1368 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 1368—1371 (1983) [Vol. 56, No. 5

Mono-complex Formation Kinetics of 2-Thenoyltrifluoroacetone with Nickel(II) and Copper(II) Ions in Aqueous Solution

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(Received July 29, 1982)

The mono-complex formation of 2-thenoyltrifluoroacetone (HTTA) with nickel(II) and copper(II) ions was studied in aqueous solution at 25.0 °C and an ionic strength of 0.20 mol dm^{-3} by means of a stopped-flow method. The rate-[H$^+$] profiles for the formation of these mono-complexes revealed that the rate-determining step of the complex formation interchanges depending upon hydrogen-ion concentration, as in the case of the Ni(II)–bpy complex. The rate constants of the mono-complex formation with TTA$^-$, k_f, and that with HTTA, k_{fh}, were determined from the rate-[H$^+$] profile in the region of the high hydrogen-ion concentration, where the pseudo-equilibrium of acid dissociation of the ligand was maintained during the complex formation; $k_f=(9.2\pm3.0)\times10^2$, $k_{fh}=(1.3\pm0.3)\times10^{-1}$ mol^{-1} dm^3 s^{-1} for the Ni(II)–TTA complex and $k_f=(2.0\pm1.2)\times10^3$, $k_{fh}=(5.0\pm0.9)\times10^{-1}$ mol^{-1} dm^3 s^{-1} for the Cu(II)–TTA complex. The deprotonation-rate constants of HTTA could be evaluated from the apparent rate constants of the complex formation in low hydrogen-ion concentration. The values thus obtained agreed well with that determined independently by a pH jump method.

Many complex formations with the ligands which have both acidic and basic conjugated forms in aqueous solution have been investigated kinetically for various metal ions, especially nickel(II) ion.[1–6] In those studies the concentration ratio at protolytic equilibrium (the pseudo-equilibrium of acid dissociation) of the ligand has been taken as constant throughout the course of the complex formation. However, the pseudo-equilibrium may fail in a complex formation with the ligand undergoing a slow proton-transfer reaction. Recently we found the first such example, so far as we know, in the mono-complex formation of Ni(II)–bpy at low hydrogen-ion concentration.[7] The kinetic measurements under such conditions lead to erroneous rate constants because of the failure of the pseudo-equilibrium of the ligand. It is, therefore, essential in the kinetic study of the complex formation with such a ligand to make sure the maintenance of the acid-base pseudo-equilibrium of the ligand during the complex formation.

β-Diketones undergo a slow proton-transfer reaction[8–11] and also form the complexes with various metal ions.[10–16] Hence, further results are expected to prove that the proton-transfer process of β-diketones is the rate-determining step of the complex formation in some experimental conditions, especially in low hydrogen-ion concentration. In this study we investigated fully the rate-[H$^+$] profiles for the complex formation of nickel(II) and copper(II) ions with 2-thenoyltrifluoroacetone (HTTA) as an available β-diketone. The results showed that the deprotonation process of HTTA could be the rate-determining step of these complex formations under some given conditions.

This phenomenon provided a new method of the estimation of the deprotonation-rate constant of the ligand, by measuring the complex-formation rate.

Experimental

Materials and Sample Solutions. Nickel(II) and copper(II) sulfates were purchased from Wako Pure Chemical Industries and were purified by recrystalization from water before use. 2-Thenoyltrifluoroacetone (Dotite TTA) was purchased from Dojindo Laboratories and used without further purification. All other chemicals were of guaranteed reagent grade and used without further purification, unless otherwise noted.

The stock solution of nickel(II) or copper(II) ion was prepared by dissolving the corresponding sulfate in water acidified faintly with sulfuric acid, and the metal-ion concentration of the solution was determined by edta titration. The stock solution of HTTA was prepared by dissolving a desired amount of it in water. Deionized-distilled water was used for all preparations of the solution.

These stock solutions were appropriately diluted for kinetic measurements. The ionic strength of the resulting solution was adjusted to 0.20 mol dm^{-3} with sodium sulfate, and the sample solution contained no buffer.

For the measurement of the acid dissociation constant of HTTA, the ionic strength of the sample solutions was adjusted to 0.20 mol dm^{-3} with sodium chloride, and the pH of them was adjusted with the following buffers: acetate buffer at pH 4—6.5, phosphate buffer at pH 5.5—8. Each buffer was added at the concentration smaller than 0.05 mol dm^{-3}.

Kinetic Measurement of Proton Transfer. The rates of proton-transfer of the ligand were measured at 25.0 °C by the pH jump technique[17,18] according to the following procedure. The solution of HTTA in dilute sulfuric acid (pH 4—4.5) was rapidly mixed with a dilute sodium hydroxide solution at the same ionic strength in a Union RA-1300 stopped-flow spectrophotometer. The increase of TTA$^-$ concentration caused by pH jumping was followed as the increase in absorbance at 339 nm, the wavelength of maximum absorption of TTA$^-$. The apparent first-order rate constant for the deprotonation of HTTA at reaction time zero, k_{dpo}, was evaluated according to a previous method.[17,18] Each k_{dpo} value was obtained from fifteen kinetic runs.

Kinetic Measurement of Complex Formation. The complex formation was followed at 349 nm and 25.0 °C by means of a Union RA-1300 stopped-flow spectrophotometer, as reported previously.[7] The concentration of metal ion was always kept in large excess (400 or more times that of HTTA) in order to ensure only the mono-complex formation. The complex formation obeyed first-order kinetics within the 50% conversion. Each pseudo first-order rate constant, k_{obsd}, was obtained from ten kinetic runs.

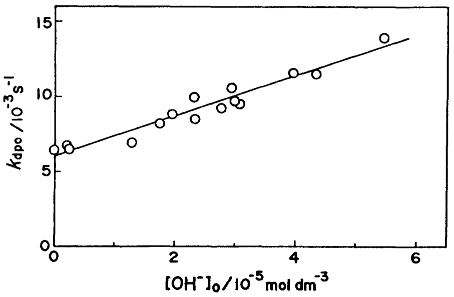

Fig. 1. Plot of k_{dpo} against $[OH^-]_0$ for 2-thenoyltrifluoroacetone.
The solid line is the linear regression line for the plot.

Measurement of Acid Dissociation Constant. Absorption spectra of HTTA in aqueous solution were recorded on a Hitachi 323 recording spectrophotometer. The acid dissociation constant, K_a, of HTTA was measured by the spectrophotometric titration at 339 nm and 25.0 °C by means of a JASCO Uvidec-2 digital spectrophotometer equipped with a thermostated cell holder.

Results and Discussion

Deprotonation Reaction of HTTA. The absorbance of HTTA at 339 nm remarkably increases with increasing pH. A spectrophotometric titration over the pH range of 2 to 8 at this wavelength yielded the number of transferred protons of 1.03±0.01 and the pK_a value of 6.35±0.01, indicating that the spectral change should be ascribed to the acid dissociation of HTTA to TTA$^-$. This pK_a value is in good agreement with the literature value.[19] The same spectral change was also observed on the heels of a pH jump in the stopped-flow apparatus by a rapid scanning technique. Consequently the apparent first-order rate constants for the deprotonation reaction of HTTA, k_{dpo}, can be determined by the stopped-flow pH jump technique.

The proton transfer of HTTA presumably proceeds through the following two simultaneous reaction paths, as in the cases of phen, pyridine and its derivatives:[17,18]

$$\mathrm{HTTA} \underset{k_p}{\overset{k_{dp}}{\rightleftharpoons}} \mathrm{TTA^-} + \mathrm{H^+}, \tag{1}$$

$$\mathrm{HTTA} + \mathrm{OH^-} \underset{k_{H_2O}}{\overset{k_{OH}}{\rightleftharpoons}} \mathrm{TTA^-} + \mathrm{H_2O}, \tag{2}$$

where k_{dp}, k_p, k_{OH}, and k_{H_2O} are the rate constants in Reactions 1 and 2, respectively. Since the decreasing rate of HTTA concentration is expressed by

$$\begin{aligned} -\mathrm{d[HTTA]}/\mathrm{d}t &= (k_{dp}+k_{OH}[\mathrm{OH^-}])[\mathrm{HTTA}] \\ &\quad - (k_p+k_{H_2O}[\mathrm{H_2O}]/[\mathrm{H^+}])[\mathrm{TTA^-}][\mathrm{H^+}], \end{aligned} \tag{3}$$

at reaction time zero k_{dpo} can be expressed as a function of hydroxide-ion concentration at reaction time zero, $[OH^-]_0$;

$$k_{dpo} = k_{dp} + k_{OH}[\mathrm{OH^-}]_0. \tag{4}$$

The plot of k_{dpo} against $[OH^-]_0$ gave a straight line, as shown in Fig. 1. The values of k_{dp} and k_{OH} given in Table 1 were obtained from the intercept and the slope of the linear regression line in Fig. 1. The k_{dp} value was in good agreement with the rate constant of the enolation of keto tautomer of HTTA, $(8.4\pm0.3)\times10^{-3}$ s^{-1} obtained by the bromination method.[11] According to Jaffe and co-workers,[11] the concentration ratio of enol to keto tautomer in aqueous HTTA solution is 4.4×10^{-3} and the rate-determining step of the enolation is the deprotonation of keto tautomer. Therefore, k_{dp} in this study corresponds to the enolation-rate constant of keto form. This k_{dp} value is also comparable to that of other β-diketones.[20]

TABLE 1. RATE CONSTANTS FOR THE MONO-COMPLEX FORMATION AND THE PROTON-TRANSFER REACTION OF 2-THENOYLTRIFLUOROACETONE AT 25.0 °C AND 0.20 mol dm^{-3} IONIC STRENGTH

Rate constant	Ni-TTA	Cu-TTA
k_f/mol^{-1} dm^3 s^{-1}	$(9.2\pm3.0)\times10^2$	$(2.0\pm1.2)\times10^3$
k_{fh}/mol^{-1} dm^3 s^{-1}	$(1.3\pm0.3)\times10^{-1}$	$(5.0\pm0.9)\times10^{-1}$
k_{dp}/s^{-1}	$(7.2\pm1.1)\times10^{-3}$ a) $(6.0\pm0.6)\times10^{-3}$ b)	$(2.8\pm1.0)\times10^{-3}$ a)
k_{OH}/mol^{-1} dm^3 s^{-1}	$(1.3\pm0.2)\times10^2$ b)	

a) The values were obtained from the data of the complex formation rates. b) The value was obtained by the pH jump method.

Complex Formation Kinetics. The mono-complex formation of nickel(II) and copper(II) ions with HTTA is thought to proceed through the following two concurrent reaction paths:

$$\mathrm{M^{2+}} + \mathrm{TTA^-} \xrightarrow{k_f} \mathrm{MTTA^+}, \tag{5}$$

$$\mathrm{M^{2+}} + \mathrm{HTTA} \xrightarrow{k_{fh}} \mathrm{MTTA^+} + \mathrm{H^+}, \tag{6}$$

where k_f and k_{fh} are the second-order rate constants in Reactions 5 and 6, respectively. As long as the pseudo-equilibrium of the acid dissociation of HTTA holds throughout the complex formation, the rate of the complex formation is expressed by

$$\begin{aligned} \mathrm{d[MTTA^+]}/\mathrm{d}t &= (k_f[\mathrm{TTA^-}] + k_{fh}[\mathrm{HTTA}])[\mathrm{M^{2+}}] \\ &= \{(k_f+k_{fh}[\mathrm{H^+}]/K_a)/(1+[\mathrm{H^+}]/K_a)\} \\ &\quad \times[\mathrm{M^{2+}}][\mathrm{TTA'}], \end{aligned} \tag{7}$$

where [TTA′] denotes the analytical concentration of HTTA, in the early stage of the complex formation, in which the dissociation of the complex can be ignored. Therefore, the pseudo first-order rate constant, k_{obsd}, is correlated with k_f and k_{fh} by

$$k_{obsd}(1+[\mathrm{H^+}]/K_a)/[\mathrm{M^{2+}}] = k_f + k_{fh}[\mathrm{H^+}]/K_a. \tag{8}$$

Figure 2 shows the plots of k_{obsd} values against [H$^+$] according to Eq. 8 for the formation of the mono-complexes of Ni(II)- and Cu(II)-TTA. In both cases, the plots in the [H$^+$]-region higher than around 2×10^{-3} mol dm^{-3} yield linear relationships, while the data at lower [H$^+$] deviate below the straight lines extrapolated from the high [H$^+$]-region. This suggests that the pseudo-equilibrium of the acid dissociation of HTTA holds only in the high [H$^+$]-region, on the analogy of the mono-complex formation of Ni(II)-bpy.[7] Hence, the k_f and k_{fh} values given in Table 1 were obtained from the intercept and the slope of the straight lines in the high [H$^+$]-region where the pseudo-equilibrium seems to hold.

In order to verify the establishment of the pseudo-

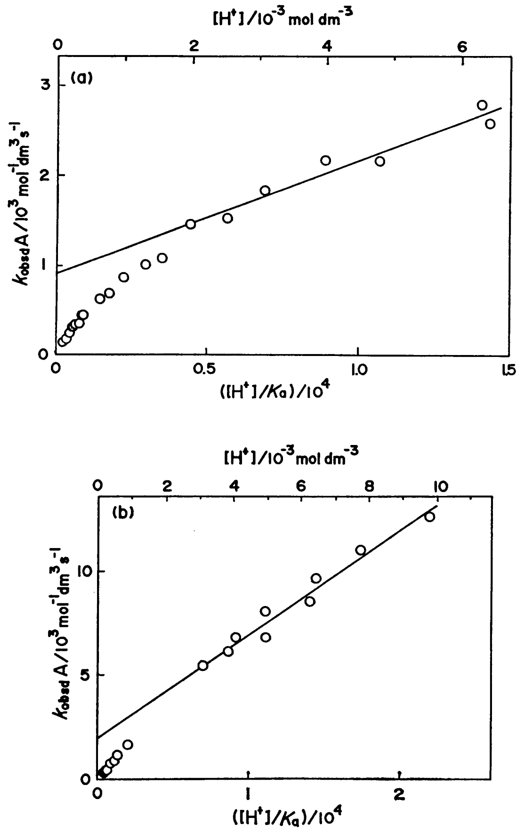

Fig. 2. Plots of $k_{obsd}A$ against $[H^+]/K_a$. $A=(1+[H^+]/K_a)/[M^{2+}]$. (a) Ni(II)–TTA complex; $[Ni^{2+}]=2.00\times10^{-2}$ mol dm^{-3}, $[HTTA]=5.00\times10^{-5}$ mol dm^{-3}. (b) Cu(II)–TTA complex; $[Cu^{2+}]=1.02\times10^{-2}$ mol dm^{-3}, $[HTTA]=1.04\times10^{-5}$ mol dm^{-3}.

equilibrium of the acid dissociation of HTTA in the $[H^+]$-region where the k_f and k_{fh} values evaluated, the initial rates of the processes concerned were compared with each other. Figure 3 illustrates the initial rates for the Ni(II)–TTA system as a function of pH, where (rate f), (rate fh), (rate dp), and (rate p) are the rates of the complex formation in Reactions 5 and 6, and those of the deprotonation of HTTA and the protonation of TTA⁻ through Reaction 1, respectively. The subscript 0 denotes the values at reaction time zero. The deprotonation rate in Reaction 2 was ignored because of its negligible contribution to (rate dp) in acidic solution. These initial rates were calculated using the k_f, k_{fh}, and k_{dp} values obtained and the initial concentrations of the species participating in the reactions. As the equilibrium of the acid dissociation of HTTA holds at reaction time zero, $(\text{rate p})_0$ must be equal to $(\text{rate dp})_0$. As can be seen in Fig. 3, with the Ni(II)–TTA system the pseudo-equilibrium mentioned above proved to hold over the pH range where the k_f and k_{fh} values were evaluated, because at pH below 3 $(\text{rate dp})_0$ is larger than $(\text{rate f})_0$, and $(\text{rate p})_0$ is larger than $(\text{rate fh})_0$. With Cu(II)–TTA system, the establishment of the pseudo-equilibrium was also confirmed in the high $[H^+]$-region.

In order to establish the mechanism assumed in this study, the k_{dp} value of HTTA was evaluated from the data of the complex formation in the pH range where the rate was controlled by the deprotonation rate, and was compared to that obtained by the pH jump method. At the pH beyond 3, $(\text{rate dp})_0$ is less than $(\text{rate f})_0$ and comparable to $(\text{rate fh})_0$, as shown in Fig. 3. Therefore, the rate of the complex formation should be controlled by (rate dp) and (rate fh), after having been stationary with respect to [TTA⁻]. Under such conditions, the rate of the complex formation is expressed by

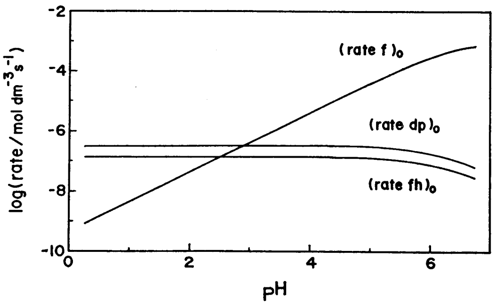

Fig. 3. Relationship between initial rates and pH for the Ni(II)–TTA complex at 25.0 °C.

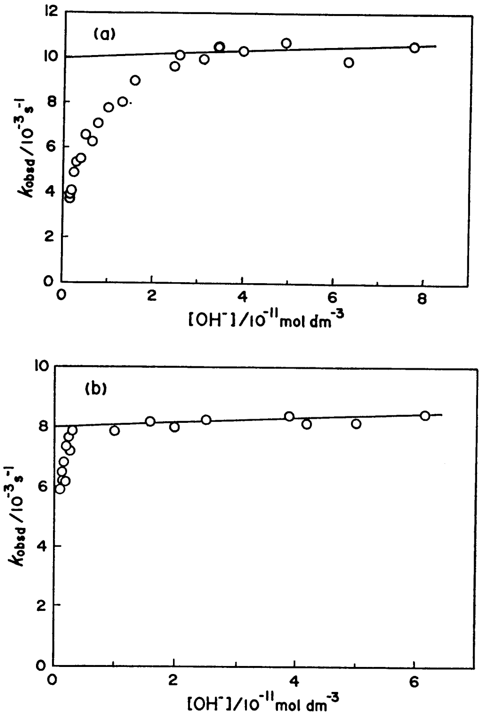

Fig. 4. Plots of k_{obsd} against [OH⁻] for (a) Ni(II)–TTA and (b) Cu(II)–TTA complex.
Data were taken from Fig. 2.

$$d[MTTA^+]/dt = (k_{dp}+k_{OH}[OH^-]+k_{fh}[M^{2+}])[HTTA]. \qquad (9)$$

Accordingly,

$$k_{obsd} = k_{OH}[OH^-] + (k_{dp}+k_{fh}[M^{2+}]). \qquad (10)$$

Figure 4 shows the plots of k_{obsd} against [OH⁻] for the Ni(II)- and Cu(II)–TTA systems. The k_{obsd} values were evaluated from the absorbance change after the reaction became stationary. The k_{dp} values of HTTA in both systems were evaluated from the intercepts of these straight lines at relatively high [OH$^-$], using [M^{2+}] and k_{fh} values. Although the k_{OH} values were also evaluated from their slopes, no significant value was obtained because of the experimental error due to the extremely low hydroxide-ion concentration. The k_{dp} values are summarized in Table 1 together with the k_{dp} and k_{OH} values obtained by the pH jump method. The average value of k_{dp} obtained by the complex-formation experiments is in excellent agreement with that by the pH jump method. This fact strongly supports the conclusion that the proton-transfer reaction of the ligand can be the rate-determining step of the complex formation depending upon the hydrogen-ion concentration. Additionally, it should be noted that the k_{dp} value of the ligand could be evaluated from the data of the complex-formation kinetics.

Jaffe and co-workers studied the same systems on the assumption that keto form of HTTA does not react directly with metal ion.[11] According to their description, the present k_f corresponds to the complex-formation rate constant of enolate ion, k_{fh} to the complex-formation rate constant of enol tautomer or to the enolation-rate constant of keto tautomer, and k_{dp} to the enolation-rate constant. Our values of k_f and k_{fh} for the Ni(II)–TTA system differ from their corresponding values, 1.0×10^4 and 2.3 mol^{-1} dm^3 s^{-1}, respectively. For the Cu(II)–TTA system, the k_f value in this study is remarkably different from their's, $\geqq 3\times10^6$ mol^{-1} dm^3 s^{-1}. Since k_{fh} is the overall rate constant, irrespective of keto or enol form of HTTA, the small value of k_{fh} may be partly ascribed to the unreactivity of the keto form. M. R. Jaffe *et al.* assumed that the equilibrium between enol tautomer and enolate ion of HTTA is always maintained throughout the reaction. This assumption seems to be reasonable only just after the reaction occurred. However, the direct deprotonation and/or the deprotonation *via* enol from keto form of HTTA become significant during the progress of the reaction. Comparing the initial rates of the complex-formation processes and the proton-transfer process, (rate f) and/or (rate fh) are larger than (rate dp) in both Ni(II)- and Cu(II)–TTA systems under their experimental conditions. This suggests that the pseudo-equilibrium for the acid dissociation or the enolation of the ligand failed in the course of the complex formation. This presumably explains the discrepancies of the rate constants between Jaffe's and our study. The fact that the rate constants in this study are not characteristic for metal ions should support the conclusion that in the complex formation forming the six-membered chelate ring the closure of the chelate ring is the rate-determining step.[15]

In conclusion, we obtained further evidence that the proton-transfer reaction of the ligand became the rate-determining step of the complex formation depending on the hydrogen-ion concentration, as in the case of the Ni(II)–bpy complex. Under such conditions, the deprotonation-rate constant of the ligand could be determined from the complex-formation rate, as well as by the pH jump method.

The authors wish to thank Professor S. Kida and Professor T. Taketatsu of Kyushu University for valuable discussions and encouragement. The present work was partially supported by a grant from the Central Research Institute of Fukuoka University.

References

1) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 107 (1970).

2) D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970).

3) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

4) J. E. Letter, Jr., and R. B. Jordan, *Inorg. Chem.*, **10**, 2692 (1971).

5) J. C. Cassatt, W. A. Johnson, L. M. Smith, and R. G. Wilkins, *J. Am. Chem. Soc.*, **94**, 8399 (1972).

6) R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, *Inorg. Chem.*, **13**, 1282 (1974).

7) I. Ando, S. Nishijima, K. Ujimoto, and H. Kurihara, *Bull. Chem. Soc. Jpn.*, **55**, 2881 (1982).

8) F. Hibbert, "Comprehensive Chemical Kinetics," ed by C. H. Bamford and C. H. F. Tipper, Elsevier, Amsterdam (1977), Vol. 8, Chap. 2.

9) J. C. Reid and M. Calbin, *J. Am. Chem. Soc.*, **72**, 2948 (1950).

10) R. W. Taft, Jr., and E. H. Cook, *J. Am. Chem. Soc.*, **81**, 46 (1959).

11) M. R. Jaffe, P. Fay, M. Cefola, and N. Sutin, *J. Am. Chem. Soc.*, **93**, 2878 (1971).

12) A. V. Celiano, M. Cefola, and P. S. Gentile, *J. Phys. Chem.*, **65**, 2194 (1961).

13) A. V. Celiano, M. Cefola, and P. S. Gentile, *J. Phys. Chem.*, **66**, 1132 (1962).

14) W. K. Ong and R. H. Prince, *J. Chem. Soc., A*, **1966**, 458.

15) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).

16) A. Adin and L. Newman, *J. Inorg. Nucl. Chem.*, **32**, 3321 (1970).

17) I. Ando, J. Saito, K. Ujimoto, and H. Kurihara, *Fukuoka Univ. Sci. Reports*, **11**, 47 (1981).

18) I. Ando, K. Ujimoto, and H. Kurihara, *Bull. Chem. Scc. Jpn.*, **55**, 713 (1982).

19) V. M. Peshkova and P. Ang, *Russ. J. Inorg. Chem.*, **7**, 765 (1962).

20) J. R. Jones, *Prog. Phys. Org. Chem.*, **9**, 241 (1972).