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

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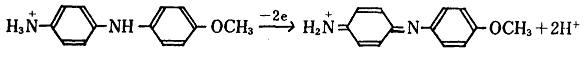
The kinetics of the non-complementary reaction of Fe(III) with Variamine Blue was studied under nitrogen atmosphere in perchlorate media of ionic strength $\mu = 1.0$ M. The iminoquinone form of Variamine Blue was followed spectrophotometrically by a stopped-flow technique. The rate constants of the stepwise reaction, $\mathrm{Fe(III)} + (\mathrm{V.B.}) \underset{k_\gamma}{\overset{k_\alpha}{\rightleftarrows}} \mathrm{Fe(II)} + (\mathrm{V.B.})_{\mathrm{sox}}$, $\mathrm{Fe(III)} + (\mathrm{V.B.})_{\mathrm{sox}} \xrightarrow{k_\beta} \mathrm{Fe(II)} + (\mathrm{V.B.})_{\mathrm{ox}} + 2\,\mathrm{H}^+$, were evaluated to be $k_\alpha = 3.28 \times 10^2$ and $k_\beta = 4.29 \times 10^2$ M^{-1} sec^{-1} at pH$\simeq$2.2 and 25°C. The apparent activation energy was 10 ± 1 kcal·mol^{-1} for both k_α and k_β. The formation rate was not seriously affected by hydrogen ion concentration (pH 2.2—0.77).

Variamine Blue (abbr. V.B.) is used as a redox indicator with many applications.[1] It has been reported that the colorless solution of V.B. undergoes two-electron oxidation to a violet-red iminoquinone (abbr. $(\mathrm{V.B.})_{\mathrm{ox}}$) by oxidizing agents such as Ce(IV), Fe(III) and I_2, as follows.[2,3]



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

Erdey *et al.*[4–6] suggest the following reaction scheme of V.B. with oxidizing agents.

$$(\mathrm{V.B.}) \rightleftarrows (\mathrm{V.B.})_{\mathrm{S}} \rightleftarrows 1/2(\mathrm{V.B.})_{\mathrm{D}} \rightleftarrows (\mathrm{V.B.})_{\mathrm{ox}},$$

where $(\mathrm{V.B.})_{\mathrm{S}}$ is a semiquinone form, and $(\mathrm{V.B.})_{\mathrm{D}}$ a dimeric one.

We are interested in the possibility of the existence of such intermediates during the course of the reaction, and the mechanisms of the reactions of V.B. with various oxidizing agents such as Co(III), Ce(IV), Tl(III), Fe(III), and I_2.

The present paper reports the reaction of V.B. with Fe(III) in 1.0 M perchlorate media. The reaction was spectrophotometrically followed by a stopped-flow technique at 550 nm corresponding to the λ_{max} of $(\mathrm{V.B.})_{\mathrm{ox}}$ under the condition $[\mathrm{Fe(III)}] \gg [\mathrm{V.B.}]$.

Experimental

Measurements. A Hitachi recording spectrophotometer model EPS-3T was used for spectral measurements. Variations of spectra with time were measured at wavelengths 350—700 nm with a Hitachi RPS-1 rapid scan apparatus. The rates of rapid reactions were measured using a Yanagimoto stopped-flow apparatus SPS-1. Purified nitrogen gas was passed through the reservoirs of the solutions during the course of measurements.

Materials. Deionized and distilled water was used. Iron(III) perchlorate was prepared by heating iron(III) chloride with a small excess of 60% perchloric acid under reduced pressure at about 60—65°C until no trace of chloride ion was detected. Sexihydrate thus obtained was dissolved in water. The concentration of Fe(III) was determined with EDTA titrimetrically.

Iron(II) perchlorate solution was prepared by electrolytic reduction of 1.07×10^{-2} M iron(III) perchlorate in 0.2 M perchloric acid under nitrogen atmosphere until negative tests were attained with thiocyanate. The solution was titrated with Ce(IV) using ferroin as an indicator and stored in a Pyrex bottle under nitrogen atmosphere.

Reagent grade sodium perchlorate and perchloric acid were used to maintain ionic strength at $\mu = 1.0$. Sodium perchlorate solution was standardized by titrating with sodium hydroxide the hydrogen ions eluted from a column of Dowex 50W-X8 in the hydrogen form.

Variamine Blue hydrochloride (Dojindo, Kumamoto) was dissolved in water free from oxygen by bubbling with nitrogen purified through an alkaline pyrogallol solution. Variamine Blue solution was freshly prepared before use.

Results

Spectra. The violet solution formed by mixing a large excess of Fe(III) and V.B. has a single absorption peak at 550 nm. With oxidizing agents such as Co(III), Ce(IV), Tl(III), and I_2 the solution also gave similar spectra with a single peak at 550 nm. We have thus ascribed the absorption peak at 550 nm to the iminoquinone form of the Variamine Blue, $(\mathrm{V.B.})_{\mathrm{ox}}$.

The absorbance in acidic media was gradually reduced over the visible range, while the absorption peak at 550 nm showed no shift.

Figure 1 shows the fast spectral change in the visible region just after the mixing of Variamine Blue with Fe(III) at pH$\simeq$2.2. Each scan requires 300 millisec. Fourteen scans were manually triggered for about 12 seconds just after mixing the Variamine Blue with Fe(III) in the optical cell from the sample syringes. In the course of the reaction, the peak at 550 nm showed no shift. Thus, under the experimental conditions, any species other than $(\mathrm{V.B.})_{\mathrm{ox}}$ do not interfere with the kinetic measurements of the $(\mathrm{V.B.})_{\mathrm{ox}}$ using the absorbance at 550 nm.

Reaction Stoichiometry. Erdey reported on the polarographic data suggesting the two-electron transfer reaction between Fe(III) and V.B.[1] We have

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[1] L. Erdey, *Chemist-Analyst*, **48**, 106 (1959).

[2] L. Erdey and A. Bodor, *Z. Analyt. Chem.*, **137**, 410 (1953); L. Erdey and F. Szabadvery, *ibid.*, **155**, 90 (1957); *Acta Chem. Acad. Sci. Hung.*, **13**, 335 (1958).

[3] E. Banyai and P. Zuman, *Collection Czech. Chem. Commun.*, **24**, 522, (1959).

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

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

[6] L. Erdey, T. Meisel, B. Mohos, and F. Tudos, *ibid.*, **14**, 1477 (1967).

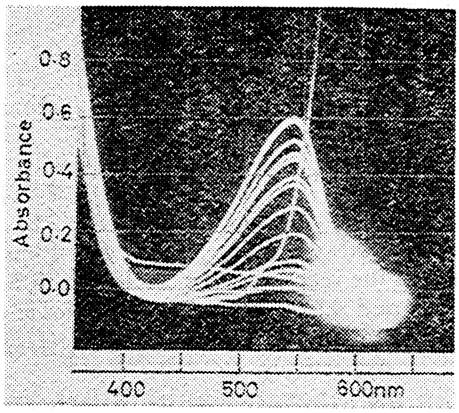

Fig. 1. Fast spectral change in the visible region. $[Fe(III)]_0 = 1.07\times10^{-3}$ M, $[V.B.]_0 = 5.00\times10^{-5}$ M, pH$\simeq$2.2, room temperature ($\simeq$20°C).

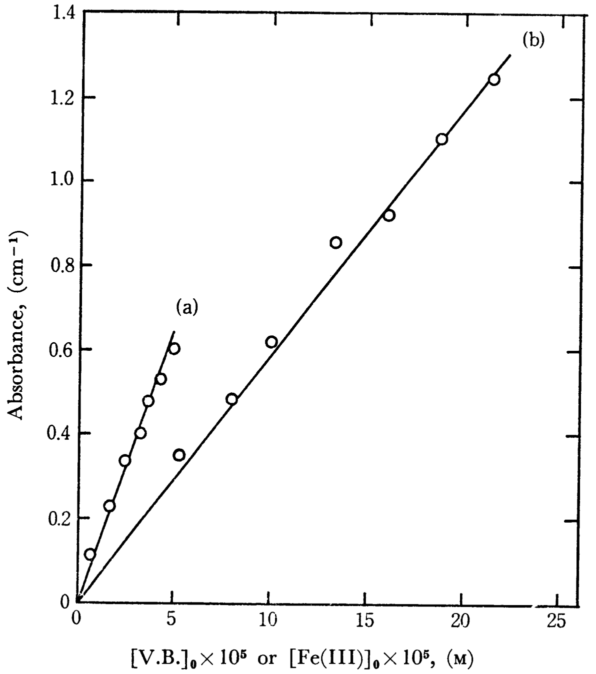

Fig. 2. Absorbance at 550 nm with varying concentration of Variamine Blue or Fe(III) at 25.0°C and $\mu = 1.0$ M.
(a) $[Fe(III)]_0 = 1.07\times10^{-3}$ M, $[V.B.]_0$=abscissa, pH=2.20,
(b) $[Fe(III)]_0$=abscissa, $[V.B.]_0 = 2.50\times10^{-4}$ M, pH=1.76.

determined the reaction stoichiometry spectrophotometrically at 550 nm by the stopped-flow technique assuming $(V.B.)_{ox}$ as the main product of the reaction even under the condition $[Fe(III)]_0 < [V.B.]_0$. Figure 2 suggests that the reaction of Variamine Blue with Fe(III) requires 2 moles of Fe(III) for 1 mole of Variamine Blue, *viz.*, a two-electron transfer reaction.

The molar absorption coefficient of $(V.B.)_{ox}$ in the protonated form at 550 nm was found to be 1.3×10^4 M^{-1} cm^{-1} in the acidic media at 25°C and ionic strength $\mu = 1.0$.

Kinetics. In the following two-electron transfer reaction

$$V.B. \xrightarrow{-2e} (V.B.)_{ox} + 2H^+$$

the rate of formation of $(V.B.)_{ox}$ in the presence of large excess of Fe(III) does not obey the first-order rate law. It is assumed that there are some intermediate oxidation states of Variamine Blue in the course of the reaction due to a non-complementary reaction between one mole of reductant, Variamine Blue, and two moles of oxidant, Fe(III).

With Tl(III) as an oxidizing agent under the same conditions, however, the formation rate of $(V.B.)_{ox}$ was expressed by a pseudo-first-order rate law.[7]

Hydrogen Ion Concentration Dependence. The formation rate of $(V.B.)_{ox}$ was not seriously influenced by the hydrogen ion concentration between pH 2.20 and 0.77. The final concentration of $(V.B.)_{ox}$ of this reaction was also not affected by the hydrogen ion concentration (Fig. 3).

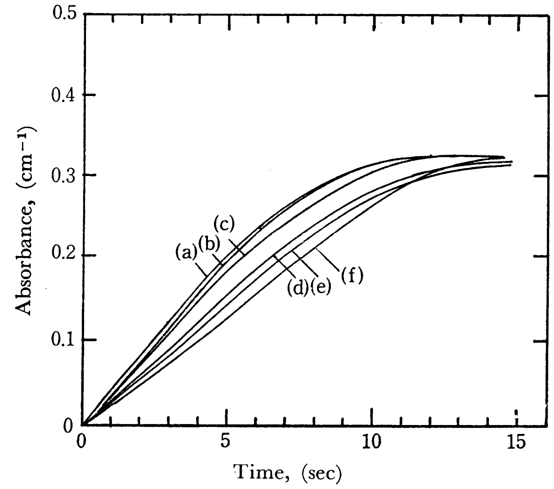

Fig. 3. Hydrogen ion concentration dependence. $[Fe(III)]_0 = 1.07\times10^{-3}$ M, $[V.B.]_0 = 2.50\times10^{-5}$ M, 25°C, $\mu = 1.0$: (a) pH=2.195, (b) pH=1.90, (c) pH=1.74, (d) pH=1.20, (e) pH=0.935, (f) pH=0.77.

The initial rate of the formation of $(V.B.)_{ox}$ at pH 2.2 was proportional to the initial concentration of Variamine Blue, the half-life being independent of the initial concentration (Fig. 4).

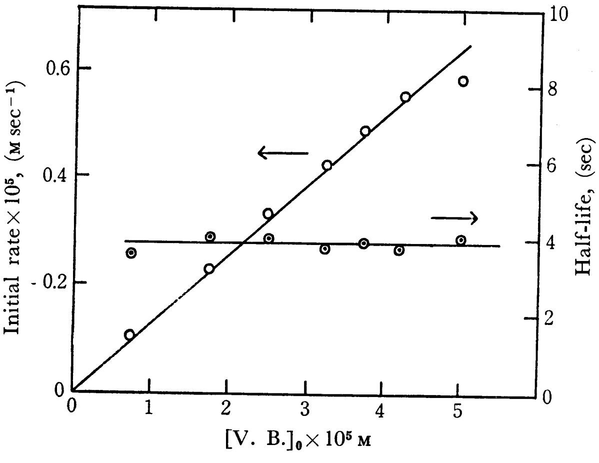

Fig. 4. Initial rate and half-life of the formation of $(V.B.)_{ox}$. $[Fe(III)]_0 = 1.07\times10^{-3}$ M, pH=2.20, $\mu = 1.0$, 25°C.

Effects of Fe(II). Figure 5 shows the effects of Fe(II) on the rate of formation of $(V.B.)_{ox}$. It is

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[7] T. Imamura and M. Fujimoto, This Bulletin, **45**, 442 (1972).

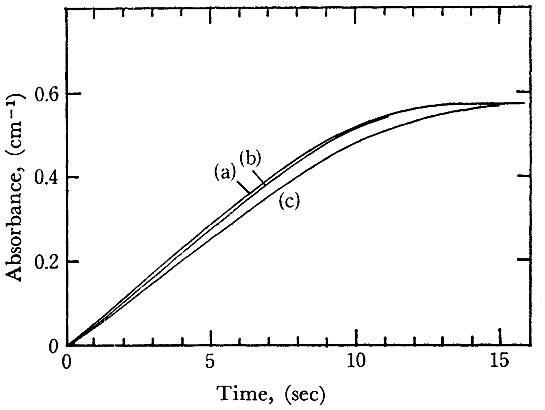


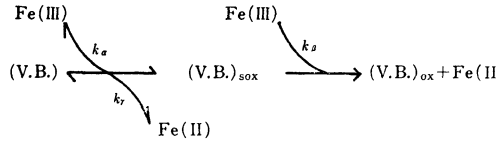
Fig. 5. Effects of Fe(II) on the formation of $(V.B.)_{ox}$ at 25°C and $\mu=1.0$ M.
$[Fe(III)]_0=1.07\times10^{-3}$ M, $[V.B.]_0=5.00\times10^{-5}$ M: (a) $[Fe(II)]_0=0$ M, (b) $[Fe(II)]_0=1.01\times10^{-3}$ M, (c) $[Fe(II)]_0=2.02\times10^{-3}$ M.

suggested that the formation rate of $(V.B.)_{ox}$ was not affected even for $[Fe(II)]_0 \geq [Fe(III)]_0 \gg [V.B.]_0$.

Discussion

Kinetics. The formation of $(V.B.)_{ox}$ in the reaction of Variamine Blue and Fe(III) does not obey the pseudo first-order rate law even with a large excess of Fe(III). It was ascribed to the fact that the intermediate of V.B. was to be considered and the reaction was a non-complementary one.

The overall reaction scheme would be as follows.



or

$$(V.B.) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (V.B.)_{sox} \xrightarrow{k_2} (V.B.)_{ox}+2H^+$$

where $(V.B.)_{sox}$ shows a semi-oxidized form of Variamine Blue as semiquinone.

With large excess of $[Fe(III)]_0$ and $[Fe(II)]_0$, the formation of $(V.B.)_{ox}$ is expressed as follows.

$$[(V.B.)_{ox}] = \frac{[(V.B.)]_0}{2q} e^{-pt}[-(p+q)e^{qt}+(p-q)e^{-qt}] + [(V.B.)]_0 \qquad (1)$$

where $p = \dfrac{k_1+k_{-1}+k_2}{2}$, $q = \dfrac{\sqrt{(k_1+k_{-1}+k_2)^2-4k_1k_2}}{2}$

and $k_1=k_\alpha[Fe(III)]_0$, $k_2=k_\beta[Fe(III)]_0$, $k_{-1}=k_\gamma[Fe(II)]_0$.

The effect of Fe(II) and hydrogen ion on the formation rate of $(V.B.)_{ox}$ was so small that k_{-1} in the equation was negligible.

Equation (1) is rewritten as follows:

$$[(V.B.)_{ox}] = [(V.B.)]_0\left[1 + \frac{1}{k_1-k_2}(k_2e^{-k_1t}-k_1e^{-k_2t})\right]. \qquad (2)$$

Let $\tau=k_1t$ and $\kappa=k_2/k_1$, then the equation becomes

$$r = \frac{[(V.B.)_{ox}]}{[(V.B.)]_0} = 1 + \frac{1}{1-\kappa}(\kappa e^{-\tau}-e^{-\kappa\tau}) \qquad (3)$$

where r is the ratio of $[(V.B.)_{ox}]$ to $[(V.B.)]_0$, that is, $r=0$ in the initial state of the reaction, and $r=1$ in the final state, when the reaction is complete. The value of the relative rate constant, $\kappa=k_2/k_1$, obtained by the time ratio method[8,9] was 1.5 at 25°C. The value of k_1 was calculated to be 0.525 sec⁻¹ with the observed reaction at $\mu=1.0$, $[Fe(III)]_0=1.067\times10^{-3}$, $[V.B.]_0=5.00\times10^{-5}$ M, 25°C, and pH=2.2.

The specific rates k_α and k_β for the first step and the second step of the reaction were calculated to be 3.28×10^2 M⁻¹ sec⁻¹ and 4.92×10^2 M⁻¹ sec⁻¹, at ionic strength 1.0, pH≃2.2 and 25°C from $k_1/[Fe(III)]_0$ and $k_2/[Fe(III)]_0$, respectively.

In Fig. 6 the concentrations of $(V.B.)_{ox}$ calculated from these values are plotted as a function of time. It is shown that the calculated concentrations of $(V.B.)_{ox}$ agree with the observed ones in the course of the reaction.

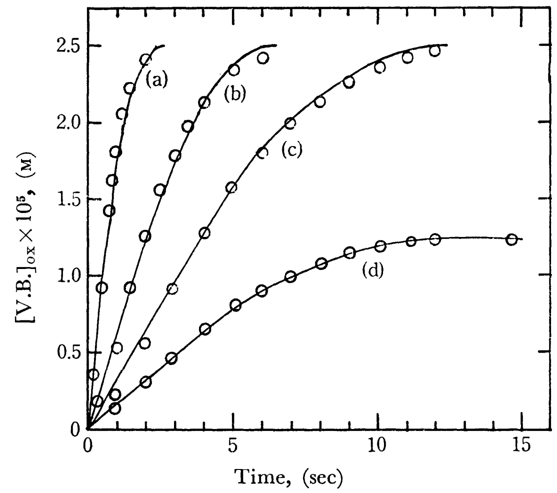


Fig. 6. Calculated concentration of $(V.B.)_{ox}$. Solid lines show the observed concentrations of $(V.B.)_{ox}$.
○ indicate the concentrations of $(V.B.)_{ox}$ calculated with the values, $k_\alpha=3.28\times10^2$ and $k_\beta=4.29\times10^2$ M⁻¹ sec⁻¹ at 25°C and $\mu=1.0$: (a) $[Fe(III)]_0=6.40\times10^{-3}$ M, $[V.B.]_0=2.50\times10^{-5}$ M, (b) $[Fe(III)]_0=2.13\times10^{-3}$ M, $[V.B.]_0=2.50\times10^{-5}$ M, (c) $[Fe(III)]_0=1.07\times10^{-3}$ M, $[V.B.]_0=2.50\times10^{-5}$ M, (d) $[Fe(III)]_0=1.07\times10^{-3}$ M, $[V.B.]_0=1.25\times10^{-5}$ M.

Temperature Dependence. Values calculated for (k_α, k_β) at 15, 20, 25, 30, and 35°C were found to be (197, 295), (272, 407), (328, 492), (487, 731), and (675, 1010 M⁻¹ sec⁻¹) at ionic strength $\mu=1.0$ and pH≃2.2 (see Fig. 7). Apparent energies of activation calculated from these values are 10±1 kcal·mol⁻¹ for both k_α and k_β.

Influence of Chloride Ion. Chloride ion was added to the solutions of the reactants in order to investigate the dependence of the reaction rate on the formation of iron(III) chloride complexes.

The formation rate of $(V.B.)_{ox}$ in the presence of large excess of chloride ion was higher than that with

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[8] A. Frost, R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, London (1961), p. 170.

[9] A. A. Frost and W. C. Schwement, *J. Amer. Chem. Soc.*, **74**, 1268 (1952); W. C. Schwemer and A. A. Frost, *ibid.*, **73**, 4541 (1951).

no chloride ion added (Fig. 8). However, the chloride ion affects the reaction rate only slightly.

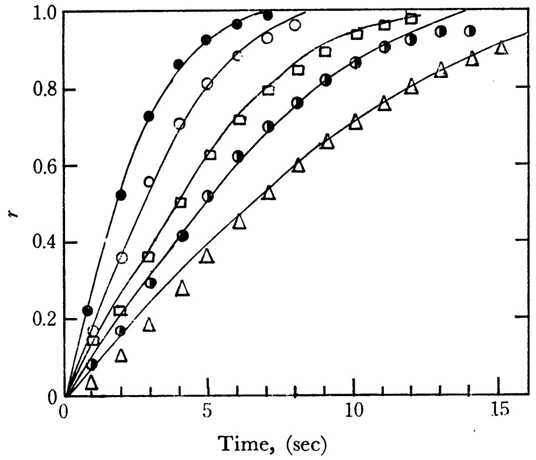


Fig. 7. Temperature dependence.
Solid lines show the observed concentrations of $(V.B.)_{ox}$. ●, ○, □, ◑, and △ indicate the calculated concentrations of $(V.B.)_{ox}$ at 35, 30, 25, 20, and 15°C, respectively: $[Fe(III)]_0=1.07\times10^{-3}$ M, $[V.B.]_0=2.5\times10^{-5}$ M, pH≃2.2, $\mu=1.0$ M.

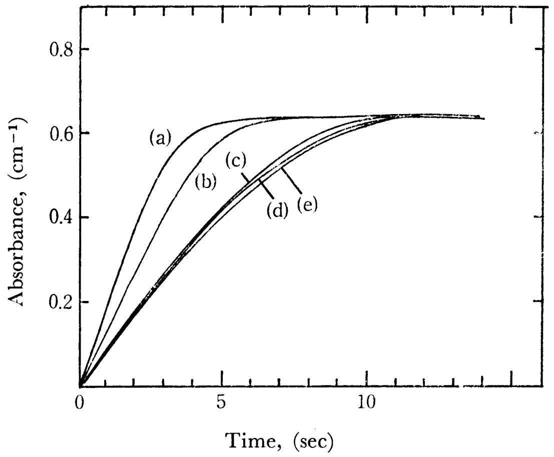
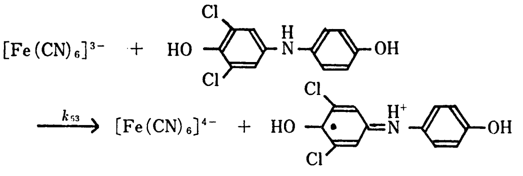


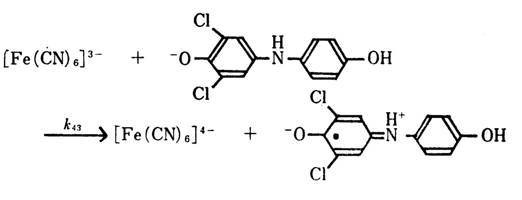
Fig. 8. Influence of chloride ion.
$[Fe(III)]_0=1.07\times10^{-3}$ M, $[V.B.]_0=5.00\times10^{-5}$ M, pH=2.2, 25°C, $\mu=1.0$ M, (a) $[NaCl]=1.0\times10^{-1}$ M, (b) 5.0×10^{-2} M, (c) 1.0×10^{-2} M, (d) 5.0×10^{-3} M, (e) 0 M.

In the reaction of hydroquinone and Fe(III),[10] it was reported that the reaction was either inner- or outer-sphere mechanism. In the reaction of V.B. and Fe(III), it is not clear whether the reaction proceeds by an inner-sphere mechanism or outer-sphere mechanism, as the kinetics was followed by Variamine Blue oxidized form.

That the formation rate of $(V.B.)_{ox}$ is not affected by acid concentration suggests the possibility of the inner-sphere mechanism for the reaction, since $FeOH^{2+}$ would influence the reaction rate for the outer-sphere mechanism. The rate constants as reported in the reaction of $[Fe(CN)_6]^{3-}$ with dichloroindophenol[11] that proceeds by outer-sphere mechanism or by hydrogen-atom transfer are much higher than those in the reaction of Fe(III) with V.B., *viz.*,



k_{53} = 1.2 (±0.3) × 10^4 $M^{-1}sec^{-1}$



k_{43} = 3.3 (±0.8) × 10^7 $M^{-1}sec^{-1}$

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[10] J. H. Baxendale, H. R. Hardy, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **47**, 963 (1951).

[11] H. Diebler. *Ber. Bunsenges. physik. Chem.*, **4**, 395 (1963).