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Wavelength and Temperature Dependence in the Photolysis of the Chemical Actinometer, Potassium trisoxalatoferrate(III), at Longer Wavelengths*

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In 1976, Betts and Buchannon reported that there was $^{12}C/^{13}C$ isotope fractionation in the long wavelength tail of the action spectrum for CO_2 production from $Fe(C_2O_4)_3^{3-}$ [1]. Such fractionation was *not* observed in the near UV region where the quantum yield is approximately constant. Betts and Buchannon [1] postulated involvement of two states in photolysis of $K_3Fe(C_2O_4)_3$ in solution. To explore their proposal, we have measured the quantum yield for Fe^{2+} formation and its temperature dependence at 457.9, 488.0 and 514.1 nm using Ar-ion laser irradiation and the *trans*$[Cr(NH_3)_2(NCS)_4]^-$ chemical actinometer [2]. Also, we have identified a new spectroscopic state in this region using magnetic circular dichroism, MCD, spectroscopy.

The experimental methods for accurate quantum yield determination at the precisely defined wavelengths available from the laser are those introduced by Adamson *et al.* [3] to measure the small quantum yields of photosubstitution at Co(III) centres. Our adaptation of these and the methods for determining Fe^{2+} are as in earlier work [4, 5]. Quantum yields for Fe^{2+} production, $\phi_{Fe^{2+}}$, (2x the yields for CO_2) are recorded in Table I as a function of wavelength, λ, and temperature, T. Fig. 1 shows the MCD spectrum of $Fe(C_2O_4)_3^{3-}$ near 20,000 kK.

The first point to note is that the gentle, nearly linear, decline of $\phi_{Fe^{2+}}$ as λ increases in the tail of the action spectrum which was discussed by Betts and Buchannon [1] is an artifact of low λ resolution available from conventional light sources. $\phi_{Fe^{2+}}$ at 514.1 nm is not much lower (at room T) than $\phi_{Fe^{2+}}$ at 488 nm. The action spectrum is more nearly L shaped with a sharp cut-off. Second, observe that only $\phi_{Fe^{2+}}$ at 514 nm is T dependent and that its values pass from values below $\phi_{Fe^{2+}}$ at 488 at lower T to values above $\phi_{Fe^{2+}}$ at 488 at higher T.

TABLE I. Quantum Yields for Photolysis of $Fe(C_2O_4)_3^{3-}$.

Wavelength (nm)	Temperature (C)	Quantum Yield $\phi_{Fe^{2+}}$	Concentration of $Fe(C_2O_4)_3^{3-}$ (*M*)
457.9	40.8	1.02	0.0154
	40.8	1.02	0.0154
	32.0	1.18	0.0102
	31.0	1.13	0.0154
	21.7	1.09	0.0154
	21.7	1.05	0.0154
	23.0	1.12	0.0102
	12.0	1.09	0.0154
	12.0	1.09	0.0154
488.0	40.3	1.08	0.0816
	40.3	1.04	0.0816
	31.0	1.03	0.0816
	31.0	1.03	0.0816
	30.8	1.03	0.0833
	30.8	1.02	0.0833
	23.0	1.08	0.0816
	23.0	1.08	0.0816
	12.8	1.09	0.0814
	12.8	1.09	0.0814
514.5	42.0	1.49	0.163
	41.5	1.39	0.204
	41.5	1.42	0.204
	31.5	1.23	0.204
	31.9	1.21	0.204
	31.9	1.23	0.204
	22.7	0.93	0.204
	21.3	0.90	0.163
	12.0	0.84	0.163
	12.5	0.89	0.163
	23.5	0.87	0.204
	21.3	0.90	0.163

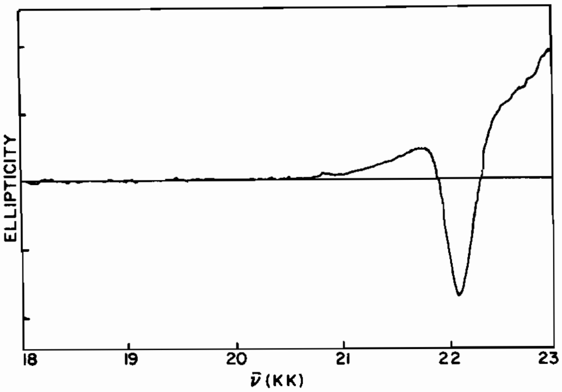

Fig. 1. The MCD spectrum of a 0.2 *M* solution of $K_3Fe(C_2O_4)_3$. The ellipticity axis is arbitrary.

The two state hypothesis of Betts and Buchannon is confirmed. The probable nature of the state important in the low energy tail is revealed by the MCD

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spectrum in Fig. 1. A "C" term (6) at approx. 22,000 cm^{-1} is consistent with an assignment to the ligand field transition $^4T_2 \leftarrow {}^6A_1$ [7] suggested by the Tanabe–Sugano diagram for high spin d^5 and the assignments of the spectrum of Fe^{3+} in beryl [7]. It seems quite likely that the second state responsible for initiating a different pathway at longer wavelength is this LF state. It is noteworthy that the $^4T_2$ state is (as are all LF states) restricted by a spin selection rule from return to the ground state and consequently may have a relatively long lifetime.

At this point, the facts concerning photolysis of $Fe(C_2O_4)_3^{3-}$ in the tail of the action spectrum can be summarized to indicate what any mechanistic proposal must satisfy. (i) Yields are nearly constant in the near UV and up to 488 nm. (ii) At 514 nm the yields are somewhat reduced at room T but are T dependent and exceed yield for shorter wavelength at T > 30 C. (iii) As reported by Betts and Buchannon (1), the isotope ratio $\phi(^{12}C)/\phi(^{13}C)$ decreases linearly from 1.05 at 20 kK to 1.00 at 28 kK. These facts are consistent with a specific and non-thermal relaxation of the state populated at higher energy in a manner partly analogous to the behaviour of a dissociative state of a diatomic molecule (except that in polyatomics this may correspond to a bound state because only one degree of freedom is pathological). Similarly, the facts are consistent with a thermally activated relaxation of the state (probably much longer lived) populated at longer wavelength.

If we assume that the primary product of photolysis of $Fe(C_2O_4)_3^{3-}$ is a radical pair $Fe^{2+}{\cdot}OOC-$ [8], then the relaxation process from the primary charge transfer (CT) excited state involves a nuclear motion which removes the high symmetry of the ground state and selects one carboxylate group from the six as the site of oxidation. Relaxation from the initial ligand field (LF) state may involve the transfer of an electron from one carboxylate to reduce the excited and therefore more reducible Fe centre. If so, as an adiabatic electron transfer, it would again involve motion along nuclear coordinates lifting the symmetry of the oxalates. Consequently, the two processes may be qualitatively represented with the same nuclear coordinate (Fig. 2). Filling the lowest metal d orbital of $^4T_2$ to reduce Fe leads to the ^2E excited state configuration around Fe^{2+}. These considerations lead to a plausible diagram of the reaction as shown in Fig. 2. This Figure is offered as a basis for further discussion and possibly a stimulus for new experiments. It is consistent with the facts, but not uniquely so.

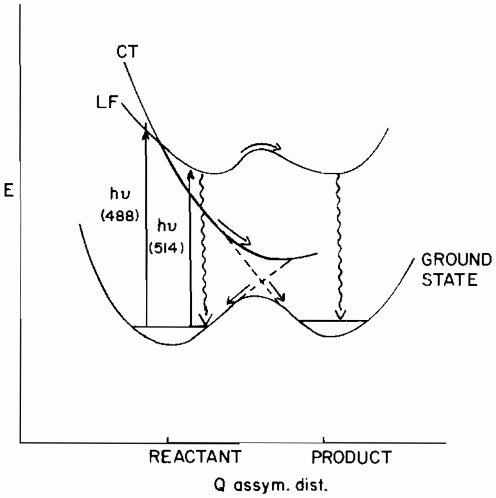

Fig. 2. An impressionistic potential surface for the reaction paths which is consistent with the collected facts. Solid arrows represent absorption of photons or 'motion on the potential surface'. Wavy arrows represent radiationless transitions.

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