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The Photolysis of Trioxalatogermanate(IV) in Aqueous Solution*. I. Photochemical Behaviour

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The photochemical behaviour of the trioxalatogermanate(IV) ion has been studied. A distinctive spectral change in the ultraviolet absorption region of the complex ion is related to the formation of a photolysis product, the yield of which depends on a preequilibration prior to irradiation. The formation of glycolate during the reverse reaction of the thermally unstable photolysis product is ascribed to the reduction of free oxalate, by which indirect evidence of a photochemical redox reaction is provided. The investigation of the preequilibration and the identification of the photolysis product are discussed.

Introduction

Our investigations of photochemical behaviour during the past few years have mainly been devoted to the oxalato complexes of the transition metals, resulting in limited photochemical data for the non-transition metal analogues. It was recently shown that the ions $Sb(C_2O_4)_3^{3-}$ and $Sb(C_2O_4)_2^-$ decompose photochemically to antimony metal and carbon dioxide, presenting a single known example of the photochemical behaviour of non-transition metal oxalato complexes.[1]

Germanium exhibits both the 4+ and 2+ oxidation states, enhancing the possibility of a photochemical redox reaction in the case of the $Ge(C_2O_4)_3^{2-}$ ion, which shows a distinctive absorption band in the ultraviolet region ($\lambda_{max} = 265$ nm, $\varepsilon_{max} = 10^2$). The present investigation on its photochemical behaviour provides more data concerning the photochemistry of non-transition metal oxalato complexes and extends the limited literature on the chemistry of germanium and its compounds.

Experimental

The complex $K_2Ge(C_2O_4)_3 \cdot H_2O$ was prepared according to literature[2], giving the following results on analysis:

Experimental Analysis	Theoretical Percentage	Experimental Percentage
oxalate[3]	61.0	60.7
germanium[4]	16.8	17.1
potassium[2]	18.1	18.3

An infrared spectrum shows the typical absorptions for oxalato complexes and confirms the covalent nature of the bonds.[5]

Test solutions were prepared by dissolving the complex in an oxalate buffer solution, adjusting the pH with potassium hydroxide and the ionic strength with potassium chloride. In a few experiments test solutions were sensitized by uranyl ion.

The test and corresponding blank solutions were irradiated in identical quartz tubes placed in equally spaced sample holders surrounding an ultraviolet burner (type Q700, Quarzlampen Gesellschaft Hanau, $\lambda_{max} = 253$ nm) mounted in a thermostated reaction vessel. The intensity of the incident light for each sample holder was controlled individually by selecting an appropriate slitwidth, while the temperature of the entire reaction vessel was kept constant within 0.5° over the range 14–50° C.

Experiments were performed to check the constancy of the light intensity and the reproducibility of the various irradiation positions within the reaction vessel. The results indicated that the light intensity remained virtually constant over the entire irradiation period and that the geometric reproducibility has an accuracy within 5%.

The spectrophotometric analyses were performed on a Unicam SP800 and a Zeiss PMQ II spectrophotometer, the spectra being recorded against corresponding blank oxalate buffer solutions. The blank and test solutions were irradiated simultaneously to correct for oxalate buffer decomposition.[6] Other instruments used

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in this investigation include a Unicam 292 pH meter, a Metrohm E382 conductivity meter, a Bellingham and Stanley polarimeter, a Metrohm E261 polarograph and a Packard 3003 Tri Carb liquid scintillation counter.

Results and Discussion

The discussion of the experimental results, conveniently presented in four subdivisions, is simplified by using the following symbols:

[X]	complex ion concentration (mole liter^{-1})
$[\mathrm{Ox}]_T$	total oxalate concentration (mole liter^{-1})
$[\mathrm{H}^+]$	hydrogen ion concentration (mole liter^{-1})
[SENS]	uranyl ion concentration (mole liter^{-1})
A	spectrophotometric absorbance of photolysis product
t	irradiation time (min)
d	slitwidth (cm)
T	temperature (K)

The parameters represented by these symbols were varied individually, maintaining the remaining parameters at a constant value of $[X] = 1.5 \times 10^{-2}$; $[\mathrm{Ox}]_T = 3.0 \times 10^{-2}$; $[\mathrm{SENS}] = 3.0 \times 10^{-4}$; pH = 2.8; d = 0.95; T = 287.

Preliminary and Qualitative Results

These results follow from an investigation of the influence of the reaction medium on the formation of the photolysis product which shows a distinctive absorption at 294 nm. The course of the reaction in non-sensitized and sensitized non-buffered and buffered test solutions is visualized in Figure 1.

The newly appeared absorption peak at 294 nm shows that the same photolysis product is formed in all cases, but the yield differs. The absorption change at 265 nm is interpreted as a change in complex species. The photolysis rate is enhanced in oxalate buffer whether the complex ion is non-sensitized or sensitized. The photoactivity of a non-buffered solution is decreased by the addition of sensitizer while a buffered solution, though initially showing a decrease in photoactivity due to an induction period, finally gives an increased yield of the product.

The various influences are more clearly seen from the results in Tables I, II and III. With constant [X] (Table I) an increase in [SENS] slightly decreases the photoactivity. An increase in [X] definitely increases the photoactivity when [SENS] is kept constant (Table II). A simultaneous increase in [X] and [SENS] (Table III) only slightly increases the photoactivity. It seems reasonable to conclude that the presence of an oxalate buffer and the influence of [X] are the predominant factors controlling the photolysis as far

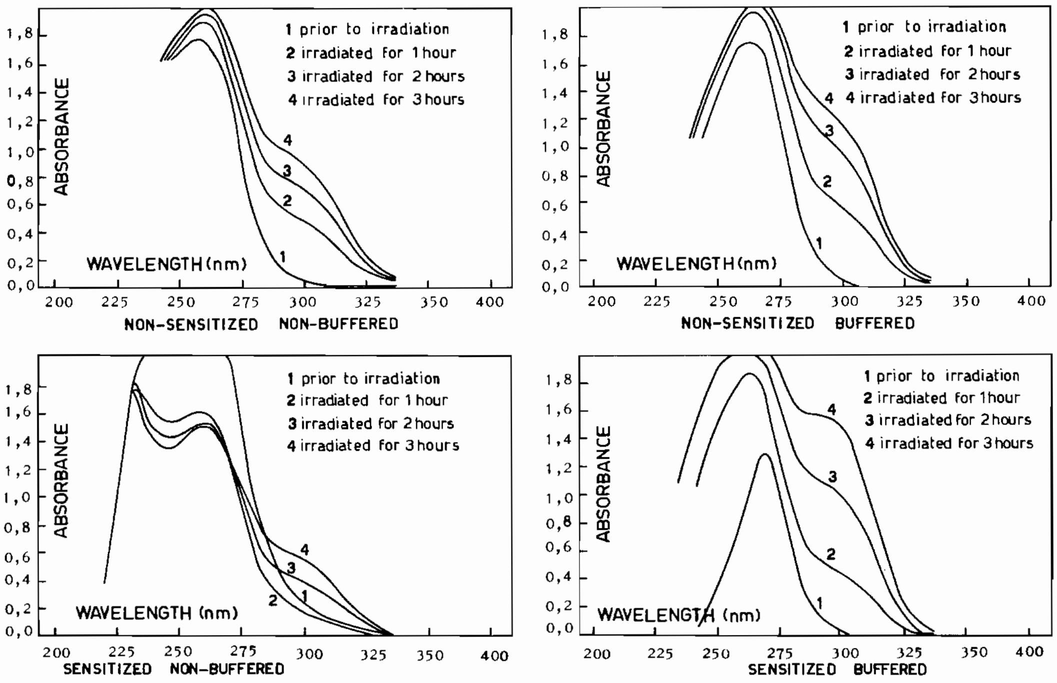

Figure 1. Photolysis in various reaction media.

TABLE I. Influence of [SENS].

t	A at 294 nm			
	[SENS] 0.0×10^{-4}	1.0×10^{-4}	2.0×10^{-4}	3.0×10^{-4}
30	0.16	0.14	0.09	0.04
60	0.50	0.37	0.34	0.33
90	0.70	0.53	0.51	0.52
120	0.90	0.80	0.72	0.66
150	1.04	1.05	0.92	0.86
180	1.08	1.15	1.10	1.02

TABLE II. Influence of [X].

t	A at 294 nm			
	[X] 0.5×10^{-2}	1.0×10^{-2}	1.5×10^{-2}	2.0×10^{-2}
30	0.00	0.00	0.05	0.11
60	0.12	0.18	0.33	0.44
90	0.18	0.31	0.51	0.64
120	0.31	0.54	0.66	0.89
150	0.40	0.72	0.86	1.21
180	0.49	0.86	1.02	1.50

TABLE III. Influence of [SENS] Proportional to [X].

t	A at 294 nm			
	[X] 0.5×10^{-2}	1.0×10^{-2}	1.5×10^{-2}	2.0×10^{-2}
	[SENS] 1.0×10^{-4}	2.0×10^{-4}	3.0×10^{-4}	4.0×10^{-4}
30	0.05	0.02	0.05	0.02
60	0.24	0.26	0.33	0.31
90	0.42	0.41	0.51	0.48
120	0.62	0.65	0.66	0.72
150	0.75	0.86	0.86	0.89
180	0.88	0.93	1.02	1.04

as the reaction medium is concerned. The neglegtibly small influence of [SENS] allows sensitizer to be ruled out as a complicating factor.

Preequilibration

A principal feature of freshly prepared test solutions is the absence of photoactivity. Apparently the photoactivatable species forms by a slow equilibrium that reaches completion after about eight hours in the dark at room temperature. A thorough investigation showed that no change in the absorption spectrum and optical rotation occurs during the preequilibration but the pH decreases and the conductivity increases as shown in Figure 2.

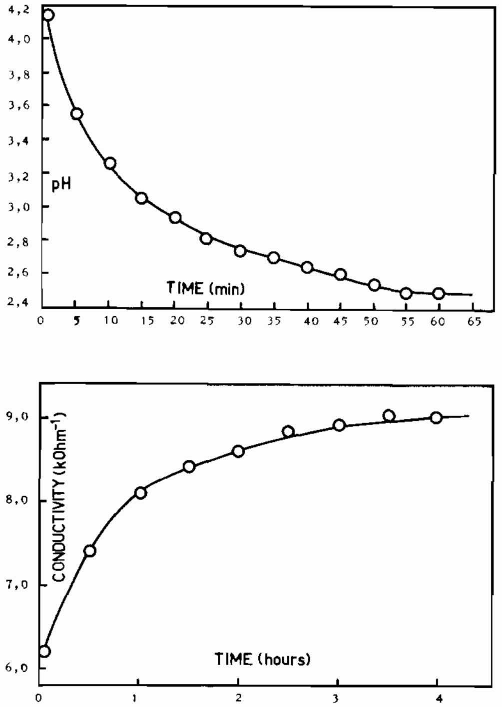

Figure 2. Change in pH and conductivity during preequilibration.

These changes can only be explained by the preequilibration

$$\begin{array}{lcl} Ge(C_2O_4)_3^{2-} + H_2O + H_3O^+ & \rightleftharpoons & Ge(C_2O_4)_2(OH)_2^{2-} + 2H^+ + HC_2O_4^- \\ Ge(C_2O_4)_2(OH)_2^{2-} & \rightarrow & GeO(C_2O_4)_2^{2-} + H_2O \\ \hline Ge(C_2O_4)_3^{2-} + H_2O & \rightleftharpoons & GeO(C_2O_4)_2^{2-} + H^+ + HC_2O_4^- \end{array}$$

and

$$\begin{array}{lcl} Ge(C_2O_4)_3^{2-} + H_2O + OH^- & \rightleftharpoons & Ge(C_2O_4)_2(OH)_2^{2-} + HC_2O_4^- \\ Ge(C_2O_4)_2(OH)_2^{2-} & \rightarrow & GeO(C_2O_4)_2^{2-} + H_2O \\ \hline Ge(C_2O_4)_3^{2-} + OH^- & \rightleftharpoons & GeO(C_2O_4)_2^{2-} + HC_2O_4^- \end{array}$$

for the pH at which experiments were performed, because (i) the decrease in pH implies an equilibrium in which hydrogen ions are released or hydroxyl ions are consumed, (ii) the release of hydrogen and bioxalate ions explains the increase in conductivity, (iii) the spectrophotometric analysis of a test solution passed through a cation exchanger (Dowex 50W–X4) after the preequilibration showed that the final complex species is negatively charged, (iv) the final complex species must be a germanium(IV) oxalato compound resembling the initial complex ion as far as the metal–oxygen bonds to the oxalate chelate ligands are concerned, explaining why no change in the absorption spectrum is observed during the preequilibration, (v) the possible existence of the complex ion $GeO(C_2O_4)_2^{2-}$ at pH 3–6 as inferred from determinations of germanium/oxalate ratios is claimed in literature[7].

The changes in pH and conductivity mainly occur during the first hour of the preequilibration period of about eight hours required for maximum photoactivity. This is explained by the minimal influence the slow conversion of the ion $Ge(C_2O_4)_2(OH)_2^{2-}$ to $GeO(C_2O_4)_2^{2-}$ will have on the pH and the conductivity.

Thermal Reverse Reaction

Irradiated test solutions show a slow thermal reverse reaction by which the photolysis product is reconverted to the original complex ion. The course of the reverse reaction is illustrated in Figure 3.

The sensitivity of the reverse reaction to oxygen suggests the possibility that the photolysis product is oxidised to the original complex ion. In such a case free oxalate must necessarily be reduced as the reverse reaction even occurs in an inactive nitrogen atmosphere, excluding the possibility that only oxidation by air is responsible for the reverse reaction.

Identification of Photolysis Product

A variety of techniques including spectrophotometry, polarimetry, polarography, electrometry and radiochemistry were adopted in an effort to identify the photolysis product.

The possibility of photo-isomerisation in which the photolysis product is an isomeric intermediate, was investigated. According to literature[8] the separation of the optical isomers of the complex ion is effected by fractional crystallisation of the quinine derivative $Q_2Ge(C_2O_4)_3$ ($Q = C_{20}H_{24}O_2N_2$), followed by the elimination of the quinine group with solid potassium iodide thus obtaining the corresponding potassium derivative. We have been able to show that the observed rotation is not due to the separation of the isomers but to traces of quinine iodide that remain in solution. This result is in agreement with comment in literature[9] on the claimed separation of the optical isomers of the complex ion $U(C_2O_4)_4^{4-}$, indicating that quinine iodide is not really as insoluble as was stated by the authors concerned.

The photoreduction of the complex ion to a germanium(II) oxalato species is another possibility explored. A variety of methods were applied to synthesize such a species. The hydroxide $Ge(OH)_2$ prepared according to literature[10] was treated with a variety of oxalate solutions, but owing to its unreactivity and insolubility at temperatures sufficiently low for the photolysis product to exist, no synthesis could be accomplished. Only on vigorous heating does the hydroxide dissolve slightly, but the ultraviolet spectrum of the solution so obtained corresponds with that of the trioxalatogermanate(IV) ion. Direct reduction of the complex ion using strong reducing agents like sodium amalgam and hypophosphorous acid failed.

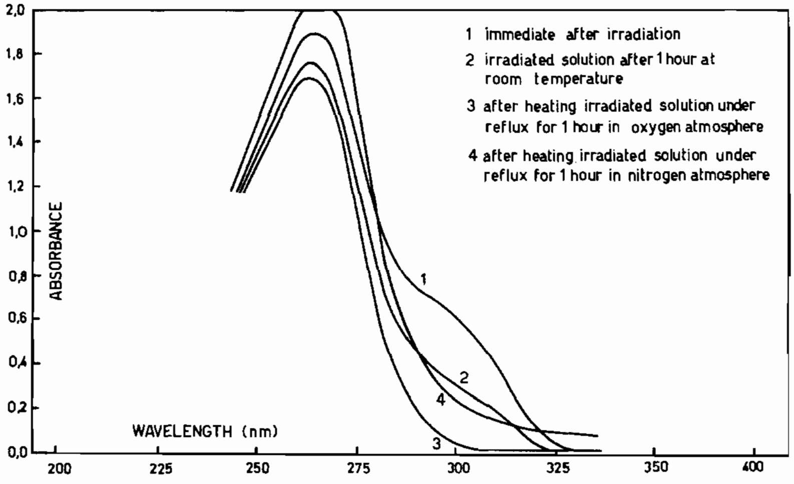

Figure 3. Thermal reverse reaction.

The difference in the standard electrode potentials for Ge(II)/Ge(0) and Ge(IV)/Ge(0) is sufficiently large (0.15 volt)[11] to expect a change in the polarographic halfwave potential and the emf of a test solution during irradiation. The polarographic results do not lead to any conclusion as we found the obtained polarograms to be those of the oxalate buffer acting as the electrolyte. A germanium electrode was constructed by coating a platinum electrode with molten germanium metal. The unrealistic emf values obtained with this electrode versus a standard calomel electrode show that we did not succeed in measuring either of the above-mentioned potentials. Both the polarographic and emf results illustrate that germanium is stabilised to such an extent by complexation with oxalate that electrode reduction is not easily effected.

A radiochemical liquid scintillation technique[12] was adopted to indicate whether radioactive carbon dioxide is produced photochemically when ^{14}C-labelled oxalate is used. The results provide direct evidence for the presence of radioactive carbon dioxide as decomposition product of the complex ion. The oxidation of the oxalate ligand to carbon dioxide is a principal feature of the photoreduction of various transition metal oxalato complexes.[13]

In the discussion of the thermal reverse reaction the conclusion was reached that oxidation of the photolysis product to the original complex ion necessarily implies reduction of free oxalate. An example of such a reaction found in literature[14] is the reduction of free oxalate by chromium(II) to glycolate, the presence of which is indicated by the 2,7-dihydroxynaphtalene test.[15] If it is assumed that the photolysis product is an unstable germanium(II) species, the oxidation to the original germanium(IV) species during the reverse reaction could readily be expected to proceed along a similar reaction path because of the strong reducing properties of germanium(II) compounds in solution.[16]

TABLE IV. Glycolate Formation.

Tested for Glycolate	A at 294 nm		Glycolate Absorbance at 540 nm	
	Non-buffered	Buffered	Non-buffered	Buffered
Prior to Irradiation	0.00	0.00	0.00	0.00
Immediate after Irradiation for Three Hours	0.83	1.40	0.03	0.08
After Heating the Irradiated Solution under Reflux for one Hour	0.24	0.14	1.40	0.39

The characteristic absorbance of glycolate at 540 nm obeys Beer's relation, making a quantitative spectrophotometric glycolate determination feasible. The results in Table IV confirm the formation of glycolate during the reverse reaction, thereby providing evidence of a photochemical redox reaction. The lower glycolate absorbance of buffered test solutions is due to a different molar extinction coefficient in oxalate medium. The inability to prepare a germanium(II) oxalato compound may be attributed to oxidation to the germanium(IV) derivative on heating germanium(II) hydroxide in the presence of oxalate.

The available results suggest that the photolysis product could be an unstable germanium(II) oxalato species, the composition of which is yet unknown. The results show a characteristic time dependence and are sufficiently reproducible to allow for a reaction kinetic investigation of the formation of the photolysis product. This may throw more light on the hitherto unknown reaction mechanism and thus add to the understanding of the photochemical behaviour of the trioxalatogermanate(IV) ion.

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