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Inorganica Chimica Acta 342 (2003) 97-106

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Kinetics and mechanism of ligand substitution in β-diketone complexes of iron(III).Solvolysis controlling the substitution process in alcohol media

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Received 4 February 2002; accepted 24 May 2002

Abstract

Conventional and stopped-flow spectrophotometry was used to study the kinetics of ligand substitution in a number of tris β -diketone iron(III) complexes, Fe(O^O)_3, by 8-hydroxyquinoline (=HO^N) in alcohol media (O^O^- = anion of the β -diketones pentane-2,4-dione, 2,6-dimethylheptane-3,5-dione, 2,2,6,6-tetramethylheptane-3,5-dione, 1-phenylbutane-1,3-dione, 1,3-diphenyl-propane-2,3-dione, and 1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dione). As shown by spectrophotometry, the solutions of complexes Fe(O^O)_3 in alcohols ROH are subject to solvolytic dissociation, leading to solvento species Fe(O^O)_2S_2 and to binuclear complexes [Fe(O^O)_2(RO)]_2 (S = ROH and RO^-, respectively). The reaction of complexes Fe(O^O)_3 with HO^N in alcohol media, leading to Fe(O^N)_3, is triphasic. The corresponding first-order rate constants k_1 , k_2 , and k_3 are independent of the concentration of the entering ligand HO^N and follow the order $k_1 > k_2 > k_3$, with $k_1/k_2 \approx 10$ and $k_1/k_3 \approx 10^2$. For a given system Fe(O^O)_3/HO^N/ROH, the size of k_1 , k_2 , and k_3 correlates with the solvent polarity parameter $E_T(30)$. Rate constant k_1 describes the solvolytic dissociation of the complexes Fe(O^O)_3 and rate constant k_3 the solvent-initiated splitting of the binuclear complexes [Fe(O^O)_2(RO)]_2. Rate constant k_2 is assigned to the solvolytic dissociation of the intermediate complex Fe(O^O)_2(O^N). Depending on the nature of the coordinated β -diketone and solvent ROH, k_1 ranges from 0.04 to 2 s⁻¹, k_2 from 0.007 to 0.2 s⁻¹, and k_3 from 0.002 to 0.01 s⁻¹ at 298 K. The mechanism of the ligand substitution processes is discussed.

Keywords: Iron(III) complexes; β-diketones; Ligand substitution; Kinetics; Mechanism

1. Introduction

One of the most conspicuous features of ferric ion in aqueous solution is its tendency to hydrolyze [1]. In the course of hydroysis doubly bridged μ -hydroxo and/or μ oxo complexes such as 1 and 2 (see Chart 1) are formed that can be structurally described as two edge sharing octahedra. In alcohol media, alcoholysis of ferric ion leads to the corresponding μ -alkoxo complexes 3. Binuclear iron(III) complexes such as 1–3 are receiving considerable attention because of their possible relevance to the understanding of certain aspects of the biochemistry of iron. The correlation of magnetic and structural properties of these complexes has therefore been studied intensively [2-4].

In earlier studies [5] we investigated the kinetics and mechanism of ligand substitution in neutral bis chelate complexes MA_2 in organic media according to Eq. (1)

$$MA_2 + 2HB \rightleftharpoons MB_2 + 2HA \tag{1}$$

(M = divalent metal; HA, HB = N-alkylsalicylaldimines). These studies showed that the rate of substitution follows a two-term rate law, rate = $(k_s + k_{HB} \times$ [HB]) × [MA₂], composed of a 'solvent path', $k_s \times$ [MA₂], and a 'ligand path', $k_{HB} \times$ [HB] × [MA₂]. In alcohol media, the solvent-initiated rate contribution, $k_s \times$ [MA₂], dominates for M = Cu(II) and Ni(II) [5a]. The size of rate constant k_s depends characteristically on the acidity of the alcohol ROH applied as solvent [5a,5c,5f,5g] and for acetonitrile–alcohol solvent mixtures it was shown that the rate of substitution is first-

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Chart 1. Binuclear μ -hydroxo, μ -oxo and μ -alkoxo complexes of iron(III) (L = H₂O, monodentate or bidentate ligand).

order in alcohol, according to rate $= k_{\text{ROH}} \times [\text{ROH}] \times [\text{MA}_2]$ [5a]. Furthermore, the appearance of mass law retardation suggested that, in alcohol media such as methanol, solvento species CuA(CH₃O)(CH₃OH) are formed as intermediates [5d].

The active role of alcohol solvents in the kinetics of ligand substitution in four-coordinate bis chelate complexes CuA₂ and NiA₂ (HA = *N*-alkylsalicylaldimine) led us to extend this sort of study in alcohol media to the kinetics of substitution in neutral octahedral chelate complexes of iron(III) and in the corresponding binuclear iron(III) complexes according to Eq. (2) and (3), respectively. Complexes Fe(O^OO)₃ are tris β -diketone complexes of iron(III) that react with an excess of

$$Fe(O^{\frown}O)_{3} + 3HO^{\frown}N \xrightarrow{ROH} Fe(O^{\frown}N)_{3} + 3HO^{\frown}O$$
(2)

$$[Fe(O^{\circ}O)_{2}(RO)]_{2} + 6HO^{\circ}N \xrightarrow{ROH} 2Fe(O^{\circ}N)_{3} + 4HO^{\circ}O + 2ROH$$
(3)

8-hydroxyquinoline (=HO^N) to form the complex Fe(O^N)₃. The β -diketonate complexes of iron(III) were chosen for two reasons, namely, (i) in addition to HO^OO = pentane-2,4-dione (acetylacetone), there are numerous derivatives of this β -diketone, differing in acidity and thus allowing the investigation of a broad range of complexes Fe(O^OO)₃, and (ii) in the literature, detailed information on binuclear β -diketone alcoxo complexes [Fe(O^OO)₂(OR)]₂ is available [6,4], which means that this type of complex, anticipated to be formed in alcohol solutions of complexes Fe(O^OO)₃, can be studied separately according to Eq. (3).

The present contribution summarizes the results obtained in the investigation of the alcoholysis of a variety of complexes $Fe(O^{\circ}O)_3$ and $[Fe(O^{\circ}O)_2(OR)]_2$ (see Chart 2, [7]) and the kinetics of ligand substituion in complexes $Fe(O^{\circ}O)_3$ and $[Fe(O^{\circ}O)_2(OR)]_2$ according to Eq. (2) and (3), as studied in a series of alcohol solvents. The results are discussed mechanistically, with the difference in reactivity between mono nuclear complexes $Fe(O^{\circ}O)_3$ and binuclear complexes $[Fe(O^{\circ}O)_2(OR)]_2$ being a focus of attention. The kinetic data are compared with those in the literature [8] on ligand exchange and substitution in complexes $Fe(O^{\circ}O)_3$, as obtained in aprotic organic media.

<u>ß-diketones</u>	\mathbf{R}^1	R^2	ноо		
	Me	Me	Hacac		
1 2	<i>i</i> -Pr	<i>i</i> -Pr	Hdibm		
	<i>t</i> -Bu	<i>t</i> -Bu	Hdpm		
88	Me	Ph	Hbza		
	Ph	Ph	Hdbm		
	\sqrt{s}	CF ₃	Httfa		
complexes					
Fe(acac)) ₃ Fe(dit	om) ₃	Fe(dpm) ₃		
Fe(bza)	, Fe(db	om) ₃	Fe(ttfa) ₃		
$[Fe(acac)_2(EtO)]_2 [Fe(dpm)_2(MeO)]_2$					

Chart 2. β -Diketone ligands HO^{\circ}O^a and iron(III) complexes. ^a For abbreviations, see Ref. [7].

2. Experimental

2.1. Solvents and ligands

The solvents MeOH, EtOH, PrOH, *i*-PrOH, BuOH, and *t*-PeOH, the β -diketones Hacac, Hbza, and Httfa and the ligand HO^{\circ}N [6] were commercially available in reagent grade quality; they were used without further purification. Commercial HpOH and 3-PeOH were distilled before use (bp 93 °C/16 mm Hg and bp 115 °C, respectively). Commercial Hdbm (EGA-Chemie) was recrystallized from EtOH (mp 78 °C) and commercial Hdpm (EGA-Chemie) was distilled (bp 58 °C/2 mm Hg). The β -diketone Hdibm was prepared from 2-methylpropionic acid methyl ester and 3-methyl-2-butanone as described [9].

2.2. Complexes

Based on a corresponding note in the literature [10], the complexes $Fe(O^O)_3$, listed in Chart 2, and the complex $Fe(O^N)_3$ were prepared from the ligands HO^O and HO^N and the iron(III) salt of 2-ethylhexanoic acid, $Fe(ehx)_3$ [7] (Ventron Alfa) according to Eq. (4) and (5), respectively. The binuclear complexes [Fe(acac)₂(EtO)]₂ and [Fe(dpm)₂(MeO)]₂ (see Chart 2) were prepared according to Eq. (6).

$$Fe(ehx)_3 + 3HO^{\circ}O \rightarrow Fe(O^{\circ}O)_3 + 3Hehx$$
(4)

$$Fe(ehx)_3 + 3HO^{\circ}N \rightarrow Fe(O^{\circ}N)_3 + 3Hehx$$
(5)



The purity of all of the iron complexes listed in Chart 2 and of the complex $Fe(O^{\cap}N)_3$ was confirmed by elemental analysis (C,H,N).

2.2.1. Procedure for complexes $Fe(O^{\cap}O)_3$ and $Fe(O^{\cap}N)_3$

A solution of 0.01 mol of Fe(ehx)₃ in 100 ml of petrol ether (bp 120–140 °C) is dropwise added to a warm solution (70–80 °C) of 0.03 mol of the corresponding ligand in 60 ml of dry toluene under stirring. Precipitation of the product Fe(O^OO)₃ and Fe(O^ON)₃, respectively, begins upon addition of the iron salt and is completed by cooling of the reaction mixture. The product is separated by filtration and recrystallized from toluene, petrol ether or a mixture of both solvents (yield: 70–90%). For final purification the complexes Fe(dpm)₃ and Fe(dibm)₃ are sublimed in vacuo.

2.2.2. Procedure for complexes $[Fe(O^{\cap}O)_2(RO)]_2$

A 0.5 M solution of NaOR in ROH (prepared by dissolution of the corresponding amount of Na in dry ROH and calibrated by titration) is added dropwise to a solution of 0.003 mol of $Fe(O^O)_3$ in 30–60 ml of ROH under stirring, until the equivalent of 0.003 mol of NaOR has been added. After stirring for another 30 min at ambient temperature, the reaction mixture is cooled for 15 h. The precipitate is separated by filtration and washed repeatedly with cold ROH (yield: 60–80%).

2.3. Instrumentation

UV–Vis spectra: diode array spectrophotometer (HP, type 8451A); kinetic measurements: diode array spectrophotometer for reactions with $t_{1/2} > 3$ min and modified [5a] stopped-flow spetrophotometer (Durrum, D110) for faster reactions.

2.4. Rate constants for ligand substitution

The kinetics of ligand substitution according to Eq. (2) and (3), as monitored spectrophotometrically in alcohol solution, were studied under pseudo-first-order conditions ([HO^{\circ}N]₀ > 10 × [iron complex]₀). The (*A*, *t*) data obtained (*A* = absorbance) were computer-fitted to one of the Eqs. (7)–(9) to obtain the experimental rate constants k_{obsd} . The programs used were based on the least-squares method. The parameters A_0 and A_{∞} refer to the absorbance at t = 0 and $t = \infty$, respectively, and the amplitudes a_1 , a_2 and a_3 describe the relative contributions of the single exponentials to the overall absorbance.

$$A = (A_0 - A_\infty) \times [\exp(-k_{\text{obsd}} \times t)] + A_\infty$$
(7)

$$A = a_1 \times [\exp(-k_{obsd(1)} \times t)] + a_2$$

$$\times [\exp(-k_{obsd(2)} \times t] + A_{\infty} \qquad (8)$$

$$A = a_1 \times [\exp(-k_{obsd(1)} \times t)] + a_2 \times [\exp(-k_{obsd(2)} \times t)]$$

$$+ a_3 [\exp(-k_{obsd(3)} \times t)] + A_{\infty} \qquad (9)$$

3. Results and discussion

3.1. UV–Vis absorption of the complexes

All of the iron(III) complexes listed in Chart 2 represent high-spin d⁵ systems for the absorption spectra of which ligand field bands are not to be expected. The intensive absorption bands in the wavelength range 250-700 nm, observed for solutions of the complexes $Fe(O^{\cap}O)_3$ and $[Fe(O^{\cap}O)_2(RO)]_2$ in the non-coordinating solvent dichloromethane (see Table 1), are based on ligand excitation and charge transfer of both the $M \rightarrow L$ and $M \leftarrow L$ type [11,12]. Modification of the alkyl according to the series $Fe(acac)_3 \rightarrow$ groups $Fe(dibm)_3 \rightarrow Fe(dpm)_3$ (corresponding to $R^1 = R^2 =$ methyl, i-propyl and t-butyl, respectively; see Chart 2) has practically no effect on the absorption spectra, characterized by absorption bands at approximately 270, 350 and 440 nm. The introduction of phenyl groups, as in Fe(bza)₃ and Fe(dbm)₃, causes however a small red shift of these three characteristic bands. The spectra of the binuclear complexes [Fe(acac)₂(EtO)]₂ and [Fe(dpm)₂(MeO)]₂ are practically identical and only slightly different from those of the mononuclear complexes $Fe(acac)_3$ and $Fe(dpm)_3$. The absorption of the complex $Fe(O^{\cap}N)_3$, generated as product in substitution reactions (2) and (3), is characterized by four bands in the range 300-600 nm, which allows convenient spectrophotometric monitoring of the substitution process.

Table 1

UV–Vis absorption data of the various iron complexes in the solvent methylene chloride at 298 K (the data are presented in the form λ_{max} (nm)/ ϵ_{max} (M⁻¹ cm⁻¹))

Fe(acac) ₃	274/25870	354/3500	438/3480	
Fe(dibm) ₃	270/25 880	356/3740	438/3730	
Fe(dpm) ₃	270/25 490	358/3850	434/3780	
[Fe(dpm) ₂ MeO] ₂ ^a	272/16650	354/3230	422/2390	
Fe(bza) ₃	302/39 580	386/6340	452/3790	
Fe(dbm) ₃	314/49 300	408/	471/4070	
		14530	(sh)	
Fe(ttfa) ₃	338/48 200	388/	434/7400	
()3		22730	(sh)	
Fe(O [∩] N) ₃	314/5090 (sh)	368/4570	466/5450	582/
	~ /			3550

^a Absorptivity ε referenced to one iron atom; (sh) = shoulder.

3.2. Solvolysis of the complexes $Fe(O^{\frown}O)_3$ in alcohol media

In protic coordinating solvents such as alcohols, all of the complexes $Fe(O^{\circ}O)_3$ and $[Fe(O^{\circ}O)_2(RO)]_2$ are subject to solvolysis. The absorption spectra of the complexes $Fe(O^{\circ}O)_3$ in alcohol solution are concentration-dependent, as indicated by a decrease of the absorption band at approximately 440 nm with increasing dilution. The nature of the alcohol solvent is essential in that dissociation of the complexes in less polar and less acidic alcohols (such as *t*-PeOH) is less pronounced than in more polar and acidic alcohols (such as MeOH).

The addition of an excess of free ligand Hacac to a dilute solution of $Fe(acac)_3$ in methanol causes a spectral change and the spectrum obtained corresponds to that of $Fe(acac)_3$ in non-coordinating dichloromethane. Furthermore, when an excess of free ligand Hacac is admixed to a dilute solution of the binuclear complex [$Fe(acac)_2(EtO)$]₂ in ethanol, the spectrum obtained again corresponds to that of $Fe(acac)_3$ in dichloromethane. These experimental findings suggest that equilibria (10) and (11) are involved. Condensation and formation of doubly bridged units according to Eq. (11) corresponds to what is well known for iron(III) hydroxo species in aqueous solution [1].



Fig. 1. Spectral changes with time for the reaction of Fe(acac)₃ with HO^{N} in 2-propanol ((1) spectrum before mixing of the reaction partners; (20) spectrum at the end of the reaction; $\Delta t = 5$ s; [Fe(acac)₃] = 1 × 10⁻⁴ M; [HO^{N}] = 2 × 10⁻³ M; 298 K).

For most of the systems $Fe(O^{\circ}O)_3/HO^{\circ}N/ROH$, the kinetics of ligand substitution according to Eq. (2) were found to be triphasic, initiated by a sharp change in absorbance, ΔA , too fast to be followed by stopped-flow spectrophotometry (as an example, see Figure S1). The (A_{580},t) data $(A_{580} = absorbance$ at 580 nm) were satisfyingly fitted with Eq. (9), which led to the experimental rate constants $k_{obsd(1)}$, $k_{obsd(2)}$, and $k_{obsd(3)}$. It was found for all of the complexes Fe(O^{\circ}O)_3 studied

$$\operatorname{Fe}(\overrightarrow{OO})_3 \xrightarrow{\operatorname{ROH}} \operatorname{Fe}(\overrightarrow{OO})_2(\operatorname{ROH})_2^+ + \overrightarrow{OO} \xrightarrow{} \operatorname{Fe}(\overrightarrow{OO})_2(\operatorname{ROH})(\operatorname{RO}) + \operatorname{Ho}$$

$$2 \operatorname{Fe}(OO)_2(\operatorname{ROH})(\operatorname{RO}) \iff [\operatorname{Fe}(OO)_2(\operatorname{RO})]_2 + 2 \operatorname{ROH} (11)$$

3.3. Kinetics of ligand substitution in the complexes $Fe(O^{\cap}O)_3$ according to Eq. (2)

As documented by the overall complex formation constants β_3 for the medium water, the tris 2-hydroxyquinolato complex Fe(O^N)₃ (log $\beta_3 = 36.9$ [13]) is more stable than the complex Fe(acac)₃ (log $\beta_3 = 26.8$ [14]) by ten orders of magnitude. One can expect that the thermodynamic stability of the complex Fe(O^N)₃ exceeds that of Fe(acac)₃ and of the other complexes Fe(O^OO)₃ in alcohol media as well. In agreement with this expectation, ligand substitution according to Eq. (2) in the presence of an excess of the entering ligand HO^N was found to be a practically irreversible process, conveniently traceable at 580 nm by stoppedflow spectrophotometry. As an example, Fig. 1 shows the spectral changes with time for the reaction of Fe(acac)₃ with HO^N in 2-propanol.



Fig. 2. Plot of $k_{obsd(1)}$, $k_{obsd(2)}$, and $k_{obsd(3)}$ vs. $[HO^{\cap}N]$ for the reaction of Fe(acac)₃ with HO^{\(\nef N\)} in MeOH ([Fe(acac)₃] = 1 × 10⁻⁴ M; 298 K).

Table 2

Rate constants k_1 , k_2 and k_3 describing the ligand substitution in the complexes Fe(O^OO)₃ by 8-hydroxyquinoline according to Eq. (2) in methanol at 298 K

Complex	k_1, s^{-1}	k_2, s^{-1}	$10^3 \times k_3, \mathrm{s}^{-1}$
Fe(ttfa) ₃	1.86 ± 0.12	0.114 ± 0.006	9.37 ± 0.40
Fe(acac) ₃	$\begin{array}{c} 1.04 \pm 0.04 \\ 1.06 \pm 0.06 \end{array}^{a} \end{array}$	$\begin{array}{c} 0.171 \pm 0.008 \\ 0.173 \pm 0.018 \end{array} ^{\rm a}$	8.97 ± 0.38 n.o. ^b
Fe(bza) ₃	1.16 ± 0.06	0.115 ± 0.007	9.24 ± 0.46
Fe(dbm) ₃	0.983 ± 0.018	0.090 ± 0.004	7.15 ± 0.24
Fe(dibm) ₃	0.502 ± 0.024	0.102 ± 0.004	14.2 ± 0.6
Fe(dpm) ₃	n.o. ^b	0.082 ± 0.003	6.96 ± 0.52

^a Data obtained in the presence of additional Hacac; see Fig. S2.
 ^b Not observed.

that the size of these experimental rate constants does not depend on the concentration of the entering ligand HO^{\circ}N. As an example, Fig. 2 shows the plot of k_{obsd} versus [HO^{\circ}N] for the reaction of Fe(acac)₃ with HO^{\circ}N in MeOH. The data for k_1 (= mean of $k_{obsd(1)}$), k_2 (= mean of $k_{obsd(2)}$), and k_3 (= mean of $k_{obsd(3)}$), as obtained for the various complexes Fe(O^{\circ}O)₃ in methanol, are summarized in Table 2. It is essential to note that, in the presence of additional Hacac, the triphasic reaction of Fe(acac)₃ with HO^{\circ}N in MeOH becomes biphasic. The slowest k_3 step is no longer observed, whereas the data for k_1 and k_2 agree with those obtained in the absence of additional Hacac.

When studied in branched alcohols such as 2-propanol (and also 3-pentanol and 2-methyl-2-butanol), the



Fig. 3. Plot of $k_{obsd(1)}$ and $k_{obsd(2)}$ vs. [HO^{\land}N] for the reaction of Fe(acac)₃ with HO^{\land}N in 2-propanol ([Fe(acac)₃] = 1 × 10⁻⁴ M; 298 K).

kinetics of ligand substitution in Fe(acac)₃ by HO^{\circ}N are found to be biphasic only. The experimental rate constants $k_{obsd(1)}$ and $k_{obsd(2)}$ increase initially with [HO^{\circ}N] to level off at high concentrations of HO^{\circ}N, as described by Eq. (12a) and (12b).

$$k_{\text{obsd}(1)} = k_1 \times K_1 \times \frac{[\text{HO}^{\circ} \text{N}]}{(1 + K_1[\text{HO}^{\circ} \text{N}])}$$
 (12a)

$$k_{\text{obsd}(2)} = k_2 \times K_2 \times \frac{[\text{HO}^{\circ} \text{N}]}{(1 + K_2[\text{HO}^{\circ} \text{N}])}$$
 (12b)

Fig. 3 shows this sort of saturation behavior for the system $Fe(acac)_3/HO^{\cap}N/i$ -PrOH. One might assume that the observed dependence of $k_{obsd(1)}$ and $k_{obsd(2)}$ on $[HO^{\cap}N]$ is due to outer-sphere complex formation according to reaction sequence (13) (HA = Hacac; HB = HO^{\cap}N).

$$\operatorname{FeA}_3 + \operatorname{HB} \stackrel{k_{os}}{\rightleftharpoons} \{\operatorname{FeA}_3, \operatorname{HB}\} \xrightarrow{k} \operatorname{FeA}_2 \operatorname{B} + \operatorname{HA}$$
(13)

If so, the experimental rate constant should follow Eq. (14). Fitting of the $(k_{obsd},[HO^{\cap}N])$ data with Eq. (14)

$$k_{\rm obsd} = \frac{(k \times K_{\rm os} \times [\rm HO^{\frown} N])}{(1 + K_{\rm os} \times [\rm HO^{\frown} N])}$$
(14)

leads however to K_{os} values of approximately 1000 M⁻¹ for both $k_{obsd(1)}$ and $k_{obsd(2)}$, which is unrealistically high for outer-sphere complex formation.

A more adequate explanation for the non-linear dependence shown in Fig. 3 follows from the reversibility of the solvolysis step. As shown in reaction sequence (15), the entering ligand HB and the leaving ligand HA compete for the reaction with the solvento



Fig. 4. Plot of $k_{obsd(1)}$ and $k_{obsd(2)}$ vs. [Hacac] for the reaction of Fe(acac)₃ with HO^{\circ}N in 2-propanol at 298 K ([Fe(acac)₃] = 1×10^{-4} M, [HO^{\circ}N] = 0.025 M).

species FeA_2S_2 (S = ROH and RO⁻, respectively). For the condition of stationary state, the rate of formation of the species FeA₂B according to Eq. (15) is described by Eqs. (16) and (17). The validity of Eq. (17) was scrutinized by investigating the ligand substitution in $Fe(acac)_3$ by HO^{\cap}N in 2-propanol under pseudo-first order conditions ($[HO^{\cap}N]_0 \gg [Fe(acac)_3]_0$) in the presence of an excess of the leaving ligand Hacac $([Hacac]_0 \gg [Fe(acac)_3]_0)$. The result is shown in Fig. 4. The observed kinetic mass law effect for both the $k_{obsd(1)}$ step and $k_{obsd(2)}$ step, as induced by additional leaving ligand Hacac, supports the interpretation that both steps are related to solvolytic equilibria. Fitting of the data $k_{obsd} = f([HB]/[HA)]$ according to Eq. (17) leads to the parameters k_{solv} and k_{HB}/k_{HA} . The data obtained for $k_{\text{solv}} (k_{\text{solv}(1)} = 0.198 \text{ s}^{-1} \text{ and } k_{\text{solv}(2)} = 0.0281 \text{ s}^{-1}) \text{ agree}$ with those of rate constants k_1 and k_2 (see Table 3). The ratio $k_{\text{HB}}/k_{\text{HA}} = 0.18$ ($k_{\text{obsd(1)}}$ step) and $k_{\text{HB}}/k_{\text{HA}} = 0.26$ $(k_{obsd(2)} \text{ step})$ indicates that in both steps the solvento species prefer to react with acetylacetone rather than with 8-hydroxyquinoline.

$$\operatorname{FeA}_{3} \underset{k_{\operatorname{HA}}}{\overset{k_{\operatorname{solv}}}{\longrightarrow}} \operatorname{FeA}_{2}S_{2} + \operatorname{HA} \overset{+\operatorname{HB}}{\xrightarrow{}} \operatorname{FeA}_{2}B + \operatorname{HA}$$
(15)

$$rate = k_{obsd} \times [FeA_3]$$

$$k_{obsd} = k_{solv}$$
(16)

$$\times \{k_{\rm HB}[{\rm HB}]/(k_{\rm HA} \times [{\rm HA}])\}/\{1 + k_{\rm HB} \\ \times [{\rm HB}]/(k_{\rm HA} \times [{\rm HA}])\}$$
(17)

The different reaction pattern observed in methanol (3 steps) and in 2-propanol (two steps) led us to study the effect of the alcohol solvent on the ligand substitution in the system Fe(acac)₃/HO^{\circ}N in some primary, secondary and tertiary alcohols ROH. The results are summarized in Table 3. In primary alcohols, three steps are observed whereas in secondary and tertiary alcohols the third step is missing. The size of rate constants k_1 , k_2 , and k_3 follows the solvent polarity parameter $E_T(30)$ [15] (see Fig. 5).



Fig. 5. Plot of log k_1 , log k_2 and log k_3 vs. $E_T(30)$ for ligand substitution in the complex Fe(acac)₃ by 8-hydroxyquinoline according to Eq. (2) in various alcohol solvents at 298 K (1 = MeOH, 2 = EtOH, 3 = PrOH, 4 = BuOH, 5 = HpOH, 6 = i-PrOH, 7 = 3-PeOH, 8 = t-PeOH).

3.4. Kinetics of ligand substitution in the binuclear complexes $[Fe(O^{\frown}O)_2(RO)]_2$ according to Eq. (3)

As discussed above, the absorption spectra of the complexes $Fe(acac)_3$ and $[Fe(O^{\circ}O)_2(RO)]_2$ in alcohol media suggest solvolytic dissociation and formation of binuclear species according to Eq. (18) (S = ROH and RO⁻, respectively; charges omitted). The two equilibria involved imply that the kinetic data, as resulting from ligand substitution experiments with solutions of $Fe(O^{\circ}O)_3$, should agree with those based on experiments with solutions of the corresponding binuclear complex $[Fe(O^{\circ}O)_2(RO)]_2$. The results obtained for the complexes $Fe(acac)_3$ and $[Fe(acac)_2(EtO)]_2$ in ethanol

Table 3

First-order rate constants k_1 , k_2 and k_3 describing the ligand substitution in the complex Fe(acac)₃ by 8-hydroxyquinoline according to eq. Eq. (2) in different alcohol solvents at 298 K

Alcohol ^a	$k_1 (s^{-1})$	$k_2 (s^{-1})$	$10^3 \times k_3 \ (\text{s}^{-1})$	k_1/k_2	k_1/k_3
МеОН	1.04 ± 0.04	0.171 ± 0.008	8.97 ± 0.38	6.08	116
MeOH	n.o. ^{b,c}	n.o. ^{b,c}	$199.0 \pm 6^{c,d}$		
EtOH	0.450 ± 0.009	0.0647 ± 0.0033	7.02 ± 0.28	6.96	64
PrOH	0.378 ± 0.009	0.0560 ± 0.0036	6.12 ± 0.22	6.75	61.8
BuOH	0.375 ± 0.006	0.0531 ± 0.0025	4.01 ± 0.20	7.06	93.5
НрОН	0.376 ± 0.010	0.0479 ± 0.0018	2.76 ± 0.36	7.85	136
i-PrOH	0.209 ± 0.008	0.0286 ± 0.0012	n.o. ^b	7.31	
3-PeOH	0.102 ± 0.004	0.0251 ± 0.0016	n.o. ^b	4.06	
t-PeOH	0.0422 ± 0.0015	0.0076 ± 0.0004	n.o. ^b	5.55	

^a For abbreviations see ref. [7].

^b Not observed.

² Reaction of the complex Fe(acac)₃ with Hacac in the absence of 8-hydroxyquinoline.

^d Rate constant k_{obsd} (as obtained according to Eq. (7)), independent of [Hacac].

Table 4

First-order rate constants k_1 , k_2 and k_3 describing the ligand substitution in the binuclear complexes $[Fe(O^{\cap}O)_2(RO)]_2$ by 8-hydroxyquinoline according to Eq. (3) and rate data for the corresponding complexes $Fe(O^{\cap}O)_3$ for comparison (298 K)

Complex	Solvent	$k_1 (s^{-1})$	$k_2 (s^{-1})$	$10^3 \times k_3 ({ m s}^{-1})$
Fe(acac) ₃	EtOH	0.450 ± 0.009	0.0647 ± 0.0033	7.02 ± 0.28
$[Fe(aca-c)_2(EtO)]_2$	EtOH	0.513 ± 0.018	0.0576 ± 0.0037	8.41 ± 0.24
Fe(dpm) ₃	MeOH	n.o. ^a	0.0820 ± 0.0030	6.96 ± 0.52
$[Fe(dpm)_2 (MeO)]_2$	MeOH	n.o. ^a	0.0732 ± 0.0041	6.82 ± 0.81
Fe(acac) ₃	EtOH	n.o. ^{a,b}	n.o. ^{a,b}	$147.0 \pm 12^{b,c}$
$[Fe(aca-c)_2(EtO)]_2$	EtOH	n.o. ^{a,b}	n.o. ^{a,b}	167.0±9 ^{b,c}

^a Not observed.

^b Reaction of the complex with Hacac in the absence of 8-hydroxyquinoline.

^c Rate constant k_{obsd} (as obtained according to Eq. (7)), independent of [Hacac].

and for the complexes $Fe(dpm)_3$ and $[Fe(dpm)_2(MeO)]_2$ in methanol are compiled in Table 4. They confirm that the equilibria described in Eq. (18) can obviously be established 'from both sides', by dissolving either $Fe(O^O)_3$ or $[Fe(O^O)_2(RO)]_2$ in ROH. The kinetic pattern is the same for both types of experiments and most of the corresponding rate constants agree within the limits of error.

As a matter of fact, none of the steps describing the ligand substitution in the complexes $Fe(O^{\frown}O)_3$ by 8-hydroxyquinoline depends on the concentration of the

that, to our knowledge, binuclear complexes [Fe(acac)₂(RO)]₂ with branched alkoxo groups RO have not been reported so far. They are obviously of very limited stability. In summary, it is found that the appearence of the k_3 pathway is bound to the presence of the binuclear species [Fe(O^OO)₂(RO)]₂.

It is interesting to see that the k_1 step is missing in the reaction of the complexes Fe(dpm)₃ and [Fe(dpm)₂- $(MeO)]_2$ with HO^{\cap}N in methanol (Table 4). The most straightforward interpretation is that, in solutions of $Fe(dpm)_3$ or $[Fe(dpm)_2(MeO)]_2$ in methanol, there are no appreciable amounts of the tris complex Fe(dpm)₃ present. Solvolysis leads to a certain amount of the solvento species $Fe(dpm)_2S_2$ (S = MeO and MeOH, respectively) and mainly to the binuclear complex $[Fe(dpm)_2(MeO)]_2$ (as a matter of fact, pure [Fe(dpm)₂(MeO)]₂ precipitates from sufficiently concentrated solutions of Fe(dpm)₃ in methanol). The absence of the k_1 pathway in the system Fe(dpm)₃/ HO^{\cap N/MeOH} (and in the system [Fe(dpm)₂(MeO)]₂/ HO^{\cap}N/MeOH) suggests therefore that the k_1 step describes the solvolysis of the tris β -diketonato complexes $Fe(O^{\circ}O)_3$ (see Eq. (18)).

To shed some further light on the equilibria described in Eq. (18), the reaction of the leaving ligand Hacac with Fe(acac)₃ in MeOH (Table 3) and with Fe(acac)₃ and [Fe(acac)₂(EtO)]₂ in EtOH (Table 4) was studied kinetically. Spectrophotometric monitoring showed two-step kinetics, consisting of an initial jump in absorbance (too fast to be followed by stopped-flow spectrophotometry) followed by an exponential change of absorbance with time according to Eq. (7). The (A, t) data led to a first-

$$\operatorname{Fe}(\widehat{OO})_{3} \xrightarrow{k_{1}} \operatorname{Fe}(\widehat{OO})_{2}S_{2} + \operatorname{HOO} \xrightarrow{k_{3}} 1/2 \left[\operatorname{Fe}(\widehat{OO})_{2}(\operatorname{RO}) \right]_{2} + \operatorname{HOO}$$
(18)

entering ligand. This fact and the observed solventdependence of the rate data strongly suggest that all of the steps are solvent-induced processes.

The experimental findings allow to assign rate constant k_3 to the solvent-induced splitting of the binuclear species [Fe(O^OO)₂(RO)₂]. This assignment is based on the following observations for the reaction of Fe(acac)₃ with 8-hydroxyquinoline, (i) in MeOH, the triphasic reaction (rate constants k_1 , k_2 , and k_3) becomes biphasic (rate constants k_1 and k_2) in the presence of admixed Hacac (see Table 2), and (ii) in branched alcohols such as i-PrOH, 3-PeOH, and t-PeOH, the k_3 step is not at all observed (see Table 3). The plausible explanation for the first observation is that additional Hacac shifts equilibria (18) to the left and lets the fraction of [Fe(acac)₂(MeO)]₂ decrease to a minor percentage. The second observation finds its explanation in the fact order rate constant k_{obsd} that was found to be independent of [Hacac]. The initial sharp change in absorbance is obviously due to the fast anation of the solvento species Fe(acac)₂S₂ by Hacac, whereas the first-order rate constant describes the splitting of the binuclear species [Fe(acac)₂(MeO)]₂ and [Fe(acac)₂(EtO)]₂, respectively, by solvent attack¹.

¹ One should note that rate constants k_{obsd} , as obtained for the splitting of the binuclear complexes in the systems Fe(acac)₃/Hacac/MeOH (Table 3) and Fe(acac)₃/Hacac/EtOH (Table 4), are by a factor of approximately twenty higher than rate constants k_3 , descibing the splitting of the binuclear complexes in the systems Fe(acac)₃/HO[^]N/MeOH and Fe(acac)₃/HO[^]N/EtOH (Table 3). Since neither Hacac nor HO[^]N are directly involved in the splitting process, the difference in rate is probably due to a medium effect. Hacac is considerably more acidic than HO[^]N [13,14,16], which might mean that proton transfer as the initial step of the splitting process occurs more easily in ROH/Hacac media than in ROH/HO[^]N media.

3.5. Mechanistic interpretation of the kinetic data obtained for ligand substitution in the systems $Fe(O^{\circ}O)_{3}|HO^{\circ}N|ROH$

The overall process of ligand substitution in the complexes $Fe(O^{\cap}O)_3$ by 8-hydroxyquinoline in alcohol media according to Eq. (2) involves four steps. In addition to three spectrophotometrically traceable steps, characterized by first-order rate constants k_1 , k_2 and k_3 (see Tables 2 and 3), one has to consider the initial sharp change in absorbance, ΔA , as the first and fastest step. This initial jump in absorbance (e.g. see Figure S1) is too fast to be followed by the stopped-flow technique applied. The size of ΔA correlates with the extent of solvolysis. In the system Fe(acac)₃/HO^{\cap}N/MeOH, ΔA corresponds to approximately 5% of the total change in absorbance observed for the overall reaction. Addition of acetylacetone to this system lets ΔA disappear. In the more strongly solvolyzed system Fe(dpm)₃/HO^{\circ}N/ MeOH, ΔA amounts to approximately 15% of the total change in absorbance. As pointed out above, the initial ΔA step obviously describes the fast reaction of the $Fe(O^{O}O)_2(ROH)_2^+$ solvento species and $Fe(O^{\cap}O)_2(RO)(ROH)$, respectively, with HO^{\cap}N^2. The higher the fraction of those kinetically labile species is, the more ΔA increases.

Scheme 1 presents a mechanistic interpretation of the overall process of substitution, as based on the experimental evidence obtained for the single steps. The kinetics of substitution are dominated by solvolysis. The alcohol solutions of the complexes $Fe(O^{\cap}O)_3$) offer the species $Fe(O^{\cap}O)_3$, $Fe(O^{\cap}O)_2(ROH)_2^+$, $Fe(O^{\cap}O)_2^-$ (RO)(ROH), $[Fe(O^{\cap}O)_2(RO)]_2$, $O^{\cap}O^-$, and $HO^{\cap}O$. The ratio $[Fe(O^{\circ}O)_2(ROH)_2^+]/[Fe(O^{\circ}O)_2(RO)(ROH)]$ is determined by the acidity of the β -diketone HO^OO and of the alcohol ROH. The assignment of first-order rate constants k_1 (solvolytic dissociation of Fe(O^OO)₃) and k_3 (solvent-induced splitting of the binuclear species $[Fe(O^O)_2(RO)]_2$) has been substantiated and discussed above. In the fastest of the four steps involved the entering ligand HO^{\chi}N 'catches' the initially present fraction of the solvento species $Fe(O^{\circ}O)_2(ROH)_2^+$ and $Fe(O^{\cap}O)_2(RO)(ROH)$, respectively, which is documented by a sharp jump in absorbance (ΔA). The rate of formation of further intermediate 'mixed' complex $Fe(O^{\cap}O)_2(O^{\cap}N)$ is thus controlled by the re-establishment of the solvolytic equilibria, which means solvolysis of the tris complex $Fe(O^{\circ}O)_3$ (k_1 path) and splitting of the species $[Fe(O^{\circ}O)_2(RO)]_2$ (k_3 path).

The assignment of rate constant k_2 is based on experimental evidence as well as on plausibility. It is experimentally found that (i) both k_1 and k_2 are firstorder rate constants that do not depend on the concentration of the entering ligand, (ii) the solvent dependence of k_1 and k_2 is very similar (see Table 3 and Fig. 5), and (iii) for all of the alcohol media studied, the ratio k_1/k_2 is more or less constant (see Table 3). These facts suggest strongly that k_1 as well as k_2 describe solvent-initiated dissociation processes. Rate constant k_1 refers to the solvolysis of the tris complex $Fe(O^{\frown}O)_3$) and rate constant k_3 describes the splitting of the binuclear complex $[Fe(O^{\circ}O)_2(RO)]_2$ (see Section 3 above). Since k_2 is not observed for the reaction of $Fe(acac)_3$ with Hacac (see Table 3), it is concluded that k_2 has to be ascribed to the solvolytic dissociation of one of the intermediate complexes, $Fe(O^{\cap}O)_2(O^{\cap}N)$ or $Fe(O^{\cap}O)(O^{\cap}N)_2$. Assuming that the intermediate $Fe(O \cap O)(O \cap N)_2$ solvolyses more rapidly than $Fe(O^{\cap}O)_2(O^{\cap}N)$, we assign k_2 to the solvolysis of the intermediate species $Fe(O^{\cap}O)_2(O^{\cap}N)$ (see Scheme 1). The solvolysis of $Fe(O^{\cap}O)(O^{\cap}N)_2$ is thus assumed to be a fast consecutive step.

From the point of formal kinetics, ligand substitution in the complexes $Fe(O^{\circ}O)_3$ by 8-hydroxyquinoline in alcohol media is a remarkable process in that none of the steps observed is found to depend on the concentration of the entering ligand, present in excess. This kinetic pattern is different from the ones reported for the homo and hetero β -diketone exchange in a wide spectrum of complexes $M(O^{\circ}O)_n$ studied in aprotic organic media (M = metal cation; n = 3, 4). As summarized by Hynes [17], in the absence of catalysts (such as acids) the rate of homo β -diketone exchange according to Eq. (19) can be described by two-term rate law (20) (HO^{\circ}O^* = isotopically labelled β -diketone).

$$M(\widehat{OO}^*)_n + H\widehat{OO} \implies M(\widehat{OO}^*)_{n-1}(\widehat{OO}) + H\widehat{OO}^*$$
(19)

$$rate = (k_1 + k_2 \times [H_2O]) \times [HO^{\frown}O]^x \times [M(O^{\frown}O)_n] \quad (20)$$

For many systems $M(O^{\circ}O^*)_n/HO^{\circ}O$, when studied in aprotic solvents, the k_1 path was found to be liganddependent, following second-order kinetics (x = 1) [17]. In the presence of water, there is an additional k_2 pathway. In the system Fe(acac*)₃/Hacac, with the weak acid Hacac being the solvent, the k_1 path is independent of [HO^{O}] (x = 0), which corresponds to rate law (21) [8d].

$$rate = (k_1 + k_2 \times [H_2O]) \times [M(O^{\frown}O)_n]$$
(21)

Sekine and Inaba studied hetero β -diketone exchange reactions in the systems Fe(O^OO¹)₃/HO^OO² (HO^OO¹, HO^OO² = Hacac, Httfa, trifluoroacetylacetone) accord-

² To our knowledge, there are no data available to describe the rate of solvent exchange at iron(III) species comparable to the solvento species $Fe(O^{\circ}O)_2(ROH)_2^+$ and $Fe(O^{\circ}O)_2(RO)(ROH)$. On the basis of $k_{ex} \approx 10^4 \text{ s}^{-1}$ for solvated Fe^{3+} in MeOH and EtOH (J. Burgess, *Metal Ions in Solution*, Ellis Horwood: Chichester, England, 1978; p. 317) one can estimate $k_{ex} \ge 10^5 \text{ s}^{-1}$ in the case of $Fe(O^{\circ}O)_2(ROH)_2^+$ and $Fe(O^{\circ}O)_2(RO)(ROH)$, respectively. This means that the time scale of the stopped-flow method is indeed not suited to resolve the reaction of these species with HO^N.



Scheme 1. Schematic description of the various steps controlling the solvolysis of the complexes $Fe(O^{\circ}O)_3$ in alcohol media and the reaction with 8-hydroxyquinoline according to Eq. (2).

ing to Eq. (22). In the aprotic solvent CCl₄, they observed ligand-dependent as well as ligand independent pathways [8b]. The authors discuss the role of the ligands HO^OO as catalyzing acids and possible kinetic effects caused by protic impurities such as water. Nelwamondo reported for reaction (22), as studied in CCl₄ solution with four complexes $Fe(O^OO^1)_3$ and $HO^OO^2 = Hacac$, that the rate of substitution is first-order in $Fe(O^OO^1)_3$ and inversely dependent on [Hacac] [8e].

$$\operatorname{Fe}(\widehat{OO}^{1})_{3} + \operatorname{HOO}^{2} \Longrightarrow \operatorname{Fe}(\widehat{OO}^{1})_{2}(\widehat{OO}^{2}) + \operatorname{HOO}^{1}$$
(22)

As a general result, the kinetic data reported for β diketone exchange and β -diketone substitution in complexes $M(O^{\circ}O)_n$ in aprotic media clearly reflect that protic components are kinetically very effective. Especially in the case of the iron(III) complexes $Fe(O^{\circ}O)_3$, water and the more or less weak acidic ligands $HO^{\circ}O$ involved open additional pathways, which stresses the crucial role of proton transfer in these exchange and substitution reactions. In line with the kinetic role of water and acids in aprotic media it was found by Graham [18] that the kinetics of ligand exchange between tris(acetohydoxamato)iron(III) complexes and EDTA in the medium water are pH-dependent.

With regard to the present study, one can extrapolate that alcohols ROH, when admixed to solutions of the complexes $Fe(O^{\cap}O)_3$ in an aprotic solvent, open an alcohol-induced reaction channel according to rate law (23). The continuous increase of [ROH] will let the term

 $k_2 \times [\text{ROH}]$ dominate so much that, in pure ROH as the solvent, rate law (23) takes the simple first-order form described by Eq. (24).

$$rate = (k_1 + k_2 \times [ROH]) \times [Fe(O^{\circ}O)_3]$$
(23)

$$rate = k_2 \times [\text{ROH}] \times [\text{Fe}(O^{\circ}O)_3]$$

$$= k_{\rm ROH} \times [\rm{Fe}(O^{-}O)_3]$$
(24)

4. Conclusions

In alcohol media, tris β -diketonate complexes $Fe(O^{\circ}O)_3$ are subject to solvolytic dissociation, leading to the solvento species, $Fe(O^{\cap}O)_2(ROH)_2^+$ and $Fe(O^{O}O)_2(ROH)(RO)$, respectively, as well as to binuclear complexes $[Fe(O^{\circ}O)_2(RO)]_2$. In alcohol solution, ligand substitution in the complexes $Fe(O^{\frown}O)_3$ by 8-hydroxyquinoline (= $HO^{\cap}N$) according to (a) occurs via the kinetically most labile solvento species. There is no direct second-order reaction between the entering ligand HO^{\cap}N and the intact complexes Fe(O^{\cap}O)₃ or the binuclear complexes $[Fe(O^{\circ}O)_2(RO)]_2$. The kinetics of ligand substitution according to reaction (a) are triphasic. The substitution process is controlled by three first-order rate constants, following the order $k_1 > k_2 >$ k_3 . All three of them do not depend on the concentration of the entering ligand HO^{\circ}N. The size of these rate constants follows the solvent polarity parameter $E_{\rm T}(30)$. Rate constant k_1 describes the solvolytic dissociation of

the complexes $Fe(O^{\cap}O)_3$, whereas k_3 can be assigned to the solvent-initiated splitting of the binuclear complexes $[Fe(O^{\cap}O)_2(RO)]_2$, which is by approximately two orders of magnitude slower $(k_1/k_3 \approx 10^2)$. Rate constant k_2 refers, most probably, to the solvolytic dissociation of the intermediate complex $Fe(O^{\cap}O)_2(O^{\cap}N)$. In a given alcohol solvent, the effect of the nature of the coordinated β -diketone in the complexes $Fe(O^{\cap}O)_3$ on the size of k_1 , k_2 and k_3 is rather minor.

$$Fe(O^{\cap}O)_3 + 3HO^{\cap}N \xrightarrow{ROH} Fe(O^{\cap}N)_3 + 3HO^{\cap}O$$
 (a)

From the preparative point of view one learns that the rate of reactions such as (a) (see above), leading to thermodynamically more stable complexes $Fe(A^{\cap}B)_3$ $(A^{\cap}B = bidentate anion of a weak acid HA^{\cap}B)$, is not enhanced by an excess of HA^B.

5. Supplementary material

Figures S1 and S2, offering further kinetic details concerning the substitution processes under study, can be obtained from the authors upon request.

Acknowledgements

Sponsorship of this work by the Deutsche Forschungsgemeinschaft and Verband der Chemischen Industrie E.V. is gratefully acknowledged.

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