Kinetics and Mechanisms of the Reactions of Nickel(II), Cobalt(II), Copper(II), and Iron(III) with 1,1,1-Trifluoropentane-2,4-dione

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The kinetics and mechanisms of the reactions of 1,1,1-trifluoropentane-2,4-dione (Htfpd) with nickel(II), cobalt(II), copper(II), and iron(III) to form the mono complexes have been studied in aqueous solution at 25 °C and 0.5 mol dm^{-3} ionic strength. The equilibrium constants for these reactions have also been measured. The kinetic data are consistent with a mechanism in which the metal ion reacts exclusively with the enol tautomer of the β-diketone. The keto-tautomer is inert in all instances.

A number of papers have reported the results of studies on the kinetics and mechanisms of the formation reactions of the 1 : 1 complexes formed between metal ions and β-diketones.[1-8] It is now clear that during the formation of these complexes ligand penetration into the co-ordination sphere does not follow the Eigen mechanism. The kinetics and mechanisms of the reactions of Ni^{II}, Co^{II}, Cu^{II}, and Fe^{III} with the β-diketone 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) to form the mono complexes have been investigated in detail.[2] 1,1,1-Trifluoropentane-2,4-dione (Htfpd) has a very similar basicity to Htftbd. However, the steric properties are quite different. As part of our continuing investigations into the kinetics and mechanisms of the reactions of metal ions with β-diketones we now report on the reactions of Ni^{II}, Co^{II}, and Fe^{III} with Htfpd in aqueous solution.

Experimental

1,1,1-Trifluoropentane-2,4-dione (Htfpd) was purchased from Koch-Light and was freshly distilled under reduced pressure prior to use. Nickel perchlorate, copper perchlorate, and cobalt perchlorate were prepared as follows. The metal carbonates were first prepared by adding a stoicheiometric amount of sodium carbonate to aqueous solutions of the AnalaR metal chlorides (B.D.H.). The metal carbonate precipitate obtained was repeatedly washed with distilled water until the supernatant was free from chloride. The metal carbonate suspension was then acidified to pH 4 using concentrated perchloric acid. Slow evaporation yielded the required metal perchlorate. Stock solutions of nickel perchlorate and cobalt perchlorate were analysed by titration with ethylenediaminetetra-acetate using Bromopyrogallol Red and Xylenol Orange indicators respectively. Stock solutions of copper perchlorate were standardized against sodium thiosulphate which had been previously standardized against potassium iodate. AnalaR $Fe(NO_3)_3 \cdot 9H_2O$ was used as the source of Fe^{III}. Solutions were standardized colorimetrically using potassium thiocyanate.

Spectra were recorded using a Beckman DB-GT u.v.–visible spectrophotometer equipped with a chart recorder. pH Measurements were made with a Pye model 290 pH meter equipped with a Pye Ingold E_0[7] combination electrode. The potassium chloride solution in the reference compartment was replaced by a 3 mol dm^{-3} sodium chloride solution. The ionic strength of solutions was adjusted using sodium perchlorate as the inert electrolyte and the pH was adjusted using sodium hydroxide and perchloric acid.

The rate constants for the reactions of Co^{II}, Ni^{II}, and Cu^{II} with Htfpd were measured using an Applied Photophysics stopped-flow device. The drive syringes and mixing chamber were thermostatted at 25.0 ± 0.1 °C. The rate constants for the Fe^{III} reactions were measured using the spectrophotometer and chart recorder. The stopped-flow kinetic data were recorded using a Tektronix model 5100 storage oscilloscope. The stored traces were photographed. In all cases rate constants were calculated from plots of $-\ln(A - A_\infty)$ against time (A = optical density).

The reactions could be run in the forward or reverse direction. Due to the low values of the equilibrium constants it was more convenient to run the Ni^{II}, Co^{II}, and Cu^{II} reactions in the reverse direction. The reverse reaction was studied by mixing solutions of the complex prepared *in situ* with an excess of acid. Studying the reactions in the forward direction involved mixing solutions of the metal and the ligand both of which were adjusted to the appropriate pH and ionic strength prior to mixing. The metal was maintained in at least ten-fold excess to ensure the formation of only the mono complex. This also ensured that the reactions were carried out under pseudo-first-order conditions.

The pK of Htfpd was determined by titrating an approximately 0.01 mol dm^{-3} solution with sodium hydroxide. The titration was carried out at 25 °C under nitrogen. The activity coefficient of H^+ at an ionic strength of 0.5 mol dm^{-3} $Na[ClO_4]$ was taken as 0.738.[9] The pK was calculated using equation (1)

$$pK_a = -\log[H^+] + \log\{([HL]_T - [Na^+] - [H^+] + [OH^-])/([Na^+] + [H^+] - [OH^-])\} \quad (1)$$

where $[HL]_T$ is the total ligand concentration. Due to the uncertainty in the value of $[HL]_T$ it was estimated using a graphical method which does not require knowledge of an accurate value of $[HL]_T$.[10] The dissociation constant (K_a) may be written as equation (2) which may be rewritten as equation (3) where $[HL]_T = [HL] + [L^-]$; $[L^-]$ may be approximated

$$K_a = a_{H^+}[L^-]\gamma_L/[HL] \text{ (assuming } \gamma_{HL} = 1) \quad (2)$$

$$(K_a[HL]_T/[L^-]) - K_a = a_{H^+}\gamma_L \quad (3)$$

without serious error to $[Na^+]$ so that a plot of $1/[L^-]$ against $a_{H^+}\gamma_L$ gives a straight line of slope $K_a[HL]_T$ and intercept $-K_a$. The value of $[HL]_T$ obtained is then used in equation (1) to obtain the concentration pK.

The equilibrium constants for reaction of Co^{2+}, Ni^{2+}, and Cu^{2+} with Htfpd were determined by titrating the ligand in the presence of an excess of metal. The constants are expressed as concentration quotients. The equilibrium constant K_1 for reaction of Fe^{3+} with Htfpd was determined spectroscopically using equation (4), where $[Fe^{3+}]_0$ and $[HL]_0$ are

$$[Fe]_0[HL]_0/Ah[H^+] = [Fe]_0 + [HL]_0/\varepsilon h[H^+] + 1/\varepsilon K_1 \quad (4)$$

the total concentrations of Fe^{3+} and Htfpd respectively, $h = (1 + K_h/[H^+])$ where K_h is the hydrolysis constant of Fe^{III}

Table 1. Equilibrium constants for formation of mono-β-diketone complexes of Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}

Metal	K_1	K_K	K_E
Ni^{II}	11.23×10^{-3}	11.30×10^{-3}	1.51
Co^{II}	2.81×10^{-3}	2.83×10^{-3}	0.38
Cu^{II}	0.463	0.467	62.3
Fe^{III}	3.39	3.42	455.3

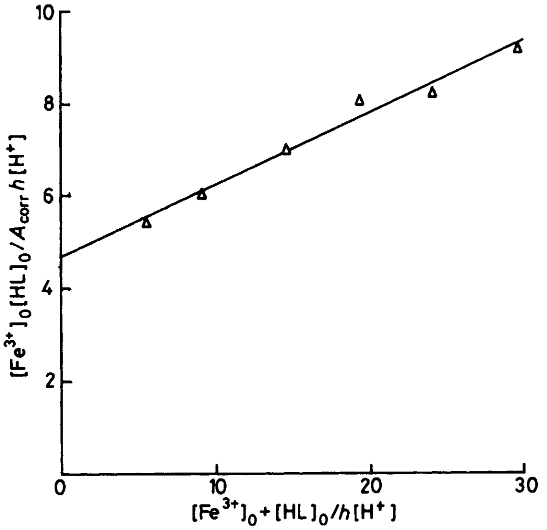


Figure 1. Plot of equation (4) for reaction of Fe^{3+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}; A_{corr} is the measured optical density corrected for the contribution from free Fe^{3+}

(1.65×10^{-3} mol dm^{-3} at 25 °C [11]), and ε is the absorption coefficient of [FeL]$^{2+}$ at the analytical wavelengths. A plot of the left-hand side of equation (4) against ([Fe^{3+}]$_0$ + [HL]$_0$)/h[H$^+$] should give a straight line of slope 1/ε and intercept $1/\varepsilon K_1$. Figure 1 shows the plot suggested by equation (4) for reaction of Fe^{3+} with Htfpd.

Results and Discussion

The apparent dissociation constant (K_{HL}) of Htfpd was found to be 8.81×10^{-7} mol dm^{-3}. This gives values of 1.18×10^{-4} mol dm^{-3} for K_{HE} (the dissociation constant of the enol tautomer) and 8.87×10^{-3} mol dm^{-3} for K_{HK} (the dissociation constant of the keto tautomer). Table 1 gives the equilibrium constants for reaction of Ni^{II}, Co^{II}, Cu^{II}, and Fe^{III} with Htfpd together with the values of the equilibrium constants K_E and K_K calculated using equation (5) where K_E and K_K are as defined by equations (6) and (7) respectively and HK, HE,

$$1/K_1 = (1/K_E) + (1/K_K) \text{ and } [HE]/[HK] = K_K/K_E \quad (5)$$

$$M^{n+} + HE \rightleftharpoons ME^{(n-1)+} + H^+ \quad (K_E) \quad (6)$$

$$M^{n+} + HK \rightleftharpoons ME^{(n-1)+} + H^+ \quad (K_K) \quad (7)$$

and E$^-$ are the keto and enol tautomers and enolate ion repectively. The ratio [HE]/[HK] has been previously estimated to be 7.5×10^{-3} under the experimental conditions of the present investigation.[12] The stability constants follow the order: Fe^{III} > Cu^{II} > Ni^{II} > Co^{II}. This is the same order as that obtained for the pentane-2,4-dione and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione complexes of these metals.

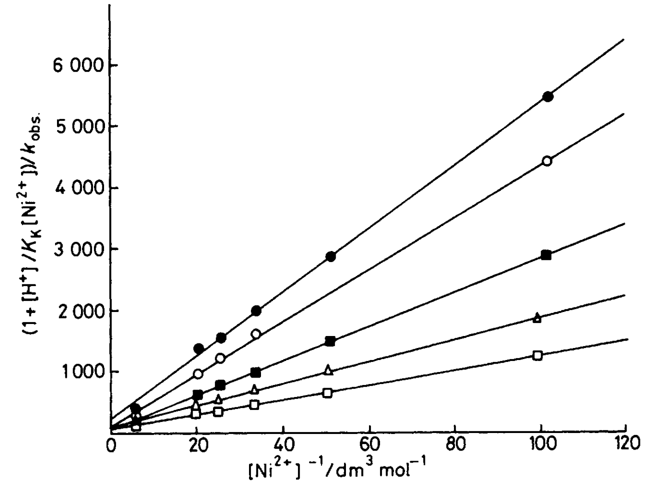


Figure 2. Plot suggested by equation (9) for reaction of Ni^{2+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}. [H$^+$] = 3.66×10^{-2} (□), 5.65×10^{-2} (△), 9.15×10^{-2} (■), 18.95×10^{-2} (○), and 26.6×10^{-2} mol dm^{-3} (●)

Tables 2—5 give the kinetic data for reactions of Ni^{II}, Co^{II}, Cu^{II}, and Fe^{II} respectively with Htfpd in aqueous solutions. The kinetic data are consistent with a reaction scheme in which the metal ion does not react directly with the keto-tautomer of the β-diketone although this is the predominant species in solution. Complex formation takes place through reaction of the metal ion with the enol form of the diketone as outlined in equation (8). In terms of this scheme $k'_{HE} = k_{HE}[M^{n+}]$, $k'_{-HE} = k_{-HE}[H^+]$, $K_E = k_{HE}/k_{-HE}$, and k_e and k_f

$$HK \underset{k_f}{\overset{k_e}{\rightleftharpoons}} HE \underset{k'_{-HE}}{\overset{k'_{HE}}{\rightleftharpoons}} ME \quad (8)$$

are the rates of enolization and ketolization of the β-diketone respectively.

The determination of the rate equations for the reaction scheme (8) has been previously described and gives rise to two possible reactions irrespective of whether the reactions are studied in the forward or reverse direction.[13,14] Under the experimental conditions of the present investigation only one relaxation was observed, and in this instance the data are consistent with the slower of the two possible reactions. Using the fact that $k_f \gg k_e$, equation (9) may be derived for $k_{obs.}$. Thus

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

a plot of the left-hand side of equation (9) against 1/[M] should yield a straight line of intercept $1/k_e$ and slope S [equation (10)]. Equation (10) may be more conveniently written as equation (11).

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

$$1/\{S - ([H^+]/k_e K_E)\} = k_e k_{HE}/k_f \quad (11)$$

Reaction of Ni^{II} *with* Htfpd.—Figure 2 shows the plots suggested by equation (9) at various values of [H$^+$]. In all instances the kinetic data are consistent with the proposed

Table 2. Observed rate constants for the reaction of Ni^{2+} with Htfpd in aqueous solution *

Expt.	$10^2[Ni^{2+}]$/ mol dm^{-3}	$10[H^+]$/ mol dm^{-3}	$10k_{obs.}$/s^{-1}
1	1.01	0.366	2.58
2	2.01	0.366	2.43
3	3.02	0.366	2.27
4	4.03	0.366	2.00
5	5.03	0.366	2.04
6	17.00	0.366	1.55
7	1.01	0.565	2.71
8	2.01	0.565	2.52
9	3.02	0.565	2.39
10	4.03	0.565	2.29
11	5.03	0.565	2.20
12	17.00	0.565	1.73
13	0.98	0.915	2.88
14	1.97	0.915	2.74
15	2.95	0.915	2.73
16	3.94	0.915	2.66
17	4.92	0.915	2.67
18	17.00	0.915	2.50
19	0.98	1.895	3.87
20	1.97	1.895	3.87
21	2.95	1.895	3.54
22	3.94	1.895	3.51
23	4.92	1.895	3.54
24	17.00	1.895	3.60
25	0.98	2.66	4.40
26	1.96	2.66	4.21
27	2.93	2.66	4.02
28	3.91	2.66	3.90
29	4.89	2.66	3.50
30	17.00	2.66	3.47

* [Htfpd] = 5×10^{-4} mol dm^{-3}, λ in the range 310—325 nm, $I = 0.5$ mol dm^{-3} Na[ClO$_4$].

mechanism and the values of k_e calculated from the intercepts are in good agreement with the experimentally determined value of 0.015 s^{-1}.[15] In order to determine the acid dependence of k_{HE}, trial substitutions were made for k_{HE} in equation (11), for example equations (12) and (13). Plots of $1/\{S - ([H^+]/k_eK_E)\}$ against $1/[H^+]$ are linear showing that k_{HE} has the form of equation (12). Therefore equation (11) may be written as (14). From the slopes and intercepts of the plots shown in Figure 3 values of a and b are found to be 1.74 dm^3 mol^{-1} s^{-1} and 0.40 s^{-1} respectively.

$$k_{HE} = a + b/[H^+] \qquad (12)$$

$$k_{HE} = a + b[H^+] \qquad (13)$$

It has previously been shown that the form of the rate law obtained here is consistent with the mechanism outlined in the Scheme where $[MHE^*]^{2+}$ and $[ME^*]^+$ are unstable intermediates in which one end of the diketone is attached to the metal centre. Assuming that HE and E^- are maintained in equilibrium, application of the steady-state approximation leads to equation (15) for k_{HE}.

$$1/\{S - ([H^+]/k_eK_E)\} = (k_e/k_f)a + (k_e/k_f)b/[H^+] \qquad (14)$$

$$k_{HE} = (k_1 + K_{HE}k_4[H^+]^{-1})\Big/\left(1 + \frac{k_{-1} + K_{MHE}k_{-4}[H^+]^{-1}}{k_2 + K_{MHE}k_3[H^+]^{-1}}\right) \qquad (15)$$

If $(k_2 + K_{MHE}k_3[H^+]^{-1}) \gg (k_{-1} + K_{MHE}k_{-4}[H^+]^{-1})$ then $k_{HE} = k_1 + K_{HE}k_4[H^+]^{-1}$. In this case $a = k_1$ and $b = K_{HE}k_4$.

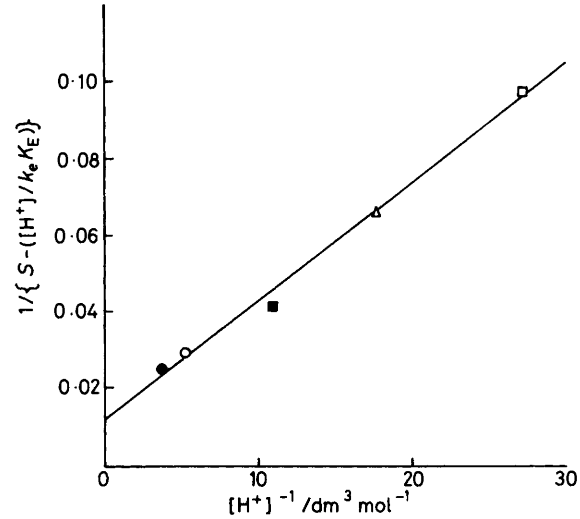
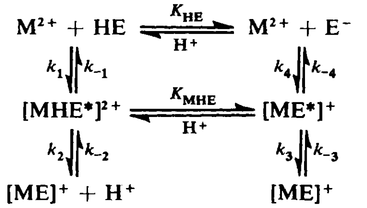


Figure 3. Plot suggested by equation (14) for reaction of Ni^{2+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}. $[H^+] = 3.66 \times 10^{-2}$ (□), 5.65×10^{-2} (△), 9.15×10^{-2} (■), 18.95×10^{-2} (○), and 26.6×10^{-2} mol dm^{-3} (●)



Scheme.

Alternatively, if $(k_2 + K_{MHE}k_3[H^+]^{-1}) \ll (k_{-1} + K_{MHE}k_{-4}[H^+]^{-1})$ equation (15) reduces to (16), where $K_1 = k_1/k_{-1}$ and $K_4 = k_4/k_{-4}$. Using the values of a and b obtained from the plots suggested by equation (11) the values of k_1 and k_4 are calculated to be 1.74 and 3.4×10^3 dm^3 mol^{-1} respectively. While the acid independent term clearly represents the rate of reaction between Ni^{2+} and the enol tautomer of Htfpd, the acid dependent term may be formulated as Ni^{2+} and E^- or alternatively as $[Ni(OH)]^+$ and HE. However, in view of the negligible degree of hydrolysis of Ni^{II} under the experimental conditions, the former is the more reasonable pathway.

$$k_{HE} = K_1k_2 + (K_{HE}K_4k_3/[H^+]) \qquad (16)$$

Reactions of Co^{II} *and* Cu^{II} *with* Htfpd.—Figure 4 shows the plot suggested by equation (9) for reaction of Co^{2+} with Htfpd. The values of k_e calculated from the intercepts are in good agreement with the directly determined value of 0.015 s^{-1}.[15] In this instance however, the slopes of the lines are in each case approximately equal to $[H^+]/k_eK_E$ and consequently plots of the left hand side of equation (11) against either $[H^+]$ or $1/[H^+]$ could not be obtained. A similar situation pertains for the reactions of Co^{II} with Htftbd.[2] Certain simplifications of equation (9) are however possible. Under the experimental conditions used $[H^+]/K_K[M^{2+}] \gg 1$ and in the event that $k_{HE}[H^+]/K_E \gg k_f$, equation (9) reduces to equation (17). Figure 5 shows the plot suggested by equation

$$1/k_{obs.} = 1/k_f + K_E[M^{2+}]/k_f[H^+] \qquad (17)$$

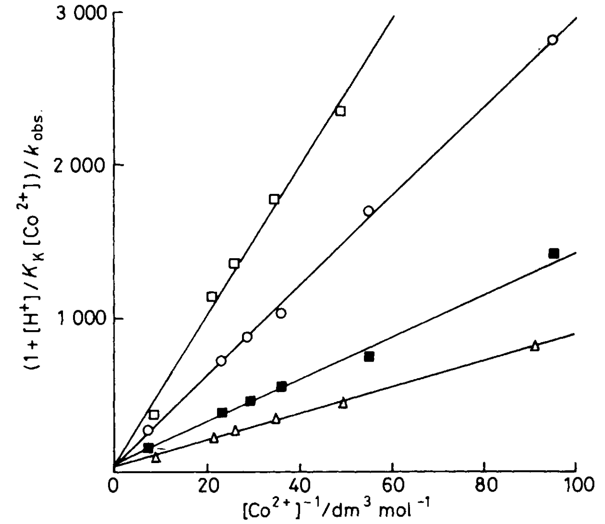


Figure 4. Plot suggested by equation (9) for reaction of Co^{2+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}. $[H^+] = 5.23 \times 10^{-2}$ (△), 8.90×10^{-2} (■), 17.95×10^{-2} (○), and 28.60×10^{-2} mol dm^{-3} (□)

Table 3. Observed rate constants for reaction of Co^{2+} with Htfpd in aqueous solution *

Expt.	$10^2[Co^{2+}]$/ mol dm^{-3}	$10[H^+]$/ mol dm^{-3}	$k_{obs.}/s^{-1}$
1	1.10	0.523	2.06
2	2.04	0.523	1.99
3	2.87	0.523	1.88
4	3.86	0.523	1.74
5	4.70	0.523	1.69
6	16.00	0.523	1.20
7	1.05	0.89	2.12
8	1.82	0.89	2.33
9	2.77	0.89	2.06
10	3.44	0.89	1.96
11	4.30	0.89	1.89
12	14.00	0.89	1.40
13	1.05	1.795	2.15
14	1.82	1.795	2.07
15	2.77	1.795	2.22
16	3.44	1.795	2.12
17	4.30	1.795	2.04
18	14.00	1.795	1.67
19	2.04	2.86	2.11
20	2.87	2.86	1.99
21	3.86	2.86	1.92
22	4.70	2.86	1.88
23	16.00	2.86	1.66

* [Htfpd] $= 5 \times 10^{-4}$ mol dm^{-3}, λ in the range 310—320 nm, $I = 0.5$ mol dm^{-3} Na[ClO$_4$].

(17). The intercept and slope of the plot in Figure 5 give values of 2.2 s^{-1} and 0.37 respectively for k_f and K_E compared to the directly determined values of 1.99 s^{-1} and 0.38. If $k_{HE}[H^+]K_E \gg k_f$, and if it is assumed that k_{HE} has the form of equation (12), the lower limits for reaction of Co^{2+} with the enol tautomer and the enolate ion of Htfpd are readily estimated as 76 dm^3 mol^{-1} s^{-1} and 3×10^4 dm^3 mol^{-1} s^{-1} respectively.

The kinetic data for reaction of Cu^{2+} with Htfpd (Table 4) are not consistent with equation (9). Additionally, the approximation $[H^+]/K_K[M^{2+}] \gg 1$ is not valid for some of the data and the plot suggested by equation (9) cannot be obtained. As a result of this, no limits can be set on the rate of reactions of Cu^{2+} with either the enol tautomer or enolate ion of Htfpd.

Table 4. Observed rate constants for reaction of Cu^{2+} with Htfpd in aqueous solution *

Expt.	$10^2[Cu^{2+}]$/ mol dm^{-3}	$10[H^+]$/ mol dm^{-3}	$k_{obs.}/s^{-1}$
1	0.85	1.37	0.740
2	1.70	1.37	0.444
3	2.55	1.37	0.314
4	3.40	1.37	0.248
5	4.25	1.37	0.210
6	14.45	1.37	0.073
7	0.80	1.75	0.979
8	1.60	1.75	0.640
9	2.40	1.75	0.453
10	0.80	0.867	0.654
11	1.60	0.867	0.355
12	2.40	0.867	0.257
13	3.20	0.867	0.205
14	4.00	0.867	0.164
15	0.85	2.70	1.250
16	1.70	2.70	0.857
17	2.55	2.70	0.633
18	3.40	2.70	0.522
19	4.25	2.70	0.433

* [Htfpd] $= 5 \times 10^{-4}$ mol dm^{-3}, λ = 325 nm, $I = 0.5$ mol dm^{-3} Na[ClO$_4$].

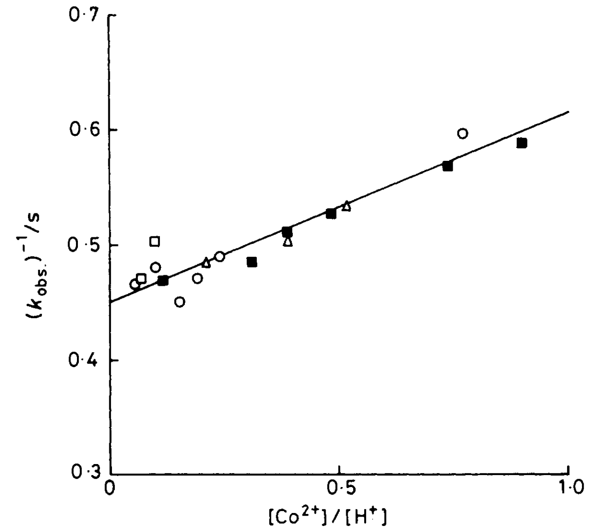


Figure 5. Plot suggested by equation (17) for reaction of Co^{2+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}. $[H^+] = 5.23 \times 10^{-2}$ (△), 8.90×10^{-2} (■), 17.95×10^{-2} (○), and 28.60×10^{-2} mol dm^{-3} (□)

Reaction of Fe^{III} *and* Htfpd.—Figure 6 shows the plots suggested by equation (9) and Figure 7 shows the plots suggested by equation (14). The values of *a* and *b* are 19.6 dm^3 mol^{-1} s^{-1} and 3.06 s^{-1} respectively. This gives a value of 19.6 dm^3 mol^{-1} s^{-1} for k_1, the acid independent pathway. If the acid dependent pathway is formulated as the reaction between Fe^{3+} and E^-, k_4 is calculated to be 2.58×10^4 dm^3 mol^{-1} s^{-1}. Alternatively, this pathway may be formulated as the reaction between $[Fe(OH)]^{2+}$ and HE and in this instance $k_5 = b/K_h = 1.85 \times 10^3$ dm^3 mol^{-1} s^{-1}.

Table 5. Observed rate constants for reaction of Fe^{3+} with Htfpd in aqueous solution *

Expt.	$10^3[Fe^{3+}]$/ mol dm^{-3}	$10^2[H^+]$/ mol dm^{-3}	$10^2k_{obs.}/s^{-1}$
1	1.92	1.99	1.23
2	2.89	1.99	1.29
3	4.81	1.99	1.20
4	5.77	1.99	1.27
5	9.62	1.99	1.02
6	3.43	3.24	1.00
7	5.15	3.24	1.02
8	6.87	3.24	1.11
9	8.59	3.24	1.03
10	10.31	3.24	1.24
11	1.72	3.95	1.11
12	3.43	3.95	1.14
13	5.15	3.95	1.16
14	8.59	3.95	1.48
15	3.43	4.69	1.29
16	5.15	4.69	1.04
17	6.87	4.69	1.13
18	8.59	4.69	1.10
19	10.31	4.69	1.60
20	3.94	6.19	1.09
21	5.90	6.19	0.81
22	7.87	6.19	0.98
23	9.84	6.19	1.00
24	20.00	6.19	1.11
25	30.00	6.19	1.10
26	40.00	6.19	1.09
27	3.43	12.38	1.13
28	5.15	12.38	1.18
29	6.87	12.38	1.00
30	8.59	12.38	1.10
31	10.31	12.38	1.20
32	1.92	12.65	1.03
33	3.85	12.65	1.04
34	5.77	12.65	1.20
35	7.69	12.65	1.30
36	9.62	12.65	1.17
37	11.50	12.65	1.17

* [Htfpd] = 2.5×10^{-4} (expts. 1—31), 1.6×10^{-3} mol dm^{-3} (expts. 32—37), $\lambda = 450$ nm, $I = 0.5$ mol dm^{-3} $Na[ClO_4]$.

Table 6 summarizes the rate constants obtained in the present investigation together with those obtained for the corresponding reactions with Htftbd as ligand. It is immediately apparent that there is a close relationship between the two data sets. In addition, in order to facilitate discussion as to whether the formation rate constants are normal or not, values of R are tabulated. The parameter R is dimensionless, given by $R = 4k_f/3K_ok_s$[16] where here k_f is the rate of complex formation, K_o is the outer-sphere association constant, and k_s is the solvent exchange rate. The values of k_s used were 3×10^4 (Ni^{2+}),[17] 2.4×10^6 (Co^{2+}),[18] 8×10^9 (Cu^{2+}),[19] 1.6×10^2 (Fe^{3+}),[20] and 1.2×10^5 s^{-1} {$[Fe(OH)]^{2+}$}.[20] The values for Fe^{3+} and $[Fe(OH)]^{2+}$ are the most recent available and differ considerably from previous values. For ' normal ' substitution of co-ordinated water by the Eigen–Wilkins mechanism, R should have a value close to unity.[16] Recent high-pressure n.m.r. work [21,22] shows that $[Ni(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ undergo complex formation reactions by a dissociative interchange (I_d) process in accordance with the Eigen–Wilkins mechanism. The activation volumes for complex formation by $[Cu(H_2O)_6]^{2+}$ have not yet been reported. However, it is probable that $[Fe(H_2O)_6]^{3+}$ reacts by an associative interchange (I_a) mechanism.[23,24]

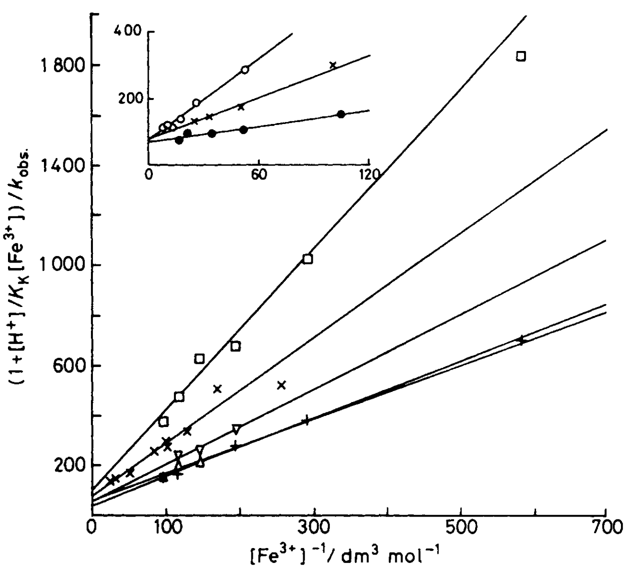


Figure 6. Plot suggested by equation (9) for reaction of Fe^{3+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}. $[H^+] = 1.99 \times 10^{-2}$ (●), 3.24×10^{-2} (△), 3.95×10^{-2} (+), 4.69×10^{-2} (▽), 6.19×10^2 (×), 12.38×10^{-2} (□), and 12.65×10^{-2} mol dm^{-3} (○)

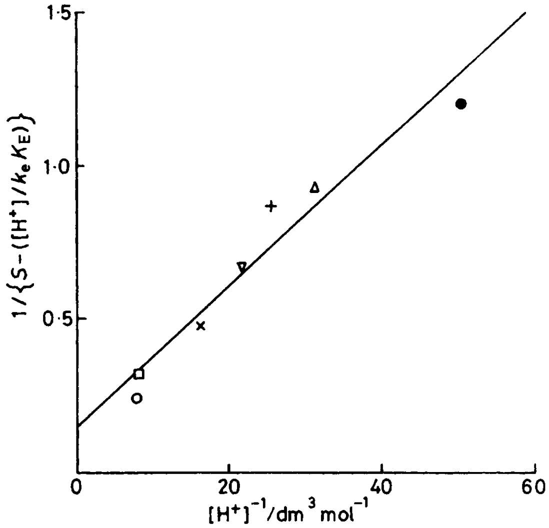


Figure 7. Plot suggested by equation (14) for reaction of Fe^{3+} with Htfpd in aqueous solution at 25 °C and $I = 0.5$ mol dm^{-3}. $[H^+] = 1.99 \times 10^{-2}$ (●), 3.24×10^{-2} (△), 3.95×10^{-2} (+), 4.69×10^{-2} (▽), 6.19×10^{-2} (×), 12.38×10^{-2} (□), and 12.65×10^{-2} mol dm^{-3} (○)

It is apparent from Table 6 that the reactions of Ni^{2+} with the enol tautomers of both Htfpd and Htftbd are considerably retarded ($R \ll 1$) compared to predictions based on solvent exchange rates. The reactions of Ni^{2+} (the only metal species for which exact data are available) with the enolate form of both ligands also have R values of less than unity, but the degree of retardation is considerably less than for the reactions with the enol tautomers. The reaction of Fe^{3+} with HE results in R values of 0.55 and 0.038 for Htfpd and Htftbd respectively. Similar values are obtained for reaction of $[Fe(OH)]^{2+}$. Assuming that in the case of the Fe^{III} reac-

Table 6. Rate constants for formation of mono complexes of β-diketones in aqueous solution

	Htfpd		Htftbd *	
Reaction	k/dm^3 mol^{-1} s^{-1}	R	k/dm^3 mol^{-1} s^{-1}	R
Ni^{2+} + HE	1.7	2.5×10^{-4}	2.3	3.4×10^{-4}
Ni^{2+} + E^-	3.4×10^3	0.12	1×10^4	0.48
Co^{2+} + HE	$\geqslant 76$	$\geqslant 1.4 \times 10^{-4}$	$\geqslant 300$	$\geqslant 5.5 \times 10^{-4}$
Co^{2+} + E^-	$\geqslant 3 \times 10^4$	$\geqslant 0.014$	$\geqslant 3 \times 10^4$	$\geqslant 0.017$
Cu^{2+} + HE	—	—	$\geqslant 3 \times 10^4$	$\geqslant 1.6 \times 10^{-5}$
Cu^{2+} + E^-	—	—	$\geqslant 3 \times 10^6$	$\geqslant 5.4 \times 10^{-4}$
Fe^{3+} + HE	19.6	0.55	1.4	3.8×10^{-2}
Fe^{3+} + E^-	2.6×10^4	94	2.4×10^4	125.0
$[Fe(OH)]^{2+}$ + HE	1.85×10^3	6.8×10^{-2}	1.3×10^3	4.8×10^{-2}

* Data from ref. 2.

tions the acid dependent pathway represents the reaction of Fe^{3+} with the enolate ion, a value of 94 is calculated for R. This is clearly unreasonably high and strongly supports the alternative formulation.

The reactivity order of metal ions with Htfpd is enolate ion > enol > keto. The keto-tautomer is unreactive towards metal ions. The unreactivity of the keto-tautomer of Htftbd has been ascribed to its unsymmetrical hydrate structure. However, we can find no evidence for the presence or absence of a similar structure in the case of Htfpd. The slow rate of reaction of HE with metal ions may be due to a slow first step (k_1) or to slow ring-closure step (k_2). Some support for the former comes from the fact that the reaction of Ni^{2+} with the enolate ion is more rapid than its reactions with the protonated enol form. However, the lower rate of reaction with HE compared to E^- may be due to the lower stability of the intermediate $[M(HE)]^{2+}$. In this event $k_{-1} \gg k_2$ and the second step could then be rate determining.[25]

Although the reaction of Ni^{2+} with the enolate form of the β-diketone is considerably more rapid than its reaction with HE, it is still slower than expected for reaction of a +2 metal species with a singly charged anion. In fact the R value obtained (Table 6) is comparable with that obtained for reaction of Fe^{3+} with HE. Obviously the degree of retardation in the case of the reaction of Fe^{3+} with HE is considerably less than the corresponding reaction with Ni^{2+}. There are two possible reasons for this. Firstly, due to its higher charge, Fe^{3+} may be more effective in breaking the intramolecular hydrogen bonds during the formation of the initial bond between the metal and the enol tautomer. This would result in a smaller degree of reduction in k_1. Secondly, Fe^{3+} is less labile than Ni^{2+}, and the retardation in its reaction rates may not be as readily apparent as in the case of more labile metal ions. The fact that Fe^{3+} may react by an I_a mechanism must also be borne in mind. The Fe^{3+} is a ' hard ' acid while β-diketones are ' hard ' bases. Consequently, the matching between acid and base is much better in the case of Fe^{3+} reactions than in the case of the Ni^{2+} reactions and reactions involving the former should therefore be more rapid, as is indeed observed. Further reactions with other ' hard ' acids are being carried out to test the universality of this observation.

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Received 24th May 1982; *Paper* 2/858