions was detected by the appearance of the characteristic yellow colour when $\text{Ti}(\text{SO}_4)_2$ reagent was added (see Fig. 2). Moreover a pH increase of about 2 units occurred during the photolysis. This result can be explained by the following sequence:



This sequence was adapted from that given by Gupta and Ghosh [11] and has also been used for the thermal decomposition of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ in DMF [12].

The value we obtained for the quantum yield in the primary step, *i.e.* 0.65 ± 0.07 , is probably the result of the internal conversion of excited molecules of the complex to the ground state (reaction (3)).

In order to obtain some information about the intermediates in the reaction scheme, we carried out irradiations in frozen DMF solutions of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ at 77 K. Qualitatively we observed that the reddish colour of the complex turned to yellow, similar to the results of Posnyak *et al.* [3]. The yellow compound was destroyed if the irradiation lasted longer than 10 - 20 min, showing that it is also photosensitive. Subsequent to the formation of the yellow compound we obtained an EPR spectrum similar to that recorded for $[\text{Mn}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{K}$ under the same conditions [4].

We obtained more information about the intermediates by using the flash photolysis technique. Thus, in accordance with our suppositions, we

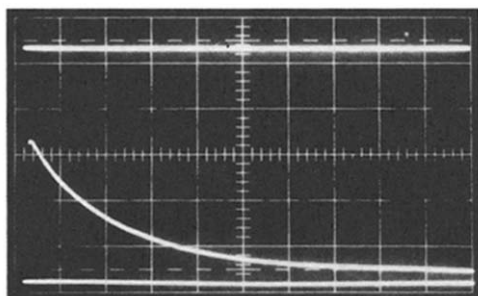


Fig. 3. A typical decay curve of the intermediate which absorbed at 400 nm in a DMF deoxygenated solution of $[\text{Mn}(\text{C}_2\text{O}_4)_3]\text{K}_3$ at 27 °C: 1000 J integral light; horizontal scale, 0.5 ms cm^{-1} ; vertical scale, 0.5 V cm^{-1} .

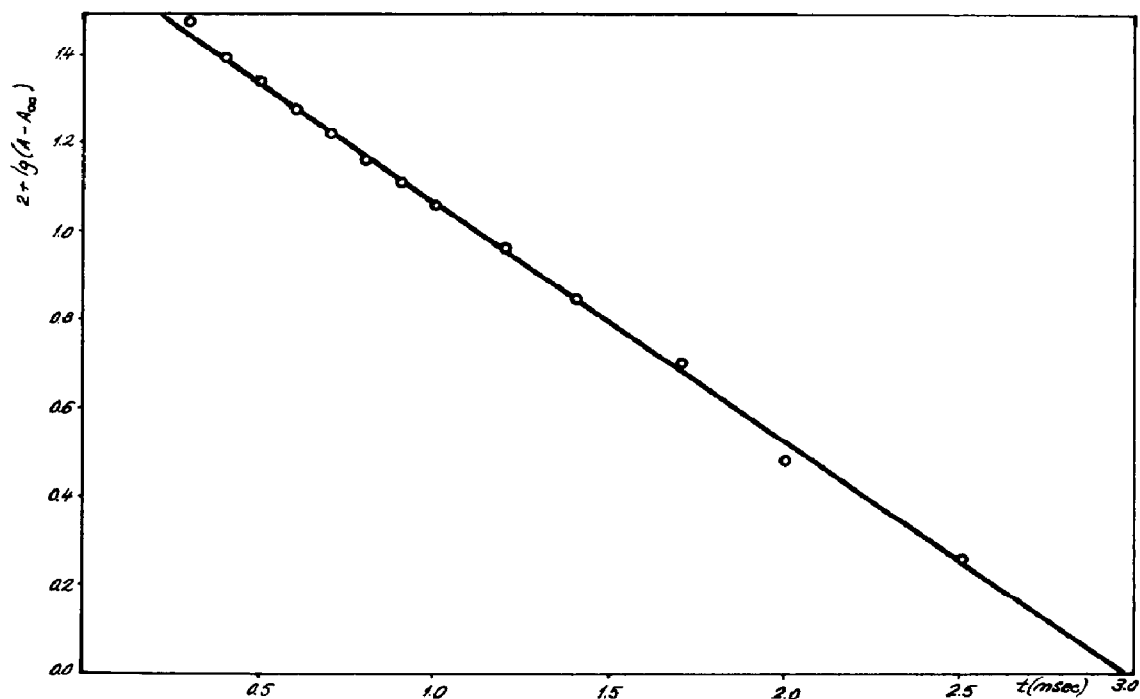


Fig. 4. First order kinetic plot for the decay of the intermediate which absorbed at 400 nm ($k_4 = 1.31 \times 10^3 \text{ s}^{-1}$).

detected in a deoxygenated solution an intermediate which absorbed at $\lambda = 400 \text{ nm}$, which is in agreement with the colour change just described. We used 1000 J flashes of integral (UV + visible) or just visible light with a half-time of 3 - 5 μs . A typical decay curve of the observed intermediate is shown in Fig. 3. It can be seen in Fig. 4 that the decay of the intermediate obeyed first order kinetics. If the solution was only partially deoxygenated, the intermediate absorption was lowered and the reaction order exceeded unity (e.g. 1.5); this means that O_2 quenching competed efficiently with the natural decay of the intermediate. In thoroughly deoxygenated solutions we obtained

a rate constant value of $1.31 \times 10^3 \text{ s}^{-1}$ which is 5 - 6 times larger than that obtained in $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{K}_3$ flash photolysis [13, 14]. Our preliminary results are also different from those obtained for $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$ flash photolysis [15] when two long-lived intermediates were detected.

As far as the structure of $[\text{Mn}(\text{C}_2\text{O}_4)_2(\text{C}_2\text{O}_4^{\cdot-})]^{\cdot 3-}$ is concerned, we cannot say precisely whether it involves a bidentate or a monodentate $\text{C}_2\text{O}_4^{\cdot-}$ radical coordinated to the Mn(II) centre. However, the difference between the rate constants for the Mn(II) intermediate ($k_4 = 1.31 \times 10^3 \text{ s}^{-1}$) and the Co(II) intermediate ($k = 58 \text{ s}^{-1}$) indicates that the monodentate intermediate is more favoured.

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