Kinetics and Mechanisms of the Reactions of Nickel(II) with 4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dione in Aqueous Solution

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The kinetics and mechanisms of the reactions of nickel(II) with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) to form the 1 : 1 complex have been studied in aqueous solution at 25 °C and $I = 0.2$ mol dm^{-3} adjusted using sodium sulphate. The equilibrium constants for reaction of Htftbd with proton and Ni^{2+} have also been determined. The kinetic data are consistent with a mechanism in which the metal ion reacts with the enol tautomer of the ligand by acid-independent and inverse-acid paths. The rate constants for reaction of Ni^{2+} with the protonated enol tautomer and with the enolate ion are 11.3 and 1 294 dm^3 mol^{-1} s^{-1} respectively.

The kinetics and mechanisms of reactions of nickel(II), cobalt(II), copper(II), and iron(III) with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) were investigated some years ago by Sutin and co-workers.[1] They interpreted their results in terms of a mechanism in which the metal ion reacts with the enol tautomer of the ligand by both acid-dependent and acid-independent pathways. The keto form of the ligand did not react with metal ions. The ionic strength used in these investigations was 1.0 mol dm^{-3} $NaClO_4$. The values of the rate constants for reaction of Ni^{2+} with the enol tautomer and with the enolate ion were 2.3 and 1×10^4 dm^3 mol^{-1} s^{-1} respectively.

More recently, Ando *et al.*[2] reported the results of investigations of the kinetics of mono complex formation of Htftbd with Ni^{II} and Cu^{II} in aqueous solution. The ionic strength was adjusted to 0.2 mol dm^{-3} using sodium sulphate, and the acid dissociation constant was measured in 0.2 mol dm^{-3} sodium chloride. The kinetic data gave a rate constant of 0.13 dm^3 mol^{-1} s^{-1} for reaction of Ni^{2+} with the protonated form of the ligand and 920 dm^3 mol^{-1} s^{-1} for reaction with the enolate ion which is formed on dissociation of either the keto or the enol tautomers. These values are at variance with the values reported by Sutin and co-workers.[1] Although Ando *et al.* do not report the individual rate constants obtained, nevertheless it is possible from an examination of their Figure 2 to calculate reasonable estimates of the $k_{obs.}$ values they would have obtained under a given set of experimental conditions. They show a large divergence from the values reported previously.[1]

In view of the foregoing, we decided to investigate the reactions of Ni^{II} with Htftbd in a medium of ionic strength 0.20 mol dm^{-3}, adjusted using sodium sulphate. Furthermore, in order to standardize the data, we also measured both the dissociation constant of Htftbd and its stability constant with Ni^{II} in this medium.

Experimental

AnalaR grade $NiSO_4 \cdot 7H_2O$ (BDH) was used as the source of nickel. Stock solutions were standardized using ethylenediaminetetra-acetate with bromopyrogallol red as indicator. The ligand Htftbd (Koch-Light) was used as supplied. Stock solutions were standardized by titration with standard sodium hydroxide. End-points were determined using an iterative computer program based on the method of Gran and Johansson.[3] AnalaR grade Na_2SO_4 (BDH) was used to adjust the ionic strength to 0.2 mol dm^{-3}. The contribution of any sulphuric acid present was taken into account when adjusting the final ionic strength. AnalaR grade sulphuric acid was used as the source of hydrogen ions for both hydrolysis reactions and pH adjustment.

The pH measurements were made using a PTI-6 pH meter equipped with a Russell combination electrode. The pH electrode was calibrated to read in hydrogen-ion concentration as follows. Acid solutions having an ionic strength of 0.2 mol dm^{-3} Na_2SO_4 were titrated with standard sodium hydroxide. The end-points were determined by the Gran method.[4] The linearity of the electrode was established using buffers of pH 4, 7, and 9. The following relationship was obtained between the measured pH and the hydrogen-ion concentration: $p[H^+] = pH - 0.414$.

Kinetic measurements were made using a HiTech SF-20 stopped-flow mixing device interfaced to a BBC microcomputer. Pseudo-first-order rate constants were calculated as previously described.[5] Stability constant refinement was carried out using the computer program SUPERQUAD.[6]

The tautomerization reactions were studied using the stopped-flow device with the ligand in excess. The procedure followed for the determination of k_e the rate constant for enolization is similar to that used by Sutin and co-workers,[1] apart from the fact that in our case absorbance measurements were made using the stopped-flow apparatus whereas they used a spectrophotometer. The procedure adopted for the determination of k_f was identical to that used in ref. 1. In the enolization reactions the bromine concentrations were determined by recording the zero-time absorbances in the stopped-flow device and using the absorption coefficient of Br_2 at 452 nm (103 dm^3 mol^{-1} cm^{-1}).

All measurements were carried out at 25 °C.

Results and Discussion

Tautomerization Reactions.—The equilibrium between the keto and enol form of Htftbd can be described by equation (1)

$$\mathrm{HK} \underset{k_f}{\overset{k_e}{\rightleftharpoons}} \mathrm{HE} \qquad (1)$$

where k_e is the rate of enolization and k_f is the rate of ketonization. Rate constant k_e can be evaluated by plotting the left-hand side of equation (2) against time, where A is the

$$-\ln[(A/\varepsilon l) + a - b] = k_e t + c \qquad (2)$$

absorbance at time t, ε is the absorption coefficient of Br_2, l is the pathlength, a is the initial concentration of ketone, and b is the initial bromine concentration. The value of k_e at 25 °C and at $I = 0.20$ mol dm^{-3} (sodium sulphate) was found to be $(8.73 \pm 0.36) \times 10^{-3}$ s^{-1}, independent of acidity in the range 0.0067—0.067 mol dm^{-3} H_2SO_4. The observed rate constant in the ketonization reactions measures the rate of approach to equilibrium and is equal to $(k_e + k_f)$. The value of k_f was found to be 3.10 ± 0.06 s^{-1}. The ratio k_e/k_f is equal to the ratio of the

Table 1. Enolization (k_e) and ketonization (k_f) rate constants, ratio of keto to enol tautomers, and equilibrium constants for the Ni^{2+}–Htftbd system at 25 °C and $I = 0.2$ mol dm^{-3} (sulphate medium)

$$k_e = 8.73 \times 10^{-3}\ s^{-1}$$
$$k_f = 3.10\ s^{-1}$$
$$[HE]/[HK] = 2.82 \times 10^{-3}$$
$$K_{HA} \approx K_{HK} = 3.55 \times 10^{-6}\ mol\ dm^{-3}$$
$$K_{HE} = 1.26 \times 10^{-3}\ mol\ dm^{-3}$$
$$K_1 \approx K_K = 1.0 \times 10^{-2}$$
$$K_E = 3.55$$

amounts of enol and keto tautomers present in solution. The present data give a value of 2.82×10^{-3} compared to 4.4×10^{-3} found in 1.0 mol dm^{-3} $NaClO_4$.[1]

Equilibrium Measurements.—The equilibrium data are summarized in Table 1. The relationship between the measured dissociation constant (K_{HA}) and K_{HE} and K_{HK} is given by equation (3) where K_{HK} and K_{HE} are the dissociation constants

$$\frac{1}{K_{HA}} = \frac{1}{K_{HE}} + \frac{1}{K_{HK}} \tag{3}$$

of the keto and enol tautomers of Htftbd respectively and $K_{HK}/K_{HE} = [HE]/[HK] = k_e/k_f$. Similarly, the equilibrium constant K_1 for reaction of Ni^{2+} with Htftbd can be partitioned between the equilibrium constants K_K and K_E for reaction with the keto and enol tautomers respectively [equations (4)—(6)].

$$Ni^{2+} + HK \rightleftharpoons [NiE]^+ + H^+;\ K_K \tag{4}$$

$$Ni^{2+} + HE \rightleftharpoons [NiE]^+ + H^+;\ K_E \tag{5}$$

$$\frac{1}{K_1} = \frac{1}{K_E} + \frac{1}{K_K} \text{ and } \frac{[HE]}{[HK]} = \frac{K_K}{K_E} \tag{6}$$

The pK of Htftbd decreases from a value of 6.35 in 1.0 mol dm^{-3} $NaClO_4$ to 5.45 in the sulphate medium used in the present study, while the value of log β_1 decreases from 4.30 to 3.45.

Kinetic Measurements.—The kinetic data are given in Table 2. They are consistent with the mechanism shown in equation (7) previously described by Sutin and co-workers.[1] Complex

$$HK \underset{k_f}{\overset{k_e}{\rightleftharpoons}} HE \underset{k'_{-HE}}{\overset{k'_{HE}}{\rightleftharpoons}} [ME]^+ \tag{7}$$

formation takes place *via* a mechanism in which the metal ion reacts exclusively with the enol tautomer of the ligand. The keto tautomer is totally inert. In terms of this scheme, $k'_{HE} = k_{HE}[Ni^{2+}]$ and $k'_{-HE} = k_{-HE}[H^+]$, and $k_{obs.}$ is predicted to have the form of equation (8) where ($k_e + k_f$) has been replaced by k_f since $k_f \gg k_e$.[6,7] The formation or dissociation of the complex is characterized by two consecutive reactions. However, under our experimental conditions only a single reaction step was observed. Either the half-lives of the two relaxations are very similar or the amplitude of the faster of the two is very small. Equation (8) can be rearranged to give (9). Figure 1 shows plots of the left-hand side of equation (9) against $1/[Ni^{2+}]$ and it is evident that the data are consistent with this equation. The slope S of these plots is given by equation (10). The average

$$k_{obs.} = \frac{k_e k_{HE}[Ni^{2+}]}{k_{HE}[Ni^{2+}] + k_f + k_{HE}[H^+]/K_E \; (1 + [H^+]/K_K[Ni^{2+}])} \tag{8}$$

$$\frac{1 + [H^+]/K_K[Ni^{2+}]}{k_{obs.}} = \frac{1}{k_e} + \frac{1}{[Ni^{2+}]}\left(\frac{k_f}{k_e k_{HE}} + \frac{[H^+]}{k_e K_E}\right) \tag{9}$$

Table 2. First-order rate constants for reaction of Ni^{2+} with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) at 25 °C and $I = 0.2$ mol dm^{-3} (sulphate medium). [Htftbd] = 1.0×10^{-4} mol dm^{-3}, λ = 355 nm

$10^2[H^+]$	$10^3[Ni^{2+}]$	
mol dm^{-3}		$k_{obs.}/s^{-1}$
0.50	5.20	0.263
0.50	10.4	0.197
0.50	15.6	0.158
0.50	20.8	0.133
0.50	25.0	0.111
1.00	5.20	0.333
1.00	10.4	0.274
1.00	15.6	0.232
1.00	20.8	0.202
1.00	25.0	0.180
2.00	5.20	0.400
2.00	10.4	0.343
2.00	15.6	0.314
2.00	20.8	0.288
2.00	25.0	0.266
4.00	5.20	0.452
4.00	10.4	0.419
4.00	15.6	0.386
4.00	20.8	0.377
4.00	25.0	0.359
6.70	5.20	0.480
6.70	10.4	0.460
6.70	15.6	0.436
6.70	20.8	0.419
6.70	25.0	0.394

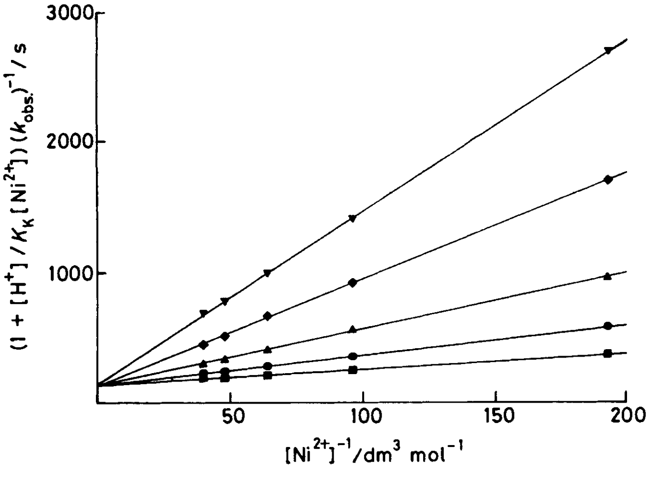


Figure 1. Plot suggested by equation (9) for reaction of Ni^{2+} with Htftbd in aqueous solution at 25 °C and $I = 0.2$ mol dm^{-3}, $[H^+] = 0.50 \times 10^{-2}$ (■), 1.00×10^{-2} (●), 2.00×10^{-2} (▲), 4.0×10^{-2} (◆), and 6.70×10^{-2} mol dm^{-3} (▼)

$$S = \frac{k_f}{k_e k_{HE}} + \frac{[H^+]}{k_e K_E} \tag{10}$$

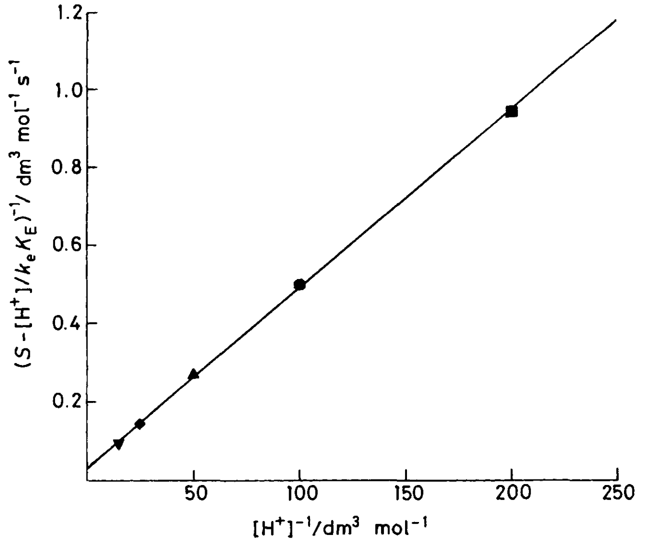


Figure 2. Plot suggested by equation (12) for reaction of Ni^{2+} with Htftbd in aqueous solution at 25 °C and I = 0.2 mol dm^{-3} (sulphate medium). Symbols as in Figure 1

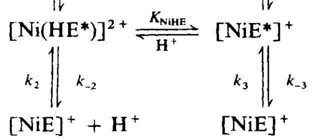
value of the intercepts of the plots in Figure 1 is 133 ± 6. According to equation (9) this should be equal to $1/k_e$ This gives a value of 7.52×10^{-3} s^{-1} for k_e compared to the directly determined value in the bromination experiment of 8.7×10^{-3} s^{-1}. The agreement is quite satisfactory. Plots of $1/\{S - ([H^+]/k_eK_E)\}$ against $1/[H^+]$, where S is the slope of the plots in Figure 1, were linear (Figure 2) suggesting that k_{HE} has the form in equation (11). Therefore equation (10) may be rearranged to give (12). The intercept and slope of the plot in

$$k_{HE} = a + b/[H^+] \tag{11}$$

$$1/\{S - ([H^+]/k_eK_E)\} = (k_e/k_f)a + (k_e/k_f)b/[H^+] \tag{12}$$

Figure 2 gives values of 11.3 dm^3 mol^{-1} s^{-1} and 1.63 s^{-1} respectively for a and b in equation (12). A detailed analysis of the sensitivity of a and b to small changes in the values of K_E and K_K was carried out using a non-linear least-squares curve-fitting routine. It was found that while the values obtained for b were stable, small variations in the values of the equilibrium constants led to unpredictable fluctuations in the values of a. Consequently, the value of a cannot be considered totally reliable.

It has previously been shown that the rate law outlined above is consistent with the mechanism shown in the Scheme, where



Scheme.

$[Ni(HE^*)]^{2+}$ and $[NiE^*]^+$ are unstable intermediates in which only one donor atom of the β-diketone is bonded to the metal species. Assuming that equilibrium is maintained between HE and E^- and $[Ni(HE^*)]^{2+}$ and $[NiE^*]^+$, equation (13) is

$$k_{HE} = \frac{k_1 + (K_{HE}k_4/[H^+])}{1 + \left(\dfrac{k_{-1} + K_{NiHE}k_{-4}/[H^+]}{k_2 + K_{NiHE}k_3/[H^+]}\right)} \tag{13}$$

derived for k_{HE}. If $\{k_2 + (K_{NiHE}k_3/[H^+])\} \gg \{k_{-1} + (K_{NiHE}k_{-4}/[H^+])\}$ then equation (14) is obtained. Thus a in equation (12)

$$k_{HE} = k_1 + (K_{HE}k_4/[H^+]) \tag{14}$$

may be equated to k_1 while b may be equated to $K_{HE}k_4$. Thus k_1 = 11.3 dm^3 mol^{-1} s^{-1} and k_4 = 1 294 dm^3 mol^{-1} s^{-1}.

It is apparent that the mechanism proposed is obeyed over a relatively wide range of $[H^+]$ and $[Ni^{2+}]$. The hydrogen-ion concentration is limited at the upper end by the need to maintain the ionic strength constant. The intercepts of the plots suggested by equation (9) are in good agreement with that calculated using the directly determined value of k_e. Ando *et al.*[2] obtained a value of 920 for the rate constant for reaction of Ni^{2+} with the deprotonated form of Htftbd. This corresponds to k_4 in the present mechanism. The agreement between the two values is fair. However, the value obtained by Ando *et al.*[2] for k_{fh} the rate constant for reaction with the fully protonated form of the ligand, is 0.13 dm^3 mol^{-1} s^{-1}. The differences between the rate constants reported in ref. 2 and those obtained here may be partly due to possible deficiencies in the mechanism proposed in the former investigation. Despite the fact that under their experimental conditions less than 10% of the ligand was present as the metal complex, the mechanism proposed takes no account of the reverse reaction. Unfortunately, the raw kinetic data were not reported, however, it appears that all the kinetic data for nickel were obtained at a single metal-ion concentration. It is apparent from our kinetic data that, at all the hydrogen-ion concentrations studied, $k_{obs.}$ decreases or remains relatively constant with increasing metal-ion concentration (as in Sutin's original work). The mechanism proposed in ref. 2 demands that, at constant $[H^+]$, $k_{obs.}$ should increase linearly with $[Ni^{2+}]$. This is clearly not the case. Additionally, the disparity between the media used to control the ionic strength in the kinetic experiments and that used in the equilibrium measurements ensured that incorrect values of both the dissociation constant and the stability constant were used. Furthermore, Ando's assertion that under the experimental conditions of Sutin's kinetic experiments equilibrium was not maintained between the enol tautomer of Htftbd and the enolate ion is untenable. The ionization rate constant for the enol tautomer would be of the order of 1×10^7 s^{-1}, while the rate constant for recombination with the hydrogen ion would be expected to be close to diffusion controlled as is the case with pentane-2,4-dione (Hpd).[8] The difference in the ionization rate constants arises from the large difference in the pK values of the enol tautomers of Htftbd and Hpd (8.0 *versus* 2.90).

The present work would appear to support the general mechanism proposed by Sutin and co-workers[1] for the reactions of metal-ion species with both the protonated form and the enolate ion of Htftbd. However, it is also clear that in sulphate media the rate constants are different to those obtained in perchlorate media. In particular, the reaction with the enolate ion is retarded by a factor of 7.7 and the reason for this is not at all clear. Unfortunately, data on the kinetics of metal complex formation in sulphate media are relatively sparse[9] and direct comparisons cannot readily be made. However, it is now apparent that extreme caution must be exercised when evaluating results obtained in sulphate media and where at all possible an alternative medium should be used.

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