Inorganica Chimica Acta, 21 (1977) 89–93

The Photolysis of Potassium-μ-oxalato-di[trisoxalatostannate(IV)] Tetrahydrate in Aqueous Acidic Solution.
I. Photochemical Behaviour

E. L. J. BREET and R. van ELDIK

Research Unit for Chemical Kinetics, Department of Chemistry, Potchefstroom University for C. H. E., Potchefstroom 2520, Republic of South Africa

Received June 9, 1976

The photolysis process of the complex $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ in aqueous acidic solution comprises photoreduction of Sn(IV) to Sn(II), accompanied by oxidation of an oxalate ligand to CO_2. The thermally unstable photolysis product is slowly converted to the original complex species through oxidation by air and/or oxalate, the latter being indicated by the formation of glycolate. The results were obtained by employing spectrophotometric and radiochemical techniques.

Introduction

The importance of photochemical studies of the metal oxalato complexes is demonstrated by the large number of papers concerning the subject, many of which are mentioned in the reviews of Adamson [1], Krishnamurty and Harris [2] and Wehry [3]. The photolysis processes of various metal oxalato complexes have been analysed in this laboratory [4–8]. These investigations have mainly been devoted to the oxalato complexes of the transition metals, resulting in a lack of photochemical information concerning the non-transition metal oxalato complexes. This may obstruct the formulation of a composite theory for the photochemistry of these complexes.

Studies on the photolysis of the complexes $Sb(C_2O_4)_3^{3-}$ [9] and $Ge(C_2O_4)_3^{2-}$ [10, 11] have recently been completed in the view of this shortcoming. These investigations have created interest in the photochemical process of complexes of Sn(IV), since such studies would permit a valuable comparison to be drawn between the photochemical reaction modes of metal oxalato complexes of which the central metal atoms belong to neighbouring positions in the periodic table of the elements. The present investigation is aimed at the disclosure of the photochemical behaviour of the oxalato complex $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ in aqueous acidic solution, on which no literature data are available.

Experimental

A simplified procedure for the synthesis of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ was adopted, the crystalline product being checked by chemical analysis and by determining the crystal structure by X-ray diffraction [12].

Test solutions were prepared by dissolving the complex in distilled water, the pH being regulated with HCl or KOH and the ionic strength with KCl. It was indicated in a previous paper [13] that three oxalate groups become available on dissolution of each complex molecule. Thus the test solutions are self-buffering and no additional free oxalate was added.

The test and corresponding blank solutions were irradiated in identical quartz tubes in a newly-designed, improved version of the photolysis reaction vessel employed in a previous investigation [10]. The geometric reproducibility of the six irradiation positions has been improved to an accuracy of 2%. The irradiation intensity of the ultraviolet burner (Q 700, Quarzlampen Gesellschaft Hanau, λ_{max} = 253 nm) was kept constant regardless of voltage fluctuations by an a.c. voltage stabiliser (Philips PE 1602) and individually controlled for each sample holder by selecting an appropriate slitwidth. The temperature of the entire photolysis reaction vessel was kept constant within 0.5 °C with the aid of a thermostatically controlled cooling unit (Lauda Ultra Kryomat TK 30D).

The photolysis process was followed spectrophotometrically by measuring the absorbance at 258 nm (λ_{max} = 258 nm, $\epsilon = 285\ M^{-1}\ cm^{-1}$). The non-irradiated and irradiated test solutions were measured against corresponding non-irradiated and irradiated blank solutions by means of a Unicam SP 1800 spectrophotometer. A radiochemical liquid scintillation technique developed in this laboratory [14], was used to confirm some of the spectrophotometric measurements. The technique is based on the exchange of oxalate ligands of the complex with C^{14} labelled oxalate ions in solution to yield radioactive carbon dioxide whenever a photochemical redox reaction occurs. The carbon dioxide is collected in a suitable scintillation liquid for measurement in a liquid scintillation counter.

Results and Discussion

The graphical representation 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] added free oxalate ion concentration (mol liter^{-1})
μ ionic strength (mol liter^{-1})
d slitwidth (mm)
T temperature (K)
A spectrophotometric absorbance
t irradiation time (min)

The change of the ultraviolet absorption spectrum of an aqueous solution of the complex during ultraviolet irradiation, is given in Figure 1. It is illustrated in the same figure that comparable changes can be effected by adding Sn(II) as an aqueous solution of anhydrous $SnCl_2$ to the complex solution. Thus the complex species in solution, with Sn in the 4+ oxidation state, undergoes photoreduction. This was confirmed radiochemically by the detection of liberated carbon dioxide as the result of photooxidation of an oxalate ligand. It was indicated experimentally by means of a mass spectrometric gasanalysis, sensitive to molecules with low molecular mass, that no carbon monoxide is liberated during photolysis and that the gaseous product is exclusively carbon dioxide.

The ultraviolet absorption spectrum of the solution irradiated for 60 minutes (Figure 1) is given by the broken line after a period of 24 hours following irradiation. This indicates thermal reverse oxidation

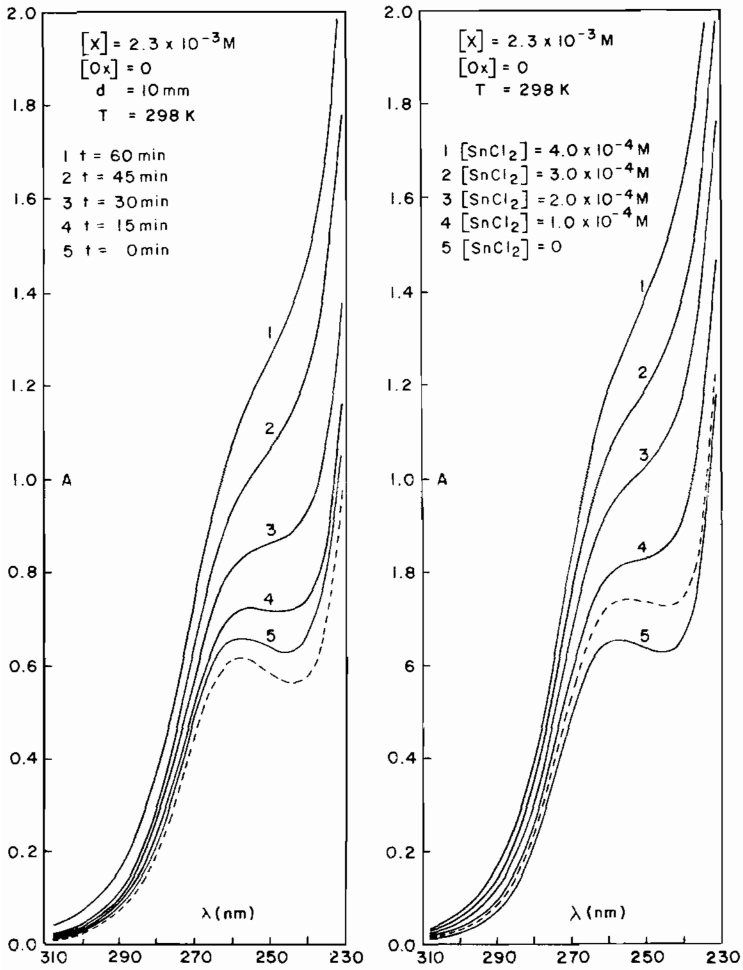

Fig. 1. Change of ultraviolet absorption spectrum of aqueous solution of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ during photolysis (left) and by addition of anhydrous tin(II) chloride (right).

of the photolysis product to the original complex species in the absence of ultraviolet light. This reverse reaction requires oxalate in the place of the bonded oxalate lost as carbon dioxide during ultraviolet irradiation. The existing free oxalate in solution (three oxalate groups per complex molecule) is partly consumed, leading to a lower complex absorbance as indicated previously [13]. The reverse oxidation obviously takes place according to two completely different reaction paths. The principal way in which the photolysis product is converted to the original complex species seems to be through direct oxidation by molecular oxygen. It is known that Sn(II) solutions are readily oxidised by air (especially in light) and always, unless stringent precautions are taken, contain some Sn(IV) [15]. A similar sensitivity to oxygen is observed in the redox photolysis of $Fe(C_2O_4)_3^{3-}$, the effect being ascribed to direct oxidation of the formed ferrous salt and free radical by molecular oxygen [2]. The reverse oxidation is also effected to a lesser degree by the reduction of oxalate to glycolate, as was confirmed experimentally by means of the 2,7-dihydroxynaphtalene test [16]. This test served as an only indirect indication of a photochemical redox reaction in the case of the complex $K_2Ge(C_2O_4)_3 \cdot H_2O$, the photolysis product of which exhibits a corresponding thermal instability [10]. The relative unavailability of suitable Ge(II) compounds prevented a direct identification of the photolysis process as described above. The thermal

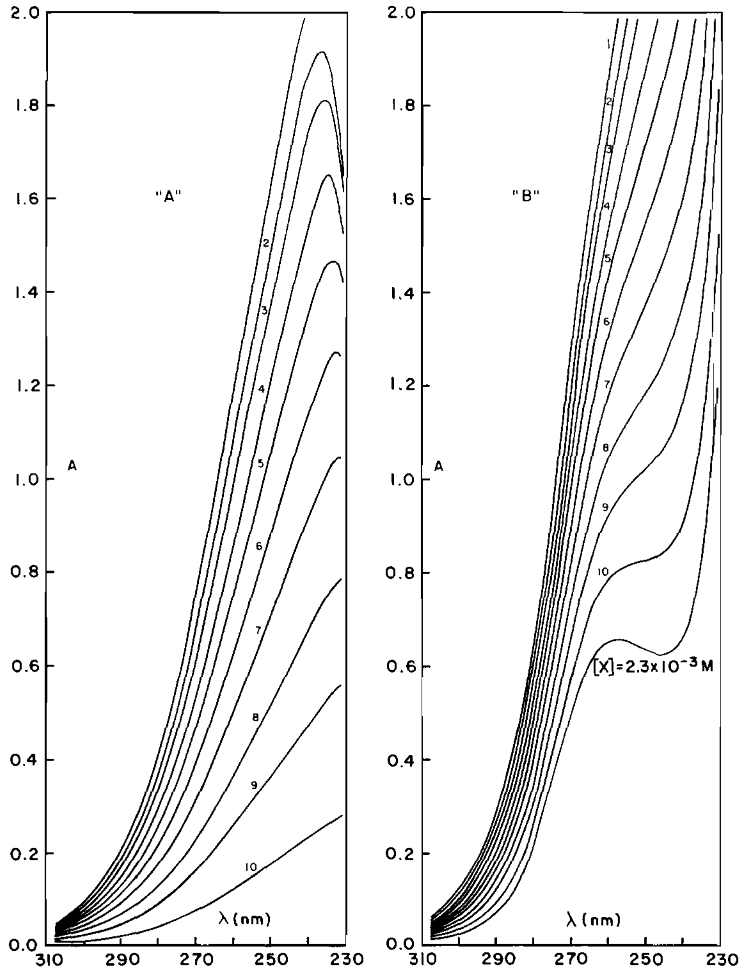

Fig. 2. Calibration of photolysis product absorbance at 258 nm using monovariant tin(II) chloride-complex mixtures.
1 $[SnCl_2] = 1.0 \times 10^{-3}$ *M*, 2 $[SnCl_2] = 9.0 \times 10^{-4}$ *M*
3 $[SnCl_2] = 8.0 \times 10^{-4}$ *M*, 4 $[SnCl_2] = 7.0 \times 10^{-4}$ *M*,
5 $[SnCl_2] = 6.0 \times 10^{-4}$ *M*, 6 $[SnCl_2] = 5.0 \times 10^{-4}$ *M*,
7 $[SnCl_2] = 4.0 \times 10^{-4}$ *M*, 8 $[SnCl_2] = 3.0 \times 10^{-4}$ *M*,
9 $[SnCl_2] = 2.0 \times 10^{-4}$ *M*, 10 $[SnCl_2] = 1.0 \times 10^{-4}$ *M*.

"A" $SnCl_2$ added to $[X] = 2.3 \times 10^{-3}$ *M* and registered with reference to $[X] = 2.3 \times 10^{-3}$ *M*.
"B" $SnCl_2$ added to $[X] = 2.3 \times 10^{-3}$ *M* and registered with reference to H_2O.

instability of the photolysis product of both the germanium and tin oxalato complexes explains why it could not be isolated or its structural characteristics experimentally determined.

The thermal reverse reaction is also observable for the complex solutions to which anhydrous $SnCl_2$, was added. It is illustrated by a broken line in Figure 1 for the solution to which 4×10^{-4} *M* $SnCl_2$ was added. The reverse reaction evidently proceeds in an analogous way as in the case of the irradiated solutions but, as the original complex species does not decompose photochemically in this case and an additional quantity of the complex species is formed during the reverse reaction, the final absorbance is higher than the initial absorbance.

The molar extinction coefficient of the photolysis product was determined experimentally by adopting the method of monovariance, *i.e.* various molar concentrations (1×10^{-4}–1×10^{-3} *M*) $SnCl_2$ were added to a fixed complex concentration ($[X] = 2.3 \times 10^{-3}$ *M*). Figure 2 presents the ultraviolet spectrum of each mixture registered with reference to a complex solution with molar concentration 2.3×10^{-3} *M* (spectra "A") and water (spectra "B") immediately after mixing. The absorbances at 258 nm of the various molar concentrations $SnCl_2$ can be read directly from spectra "A". These values are, except for minor differences due to the slow thermal reverse reaction, in excellent agreement with those calculated from spectra "B" as the difference between the observed absorbances and that of the complex solution at the same wavelength. This illustrates that at 258 nm the absorbances of the various molar concentrations $SnCl_2$ are linearly additive with respect to the absorbance of the complex species. The conclusion also follows from the linear variation of the absorbances with molar concentration $SnCl_2$, since the absorbance of the complex species obeys the Beer–Lambert law at the wavelength mentioned. The extinction coefficient of $SnCl_2$ at 258 nm was determined as $\epsilon = 1325\ M^{-1}\ cm^{-1}$ from the slope of the linear relation. It can be considered as the molar extinction coefficient of the photolysis product at this wavelength, since the large difference between the numerical values obtained for similar determinations, *viz.* $\epsilon \sim 350\ M^{-1}\ cm^{-1}$ in the case of an aqueous solution and $\epsilon = 2000\ M^{-1}\ cm^{-1}$ in the case of a 1.6×10^{-2} *M* oxalate solution, indicates that a complex is formed between the added $SnCl_2$ and the free oxalate in solution.

The large numerical value of the extinction coefficient of the photolysis product at 258 nm explains why, as a result of the thermal reverse reaction (oxidation by oxygen and glycolate forming oxalate reduction), the observed absorbance of an irradiated solution cannot be measured accurately. However, the oxidation by air was eliminated by carrying out the photolysis process in nitrogen atmosphere. The thermal reverse reaction by oxalate reduction is not eliminated in this way, but it proceeds so slowly that its influence on the immediate spectrophotometric measurement after irradiation, is negligible. The measured absorbances at 258 nm were nevertheless registered as time-calibrated lines, so that if they would exhibit slopes worth mentioning due to considerable reverse reaction, the desired values could be obtained by extrapolation. The results in Figure 3 indicate the effective elimination of the reverse reaction in nitrogen atmosphere.

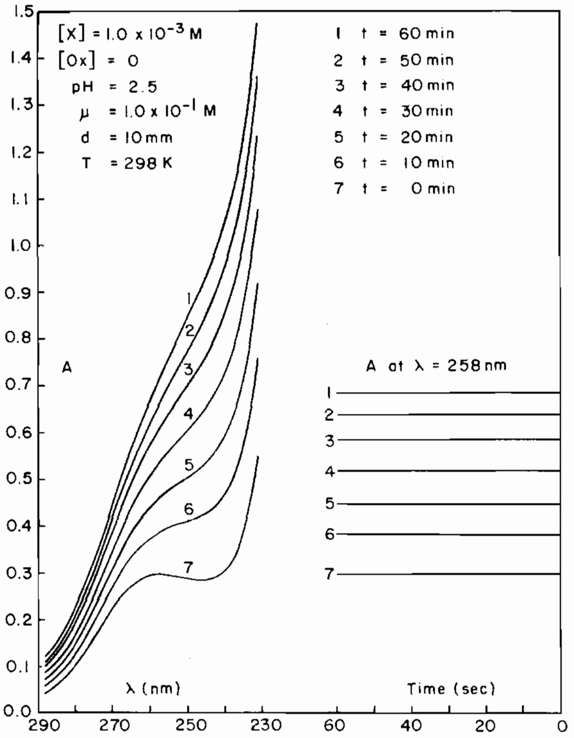

Fig. 3. Illustration of spectrophotometric measurement of photolysis product absorbance.

The absorbance versus time curve obtained from the spectrophotometric measurements in Figure 3, is in Figure 4 compared to the count rate versus time curve obtained under identical experimental conditions by radiochemical measurement of the radioactive carbon dioxide liberated when C^{14} labelled oxalic acid ($2\mu Ci/20\ cm^3$ of a mother solution of $50\mu Ci/10\ cm^3$ for $[X] = 1.0 \times 10^{-3}$ *M* and $[Ox] = 0$) is used. It is clear that the same result is obtained whether the increase in absorbance due to the photoreduction of Sn(IV) to Sn(II) or the increase in count rate due to the photooxidation of oxalate to carbon dioxide is measured. The photolysis can thus be followed spectrophotometrically and radiochemically. The large value of the molar extinction coefficient leads to relatively large differences between the spectrophotometrically measured absorbances for va-

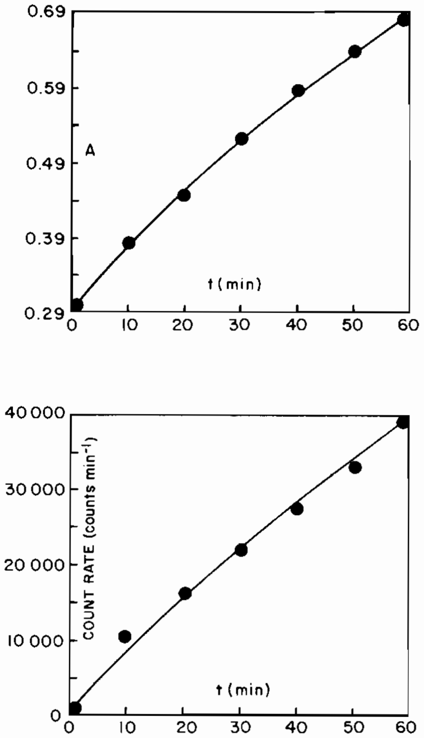

Fig. 4. Comparison of absorbance *versus* time and count rate *versus* time curves.

rious irradiation times, though they are not indicative of a rapid photolysis process. The average absorbance at 258 nm represents decomposition of merely 5% of the complex species, and the corresponding amount of liberated carbon dioxide is insufficient for accurate radiochemical analysis of the photolysis process. A spectrophotometric analysis of the photolysis process is thus favoured since long irradiation times are for various reasons undesirable.

The gradual termination of the measured absorbance or count rate with irradiation time (Figures 3 and 4) is the result of the simultaneous occurrence of the competitive processes

$$\mathrm{Sn(IV)} \xrightarrow{h\nu} \mathrm{Sn(II)} + \mathrm{CO_2}$$

and

$$\mathrm{Sn(II)} \xrightarrow{\Delta} \mathrm{Sn(IV)} + \text{glycolate}$$

The results of a kinetic analysis of the overall process and the forward photochemical reaction, are presented in a separate paper [17]. The principal considerations for such an analysis is to reveal the hitherto unknown photolysis mechanism and thus add to the understanding of the photochemical behaviour described above, and to afford a possible choice between the two proposed dioxalato species that result from the dissolution of the complex [13].

Acknowledgement

The authors gratefully acknowledge financial support from the S.A. Council for Scientific and Industrial Research and the S.A. Atomic Energy Board.

References

1 A. W. Adamson *et al.*, *Chem. Rev.*, *68*, 541 (1968).
2 K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, *61*, 213 (1961).
3 E. L. Wehry, *Quart. Rev.*, *21*, 213 (1967).
4 D. J. A. de Waal and J. A. van den Berg, *Tydskrif vir Natuurwetenskappe*, *9*, 1 (1969).
5 R. van Eldik and J. A. van den Berg, *J. S. Afr. Chem. Inst.*, *22*, 19 (1969).
6 R. van Eldik and J. A. van den Berg, *J. S. Afr. Chem. Inst.*, *22*, 24 (1969).
7 B. S. Maritz, R. van Eldik and J. A. van den Berg, *J. S. Afr. Chem. Inst.*, *28*, 14 (1975).
8 A. G. Brits, R. van Eldik and J. A. van den Berg, *Z. Physik. Chem.*, Neue Folge, in the press.
9 J. J. Prinsloo and J. A. van den Berg, *Tydskrif vir Natuurwetenskappe*, *10*, 76 (1970).
10 E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta*, *9*, 177 (1974).
11 E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta*, *9*, 183 (1974).
12 G. J. Kruger, E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta*, *19*, 151 (1976).
13 E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta*, *20*, 99 (1976).
14 R. van Eldik and R. Alberts, *J. S. Afr. Chem. Inst.*, *25*, 17 (1972).
15 F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York p. 482 (1966).
16 F. Feigl, "Spot Tests in Organic Analysis", Elsevier, Amsterdam, p. 465 (1966).
17 E. L. J. Breet and K. van Eldik, *Inorg. Chim. Acta*, *21*, 95 (1977).