

## PHOTOLYSIS OF $K_3[Fe(C_2O_4)_3]$ IN DIMETHYLFORMAMIDE

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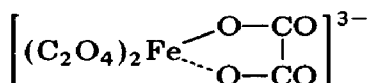
### Summary

The photolysis of  $K_3[Fe(C_2O_4)_3]$  in deoxygenated dimethylformamide solutions at wavelengths of 313 and 366 nm in the ligand-to-metal charge transfer (LMCT) absorption band of the complex was studied. The overall reaction quantum yield was independent of the irradiation wavelength and of the concentration of the complex in the range  $10^{-5}$  -  $10^{-4}$  M at 25 °C. A reaction intermediate, which is believed to be a  $C_2O_4^{\cdot-}$  radical coordinated to an iron(II) complex oxalate, was detected by flash photolysis experiments and was found to have a decay constant of  $(1.5 \pm 0.1) \times 10^3 s^{-1}$ . The proposed photolysis mechanism enables the efficiency of the intramolecular LMCT deactivation process to be estimated.

### 1. Introduction

The photolysis of  $K_3[Fe(C_2O_4)_3]$  in acidic aqueous solutions has been studied extensively, particularly in connection with UV and visible chemical actinometry [1 - 5], and the dissolved oxygen has been found to have little effect on the overall reaction quantum yields. Low pH values were used to prevent the precipitation of  $FeC_2O_4$  so that the main photosensitive species studied were  $[Fe(C_2O_4)_2(H_2O)_2]^-$  and  $[Fe(C_2O_4)(H_2O)_4]^+$  [6, 7]. The work of Allmand and coworkers [8, 9] appears to be the only study of the photochemistry of  $[Fe(C_2O_4)_3]^{3-}$  species in aqueous solution performed using continuous irradiation. Their experiments revealed that oxygen had some effects on the ferrioxalate decomposition but these were not sufficient to postulate a consistent reaction mechanism.

The results of flash photolysis experiments performed in acid or neutral aqueous ferrioxalate solutions [6, 7, 10] and of low temperature photolysis in glassy solutions [11] confirmed a reaction mechanism involving the transient species



( $k = 2.6 \times 10^2 \text{ s}^{-1}$ ) and  $\text{C}_2\text{O}_4^{\cdot-}$  ( $\tau < 50 \mu\text{s}$ ) [10]. Observation of the solid state photolysis of some ferrioxalates using Mössbauer spectroscopy has revealed the presence of the ferro-oxalate transient [12].

The aim of this work was to provide original data on the photolysis of  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  in dimethylformamide (DMF) solutions to establish the reaction mechanism. Some parallels are drawn with the photochemistry of manganese(III) complex oxalates in the same solvent [13 - 15].

## 2. Experimental details

The complex  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  was prepared using the method described by Parker and coworkers [1, 2]. Merck Uvasol DMF was used as the solvent without further purification. The concentration range of the complex was limited to  $10^{-5}$  -  $10^{-4}$  M because of its low solubility in DMF. The photolysis experiments were carried out in deoxygenated solutions only because the presence of oxygen produced substantial turbidity, even after short irradiation times, which hindered quantitative evaluation. The solutions were deoxygenated by bubbling argon through for more than 30 min before each experiment.

The irradiation at 313 and 366 nm was performed using a photochemical apparatus and an irradiation procedure which have been described elsewhere [16]. The UV and visible spectra of the reaction system were recorded using a Pye Unicam SP-8000 instrument.

Reaction quantum yield determinations were performed using a kinetic method similar to the procedures described by Kling *et al.* [17] and Gauglitz [18]. Standard mathematical manipulation leads to the equation

$$\ln\left(\frac{c_0}{c}\right) = \overline{f(A)} \overline{Q}_0 \epsilon_1 \phi_R l t \quad (1)$$

which is characteristic of first-order kinetics. In eqn. (1)  $c_0$  is the initial complex concentration in moles per litre,  $c$  is the complex concentration after an irradiation time  $t$  in minutes,  $\overline{Q}_0$  is the mean intensity of the incident light in moles per litre per minute,  $\epsilon_1$  is the complex molar absorptivity at the irradiation wavelength ( $\epsilon_1 = 2.50 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 313 nm and  $\epsilon_1 = 1.15 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 366 nm),  $l$  is the length of the quartz irradiation cell in centimetres,  $\phi_R$  is the reaction quantum yield and  $\overline{f(A)}$  is the mean value of the ratio

$$f(A) = \frac{(1 - 10^{-A})(1 + F \times 10^{-A})}{A} \quad (2)$$

where  $A$  is the absorbance of the system and  $F$  is the reflectance index of the air-quartz interface at the irradiation wavelength.  $f(A)$  was constant to within 5% - 10% over 80% conversion of the original complex. The mixture of the final reaction products  $\text{FeC}_2\text{O}_4$  and  $\text{K}_2\text{C}_2\text{O}_4$  has an absorption band centred at 410 nm with  $\epsilon_2 = 2.44 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  which is suitable for analytical measurements. If the relation

$$\frac{c_0}{c} = \frac{A'_\infty - A'_0}{A'_\infty - A'} \quad (3)$$

holds, where  $A'_0$ ,  $A'_\infty$  and  $A'$  are the absorbances of the system in the reaction product absorption band at  $t = 0$ ,  $t = \infty$  and variable irradiation times respectively, the slopes  $m$  of the  $\ln\{(A'_\infty - A'_0)/(A'_\infty - A')\}$  versus  $f(t)$  plots give the  $\phi_R$  values from the equation

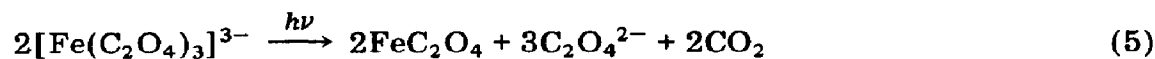
$$\phi_R = \frac{m}{\bar{f}(A)Q_0l\epsilon_1} \quad (4)$$

This kinetic method is valid only if the Beer-Lambert law is obeyed and the system involves a single partial linear independent reaction [19]. Therefore we performed some preliminary investigations to establish whether these conditions were satisfactorily fulfilled. An important feature of this approach is that the values of the molar absorptivities of the products are not explicitly required.

The flash photolysis experiments were carried out using an Applied Photophysics D-10 apparatus.

### 3. Results and discussion

The overall photochemical reaction investigated is



This irreversible reaction is fairly photosensitive. The spectra of the reaction system recorded at various times during the photolysis are shown in Fig. 1.

The photolysis could be performed up to a total conversion  $\alpha$  of the original complex into products. We prepared deoxygenated solutions of the products corresponding to various initial concentrations of the original com-

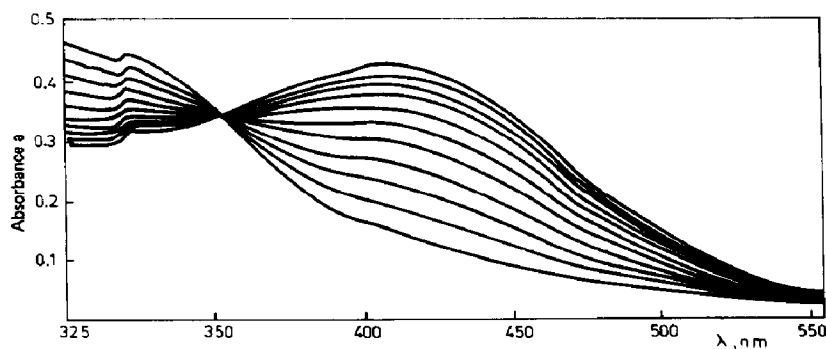


Fig. 1. Absorption spectra of  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  in DMF at 25 °C for various photolysis times ( $c_0 = 5.83 \times 10^{-5}$  M;  $\lambda = 313$  nm;  $Q_0 = 1.83 \times 10^{-5}$  M min $^{-1}$ ;  $l = 4$  cm;  $\Delta t = 0.5$  min).

TABLE 1

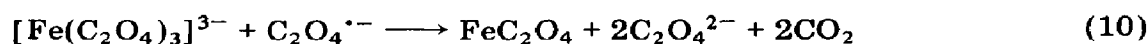
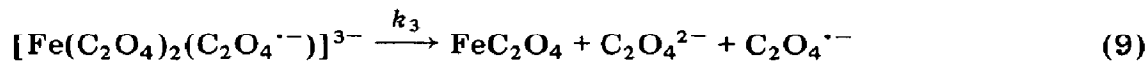
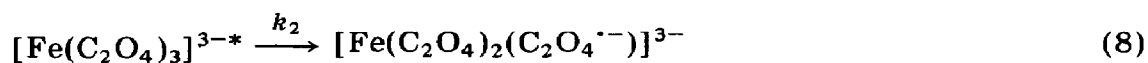
Kinetic and quantum yield data for the photolysis of  $K_3[Fe(C_2O_4)_3]$  in deoxygenated dimethylformamide solutions

$t$ (min)	$A_{410}$	$\alpha$ (%)	$\ln\{(A'_\infty - A'_0)/(A'_\infty - A'_t)\}$	$\epsilon_1 \bar{Q}_0 l \overline{f(A)} t$	$\phi_R$
0	0.140	0.0	0.000	0.000	—
0.5	0.180	9.3	0.098	0.154	0.64
1.0	0.215	17.5	0.192	0.308	0.63
1.5	0.255	26.8	0.311	0.462	0.68
2.0	0.290	34.9	0.429	0.616	0.70
2.5	0.320	41.9	0.542	0.770	0.71
3.0	0.345	47.7	0.648	0.923	0.70
3.5	0.370	53.5	0.766	1.077	0.71
4.0	0.385	57.0	0.843	1.231	0.69
4.5	0.400	60.5	0.928	1.385	0.67
5.0	0.420	65.1	1.053	1.539	0.68
$\infty$	0.570	100.0	—	—	—
					$0.68 \pm 0.03$

$T = 298$  K;  $c_0 = 5.83 \times 10^{-5}$  M;  $\bar{Q}_0 = 1.83 \times 10^{-5}$  M min $^{-1}$ ;  $\overline{f(A)} = 1.682$ ;  $l = 4$  cm;  $v = 12$  cm $^3$ ;  $\lambda = 313$  nm.

plex and their spectra fitted the spectra of the totally photolysed complex solutions to within  $\pm 0.005$  absorbance units, thus confirming reaction (5). The photolysis obeyed approximately first-order kinetics at both 313 and 366 nm. Typical kinetic data are shown in Table 1.

Statistical treatment of the data given in Table 1 leads to a first-order rate constant  $k_1 = m = 0.212$  min $^{-1}$  with a correlation factor  $r = 0.980$  and a quantum yield  $\phi_R = 0.69 \pm 0.03$ . Better correlation ( $r = 0.995 - 1.000$ ) was obtained for irradiation at 366 nm. Reaction quantum yields of  $0.69 \pm 0.07$  and  $0.69 \pm 0.05$  were obtained for irradiation wavelengths of 313 nm and 366 nm respectively as expected for complex excitation in the ligand-to-metal charge transfer band. These experimental data and the similarities with the photochemistry of  $K_3[Mn(C_2O_4)_3]$  in DMF solutions [13 - 15] led us to consider the following reaction sequence:



where  $k_1$ ,  $k_2$  and  $k_3$  are the rate constants. To determine whether this reaction sequence was correct, we sought the  $[\text{Fe}(\text{C}_2\text{O}_4)_2(\text{C}_2\text{O}_4^{\cdot-})]^{3-}$  intermediate only because  $\text{C}_2\text{O}_4^{\cdot-}$  is a common intermediate in the photochemistry of  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  [7, 10, 11]. Our preliminary flash spectroscopy investigations provided evidence for a transient species corresponding to that detected by Poznyak [11] at low temperatures in glassy irradiated solutions. The transient absorption band is centred near 420 nm and overlaps the spectra of the original complex and the reaction products. We attributed this spectrum to the transient of the iron(II) complex oxalate and we studied its decay curve by flash spectrophotometry. A typical decay curve for this transient is shown in Fig. 2. The signal intensity is similar to that obtained by Parker and Hatchard [6] and is characterized by a substantial overlapping of the transient spectrum with the spectra corresponding to the original complex and the reaction products. The transient decay obeyed first-order kinetics as can be seen in Fig. 3.

The correlation factor for the plot in Fig. 3 was  $r = 0.998$  and a rate constant  $k_3$  of  $(1.5 \pm 0.1) \times 10^3 \text{ s}^{-1}$  was found for the transient decay. This value is about a factor of 10 - 100 greater than the results obtained for the intermediates detected in flash photolysis studies of  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  and  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  [6, 7, 10, 20, 21]. This large difference indicates that a transient complex consisting of a  $\text{C}_2\text{O}_4^{\cdot-}$  radical in monodentate coordination with the corresponding iron(II) complex oxalate is more likely than a bidentate coordinated complex [20].

Kinetic treatment of the reaction sequence (6) - (10) led to the relation

$$\phi_R = 2(1 - \phi_{IC}) \quad (11)$$

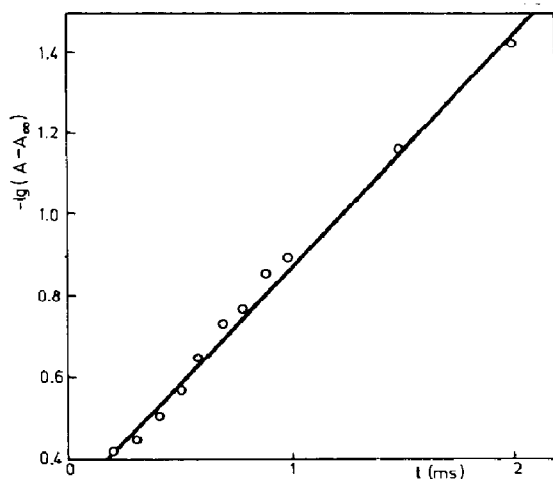
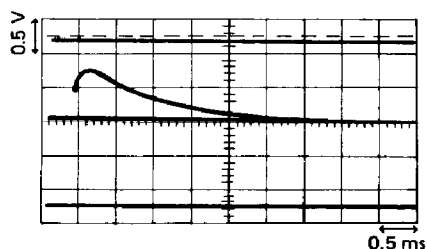


Fig. 2. Typical decay curve for the reaction intermediate ( $T = 300 \text{ K}$ ;  $c_0 = 2.2 \times 10^{-5} \text{ M}$ ;  $\lambda = 400 \text{ nm}$ ; 1000 J integral light flashes; sensitivity,  $0.5 \text{ V cm}^{-1}$ ; time scale,  $0.5 \text{ ms cm}^{-1}$ ).

Fig. 3. First-order kinetic plot for the decay of the reaction intermediate (data derived from Fig. 2).

where  $\phi_{IC}$  is the quantum efficiency of the primary internal conversion deactivation process (reaction (7)) and is defined as follows:

$$\phi_{IC} = \frac{k_1}{k_1 + k_2} \quad (12)$$

The quantum efficiency of the primary charge transfer process (reaction (8)) is

$$\phi_{CT} = 1 - \phi_{IC} \quad (13)$$

and hence we can estimate the values of these parameters starting from the experimental  $\phi_R$  values. The results are as follows:  $\phi_{IC} = 0.65$ ,  $\phi_{CT} = 0.35$  and  $k_1/k_2 \approx 2$ . This last value is about four times larger than the corresponding value for the photolysis of  $K_3[Mn(C_2O_4)_3]$  under the same conditions [14, 15] in agreement with the theoretical photoredox reactivity series proposed by Murgulescu *et al.* [22]. Reaction (10) is a scavenging process and probably obeys the Noyes equation [23]. We could not verify this assumption because of the low solubility of the complex in DMF, but such behaviour is probable by analogy with the behaviour of the corresponding manganese(III) oxalate complex [15].

Further photochemical studies of  $K_3[Fe(C_2O_4)_3]$  in aqueous  $K_2C_2O_4$  solutions which reveal some interesting novel features of the photochemistry of this complex are in progress in our laboratory.

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