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The Photolysis of Potassium-μ-oxalato-di[trisoxalatostannate(IV)] Tetrahydrate in Aqueous Acidic Solution.
II. Kinetics and Mechanism

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The photolysis process of the complex $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ in aqueous acidic solution has been analysed kinetically. The proposed photolysis mechanism is based on both kinetic data and structural considerations regarding the way in which the complex exists in aqueous acidic solution. The photoreduction of the final complex species is facilitated by decarboxylation during primary photoactivation and by interaction between the complex species and a photoactivated bioxalate ion.

Introduction

Previous papers [1–3] respectively deal with the synthesis and crystal structure, water dissolution process and photochemical behaviour in aqueous acidic solution of the complex $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$. The present investigation is aimed at the disclosure of the photolysis mechanism by reaction kinetics.

A principal problem concerning the proposition of a photolysis mechanism is knowledge of the way in which the complex exists in aqueous acidic solution. The proposed mechanism is most reliable when based on both kinetic data and structural detail. The two possible dissolution processes

$$K_6Sn_2(C_2O_4)_7 + 6H_2O \rightarrow 2Sn(C_2O_4)(OC_2O_3H)\text{-}$$
$$(H_2O)(OH)_2^- + H^+ + HC_2O_4^- + 2C_2O_4^{2-} + 6K^+$$
$$2Sn(C_2O_4)(OC_2O_3H)(H_2O)(OH)_2^- \rightleftarrows$$
$$\rightleftarrows 2Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-} + 2H^+ \qquad \text{(A)}$$

and

$$K_6Sn_2(C_2O_4)_7 + 4H_2O \rightarrow 2Sn(C_2O_4)_2(H_2O)(OH)^-$$
$$+ H^+ + HC_2O_4^- + 2C_2O_4^{2-} + 6K^+ \; 2SN(C_2O_4)_2(H_2O)$$
$$(OH)^- \rightleftarrows 2Sn(C_2O_4)_2(OH)_2^{2-} + 2H^+ \qquad \text{(B)}$$

formulated previously [2], lead to different dioxalato complex species. It is attempted to favour the participation of one of these species by virtue of the available kinetic data.

Experimental

The synthesis and analysis of the complex, the construction of the photolysis reaction vessel and the employed spectrophotometric and radiochemical techniques were described in previous papers [1, 3]. The preparation of the various test and corresponding blank solutions was based on monovariance. The pH was adjusted with HCl or KOH and the ionic strength with KCl. The free oxalate in solution was varied by the addition of oxalic acid, the values $K_1 = 4.3 \times 10^{-2}$ and $K_2 = 1.56 \times 10^{-4}$ *M* of McAuley and Nancollas [4] being used to calculate $[H_2C_2O_4]$, $[HC_2O_4^-]$ and $[C_2O_4^{2-}]$ at a given pH and ionic strength for the estimation of the required amounts of HCl or KOH and KCl. The test solutions were irradiated under nitrogen atmosphere to exclude the reverse oxidation by air dealt with previously [3].

Results and Discussion

The presentation and discussion of the experimental results is simplified by using the following symbols:

[X]	complex concentration (mol liter^{-1}, weighed as $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$)
$[Ox]_T$	total (bonded and free) oxalate ion concentration (mol liter^{-1})
$[Ox]_F$	free oxalate ion concentration (mol liter^{-1})
$[Ox]_B$	bonded oxalate ion concentration (mol liter^{-1})
$[Ox]_A$	added oxalate ion concentration (mol liter^{-1})
μ	ionic strength (mol liter^{-1})
I	irradiation intensity
d	slitwidth (mm)
T	temperature (K)
A	spectrophotometric absorbance
t	irradiation time (min)
R	initial photolysis rate (mol liter^{-1} min^{-1})
k	rate constant
K	equilibrium constant

The photolysis process was followed kinetically by measuring A at 258 nm as function of t (10, 20, 30, 40, 50, 60 min) for the rate parameters $0.25 \times 10^{-3} \leqslant [X] \leqslant 1.25 \times 10^{-3}\ M$; $0 \leqslant [Ox]_A \leqslant 3.0 \times 10^{-3}\ M$; $1.5 \leqslant pH \leqslant 3.5$; $\mu = 1.0 \times 10^{-1}\ M$; $2 \leqslant d \leqslant 10$ mm; $298 \leqslant T \leqslant 317$ K.

The kinetic analysis of the overall process [3]

$$Sn(IV) \underset{\Delta,\, k_{II}}{\overset{h\nu,\, k_I}{\rightleftharpoons}} Sn(II) + CO_2$$

is based on the variation of log $\dfrac{A_\infty - A_t}{A_\infty - A_0}$

with t, $A_t = [X](1 - x)\epsilon_1 + [X]x\epsilon_2$ being the observed absorbance at 258 nm at time t, A_0 the complex absorbance prior to irradiation and $\epsilon_1 = 285\ M^{-1}\ cm^{-1}$ [2] and $\epsilon_2 = 1375\ M^{-1}\ cm^{-1}$ [3] the extinction coefficients of the complex and the photolysis product at 258 nm respectively. The infinity absorbance A_∞ is calculated by substituting the second-order polynomial regression coefficients a and b and the ordinate intercept c in the equation $Y = aX^2 + bX + c$ after determining X by equating $dY/dX = 0$. The first-order rate constant $k = k_I + k_{II}$ is then obtainable from the graphically determined half-life period. However, the termination to the infinity absorbance A_∞ is so gradual that even after an irradiation of 60 minutes no equilibrium is attained, merely 5% of the complex being decomposed into the photolysis products. Thus the values of A_∞ obtained as described above, are unrealistic. Although the differences between the observed absorbances are large because of the high extinction coefficient of the photolysis product, they are no true indication of how far the process has proceeded at a given time.

The analysis of the photochemical forward reaction requires utilization of initial rate data to exclude the thermal reverse reaction. From the relations

$$A_1 = \epsilon_1 C_1 + 2(C_0 - C_1)\epsilon_2$$

and

$$A_2 = \epsilon_1 C_2 + 2(C_0 - C_2)\epsilon_2$$

with A the absorbance at 258 nm, C the molar concentration of the complex solution at a given time during photolysis and C_0 the initial concentration of the complex solution, it follows that

$$\Delta A = A_2 - A_1 = \Delta C(\epsilon_1 - 2\epsilon_2)$$

Thus the initial photolysis rate can for short irradiation periods be calculated as

$$R = \frac{\Delta C}{\Delta t} = \frac{\Delta A}{(2\epsilon_2 - \epsilon_1)\Delta t} = \frac{\Delta A}{2365\Delta t}$$

with $\Delta A/\Delta t$ the initial slope of the absorbance *versus* time curves, as illustrated for [X] as rate parameter in Figure 1. The values of R calculated from Figure 1 vary linearly with [X] as Figure 2 illustrates.

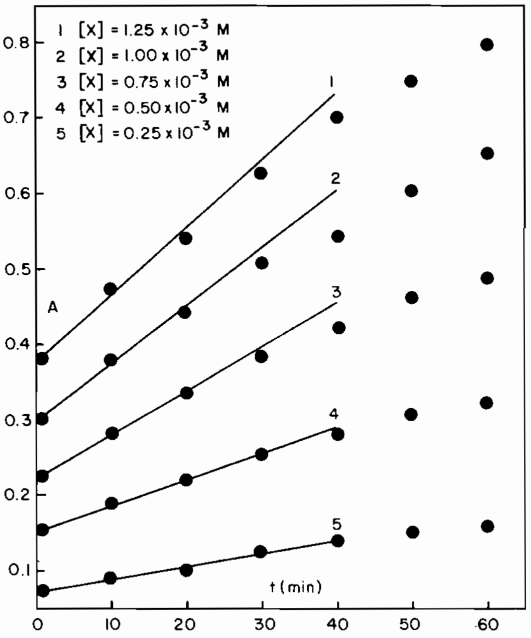

Figure 1. Determination of $\Delta A/\Delta t$ from absorbance *versus* time curves for [X] as rate parameter. $[Ox]_A = 0$; pH = 2.5; $\mu = 1.0 \times 10^{-1}\ M$; d = 10 mm; T = 298 K.

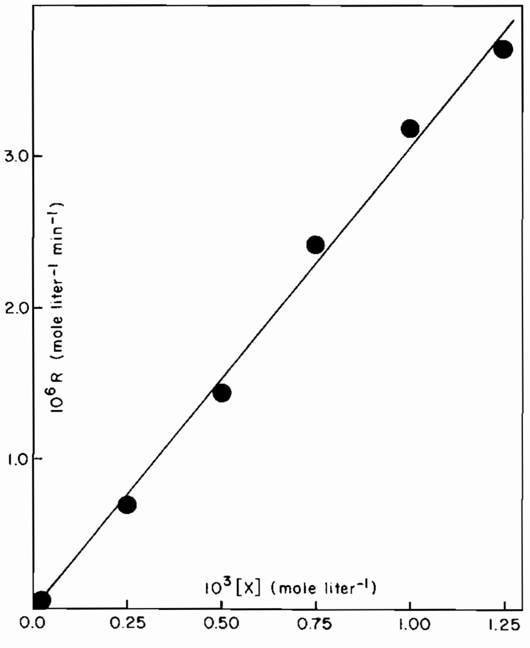

Figure 2. R as function of [X].

The equation

$$R = k_1 [X] \tag{1}$$

mathematically describes the linear relation, the numerical value of the first-order rate constant k_1 being $3.09 \times 10^{-3}\ min^{-1}$.

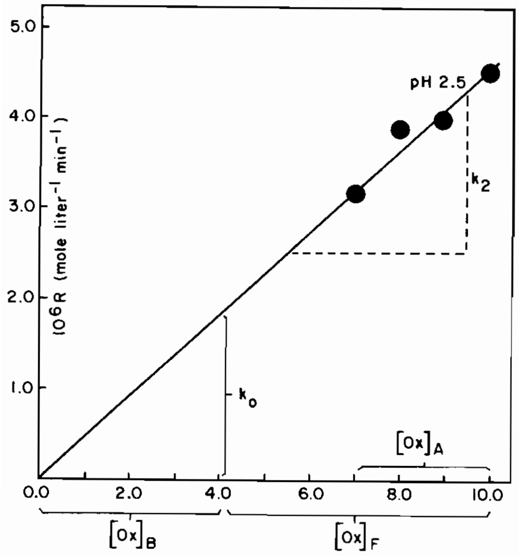

Figure 3. Graphical representation of contribution of bonded and free oxalate.

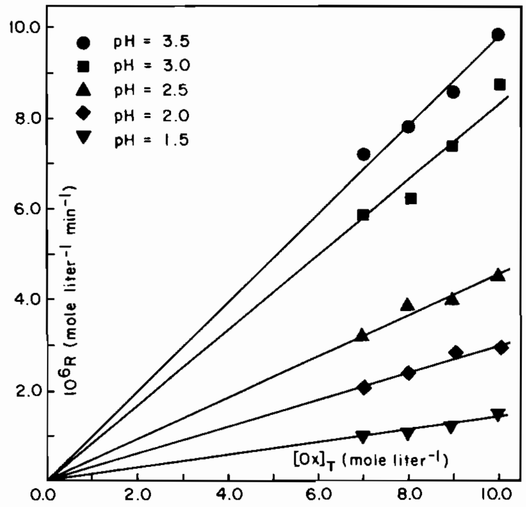

Figure 4. R as function of $[Ox]_T$ for pH as rate parameter. $[X] = 1.0 \times 10^{-3}$ *M*; $\mu = 1.0 \times 10^{-1}$ *M*; d = 10 mm; T = 298 K.

The influence of oxalate on R at a given pH is illustrated in Figure 3. The graphical representation of the contribution of the bonded and free oxalate in this figure is based on the experimental result that three oxalate groups per complex molecule exist freely in solution [2]. A striking feature of the photolysis process is that the linear relation can mathematically either be written as

$$R = k_2[Ox]_T$$

or

$$R = k_0 + k_2[Ox]_F \tag{2}$$

where k_0 represents the constant contribution of $[Ox]_B$ for constant [X]. The conclusion is that the bonded and free oxalate in solution are equally photoactive. This statement is supported by results reported later in this paper and is important for the proposition of a photolysis mechanism. The validity of the mathematical relations applies to the results obtained at all pH values concerned, as Figure 4 depicts.

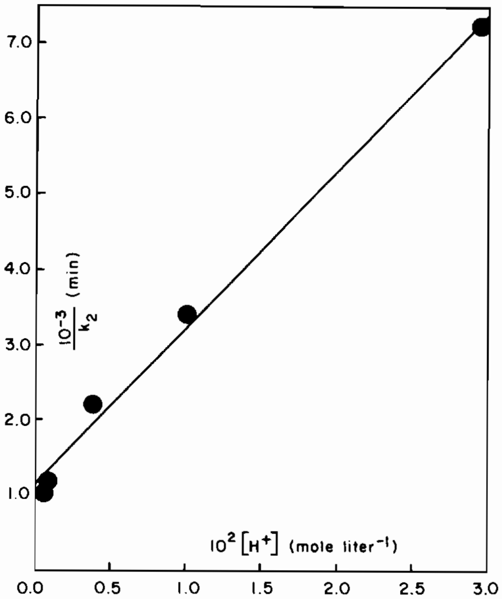

Figure 5. k_2 as function of $[H^+]$.

Figure 5 indicates that, if $1/k_2$ is plotted as a function of $[H^+]$, a straight line with intercept $k' = 1.15 \times 10^3$ min and slope $k'' = 2.07 \times 10^5$ M^{-1} min is obtained. The pH dependence is given mathematically by the equation

$$k_2 = \frac{1}{k' + k''[H^+]} = \frac{1/k''}{k'/k'' + [H^+]} = \frac{k_3}{k''' + [H^+]} \tag{3}$$

with $k_3 = 1/k'' = 4.82 \times 10^{-6}$ *M* min^{-1} and $k''' = k'/k'' = 5.53 \times 10^{-3}$ *M*.

The inflection at pH 2.5 observed in Figure 6 by plotting k_2 *versus* pH, is an indication of an acid–base equilibrium that brings about a sevenfold acceleration of the photolysis process for a change in pH from 1.5 to 3.5. In a previous paper [3] multiple additional indications of the occurrence of an acid–base equilibrium were given. It is evident by extrapolating the curve in Figure 6 that theoretically no photolysis takes place at pH = 0. The acid–base equilibrium evidently converts a non-photoactive complex species into a photoreactive complex species. The pK value 2.5 implies that in a 1.0×10^{-3} *M* aqueous complex solution for which the pH is 2.92, the non-photoactive and photoreactive species are present in approximately equal concentrations, explaining why

TABLE I. R as Function of $[Ox]_A$ for d and T as Rate Parameters.

$[X] = 1.0 \times 10^{-3}\ M$				$pH = 2.5$			$\mu = 1.0 \times 10^{-1}\ M$		
d (mm)	2	4	6	8	10	10	10	10	10
T (K)	298	298	298	298	298	303	307	312	317
$10^3[Ox]_A (M)$				$10^6 R\ (M\ min^{-1})$					
0.0	0.740	1.496	1.776	2.537	3.185	5.243	6.427	9.40	13.00
1.0	1.117	2.020	2.135	3.326	3.862	6.202	7.780	10.82	14.09
2.0	1.247	2.067	2.805	3.665	3.975	6.342	9.201	12.12	17.56
3.0	1.679	2.283	3.383	4.017	4.461	7.702	10.235	13.67	18.35

TABLE II. Rate Constants k_2 (min^{-1}) and k_o ($M\ min^{-1}$) for pH, d and T as Rate Parameters.

pH	$10^3k_2^a$	10^6k_o	d	$10^3k_2^b$	10^6k_o	T	10^3k_2	10^5k_o
1.5	0.139	0.56	2	0.146	0.57	298	0.453	0.18
2.0	0.293	1.18	4	0.232	0.93	303	0.750	0.30
2.5	0.453	1.80	6	0.310	1.20	307	0.999	0.40
3.0	0.832	3.32	8	0.402	1.60	312	1.358	0.54
3.5	0.974	3.92	10	0.452	1.83	317	1.861	0.74

[a] Plotted in Figures 5 and 6. [b] Zeropoint inserted for calculation of k_2 due to experimental deviations for small values of d.

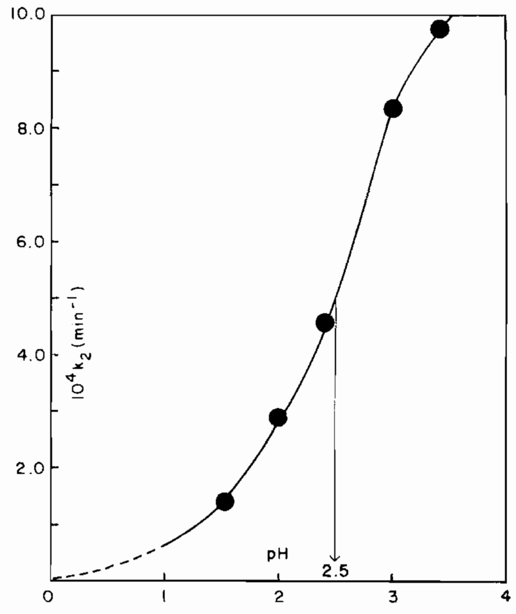

Figure 6. k_2 as function of pH.

the photolysis proceeds favourably under such conditions. The equilibrium is connected with the deprotonation of bonded oxalate or bonded water as indicated in the proposed dissolution processes (A) and (B) since (i) each deprotonating type in conjunction with the proposed dissolution step satisfies the requirement that three oxalate groups and one hydrogen ion are released by each complex molecule; (ii) both deprotonation types permit the derivation of the pH dependence obtained from Figure 5 provided k''' represents the equilibrium constant K of the acid–base equilibrium, and this requirement is met as the numerical value of k''' indicates a pK value of 2.3.

The values of R as function of $[Ox]_A$ for d and T as rate parameters are given in Table I. The rate constants k_2 obtained by plotting these values in the same way as in Figure 4, are given in Table II. They allow the influence of I on the photolysis process to be written as

$$k_2 = k_4 I \qquad (4)$$

and the activation parameters to be calculated as $\Delta H^* = 53.8 \pm 3.2$ kJ mol^{-1} and $\Delta S^* = -161.8 \pm 11.8$ J K^{-1} mol^{-1}.

The results are the same if, instead of the rate constant k_2, the rate constant k_o (Figure 3), whose numerical values for pH, d and T as rate parameters are also listed in Table II, are plotted as function of the corresponding rate parameter. This is reflected by the derivation of the corresponding relations

$$k_o = \frac{k_5}{k''' + [H^+]} \qquad (5)$$

and

TABLE III. pK and ΔH^* using k_2 or k_o.

pK		ΔH^* (kJ mol^{-1})	
k_2	k_o	k_2	k_o
2.26	2.25	53.8 ± 3.2	53.7 ± 2.6

$$k_o = k_6 I \qquad (6)$$

and the comparability of the values of two kinetically measured parameters in Table III. These results also lead to the conclusion that the bonded and free oxalate are photoactivated with equal ease.

The experimental rate equation

$$R = \frac{\{k_a + k_b[Ox]_F\}[X]\ I}{K + [H^+]}$$

is obtained by combining equations (1), (2), (3), (4), (5) and (6), where $K = k'''$ ($pK = 2.3$–2.5) is the kinetically measured equilibrium constant for the acid–base equilibrium by which the photoreactive complex species $Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}$ process (A)) or $Sn(C_2O_4)_2(OH)_2^{2-}$ (process (B)) originates in solution and $k_a = 2.03 \times 10^{-6}$ *M* min^{-1} mm^{-1} and $k_b = 5.11 \times 10^{-4}$ min^{-1} mm^{-1} are arbitrary constants.

It is noteworthy that the pH dependence corresponds with that of the photolysis process of the complex $K_2Ge(C_2O_4)_3 \cdot H_2O$ under comparable conditions [5, 6]. Since the photoreactive complex species in both cases originate in solution by acid–base equilibria and the kinetically measured pK values of 2.0–2.2 and 2.3–2.5 are in close agreement, it was expected that the complex species $Sn(C_2O_4)_2(OH)_2^2$ (or more probably $SnO(C_2O_4)_2^{2-}$, formed by loss of H_2O) participates in the photolysis process of the tin oxalato complex after the analogy of the complex species $GeO(C_2O_4)_2^{2-}$, that participates in the photolysis process of the germanium oxalato complex. However, the pK values for the deprotonating equilibria of bonded water for analogous complex species, *e.g.* $Cr(C_2O_4)_2(H_2O)_2^-$, are markedly different from the kinetically measured pK value. It is $pK_1 = 7.1$ and $pK_2 = 9.3$ for *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ [7] and $pK_1 = 7.5$ and $pK_2 = 10.5$ for *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ [8]. On the contrary, the examples below illustrate over how wide a pK region the acid character of bonded water may vary:

$Al(H_2O)_6^{3+} \rightleftarrows Al(H_2O)_5(OH)^{2+} + H^+$ $pK = 4.95$ [9]

$Cr(H_2O)_6^{3+} \rightleftarrows Cr(H_2O)_5(OH)^{2+} + H^+$ $pK = 3.90$ [9]

$Fe(H_2O)_6^{3+} \rightleftarrows Fe(H_2O)_5(OH)^{2+} + H^+$ $pK = 2.20$ [9]

$Co(NH_3)_5(H_2O)^{3+} \rightleftarrows Co(NH_3)_5(OH)^{2+} + H^+$
$pK = 5.70$ [9]

$Pt(NH_3)_4(H_2O)_2^{4+} \rightleftarrows Pt(NH_3)_4(H_2O)(OH)^{3+} + H^+$
$pK = 2.00$ [9]

$Cr(C_2O_4)(H_2O)_4^+ \rightleftarrows Cr(C_2O_4)(H_2O)_3(OH) + H^+$
$pK = 5.60$ [7]

$AuCl_3(H_2O) \rightleftarrows AuCl_3(OH)^- + H^+$ $pK = 0.60$ [10]

The kinetically measured pK value 2.3–2.5 is in good agreement with the pK value 2.2 for the equilibrium [11]

$$Co(NH_3)_5(OC_2O_3H)^{2+} \rightleftarrows Co(NH_3)_5(OC_2O_3)^+ + H^+$$

Thus the occurrence of the equilibrium by which bonded oxalate is deprotonated, is also quite probable. The problem is to make a choice between the two possible acid–base equilibria and thus determine which complex species participates in the photolysis process.

Since it is known from the kinetic results that the acid–base equilibrium converts a non-photoactive complex species into a photoreactive species, the reasons for the photoreactivity of the deprotonated species $Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}$ and $Sn(C_2O_4)_2(OH)_2^{2-}$ or more probably $SnO(C_2O_4)_2^{2-}$ were taken as an approach to determine which one participates. The photoreactivity of $SnO(C_2O_4)_2^{2-}$ probably lies in oxygen ring opening by primary or secondary photoactivation as proposed in the case of the photolysis process of the complex species $GeO(C_2O_4)_2^{2-}$ [6]. In either complex species $Sn(C_2O_4)(OC_2O_3H)(H_2O)(OH)_2^-$ or $Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}$ ring closing is prevented by the water molecule that occupies the vacant position in the coordination sphere, but quasi ring closing may occur for the protonated species by hydrogen bonding. However, this is not quite convincing for the conversion of a non-photoactive into a photoreactive species when the strength of hydrogen bonds [12] on the one hand and its influence on a pK value [13] on the other hand, are taken into consideration. The photoreactivity rather lies in decarboxylation [14] of the deprotonated complex species by which photoactivation directly leads to electron transfer. This provides a possible explanation for the experimental result that the photoactivation of bonded and free oxalate occurs with equal ease. The removal of the carboxylic group as carbon dioxide in alkaline medium in which mainly the deprotonated form exists, is a well-known process in the synthetic organic chemistry [15].

A definite choice could not be made by only taking the above considerations into account. There are, however, differences between the photolysis processes of the complexes $K_2Ge(C_2O_4)_3 \cdot H_2O$ and $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ in aqueous acidic solution with

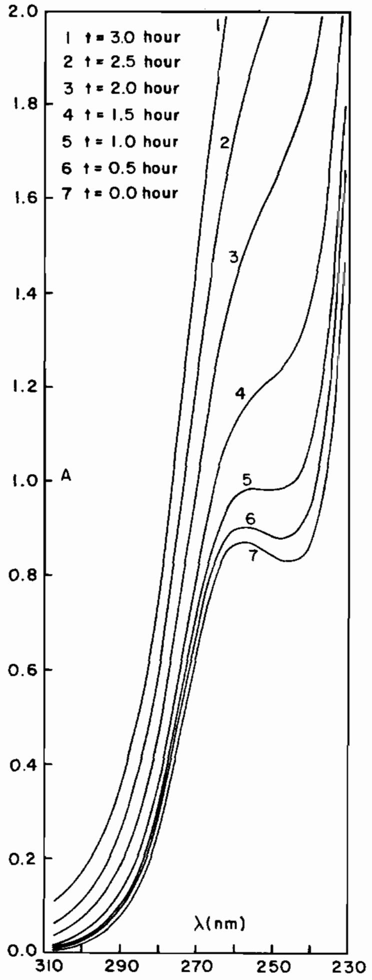

Figure 7. Thermal reduction of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ in aqueous solution at 70 °C. [X] = 3.0×10^{-3} *M*; $[Ox]_A = 0$; pH = 2.5.

regard to thermal instability and activation enthalpy on account of which the participation of the complex species $Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}$ is favoured.

Figure 7 provides spectrophotometric evidence that the complex $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ undergoes thermal reduction in aqueous acidic solution at 70 °C, yielding the same product as that formed during photolysis. The complex $K_2Ge(C_2O_4)_3 \cdot H_2O$ exhibits no thermal redox reaction under similar conditions. The difference in the standard reduction potentials for the reactions

$$GeO_2 + 4H^+ + 2e^- \rightleftharpoons Ge^{2+} + 2H_2O \qquad E^0 = -0.15\ \mathrm{V} \quad [16]$$

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+} \qquad E^0 = +0.15\ \mathrm{V} \quad [17]$$

may probably be related to the difference in thermal reactivity of these complexes. The fact that only the tin oxalato complex decomposes thermally, favours the participation of the complex species $Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}$. The direct electron transfer by decarboxylation is considered beneficial to thermal reduction. Moreover, support for the participation of the complex species $Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}$ is provided by the result that the bonded and free oxalate are photoactivated with equal ease since the ring opened oxalate ligand is similarly photoactivated as a free bioxalate ion. There is no evidence that the complex species $Sn(C_2O_4)_2(OH)_2^{2-}$ or $SnO(C_2O_4)_2^{2-}$ is directly photoactivated. Provision was made for the direct photoactivation of the complex species $GeO(C_2O_4)_2^{2-}$ in the proposed photolysis mechanism of the germanium oxalato complex, but the photoreduction is facilitated by the interaction between the photoactivated complex species and a photoactivated bioxalate ion [6].

The activation enthalpy for the photolysis process of the germanium and tin oxalato complex in aqueous acidic solution is 10.8 and 53.8 kJ mol^{-1} respectively. It is unlikely that these values would differ so drastically if an oxyoxalato complex species participates in both photolysis processes. The relative low value in the case of the germanium oxalato complex provides for energy transfer rather than for primary photoactivation, for which a greater energy demand exists. The relatively high activation enthalpy in the case of the tin oxalato complex may probably be attributed to a process comprising both energy transfer and direct photoactivation.

The proposed photolysis mechanism is based on the result that both the bonded and free oxalate are photoactivated. The bonded oxalate is represented by the complex species that originates in solution by the deprotonation equilibrium

$$Sn(C_2O_4)(OC_2O_3H)(H_2O)(OH)_2^- \overset{K}{\rightleftharpoons} Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-} + H^+$$

favoured by the various considerations dealt with above. The free oxalate is mainly present as bioxalate ions in the pH region concerned. The primary photoactivation comprises the steps

$$Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-} \xrightarrow[k_1, I]{h\nu} Sn(C_2O_4)(OC_2O_3^*)(H_2O)(OH)_2^{2-} \qquad (1)$$

and

$$HC_2O_4^- \xrightarrow[k_2, I]{h\nu} [HC_2O_4^-]^* \qquad (2)$$

and is followed by the rate-determining steps

$$Sn(C_2O_4)(OC_2O_3^*)(H_2O)(OH)_2^{2-} \xrightarrow[k_3]{} Sn(C_2O_4)(OH)_2^{2-} + 2CO_2 + H_2O \qquad (3)$$

and

$$\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-} + [HC_2O_4^-]^*} \xrightarrow[k_4]{} \mathrm{Sn(C_2O_4)(OH)_2^{2-} + HC_2O_4^- + 2CO_2 + H_2O} \quad (4)$$

The suggestion that both electron transfer by decarboxylation of a photoactived ring opened oxalate ligand (step 3) and indirect photoactivation of a complex molecule by energy transfer from a primarily photoactivated bioxalate ion during thermal collision (step 4) are rate-determining, is in agreement with the relatively high activation enthalpy. The liberation of carbon dioxide as the only gaseous product was verified by radiochemical and mass spectrometric techniques previously described [3]. The structural characteristics of the photolysis product could not be determined. In a previous paper [3] it was indicated that a Sn(II) oxalate species is formed during photolysis, which may be a simple oxalate or an oxalato complex.

The theoretical rate equation is derived after obtaining a concentration expression for the participating complex species in terms of [X] from the deprotonation equilibrium in the dissolution process (A).

$$2[\mathrm{X}] = [\mathrm{Sn(C_2O_4)(OC_2O_3H)(H_2O)(OH)_2^-}] + [\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}]$$

$$= \frac{[\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}]\,[\mathrm{H^+}]}{\mathrm{K}} + [\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}]$$

or

$$[\mathrm{X}] = \frac{\mathrm{K} + [\mathrm{H^+}]}{2\mathrm{K}}\,[\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}]$$

or

$$[\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}] = \frac{2\mathrm{K}}{\mathrm{K} + [\mathrm{H^+}]}\,[\mathrm{X}]$$

The initial photolysis rate is theoretically

$$\mathrm{R} = \mathrm{k_3}[\mathrm{Sn(C_2O_4)(OC_2O_3{}^*)(H_2O)(OH)_2^{2-}}] + \mathrm{k_4}[\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}][\mathrm{HC_2O_4^-}]^*$$

$$= \mathrm{k_3k_1I}[\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}] + \mathrm{k_4k_2I}[\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}][\mathrm{HC_2O_4^-}]$$

$$= \{\mathrm{k_3k_1} + \mathrm{k_4k_2}[\mathrm{HC_2O_4^-}]\} \times [\mathrm{Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-}}]\,\mathrm{I}$$

$$= \frac{2\mathrm{K}\{\mathrm{k_3k_1} + \mathrm{k_4k_2}[\mathrm{HC_2O_4^-}]\}[\mathrm{X}]\,\mathrm{I}}{\mathrm{K} + [\mathrm{H^+}]}$$

$$= \frac{\{\mathrm{k_a} + \mathrm{k_b}[\mathrm{Ox}]_\mathrm{F}\}[\mathrm{X}]\,\mathrm{I}}{\mathrm{K} + [\mathrm{H^+}]}$$

This is in agreement with the experimental expression for $k_a = 2Kk_3k_1$, $k_b = 2Kk_4k_2$ and $[Ox]_F = [HC_2O_4^-]$ in the pH region concerned.

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