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THE PHOTOLYSIS MECHANISM OF SOME MANGANESE(III) OXALATE COMPLEXES IN DIMETHYL FORMAMIDE

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Summary

Previous results concerning the photolysis of $[Mn(C_2O_4)_3]K_3$ and *trans*-$[Mn(C_2O_4)_2(H_2O)_2]K$ in dimethyl formamide together with recent flash photolysis data on the substituted complex are used in the development of a general photolysis mechanism which shows some differences from earlier models. This mechanism involves processes that can be treated using Noyes' concept of geminate recombination and enables the rate constants and quantum efficiencies of primary processes such as internal conversion and ligand-to-metal charge transfer to be estimated. These data are consistent with structural predictions.

1. Introduction

In contrast with the data obtained from investigations involving the continuous irradiation of aqueous solutions of manganese(III) oxalate complexes [1 - 3], the results of experiments carried out in dimethyl formamide (DMF) [4, 5] showed that the quantum yields of the overall reaction depended strongly on the concentrations of oxygen and the complex. Our results, which were obtained by irradiating frozen DMF solutions of these complexes, were consistent with those obtained by Shagisultanova and coworkers [6, 7] for $[Mn(C_2O_4)_3]K_3$ in mixed solvent glasses at 77 K. Electron paramagnetic spectroscopy revealed both a manganese(II) oxalate complex intermediate and the $C_2O_4^{\cdot -}$ radical [8]. The $C_2O_4^{\cdot -}$ radical was generated by the thermal decomposition of the manganese(II) oxalate complex intermediate. In the case of $[Mn(C_2O_4)_3]K_3$ we succeeded only in determining the presence of $C_2O_4^{\cdot -}$ [5] but qualitative optical observations confirmed the formation of a reactive photosensitive intermediate, presumably a manganese(II) oxalate complex. With regard to the radical species involved in the reaction we agree with Simon's opinion [9] that the $C_2O_4^{\cdot -}$ radicals are sufficiently stable to react with the original complex molecules prior to their thermal decomposition to CO_2 and $CO_2^{\cdot -}$.

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The flash photolysis experiments in DMF [5, 10] revealed features common to $[Mn(C_2O_4)_3]K_3$ and *trans*-$[Mn(C_2O_4)_2(H_2O)_2]K$. Reactive intermediates with broad structureless spectra centred at 400 nm similar to those obtained in glassy solutions at 77 K [6, 7] were generated by flash irradiation of these complexes at room temperature. These intermediates are presumably $[Mn^{II}(C_2O_4)_2(C_2O_4^{\bullet -})]^{3-}$ and $[Mn^{II}(H_2O)_2(C_2O_4)(C_2O_4^{\bullet -})]^{-}$ which, in the absence of O_2, decay with approximately first-order kinetics with rate constants of $(3.3 \pm 0.3) \times 10^3\ s^{-1}$ [5] and $(1.8 \pm 0.1) \times 10^3\ s^{-1}$ respectively [10]. These relatively short-lived intermediates probably consist of $C_2O_4^{\bullet -}$ radicals in monodentate coordination with the corresponding manganese(II) oxalate complexes analogous to the cobalt(II) oxalate intermediates described by Rowan *et al.* [11].

Our attempts to detect excited states by luminescence experiments in manganese(III) oxalate complexes in DMF solutions were unsuccessful [10] and we concluded that non-radiative deactivation by internal conversion and particularly by internal ligand-to-metal charge transfer (CT) is a very fast and efficient process. Consequently we have modified the reaction mechanism proposed previously [4, 5] in order to take into account all the facts discussed above.

2. Results and discussion

The general photolysis mechanism for manganese(III) oxalate complexes in DMF can be illustrated by the photolysis of $[Mn(C_2O_4)_3]K_3$:

$$[Mn^{III}(C_2O_4)_3]^{3-} \xrightarrow[Q_a]{h\nu} [Mn(C_2O_4)_3]^{*3-} \qquad \text{CT} \tag{1}$$

$$[Mn(C_2O_4)_3]^{*3-} \xrightarrow{k_2} [Mn^{III}(C_2O_4)_3]^{3-} \tag{2}$$

$$[Mn(C_2O_4)_3]^{*3-} \xrightarrow{k_3} [Mn^{II}(C_2O_4)_2(C_2O_4^{\bullet -})]^{3-} \tag{3}$$

$$[Mn^{II}(C_2O_4)_2(C_2O_4^{\bullet -})]^{3-} \xrightarrow{k_4} MnC_2O_4 + C_2O_4^{2-} + C_2O_4^{\bullet -} \tag{4}$$

$$[Mn^{III}(C_2O_4)_3]^{3-} + C_2O_4^{\bullet -} \xrightarrow{k_5} MnC_2O_4 + 2C_2O_4^{2-} + 2CO_2 \tag{5}$$

$$[Mn^{II}(C_2O_4)_2(C_2O_4^{\bullet -})]^{3-} + O_2 \xrightarrow{k_6} MnC_2O_4 + C_2O_4^{2-} + O_2^{-} + 2CO_2 \tag{6}$$

$$C_2O_4^{\bullet -} + O_2 \xrightarrow{k_7} 2CO_2 + O_2^{-} \tag{7}$$

The reaction sequence (1) - (5) is valid for deoxygenated complex solutions, and reactions (6) and (7) describe the influence of dissolved O_2 in hindering both the generation and the scavenging of the $C_2O_4^{\bullet -}$ radicals.

The internal conversion to the ground state of the complex (rate constant k_2) is a very fast non-radiative deactivation process in coordination compounds and therefore it seems unlikely that the excited CT state of $[Mn(C_2O_4)_3]^{3-}$ is the transient species observed elsewhere [5] by flash photolysis ($k_4 = (3.3 \pm 0.3) \times 10^3\ s^{-1}$). Under these conditions and in view of the observations discussed in Section 1 it seems reasonable to postulate process (3) which results in the formation of the $[Mn^{II}(C_2O_4)_2(C_2O_4^{\cdot -})]^{3-}$ intermediate. Reaction (3) must be a very fast ligand-to-metal CT chemical deactivation which is able to compete efficiently with the internal conversion to the ground state. This modification to the mechanism proposed earlier [5] leads to important results concerning the photolysis of manganese(III) oxalate complexes in DMF solutions.

Conventional kinetic treatment of the above mechanism results in the following formula [10]:

$$\varphi_R = (1 - \varphi_{IC})\left\{1 + \frac{k_4 k_5 [C]}{(k_4 + k_6[O_2])(k_5[C] + k_7[O_2])}\right\} \tag{8}$$

where φ_R is the overall reaction quantum yield, φ_{IC} is the primary internal conversion quantum yield defined by

$$\varphi_{IC} = \frac{k_2}{k_2 + k_3} \tag{9}$$

[C] is the complex concentration (M), $[O_2]$ is the O_2 concentration (M), k_2 - k_7 are the rate constants of reactions (2) - (7) and Q_a is the absorbed light intensity (M min^{-1}). We do not intend to discuss here the evidence for the existence of the reaction intermediates because it has been presented elsewhere [4, 5]. Our task is to consider the consequences of eqn. (8). In deoxygenated solutions, *i.e.* $[O_2] = 0$, we obtain

$$\varphi_R = 2(1 - \varphi_{IC}) \tag{10}$$

while in the presence of O_2 k_4 is very much less than $k_6[O_2]$, as the flash photolysis experiments confirm [5, 10], and we obtain

$$\varphi_R \approx 1 - \varphi_{IC} \tag{11}$$

Because of the quantum efficiency of the primary intramolecular ligand-to-metal CT deactivation process (3), φ_{CT} is given by

$$\varphi_{CT} = 1 - \varphi_{IC} \tag{12}$$

and the ratio k_2/k_3 is given by

$$\frac{k_2}{k_3} = \frac{\varphi_{IC}}{\varphi_{CT}} \tag{13}$$

The values of all these parameters can be estimated from φ_R only if the kinetic results (10) and (11) are correct.

Our determinations of the reaction quantum yield confirm the kinetic results. Thus for the photolysis of $[Mn(C_2O_4)_2(H_2O)_2]K$ in DMF at λ = 313 nm, T = 298 K and low complex concentrations (about 10^{-4} M), φ_R is 1.81 ± 0.08 in the absence of O_2 and 0.99 ± 0.04 in the presence of O_2 [4].

For the photolysis of $[Mn(C_2O_4)_3]K_3$ under the same conditions φ_R is 1.23 ± 0.12 in the absence of O_2 and 0.65 ± 0.07 in the presence of O_2 [5]. we obtained $\varphi_{IC} \approx 0$, $\varphi_{CT} \approx 1$ and $k_2/k_3 \approx 0$ for the photolysis of $[Mn(C_2O_4)_2(H_2O)_2]K$ and $\varphi_{IC} \approx 0.35$, $\varphi_{CT} \approx 0.65$ and $k_2/k_3 \approx 0.54$ for the photolysis of $[Mn(C_2O_4)_3]K_3$. These values for φ_{CT} and k_2/k_3 are fairly consistent with the theoretical photoredox reactivity series proposed by Murgulescu *et al.* [12]. We can also conclude that intramolecular ligand-to-metal CT is one of the fastest chemical deactivation primary processes in manganese(III) oxalate complex photochemistry.

Although eqn. (8) can explain the effect of O_2 on the quantum yield of the overall reaction in the two limiting cases and provides important data concerning the primary processes implied in the reaction mechanism, it cannot be used to explain the dependence of φ_R on the original complex concentration $[C_0]$. This dependence was observed only for the photolysis of the bisoxalate complex of manganese(III) in DMF owing to its high solubility in this solvent (up to 10^{-2} M) [4]. Typical φ_R data are shown in Table 1.

TABLE 1

Dependence of the reaction quantum yield on the complex concentration in the presence of O_2 (irradiation at $\lambda = 313$ nm and $T = 298$ K)

$[C_0] \times 10^4$ (M)	0.84	1.02	2.57	6.00	11.00	14.10	17.90	21.50	25.50
φ_R	0.93	0.99	1.08	1.12	1.26	1.54	1.77	1.89	1.94

In order to check eqn. (8) we recast it in a more convenient form, remembering that φ_{IC} is approximately zero:

$$(\varphi_R - 1)^{-1} = \frac{k_4k_5 + k_5k_6[O_2]}{k_4k_5} + \frac{k_7[O_2]}{k_4k_5}(k_4 + k_6[O_2])[C]^{-1} \tag{14}$$

The O_2 concentration is constant in the complex concentration range 10^{-4} - 3×10^{-3} M and therefore a plot of $(\varphi_R - 1)^{-1}$ against $[C]^{-1}$ should show a linear dependence. We checked eqn. (14) and found that it was not valid [10]. This negative result was explained by assuming that at least one of the reactions involved in the mechanism cannot be treated by means of the conventional rate constant formalism. Thus there is competition between O_2 and the complex molecules for the consumption of $C_2O_4{}^{\bullet-}$ radicals ejected from the solvent cage in the sequence (1) - (4). The existence of this competition led us to consider Noyes' model of geminate recombination [13, 14] which has some similarities with our mechanism particularly with regard to the original complex which acts as a scavenger for the $C_2O_4{}^{\bullet-}$ radicals. We therefore checked the simplest φ_R dependence on the scavenger concentration [C] proposed by Noyes [13, 14]:

$$\varphi_R = \varphi_R{}^0 + 2a(2\pi k_s)^{1/2}[C]^{1/2} \tag{15}$$

In this equation $\varphi_R{}^0$ is the limiting value of φ_R in the absence of the scavenger, *i.e.* at zero extrapolated complex concentration ($\varphi_R{}^0 = 1$) in our case, a is a parameter describing the random motion of the solvent molecules and k_s is a "long time" pseudo rate constant. Surprisingly, our experimental data provided a satisfactory verification of eqn. (15), and we obtained a correlation factor r of 0.96 and a slope value $2a(2\pi k_s)^{1/2}$ of 23.5 $M^{-1/2}$ with an error of ±17%. By using the value of $a = 1.6 \times 10^{-6}$ $s^{1/2}$ proposed by Noyes [13] and the value for the slope given above we estimated a lifetime τ of 10^{-10} s for the $C_2O_4{}^{\cdot-}$ radicals at a complex concentration [C] of 10^{-3} M [10]. This value is in the middle of the time range 10^{-11} - 10^{-9} s characteristic of this type of scavenging process. Under these conditions it is not correct to describe reactions (5) and (7) in terms of conventional rate constant kinetics. Noyes' [13, 14] model has been verified for the photochemistry of I^- ions in aqueous solutions [15, 16]. We believe that such processes are frequent in the photochemistry of transition metal oxalate complexes and further work concerning this aspect of the photolysis of $[Mn(C_2O_4)_3]K_3$ in aqueous solutions is in progress in this laboratory.

Finally we considered values of φ_R obtained previously [4, 8] for the photolysis of *trans*-$[Mn(C_2O_4)_2(H_2O)_2]K$ in DMF on irradiation at wavelengths of 405 and 436 nm in the ligand field absorption band (L) of the complex. φ_R values of 1.22 ± 0.12 and 0.74 ± 0.04 were obtained at 405 nm and 436 nm respectively in concentrated complex solutions ((2 - 3) × 10^{-3} M) in the presence of O_2. The reaction products were the same as those obtained in the UV excitation of the complex. Therefore we explained our data by taking into account the intersystem crossing (k_{IS}) and internal conversion (k_{IC}) primary deactivation processes of the ligand field excited state of the complex as can be seen in the following sequence:

$$[Mn^{III}(C_2O_4)_2(H_2O)_2]^- \xrightarrow[Q_a]{h\nu} [Mn^{III}(C_2O_4)_2(H_2O)_2]^{**-} \qquad L \qquad (16)$$

$$[Mn^{III}(C_2O_4)_2(H_2O)_2]^{**-} \xrightarrow{k_{IC}} [Mn^{III}(C_2O_4)_2(H_2O)_2]^- \qquad (17)$$

$$[Mn^{III}(C_2O_4)_2(H_2O)_2]^{**-} \xrightarrow{k_{IS}} [Mn(C_2O_4)_2(H_2O)_2]^{*-} \qquad CT \qquad (18)$$

Process (18) is supported by the energy level diagram of manganese(III) oxalate complexes [17]. The sequence (16) - (18) precedes reactions (1) - (7).

A similar kinetic treatment to that described above led to the relationships [10]

$$\begin{aligned} \varphi_R &= 2\varphi_{IS} \\ \varphi_{IC} &= 1 - \varphi_{IS} \end{aligned} \qquad (19)$$

from which we obtained $\varphi_{IC} = 0.63$, $\varphi_{IS} = 0.37$ for $\lambda = 436$ nm and $\varphi_{IC} = 0.35$, $\varphi_{IS} = 0.65$ for $\lambda = 405$ nm. These results explain the dependence of φ_R on the irradiation wavelength λ for manganese(III) oxalate complexes [1, 4, 8] in terms of the increased efficiency of the intersystem crossing process between the L and CT states on going from the visible to the UV excitation process.

References

1 G. B. Porter, J. G. W. Doering and S. Karanka, *J. Am. Chem. Soc.*, *84* (1962) 4027.
2 B. Rackov, *Z. Chem.*, *5* (1965) 397.
3 B. Rackov, *Z. Phys. Chem. (Leipzig)*, *233* (1966) 103, 110, 113.
4 T. Oncescu, S. G. Ionescu and C. Andreescu, *Rev. Roum. Chim.*, *22* (1977) 697.
5 T. Oncescu and S. G. Ionescu, *J. Photochem.*, *13* (1980) 181.
6 G. A. Shagisultanova, L. N. Neokladnova and A. L. Pozniak, *Dokl. Akad. Nauk S.S.S.R.*, *162* (1965) 1333.
7 A. L. Pozniak, G. A. Shagisultanova and L. N. Neokladnova, *Teor. Eksp. Khim.*, *4* (1968) 567.
8 I. G. Murgulescu, T. Oncescu and S. G. Ionescu, *Rev. Roum. Chim.*, *17* (1972) 423.
9 Z. Simon, *Rev. Roum. Chim.*, *14* (1969) 705.
10 S. G. Ionescu, *Doctoral Thesis*, Bucharest, 1980.
11 R. N. Rowan, M. Hoffman and R. Milburn, *J. Phys. Chem.*, *96* (1974) 6060.
12 I. G. Murgulescu, T. Oncescu and Z. Simon, *Rev. Roum. Chim.*, *12* (1967) 755.
13 R. M. Noyes, *J. Am. Chem. Soc.*, *77* (1955) 2042.
14 R. M. Noyes, *J. Am. Chem. Soc.*, *78* (1956) 5486.
15 J. Jortner, M. Ottolenghi and G. Stein, *J. Phys. Chem.*, *67* (1962) 1271.
16 J. Jortner, M. Ottolenghi, J. Rabani and G. Stein, *J. Phys. Chem.*, *37* (1962) 2488.
17 I. G. Murgulescu, T. Oncescu and Z. Simon, *Rev. Roum. Chim.*, *12* (1967) 737.