BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3399—3400 (1975)

A Kinetic Study on the Complex Formation of Iron(III) with *o*-Cresolsulfonphthalein: A Quinoidal Complex*

Hiroaki NAKAYAMA** and Masatoshi FUJIMOTO
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received May 22, 1975)

Synopsis. The kinetics of the 1 : 1 complex formation of Fe(III) with *o*-Cresol Red is studied. The reaction scheme is quite different from that for the monophenolato complexes of Fe(III), and interpreted by the formation of a quinoidal complex.

A pH indicator *o*-Cresolsulfonphthalein, *o*-Cresol Red (abbr. CR), is a phenolic and quinoidal ligand with conjugated π-systems and hardly behaves as a chelating agent. It is interesting to note whether the given ligand forms a phenolato complex or a quinoidal complex with tervalent iron, and in what mechanism it reacts with the metal ion in comparison with monophenols.[1]

Experimental

Reagent grade *o*-Cresol Red (Wako), which gave only one spot on paper chromatogram,[2] was used. Other reagents and apparatus were described in detail in a previous report.[1]

Kinetic measurements were performed in aqueous perchlorate media of $\mu=0.1$ and at 25.0±0.2 °C. Analytical concentration of the ligand, C_{CR}, was kept at 1.00×10^{-4} M. C_{Fe} was changed from 3.62 to 51.2×10^{-3} M. Hydrogen-ion concentration [H] was calculated from the observed pH value without correction of the activity coefficients. Absorbance change was followed at 580 nm, where the absorption of the ligand was weak.

Results and Discussion

Owing to the strong absorption band of the ligand chromophore in the visible region[3] it was rather difficult to obtain the absorption spectra of the unstable complex of Fe(III) with Cresol Red except for the distinct increase in absorbance at 550—600 nm in the tail region of the absorption band of the ligand. Observed difference spectra are shown in Fig. 1.

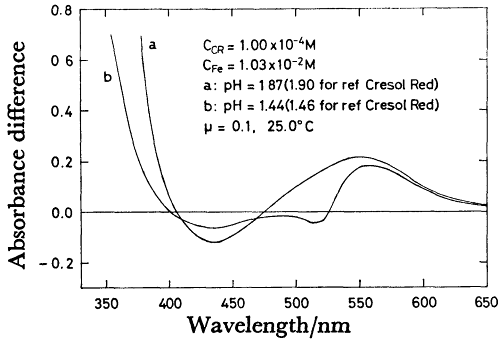


Fig. 1. Difference spectra between Fe(III)-Cresol Red and Cresol Red.

Formation constant of the complex could not be determined by the usual spectrophotometric method, since some slow side-reactions[5] involving the decomposition of the ligand ensued. At 580 nm, however, pseudo-first-order relaxation curves were obtained for the fast reaction process under the conditions of a large excess of Fe(III). Following discussions are concerned with this fast process regarded as the complex formation.

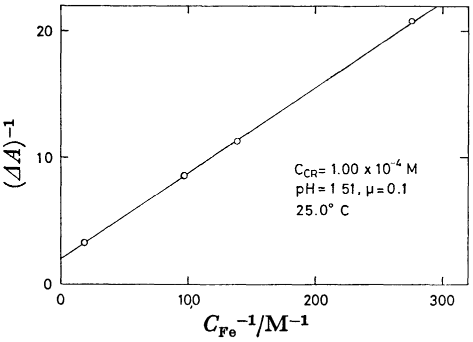
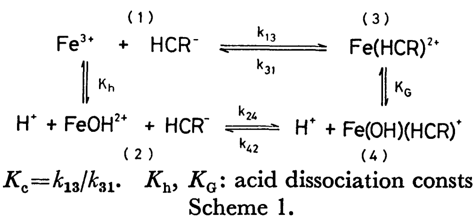


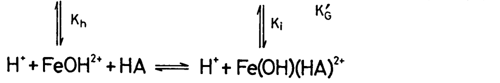
Fig. 2. Plot of $1/\Delta A$ at 580 nm *vs.* $1/C_{Fe}$.

Apparent rate constant k_{obsd} decreased with increasing [H]. It showed no significant change through more than ten-fold change in C_{Fe}. Absorbance changes, ΔA, on the complex formation were obtained from the difference in absorbance in the stopped-flow signals.[6] The values of ΔA showed no significant dependence on [H], but depends on C_{Fe} (see Fig. 2). Scheme 1 is proposed to account for these results. It clearly contrasts with the Scheme 2 for the complex formation between Fe(III) and monophenols (HA).[1]



$K_c=k_{13}/k_{31}$. K_h, K_G: acid dissociation consts.

Scheme 1.



Scheme 2.[1]

The predominant species after the fast complex formation reached equilibrium may be Fe^{3+}, HCR^-, and $Fe(HCR)^{2+}$. The following approximate equation is derived:

$$1/\Delta A = (1+1/C_{Fe}\cdot K_c)/\Delta\varepsilon\cdot C_{CR},$$

$$\Delta\varepsilon = \varepsilon_{FeHCR} - \varepsilon_{HCR},$$

where ε_{FeHCR} and ε_{HCR} denote the apparent molar ex-

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* Presented in part at the 1971 Winter Meeting in Hokkaido of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, Sapporo, February, 1971.

** Present address: Kagawa Nutrition College, Sakadomachi, Saitama.

tinction coefficient at 580 nm, and $K_C=[Fe(HCR)^{2+}]/[Fe^{3+}][HCR^-]$. Thus ΔA becomes independent of [H]. The linear plot of $(\Delta A)^{-1}$ *versus* C_{Fe}^{-1} as shown in Fig. 2 confirms that only 1 : 1 complex formation is concerned. From the slope and the intercept,[7] $\Delta\varepsilon=5.05\times10^3$ $M^{-1}\,cm^{-1}$ and $K_C=29.3\ M^{-1}$.

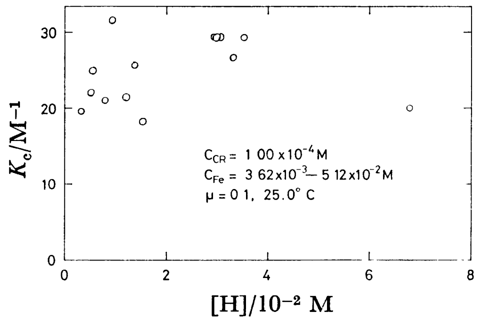


Fig. 3. Apparent stability constants K_c calculated from the absorbance change in the stopped-flow signals.

Spectrophotometric measurement gave $\varepsilon_{HCR}\leqq170$ so that ε_{FeHCR} is $5.2\times10^3\ M^{-1}cm^{-1}$. Assuming the one-step mechanism[8] and the equilibrium for very fast proton transfer during the relaxation process, we obtained

$$k_{obsd}\simeq k_fC_{Fe}+k_r,$$

$$k_f=([H]k_{13}+K_hk_{24})/([H]+K_h)$$

$$\text{and}\quad k_r=([H]k_{31}+K_Gk_{42})/([H]+K_G).$$

Here, k_{obsd} was independent of C_{Fe}, so that $k_{obsd}=k_r$. Considering the Coulombic factor in the dissociative process, we assumed that $[H]k_{31}\ll K_Gk_{42}$, giving the approximation

$$k_{obsd}^{-1}\simeq[H]/K_G\cdot k_{42}+1/k_{42}.$$

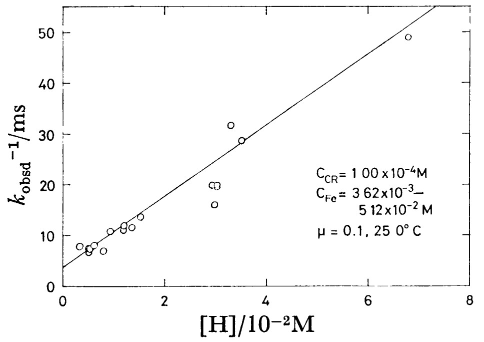
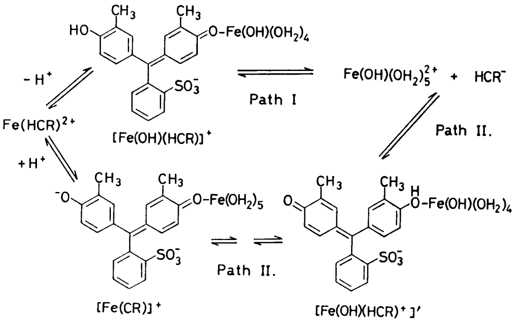


Fig. 4. Plot of $1/k_{obsd}$ *vs.* hydrogen-ion concentration.

A plot of k_{obsd}^{-1} *versus* [H] gave a straight line (Fig. 4). From the slope and the intercept, $k_{42}=270\ s^{-1}$ and $K_G=5.6\times10^{-3}$ M. An anionic ligand HCR^- thus may be a comparably weak donor as H_2O, for the K_G is in the same order of magnitude as K_h (4.1×10^{-3} M).[9] The rate constant k_{24} was calculated from the given data to be $k_{24}=(K_GK_C/K_h)\cdot k_{42}=1.1\times10^4\ M^{-1}s^{-1}$. This value is similar to the complex formation rate for Br^- and $Fe(OH)^{2+}$,[10] and significantly larger than that for monophenols and $Fe(OH)^{2+}$ ($1\times10^3\ M^{-1}s^{-1}$).[1,11] Thus, the experimental results are consistently interpreted on the basis of the Scheme 1, regarding k_{obsd} as k_r.

Though the following Path I is postulated in the Scheme 1, another intermediate $Fe(CR)^+$, which is isoprotonic to $Fe(OH)(HCR)^+$, can also be taken into consideration (Path II).



Going along the dissociative process, electronic configuration change of $Fe(CR)^+$ followed by intramolecular proton transfer results another isoprotonic intermediate $[Fe(OH)(HCR)^+]'$, which readily releases HCR^-. The observed K_G value is, however, only slightly larger than K_h and much larger than the acid dissociation constant of HCR^-. It is thus approved that the observed K_G concerns rather with the coordinated water than the phenolic hydroxyl group, though the coordination of quinoidal oxygen to Fe(III) may increase the dissociation of phenolic proton. Moreover, Path I is more favorable than Path II for the complex formation process when the charge densities on the two oxygen atoms of the ligand are considered.[12]

Temperature dependence of k_{obsd} was investigated at pH 1.81 and $C_{Fe}=1.65\times10^{-2}$ M. Apparent activation energy was found to be 68.81 kJ·mol⁻¹.

References

1) K. Nakamura, T. Tsuchida, A. Yamagishi, and M. Fujimoto, This Bulletin, **46**, 456 (1973).

2) Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, *ibid.*, **45**, 1417 (1972).

3) Molar extinction coefficient of HCR^- at 435 nm (ε_{max}) was reported to be $1.80\times10^4\ M^{-1}\ cm^{-1}$.[4]

4) M. Murakami, T. Yoshino, and S. Harasawa, *Talanta*, **14**, 1293 (1967).

5) At 435 nm the difference of the absorbance decreased monotonously, at 550 nm once increased and then decreased, and at 500 nm showed complicated feature.

6) Dead time of the stopped-flow apparatus was 1.7±0.2 ms. In the present experiment absorbance may be estimated too small in the case of lower [H], with $k_{obsd}^{-1}=7$ ms.

7) Using the intercept value 1.98, each set of C_{Fe} and ΔA derives the value of K_c, which is plotted against [H] (Fig. 3).

8) Two-step mechanism involving a very stable intermediate gives k_{obsd} which is independent of C_{metal} and is concerned with the formation process. See Eq. (2) in Ref. 2.

9) R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **77**, 1352 (1955).

10) P. Matthies and H. Wendt, *Z. Physik. Chem.*, *N. F.*, **30**, 137 (1961).

11) According to the authors' mind the pre-equilibrium constants[2] for the ion-pair formation, which depend mainly on the charges and the radii of the solvated species involved, may characterize the complex formation rate constants of $Fe(OH)^{2+}$ with various ligands.

12) The possibility of the direct protolytic transformation between species $[Fe(OH)(HCR)]^+$ (A) and $[Fe(OH)(HCR)^+]'$ (B) is assumed to be quite small, since the contribution of the intervening resonance forms involving an intermediate protonated quinoid cation to the proton transfer between A and B is lowered because of the propeller-like distortion of the π-systems in the benzene and the quinoidal ring.