

KINETICS AND MECHANISMS OF THE REACTION OF IRON(III) AND 2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONE IN AQUEOUS SOLUTIONJose M.^a HERNANDO, Carlos BLANCO* and Manuel MATEO*Departamento de Química Física, Facultad de Ciencias,
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In this work the kinetic of formation of (2,2,6,6-tetramethyl-3,5-heptanedione)iron(III) complex (stoichiometry 1 : 1) has been studied in aqueous solution. It was found that the reaction is of first order with respect to diketone. The influence of several factors such as reagent concentrations, pH, ionic strength and temperature was systematically examined. A mechanism S_N1 is proposed for the complexation process that accounts successfully for the experimental results.

The reactions between metal ions and β -diketones have been the subject of considerable investigation, but few studies on the formation of the complexes of iron(III) with 2,2,6,6-tetramethyl-3,5-heptanedione have been reported. Actually, the chemical literature only refers^{1,2} to the tris(2,2,6,6-tetramethyl-3,5-heptanedione)iron(III), nevertheless the formation of the monochelated complexes of metal ions with β -diketones has already been studied³⁻⁵ and because of this, in this paper we carry out the study of the 1 : 1 complex.

Before the kinetic study of the complex formation its composition has been determined at the lowest range of pH. The stability constant of the monochelate has been estimated using the ionization constant value, which was determined by the "Method of the parallel straights" (ref.⁶).

The kinetic study was carried out in a narrow range of pH, and simultaneously the iron(III) concentration was maintained in excess of the ligand to avoid formation of the complexes with the higher stoichiometries.

EXPERIMENTAL

The solutions of Fe(III) were prepared from reagent grade $Fe(NO_3)_3 \cdot 9 H_2O$ and standardized by gravimetric analysis. Reagent grade 2,2,6,6-tetramethyl-3,5-heptanedione (TMH) was obtained from Sigma. Ethanol-water mixtures were prepared, and $HClO_4$ - $NaClO_4$ were used to adjust the ionic strength to 0.5 mol dm^{-3} . For the measurement of the acid dissociation constant of TMH, the pH of the sample solutions was adjusted with NaOH and $Na_2HPO_4 \cdot 12 H_2O$.

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pH Measurements were made with a Crison model 501 pH-meter equipped with an Ingold combined glass-and-reference electrode.

Absorption spectra were recorded on a Spectronic 1 201 UV-VIS spectrophotometer and the rates of reactions were measured using a computer coupled with it.

RESULTS

Composition of the Complex

The composition of the complex that iron(III) forms with 2,2,6,6-tetramethyl-3,5-heptanedione in water-ethanol mixture (85 vol. %) has been investigated spectrophotometrically by several methods: continuous variations⁷, molar ratio⁸, and slopes ratio⁹. The measurements were made at 490 nm, the pH range was low enough to prevent formation of hydrolysis products and their interferences. The ionic strength was kept constant ($I = 0.5$) with NaClO_4 .

Method of the continuous variations. In all series of solutions the total concentration, $[\text{Fe(III)}] + [\text{TMH}]$, was kept at $1.0 \cdot 10^{-3} \text{ mol dm}^{-3}$. In every case the maximum observed corresponds to 1 : 1 ratio of iron(III) to the ligand in the complex formed. The results at all pH values agree, and no evidence was found to indicate complexes other than the 1 : 1.

Method of molar ratio. For this method we prepared several series of solutions where the concentration of iron(III) was $1.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, and changing the TMH concentration in the way that $[\text{TMH}]/[\text{Fe(III)}]$ ratio ranged from 0 to 4. The data obtained agree for each pH value again with a 1 : 1 stoichiometry.

Method of slopes ratio. Two series of solutions were prepared, one of them keeping the Fe(III) concentration constant and changing the TMH concentration. The other one with a constant concentration of diketone and changing the amount of iron(III). In both series of solutions there was a large excess of the reagent in constant concentration in order to avoid complex dissociation. Plotting the absorption of these solutions against the molar concentration of the changing reagent we find two straight lines, and their slopes were determined by the least squares method.

The ratio s_1/s_2 between the slope for the line absorption = $f([\text{Fe(III)}])$, s_1 , and the slope for the line absorption = $f'([\text{TMH}])$, s_2 , has the approximate value of 1 (Table I) confirming once more a 1 : 1 composition.

The analysis of the results of all three methods can be interpreted in the following way. The stability of the complex is a function of acidity, at low pH values increases the dissociation, nevertheless at pH higher than 1.30 or 1.50 the composition of the complex diverges slightly from the 1 : 1 composition.

Stability Constant of Complex

The iron(III) in acid aqueous solution has six water molecules in octahedral coordination and by an S_N1 mechanism two of the coordination positions are utilized by the bidentate ligand in the formation of the chelate.

The complex ion which will be studied in this work is $[\text{Fe}(\text{H}_2\text{O})_4\text{TM}]^{2+}$, and for the sake of simplicity, the solvent molecules will not be written, so the stability constant of $[\text{FeTM}]^{2+}$ complex can be written as

$$\beta = [\text{FeTM}^{2+}]/[\text{Fe}][\text{TM}^-]. \quad (1)$$

The direct determination of this constant is rather complicated because several competitive reactions can take place and, all of these side reactions affect the extent of the formation of monocomplex, this is quantitatively expressed by the conditional constant:

$$\beta' = [\text{FeTM}^{2+}]/[\text{Fe}'][\text{TM}^{-'}], \quad (2)$$

where $[\text{Fe}']$ and $[\text{TM}^{-'}]$ are the total concentration of iron and the total concentration of ligand that does not form the complex respectively¹⁰. In such a way the stability constant can be connected with the conditional constant by the following

TABLE I
Method of slopes ratio

pH	[TMH], mol dm ⁻³	[Fe(III)], mol dm ⁻³	s_1	s_2	s_1/s_2
1.0	variable	$1.00 \cdot 10^{-2}$	753		1.02
1.0	$1.0 \cdot 10^{-3}$	variable		739	
1.3	variable	$1.00 \cdot 10^{-2}$	860		1.01
1.3	$1.0 \cdot 10^{-3}$	variable		851	
1.5	variable	$1.00 \cdot 10^{-2}$	933		1.07
1.5	$1.0 \cdot 10^{-3}$	variable		870	
2.0	variable	$1.00 \cdot 10^{-2}$	962		1.08
2.0	$1.0 \cdot 10^{-3}$	variable		887	

equation:

$$\beta = \beta' \left(1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + 2K_3 \frac{[Fe^{3+}]}{[H^+]^2} + 3K_4 \frac{[Fe^{3+}]^2}{[H^+]^4} \right) \left(1 + \frac{[H^+]}{K_1} \right), \quad (3)$$

where K_1 , K_2 , K_3 , and K_4 are the hydrolysis constants of the Fe^{3+} to form $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, and $Fe_3(OH)_4^{5+}$, which are taken from the literature¹¹: $10^{-2.3}$, $10^{-5.7}$, $10^{-2.9}$, and $10^{-6.3}$, respectively.

The 2,2,6,6-tetramethyl-3,5-heptanedione exists in three forms in aqueous solution: the keto and enol forms (TMH), and the anionic form, which is the common product of ionization of either tautomer and may be referred to simply as TM^- . Thus, K_1 stands for the ionization constant of the ligand, which can be written as

$$K_1 = a_{TM^-} a_{H^+} / a_{TMH}. \quad (4)$$

The K_1 value has been determined spectrophotometrically by the "Method of the parallel straight lines" (ref.⁶), since in this method it is not necessary to determine the diketone absorption coefficient in alkaline medium where the β -diketones undergo fragmentation reactions¹². From this, the ionization constant K_1 is related to absorption coefficients through the equation:

$$\varepsilon = \varepsilon_{TM^-} - \frac{1}{K_1} (\varepsilon - \varepsilon_{TMH}) \gamma_{TM^-} \cdot a_{H^+}, \quad (5)$$

where ε_{TMH} , ε_{TM^-} , and ε are the absorption coefficients of the 2,2,6,6-tetramethyl-3,5-heptanedione in its molecular form, ionic form and their mixture, respectively. The activity coefficient of the ionic form of the diketone is γ_{TM^-} and a_{H^+} is the proton activity.

The buffer solutions were mixtures of Na_2HPO_4 0.05 mol dm^{-3} and $NaOH$ 0.1 mol dm^{-3} . The wavelengths were selected at regular intervals around the absorption maximum which the diketone showed at $\lambda = 295 \text{ nm}$. On plotting the values of ε against $(\varepsilon - \varepsilon_{TMH}) \gamma_{TM^-} \cdot a_{H^+}$ for all wavelengths an association of straight parallel lines was obtained, from whose slopes the K_1 values were determined (Table II).

The conditional constant β' was determined from absorption spectra values in the stoichiometric point according to the continuous variations and molar ratio methods in the same way as we made in a previous paper¹³. When the values of β' are inserted in Eq. (3), the stability constant $\beta = 1.1 \cdot 10^{14}$ of the complex results.

Kinetic Study

The metal ions yield complexes with β -diketones through successive stages. The conditions were chosen so that only the mono-chelated complex was observed.

Higher complexes formation was prevented under the conditions of high acidity and low ligand concentration. The pH was kept within a range from 1.00 to 1.30. This was so chosen because of the high degree of dissociation of the complex for a hydrogen-ion concentration above $10^{-1} \text{ mol dm}^{-3}$. On the other hand for a pH greater than 1.30 the intended¹⁴ presence of complexes of stoichiometry other than the 1 : 1 and the presence of some iron hydrolysis products such as $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe}(\text{OH})_2^+$ with absorption maxima near the complex, make its spectrophotometric study difficult.

The metal ion was maintained in at least twelve-fold excess of the ligand to ensure the formation of only the $[\text{FeTM}]^{2+}$ complex. This also ensured that the reactions were carried out under pseudo-first-order conditions. The temperature was maintained at $10.0 \pm 0.1^\circ\text{C}$.

Reaction order. By keeping constant the ferric ion concentration, the hydrogen ion concentration, the ionic strength, and the temperature, the variation of rate

TABLE II

ionization constant of TMH determined by the method of parallel straight lines. $\varepsilon' = (\varepsilon - \varepsilon_{\text{TMH}}) \nu_{\text{TM}^-} \alpha_{\text{H}^+} \cdot 10^9$, ε in $\text{m}^2 \text{ mol}^{-1}$

pH	λ , nm				
	285	290	295	300	305
	ε/ε'				
12.31	11 420	13 400	14 040	13 180	10 520
12.31	3.3504	4.1953	4.5700	4.4084	3.5855
12.17	10 040	11 720	12 120	11 380	9 140
12.17	3.9568	4.9792	5.3779	5.2143	4.2839
11.91	8 740	9 980	10 260	9 540	7 680
11.91	6.0407	7.5040	8.1230	7.8416	6.4909
11.73	7 320	8 180	8 300	7 660	6 260
11.73	7.1730	8.8591	9.5736	9.2592	7.8589
11.53	6 065	6 626	6 589	6 001	4 883
11.53	8.5718	10.5775	11.3583	10.9760	9.3868
	ε_{TMH}				
0.1M-HCl	2 300	1 980	1 600	1 180	760
	$\text{p}K$				
	11.984	12.003	12.014	12.014	11.963

with the concentration of TMH was studied. The absorptions at 490 nm were measured at certain time intervals after the metal ion and the ligand solutions had been mixed. The results were plotted as $-\log(A_\infty - A)$ against time, where A is the complex absorption at a time t and A_∞ corresponds to the absorption when the reaction is over.

The result comes out as a straight line, corresponding to an integrated kinetic equation of first-order. By changing the amount of Fe(III) the rate equation remains a first-order as shown in Table III.

Ferric ion and hydrogen ion concentration dependences. For the best analysis of the relationship that can be seen in Table III, four series of experiments have been developed to study the influence on the rate constant of the Fe(III) concentration, where the 2,2,6,6-tetramethyl-3,5-heptanedione concentration, the ionic strength, the temperature and the pH of the solutions remain constant for each one of the series. The variation of first-order rate constant on the concentration of ferric ions was evaluated by plotting k_{obs} against $[\text{Fe(III)}]$, (Fig. 1).

Ionic strength dependence. This influence has been analyzed according to the Debye-Huckel's law. All the experiments show that on changing the ionic strength by adding amounts of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ the slope of the straight line, obtained by plotting the values of $\log k_{\text{obs}}$ against $I^{1/2}(1 + I^{1/2})$, is negative. This fact confirms the presence of the 2,2,6,6-tetramethyl-3,5-heptanedione in its ionic form when it reacts with Fe(III).

TABLE III

Variation of observed rate constant, k_{obs} , with $[\text{Fe(III)}]$ and $[\text{TMH}]$. pH = 1.15, $T = 283 \text{ K}$, $I = 0.5 \text{ mol dm}^{-3}$

$[\text{Fe(III)}] \cdot 10^3$ mol dm^{-3}	$[\text{TMH}] \cdot 10^3$ mol dm^{-3}	$k_{\text{obs}} \cdot 10^3$ s^{-1}	$[\text{Fe(III)}] \cdot 10^3$ mol dm^{-3}	$[\text{TMH}] \cdot 10^3$ mol dm^{-3}	$k_{\text{obs}} \cdot 10^3$ s^{-1}
7.0	3.0	7.0	9.0	3.0	9.0
7.0	3.5	7.3	9.0	3.5	8.7
7.0	4.0	7.3	9.0	4.0	8.8
7.0	4.5	7.1	9.0	4.5	8.9
7.0	5.0	7.0	9.0	5.0	8.8
7.0	5.5	7.2	9.0	5.5	9.0
8.0	3.0	8.1	10.0	3.0	10.2
8.0	3.5	7.8	10.0	3.5	10.3
8.0	4.0	8.1	10.0	4.0	10.5
8.0	4.5	7.9	10.0	4.5	10.1
8.0	5.0	8.0	10.0	5.0	10.1
8.0	5.5	8.1	10.0	5.5	10.3

Temperature dependence. The temperature variation of the rate constant (which follows the Arrhenius equation to reasonable precision) is shown in Fig. 2. The values of activation energies were determined from the slope of that plot by the method of least squares.

The values of ΔH^\ddagger and ΔS^\ddagger corresponding to the complex formation were calculated from the plot of $\ln k_{\text{obs}}/T$ against $1/T$ and they were 82.8 kJ mol^{-1} and $6.1 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

Reaction Mechanism

The kinetics of the complexation reactions of transition metal ions have been studied using a variety of rapid reaction techniques¹⁵. In the case of the fully hydrated metal ion and a normal bidentate ligand, such as a β -diketone, the substitution requires at least three steps¹⁶. First, there is the diffusion-limited step with an ion pair formation between the aquated metal ion, $M(\text{H}_2\text{O})_n$, and the reactant ligand A-B to form $[\text{A-B}, M(\text{H}_2\text{O})_n]$. After that, substitution of a water from the inner coordination sphere of the metal ion occurs yielding $\text{A-B}-M(\text{H}_2\text{O})_{n-1}$. Further water molecule coordinated can be eventually replaced by the second ligating atom of the bidentate

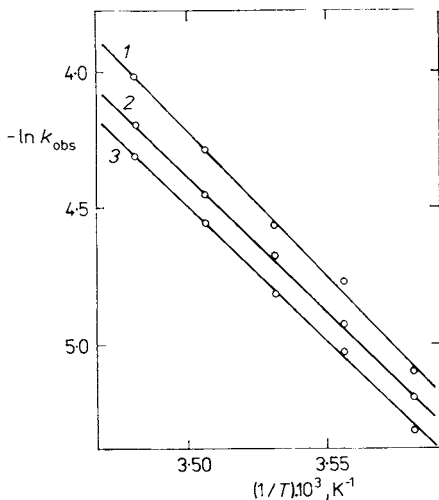


FIG. 1

Variation of observed rate constant k_{obs} with Fe(III) and pH. $[\text{TMH}] = 1 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $T = 283 \text{ K}$; pH: 1 1.00, 2 1.10, 3 1.20, 4 1.30

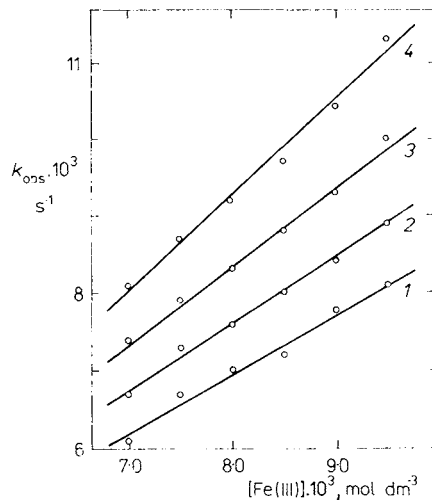
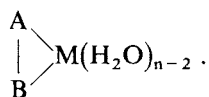


FIG. 2

Variation of observed rate constants as a function of temperature. $[\text{TMH}] = 4 \cdot 10^{-4} \text{ mol dm}^{-3}$, pH = 1.20 and $I = 0.5 \text{ mol dm}^{-3}$; $[\text{Fe(III)}]$: 1 $9 \cdot 10^{-3}$, 2 $8 \cdot 10^{-3}$, 3 $7 \cdot 10^{-3} \text{ mol dm}^{-3}$

ligand giving:



The mono-complex formation of iron(III) ion with the β -diketone is thought to proceed through a mechanism which is connected with the experimental conditions.

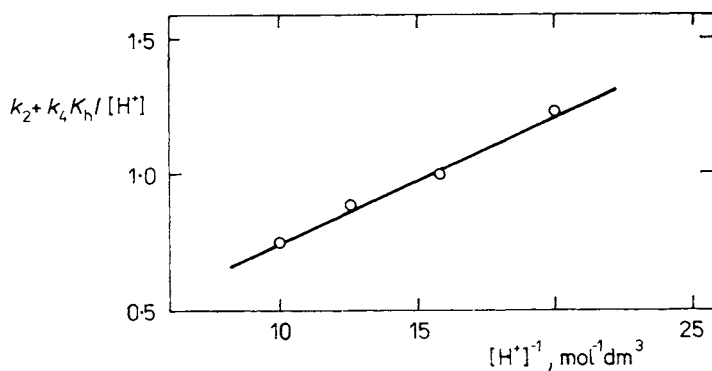


FIG. 3

Plot suggested by Eq. (9) for reaction of Fe(III) with TMH. $[\text{TMH}] = 4 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $T = 283 \text{ K}$

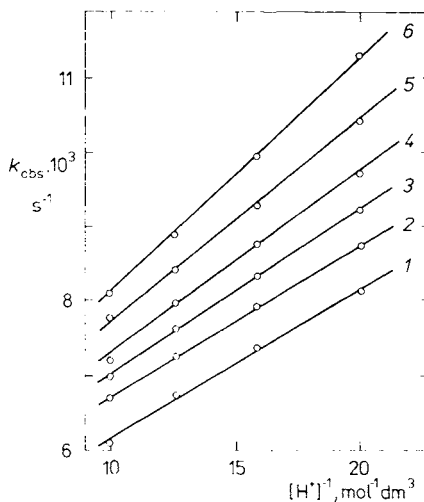
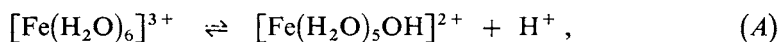


FIG. 4

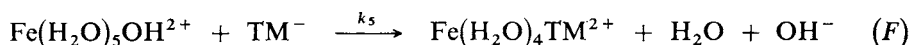
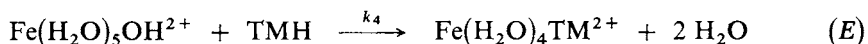
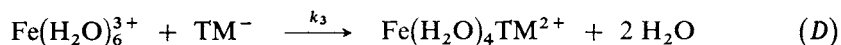
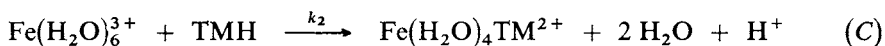
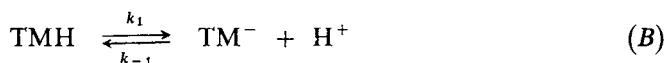
Plot suggested by Eq. (10) for reaction of Fe(III) with TMH. $[\text{TMH}] = 4 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $T = 283 \text{ K}$; $[\text{Fe(III)}]$: 1 $7 \cdot 10^{-3}$, 2 $7.5 \cdot 10^{-3}$, 3 $8 \cdot 10^{-3}$, 4 $8.5 \cdot 10^{-3}$, 5 $9 \cdot 10^{-3}$, 6 $9.5 \cdot 10^{-3} \text{ mol dm}^{-3}$

The iron(III) can be hydrolyzed mainly according to the following reaction:



since the rest of the possible species from hydrolysis, like $\text{Fe}(\text{OH})_2^+$ or $\text{Fe}_2(\text{OH})_2^{4+}$, are in a negligible concentration at $\text{pH} < 1.30$.

As we could see, the ionization constant of the diketone shows that in acid solution it is almost completely in the molecular form. However, this does not mean that the diketone cannot be ionized and the complex formation could take place between hydrated metal ion and the β -diketone in the ionic form. In these conditions, it is assumed that the following reaction routes are possible.



Making the steady-state approximation for the enolate, which in these conditions can be produced to react with the two ferric species

$$[\text{TM}^-] = \frac{k_1[\text{TMH}]}{k_{-1}[\text{H}^+] + k_3[\text{Fe}(\text{H}_2\text{O})_6^{3+}] + k_5[\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}]}, \quad (\text{G})$$

where it can be considered that the reverse reaction in the equilibrium (B) is quantitatively negligible and that $k_3[\text{Fe}(\text{H}_2\text{O})_6^{3+}] \gg k_5[\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}]$ since $[\text{Fe}(\text{H}_2\text{O})_6^{3+}] \gg [\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}]$.

Substituting the enolate concentration obtained after making the above approximations in the expression (G) and the hydrolysis constant corresponding to reaction (A) in the rate equation of complex formation, we then have for overall rate reaction:

$$v = k_2[\text{Fe}(\text{H}_2\text{O})_6^{3+}][\text{TMH}] + k_1[\text{TMH}] + k_4K_h \frac{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]}{[\text{H}^+]} [\text{TMH}] + \frac{k_5k_1K_h}{k_3[\text{H}^+]} [\text{TMH}], \quad (\text{H})$$

it can be seen that the $[\text{TMH}]$ is a common factor in all terms. This agrees with a pseudo-first-order reaction $v = k_{\text{obs}}[\text{TMH}]$ and then

$$k_{\text{obs}} = k_1 + k_2[\text{Fe}(\text{H}_2\text{O})_6^{3+}] + k_4K_h \frac{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]}{[\text{H}^+]} + \frac{k_5k_1K_h}{k_3} \frac{1}{[\text{H}^+]}, \quad (8)$$

this expression can be explained if the last term is considered negligible in comparison with the rest of the terms, which voids the stage (F). This is justified if we consider the relatively low concentration of the two species, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ and TM^- , that is found in this stage. A new rate constant (9) will be, therefore, used to discussing the results. Thus, a plot of the slopes obtained for each pH value in Fig. 1 against $[\text{H}^+]^{-1}$, which is linear (Fig. 3), can justify the proton dependence expressed by equation:

$$k_{\text{obs}} = k_1 + \left(k_2 + \frac{k_4K_h}{[\text{H}^+]} \right) [\text{Fe}(\text{H}_2\text{O})_6^{3+}]. \quad (9)$$

The double influence of iron concentration in k_{obs} can be justified by plotting k_{obs} values which were obtained in Fig. 2 against $[\text{H}^+]^{-1}$.

$$k_{\text{obs}} = (k_1 + k_2[\text{Fe}(\text{H}_2\text{O})_6^{3+}]) + k_4K_h[\text{Fe}(\text{H}_2\text{O})_6^{3+}] \frac{1}{[\text{H}^+]}. \quad (10)$$

The plot should yield straight lines of slopes $k_4K_h[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$ and intercepts $k_1 + k_2[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$. Actually, Fig. 4 is in good agreement with this, since both, slopes and intercepts, increase in connection with the iron concentration.

The constants k_1 , k_2 , and k_4 have been determined from the results shown in Figs 3 and 4 in such a way that at 283 K and $I = 0.5$ the rate equation became:

$$v = \left(0.0035 + 0.15[\text{Fe}(\text{H}_2\text{O})_6^{3+}] + 0.040 \frac{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]}{[\text{H}^+]} \right) [\text{TMH}]. \quad (11)$$

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