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Reactions of metal ions with protonated ligands. Kinetics and mechanisms of the reactions of iron(III) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3}

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Abstract

The equilibria and kinetics of the reactions of iron(III) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) have been investigated in methanol–water (70:30 vol./vol.) solution at 25 °C and ionic strength 0.5 mol dm^{-3}. The hydrolysis reactions of Fe^{3+} and $[Fe(Hhto)]^{2+}$ have also been investigated under the same conditions. A mechanism is proposed which accounts satisfactorily for the kinetic data. Fe^{3+} reacts with the fully protonated forms of H_2hto, H_2phto and H_2dppto with rate constants of 110, 97.4 and 61.9 mol^{-1} s^{-1}, respectively, while $Fe(OH)^{2+}$ reacts with the fully protonated forms of H_2hto, H_2phto and H_2dppto with rate constants of 1.86×10^3, 1.13×10^3 and 0.910×10^3 dm^3 mol^{-1} s^{-1}, respectively.

Introduction

We have recently reported the kinetics and mechanisms of the reactions of nickel(II) [1–3], cobalt(II) [1–3], copper(II) [4] and dioxouranium(VI) [5] with a series of triketones. In general, complex formation reactions of nickel(II), cobalt(II) and copper(II) take place via an I_d mechanism [6, 7] so that the rate constants should be similar to those predicted by the Eigen–Wilkins–Tamm mechanism. The position is much less clear in the case of dioxouranium(VI) [5, 8]. In our investigations, it was shown that the rate constants for reaction of Ni^{2+}, Co^{2+} and Cu^{2+} with the mono-anions derived from the triketones were broadly in agreement with those predicted on the basis of the solvent exchange rates and the outer-sphere association constant. The rate of reaction of $[UO_2]^{2+}$ with the mono-anions appeared to be greater than would be expected from predictions based solely on the above criteria. However, all the metal ions reacted with the fully protonated forms of the ligands at rates that were much less than the rates of solvent exchange.

In 1974 it was first pointed out that the rates of substitution of water by other ligands in aqueous solutions of $[Fe(H_2O)_5OH]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ were consistent with dissociative activation in the former and associative activation in the latter [9]. Grant and Jordan [10] measured the rates of water exchange on both the above iron(III) species and on the basis of their own results together with a consideration of published data on the rates of formation of iron(III) complexes, they reached a conclusion similar to that of Swaddle. Swaddle and Merbach subsequently extended the atmospheric pressure study of Grant and Jordan to higher pressures and reported the volumes of activation for water exchange on $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5OH]^{2+}$ to be -5.4 and $+7.0$ cm^3 mol^{-1}, respectively [11]. These data confirmed the associative (I_a) and dissociative (I_d) modes of reaction of $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5OH]^{2+}$, respectively, in aqueous solution. However, in bulky solvents, the situation is less clear [12].

The reactions of iron(III) are of considerable interest in the light of the above results and since the work of Swaddle and Merbach a number of other workers have studied the complex formation reactions of iron(III) in various solvents [13–17]. In addition, it has previously been shown that the rate constants for complex formation reactions of many metal ions with protonated ligands are considerably less than those predicted on the basis of the Ei-

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gen–Wilkins–Tamm mechanism [6]. Interestingly however, Fe^{3+} complex formation reactions with protonated ligands are considerably less retarded than those of many other metal ions [18–20]. Consequently, an investigation of the kinetics and mechanisms of the reactions of iron(III) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) was pertinent. These results are also important for a full understanding of the electron transfer reactions of these complexes [21].

Experimental

H_2hto was prepared according to the method of Bethell and Maitland [22] and was purified prior to use by distillation under reduced pressure. H_2phto was prepared by condensation of pentane-2,4-dione with methyl benzoate as described by Hauser *et al.* [23]. H_2dppto was prepared by condensation of 1-phenyl-butane-1,3-dione with methyl benzoate as described by Hauser *et al.* [23]. Stock solutions of iron(III) were prepared from AnalaR grade $Fe(ClO_4)_3 \cdot 6H_2O$ (Johnson Matthey). These solutions were standardized by reaction with excess potassium iodide. The liberated iodine was titrated with standard sodium thiosulfate solution using starch as an indicator. Stock solutions of sodium hydroxide were prepared from reagent grade NaOH (Riedel–de Haën). The solutions were decarbonated by passing them over Zerolit FF anion exchange resin which had been preconditioned with 2 mol dm^{-3} sodium hydroxide. The sodium hydroxide was then standardized against AnalaR grade potassium hydrogen phthalate (BDH).

All the investigations were carried out in methanol:water solutions (70:30 vol./vol.). The ligands and their iron(III) complexes have sufficient solubility in this medium to enable equilibrium and kinetic investigations to be carried out. The ionic strength of all solutions was adjusted to 0.5 mol dm^{-3} using reagent grade sodium perchlorate (Riedel–de Haën).

UV–Vis spectra were recorded on a Shimadzu UV260 spectrophotometer. pH measurements were made with a PTI6 pH meter equipped with a Russell combination electrode. The filling solution of the reference section was a 3 mol dm^{-3} aqueous solution of sodium chloride. The pH meter was calibrated to read hydrogen ion concentration directly by titrating solutions of perchloric acid (0.001–0.005 mol dm^{-3}) with standard sodium hydroxide solutions. The endpoints of these titrations were determined using the method of Johansson [24].

Metal ions stability constants were determined using both spectrophotometric and potentiometric methods. Stability constant refinement was carried out using the computer programs SUPERQUAD [25] and SQUAD [26]. The details of the ligand and metal concentrations used are shown in Table 1.

The hydrolysis constant (K_h) of iron(III) in methanol–water (70:30 vol./vol.) was determined by recording ten spectra of a solution of iron(III) (4.0×10^{-4} mol dm^{-3}) at hydrogen ion concentrations which varied from 0.02 to 0.001 mol dm^{-3}. The molar absorptivities of $[Fe(H_2O)_6]^{3+}$ at various wavelengths were determined by recording a spectrum of 0.001 mol dm^{-3} iron(III) in 0.5 mol dm^{-3} $HClO_4$. At this hydrogen ion concentration, the concentrations of hydrolytic species were negligible. The spectral data were refined using SQUAD [26].

Kinetic measurements were made on a Hi-Tech SF-20 stopped-flow apparatus interfaced to a BBC microcomputer. Pseudo-first-order rate constants were calculated by fitting the absorbance data (70–100 data points) to eqn. (1) using a three-parameter curve-fitting routine in which the absorbance at zero time, A_0, the absorbance at infinite time, A_∞, and the rate constants k were treated as variables. Data for from three to four reaction half-lives were used in these calculations. The reported rate constants are the average of at least three determinations. The standard deviations in individual runs were usually less than 1%.

$$A = A_\infty(1 - \exp(-kt)) + A_0\exp(-kt) \qquad (1)$$

Results and discussion

Table 1 lists the equilibrium data for the 1:1 complexes of iron(III) with H_2hto, H_2phto and H_2dppto. The equilibrium constants for formation of the 1:1 complexes with Fe^{3+} are much greater than those for either the copper(II) or dioxouranium(VI) complexes. For H_2hto for example, log β_1(copper(II)) is 8.99 [4] while log β_1(dioxouranium(VI)) is 8.48 [5]. The order of stability of the iron(III) complexes is $H_2\text{hto} \sim H_2\text{phto} > H_2\text{dppto}$. The value obtained for the hydrolysis constant of Fe^{3+} ($\log K_h = -1.79 \pm 0.01$) is much greater in methanol:water (70:30 vol./vol.) than in water ($\log K_h = -2.73$ [27]). At $-\log[H^+]$ concentrations greater than 1, $[Fe(H_2O)_5OH]^{2+}$ becomes an important reacting species.

Potentiometric titrations of methanol:water (70:30 vol./vol.) solutions of $[Fe(Hhto)]^{2+}$ in the concentration range 0.001–0.003 mol dm^{-3} were carried out using sodium hydroxide as titrant. Using SUPERQUAD, an extensive analysis of the data was carried out. It was found that $[Fe(Hhto)]^{2+}$ consumes two moles of sodium hydroxide per mole of complex

TABLE 1. Equilibrium data for reaction of iron(III) with triketones

	H_2hto	H_2phto	H_2dppto
Solution composition (mol dm^{-3})			
$[T_L]$ range		1.00×10^{-4}–2.00×10^{-4}	
$[T_M]$ range		2.50×10^{-5}–8.00×10^{-4}	
ionic strength, electrolyte		0.5 $NaClO_4$	
$[H^+]$		≈ 0.50	
Experimental method		spectrophotometric determination	
Temperature (°C)		25	
Total number of data points	160	160	160
Method of calculation		SQUAD [26]	
Stability constants log β_{MHL}	12.24 ± 0.02	12.30 ± 0.02	11.84 ± 0.01

between pH 2.2 and 5.0. Under the experimental conditions used for these titrations, formation of $[Fe(Hhto)]^{2+}$ is complete at pH 2.2. Rather surprisingly, it appears that the loss of the two protons is a concerted process and despite all efforts is proved impossible to resolve the two equilibrium constants. One composite equilibrium was obtained for the process represented by eqn. (2). The log of the equilibrium constant for eqn. (3) is 5.28 ± 0.04.

$$Fe^{3+} + Hhto^- + 2H_2O \rightleftharpoons [Fe(Hhto)(OH)_2] + 2H^+ \quad (2)$$

The hydrolysis product in eqn. (2) could reasonably be formulated as $[Fe(Hhto)(OH)_2]$ or as $[Fe(hto)(OH)]$. The former represents the situation where two coordinated water molecules on the iron are hydrolyzed while the latter represents the situation where one coordinated water molecule on the iron is hydrolyzed concurrently with loss of the second acidic proton from the ligand. Initially, it did not prove possible to determine which of these formulations was correct. However, an investigation of the hydrolysis of the monocomplex for Fe^{3+} with 1-phenyl-1,3-butanedione (Hpbd) gave a similar result with only one equilibrium constant corresponding to the formation of $[Fe(pbd)(OH)_2]$ being resolved [28]. In this instance, this is the only reasonable formulation of the hydrolysis as there is no dissociable ligand proton in $[Fe(pbd)]^{2+}$. Therefore, it is reasonable to assume that the correct formulation of the hydrolytic species in the present investigation is $[Fe(Hhto)(OH)_2]$. Experiments at different iron(III) concentrations gave no evidence of dimer formation.

When solutions of the ligands were reacted with solutions containing a pseudo-first-order excess of iron(III) in the stopped-flow apparatus, a single first-order reaction was observed. Table 2 lists the kinetic data for formation of the 1:1 complexes with all three ligands. The mechanism proposed to account for the kinetic data is shown in Scheme 1. In this Scheme, H_2L represents the triketone.

For the mechanism in Scheme 1, assuming that the reactions go to completion, k_{obs} has the form of eqn. (3), K_a is the first dissociation constant of the ligand*, K_h is the hydrolysis constant of Fe^{3+} and $[Fe^{III}]_0$ is the total iron(III) concentration.

$$k_{obs} = \frac{[Fe^{III}]_0}{\{1+K_h/[H^+]\}}\left[k_1 + \frac{k_2K_a + k_3K_h}{[H^+]}\right] \quad (3)$$

Equation (3) predicts that a plot of k_{obs} against $[Fe^{III}]_0/\{1+K_h/[H^+]\}$ at constant $[H^+]$ should give a straight line having zero intercept and slope $\{k_1 + (k_2K_a + k_3K_h)[H^+]^{-1}\}$. Figures 1, 2 and 3 show this to be the case for all three ligands. A plot of the slopes of the lines in Figs. 1–3 against $1/[H^+]$ should give straight lines with intercepts of k_1 and slopes of $(k_2K_a + k_3K_h)$. Figure 4 shows this to be the case.

The kinetic data were fitted to eqn. (3) using a two-parameter curve-fitting routine in which k_1 and $(k_2K_a + k_3K_h)$ were treated as variables. The values obtained for k_1 using this procedure are given in Table 3. $(k_2K_a + k_3K_h)$ was found to be 30.2 (±0.4), 18.4 (±0.3) and 14.8 (±0.2) for H_2hto, H_2phto and H_2dppto, respectively. These values are in good

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*$10^{-8.27}$ for H_2hto and H_2dppto and $10^{-8.39}$ for H_2phto [29].

TABLE 2. Kinetic data for reaction of iron(III) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) at 25 °C and $I=0.5$ mol dm^{-3}

Ligand	$10^3\times[Fe^{III}]$ (mol dm^{-3})	$10^2\times[H^+]$ (mol dm^{-3})	k_{obs} (s^{-1})	k_{calc}[a] (s^{-1})
H_2hto[b]	0.495	10.0	0.176	0.175
	0.792	10.0	0.257	0.280
	1.19	10.0	0.404	0.420
	1.58	10.0	0.516	0.561
	1.98	10.0	0.626	0.700
	0.495	5.00	0.274	0.267
	0.792	5.00	0.440	0.427
	1.19	5.00	0.617	0.640
	1.58	5.00	0.848	0.854
	1.98	5.00	1.15	1.07
	0.502	2.38	0.443	0.412
	1.00	2.38	0.862	0.824
	1.51	2.38	1.32	1.24
	1.93	2.38	1.64	1.59
	0.502	1.39	0.524	0.529
	1.00	1.39	1.06	1.06
	1.51	1.39	1.62	1.59
	1.93	1.39	2.08	2.04
	0.495	1.00	0.550	0.593
	0.792	1.00	0.890	0.949
	1.19	1.00	1.38	1.42
	1.58	1.00	1.88	1.89
	1.98	1.00	2.30	2.37
H_2phto[c]	0.495	9.70	0.124	0.122
	0.792	9.70	0.208	0.195
	1.19	9.70	0.283	0.292
	1.58	9.70	0.393	0.390
	1.98	9.70	0.466	0.487
	0.495	4.85	0.192	0.177
	0.792	4.85	0.300	0.283
	1.19	4.85	0.434	0.425
	1.58	4.85	0.557	0.566
	1.98	4.85	0.670	0.700
	0.502	2.38	0.277	0.260
	1.00	2.38	0.560	0.520
	1.51	2.38	0.825	0.780
	1.93	2.38	1.05	1.00
	0.502	1.39	0.300	0.329
	1.00	1.39	0.650	0.658
	1.51	1.39	0.980	0.988
	1.93	1.39	1.23	1.26
	0.495	1.00	0.360	0.367
	0.792	1.00	0.610	0.587
	1.19	1.00	0.840	0.880
	1.58	1.00	1.22	1.17
	1.98	1.00	1.44	1.46
H_2dppto[d]	0.495	9.70	0.090	0.091
	0.792	9.70	0.124	0.140
	1.19	9.70	0.201	0.218
	1.58	9.70	0.267	0.291
	1.98	9.70	0.354	0.364
	0.495	4.85	0.131	0.136
	0.792	4.85	0.230	0.218
	1.19	4.85	0.325	0.327
	1.58	4.85	0.467	0.436
	1.98	4.85	0.559	0.545
	0.502	2.38	0.215	0.205
	1.00	2.38	0.441	0.410
	1.51	2.38	0.630	0.613
	1.93	2.38	0.800	0.787
	0.502	1.39	0.273	0.262
	1.00	1.39	0.536	0.523
	1.51	1.39	0.765	0.785
	1.93	1.39	1.00	1.01
	0.495	1.00	0.300	0.293
	0.792	1.00	0.477	0.468
	1.19	1.00	0.687	0.702
	1.58	1.00	0.951	0.936
	1.98	1.00	1.14	1.17

[a]On the basis of Scheme 1. [b]$\lambda=470$ nm. [c]$\lambda=540$ nm. [d]$\lambda=580$ nm.

$$\begin{tikzcd}
Fe^{3+}+H_2L \arrow[r, "k_1"] \arrow[d, shift right, "K_a"'] & {[Fe(HL)]^{2+}+H^+} \\
Fe^{3+}+HL^- \arrow[r, "k_2"] \arrow[u, shift right] \arrow[d, shift right, "K_h"'] & Fe(HL)]^{+} \\
Fe(OH)^{2+}+H_2L \arrow[r, "k_3"] \arrow[u, shift right] & {[Fe(HL)]^{2+}+H_2O}
\end{tikzcd}$$

Scheme 1.

agreement with the values obtained from the slopes of the plots in Figs. 1–3. k_2 and k_3 represent alternative formulations of the inverse-acid pathway. The k_2 pathway represents reaction of Fe^{3+} with the monoanion of the triketone while the k_2 pathway involves reaction of $Fe(OH)^{2+}$ with the fully protonated form of the ligand. If the former formulation is adopted for the acid dependent path, k_2 is obtained, whereas the latter formulation gives the value of k_3. The results of these calculations are shown in Table 3.

In general, the oxygen in alcohols is a weaker donor than the oxygen in water and many workers have found that water is strongly preferred to alcohols in the inner coordination sphere of transition metal ions [30–34]. In the case of Ni^{2+}, MacKellar and Rorabacher stated [34] that for relatively low nickel concentrations, only the nickel species containing zero, one and two methanol molecules need be considered up to 95% methanol or greater. Although no such studies have been carried out for Fe^{3+}, studies on Cr^{3+} [31, 33] have shown that a similar situation obtains. At mole fractions of methanol in the region of 0.51 (the mole fraction used in the

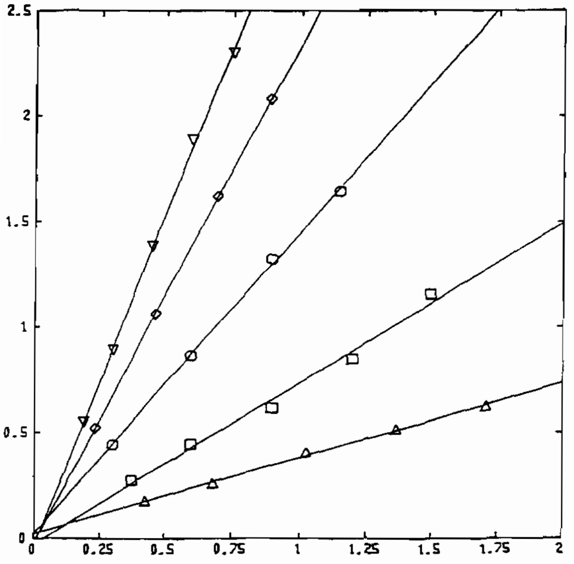

Fig. 1. Plot suggested by eqn. (3) for reaction of iron(III) with heptane-2,4,6-trione (H_2hto) in methanol:water solution (70:30 vol./vol) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$. $[H^+] = 0.100$ (△), 0.050 (□), 0.0238 (○), 0.0139 (◇), and 0.010 (▽) mol dm^{-3}. x axis: $10^3[Fe^{III}]_0/(1 + K_h/[H^+]]$; y axis: k_{obs} (s^{-1}).

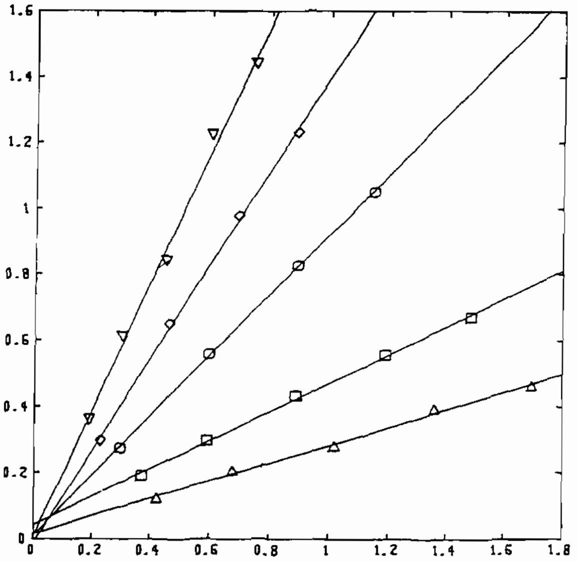

Fig. 2. Plot suggested by eqn. (3) for reaction of iron(III) with 1-phenylhexane-1,3,5-trione (H_2phto) in methanol:water solution (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$. $[H^+] = 0.097$ (△), 0.0485 (□), 0.0238 (○), 0.0139 (◇), and 0.010 (▽) mol dm^{-3}. x axis: $10^3[Fe^{III}]_0/(1 + K_h/[H^+]]$; y axis: k_{obs} (s^{-1}).

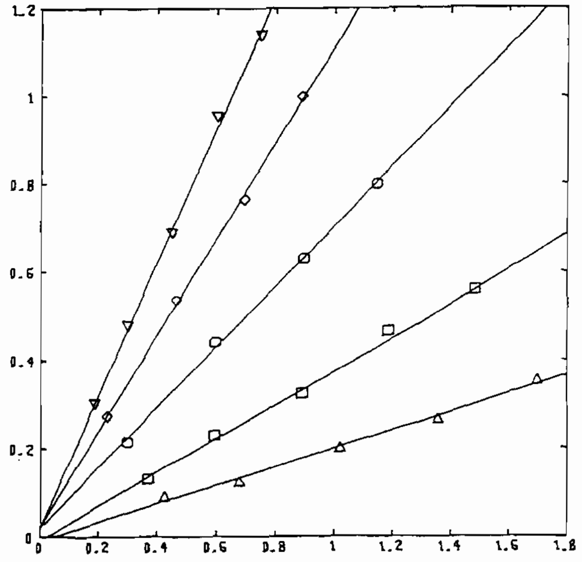

Fig. 3. Plot suggested by eqn. (3) for reaction of iron(III) with 1,5-diphenylpentane-1,3,5-trione (H_2dppto) methanol:water solution (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$. $[H^+] = 0.097$ (△), 0.0485 (□), 0.0238 (○), 0.0139 (◇), and 0.010 (▽) mol dm^{-3}. x axis: $10^3[Fe^{III}]_0/(1 + K_h/[H^+]]$; y axis: k_{obs} (s^{-1}).

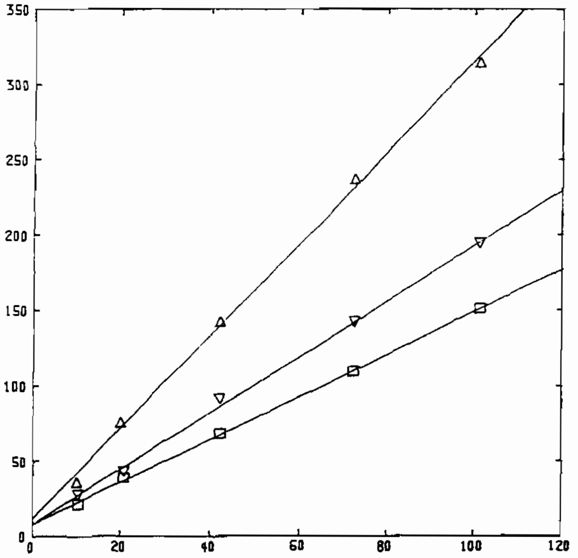

Fig. 4. Plots of the slopes obtained from Figs. 1–3 against $1/[H^+]$ for reaction of iron(III) with heptane-2,4,6-trione (△), 1-phenylhexane-1,3,5-trione (▽) and 1,5-diphenylpentane-1,3,5-trione (□) in methanol:water solution (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$. x axis: 10^{-1} slope; y axis: $1/[H^+]$ (mol^{-1} dm^3).

present investigation), chromium species containing zero and one molecule of methanol predominate. The situation is unlikely to be different for iron(III).

MacKellar and Rorabacher have carried out a careful study of the kinetics of solvated nickel(II) reacting with ammonia in methanol–water mixtures ranging from 0 to 97% ethanol by weight [34]. They have shown that for the solvent composition used in the present investigation, the outer-sphere association constant will not differ greatly from that

TABLE 3. Summary of the rate constants for formation of the monocomplexes of iron(III) with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) at 25 °C and $I=0.5$ mol dm^{-3}

Rate constant ($dm^3\ mol^{-1}\ s^{-1}$)	H_2hto	H_2phto	H_2dppto
k_1	110.0 ± 15	97.4 ± 11	61.9 ± 6.6
k_2	5.63×10^9	4.52×10^9	2.76×10^9
k_3	1.86×10^3	1.13×10^3	0.91×10^3

in pure water. Similar arguments apply to iron(III). In the case of solvent exchange on Ni^{2+}, previous calculations [1, 34] have shown that the rate of solvent exchange in methanol:water (70:30 vol./vol.), is approximately twice that in pure water. The symmetrical occupancy of the d-orbitals suggests that the situation is unlikely to be greatly different for iron(III). In view of the foregoing, the water exchange rates on Fe^{3+} and $Fe(OH)^{2+}$ form a reasonable basis for a discussion of the kinetic results obtained in the present investigation.

The rate constants for water exchange on $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ are 160 s^{-1} ($\Delta V^{\ddagger}=-5.4$ cm^3 mol^{-1}) and 1.2×10^5 s^{-1} ($\Delta V^{\ddagger}=+7.0$ cm^3 mol^{-1}), respectively [11]. For complex formation reactions which obey the Eigen–Wilkins–Tamm mechanism, the rate of complex formation k_f is given by eqn. (4) [35] where K_{os} is the outer-sphere association constant and k^{M-S} is the rate constant for solvent exchange.

$$k_f=(3/4)K_{os}k^{M-S} \tag{4}$$

The values of K_{os}, the outer-sphere association constants for $+3/0$ and $+3/-1$ interactions at an ionic strength of 0.5 mol dm^{-3} and distance of closest approach of 6 Å, are approximately 0.5 and 3.7 dm^3 mol^{-1}, respectively. The value of K_{os} for a $+2/0$ interaction is approximately 0.5 dm^3 mol^{-1}. However, in the case of $[Fe(H_2O)_6(OH)]^{2+}$, this may be enhanced due to interaction of the OH group with the ligand. The data in Table 3 demonstrate that reaction of Fe^{3+} with the fully protonated form of all three ligands proceeds at rates that are comparable to those predicted by the Eigen–Wilkins–Tamm mechanism, eqn. (4).

Assuming that the inverse acid pathway involves reaction of Fe^{3+} with HL^-, the values obtained for k_2 (Table 3) are close to diffusion controlled and this pathway will not therefore by considered further. Consequently, the inverse-acid pathway must involve reaction of $[Fe(H_2O)_5(OH)]^{2+}$ with H_2L, the fully protonated form of the triketone.

The reactions of Fe^{3+} with the fully protonated triketones appear to be 'normal' when compared to the rate constants predicted on the basis of the Eigen–Wilkins mechanism. This is quite different to the results obtained for the same reactions when either Ni^{2+}, Co^{2+} or Cu^{2+} was the metal ion [1–4]. For the latter reactions, retardation factors of 10^2–10^4 were obtained. There may be a number of reasons for this. Firstly, complex formation reactions of Fe^{3+} frequently proceed via an I_a mechanism [7] in which case the rate of solvent exchange will not be rate determining. Consequently, caution must be exercised when comparing the reactivity of Fe^{3+} with the reactivities of labile metal ions such as Ni^{2+}, Co^{2+} and Cu^{2+} which react by an I_d mechanism.

Some of the factors which must be considered when dealing with the kinetics of metal–complex formation with protonated multidentate ligands include (i) strong intramolecular hydrogen bonds which convert the protonated ligand into a poor entering group; (ii) the energetics of proton release from a unidentate intermediate which may slow down the rate of ring closure (proton controlled ring closure); (iii) ring strain associated with the formation of a six-membered ring. Factor (iii) may be eliminated on the basis that the reactions of most metal ions with the enolate anions of 1,3-diketones proceed at rates close to those predicted by eqn. (4) [20]. Sutin and co-workers have argued that intramolecular hydrogen bonding would not retard complex formation reactions by the three to four orders of magnitude observed for reaction of Ni^{2+} and Co^{2+} with protonated ligands [18]. However, it is clear that there is considerable variation in the degree to which complex formation reactions with protonated ligands are retarded compared to predictions based on eqn. (4) [20].

The present results may be reasonably rationalized in terms of the stability of a precursor complex formed as the first step in the reaction between the metal ion and the triketone, an idea originally proposed by Pearson and Anderson [36]. The stability of such a complex might be expected to be related to the hard-acid hard-base compatibility of the reacting species as outlined by a number of authors in the case of β-diketones [20]. β-δ-triketones have hard characteristics. Consequently, the most stable metal complexes would be expected to be formed by hard metal ions such as Fe^{3+} and consequently, thc degree of retardation of complex formation rate constants should be least for these metal ions.

Due to the higher charge on Fe^{3+}, the poor entering ability of the ligand may not be as apparent during initial bond formation. The metal is more likely to be able to disrupt and overcome intramolecular hydrogen bonding in the ligand, thus reducing the retardation factor. Finally Fe^{3+} is less labile than either Ni^{2+}, Co^{2+} or Cu^{2+}, therefore the retardation in its reactions may not be as readily apparent as in the case of the more labile metal ions.

It has been shown that $[Fe(H_2O)_5(OH)]^{2+}$ reacts via an I_d mechanism [7] so that the values of k_3 are rather low when compared to the values predicted by eqn. (4). The retardation factor would appear to be of the order of 10^2 even allowing for the uncertainty of the solvent exchange rate in methanol:water (70:30 vol./vol.). Thus the reactivity of $[Fe(H_2O)_5(OH)]^{2+}$ towards triketones is rather similar to that of other +2 metal ions in that the rate constants for complex formation are lower than predicted on the basis of an I_d mechanism similar to that operative for complex formation reactions of nickel(II).

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