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

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The kinetics of the non-complementary reactions of Ce(IV) and Co(III) with Variamine Blue perchlorate were studied under nitrogen atmosphere in aqueous perchlorate media of ionic strength $\mu=2.0$ M. The imino-quinone form of Variamine Blue was spectrophotometrically followed at 550 nm by stopped-flow technique. The rate constants of the stepwise reaction, $M^{n+}+(\text{V.B.})\underset{k_r}{\overset{k_\alpha}{\rightleftharpoons}}M^{(n-1)+}+(\text{V.B.})_{\text{sox}}$, $M^{n+}+(\text{V.B.})_{\text{sox}}\xrightarrow{k_\beta}M^{(n-1)+}+(\text{V.B.})_{\text{ox}}+2H^+$ were evaluated at 25 °C to be $k_\alpha=1.7\times10^5$ and $k_\beta=2.4\times10^5$ M^{-1} sec^{-1} for Ce^{4+} and $k_\alpha=1.35\times10^4$ and $k_\beta=1.53\times10^4$ M^{-1} sec^{-1} at [H]=1.0 M for Co^{3+}. The rates of Ce^{4+} were not affected by [H]. The [H]-dependence of k_α and k_β for Co^{3+} gives the mechanism $\text{Co}^{3+}_{\text{aq}}+\text{B}\overset{k_1}{\rightleftharpoons}\text{product}$, $\text{CoOH}^{2+}_{\text{aq}}+\text{B}\overset{k_2}{\rightleftharpoons}\text{product}$, $\text{Co}^{3+}_{\text{aq}}\overset{K_h}{\rightleftharpoons}\text{CoOH}^{2+}_{\text{aq}}+\text{H}^+$, with $k_2\simeq10^7$ M^{-1} sec^{-1}, suggesting an outer-sphere mechanism for the electron transfer with CoOH^{2+}.

In preceding reports we discussed the reactions of Variamine Blue (abbr. V.B.) with iron(III) and thallium(III), in which the formation of the iminoquinone form of V.B. was treated as a two-setp reaction for iron(III)[1] and as a one-step reaction for thallium(III).[2]

The question has been raised whether the two-step scheme is essential in the non-complementary reaction of V.B. with other metal ions in high oxidation states such as cerium(IV) and cobalt(III). The redox reaction rates of cobalt(III) are generally slower than those predicted from its high redox potential.[3] In the present paper the reactions of V.B. with aquo ions, cerium(IV) and cobalt(III) are reported.

Experimental

Materials. Deionized water was distilled with an all-joint Pyrex apparatus. Purified sodium perchlorate[4] was used to maintain the ionic strength at 2.0 M.

Cerium(IV) and cobalt(III) perchlorates were prepared by electrolytic oxidation from cerium(III) and cobalt(II) perchlorates, respectively. The current was kept constant at *ca.* 100 mA. The concentration of cerium(IV) was estimated by indirect spectrophotometric measurements of iron(III) formed in the reaction with iron(II) perchlorate, with $[\varepsilon^{\text{Fe(III)}}_{260\,\text{nm}}=(2.88\pm0.33)\times10^3]$.[5] Cobalt(III) was also determined similarly at 260 nm or directly at 605 nm with $[\varepsilon^{\text{Co(III)}}_{605\,\text{nm}}=35.5\pm1]$.[6] The concentrations of cobalt(III) determined by the two spectrophotometric measurements agreed with each other within experimental error.

Cerium(III) perchlorate was prepared from cerium(III) carbonate and perchloric acid. Cobalt(II) perchlorate was prepared by heating cobalt(II) chloride with a slight excess of perchloric acid and made free from chloride by repeated recrystallization.

Commercial Variamine Blue hydrochloride often becomes a faint blue-color by air-oxidation or photochemical reaction. Dilute solution of Variamine Blue, for example, *ca.* 10^{-3} M, was colorless for 1—2 days but gradually turned bluish accompanied by precipitate formation.

Variamine Blue perchlorate was prepared from commercial V.B. hydrochloride.[7] 0.1 g V.B. and 0.04 g sodium dithionite were dissolved in hot water. The solution was shaken with 0.15 g active carbon and filtered. The filtrate was mixed with 5 ml saturated sodium perchlorate solution and cooled for *ca.* 1 hr in a refrigerator. The silky crystalline precipitate was filtered and washed with cold water and dried *in vacuo*. The elemental analyses of a commercial Variamine Blue hydrochloride and the prepared Variamine Blue perchlorate are given in Table 1.

TABLE 1. ELEMENTAL ANALYSES OF VARIAMINE BLUE SPECIMENS

Specimen		C(%)	H(%)	N(%)	Cl(%)
Commercial V.B. hydrochloride	Found	60.4	5.80	10.93	15.71
	Calcd for $C_{13}H_{15}ON_2Cl$	62.2	6.03	11.17	14.14
Prepared V.B. perchlorate	Found	49.35	4.56	8.70	
	Calcd for $C_{13}H_{15}O_5N_2Cl$	49.61	4.80	8.90	

Kinetics. Yanagimoto SPS-1 stopped-flow apparatus with a 4-jet mixing chamber and a 10 mm optical cell was used for kinetic measurements. The reservoirs of the stopped-flow apparatus were thermostated by circulating water from a thermostat. Purified nitrogen gas was passed through the reservoirs of the solutions in the course of measurements. The changes in absorbance were followed on the storage-screen of an oscilloscope.

The reactions of V.B. with cerium(IV) and cobalt(III) were studied in the hydrogen-ion concentration range 0.2—2.0 M since these ions are very unstable in low acid region. The reactions were followed at 550 nm, the absorption maximum of (V.B.)$_{\text{ox}}$, the iminoquinone form of V.B., in the presence of a large excess of metal ions.

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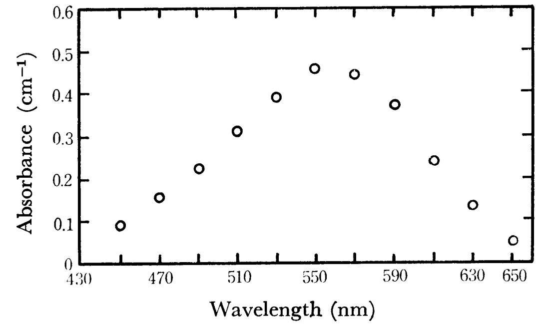


Fig. 1. Absorbance-wavelength plots at equilibrium of the initial fast reaction of V.B. with cobalt(III) measured by stopped-flow technique.
$[Co(III)]_0 = 2.6\times10^{-3}M$, $[V.B.]_0 = 2.5\times10^{-5}M$, $[H] = 0.5M$, $\mu = 2.0$ and 25 °C.

Results

The rapid initial increase in absorbance at 550 nm was followed by a comparatively slow decrease.8) Figure 1 shows the absorbance-wavelength plots at the end of the initial increase in absorbance measured by stopped-flow technique. No shift of absorption maximum at 550 nm was observed. The rates of increase in absorbances observed at any wavelengths in the visible range did not differ from each other.

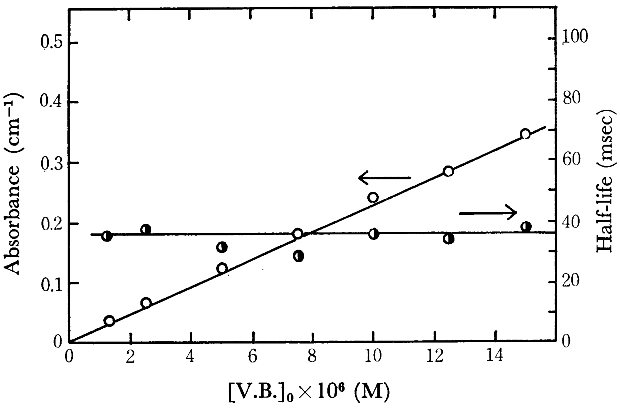


Fig. 2. Absorbance (550 nm) and half-life *vs.* initial concentration of V.B. plots in the reaction with cerium(IV).
$[Ce(IV)] = 2.14\times10^{-4}M$, $[H] = 0.5M$, $\mu = 2.0$ and 25 °C.

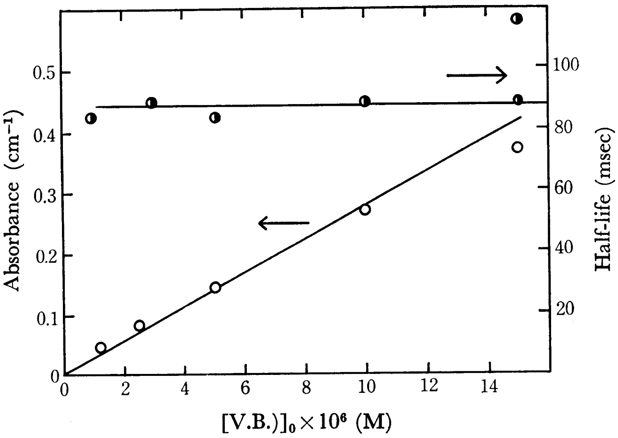


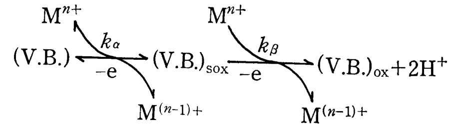
Fig. 3. Absorbance (550 nm) and half-life *vs.* initial concentration of V.B. plots in the reaction with cobalt(III).
$[Co(III)] = 1.33\times10^{-3}M$, $[H] = 1.0M$, $\mu = 2.0$ and 25 °C.

Chloride ions did not affect the rate of increase in absorbance at 550 nm.

As shown in Figs. 2 and 3, the absorbances at 550 nm increase linearly with the initial concentrations of V.B., the half-life of reaction being independent of $[V.B.]_0$ under the experimental conditions. The rate also does not obey the pseudo-first-order rate law even in the presence of a large excess of metal ions as observed in the reaction of V.B. with iron(III).

Discussion

The reactions of V.B. with Ce^{4+} and Co^{3+} are interpreted as a two-step mechanism:



$$(V.B.) \xrightarrow[-e]{k_\alpha} (V.B.)_{sox} \xrightarrow[-e]{k_\beta} (V.B.)_{ox} + 2H^+ \qquad (1)$$

The values of rate constants for Ce^{4+} are evaluated by the equation in the preceding paper1) to be $k_\alpha = 1.7\times10^5$ and $k_\beta = 2.4\times10^5\ M^{-1}\,sec^{-1}$ at 25 °C and $\mu = 2.0$. The rates were not affected by hydrogen-ion concentrations. This suggests that the reaction proceeds *via* inner-sphere mechanism.

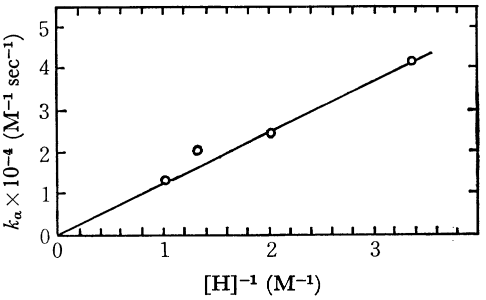


Fig. 4. Rate constant k_α *vs.* $[H]^{-1}$ plots in the reaction of V.B. with cobalt(III).

For the reaction of V.B. with Co^{3+}, the values of k_α and k_β are calculated to be 1.35×10^4 and 1.53×10^4 $M^{-1}\,sec^{-1}$, respectively, at 25 °C, $\mu = 2.0$ and $[H] = 1.0$. The rate constants k_α and k_β are inversely proportional to hydrogen-ion concentration (Fig. 4). The observed second-order rate constants at each step suggest the expression to be

$$k_{obs} = k_1 + k_2K_h/[H], \qquad (2)$$

corresponding to the reactions9)

$$Co_{aq}{}^{3+} + B \overset{k_1}{\rightleftharpoons} \text{product} \qquad (3)$$

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8) The slow decrease in absorbance suggests a subsequent redox reaction of the iminoquinone form of Variamine Blue with the oxidants, color fading being accelerated by the metal ions.

9) The reactions can proceed *via* either path of the two indistinguishable reactions;

$CoOH^{2+}$+protonated V.B.→product (6)

or

Co^{3+}+unprotonated V.B.→product. (7)

However, in the high acidity range the protonated form of Variamine Blue seems to be predominant.

$$\mathrm{CoOH_{aq}}^{2+} + \mathrm{B} \overset{k_2}{\rightleftharpoons} \text{product} \tag{4}$$

$$\mathrm{Co_{aq}}^{3+} \overset{K_h}{\rightleftharpoons} \mathrm{CoOH_{aq}}^{2+} + \mathrm{H}^+ \tag{5}$$

where B is the species of Variamine Blue in the reaction. The type of rate law is common to many reactions of Co^{3+}. It should be noted that (2) is a special case of the general rate law

$$k_{\mathrm{obs}} = (k_1 + k_2K_\mathrm{h}/[\mathrm{H}])/(1+K_\mathrm{h}/[\mathrm{H}]) \tag{8}$$

for $K_\mathrm{h} \ll [\mathrm{H}]$ as fulfilled under experimental conditions. From the slope of k_α *vs.* $[\mathrm{H}]^{-1}$-plot in Fig. 4, the value of k_2 was estimated to be in the order of magnitude of $10^7\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$ using the value $K_\mathrm{h} = (2\pm1)\times10^{-3}$ M.[10] The rapid reaction of cobalt(III) with V.B. is most likely to be of an outer-sphere mechanism as in the reactions of Co^{3+} with hydroquinone or iodide.[6] The concentrations of $(\mathrm{V.B.})_{\mathrm{ox}}$ calculated from the values of k_α and k_β are plotted as a function of time in Figs. 5 and 6. The concentrations agree with the ones observed in the course of reaction.

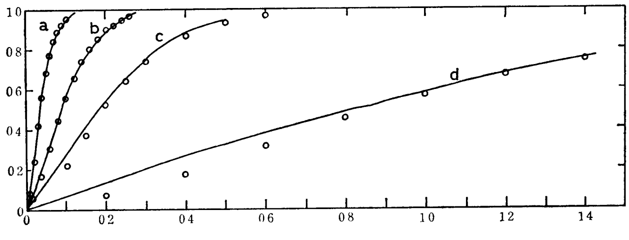

Fig. 5. Calculated concentration of $(\mathrm{V.B.})_{\mathrm{ox}}$ in the reaction with cerium(IV). Solid lines show the observed concentration of $(\mathrm{V.B.})_{\mathrm{ox}}$.
○ indicates the concentration of $(\mathrm{V.B.})_{\mathrm{ox}}$ calculated with the values $k_\alpha = 1.69\times10^5$ and $k_\beta = 2.36\times10^5\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$. $[\mathrm{V.B.}]_0 = 5.0\times10^{-6}$ M, [H] = 0.5 M, 25 °C and (a) $[\mathrm{Ce(IV)}]_0 = 8.54\times10^{-4}$, (b) 4.27×10^{-4}, (c) 2.14×10^{-4}, and (d) 8.54×10^{-5} M. $\gamma = [(\mathrm{V.B.})_{\mathrm{ox}}]/[(\mathrm{V.B.})]_0$.

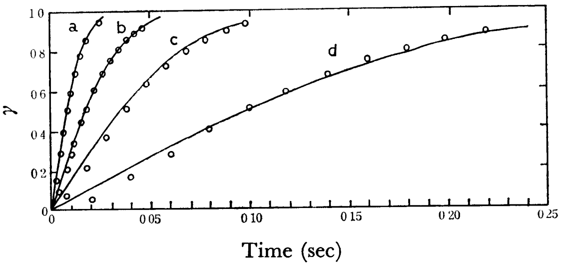

Fig. 6. Calculated concentration of $(\mathrm{V.B.})_{\mathrm{ox}}$ in the reaction with cobalt(III). Solid lines show the observed concentration of $(\mathrm{V.B.})_{\mathrm{ox}}$.
○ indicates the concentration of $(\mathrm{V.B.})_{\mathrm{ox}}$ calculated with the values $k_\alpha = 1.35\times10^4$ and $k_\beta = 1.53\times10^4\ \mathrm{M}^{-1}\mathrm{sec}^{-1}$. $[\mathrm{V.B.}]_0 = 5.0\times10^{-6}$ M, [H] = 1.0 M, 25 °C and (a) $[\mathrm{Co(III)}]_0 = 2.78\times10^{-3}$, (b) 1.11×10^{-3}, (c) 5.05×10^{-4}, and (d) 1.11×10^{-4} M. $\gamma = [(\mathrm{V.B.})_{\mathrm{ox}}]/[(\mathrm{V.B.})]_0$.

Increase in absorbance at 550 nm in the reactions with cerium(IV) and cobalt(III) was about 15—20% larger than that measured in the reaction of commercial Variamine Blue with iron(III). The difference in absorbance exceeds the experimental error ±10%.

The fact that the absorbance at 600—650 nm increases in the reaction of V.B. with iron(III)[11] in low concentrations suggests the possibility of the presence of some polymeric species of V.B.[12] which is rather stable against iron(III). The extra increase in absorbance at 550 nm observed in the reaction with cerium(IV) and cobalt(III) would be ascribed to a further reaction of these polymeric forms or to some subreactions of V.B. with the metal ions owing to their very high redox potentials.

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