REDUCTION OF THALLIUM(III) BY SODIUM HYPOPHOSPHITE IN AQUEOUS SOLUTION IN THE PRESENCE OF CERTAIN COMPLEXONES

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Chloride ions catalyze the reduction of thallium(III) by the hypophosphite ion [1, 2]. The reaction of $\text{H}_2\text{PO}_2^-$ with $\text{Tl}^{(III)}$ in the presence of complexones has not been studied. We have investigated the $\text{Tl}^{(III)}$-nitrilotriacetic acid ($\text{H}_3\text{X}$, NTA),$\text{H}_2\text{PO}_2^-$, $\text{Tl}^{(III)}$-ethylenediaminetetraacetic acid ($\text{H}_4\text{Y}$, EDTA)$\text{H}_2\text{PO}_2^-$, and $\text{Tl}^{(III)}$-diethylenetriaminepentaacetic acid ($\text{H}_5\text{L}$, DTPA)$\text{H}_2\text{PO}_2^-$ systems.

EXPERIMENTAL

Solutions of $\text{Tl}_2(\text{SO}_4)_3$ were prepared by the method in [3]. The concentrations of $\text{Tl}^{(III)}$ in solution were determined by iodimetry and complexometry [4]. Sodium hypophosphite solution was made from a precisely weighed sample of a recrystallized preparation of analytical reagent grade; solutions of the complexones were prepared from twice-recrystallized preparations of chemically pure and pure grades; their concentration were checked by titration with a solution of $\text{Ca}^{2+}$ in the presence of oxalate ions [5]. Solutions of constant ionic strength ($\mu = 1$) were made by adding $\text{Na}_2\text{SO}_4$, $\text{H}_2\text{SO}_4$, or $\text{NaOH}$ (all of chemically pure grade).

The course of the redox reaction between $\text{Tl}^{(III)}$ and $\text{H}_2\text{PO}_2^-$ was judged by means of the changes in optical density $\Delta$ of the solutions with time $\tau$ in the parts of the spectrum where the reaction products have no absorption, i.e., 266 nm for $\text{Tl}^{(III)}$-NTA, 275 nm for $\text{Tl}^{(III)}$-EDTA, and 288 nm for $\text{Tl}^{(III)}$-DTPA. The solutions of the reagents were thermostated in different side tubes of the mixer vessel. The time of inverting the vessel and mixing the solutions was taken as the start of the reaction. The optical and kinetic measurements were made in an SF-4A spectrophotometer in a thermostated cell. The acidity of the solutions was monitored by means of a pH-340 potentiometer. The solutions were thermostated by means of a U-20 ultrathermostat.

DISCUSSION OF RESULTS

For each of the three systems $\text{Tl}^{(III)}$-complexone-$\text{H}_2\text{PO}_2^-$ we observe a linear dependence of $\log \Delta$ on $\tau$ with a 40-fold excess of $\text{H}_2\text{PO}_2^-$ with respect to the $\text{Tl}^{(III)}$ concentration (Fig. 1a); thus the redox reaction is first order with respect to the oxidant. By graphical differentiation of the kinetic curves of $\Delta$ vs $\tau$ [6], we also found that the reactions are first order with respect to the oxidant for all three complexones. The pseudofirst-order rate constant ($k_1 = \tan \alpha$) remains constant as the initial concentrations of all three complexonates are varied from $1.0 \times 10^{-4}$ to $1.5 \times 10^{-3}$ mole/liter (Table 1). From the dependence of $k_1$ on the concentration of $\text{H}_2\text{PO}_2^-$ it follows that the order of reaction with respect to hypophosphite (Fig. 1b) is equal to +1 for the three complexones.

The rate of reduction of $\text{Tl}^{(III)}$ by hypophosphite does not depend on the acidity of the medium [1]. Addition of complexones to the $\text{Tl}^{(III)}$-$\text{H}_2\text{PO}_2^-$ system leads to variation of the rate of the redox reaction with $[\text{H}^+]$. As we see from Fig. 2, in the case of $\text{H}_2\text{L}$ and $\text{H}_3\text{X}$, the reaction rate sharply decreases as the pH increases. In the $\text{Tl}^{(III)}$-EDTA-$\text{H}_2\text{PO}_2^-$ system a reduction in the solution acidity to pH 3.0 also causes a fall in $k_1$; however, on further fall in acidity to pH > 4.5 the rate of the redox reaction sharply increases. The maximum rate is observed at pH 5.8–6.0; further rise in pH again leads to a fall in the rate.

If the acidity and temperature are constant, the reaction rate depends on the mole fraction of complexone (Fig. 3). From Fig. 3 we see that in all the three systems the rate decreases as the mole fraction of complexone increases. In the $\text{Tl}^{(III)}$-$\text{H}_2\text{L}$-$\text{H}_2\text{PO}_2^-$ system the rate sharply falls as $[\text{H}_2\text{L}]$ increases up to $[\text{Tl}^{(III)}]$: $[\text{H}_2\text{L}] = 1:1$; further rise in the concentration of $\text{H}_2\text{L}$ has practically no influence on the rate of reduction of $\text{Tl}^{(III)}$ by hypophosphite. An increase in the mole fraction of NTA causes a gradual decrease in the reaction rate. In the $\text{Tl}^{(III)}$-$\text{H}_4\text{Y}$-$\text{H}_2\text{PO}_2^-$ system at pH 1 or 2.0, an increase in the $\text{H}_4\text{Y}$ concentration to $[\text{Tl}^{(III)}]$: $[\text{H}_4\text{Y}] = 1:0.5$ causes a fall in the rate. A further rise in $[\text{H}_4\text{Y}]$ leads to a rise in the reaction rate, which passes through a maximum at $[\text{Tl}^{(III)}]$: $[\text{H}_4\text{Y}] = 1:1$, and then again decreases.

Fig. 1. Logarithm of optical density of solution vs time in the Tl(III) -complexone -H₃PO₂ system (a), and rates of reduction of complexones of Tl(III) vs total hypophosphite concentration (b). 1) Tl³⁺ -NTA -H₃PO₂; 2) Tl³⁺ -EDTA -H₃PO₂; 3) Tl³⁺ -DTPA -H₃PO₂. [Tl³⁺] = [H₅L] = [H₃Y] = 5 × 10⁻⁴; [H₃X] = 1 × 10⁻³; [H₃PO₂] = 2 × 10⁻² mole/liter; μ = 1.0; pH = 1.0; 70°C.

TABLE 1. Rate of Reduction of Tl(III) by Hypophosphite in the Presence of Complexones vs Concentration of Tl(III) Complexonate ([H₃PO₂] = 2 × 10⁻² mole/liter; μ = 1; pH = 1.0; 70°C)

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<tr>
<th>C_init/mole/liter</th>
<th>[Hₓ] × 10⁻² sec⁻¹</th>
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<th>[Hₓ] × 10⁻² sec⁻¹</th>
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<tbody>
<tr>
<td>1.0 × 10⁻⁴</td>
<td>1.2</td>
<td>1.5</td>
<td>5.0</td>
</tr>
<tr>
<td>2.5 × 10⁻⁴</td>
<td>1.2</td>
<td>1.7</td>
<td>6.0</td>
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<tr>
<td>5.0 × 10⁻⁴</td>
<td>1.1</td>
<td>1.6</td>
<td>5.1</td>
</tr>
<tr>
<td>7.5 × 10⁻⁴</td>
<td>1.2</td>
<td>1.6</td>
<td>5.1</td>
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<tr>
<td>1.0 × 10⁻³</td>
<td>1.2</td>
<td>1.7</td>
<td>5.3</td>
</tr>
<tr>
<td>1.5 × 10⁻³</td>
<td>1.4</td>
<td>1.5</td>
<td>5.0</td>
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Average k₁ = (1.2±0.1) × 10⁻³ = (1.6±0.1) × 10⁻³ = (5.5±0.3) × 10⁻⁴

Thus, addition of complexones has a marked influence on the kinetics of the reaction of Tl(III) with H₃PO₂. Assuming that the rate of the reaction in the presence of complexones is of the same order as the rate of reduction of H₂PO₂⁻ not combined in Tl(III) complexonate, and using the above-mentioned dependence of the reaction rate in the Tl(III) -complexone -H₃PO₂ system on the acidity and the mole fraction of complexone, we can represent the processes occurring in the solution by means of the scheme

\[
\begin{align*}
Tl^{3+} + Z & \rightleftharpoons TlZ \\
TlZ + H_3PO_2 & \rightleftharpoons H_2O + Tl^{2+} + Z + H_3PO_3 + 2 H^+ 
\end{align*}
\]

where Z is any complexone, the proton composition of which is not stated. The Tl(III) complexonate undergoes a redox reaction with the H₃PO₂⁻ but the hydrolyzed Tl(III) ions do not.

The kinetic equation of this reaction is

\[-d[TlZ]/dt = k_2 [TlZ] [H₃PO₂⁻]\]

where k₂ is the second-order rate constant of the reaction. We can show that k₂ depends both on the pH and on the mole fraction of complexone if we assume that the equilibrium of (1) is not entirely shifted to the right and that the equilibrium constant of (1) depends on [H₃O⁺].

From the temperature dependence of the reaction rate at pH 1.0 we determined the activation energies of the reduction of all the three complexonates by H₃PO₂⁻ (Table 2).