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The Kinetics and Mechanism of the Hydrolysis of the Trioxalatogermanate(IV) Ion in Aqueous Acidic Solution

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The title reaction has been studied spectrophotometrically by measuring the absorbance of released oxalate ion at 230 nm as a function of various rate parameters. The dependence of the observed first-order rate constant on these rate parameters and the results of ion exchange and pH titration techniques revealing the structural characteristics of the final hydrolysis product, jointly enable the proposition of a hydrolysis mechanism. This mainly consists of acid-dependent aquation and slightly opposing oxalate-dependent anation reactions followed by an acid–base equilibrium. The values of various kinetic parameters are reported and reference is made to the photoactivity of the hydrolysis product, whereby linkage to existing literature data is provided [*1*].

Introduction

Our previous work [2, 3] on the complex ion $Ge(C_2O_4)_3^{2-}$ was mainly concerned with its photoactivity in aqueous acidic solution. It was pointed out that the complex ion itself is not photoactive but that it is converted via hydrolysis to a photoactive complex species during the first few hours following the dissolution of the complex. Attention is now drawn to this hydrolysis process for the purpose of revealing its unknown mechanism. Since the hydrolysis process may be regarded as an integral part of the photochemical behaviour of the complex ion under consideration, an analysis of the process may valuably supplement existing literature data and also add to the relatively limited knowledge of the chemistry of germanium as a less familiar non-transition metal.

Besides the gradual conversion of a non-photoactive complex ion into a photoreactive species that facilitates photoreduction of Ge(IV) to Ge(II) on irradiation with high-intensity ultraviolet light (λ_{max} = 253 nm), three major experimentally detectable changes occur during hydrolysis. Although these will be dealt with in more detail, it is at this stage sufficient to say that at least one could be utilised efficiently for a kinetic analysis. The final proposition of a hydrolysis mechanism amply demonstrates the usefulness of this kinetic approach, especially when complemented by information obtained from various ancillary techniques.

Experimental

The complex ion $Ge(C_2O_4)_3^{2-}$ is isolable as various salts according to procedures described by Bardet and Tchakarian [4], Willard and Zuehlke [5], Dean *et al.* [6] and Kurnevich and Shagisultanova [7], the most suitable for our purposes being the potassium salt according to Arvedson and Larsen [8]. The results of the chemical analysis for C_2O_4, K and Ge are given in a previous paper [2] and are supplemented by CHN analyses yielding C 16.58% (theoretical 16.65%) and H 0.48% (theoretical 0.47%).

The test solution for each kineric run was prepared by dissolving a weighed amount of $K_2Ge(C_2O_4)_3 \cdot H_2O$ in deionised water, the pH and ionic strength being regulated by adding pre-estimated amounts of stock solutions of HCl or KOH and KCl respectively. The free oxalate in solution was varied by the addition of oxalic acid, the values $K_1 = 4.3 \times 10^{-2}$ and $K_2 = 1.56 \times 10^{-4}$ mol dm^{-3} of McAuley and Nancollas [9] 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 the above-mentioned stock solutions. A few kinetic runs were repeated using $HClO_4$ and $NaClO_4$ instead of HCl and KCl to ensure that the process under consideration was indeed hydrolysis and not complexation or substitution by chloride ion.

The hydrolysis process was followed spectrophotometrically by means of *in situ* absorbance measurements as a function of time using a Unicam SP 1800 spectrophotometer with a Techne C 100 temperature control unit. Samples of the various test solutions were thermostatted separately at the corresponding temperatures to subsequently obtain the infinity readings. Complementary to the spectro-

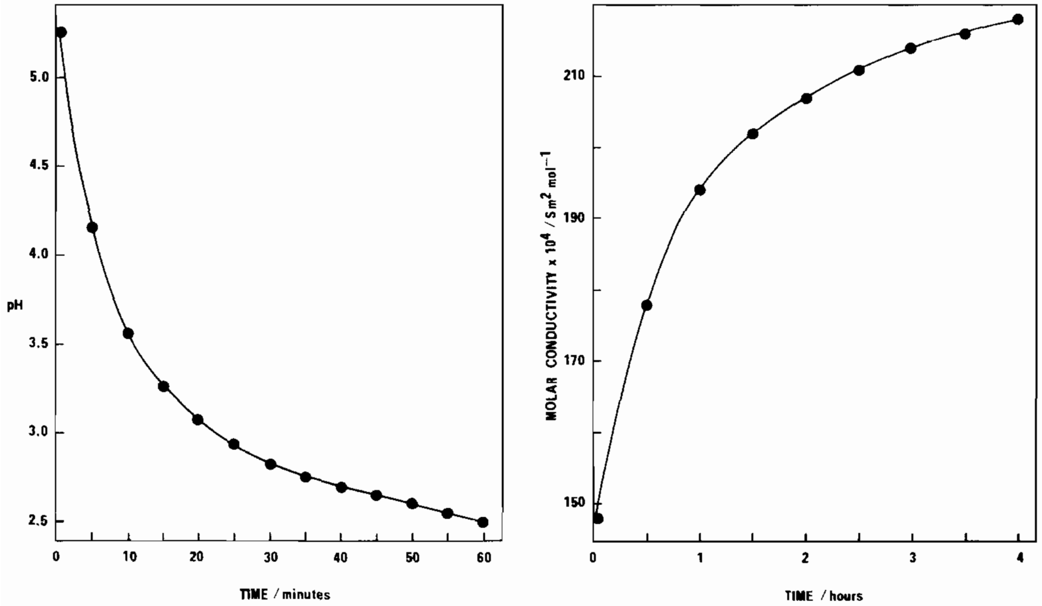

Fig. 1. Change in pH and molar conductivity during hydrolysis. [complex] = 1.5 X 10^{-2} mol dm^{-3}; [added oxalate] = 0; temperature = 25 °C.

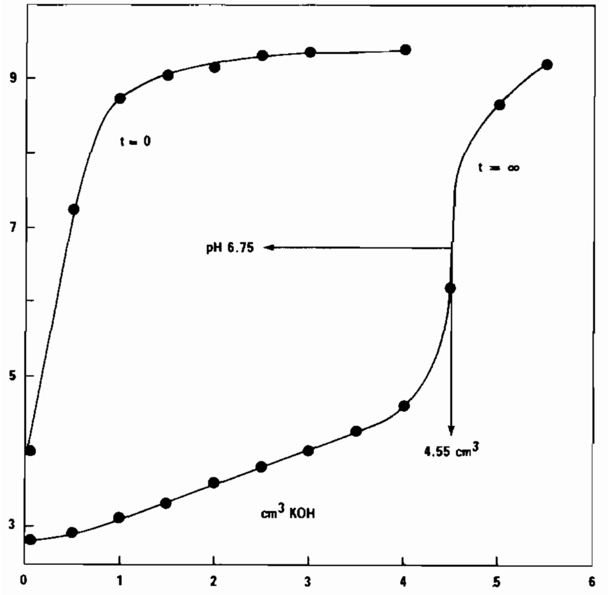

Fig. 2. pH titration of $K_2Ge(C_2O_4)_3 \cdot H_2O$ in aqueous solution. [complex] = 1 X 10^{-3} mol dm^{-3} (50 cm^3); [KOH] = 4.35 X 10^{-2} mol dm^{-3}.

photometric data various pH and conductivity measurements were performed using a Metrohm E 500 digital pH meter and a Metrohm E 382 conductometer respectively.

Results and Discussion

On dissolution of the complex various changes become detectable. Firstly there is a decrease in pH as shown in Fig. 1. The attribution of this decrease to a release of hydrogen ions instead of a consumption of hydroxyl ions is based on the difference between the pH titration curves obtained by titrating aqueous solutions with standard alkali immediately after dissolution of the complex and after termination of the pH decrease. It is evident from Fig. 2 that the endpoint in the latter case corresponds to [KOH]/[complex] = 4, a ratio to which will be referred again. The release of hydrogen ions as the reason for the observed decrease in pH is also supported by a simultaneous increase in molar conductivity as shown in Fig. 1. Finally a significant change in the ultraviolet absorption spectrum is observed as the repetitive scans in Fig. 3 indicate. The increase in absorbance at 230 nm is considered an indication of a release of oxalate ion. The latter absorbs strongly in this wavelength region and, as a comparison of the two cases in Fig. 3 shows, the external addition of oxalate markedly decreases the change in absorbance. The time dependence of this absorbance change allowed for the kinetic analysis described below. The mentioned changes are presumably due to shifts in equilibria as inferred from the distinct isosbestic points in Fig. 3 and the observation that the resulting pH is not linearly related to [complex]. To summarise then, the various changes suggest a hydrolysis process that yields free oxalate ions, hydrogen ions and a photosensitive variant of the initial complex ion and which is retarded by the external addition of free oxalate. The present investigation is aimed at the disclosure of the mechanism of this hydrolysis process.

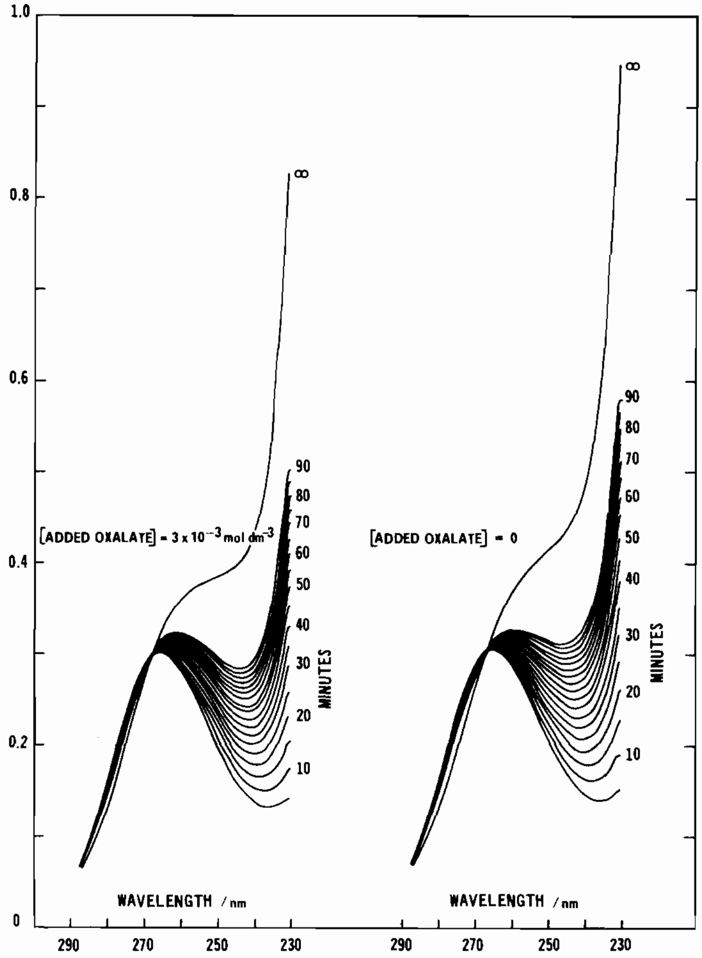

Fig. 3. Repetitive scans of ultraviolet absorption spectrum during hydrolysis. [complex] = 3 × 10^{-3} mol dm^{-3}; pH = 2.0; ionic strength = 0.1 mol dm^{-3}; temperature = 25 °C.

TABLE I. k_{obs} as a Function of [Added Oxalate]. Temperature = 25 °C, ionic strength = 0.1 mol dm^{-3}.

pH	10^3 [complex] mol dm^{-3}	10^4 k_{obs} s^{-1}					10^4 k_{av} s^{-1}
		10^3 [added oxalate] mol dm^{-3}					
		0.0	3.0	5.0	8.0	10.0	
1.0	1.0	2.13					2.13
	3.0	2.47	2.33	2.52	2.45		2.39 ± 0.13
		2.20					
	4.0	2.37					2.37
	5.0	2.43					2.43
1.5	1.0	1.98				2.17	2.08 ± 0.13
	2.0			1.85		1.83	1.84 ± 0.01
	3.0	2.23	2.15	2.18	2.13	2.15	2.17 ± 0.03
						2.17	
	4.0	2.17		2.12		2.07	2.12 ± 0.05
	5.0	2.17		2.08		2.18	2.14 ± 0.06

(continued overleaf)

TABLE I. *(continued)*

pH	10^3 [complex] mol dm^{-3}	10^4 k_{obs} s^{-1}					10^4 k_{av} s^{-1}
		10^3 [added oxalate] mol dm^{-3}					
		0.0	3.0	5.0	8.0	10.0	
2.0	3.0	1.87	1.72	1.90	1.77		1.82 ± 0.08
	5.0	1.73					1.73
2.5	1.0	1.47		1.48		1.60	1.52 ± 0.07
	2.0	1.50		1.50		1.50	1.50 ± 0.00
	3.0	1.67	1.58	1.68	1.48		1.55 ± 0.12
		1.43	1.42	1.42			
		1.68					
	4.0	1.78		1.75			1.77 ± 0.02
	5.0	1.63		1.73			1.66 ± 0.06
		1.62					
3.0	3.0	1.58	1.52	1.57	1.62		1.55 ± 0.05
		1.48		1.48			
		1.52					
		1.57					
		1.58					
	4.0	1.50					1.50
	5.0	1.58					1.58
3.5	1.0			1.42		1.40	1.41 ± 0.01
	2.0	1.52		1.55		1.53	1.53 ± 0.02
	3.0	1.58	1.63	1.63	1.73	1.70	1.65 ± 0.05
				1.65			
	4.0	1.73		1.87			1.80 ± 0.10
	5.0	1.72		1.92			1.82 ± 0.14

The kinetic analysis under the experimental conditions $1 \times 10^{-3} \leqslant$ [complex] $\leqslant 5 \times 10^{-3}$ mol dm^{-3}; $0 \leqslant$ [added oxalate] $\leqslant 1 \times 10^{-2}$ mol dm^{-3}; $1.0 \leqslant$ pH $\leqslant 3.5$; $298 \leqslant T \leqslant 318$ K; ionic strength = 0.1 mol dm^{-3} was effected by measuring the spectrophotometric absorbance A at 230 nm as a funcion of time t, Fig. 4 being an illustration of a typical result obtained by determining the influence of a single rate parameter (in this case [added oxalate]) on the hydrolysis process. The observed first-order rate constant k_{obs} was calculated from the linear plots of log $(A_\infty - A_t)$ *versus* t, the illustration in Fig. 4 being representative of its independence of [added oxalate] under all experimental conditions as exemplified by the entries in Table I and in agreement with the first-order release of oxalate. This independence of [added oxalate] is also exhibited by initial rate data presented in Table II as the initial slope $\Delta A/\Delta t$ of the absorbance *versus* time curves for [added oxalate] as rate parameter. The paradox concerning this independence is that Fig. 3 suggests retardment of the process with [added oxalate]. A possible explanation is that, although the difference between the observed absorbances in the two cases presented in Fig. 3 is large because of the high extinction in the wavelength region concerned, the actual retardation of the process is so small that it is not reflected in k_{obs}. The retarding influence of [added oxalate] could possibly be reflected in k_{obs} by enlarging the range over which [added oxalate] is varied, but that would lead to unstable and unreliable absorbance measurements since the difference in

TABLE II. $\Delta A/\Delta t$ as a Function of [Added Oxalate]. Temperature = 25 °C, [complex] = 3×10^{-3} mol dm^{-3}, Ionic Strength = 0.1 mol dm^{-3}.

pH	10^5 $\Delta A/\Delta t$ s^{-1}				
	10^3 [added oxalate] mol dm^{-3}				
	0.0	3.0	5.0	8.0	10.0
1.0	10.0	9.5	10.0	8.8	10.0
1.5	11.8	11.5	11.3	10.7	9.8
2.0	13.0	12.0	12.2	11.7	12.2
2.5	13.3	12.8	13.0	12.2	12.8
3.0	12.7	12.5	13.0	13.0	12.2
3.5	12.8	13.8	13.3	13.3	13.3

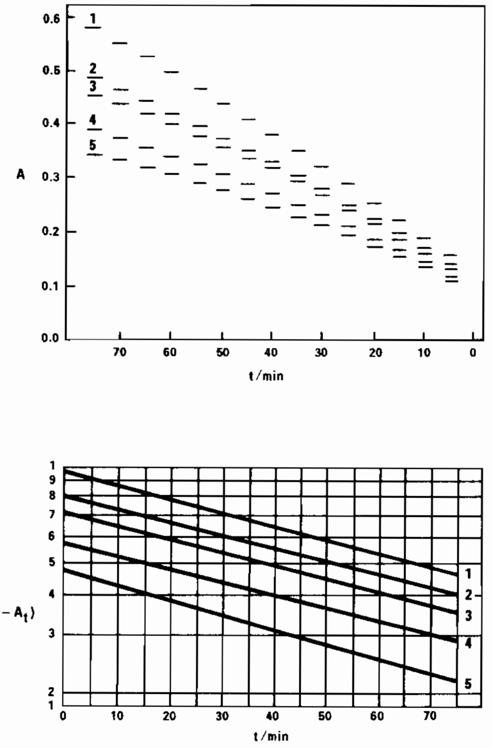

Fig. 4. Typical kinetic traces and determination of k_{obs}. [complex] = 3×10^{-3} mol dm^{-3}; pH = 2.5; ionic strength = 0.1 mol dm^{-3}; temperature = 25 °C:

number	10^3 [added oxalate] /mol dm^{-3}	A_∞
1	0.0	1.045
2	3.0	0.892
3	5.0	0.815
4	8.0	0.692
5	10.0	0.572

oxalate ion concentration between sample and reference cells becomes exceedingly small. An alternative explanation is afforded by associating the influence of [added oxalate] with a non rate-determining step. This would, however, imply a mechanism much more complex than that suggested by the distinct isosbestic points in Fig. 3. It is concluded, therefore, that for the [added oxalate] range under consideration $k_{obs} = k_{aquation} + k_{anation}[\text{oxalate}] \approx k_{aquation}$. This means that the forward aquation is so slightly opposed by oxalate-dependent anation under the experimental conditions concerned that the obtained kinetic results apply virtually only to the forward aquation step of the hydrolysis process.

The entries in the last column of Table I reflect such slight, if any dependence of k_{obs} on [complex] that it does not deserve any detailed discussion. The small variation in k_{obs} may possibly be attributed to secondary reactions such as the participation of binuclear species, resulting in slight deviations from first-order kinetics. However, a decisive answer is impossible unless more data concerning the various reaction modes of this germanium complex are available. Another independence of k_{obs} holds for ionic strength. Although the latter was maintained at a constant value throughout the kinetic analysis, a few runs were repeated varying this parameter with no effect on the hydrolysis process.

TABLE III. k_{obs} as a Function of pH. Temperature = 25 °C; [complex] = 3×10^{-3} mol dm^{-3}; [added oxalate] = 0–10 × 10^{-3} mol dm^{-3}; ionic strength = 0.1 mol dm^{-3}.

pH	$10^4\ k_{av}\ s^{-1}$
1.0	2.39 ± 0.13
1.25	2.30 ± 0.11
1.5	2.17 ± 0.03
1.75	2.03 ± 0.10
2.0	1.82 ± 0.08
2.25	1.83 ± 0.09
2.5	1.55 ± 0.12
3.0	1.55 ± 0.05
3.5	1.65 ± 0.05

The data in Table I clearly indicate a decrease in k_{obs} with increasing pH at a particular [complex]. The series at [complex] = 3×10^{-3} mol dm^{-3} was extended to include additional data summarised in Table III. These indicate a significant pH dependence which can only be ascribed to the presence of an acid-promoted path at pH < 2.5. The value of k_{obs} stays constant at pH ⩾ 2.5 with an average value of $(1.58 \pm 0.06) \times 10^{-4}\ s^{-1}$. These tendencies suggest a reaction mechanism comprising the steps

$$Ge(C_2O_4)_3^{2-} + H_3O^+ \xrightleftharpoons{K} [Ge(C_2O_4)_3^{2-}\cdot H_3O^+]$$

$$Ge(C_2O_4)_3^{2-} + H_2O \xrightarrow{k_1} Ge(C_2O_4)_2(OH_2)_2^0 + C_2O_4^{2-} \tag{1}$$

$$[Ge(C_2O_4)_3^{2-}\cdot H_3O^+] \xrightarrow{k_2} Ge(C_2O_4)_2(OH_2)_2^0 + HC_2O_4^- \tag{2}$$

Reaction (1) represents acid-independent aquation which, according to the data in Table III, occurs at pH ⩾ 2.5 such that $k_1 = (1.58 \pm 0.06) \times 10^{-4}\ s^{-1}$ at 25 °C. Reaction (2) represents acid-promoted aquation and includes the participation of a protonated germanium oxalato-intermediate presented by $[Ge(C_2O_4)_3^{2-}\cdot H_3O^+]$. The latter can be visualised as an ion-pair or a protonated, possibly ring-opened, oxalato species. Whatever its nature, the rate data should fit the rate law $k_{obs} = (k_1 + k_2K[H^+])/(1 + K[H^+])$. Since k_1 is known from the rate data at pH ⩾ 2.5, this equation can be rewritten as $k_{obs} - k_1 =$

TABLE IV. Rate Parameters for the Hydrolysis Process. [complex] = 3 × 10^{-3} mol dm^{-3}; [added oxalate] = 0–10 × 10^{-3} mol dm^{-3}; ionic strength = 0.1 mol dm^{-3}.

pH	10^4 k_{av}/s^{-1}					$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
	T = 298 K	T = 303 K	T = 308 K	T = 313 K	T = 318 K		
1.0	2.39	4.61	5.37	10.2	12.8	63 ± 7	−10 ± 22
1.5	2.17	3.26	4.74	8.78	–	68 ± 7	−9 ± 22
2.0	1.82	2.76	4.68	8.52	12.0	75 ± 4	−7 ± 12
2.5	1.55	2.64	4.69	7.75	–	81 ± 2	−5 ± 5
3.0	1.55	2.63	4.51	7.98	9.33	72 ± 6	−8 ± 20
3.5	1.65	2.58	4.67	8.02	–	80 ± 4	−5 ± 13

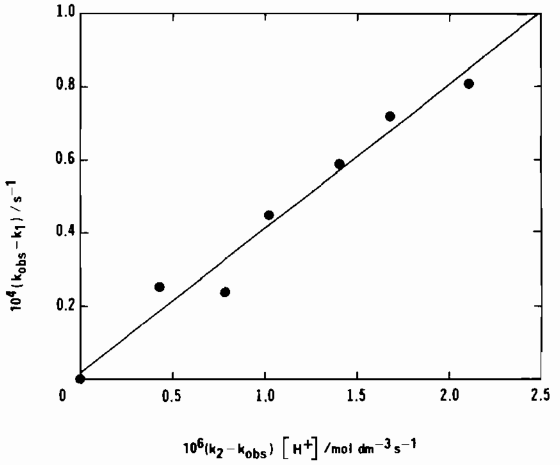

Fig. 5. pH dependence of hydrolysis process. [complex] = 3 × 10^{-3} mol dm^{-3}; [added oxalate] = 0 to 10 × 10^{-3} mol dm^{-3}; ionic strength = 0.1 mol dm^{-3}; temperature = 25 °C.

$(k_2 - k_{obs})K[H^+]$ in which k_2 and K are unknown. Since it is obvious that $k_2 \gg k_{obs}$ at pH 1.0, the data were fitted to the above equation in an indirect fashion by floating the k_2 value to find the best least-square fit. It turned out that k_2 = 2.6 × 10^{-4} s^{-1} and K = (39.4 ± 3.2) dm^3 mol^{-1} s^{-1} present the best fit of the data as shown in Fig. 5. Although $k_2 > k_1$, mutual comparison indicates a secondary or weak catalytic effect of hydrogen ions. The magnitude of K is quite high for an ion-pair formation constant of such an intermediate species, although hydrogen bonding with the oxalate ligands may contribute to the magnitude of K. On the contrary K may represent the formation constant of a protonated oxalato species such that pK = 1.60 ± 0.04. This possibility is not so far-fetched since the pK value of a similar ring-opened oxalato complex ion, *viz.* $Co(NH_3)_5C_2O_4H^{2+}$, is 2.05 ± 0.05 [10]. In the event of an acid-catalysed ring-opening reaction the pH dependence illustrates the significance of the M–O bond strength in the $Ge(C_2O_4)_3^{2-}$ ion. A similar result was reported for the acid-catalysed ring-opening reaction of $Rh(en)_2CO_3^+$ [11] and is in agreement with the principally covalent character of the bound oxalate in the complex $Ge(C_2O_4)_3^{2-}$ as inferred from a very strong IR absorption in the region 1720–1750 cm^{-1} [12].

The observed pH decrease during hydrolysis is attributed to a subsequent acid–base equilibrium

$$Ge(C_2O_4)_2(OH_2)_2^0 \rightleftharpoons Ge(C_2O_4)_2(OH)_2^{2-}n + 2H^+ \qquad (3)$$

for which support is provided by Tananaev and Avduevskaya [13] in isolating the potassium and ammonium salts of the complex ion $Ge(C_2O_4)_2(OH)_2^{2-}$. The final complex species is negatively charged according to results obtained by monitoring solutions sent through anion and cation exchangers after hydrolysis. It is probably $GeO(C_2O_4)_2^{2-}$, the existence of which is claimed by Everest [14].

$$Ge(C_2O_4)_2(OH)_2^{2-} \rightarrow GeO(C_2O_4)_2^{2-} + H_2O \qquad (4)$$

The author determined germanium/oxalate ratios in the pH range 3–6 to show that the species in solution are mainly $Ge(C_2O_4)_3^{2-}$ at pH < 3, $GeO(C_2O_4)_2^{2-}$ at pH 4.8 and $GeO_2(C_2O_4)^{2-}$ at pH 5.6. The latter complex species exists in solution up to pH 6.8, which corresponds with the endpoint at pH 6.75 of the pH titration presented in Fig. 2. The conversion of one mol $Ge(C_2O_4)_3^{2-}$ to one mol $GeO_2(C_2O_4)^{2-}$ requires four mol KOH as the ratio [KOH]/[complex] at the endpoint indicates. The complex species $GeO(C_2O_4)_2^{2-}$ is regarded as the photoactive entity in solution. The values of k_{obs} as a function of temperature are given in Table III. These were determined as a function of [added oxalate] at all pH values concerned, hence allowing the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to be tabulated as a function of pH. The average value of $\Delta H^{\neq}$ is quite typical for such aquation reactions. Its value for k_1 (pH $<$ 2.5) is slightly smaller than the value for k_2 (pH $\geqslant$ 2.5), which again refers to the promoting effect of the hydrogen ions under such conditions. The values of $\Delta S^{\neq}$ are within experimental error constant over the pH range concerned and quite typical for an interchange type of mechanism. That they are slightly negative may be an indication that the reaction is associatively activated and the possibility of a seven-coordinate intermediate is not ruled out. In this respect it is of interest to refer to our results for the very analogous Sn(IV)–oxalate system. We succeeded in isolating the seven-coordinated species $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ [15], which on dissolution yields an ultraviolet absorption spectrum almost identical to that of the hydrolysis product of the species $K_2Ge(C_2O_4)_3 \cdot H_2O$ [16]. Evidence for the presence of $SnO(C_2O_4)_2^{2-}$ as a possible photoactive species in solution was reported [17] and seems to be in good agreement with the conclusions reached in this paper.

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