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

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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:

\[
M(OH)_6^{n-} + (HO)_nM \rightleftharpoons K_c \rightleftharpoons \left[\begin{array}{c}
\text{M} \\
\text{H}_2O
\end{array}\right] + nH_2O \quad (1)
\]

\(M = \text{Sb, Sn}; \quad n = 1, 2\)

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-
grade purity or better. The general procedure followed was to dilute appropriate quantities of Na$_2$Sn(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 $L_0$ 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$_2$Sn(OH)$_6$. All the runs were carried out in a carbon dioxide-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 ∆$L$ 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 ∆$L$ 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).

<table>
<thead>
<tr>
<th>Time/h</th>
<th>L x 10$^6$/ohm$^{-1}$</th>
<th>$\frac{\Delta L}{\Delta t}$ x 10$^{-6}$/ohm$^{-1}$</th>
<th>$\Delta L$ x 10$^{-6}$/ohm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>824.5</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>818.0</td>
<td>1.25</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>812.5</td>
<td>1.10</td>
<td>8.6</td>
</tr>
<tr>
<td>15</td>
<td>807.6</td>
<td>0.98</td>
<td>14.0</td>
</tr>
<tr>
<td>20</td>
<td>803.5</td>
<td>0.80</td>
<td>21.0</td>
</tr>
<tr>
<td>25</td>
<td>799.5</td>
<td>0.80</td>
<td>23.5</td>
</tr>
<tr>
<td>30</td>
<td>796.0</td>
<td>0.70</td>
<td>25.5</td>
</tr>
<tr>
<td>35</td>
<td>793.0</td>
<td>0.60</td>
<td>30.0</td>
</tr>
<tr>
<td>40</td>
<td>790.3</td>
<td>0.54</td>
<td>32.5</td>
</tr>
<tr>
<td>45</td>
<td>787.9</td>
<td>0.48</td>
<td>35.0</td>
</tr>
<tr>
<td>50</td>
<td>785.9</td>
<td>0.40</td>
<td>38.0</td>
</tr>
<tr>
<td>55</td>
<td>784.0</td>
<td>0.38</td>
<td>39.5</td>
</tr>
<tr>
<td>60</td>
<td>782.0</td>
<td>0.40</td>
<td>41.5</td>
</tr>
<tr>
<td>65</td>
<td>780.5</td>
<td>0.30</td>
<td>42.5</td>
</tr>
<tr>
<td>120</td>
<td>774.5</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
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
\[
Kc_1 = \frac{(\Delta L)_{eq}}{C_f(L_1 - L_{eq})} = \frac{(\Delta L)_{eq}}{C_2(L_2 - L_{eq2})} = \frac{(\Delta L)_{eq}}{C_3(L_3 - L_{eq3})}
\]
(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
\[
F_{12} = \frac{q_1q_2}{4\pi\varepsilon m r^2}
\]
where the symbols have their usual meanings and \( \varepsilon_m \) is the electrical permittivity of the medium. If \( \varepsilon_m \) 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
\[
Kc_1 = \frac{(\Delta L)_{eq}}{C(L_1 - L_{eq})} = \frac{(\Delta L)_{eq}}{C[L_1 - (L_o + (\Delta L)_{eq})]} = \frac{(L_{eq} - L_o)}{C[L_1 - (L_o + L_{eq} - L_o)]}
\]
(3)

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)\(_5\), 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 \([\text{Sn(IV)}]_o \)) 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 augment these results necessitated higher concentrations of polyol for measurable changes in optical rotation to be realised. This often required much higher oxanion 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)_{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

\[
\text{Sn(OH)}_{2^+} + P \xrightarrow{k_r} \text{H}_2\text{SnO}_4\beta^{2^+} + 2\text{H}_2\text{O}
\]

\[(P = \text{polyol})\]

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

\[
R_r = k_r\text{([Sn(OH)}_{2^+}]^p\text{[P]}^q)
\]

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.

\[
R_r = k \left| \frac{d(\Delta L)}{dt} \right|
\]
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 \( \text{Sn(OH)}_6^{2-} \) 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

\[
R_i = k'_i'[\text{Sn(OH)}_6^{2-}] [\text{P}][\text{H}^+] - k'_i[H_2\text{SnO}_3\text{P}^5][\text{H}^+]'
\]  

(7)

This expression can be rearranged to relate the observed decrease in conductance \( \Delta L \) with time as

\[
k \frac{d(\Delta L)}{dt} = k'_i'\{k(L_i - L_o)\} [\text{P}][\text{H}^+]' - k'_i'\{k(L_i - L_o)\} [\text{H}^+]'
\]  

(8)

which simplifies to

\[
k \frac{d(\Delta L)}{dt} = k'_i'(\Delta L_i - (\Delta L)) [\text{P}][\text{H}^+]' - k'_i[\text{H}^+]'(\Delta L)
\]  

(9)

or further to

\[
k \frac{d(\Delta L)}{dt} = k'_i'[\text{P}][\text{H}^+]'(\Delta L_i) - \left(k'_i[\text{H}^+]' + k'_i'[\text{P}][\text{H}^+]'\right)(\Delta L)
\]  

(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

\[
k \frac{d(\Delta L)}{dt} = k'_i(\text{obs})(\Delta L_i) - \left(k'_i(\text{obs}) + k'_i\right)(\Delta L)
\]  

(11)

Equation (11) predicts a linear variation of \( \frac{\delta(\Delta L)}{\delta t} \) with \( \Delta L \). Values of \( \frac{\delta(\Delta L)}{\delta t} \) were obtained (Table 1) by measuring \( \delta(\Delta L) \) for small intervals of time \( \delta t \), and the corresponding values of \( \Delta L \) taken at the midpoints of \( \delta t \) along the conductance-time curve (Figure 1). Plots of \( \frac{\delta(\Delta L)}{\delta t} \) vs \( \Delta L \) were linear with negative slope (Figure 2) for ~75% of the reaction, and for values of \( \delta t \) ranging up to 5 hours with no alternation in slope. This was the case for all other conditions of \([\text{Sn(OH)}_6^{2-}]_o\), 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. ([oxyanion]₀ = 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)(ΔL)_f, k_r(obs) and k_f(obs) can be calculated with a knowledge of (ΔL)_f values obtainable from earlier static experiments using equation (2) at the respective [Sn(OH)₆]²⁻. 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 Kc₁, as may be checked using the values given in Table 2. It
Equilibrium and kinetic studies of the stannate(IV)-polyol reaction


is also noteworthy that the values of $k_f(\text{obs})$ lie within a narrow range of $(6.41 \pm 0.28) \times 10^{-6}$ s$^{-1}$ as to be taken practically constant while those of $k_r(\text{obs})$ show significant disparity. At the same $k(\text{obs})$ value the disparity in $K_c$ values is therefore reflected in the hydrolysis rate constants $k_r(\text{obs})$ of the complexes.

Table 2. Formation and rate constants for aqueous stannate(IV)-polyol complexes at 298.2 K, pH 11.0 and at $[\text{Na}_2\text{Sn(OH)}_6]_o = 0.0050$ M, $[\text{polyol}]_o = 0.050$ M, $I = 0.015$ M.

<table>
<thead>
<tr>
<th>Polyol</th>
<th>$K_{C1}$</th>
<th>$10^{4} k_0(\text{obs})/[H^+]$ (M$^{-1}$s$^{-1}$)</th>
<th>$10^{4} k_f$ (s$^{-1}$)</th>
<th>$10^{4} k_r(\text{obs})/[H^+]$ (M$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Arabinose</td>
<td>7.77 ± 0.13</td>
<td>6.37 ± 0.02</td>
<td>1.15</td>
<td>0.82 ± 0.01</td>
</tr>
<tr>
<td>D-Xylose</td>
<td>7.69 ± 0.18</td>
<td>6.46 ± 0.04</td>
<td>1.16</td>
<td>0.84 ± 0.03</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>6.09 ± 0.13</td>
<td>6.39 ± 0.06</td>
<td>1.15</td>
<td>1.05 ± 0.04</td>
</tr>
<tr>
<td>D-Galactose</td>
<td>9.25 ± 0.18</td>
<td>6.01 ± 0.03</td>
<td>1.08</td>
<td>0.65 ± 0.02</td>
</tr>
<tr>
<td>D-Mannose</td>
<td>17.37 ± 0.50</td>
<td>6.60 ± 0.05</td>
<td>1.19</td>
<td>0.38 ± 0.03</td>
</tr>
<tr>
<td>D-Fructose</td>
<td>23.22 ± 0.29</td>
<td>6.27 ± 0.08</td>
<td>1.13</td>
<td>0.27 ± 0.06</td>
</tr>
<tr>
<td>Lactose</td>
<td>8.60 ± 0.37</td>
<td>6.51 ± 0.04</td>
<td>1.17</td>
<td>0.35 ± 0.04</td>
</tr>
<tr>
<td>Myo-Inositol</td>
<td>5.32 ± 0.13</td>
<td>5.69 ± 0.06</td>
<td>1.07</td>
<td>1.05 ± 0.04</td>
</tr>
<tr>
<td>D-Dulcitol</td>
<td>123.00 ± 0.07</td>
<td>7.01 ± 0.09</td>
<td>1.26</td>
<td>0.057 ± 0.007</td>
</tr>
<tr>
<td>D-Mannitol</td>
<td>91.26 ± 0.09</td>
<td>6.48 ± 0.02</td>
<td>1.17</td>
<td>0.071 ± 0.002</td>
</tr>
</tbody>
</table>

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 $k_f(\text{obs})$ were however obtained for a number of polyols at various $[\text{oxyanion}]_o$ and pH. Plots of $\log k_f(\text{obs})$ 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

$$\text{Rate} = k_1 \cdot [\text{Sn(OH)}_6^{2-}] \cdot [\text{P}] \cdot [H^+] - k_2 \cdot [\text{H}_2\text{SnO}_6\text{P}^{2-}] \cdot [H^+]$$  \hspace{1cm} (12)$$

Previous workers [13, 14] have held the view that the neutral acid, in this case stannic acid $\text{H}_2\text{Sn(OH)}_6$, 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 $\text{Sn(OH)}_6^{2-}$ which allows equation (12) to be rewritten as

$$-\frac{d[H\text{Sn(OH)}_6^{2-}]}{dt} = k_1 \cdot K_2 \cdot [\text{H}\text{Sn(OH)}_6^{-}] \cdot [\text{P}] \cdot [H^+] - k_2 \cdot [\text{H}_2\text{SnO}_6\text{P}^{2-}] \cdot [H^+]$$  \hspace{1cm} (13)$$

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

It follows therefore that the forward rate constant $k_f = k_1 \cdot K_2 \cdot \frac{k_f(\text{obs})}{[H^+]}$ but the reverse constant $k_r$ is the same as $k_r = \frac{k_f(\text{obs})}{[H^+]}$. Consequently, in order to calculate $k_r$ it was necessary to obtain $k_f(\text{obs})$ through a separate measure of the forward reaction.

On the basis of these data, taking due care to distinguish between \( K \) and \( \log K \), it can be shown that the rate law may be expressed as:

\[
\frac{d[\text{Sn(OH)}_{5}^{2-}]}{dt} = \frac{k_{1}[\text{Sn(OH)}_{5}^{2-}][\text{P}][\text{H}^{+}]}{k_{1} + k_{2}[\text{P}]} - k_{3}[\text{H}_{2}\text{SnO}_{4}\text{P}^{2-}][\text{H}^{+}]
\]

Noting that in view of the expected high reactivity of the \( \text{Sn(OH)}_{5}^{2-} \) species toward the nucleophilic OH groups both in \( \text{H}_{2}\text{O} \) and in polyols \( k_{1} \) and \( k_{2} \) are comparable such that we may put \( \frac{k_{1}}{k_{2}} = 1 \), and that at large polyol concentrations \( k_{3}[\text{P}] \gg k_{4} \), so that \( k_{1} + k_{2}[\text{P}] \approx k_{3}[\text{P}] \), then

\[
\text{Rate} = \left( \frac{k_{1}}{k_{2}} \right)[\text{Sn(OH)}_{5}^{2-}][\text{H}^{+}] - \frac{k_{3}[\text{H}_{2}\text{SnO}_{4}\text{P}^{2-}][\text{H}^{+}]}{[\text{P}]} \]

\[
(19)
\]
when the quotient vanishes and the rate at constant pH becomes dependent only on the oxyanion concentration, i.e.

$$R_i = \left( \frac{k_i[H^+]}{K_2} \right) [Sn(OH)_{6}^{2-}] = k_i(\text{obs}) [Sn(OH)_{6}^{2-}] \quad (20)$$

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

$$-\frac{d[Sn(OH)_{6}^{2-}]}{dt} = \left( \frac{k_1}{K_2} \right) [Sn(OH)_{6}^{2-}][P][H^+] - k_{-1}[H_2SnO_4P^{2-}][H^+] \quad (21)$$

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 $k_1 = k_2$ and $k_{-1} = k'_{-1} = k_{-2}$, 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 polyl 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 $K_c$ values for the individual polyl 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 polyl 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 polyl-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.

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REFERENCES

10. Albeck, M.; Sredni, B. US Patent 7276628, Biologically Active Complex, 2007; Available at: www.freepatentsonline.com/7276628.html