BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (5), 1345—1346 (1977)

A Note on the Rates of Complex Formation of Indium(III) with Murexide and the Decomposition of Murexide in the Presence of Indium(III)

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(Received November 11, 1976)

Synopsis. Kinetics of the complex formation between In(III) and murexide was studied by means of the temperature-jump method and the rate of decomposition of the ligand in acid nitrate media. The complex formation of $\mathrm{InOH^{2+}}$ with murexide is about 10 times faster than that of $\mathrm{In^{3+}}$. The stability constants indirectly obtained from the decomposition rate of murexide coincide with those from direct stopped-flow measurements.

Murexide, ammonium purpurate, is a useful metallochromic indicator except for the acid region where it decomposes to uramil and alloxan.[1] Kawai *et al.* studied the kinetics on the complex formation of murexide with In(III) and the decomposition of murexide in acid perchlorate media in the presence of In(III).[2] In this study no dependence of the rate of complex formation on hydrogen-ion concentration (0.001—0.5 M) could be observed. In addition a discrepancy in the stability constants was obtained from the two methods, the indirect calculation from the rate of decomposition of murexide giving a stability constant twice as large as that from the direct stopped-flow measurement. We have reexamined the questions with use of potassium nitrate instead of sodium perchlorate for adjusting the ionic strength in order to avoid the influence of the ion-pair formed between sodium ion and murexide anion.

Experimental

Materials. In order to prepare a stock solution of In(III) containing 1 M nitric acid, indium(III) oxide (Koso) was dissolved in excess of nitric acid by warming on a water bath. The concentration of In(III) was determined by titration with EDTA using Xylenol Orange as an indicator. The freshly prepared stock solution was used within a day in order to avoid undesired polymerization of In(III). Murexide was prepared and recrystallized.[3] A weighed amount of murexide was dissolved in water immediately before use. Acidity and ionic strength of the solution were adjusted with nitric acid and potassium nitrate.

Measurements. The rate of complex formation was measured with a Union Giken co-axial-cable temperature-jump apparatus Model RA-105. A Hitachi ESP-3T spectrophotometer equipped with a recorder was used to measure the rate of decomposition. Visible spectrum of unstable purpuric acid was obtained with a Union Giken rapid-scan spectrophotometer RA-1300, and the acid dissociation constant with a Yanagimoto SPS-1 stopped-flow apparatus.

Results and Discussion

Rate of Complex Formation. The rate of complex formation between In(III) and murexide was measured at the absorption peak of the complex, 460 nm, by means of the temperature-jump method at 20 °C and ionic strength 0.2 M ($\mathrm{KNO_3}$). Acetic acid and potassium acetate were used to adjust pH. The results suggest the presence of a base-catalyzed path, the following mechanism being considered;

$$\begin{array}{ccccc}
\mathrm{In} & + & \mathrm{L} & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & \mathrm{InL} \\
K_\mathrm{a}\downarrow\uparrow & & & & K_\mathrm{b}\downarrow\uparrow \\
\mathrm{In(OH)} & + & \mathrm{L} & \underset{k_4}{\overset{k_3}{\rightleftharpoons}} & \mathrm{In(OH)L} \\
+\,\mathrm{H^+} & & & & +\,\mathrm{H^+}
\end{array}$$

$$\tau^{-1} = \frac{k_1[\mathrm{H}]+k_3K_\mathrm{a}}{[\mathrm{H}]+K_\mathrm{a}}\cdot C_\mathrm{In} + \frac{k_2[\mathrm{H}]+k_4K_\mathrm{b}}{[\mathrm{H}]+K_\mathrm{b}},$$

where C_In is the total concentration of In(III) ($C_\mathrm{In} \gg [\mathrm{L}]$). The value of K_a in literature is adopted ($K_\mathrm{a}=10^{-4.42}$ M).[4] The values of rate constants are determined to be $k_1=6.0\times10^5\ \mathrm{M^{-1}\,s^{-1}}$, $k_2=50\ \mathrm{s^{-1}}$, $k_3=6.8\times10^6\ \mathrm{M^{-1}\,s^{-1}}$, and $k_4K_\mathrm{b}=2.3\ \mathrm{M\,s^{-1}}$. The hydrolyzed form, $\mathrm{InOH^{2+}}$, reacts with the ligand about 10 times faster than the aquo form. This is in line with the tendency that the rate of complex formation of hydroxo metal ion is higher than that of the corresponding aquo metal ion.[5]

Acid Dissociation Constant of Purpuric Acid. Since murexide decomposes rapidly in an acid solution, the acid dissociation constant of protonated murexide or purpuric acid was measured by the stopped-flow method, giving $\mathrm{p}K_1=-0.24$. Rapid-scan spectroscopy gave $\lambda_\mathrm{max}=444$ nm, $\varepsilon=2.2\times10^4\ \mathrm{l\,mol^{-1}\,cm^{-1}}$ with an isosbestic point at 485 nm for purpuric acid.

Effect of [H] on the Decomposition Rate of Murexide. The decomposition of murexide is accelerated by acid. The reciprocal of the pseudo-first-order rate constant for the decomposition of murexide has a linear relationship with respect to $[\mathrm{H}]^{-1}$, as shown in Fig. 1. The reaction mechanism is as follows;

$$\mathrm{MX} + \mathrm{H} \overset{K_\mathrm{H}}{\rightleftharpoons} \mathrm{MXH} \xrightarrow[+\mathrm{H_2O}]{k} \text{Uramil} + \text{Alloxan},$$

$$k_\mathrm{obsd}^{\mathrm{dec}\;-1} = \frac{1}{k} + \frac{1}{kK_\mathrm{H}}\cdot\frac{1}{[\mathrm{H}]},$$

where MX and MXH denote purpurate anion and purpuric acid, respectively. Since the intercept of the straight line in Fig. 1 is too small for evaluation, the value obtained above is introduced into K_H ($K_\mathrm{H}=K_1^{-1}$), giving the result $k=0.13\ \mathrm{s^{-1}}$.

Rate of Decomposition of Murexide in the Presence of In(III). The rate of decomposition of murexide was measured at the absorption maximum of the complex. The rate decreases with increase in the concentration of In(III) (Fig. 2). The following reaction scheme is proposed:

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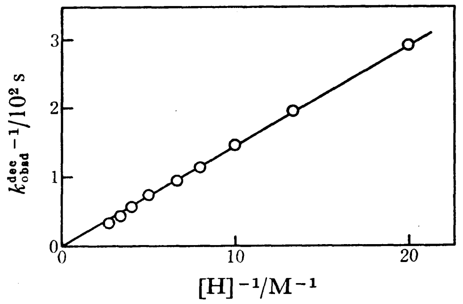

Fig. 1. Plot of $k_{obsd}^{dec\ -1}$ *vs.* inverse of hydrogen-ion concentration. At 520 nm, 10 °C, I=1.0 M (KNO_3), and $[MX]_0 = 5.0 \times 10^{-5}$ M.

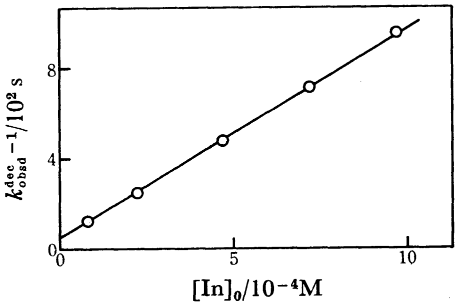

Fig. 2. Plot of $k_{obsd}^{dec\ -1}$ *vs.* total concentration of In(III). At 460 nm, 10 °C, [H]=0.25 M, I=1.0 M (KNO_3), and $[MX]_0 = 5.0 \times 10^{-5}$ M.

$$MX + In \overset{K_{In}}{\rightleftharpoons} InMX$$

$$MX + H \overset{K_H}{\rightleftharpoons} MXH \xrightarrow[+H_2O]{k} \text{Uramil} + \text{Alloxan}.$$

The rate of decomposition is given by

$$k_{obsd}^{dec\ -1} = \frac{[H]K_H + 1}{[H]kK_H} + \frac{K_{In}}{[H]kK_H} \cdot [In]_0.$$

Introduction of the above results into K_H and k leads to $K_{In} = 1.5 \times 10^4$ M^{-1}. The value coincides with the direct stopped-flow data, $K'_{In} = k_1/k_2 = 1.4 \times 10^4$ M^{-1}, I=1 M (KNO_3) at 10 °C. Agreement of the two values indicates that the proposed mechanism is correct. The terdentate structure of the complex coordinated at the central nitrogen atom of the ligand stabilizes the ligand molecule against decomposition.[6]

The discrepancy in the two stability constants derived from the direct and the indirect measurements[2] would be clarified in terms of two effects of the sodium ion: (1) Sodium ion forms an ion-pair with purpurate anion, which is fairly stable against acid. (2) The ion-pair, $Na^+ \cdots MX^-$, also forms a complex with In(III). Since the data on the ion-pair are very limited, no further discussion can be made.

The present work was supported by a grant-in-aid for Scientific Research from the Ministry of Education.

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