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Kinetics and Mechanisms of the Reaction of Tl(III) with Variamine Blue, [*N*-(*p*-Methoxyphenyl)phenylenediamine] in Aqueous Perchlorate Media

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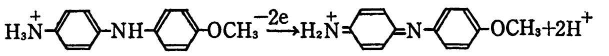
A stopped-flow apparatus was used to study the kinetics of the redox reaction of Tl(III) with Variamine Blue under nitrogen atmosphere in acid (0.2—0.6 M) perchlorate media of ionic strength $\mu = 1.0$ M. The observed second-order rate constant increases inversely with hydrogen ion concentration. The proposed mechanism involves the overall rate-determining steps

$$\mathrm{Tl^{3+} + (V.B.) \overset{k_1}{\rightleftharpoons} Tl^{+} + (V.B.)_{ox} + 2H^{+}}$$

$$\mathrm{TlOH^{2+} + (V.B.) \overset{k_2}{\rightleftharpoons} Tl^{+} + (V.B.)_{ox} + H_2O + H^{+}}$$

where (V.B.) and $\mathrm{(V.B.)_{ox}}$ are a reduced form and an oxidized form of Variamine Blue respectively. The rate constants are evaluated to be $k_1 \leq 10^2\ \mathrm{M^{-1}\,sec^{-1}}$, and $k_2 = 3.6 \times 10^4\ \mathrm{M^{-1}\,sec^{-1}}$ at 25°C. The activation energy E_2 for k_2 is $11 \pm 0.8\ \mathrm{kcal \cdot mol^{-1}}$.

It has been reported[1-3] that the aqueous solution of Variamine Blue (abbr. V.B.) undergoes two electron oxidation to yield a violet-red iminoquinone (abbr. $\mathrm{(V.B.)_{ox}}$) by oxidizing agents such as Ce(IV), Fe(III), and $\mathrm{I_2}$, as follows.



(V.B.) (V.B.)$_{\mathrm{ox}}$

In the reaction of V.B. with Fe(III)[4] and Ce(IV),[5] the formation of $\mathrm{(V.B.)_{ox}}$ does not obey the pseudo-first-order rate law in the presence of a large excess of metal ions. It was ascribed to the non-complementary reaction, where 2 mol of the oxidizing agent react with 1 mol of the reducing agent.

In the present paper we report the reaction of Tl(III) with V.B. in aqueous perchlorate media. Formation of $\mathrm{(V.B.)_{ox}}$ obeys the first order rate law under the condition $\mathrm{[Tl(III)]_0 \gg [(V.B.)_{ox}]}$. It seems that the complementary reaction of Tl(III) with V.B. does not proceed through the semioxidized form of Variamine Blue as semiquinone.

Experimental

Materials. Deionized and distilled water was used. The solution of Tl(III) perchlorate was prepared by electrolytic oxidation of Tl(I) perchlorate in 2 M perchloric acid.[6] Thallium(I) perchlorate was precipitated from solutions of Tl(OAc) and $\mathrm{HClO_4}$ and purified by repeated recrystallization. The concentration of Tl(III) was standardized with EDTA titrimetrically. Variamine Blue (hydrochloride, Dojindo, Kumamoto) was dissolved in boiled water before use.

Sodium perchlorate and perchloric acid (reagent grade, Koso, Tokyo) were used to maintain the ionic strength at $\mu = 1.0$ throughout the work. The concentration of sodium perchlorate was standardized by titrating the eluent from a column of ion-exchange resin, Dowex 50W-X8, in the acid form.

Kinetics. The reaction of V.B. with Tl(III) was followed spectrophotometrically using a stopped-flow apparatus (SPS-1, Yanagimoto, Kyoto) at 550 nm, the λ_{max} of $\mathrm{(V.B.)_{ox}}$.

Nitrogen gas purified through an alkaline pyrogallol solution was passed through the solutions in the reservoirs during the course of measurements in order to avoid undesirable air oxidation.

Since in perchloric acid media the absorbance of Variamine Blue at 280 nm decreases gradually on exposure to the air, the solution of Tl(III) in perchloric acid media was mixed with a solution of V.B. of pH about 5. No decrease in absorbance was observed when solid Variamine Blue was directly dissolved *in vacuo* in the 2 M perchloric acid solution freed from oxygen by freezing a few times.

Measurements of the reaction of V.B. with Tl(III) were performed under the conditions $5.0 \times 10^{-3} > \mathrm{[Tl(III)]} > 1.0 \times 10^{-3}$, $5.0 \times 10^{-5} \geqq \mathrm{[V.B.]_0} \geqq 5.0 \times 10^{-6}$, and $0.6 > \mathrm{[H^+]_0} \geqq 0.2$ M.

Results

Stoichiometry. The stoichiometry of the reaction of Tl(III) with V.B. was determined spectrophotometrically at 550 nm using a stopped-flow apparatus. A definite excess of Tl(III) was mixed with V.B. to determine the molar extinction coefficient of $\mathrm{(V.B.)_{ox}}$ as $1.3 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$ at 550 nm. The value agreed with that observed in the reaction of Fe(III) with V.B.[4]

Table 1 shows the concentration of $\mathrm{(V.B.)_{ox}}$ formed

Table 1. Stoichiometry of the reaction of Tl(III) with V.B.[a]

$\mathrm{[Tl(III)]_0}$ (10^{-5} M)	$\mathrm{[V.B.]_0}$ (10^{-5} M)	$\mathrm{[(V.B.)_{ox}]}$ (10^{-5} M)	$\dfrac{\mathrm{[(V.B.)_{ox}]}}{\mathrm{[V.B.]_0}}$	$\dfrac{\mathrm{[(V.B.)_{ox}]}}{\mathrm{[Tl(III)]_0}}$
168.0	0.5	0.5	1.0	
2.8	40.0	2.3		0.82
5.6	40.0	5.0		0.91

a) at $\mathrm{[H^+]} = 0.5$ M, $\mu = 1.0$, and 25°C.

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[1] L. Erdey, I. Buzas, and K. Vigh, *Talanta*, **1**, 377 (1958).

[2] L. Erdey and R. C. Pink, *ibid.*, **9**, 329 (1962).

[3] L. Erdey, T. Meisel, B. Mohos, and F. Tudos, *ibid.*, **14**, 1477 (1965).

[4] T. Imamura and M. Fujimoto, This Bulletin, **45**, 438 (1972).

[5] T. Imamura and M. Fujimoto, *ibid.*, submitted for publication.

[6] G. Biedermann, *Arkiv Kemi*, **5**, 44 (1953).

from various concentrations of Tl(III) and V.B. The derived stoichiometry is $\Delta[(\mathrm{V.B.})_{\mathrm{ox}}]/\Delta[\mathrm{Tl(III)}]_0 = -1.0$.

Kinetics. With a large excess of Tl(III) the appropriate pseudo-first-order absorbance plots gave a straight line, as shown in Fig. 1, according to the following equation.

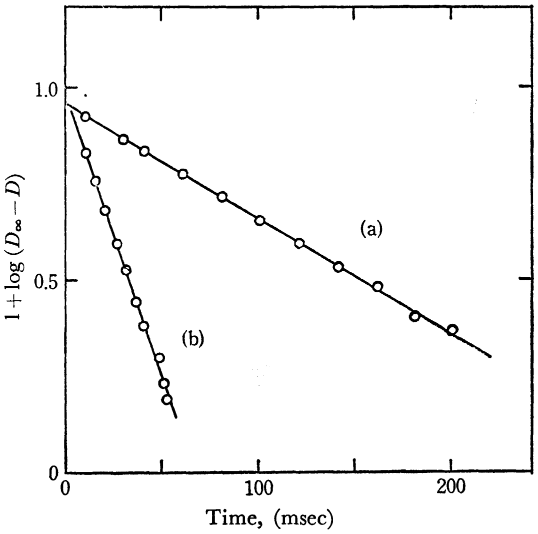

Fig. 1. Typical first-order rate plots at 25°C and $\mu=1.0$. (a) $[\mathrm{Tl(III)}]_0=1.68\times10^{-3}$ M, $[\mathrm{V.B.}]_0=5.00\times10^{-5}$ M, $[\mathrm{H^+}]=0.45$ M, (b) $[\mathrm{Tl(III)}]_0=3.36\times10^{-3}$ M, $[\mathrm{V.B.}]_0=5.00\times10^{-5}$ M, $[\mathrm{H^+}]=0.20$ M.

$$\log(D_\infty-D) = \log(D_\infty-D_0)-\frac{k'}{2.303}t$$

where D_∞, D, and D_0 are the optical densities at 550 nm at equilibrium and $t=t$ and $t=0$, respectively. The observed rate constant k' was plotted against the concentration of Tl(III). Figure 2 shows that the value of k' is proportional to the initial concentration of Tl(III) under the conditions, $\mu=1.0$, $[\mathrm{H^+}]=0.2$ M, and 25°C, suggesting the rate equation to be

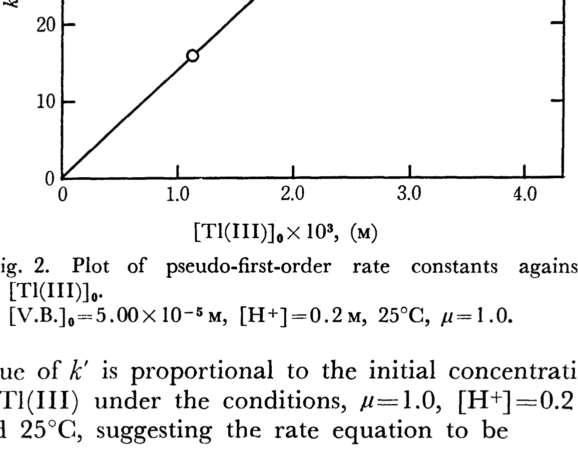

Fig. 2. Plot of pseudo-first-order rate constants against $[\mathrm{Tl(III)}]_0$.
$[\mathrm{V.B.}]_0=5.00\times10^{-5}$ M, $[\mathrm{H^+}]=0.2$ M, 25°C, $\mu=1.0$.

$$\mathrm{d}[(\mathrm{V.B.})_{\mathrm{ox}}]/\mathrm{d}t = k_a[\mathrm{Tl(III)}][(\mathrm{V.B.})]$$

The dependence of the second-order rate constant k_a on $[\mathrm{H^+}]$ and temperature was measured in a range $0.6>[\mathrm{H}]\geqq0.2$. The plots of k_a *versus* $1/[\mathrm{H}]$ at 15, 20, 25, 30, and 35°C fall on a series of straight lines with the intercepts near the origin as shown in Fig. 3.

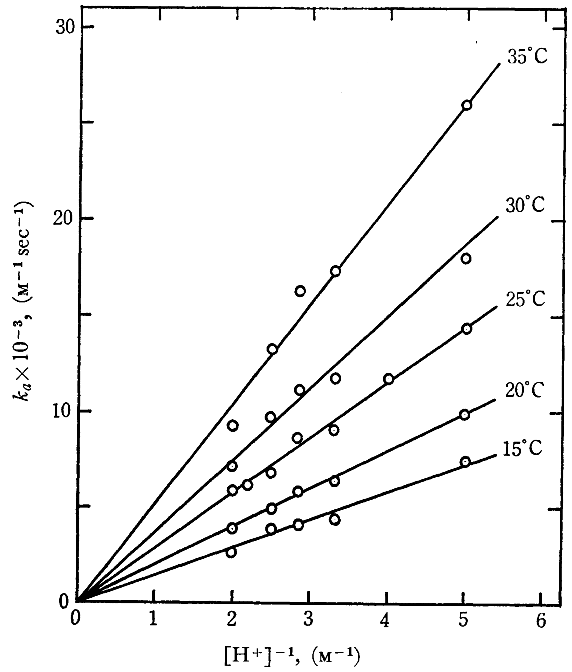

Fig. 3. Plot of second-order rate constants against $1/[\mathrm{H^+}]$.

Mechanism and Discussion

In the non-complementary reactions of Tl(III) with Fe(II), the existence of Tl(II) as an intermediate of the reaction is suggested.[7] The reactions of Tl(III) with V(III) and V(IV) also seem to proceed through the formation of Tl(II).[8] Oxidation of V.B. with Fe(III) and Ce(IV) proceeds through a semi-oxidized form of Variamine Blue as semiquinone to form $(\mathrm{V.B.})_{\mathrm{ox}}$.[4,5]

In the complementary reaction of Tl(III) with V.B., however, one mole of Tl(III) reacts with one mole of V.B., and the intermediates as Tl(II) and semiquinone of V.B. seem to be very unstable during the course of the reaction.

Assuming that all protolytic equilibria are rapidly established with respect to Tl(III) and V.B., the mechanism of the reaction is suggested to be as follows.

$$\mathrm{Tl^{3+}} \xrightleftharpoons{k_1} \mathrm{TlOH^{2+}} + \mathrm{H^+} \tag{1}$$

$$\mathrm{Tl^{3+}} + \mathrm{V.B.} \xrightarrow{k_1} \mathrm{Tl^+} + (\mathrm{V.B.})_{\mathrm{ox}} + 2\mathrm{H^+} \tag{2}$$

$$\mathrm{H^+} + \mathrm{TlOH^{2+}} + \mathrm{V.B.} \xrightarrow{k_2} \mathrm{Tl^+} + (\mathrm{V.B.})_{\mathrm{ox}} + 2\mathrm{H^+} + \mathrm{H_2O} \tag{3}$$

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[7] K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, **1953**, 3044.

[8] W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, **29**, 39 (1960).

The second-order rate constant k_a is thus rewritten as $k_a=(k_1[\mathrm{H}^+]+k_2K)/([\mathrm{H}^+]+K)$, where K is an acid dissociation constant of aqueous Tl(III), $K=7.94\times10^{-2}$.[7]

When K is neglected against $[\mathrm{H}^+]$, we have $k_a=k_1+k_2K/[\mathrm{H}^+]$. Values of $k_1\leq10^2\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ and $k_2=3.63\times10^4\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ at $\mu=1.0$ and 25°C are evaluated from the intercept and the slope of the straight line shown in Fig. 3.

In Fig. 4 the function $k_a([\mathrm{H}^+]+K)$ is plotted against $[\mathrm{H}^+]$, from which the value $k_2=3.56\times10^4\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ is obtained. The value k_2 agreed with the value obtained from the slope of the straight line in Fig. 3 within relative error of about 15%.

Activation energy for k_2, E_a, is also evaluated as $11\pm0.8\ \mathrm{kcal\cdot mol^{-1}}$ from the plot of k_2 against the reciprocal absolute temperature (Fig. 5). The activation energy of the reaction of Tl(III) with V.B. is about the same as that of Fe(III).[4] The apparent activation energy of the reaction of Ce(IV)[5] with V.B. is about zero, the same as observed in the reaction of Ce(IV) with hydroquinone.[9]

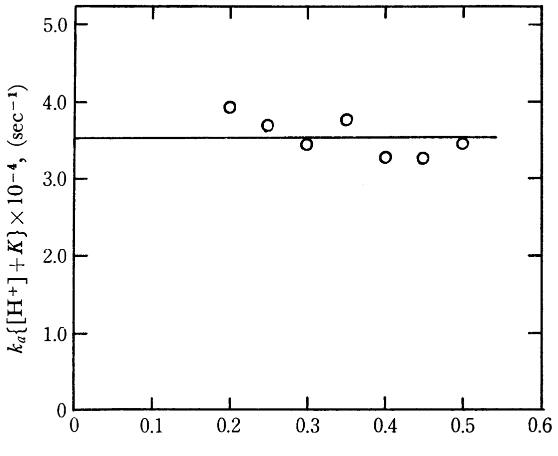

Fig. 4. Plot of $k_a\{[\mathrm{H}^+]+K\}$ against $[\mathrm{H}^+]$ at 25°C and $\mu=1.0$.

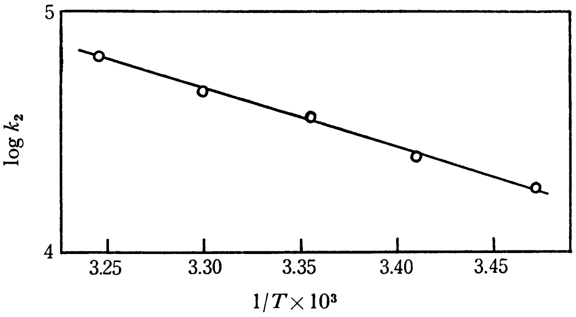

Fig. 5. Plot of second-order rate constant, k_2 against $1/T$.

The apparent rate constant of the reaction of Tl(III) with V.B. is about 10^2 times higher than that of Fe(III) with V.B. It may be ascribed to the difference in the redox potentials of metal ions, $E^0=1.28$ V for Tl(III)[6] and $E^0=0.71$ V for Fe(III).[10]

The values of the apparent second-order rate constants $(1-6)\times10^4\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$ as obtained for the complex formation of Tl(III) with Semi-xylenol Orange at $[\mathrm{H}^+]=0.2-0.5$ M and at 25°C[11] suggest the possibility of the complex formation between Tl(III) and V.B. as a rate-determining step for the redox reaction.

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9) C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.*, *A*, **1969**, 2575.

10) W. C. Schumb, M. S. Scherrill, and S. B. Sweetser, *J. Amer. Chem. Soc.*, **59**, 2360 (1937).

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