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Rate and Mechanism of the Complex Formation of Thallium(III) with 4-(2-Pyridylazo)resorcinol (PAR) in Aqueous Solution[†]

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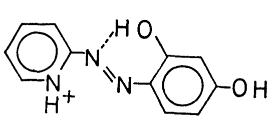
Synopsis. The kinetics of complex formation of Tl(III) with PAR (LH_3^+) was studied in aqueous solution at 25 °C, $[H^+]=0.1$—1.0 mol dm^{-3}, and ionic strength $I=2.0$ mol dm^{-3} ($NaClO_4$). The formation rate constants k_1 and k_2 assigned to the reactions of Tl^{3+} and $TlOH^{2+}$ with LH_3^+ were determined to be 4.1×10^4 and 1.8×10^5 mol$^{-1}\cdot$dm^3 s^{-1}, respectively. The rate data were discussed in comparison with those for Tl(III)-Semi-Xylenol Orange system.

Thallium(III) has been reported to form colored complexes with some *o*-hydroxy azo multidentate ligands as PAR and its analogs even in acidic media.[1,2] However, no kinetic studies have been reported so far except for our early work on the complex formation of Tl(III) with Semi-Xylenol Orange, SXO, which gives the rate constant 3×10^5 mol^{-1} dm^3 s^{-1} for the reaction of $TlOH^{2+}$ and a neutral species of SXO, H_4SXO^0.[3,4] In the present paper we report the kinetic data for the complex formation of Tl(III) with PAR, in order to compare the rate constants with those for the reaction of Tl(III) with SXO.



PAR (LH_3^+)

In the proton concentrations 0.1—1.0 mol dm^{-3} the formation of 1 : 1 Tl(III)-PAR complex was confirmed by means of the method of continuous variation at 520 nm, the absorption maximum of the complex.[5] For the kinetic measurements the total concentration of Tl(III) was kept at least in tenfold excess over the PAR concentration. The change in the absorbance at 560 nm, a shoulder of the absorption spectrum of 1 : 1 complex, was followed by stopped-flow technique. This wavelength was adopted for the measurements in order to avoid the influence of the absorbance of the free ligand. Under the experimental conditions the value of the pseudo-first-order rate constants, k_{obsd}, did not depend on the total concentrations of PAR.

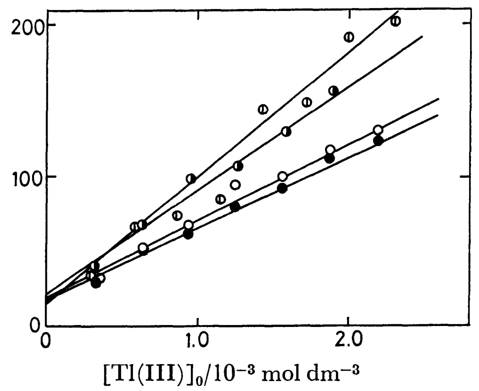
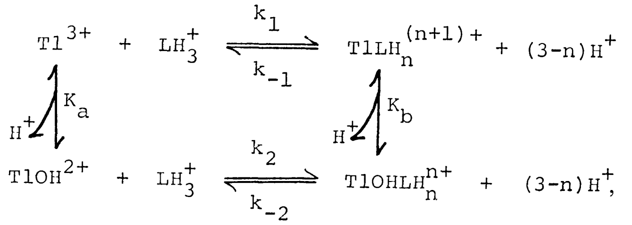


Fig. 1. Dependence of rate constants, k_{obsd}, on total concentrations of Tl(III) at various proton concentrations. $[H^+]=0.2$ (◐), 0.3 (◑), 0.5 (○), and 0.6 mol$\cdot$dm^{-3} (●). $[PAR]_0=2.49\times10^{-5}$ mol dm^{-3}. $I=2.0$ mol dm^{-3} ($NaClO_4$-$HClO_4$) and 25 °C.

Figure 1 shows the dependence of the pseudo-first-order rate constants, k_{obsd}, on the total concentration of Tl(III), $[Tl(III)]_0$, at various proton concentrations. The slopes and the intercepts of the straight lines give the overall rate constants, k_f and k_d, for the formation and dissociation of 1 : 1 complexes, respectively.

The acid-dissociation constants of PAR, $K_c=[LH_2]\times[H^+]/[LH_3^+]=10^{-3.1}$ mol dm^{-3},[1] suggests that the protonated species of PAR, LH_3^+, should be the main species responsible for the complex formation in the acidic region as $[H^+]=0.1$—1.0 mol dm^{-3}.

According to the following scheme with due considerations on the contribution of a base-catalyzed path and the equilibria for very fast protolytic reactions



$$\begin{tikzcd} Tl^{3+} + LH_3^+ \arrow[r, shift left, "k_1"] & TlLH_n^{(n+1)+} + (3-n)H^+ \arrow[l, shift left, "k_{-1}"] \\ TlOH^{2+} + LH_3^+ \arrow[u, shift left, "K_a"] \arrow[r, shift left, "k_2"] & TlOHLH_n^{n+} + (3-n)H^+, \arrow[l, shift left, "k_{-2}"] \arrow[u, shift left, "K_b"] \end{tikzcd}$$

the formation rate constant k_f can be expressed as follows,

$$k_f=\frac{k_1[H^+]+k_2K_a}{[H^+]+K_a}$$

or

$$k_f([H^+]+K_a)=k_1[H^+]+k_2K_a.$$

The plot of $k_f([H^+]+K_a)$ against $[H^+]$ gives a straight line as shown in Fig. 2.[6] From the slope and the intercept the rate constants were determined to be $k_1=4.1\times10^4$ and $k_2=1.8\times10^5$ mol^{-1} dm^3 s^{-1}, respectively.

The value of k_2 was in the same order of magnitude as the formation rate constant for the reaction of $TlOH^{2+}$ and H_4SXO^0. For the completion of the complex formation between Tl(III) and multidentate ligand SXO, the cleavage of the hydrogen-bond

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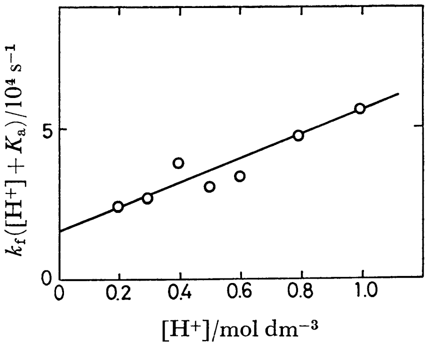

Fig. 2. Plots of $k_f([H^+]+K_a)$ *versus* $[H^+]$ at 25 °C and $I=2.0$ mol dm^{-3} ($NaClO_4$-$HClO_4$). $K_a=10^{-1.14}$ mol dm^{-3}.[10)]

between the *o*-hydroxyl group and the nitrogen of iminodiacetate group should necessarily be involved. As regards the first step of the complex formation of PAR with Tl(III) two reaction paths are possible, namely, the first attack of metal ion on the protonated pyridyl nitrogen or the first attack of metal ion on the intramolecular hydrogen-bond between the *o*-hydroxyl group and the azo nitrogen. However, the attack at the protonated unipositive pyridyl group of PAR is very unlikely as reported in the case of the Co(II)–PAR[7)] and the Ni(II)–PAR system.[8)] Furthermore, it is surprising that the rate constant for the complex formation of Tl(III) with PAR is in the same order of magnitude as that of Tl(III)–SXO despite the differences in the structure, charge type, and the donor atoms between these two ligands. This fact suggests the control of the reaction rate by the step of dissociation of the coordinated water molecule from aqua Tl(III) ion. It is likely that the first attack of Tl(III) ion occurs on the hydrogen-bond between the *o*-hydroxyl group and azo nitrogen of PAR to form the complex.[9)]

Experimental

Measurements. All measurements were carried out at 25.0±0.2 °C and ionic strength 2.0 ($NaClO_4$–$HClO_4$). The kinetic measurements were carried out with a stopped-flow spectrometer Yanagimoto SPS-1. The absorption spectra were measured with a Hitachi recording spectrophotometer EPS-3T.

Materials. All reagents are of analytical grade, unless otherwise specified. Water was deionized and distilled. A stock solution of Tl(III) perchlorate was prepared by anodic oxidation of Tl(I) perchlorate in 2 mol dm^{-3} perchloric acid.[10)] The concentration of Tl(III) was determined titrimetrically with EDTA using XO as an indicator.[11)] The stock solution was stored in the dark. The monohydrate of monosodium salt of PAR was synthesized and purified by repeating recrystallization from ethanol.[2)] The purity was confirmed by elemental analysis.[7)]

References

1) M. Hniličkovâ and L. Sommer, *Talanta*, **16**, 83 (1969).

2) S. Shibata, "2-Pyridylazo Compounds in Analytical Chemistry," in "Chelates in Analytical Chemistry," ed by H. A. Flaschka and A. J. Barnard, Jr., Marcel Dekker, Inc., New York, N. Y. (1972), Vol. 4, p. 1.

3) Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **45**, 1417 (1972).

4) Sutin estimated the characteristic rate constant for the replacement of a coordinated water molecule from hydrated Tl(III) ion to be larger than 3×10^9 s^{-1}. The value was calculated from the data for the reaction of iron(III) and chloride ion. See N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

5) Tl(III) ion was reported to form a 1 : 1 complex with PAR in aqueous solution at pH lower than 2. At higher pH a 1 : 2 complex was also formed.[1)]

6) The dependency of the value of k_d on the proton concentration is not clear owing to the large experimental error (±30%) for the intercepts in Fig. 1. The average value of k_d was calculated to be 10 ± 5 s^{-1} at various proton concentrations.

7) K. Mochizuki, T. Imamura, T. Ito, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **51**, 1743 (1978).

8) M. Fujimoto, presented at the 21st Annual Meeting on Coordination Chemistry, Nagoya, October 17, 1971, Abstracts, p. 87.

9) The results of the equilibrium measurements suggest the possibility of the formation of a bidentate PAR complex of Tl(III). Further studies using another method, *e.g.*, NMR, would be necessary to confirm whether the ligand PAR is coordinated to Tl(III) as a bidentate ligand or as a terdentate ligand under the experimental conditions.

10) G. Biedermann, *Arkiv. Kem.*, **5**, 441 (1953).

11) J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, **46**, 92 (1957).