

KINETICS AND MECHANISM OF THE REACTION OF IRON(III) WITH 6-METHYL-2,4-HEPTANEDIONE AND 3,5-HEPTANEDIONE

José M. HERNANDO, Olimpio MONTERO and Carlos BLANCO

*Departamento de Química Física, Facultad de Ciencias,
Universidad de Valladolid, 470 05 Valladolid, Spain*Received November 7, 1989
Accepted December 20, 1989

The kinetics of the reactions of iron(III) with 6-methyl-2,4-heptanedione and 3,5-heptanedione to form the corresponding monocomplexes have been studied spectrophotometrically in the range 5°C to 16°C at I 25 mol l⁻¹ in aqueous solution. In the proposed mechanism for the two complexes, the enol form reacts with the metal ion by parallel acid-independent and inverse-acid paths. The kinetic constants for both pathways have been calculated at five temperatures. Activation parameters have also been calculated. The results are consistent with an associative activation for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and dissociative activation for $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$. The differences in the results for the complexes of heptanediones studied are interpreted in terms of steric factors.

The mechanism of the complexation reactions of metal ions has been widely studied in the last years¹⁻⁹. Ligands as β -diketones have been considered very interesting in view of a number of useful applications¹⁰, and also kinetically, due to their ability to react as either keto or enol tautomer, in addition to the enolate ion.

It appears accepted that the formation of $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ proceeds through a dissociative process and formation of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ via an associative process^{11,12}. However, the influence of steric factors and of chain length of the ligand have not yet been reported.

To continue our study of these reactions⁷⁻⁹, in this paper we report on kinetic data and rate constants for the formation of the complex of iron(III) with two heptanediones, 6-methyl-2,4-heptanedione (HiBAM) and 3,5-heptanedione (HDPrM) at low temperatures.

EXPERIMENTAL

The solutions of β -diketones were prepared from Kodak reagent grade and were freshly distilled under reduced pressure prior to use. Stock aqueous $5 \cdot 12 \cdot 10^{-2}$ M-HiBAM and $4 \cdot 76 \cdot 10^{-2}$ M-HDPrM solutions were used. Merck reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ was used as a source of Fe(III), stock solutions were standardized gravimetrically.

HClO_4 (Merck) was used as a source of hydrogen ions, pH value of solutions was adjusted by using $\text{HClO}_4/\text{NaOH}$. The ionic strength of all the solutions was adjusted to $0 \cdot 25 \text{ mol dm}^{-3}$ by

using NaClO_4 and HClO_4 . Unless otherwise indicated, all the materials were of reagent grade (Merck) and were used without further purification.

Kinetic measurements were carried out in Spectronic 1201 and Coleman 55 Perkin-Elmer spectrophotometers. Temperature of the reaction solution was controlled within $\pm 0.1^\circ\text{C}$ by using a thermostatic circulating bath. The equilibrium constants of β -diketones were determined by using a Spectronic 1201 with graphic recorder BBC, SE790. pH Measurements were made with a Crison 501 pH-meter equipped with an Ingold combined glass-and-reference electrode.

RESULTS

Ionization constants of β -diketones. The constants of ionization for both β -diketones corresponding to the equilibrium expressed in Eq. (1), where HL is the β -diketone undissociated and L^- is the enolate ion, were determined by the "Parallel Straight Lines" method¹³. The concentrations of β -diketones $5.0 \cdot 10^{-5}$ mol/l for HiBAM and $4.76 \cdot 10^{-5}$ mol/l for HDPrM were used. The values obtained for $\text{p}K_1$ are shown in Table I and agree well with literature values^{14,15}.



Tautomerization equilibrium. The keto-enol tautomerization equilibrium of a β -diketone may be represented by Eq. (2), where HK and HE represent the keto and enol tautomers, respectively. The enolization rate (k_e) and the enol fraction ($y = [\text{HE}]/[\text{HL}]$) were measured by a bromination procedure^{2,9}.



The ketonization rate (k_f) may be obtained from Eq. (3).

$$y = 1/(1 + k_f/k_e) \quad (3)$$

TABLE I

Constants for the equilibrium of β -diketones at 10.0°C . $[\text{HiBAM}] = 6.87 \cdot 10^{-4}$ mol/l and $3.4 \cdot 10^{-4}$ mol/l and $[\text{HDPrM}] = 1.64 \cdot 10^{-3}$ mol/l

Compound	k_e, s^{-1}	k_f, s^{-1}	y	$\text{p}K_1$
HiBAM	$1.71 \cdot 10^{-2}$	$3.99 \cdot 10^{-2}$	0.30	9.19 ^a
HDPrM	$5.08 \cdot 10^{-3}$	$2.67 \cdot 10^{-2}$	0.16	9.81 ^a

^a $t = 25^\circ\text{C}$.

Data of k_e , k_f and enol fraction obtained for HiBAM and HDPPrM are shown in Table I.

Stability constant of complex. A stoichiometry 1 : 1 for both complexes was determined spectrophotometrically using the Job¹⁶ and Yoe-Jones¹⁷ methods. The pH range was kept at values less than 1.8. The stability constants for the complexes were determined by Eq. (4), where β is the stability constant, β' is the conditional constant, K_1 is the ionization constant of the ligand and K_1 , K_2 , and K_3 are the hydrolysis constants for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, to form $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4^+$ and $\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$, being $K_1 = 10^{-2.3}$, $K_2 = 10^{-5.7}$ and $K_3 = 10^{-2.9}$ (refs¹⁸⁻²⁰), β' can be determined from absorption values at the stoichiometric point according to Job's method in the same way as in a previous paper²¹. The values of $\log \beta$ at 25 °C are 11.08 ± 0.07 for the complex of iron(III) with HiBAM and 11.78 ± 0.05 for the complex of iron(III) with HDPPrM.

$$\beta = \beta' \left[1 + \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2} + 2 \frac{K_3[\text{Fe}(\text{H}_2\text{O})_6^{3+}]}{[\text{H}^+]^2} \right] \left[1 + \frac{[\text{H}^+]}{K_1} \right] \quad (4)$$

Kinetic measurements. The reaction of complex formation was carried out in excess of metal ion to ensure the quantitative presence of the complex of stoichiometry 1 : 1, at hydrogen ion concentration 0.01–0.1 mol/l. The pseudo-first-order rate constants were obtained from plots of $-\ln(A_\infty - A_t)$ against time, where A_∞ is the complex absorption when the reaction is over.

In order to study the influence of the Fe(III) concentration on k_{obs} , several series of experiments with constant values of ligand concentration, pH, ionic strength and temperature, were performed. Plots k_{obs} against $[\text{Fe}(\text{III})]_0$ at different pH values for each temperature yielded a linear correlation in all cases. Some experimental values are given in Table II.

DISCUSSION

Kinetic data show a linear dependence of k_{obs} with $[\text{Fe}^{3+}]_0$ and an inverse dependence with $[\text{H}^+]$, as shown in Table II. The ratio between HiBAM and HDPPrM enol fraction is 1.88 which is very similar to the ratio between k_{obs} for reactions of both β -diketones at the same temperature and $[\text{Fe}^{3+}]_0$, so we have considered that the reaction takes place via enol tautomer. Taking into account this assumption, kinetic data may be interpreted with reference to the series of reactions in Scheme 1 (coordinated H_2O is omitted for clarity).

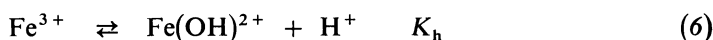
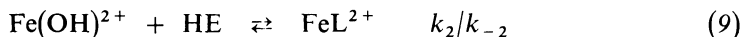
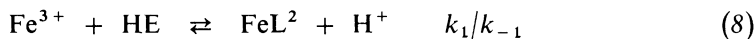
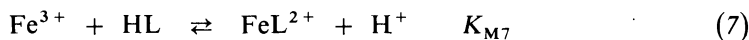


TABLE II

Experimental rate constant k_{obs} (s^{-1}) at 10.0°C ($\mu = 0.25 \text{ mol/l}$). $[\text{HiBAM}] = 5.12 \cdot 10^{-4} \text{ mol/l}$, $[\text{HDPPrM}] = 4.17 \cdot 10^{-4} \text{ mol/l}$

Complex Fe(III)-HiBAM			Complex Fe(III)-HDPPrM		
$[\text{H}^+] \cdot 10^2$ mol dm^{-3}	$[\text{Fe(III)}] \cdot 10^2$ mol dm^{-3}	$k_{\text{obs}} \cdot 10^3$ s^{-1}	$[\text{H}^+] \cdot 10^2$ mol dm^{-3}	$[\text{Fe(III)}] \cdot 10^2$ mol dm^{-3}	$k_{\text{obs}} \cdot 10^3$ s^{-1}
9.55	1.0	4.42	10.47	1.0	2.26
9.55	1.5	4.68	10.47	1.5	2.46
9.55	2.0	4.99	10.47	2.0	2.60
9.55	2.5	5.03	10.47	2.5	2.93
9.55	3.0	5.38	10.47	3.0	3.18
9.55	3.5	5.60	10.47	3.5	3.50
9.55	4.0	5.82	6.61	1.0	2.21
6.17	1.0	4.79	6.61	1.5	2.47
6.17	1.5	5.08	6.61	2.0	2.76
6.17	2.0	5.29	6.61	2.5	3.02
6.17	2.5	5.65	6.61	3.0	3.35
6.17	3.0	5.92	6.61	3.5	3.61
6.17	3.5	6.11	3.63	1.0	2.31
6.17	4.0	6.35	3.63	1.5	2.59
4.07	1.0	5.07	3.63	2.0	2.93
4.07	1.5	5.60	3.63	2.5	3.16
4.07	2.0	5.91	3.63	3.0	3.62
4.07	2.5	6.46	3.63	3.5	4.11
4.07	3.0	6.82	2.57	1.0	2.30
4.07	3.5	7.20	2.57	1.5	2.69
4.07	4.0	7.61	2.57	2.0	3.04
2.63	1.0	5.48	2.57	2.5	3.34
2.63	2.0	6.39	2.57	3.0	3.90
2.63	2.5	7.01	2.57	3.5	4.33
2.63	3.0	7.34	1.78	1.0	2.43
2.63	4.0	8.28	1.78	1.5	2.83
1.62	1.0	5.79	1.78	2.0	3.18
1.62	1.5	6.30	1.78	2.5	3.65
1.62	2.0	6.87	1.78	3.0	4.35
1.62	2.5	7.63	1.78	3.5	4.88
1.62	3.0	7.59			
1.62	3.5	8.37			
1.62	4.0	9.36			



SCHEME 1

From reactions in Scheme 1, Eq. (10) may be derived for k_{obs} (ref.⁹) when the ferric ion is in pseudo-first-order excess and the total ferric ion concentration is $[\text{Fe}]_0$.

$$k_{\text{obs}} = \left[\frac{1}{K_{\text{ML}}} + \frac{[\text{Fe}]_0}{[\text{H}^+] + K_{\text{h}}} \right] \frac{1}{1 + k_f/k_e} (k_1[\text{H}^+] + k_2K_{\text{h}}) \quad (10)$$

Values of rate constants k_1 and k_2 were determined from the intercept and the slope, respectively, in a plot of $k_{\text{obs}}/\{1/K_{\text{ML}} + [\text{Fe}]_0/([\text{H}^+] + K_{\text{h}})\} (1 + k_f/k_e)^{-1}$ against $[\text{H}^+]$. These values are given in Table III at seven temperatures in the range 5–16°C.

K_{ML} was determined using Eq. (11), where $[\text{Fe}]_0$ and $[\text{HL}]_0$ are the total concentration of Fe^{3+} and ligand respectively, $h = (1 + K_{\text{h}}/[\text{H}^+])$ and ε is the absorption coefficient of FeL^{2+} at the analytical wavelengths. A plot of left hand side of Eq. (11) against $([\text{Fe}]_0 + [\text{HL}]_0)/h[\text{H}^+]$ should give a straight line of slope $1/\varepsilon$ and intercept $1/\varepsilon K_{\text{ML}}$. Values obtained are in the range 65.7–70.4 for the complex of HiBAM and 63.3–69.3 for the complex of HDPrM.

$$[\text{Fe}]_0 [\text{HL}]_0 / Ah[\text{H}^+] = ([\text{Fe}]_0 + [\text{HL}]_0) / h\varepsilon[\text{H}^+] + 1/\varepsilon K_{\text{ML}} \quad (11)$$

From data in Table III we have calculated values of activation energy plotting $\ln k_1$ or $\ln k_2$ against $1/T$, and activation enthalpy and entropy plotting $\ln k_1/T$ or $\ln k_2/T$ against $1/T$, respectively, for the two pathways in Eqs (8) and (9). The results are shown in Table IV.

If the reaction between Fe^{3+} and enolate ion is assumed as alternative formulation of the inverse acid pathway, then a rate constant of 10^6 or 10^7 order results for this reaction if the ligands are HiBAM or HDPrM; these values are clearly too large. Furthermore, a study of the influence of the ionic strength on k_{obs} shows an insensitive participation of a species with negative charge. When complexes are iron(III)–HiBAM and iron(III)–HDPrM, the values of E_a calculated for these reactions are $5.85 \cdot 10^4$ and $7.04 \cdot 10^4 \text{ J mol}^{-1}$ respectively, and they are approximately the double of those for the reaction between FeOH^{2+} and the enol tautomer. So we conclude that reaction (9) is the correct one.

Measurements of the activation volumes have pointed out (refs^{11,12}) that ion Fe^{3+} reacts via an associative interchange mechanism (I_d). The steric strain due to

a heptacoordinate intermediate in I_a mechanism will be increased if the coordinate point of the ligand has a bulky group in its proximities, such as isopropyl group of the HiBAM, and the rate of coordination will be decreased. In I_d mechanism, the steric strain in the pentacoordinate intermediate is not so large and the presence of a bulky group will have less influence than in the I_a mechanism. In consequence, steric factors may produce an increase in the difference of the rate of reaction between both mechanisms. This has been the case in the complexes studied in this work (see Table III), since the similar structure ($R-CO-CH_2-CO-R'$) in the two β -diketones let us suppose that the rate of formation of the two complexes must be of the same order, such as it has been. Previously we got the values $k_1 = 0.15$ and $k_2 = 60.9 \text{ mol}^{-1} \text{ dm}^3$.

TABLE III
Rate constants k_1 and k_2 ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) for reactions of HE with Fe^{3+} and FeOH^{2+} respectively, at different temperatures

Complex Fe(III)-HiBAM							
$t, ^\circ\text{C}$	5.0	7.0	9.0	10.0	12.1	14.0	16.0
k_1	0.25	0.36	0.41	0.49	0.60	0.77	0.86
k_2	13.07	14.23	15.21	15.82	16.88	18.11	19.12
Complex Fe(III)-HDPPrM							
$t, ^\circ\text{C}$	5.0	7.0	8.5	10.0	12.0	14.0	16.0
k_1	0.44	0.48	0.56	0.67	0.74	0.92	1.12
k_2	8.41	9.11	9.74	10.52	11.99	13.22	12.27

TABLE IV
Activation parameters for both independent and inverse-acid pathways

Pathway	$E_a, \text{J mol}^{-1}$	$\Delta H^\ddagger, \text{J mol}^{-1}$	$\Delta S^\ddagger, \text{J mol}^{-1}$
Complex Fe(III)-HiBAM			
$\text{Fe}^{3+}-\text{HE}$	$7.25 \cdot 10^4$	$7.02 \cdot 10^4$	-2.99
$\text{Fe}(\text{OH})^{2+}-\text{HE}$	$2.32 \cdot 10^4$	$2.08 \cdot 10^4$	$-1.48 \cdot 10^2$
Complex Fe(III)-HDPPrM			
$\text{Fe}^{3+}-\text{HE}$	$5.94 \cdot 10^4$	$5.70 \cdot 10^4$	-47.50
$\text{Fe}(\text{OH})^{2+}-\text{HE}$	$3.60 \cdot 10^4$	$3.40 \cdot 10^4$	$-1.05 \cdot 10^2$

$\cdot s^{-1}$ at 10.0°C for complexation of iron(III) with 2,2,6,6-tetramethyl-3,5-heptanedione⁸. This is in agreement with the data mentioned above.

The strong bonding between the metal center and OH^- group will weaken the coordinated bonds metal-water. However, it does not explain the increase in the difference between k_1 and k_2 with increase in the size of substituents in β -diketones (R and R'). On the other hand, the activation parameters are in concordance with associative activation for Fe^{3+} and dissociative activation for FeOH^{2+} , since E_a is lower for the latter than for the first process. In the same way, the influence of steric factors is reflected in values of ΔS^\ddagger , which are about 50 times more negative for the reaction of FeOH^{2+} with HE than for that of Fe^{3+} with HE when the β -diketone is HiBAM, while this difference is only about 2 times if β -diketone is HDPrM. The values of activation parameters calculated in this work should be regarded as indicative values and not as reliable ones. Therefore, the above considerations must be taken with caution.

Values of k_1 and k_2 have been calculated at 25°C from the plot of $\ln k_1$ and $\ln k_2$ against $1/T$, respectively. They are 2.25 and $8.96 \cdot 10^{-4}$ for the complex of HiBAM and 2.28 and $7.99 \cdot 10^{-4}$ for the complex of HDPrM, i.e., they are lower than the values predicted on the basis of the Eigen mechanism.

REFERENCES

1. Fay D. P., Nichols A. R., Sutin N.: *Inorg. Chem.* 10, 2096 (1971).
2. Jaffe M. R., Fay D. P., Cefola M., Sutin N.: *J. Am. Chem. Soc.* 93, 2878 (1971).
3. Pearson R. G., Anderson D. P.: *Inorg. Chem.* 9, 39 (1970).
4. Hynes M. J., O'Regan B. D.: *J. Chem. Soc., Dalton Trans.* 1980, 1502.
5. Ando I., Yoshizumi K., Ito K., Ujimoto K., Kurihara H.: *Bull. Chem. Soc. Jpn.* 56, 1368 (1983).
6. Hynes M. J., O'Shea M. T.: *J. Chem. Soc., Dalton Trans.* 1983, 331.
7. Hernando J. M., Blanco C., Prieto T.: *Bull. Soc. Chim. Fr.* 5, 775 (1987).
8. Hernando J. M., Blanco C., Mateo M.: *Collect. Czech. Chem. Commun.* 53, 976 (1988).
9. Blanco C., Hernando J. M., Mateo M.: *Can. J. Chem.* 67, 1305 (1989).
10. Riberio Da Silva M. A.: *Nato As. Ser. Ser. C., Thermochem. Its. Appl. Chem. Biochem. Syst.* 119, 317 (1984).
11. Ishihara K., Funahashi S., Tanaka M.: *Inorg. Chem.* 22, 195 (1983).
12. Merbach A. E.: *Pure Appl. Chem.* 59, 161 (1987).
13. Maroni P., Calmon J. P.: *Bull. Soc. Chim.* 5, 519 (1961).
14. Calmon J. P., Maroni P.: *Bull. Soc. Chim.* 1964, 2525.
15. Ault J. L., Harries H. J.: *J. Chem. Soc., Dalton Trans.* 1973, 1095.
16. Job P.: *Ann. Chim.* 9, 13 (1928).
17. Yoe J. H., Jones A. L.: *Ind. Eng. Chem., Anal. Ed.* 16, 11 (1944).
18. Ringbom A. in: *Formación de complejos en Química Analítica* (S. A. Alhambra, Ed.). Madrid 1979.
19. Stunzi H., Marty W.: *Inorg. Chem.* 22, 2145 (1983).
20. Flynn C. M.: *Chem. Rev.* 84, 31 (1984).
21. Romero J. M., Blanco C., Verdú J.: *An. Quim.* 77, 182 (1981).