

## Complex Formation of Indium(III) with Murexide and the Decomposition of Murexide in the Presence of Indium(III) in Acid Perchlorate Media

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Kinetic and equilibrium data on the complex formation between In(III) and murexide are derived using stopped-flow method and also from the rate of decomposition of the ligand in acid perchlorate media. The rate of complex formation is independent of the acid concentration over the wide range of  $[H]$  between 0.001 and 0.5 M. The discrepancies of the stability constants obtained from the direct and the indirect methods are discussed.

Murexide, ammonium purpurate, has long been used as a very useful metallochromic indicator<sup>1)</sup> except for acid region, where it decomposes to uramil and alloxan.<sup>2,3)</sup> The rate of the decomposition depends on the acid concentration.<sup>2)</sup> We are interested in the reaction mechanism of the complex formation between indium(III) and murexide in connection with the possibility of catalytic action of indium(III) on the decomposition of murexide.

The rates of metal complex formations in general are affected by the acid concentration due to the contribution of hydrolyzed forms of the metal ion.<sup>4)</sup> The kinetic data on the metal complex formations with murexide in the neutral region were reported in detail by Geier.<sup>5)</sup> In the case of indium(III) and murexide, however, we observed no dependence on the hydrogen-ion concentration of the rate of complex formation. In the present report the complex formation between indium(III) and murexide and the decomposition of murexide in the presence of indium(III) ion are studied over a wide range of the hydrogen-ion concentrations 0.001—0.5 M.

### Experimental

**Materials.** Deionized water was distilled. Reagent grade materials were used unless otherwise specified. Indium(III) perchlorate solution was prepared by dissolving indium(III) oxide in a small excess of concentrated perchloric acid. The concentration was titrimetrically determined with EDTA using Xylenol Orange as indicator. Weighed amount of commercial or prepared murexide<sup>6)</sup> was dissolved in water immediately before use.

Acidity and ionic strength of the solutions were adjusted with perchloric acid and sodium perchlorate. The stock solution of perchloric acid was standardized by titration with sodium hydroxide. The stock solution of sodium perchlorate was kept for a couple of weeks to precipitate trace amount of metal impurities together with silicates and filtered through a glass filter. An aliquot of the solution was passed through a column of cation-exchange resin (Dowex 50W-X8) in the H-form and titrated with sodium hydroxide.

**Measurements.** The rates of decomposition and the spectra were measured with a Hitachi EPS-3T spectrophotometer equipped with a recorder. The thermostated reactant solutions were pipetted and mixed with shaking in a thermo-

stated optical cell.

A Yanagimoto SPS-1 stopped-flow apparatus was used to measure the rate of complex formation. The optical cell and the reservoirs were thermostated by circulating the water from a thermostat.

### Results

*Stability Constant of the Complex Measured by Stopped-flow Method at  $[H]=0.5$  M.* Equilibrium data of the complex in the acid range were directly derived from the change in absorbance as measured by stopped-flow technique.

Formation of 1:1 complex between indium(III) and murexide (MX) was confirmed by the mole ratio method. The absorption maximum of the complex (InMX) lies at 470 nm with the molar extinction coefficient  $\epsilon_{\text{InMX}}=8.82 \times 10^3$  at  $[H]=0.5$  M and ionic strength 2.0 M ( $\text{NaClO}_4$ ). The value  $\epsilon_{\text{MX}}$  at 470 nm was evaluated to be  $4.51 \times 10^3$ .

Under high acid concentration the rapid complex formation is followed by the slow decomposition of murexide. Stability constant of the complex  $K_{1a}$  at 25 °C and  $[H]=0.5$  M was calculated from the change in absorbance at 470 nm memorized on the screen of oscilloscope.

Stability constant  $K_{1a}$  is written as follows.

$$K_{1a} = \frac{[\text{InMX}]}{\{[\text{In}]_0 - [\text{InMX}]\}\{[\text{MX}]_0 - [\text{InMX}]\}},$$

$$A = \epsilon_{\text{MX}}[\text{MX}]_0 + (\epsilon_{\text{InMX}} - \epsilon_{\text{MX}})[\text{InMX}], \text{ and}$$

$$[\text{InMX}] = \frac{A - \epsilon_{\text{MX}}[\text{MX}]_0}{\epsilon_{\text{InMX}} - \epsilon_{\text{MX}}},$$

where  $[\text{In}]_0$  and  $[\text{MX}]_0$  are the initial concentrations of indium(III) and murexide respectively, and  $A$ ,  $\epsilon_{\text{InMX}}$ , and  $\epsilon_{\text{MX}}$  denote the observed absorbance, the molar extinction coefficients of the complex and the ligand at 470 nm respectively.

The plot of  $\{[\text{In}]_0 - [\text{InMX}]\}\{[\text{MX}]_0 - [\text{InMX}]\}$  versus  $[\text{InMX}]$  gave a straight line as shown in Fig. 1 and value of  $K_{1a}$  was evaluated from the slope to be  $7.2 \times 10^3 \text{ M}^{-1}$  at  $[H]=0.5$  M,  $\mu=2.0$  M ( $\text{NaClO}_4$ ) and at 25 °C.

*Rate of Complex Formation and Stability Constants.*

The rate of complex formation between indium(III) and murexide was measured by following the increase in the absorbance of the complex with time. The rate

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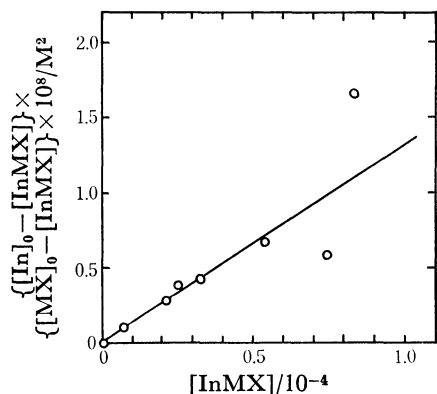


Fig. 1. Plot of  $\{[In]_0 - [InMX]\}\{[MX]_0 - [InMX]\}$  vs.  $[InMX]$  at 25 °C,  $\mu=2.0$  (NaClO<sub>4</sub>), and  $[H]=0.5$  M.

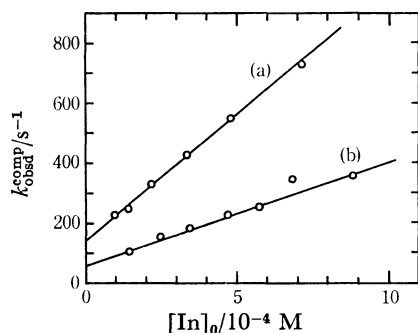
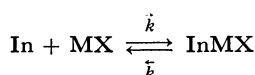


Fig. 2. Plot of  $k_{obs}^{comp}$  vs. total concentration of In(III) at  $[H]=0.5$  M and  $\mu=2.0$  (NaClO<sub>4</sub>). (a)  $[MX]_0=4.08 \times 10^{-5}$  M and at 25 °C; (b)  $[MX]_0=1.08 \times 10^{-5}$  M and at 10 °C.

of complex formation is increased with increasing concentration of indium(III). Figure 2 shows the dependence of the pseudo-first-order rate constant on indium(III) concentration under the conditions of  $[In]_0 \gg [MX]_0$ ,  $[H]=0.5$  M,  $\mu=2.0$  M (NaClO<sub>4</sub>) and at 10 or 25 °C.

The values of  $\vec{k}$ ,  $\bar{k}$  and  $K_{1b}$  for the reaction



are evaluated as shown in Table 1.

TABLE 1. KINETIC AND EQUILIBRIUM DATA OF THE INDIUM(III)-MUREXIDE COMPLEX, MEASURED AT  $[H]=0.5$  M AND  $\mu=2.0$  (NaClO<sub>4</sub>).

$T$ (°C)	$\vec{k}$ (M <sup>-1</sup> ·s <sup>-1</sup> )	$\bar{k}$ (s <sup>-1</sup> )	$K_{1b}=\vec{k}/\bar{k}$ (M <sup>-1</sup> )
10	$3.5_4 \times 10^5$	57.6	$6.1_4 \times 10^3$
25	$8.5_2 \times 10^5$	130	$6.5_5 \times 10^3$

Table 2 shows the rate constants  $k_{obs}^{comp}$ ,  $\vec{k}$  and  $\bar{k}$  for the wide range of acid concentrations at ionic strength 2.0 M (NaClO<sub>4</sub>) and 10 °C. Since the pseudo-first-order rate constant  $k_{obs}^{comp}$  does not depend on the acid concentration, it would be reasonable to conclude that the both rate constants  $\vec{k}$  and  $\bar{k}$  do not depend on the acid concentration.

*Effect of  $[MX]_0$  and  $[H]$  on the Rate of Decomposition of Murexide.* The absorption maximum of murexide

TABLE 2.  $[H]$ -DEPENDENCE OF THE RATE OF COMPLEX FORMATION BETWEEN INDIUM(III) AND MUREXIDE AT 10 °C AND  $\mu=2.0$  (NaClO<sub>4</sub>). ( $[In]_0=4.77 \times 10^{-4}$  M,  $[MX]_0=5.10 \times 10^{-5}$  M).

$[H]$ (M)	$k_{obs}^{comp}$ (s <sup>-1</sup> )	$\vec{k}=(k_{obs}^{comp}-\bar{k})/[In]_0$ (M <sup>-1</sup> ·s <sup>-1</sup> )
0.5	230	$3.61 \times 10^5$
0.4	(162) <sup>b</sup>	$(4.42)^b \times 10^5$
0.3	(156) <sup>b</sup>	$(4.17)^b \times 10^5$
0.2	190	$2.78 \times 10^5$
0.1	230	$3.61 \times 10^5$
0.05	250	$4.03 \times 10^5$
0.01	210	$3.20 \times 10^5$
0.005	220	$3.40 \times 10^5$
0.001	230	$3.61 \times 10^5$

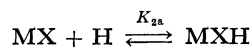
a) The value of  $\bar{k}$  was evaluated to be 57.6 s<sup>-1</sup> (see Table 1). b) The values in parentheses are those from other series of data with  $[In]_0=2.36 \times 10^{-4}$  M and  $[MX]_0=2.65 \times 10^{-5}$  M. Experimental errors for the values of  $k_{obs}^{comp}$  are ca.  $\pm 8\%$ .

TABLE 3.  $[MX]_0$ -DEPENDENCE OF THE RATE OF THE DECOMPOSITION OF MUREXIDE AT 25 °C,  $\mu=2.0$  (NaClO<sub>4</sub>) AND  $[H]=0.5$  M.

$[MX]_0$ (M)	$k_{obs}^{dec}$ (s <sup>-1</sup> )
$2.5 \times 10^{-6}$	0.11
$5.0 \times 10^{-6}$	0.11
$2.5 \times 10^{-5}$	0.10
$1.0 \times 10^{-4}$	0.093
$1.5 \times 10^{-4}$	0.085

lies at 530 nm at  $[H]=0.5$  M and  $\mu=2.0$  M (NaClO<sub>4</sub>) in the concentration range between  $[MX]_0=1.0 \times 10^{-4}$  and  $2.5 \times 10^{-6}$  M. The effect of initial concentration of murexide on the rate of decomposition is shown in Table 3. Though the rate shows some dependence on the concentration of murexide, the observed tendency of decrease was quite small despite of the large concentration change of murexide more than two orders of magnitude. The similar tendency is also reported in Ref. 2.

The decomposition of murexide is accelerated by acid. Figure 3 shows that the reciprocal of the pseudo-first-order rate constant for the decomposition of murexide has a linear relation to  $[H]^{-1}$ . The proposed reaction scheme is thus as follows.



where MX and MXH denote purpurate anion and purpuric acid respectively.

The rate of decomposition is written as

$$k_{obs}^{dec}^{-1} = \frac{1}{k_{2a}} + \frac{1}{k_{2a}K_{2a}} \cdot \frac{1}{[H]}.$$

According to the above equation the values  $k_{2a}K_{2a}$  and  $k_{2a}$  are evaluated to be  $k_{2a}K_{2a}=0.16$  M<sup>-1</sup> s<sup>-1</sup> and  $k_{2a}=1.2$  s<sup>-1</sup> from the slope and the intercept respectively. The constant  $K_{2a}$  is therefore calculated to be about 0.13 M<sup>-1</sup>. However, as the intercept passes through

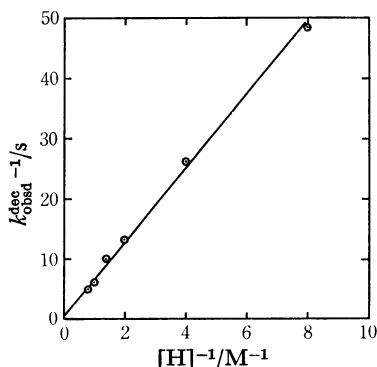
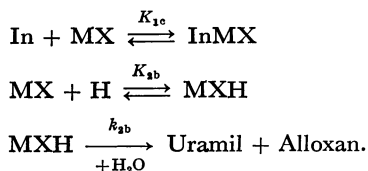


Fig. 3. Plot of  $k_{\text{obs}}^{\text{dec}} -1$  vs. inverse of hydrogen-ion concentration. at 530 nm, 25 °C,  $\mu=2.0$  (NaClO<sub>4</sub>), and  $[\text{MX}]_0 = 1.02 \times 10^{-4}$  M.

very near the origin, each value of  $k_{2a}$  and  $K_{2a}$  has eventually a great inaccuracy of 50%. More accurate value of  $K_{2a}$  is given by  $K_{2b}$  in the next section from the effect of indium(III) on the decomposition of murexide.

*Rate of Decomposition of Murexide in the Presence of Indium(III).* The rate of decomposition of murexide was also studied by following the change in absorbance at the absorption peak of the complex at constant acid concentration  $[\text{H}]=0.5$  M. The apparent rate of decomposition was decreased with increasing concentration of indium(III). This result is ascribed to the inertness of the indium(III) complex against the decomposition of the ligand murexide.

Now let us write the reaction scheme as follows.



The rate of decomposition is written as

$$k_{\text{obs}}^{\text{dec}} -1 = \frac{[\text{H}]K_{2b} + 1}{[\text{H}]k_{2b}K_{2b}} + \frac{K_{1c}}{[\text{H}]k_{2b}K_{2b}} \cdot [\text{In}]_0.$$

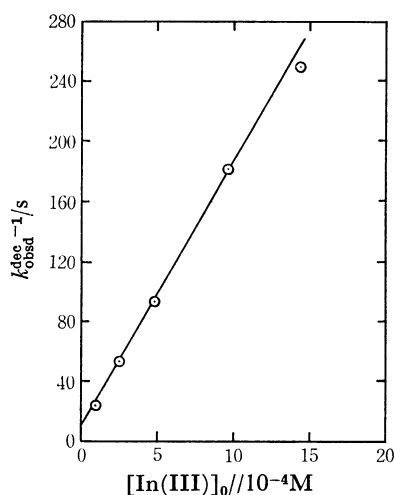


Fig. 4. Plot of  $k_{\text{obs}}^{\text{dec}} -1$  vs. total concentration of In(III). At 470 nm, 25 °C,  $[\text{H}]=0.5$ ,  $\mu=2.0$  (NaClO<sub>4</sub>), and  $[\text{MX}]_0 = 1.02 \times 10^{-4}$  M.

TABLE 4. EQUILIBRIUM DATA MEASURED AT 25 °C,  $\mu=2.0$  (NaClO<sub>4</sub>) AND  $[\text{H}]=0.5$  M.

$K_{1a} = 7.2 \times 10^3 \text{ M}^{-1}$	
$K_{1b} = 6.5 \times 10^3 \text{ M}^{-1}$	$K_{2a} = 0.13 \text{ M}^{-1}$
$K_{1c} = 14 \times 10^3 \text{ M}^{-1}$	$K_{2b} = 0.13 \text{ M}^{-1}$

From the intercept and the slope of the straight line as shown in Fig. 4, the values of  $K_{2b}$  and  $K_{1c}$  are determined to be 0.13 and  $1.4 \times 10^4 \text{ M}^{-1}$  at 25 °C, respectively. The data are summarized in Table 4.

## Discussion

Stability constant  $K_{1c}$  evaluated from the rate of decomposition is about twice as large as the constants  $K_{1a}$  and  $K_{1b}$  given by the stopped-flow measurements. These results show that the complex formation between indium(III) and murexide plays a role of negative catalysis on the decomposition of murexide under the experimental conditions.

The complex formed between metal ions and the ligand murexide does not show a large molar extinction coefficient until the "nitrogen" atom at the center of the ligand molecule *does* coordinate to the metal ion to form a terdentate structure.<sup>7)</sup> The complex followed at 470 nm is thus assigned to the one involving murexide as a terdentate ligand. The terdentate structure of the complex usually stabilizes the ligand molecule against decomposition.<sup>8,9)</sup> Therefore the observed larger value of  $K_{1c}$  suggests the existence of other type of complexes or some ion pairs that are stable and less active to the acid decomposition of murexide, though not experimentally ascertained.

The result that the rate of the complex formation between indium(III) and murexide does not depend on the acid concentration is very interesting from a point of view that the rate of complex formation of hydroxo metal ion is generally by about 100 times higher than that of the corresponding aquo metal ion.<sup>10-12)</sup> The larger value of  $K_{1c}$  from the decomposition rate of the ligand as compared with the values of  $K_{1a}$  and  $K_{1b}$ , and the lack of effect of the hydrogen-ion concentration on the rate of complex formation suggest the contribution of a sort of complex different from the one followed at 470 nm to the reaction system. Then  $K_{1c}$  may include the stability constants of the other complexes. Further details of the problem will be discussed elsewhere.

Furthermore it is of practical interest to note that the kinetic results of the acid decomposition suggest the possibility of determining the acid dissociation constant of the organic compounds which are too unstable to determine the constant by static method.

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## References

- 1) G. Schwarzenbach and H. Gysling, *Helv. Chim. Acta*, **32**, 1108, 1314 (1949). J. H. Moser and M. B. Williams, *Anal. Chem.*, **25**, 1414 (1953). G. Brunisholz, *Helv. Chim. Acta*, **37**, 1546 (1954).

- 2) N. A. Ramaiah, S. L. Gupta, and J. Vishnu, *Z. Naturforsch.*, **12b**, 189 (1957).
  - 3) R. K. Chaturvedi, *Z. Phys. Chem. (Leipzig)*, **221**, 127 (1962).
  - 4) M. Eigen, "Advances in the Chemistry of the Coordination Compounds," ed. by S. Kirschner MacMillan, New York, N.Y. (1961), p. 371.
  - 5) G. Geier, *Ber. Bunsenges. Phys. Chem.*, **69**, 617 (1965); *Helv. Chim. Acta*, **51**, 94 (1968).
  - 6) D. Davidson, *J. Amer. Chem. Soc.*, **58**, 1821 (1936).
  - 7) H. Gysling and G. Schwarzenbach, *Helv. Chim. Acta*, **52**, 1484 (1949).
  - 8) G. L. Eichorn and N. D. Marchand, *J. Amer. Chem. Soc.*, **78**, 2688 (1956).
  - 9) A. Nakahara, This Bulletin, **32**, 308 (1959).
  - 10) J. Miceli and J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 6967 (1968).
  - 11) N. D. Lukomskaya, T. V. Malikova, and K. B. Yatsimirskii, *Zh. Neorg. Khim.*, **12**, 2462 (1967).
  - 12) Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, This Bulletin, **45**, 1417 (1972).
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