Bull. Chem. Soc. Ethiop. **2010**, 24(3), 447-456. ISSN 1011-3924
Printed in Ethiopia

EQUILIBRIUM AND KINETIC STUDIES OF THE STANNATE(IV)-POLYOL REACTION

Jolocam Mbabazi*, John Wasswa and Muhammad Ntale

Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda

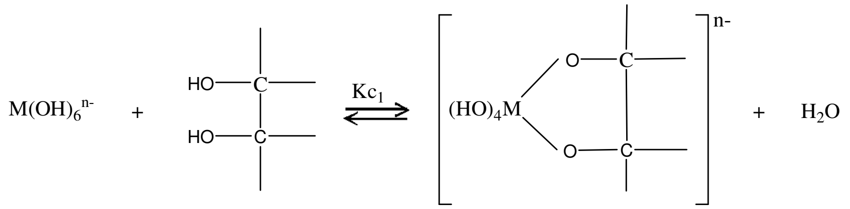
(Received June 25, 2009; revised April 22, 2010)

ABSTRACT. The stability constants of 1:1 stannate(IV)-polyol complexes in aqueous media have been determined using a conductimetric technique. The constants are fairly large, and lie in the range 5.3-123.0 for the ten ligands investigated. These values were subsequently used in conjunction with kinetic data to postulate a mechanism involving the species $Sn(OH)_5^-$ as intermediate in the formation of the chelates. The stannate(IV)-polyol reaction, though taking place at higher pH values, is acid-catalysed and follows first-order kinetics in the oxyanion, but at large ligand-oxyanion mole ratios the reaction exhibits zero-order rate dependence on the polyol. These features taken together are consistent with a unimolecular nucleophilic substitution on the oxyanion.

KEY WORDS: Hexahydroxystannate(IV), Polyol, Stability constants, Conductimetric method, Mechanism

INTRODUCTION

Chelate formation of certain weak inorganic oxyacids and their anions with organic polyhydroxy ligands continues to be a subject of research [1-9], and a biologically active complex has recently been developed and patented on the basis of this phenomenon. Related reactions in connection with this new development are quoted as having been carried out in these laboratories [10]. Extensive equilibria studies have been reported [8, 9] of the reactions of such compounds with Sn(IV), Sb(V), and Te(VI) hydroxyanions in aqueous media. The results indicate that $Sb(OH)_6^-$ and $Sn(OH)_6^{2-}$, two isostructural and isoelectronic species, form mainly 1:1 chelates presumably according to the stoichiometry:



(1)

(M = Sb, Sn; n = 1, 2)

The present paper reports on the extent of formation of some of these complexes, the results of which are used as an aid to a better understanding of the kinetics and mechanism of the stannate(IV)-polyol reaction.

EXPERIMENTAL

In these studies a Wayne-Kerr Universal Bridge B224 (UK), and a Mullard conductivity dip cell of type E7591/B (UK) with a cell constant = 1.37 cm^{-1}, were used for electrolytic conductance measurements. Sodium stannate(IV) was obtained from Hopkin and Williams (UK). Potentiometric measurements were made on a Corning Model 12 Research pH meter (UK), connected to a combined glass electrode. The organic compounds used were each of reagent-

---

*Corresponding author. E-mail: jolocammbabazi@chemistry.mak.ac.ug grade purity or better. The general procedure followed was to dilute appropriate quantities of $Na_2Sn(OH)_6$ (0.008 M) and, together with requisite volumes of polyol (usually 0.40 M), thermostat them at the desired temperature (± 0.02 ˚C) so that when mixed they gave solutions with resultant oxyanion concentrations in the range (1-5) x 10^{-3} M $Sn(OH)_6^{2-}$ in the presence of (10-20)-fold excess polyol. The conductivity cell at the same temperature and with a tight-fitting stopper was at this point quickly immersed in the solution. The lapse between mixing and the first conductance reading was ~60 seconds. Stannate-polyol reaction rates were very slow, requiring intervals of up to 6 hours for measurable changes in conductance to be observed, and so the steady reading registered within the first 10 minutes of mixing could be taken as the conductance L_o of the solution at $t = 0$ without introducing any appreciable error.

In these equilibrium and kinetic experiments, maintenance of constant pH was essential. Preliminary runs showed that at the oxyanion concentrations used the pH of the solution mixture was practically unaltered by complex-formation, so that it was essentially in equilibrium studies where allowance had to be made for the effect of dilution on the pH of the oxyanion solution. This was done by raising with a little dilute KOH prior to mixing, each of the reactant solutions to pH 11.0 which was close to that of freshly prepared 0.008 M $Na_2Sn(OH)_6$. All the runs were carried out in a carbondioxide-free atmosphere using a glove box previously flushed with nitrogen. At ambient temperatures equilibrium was attained within 3-5 days. All runs were performed at least in duplicate, and the ΔL values so obtained usually agreed to within ± 2 x 10^{-6} ohm^{-1}.

RESULTS AND DISCUSSION

Equilibrium studies

Conductance measurements confirmed that at alkaline pH values, low ionic concentrations and large polyol-oxyanion molar ratios as employed in these studies, neutral acid formation and aggregation of $Sn(OH)_6^{2-}$ ions in the test solutions was insignificant. The observed gradual decrease in conductance (Table 1) may therefore be attributed to the substitution of less mobile polyol-oxyanion chelates for free oxyanions. Under such circumstances, it may be shown that the change in conductance ΔL at any instant is proportional to the amount of complex formed.

Table 1. Sample kinetic data for complex-formation. ($[stannate]_o = 0.0050$ M; [mannitol] = 0.050 M; pH = 11.0; T = 298.2 K).

Time/h	L x 10^6/ohm^{-1}	$\frac{\lvert\delta(\Delta L)/\delta t\rvert}{10^{-6}\,ohm^{-1}\,h^{-1}}$	$\frac{\lvert\Delta L\rvert}{10^{-6}\,ohm^{-1}}$
0	824.5	---	---
5	818.0	1.25	2.5
10	812.5	1.10	8.6
15	807.6	0.98	14.0
20	803.5	0.80	21.0
25	799.5	0.80	23.5
30	796.0	0.70	25.5
35	793.0	0.60	30.0
40	790.3	0.54	32.5
45	787.9	0.48	35.0
50	785.9	0.40	38.0
55	784.0	0.38	39.5
60	782.0	0.40	41.5
65	780.5	0.30	42.5
120	774.5	---	---

Denoting the conductance of the reaction mixture at equilibrium as L_{eq} and that at complete reaction as L_f, for a constant initial oxyanion concentration but various polyol concentrations C >> $[\text{oxyanion}]_o$ we may write the expression for the equilibrium constant [11] as Kc_1 = [complex]/[polyol][oxyanion], or

$$Kc_1 = \frac{(\Delta L)eq_1}{C_1(L_f - Leq_1)} = \frac{(\Delta L)eq_2}{C_2(L_f - Leq_2)} = \frac{(\Delta L)eq_3}{C_3(L_f - Leq_3)} \tag{2}$$

The above expression, unknown in L_f, requires that the initial conductance L_o of the solution be the same at C_1, C_2, and C_3. The conductance of the mixture is instantaneously reduced by the presence of excess polyol, causing L_o to be measurably less than that of the pure salt solution at the same concentration. This effect is attributable to a decrease in electrical permittivity of the medium. The ionic mobility and hence the electrolytic conductance of a solution depends on the coulombic attractions between the ions given by $F_{12} = q_1q_2/(4\pi\varepsilon_m r^2)$, where the symbols have their usual meanings and ε_m is the electrical permittivity of the medium. If ε_m is reduced the electrostatic interionic forces increase and the conductance of the solution is lowered. The observed reduction in electrolytic conductance may be allowed for by assuming that the observed $(\Delta L)_{eq}$ values are measured from the same (arbitrary) value of L_o and adjusting the value of L_{eq} accordingly. $(\Delta L)_{eq}$ is an experimental measurable, and once a suitable arbitrary value of L_o has been chosen then $L_{eq} = L_o - |(\Delta L_{eq})|$. Absolute values of $(\Delta L)_{eq}$ must be taken since $(\Delta L)_{eq}$ is negative. A quick check with equation (2) confirms that calculation of Kc_1 is independent of the value of L_o, as

$$Kc_1 = \frac{(\Delta L)eq}{C(L_f - Leq)} = \frac{(\Delta L)eq}{C\{L_f - [L_o + (\Delta L)eq]\}} = \frac{(Leq - L_o)}{C[L_f - (L_o + Leq - L_o)]} \tag{3}$$

$$= \frac{(\Delta L)eq}{C(L_f - Leq)}, \text{ as before.}$$

This simple but important manipulation ensures that all Kc_1 values are obtained at zero polyol concentration, a thermodynamic requirement.

The stability of the complexes increases with pH [8, 9]. However, since the reaction does not entail any change in charge type [equation (1)] at constant pH the value of Kc_1 is expected to be independent of ionic strength. Also, sodium stannate solutions are very sensitive to the presence of indifferent electrolyte (this work), and attempts to control ionic strength by, for example, addition of KCl led to an immediate turbidity. The ionic strength I of the solution was in this case dependent mainly on the initial salt concentration. Calculations based on the pH values of the oxyanion-polyol mixtures showed that effects of hydrolysis of $Sn(OH)_6^{2-}$ to $HSn(OH)_6^-$ only slightly decreased I. Allowance for the small amount of KOH used to adjust the pH topped it (the ionic strength) up to its expected level.

Kc_1-stannate values at 298.2 K, pH 11.0 and at I = 0.015 M (numerically equal to 3 times $[Sn(IV)]_o$) are given in Table 2. The Kc_1-tellurate values at 298.2 K determined earlier [12], though determined at zero polyol concentration, were measured at I = 0.10 M and are not included here for comparison, but may serve to show that both tellurate and stannate anions bind polyols fairly strongly. In this, however, there is reliable evidence [8, 9] that tellurate chelates are stronger.

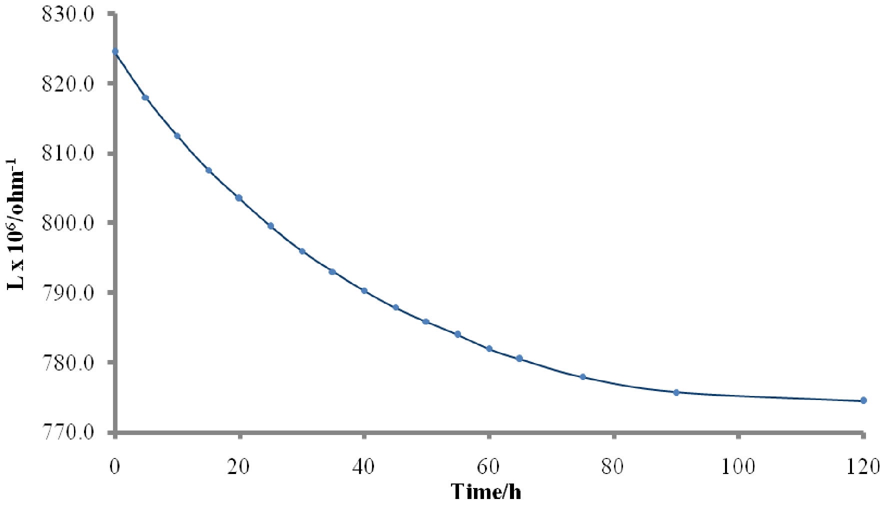


Figure 1. Behaviour of sodium stannate (0.0050 M, pH 11.0) in presence of a 10-fold excess mannitol at 298.2 K.

The use of polarimetry to augument these results necessitated higher concentrations of polyol for measurable changes in optical rotation to be realised. This often required much higher oxyanion concentrations at which polymerisation becomes much more preponderant and the stannate mixtures turbid. Spectrophotometry too had its own shortcomings, as λ_{max} values for $Sn(OH)_6^{2-}$ and the polyols were very close together (188-192 nm), and the changes in absorbance at the small concentrations dictated by the technique were small and fraught with uncertainty.

Kinetics of complex-formation

According to the equation

According to the equation

$$Sn(OH)_6{}^{2-} + P \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2SnO_4P^{2-} + 2H_2O \tag{4}$$

(P = polyol)

it seemed probable that the expression for the rate of chelation might be of the form

$$R_f = k_f(obs)[Sn(OH)_6^{2-}]^p\,[P]^q \tag{5}$$

where the symbols have their usual meanings. At the same time, it is clear that the rate of change of conductance with time is an indirect measure of how fast the complex is forming, i.e.

$$R_f = k\,\frac{d(\Delta L)}{dt} \tag{6}$$

where k is a negative proportionality constant. A striking feature of the Sn(IV)-polyol reaction, however, was its unusually slow rate (Figure 1). This, viewed in the light of the alkaline natural pH of stannate solutions and the preliminary observation that the initial rates of reaction decreased even more with higher pH, was suggestive of possible acid-catalysis. It also seemed highly probable that the rate of complex-formation depended directly on the $Sn(OH)_6^{2-}$ concentration. Further, for every initial stannate concentration the observed changes in conductance for the first 90 hours, representing ~75% of the reaction (Figure 1), were almost independent of the nature and amount of excess polyol present, indicating that the kinetics depended mainly on the oxyanion species.

Taking these facts and also the presence of the reverse reaction into account it seemed likely that the complete rate law would take the form

$$R_f = k_f'[Sn(OH)_6^{2-}][P][H^+]^y - k_r'[H_2SnO_4P^{2-}][H^+]^y \tag{7}$$

This expression can be rearranged to relate the observed decrease in conductance ΔL with time as

$$k\frac{d(\Delta L)}{dt} = k_f'\{k(L_f - L_t)\}[P][H^+]^y - k_r'\{k(L_t - L_o)\}[H^+]^y \tag{8}$$

which simplifies to

$$\frac{d(\Delta L)}{dt} = k_f'\{(\Delta L)_f - (\Delta L)\}[P][H^+]^y - k_r'[H^+]^y(\Delta L) \tag{9}$$

or further to

$$\frac{d(\Delta L)}{dt} = k_f'[P][H^+]^y(\Delta L)_f - \left(k_r'[H^+]^y + k_f'[P][H^+]^y\right)(\Delta L) \tag{10}$$

In the presence of a sufficiently large excess of polyol experiment shows (Figure 1) that the rate of chelation is independent of its concentration and nature so that at constant pH we may write equation (10) as

$$\frac{d(\Delta L)}{dt} = k_f(obs)(\Delta L)_f - \{k_r(obs) + k_f(obs)\}(\Delta L) \tag{11}$$

Equation (11) predicts a linear variation of $\frac{\delta(\Delta L)}{\delta t}$ with ΔL. Values of $\frac{\delta(\Delta L)}{\delta t}$ were obtained (Table 1) by measuring δ(ΔL) for small intervals of time δt, and the corresponding values of ΔL taken at the midpoints of δt along the conductance-time curve (Figure 1). Plots of $\left|\frac{\delta(\Delta L)}{\delta t}\right|$ *vs* |ΔL| were linear with negative slope (Figure 2) for ~75% of the reaction, and for values of δt ranging up to 5 hours with no alternation in slope. This was the case for all other conditions of $[Sn(OH)_6^{2-}]_o$, temperature, and pH in the ranges employed here, thus verifying the validity of equation (11) and the assumptions made. The formation of mainly 1:1 complexes is apparent therein. Deviation from linearity at longer reaction times (Figure 2) was indicative of the backward reaction becoming significant.

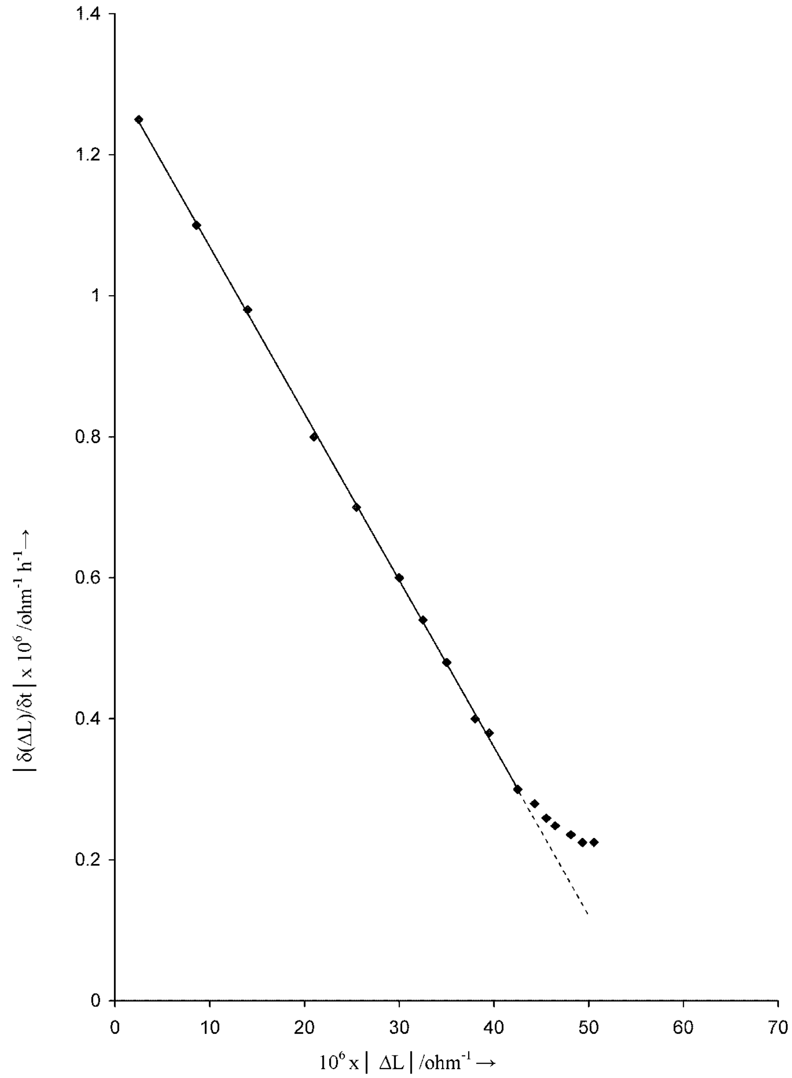


Figure 2. First order dependence of reaction rate on stannate concentration. ($[\text{oxyanion}]_o$ = 0.0050 M; [mannitol] = 0.050 M; pH = 11.0; T = 298.2 K; slope = - (2.37 ± 0.05) x 10^{-2} h^{-1}; intercept = (1.32 ± 0.05) x 10^{-6} ohm^{-1} h^{-1}).

By evaluating the slope $-\{k_r(obs) + k_f(obs)\}$ which was independent of the oxyanion concentration, and the intercept $k_f(obs)|(\Delta L)_f|$, $k_f(obs)$ and $k_r(obs)$ can be calculated with a knowledge of $(\Delta L)_f$ values obtainable from earlier static experiments using equation (2) at the respective $[Sn(OH)_6^{2-}]_o$. These values are listed in Table 2 for the ten polyols studied at 298.2 K, pH 11.0 and at I = 0.015 M. It is worthwhile to note that the ratio $k_f(obs)/k_r(obs)$ is the concentration equilibrium constant Kc_1, as may be checked using the values given in Table 2. It is also noteworthy that the values of k_f(obs) lie within a narrow range of (6.41 ± 0.28) x 10^{-6} s^{-1} as to be taken practically constant while those of k_r(obs) show significant disparity. At the same k_f(obs) value the disparity in Kc_1 values is therefore reflected in the hydrolysis rate constants k_r (obs) of the complexes.

Table 2. Formation and rate constants for aqueous stannate(IV)-polyol complexes at 298.2 K, pH 11.0 and at $[Na_2Sn(OH)_6]_o = 0.0050$ M, $[polyol]_o = 0.050$ M, I = 0.015 M.

Polyol	Kc_1	10^{-5} $k_f(obs)/[H^+]$ (M^{-1} s^{-1})	10^{+4} k_f (s^{-1})	10^{-5} $k_r(obs)/[H^+]$ (M^{-1} s^{-1})
L-Arabinose	7.77 ± 0.13	6.37 ± 0.02	1.15	0.82 ± 0.01
D-Xylose	7.69 ± .18	6.46 ± .04	1.16	0.84 ± .03
D-Glucose	6.09 ± .13	6.39 ± .06	1.15	1.05 ± .04
D-Galactose	9.25 ± .18	6.01 ± .03	1.08	0.65 ± .02
D-Mannose	17.37 ± .50	6.60 ± .05	1.19	0.38 ± .03
D-Fructose	23.22 ± .29	6.27 ± .08	1.13	0.27 ± .06
Lactose	8.60 ± .37	6.51 ± .04	1.17	0.35 ± .04
Myo-Inositol	5.32 ± .13	5.69 ± .06	1.07	1.05 ± .04
D-Dulcitol	123.00 ± .07	7.01 ± .09	1.26	0.057 ± .007
D-Mannitol	91.26 ± .09	6.48 ± .02	1.17	0.071 ± .002

We have already noted that the interaction of stannate anions with polyols is an exceedingly slow process by laboratory standards. The use of excess polyol serves to make it faster. Nevertheless efforts were made to perform kinetic runs at polyol concentrations comparable to those of the oxyanion, but in almost every case the rate was so slow that the reaction usually passed unnoticed. It was apparent therefore that at relatively low concentrations the rate also depended on the polyol, becoming independent only at higher values.

The pH of sodium stannate solutions could only be altered by raising it with KOH; it could not be lowered as the slightest addition of dilute acid produced an immediate turbidity. Values of k_f(obs) were however obtained for a number of polyols at various $[oxyanion]_o$ and pH. Plots of log k_f(obs) *vs* pH in the range 9-12 were linear with negative slopes of 0.90 ± 0.15, indicative of little deviation from first order rate dependence on $[H^+]$.

Equation (7) may now be explicitly expressed as

$$\text{Rate} = k_f'[Sn(OH)_6^{2-}][P][H^+] - k_r'[H_2SnO_4P^{2-}][H^+] \tag{12}$$

Previous workers [13, 14] have held the view that the neutral acid, in this case stannic acid $H_2Sn(OH)_6$, does not form a complex but rather an anionic form of the weak acid. In compliance, the most probable interpretation of the above rate law is that the reactive oxyanion species is the protonated form of $Sn(OH)_6^{2-}$ which allows equation (12) to be rewritten as

$$-\frac{d[HSn(OH)_6^-]}{dt} = k_f' K_2 [HSn(OH)_6^-][P] - k_r'[H_2SnO_4P^{2-}][H^+] \tag{13}$$

where K_2 is the second acid ionisation constant of stannic acid.

It follows therefore that the forward rate constant $k_f = k_f'K_2 = \frac{k_f(obs)K_2}{[H^+]}$ but the reverse constant k_r is the same as $k_r' = \frac{k_r(obs)}{[H^+]}$. Consequently, in order to calculate k_f it was necessary to calculate K_2. This was achieved by observing the pH of freshly prepared dilute solutions of $Na_2Sn(OH)_6$ at 0.005 M and calculating K_2(obs) as $\frac{[Sn(OH)_6^{2-}][H_3O^+]}{[HSn(OH)_6^-]}$ on the basis of the hydrolysis of the $Sn(OH)_6^{2-}$ anion

$$Sn(OH)_6^{2-} + H_2O \overset{K_h}{\rightleftharpoons} HSn(OH)_6^- + OH^- \tag{14}$$

and the relationship $pK_2(obs) = pK_w - pK_h(obs)$ at the operational temperature. This gave the value of pK_2 as 9.74 ± 0.02 at 298.2 K and at I = 0.015 M. Values of k_f have been calculated and listed in Table 2. The values of k_f may be summed up as $(1.15 \pm .05) \times 10^{-4}\ s^{-1}$ under the experimental conditions used.

Two aspects pertinent to the stannate(IV)-polyol reaction are derived from the foregoing study. The reaction is acid-catalysed. The very slow rate at the high natural pH of stannate solutions, equilibrium times being of the order of days, contrasts strongly with the behaviour of the isostructural and isoelectronic telluric acid $Te(OH)_6$ whose reaction with similar compounds is virtually over within minutes at pH 11 but slow in acidic media [8, 9]. Also, the reaction is first order in $[Sn(OH)_6^{2-}]$. The rate also depends on the polyol at concentrations comparable to that of the oxyanion, but becomes independent of the ligand at larger polyol-oxyanion molar ratios. The non-dependence of the forward rate constant on the nature of the polyol indicates that the rate-controlling step involves only the stannate ion; intuitively the observed acid-catalysis must be associated only with protonation of $Sn(OH)_6^{2-}$.

On the basis of these data, taking due care to distinguish between K_2 (an equilibrium constant) and k_2 along with k_{-2} (rate constants), a possible mechanism is proposed as follows:

$$Sn(OH)_6^{2-} + H_3O^+ \underset{K_2}{\rightleftharpoons} (HO)_5SnOH_2^- + H_2O \tag{15}$$

$$(HO)_5SnOH_2^- \overset{k_1}{\rightleftharpoons} [(OH)_5Sn\text{---}OH_2^-] \underset{k_1}{\rightleftharpoons} Sn(OH)_5^- + H_2O \qquad \text{slow} \tag{16}$$

$$Sn(OH)_5^- + P \overset{k_2}{\rightleftharpoons} [\ddagger] \underset{k_{-2}}{\rightleftharpoons} H_2SnO_4P^{2-} + H_3O^+ \tag{17}$$

The entity [‡] here represents the second activated state necessary for the cyclisation process to take place. Considering the rate of complex-formation as depending on the rate of elimination of water from the protonated $HSn(OH)_6^-$ ion, it can be shown that the rate law may be expressed as

$$-\frac{d[Sn(OH)_6^{2-}]}{dt} = \frac{\left(\frac{k_1k_2}{K_2}\right)[Sn(OH)_6^{2-}][P][H^+] - k_{-1}k_{-2}[H_2SnO_4P^{2-}][H^+]}{k_{-1} + k_2[P]} \tag{18}$$

Noting that in view of the expected high reactivity of the $Sn(OH)_5^-$ species toward the nucleophilic OH groups both in H_2O and in polyols k_{-1} and k_2 are comparable such that we may put $\frac{k_{-1}}{k_2} \approx 1$, and that at large polyol concentrations $k_2[P] >> k_{-1}$ so that $k_{-1} + k_2[P] \approx k_2[P]$, then

$$\text{Rate} = \left(\frac{k_1}{K_2}\right)[Sn(OH)_6^{2-}][H^+] - \frac{k_{-2}[H_2SnO_4P^{2-}][H^+]}{[P]} \tag{19}$$

when the quotient vanishes and the rate at constant pH becomes dependent only on the oxyanion concentration, i.e.

$$R_f = \left(\frac{k_1[H^+]}{K_2}\right)[Sn(OH)_6{}^{2-}] = k_f(obs)\ [Sn(OH)_6{}^{2-}] \tag{20}$$

On the other hand when [P] is progressively reduced such that $k_2[P] << k_{-1}$ then

$$-\frac{d[Sn(OH)_6{}^{2-}]}{dt} = \left(\frac{k_1}{K_2}\right)[Sn(OH)_6{}^{2-}][P][H^+] - k_{-2}[H_2SnO_4P^{2-}][H^+] \tag{21}$$

which is synchronous with the experimental rate law, equation (12). Further inspection of equation (21) and the experimental ones [equations (12) and (13)] will reveal that $k_1 = k_f$ and $k_r = k_r' = k_{-2}$, which have been measured and tabulated in Table 2.

The postulation of the $Sn(OH)_5^-$ anion deserves further discussion. A change in coordination number during reaction mechanisms is a known phenomenon in laboratory reactions [15] so that the change from coordination number 6 to 5 during the process $HSn(OH)_6^- \rightarrow Sn(OH)_5^-$ does not look impossible. It has been postulated that in chemical reactions intermediates are structurally similar to known stable compounds. Five-coordinated compounds of tin(IV) are known [16a], an example being the trigonal bipyramidal $[Sn(O_2CMe)_5]^-$ ion [16b], and a host of others from the elements surrounding Sn in the Periodic Table. Salts of $Sn(OH)_5^-$ are still unknown, but lack of this knowledge does not necessarily preclude the existence of the species. It may exist in such small amounts that it escapes detection. This possibility may in fact be used to account for its presumed high reactivity toward polyols in this instance, using its vacant sixth coordination site to bond datively with one oxygen from the polyol followed by rapid cyclisation and loss of a proton and water. Because of the usually slow fission of the C–O bond, it is presumed that the water comes as a result of fission of one Sn–O bond.

The spread in k_r values, resulting in dissimilarity of the Kc_1 values for the individual polyol ligand chelates (Table 2), may be interpreted in terms of the stereospecificity of the protonation of the oxygen in Sn–O–C bonds required to cause hydrolysis. Such protonation would largely depend on the structure of the polyol which may be such that the surroundings of the oxygens in the two Sn–O–C bonds are shielded in one chelate and more open in another. This is opposed to the initial step in which protonation of $Sn(OH)_5^-$ may take place at any of the six hydroxyls and each time give rise to a species capable of going to the transition state.

CONCLUSIONS

This study, it is hoped, puts the $Sn(OH)_6^{2-}$ species in its proper place in the wide research field of polyol-oxyanion systems. It is worthy of further investigation whether the mechanism put forward for this reaction could be extended to reactions with α-hydroxyacids in which one of the donor oxygen atoms belongs to a carboxyl moiety. A higher case in this respect would be α-aminoacids, in which nitrogen would be expected to be involved as part of the chelate bridge, i.e. in the Sn–N–C link.

ACKNOWLEDGEMENTS

We thank Makerere University Research and Publications Grants Committee for financial support and the host Department of Chemistry for laboratory facilities.

REFERENCES

1. Norkus, E. *J. Incl. Phenom. Macro*. **2009**, 65, 237.
2. Claire, K.; Giselle, S.; Jason, C.; Adam, S.; Ptolemy, P. *Chem. Commun*. **2008**, 338.
3. Benner, K.; Ihringer, J.; Klufers, P.; Marinov, D. *Angew. Chem. Int. Ed.* **2006**, 35, 5818.
4. Tomonori, S.; Hidetaka, K.; Kazuya, U.; Satoshi, T.; Akira, H.; Kyoichi, S.; Masao, T.; Takanobu, S. *J. Membr. Sci*. **2004**, 236, 65.
5. Wen-Ching, W.; Po-Hsiang, C.; Mo-Hsiung, Y. *J. Anal. At. Spectrom*. **2000**, 15, 1466.
6. Yu, E.; Alexander, D.; Yu, A. *Russ. Chem. Rev*. **1998**, 67, 649.
7. Jean-François, V.; Jean-Paul, S.; Guy-Roland, R. *Analyst* **1990**, 5, 637.
8. Mbabazi, J. *Polyhedron* **1985**, 4, 75.
9. Mbabazi, J. *Carbohydr. Res*. **1985**, 140, 151.
10. Albeck, M.; Sredni, B. *US Patent 7276628*, *Biologically Active Complex*, **2007**; Available at: *www.freepatentsonline.com/7276628.html*
11. Haight, G.P.; Paragamian, V. *Anal. Chem*. **1960**, 32, 642.
12. Mbabazi, J. *Ph.D. Thesis*, Makerere University, Uganda, **1988**.
13. Mbabazi, J.; Popiel, W.J. *J. Inorg. Nucl. Chem*. **1979**, 41, 1491.
14. Popiel, W.J.; Rustom, M.S. *J. Inorg. Nucl. Chem*. **1978**, 40, 921.
15. Katsumi, H.; Junko, I.; Yoko, N.; Kazuhiko, O.; Kazuo, K.; Hidetoshi, N.; Koji, O.; Giuseppe, D.; Norikazu, O.; Norimasa, U. *Mem. SR Cent. Ritsumeikan Univ*. **2006**, 8, 55.
16. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed., John Wiley and Sons: New York; **1988**; (a) p 272, (b) p 289.