Thermodynamics of Formation of Azide Complexes of Iron(III)

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The thermodynamic functions for the stepwise formation of the iron(III) azide complexes have been determined in an aqueous sodium perchlorate medium of unit ionic strength at 25.0 °C. The formation constants were found potentiometrically by means of a glass electrode while the enthalpy changes have been measured by a direct calorimetric determination of heats of complex formation. Five strong mononuclear complexes are formed in the range of ligand concentration used. Neither polynuclear nor acid complexes seem to exist in the range studied.

The studies of azide complexes of iron(III) beyond the first step have hitherto received no attention mainly due to experimental difficulties. First, iron(III) hydrolyses extensively even at rather low pH's of 2−3. Second, hydrazoic acid is a weak volatile acid which very easily corrodes various metallic parts of the instrument. Even in minute amounts, these corrosion products may cause violent explosions.

The study of this system has mainly been focused on the first step. The only method, so far, applied for equilibrium measurements seems to be the spectrophotometrical one.[1−5] Very few determinations of ΔH_1° exist for this system[1,2,6] and none of these has been performed calorimetrically. Therefore, an investigation of this system seems motivated. The most reliable method to obtain accurate values of the thermodynamic functions seems to be a potentiometric determination of the formation constants followed by a direct calorimetric measurement of the corresponding enthalpy changes.

All measurements have been carried out in an aqueous medium of unit ionic strength with sodium perchlorate as inert electrolyte and at a temperature of 25.0 °C. The free energy changes were calculated, from the stability constants found potentiometrically, according to eqn. (1) and finally

$$\Delta G_j^\circ = -RT\ln K_j \qquad (1)$$

the entropy changes were obtained from the relation (2).

$$T\Delta S_j^\circ = \Delta H_j^\circ - \Delta G_j^\circ \qquad (2)$$

EXPERIMENTAL

Chemicals. Standard *iron(III) perchlorate* solutions were prepared according to Ref. 7. All iron(III) perchlorate solutions should be highly acidic in order to prevent hydrolysis.[8,9] The free acid content in the stock solution has been determined potentiometrically and/or by passing aliquots of the solution through columns of Dowex-50W cation-exchange resin in the hydrogen ion form and titrating the eluate with standard sodium hydroxide. Both methods gave concordant results.

Sodium azide and *sodium perchlorate* were prepared and analyzed as described before.[10] The Ag,AgCl electrodes were prepared according to Brown.[11]
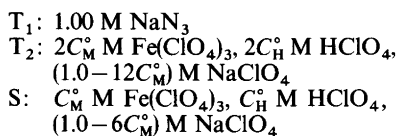
Apparatus. A Metrohm E500 Digital pH Meter equipped with a Metrohm EA109 glass electrode has been used for the potentiometric measurements. The slope of the glass electrode has been checked repeatedly and found to be 59.2 ± 0.2 mV. A magnetic stirrer was used for mixing.

The calorimeter used in this study was of the model developed and described by Grenthe *et al.*[12]

Procedure. The equilibrium measurements were

arranged as titrations at constant C_M and C_H. Equal volumes of the solutions T_1 and T_2 were added from piston burettes to V_0 ml of the solution S. These solutions had the following compositions:

T_1: 1.00 M NaN$_3$
T_2: $2C_M^\circ$ M Fe(ClO$_4$)$_3$, $2C_H^\circ$ M HClO$_4$,
    $(1.0-12C_M^\circ)$ M NaClO$_4$
S: C_M° M Fe(ClO$_4$)$_3$, C_H° M HClO$_4$,
    $(1.0-6C_M^\circ)$ M NaClO$_4$

Thus, up to $C_L = C_H$ the ionic strength is higher than 1 M. But at $C_L = C_H$, which is reached after a few points, all the free acid will practically be converted into HN$_3$. The ionic strength of the resulting solution will then be 1 M.

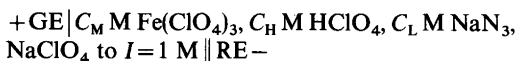Every titration was repeated at least four times with a reproducibility within 0.4 mV.

The technique of the calorimetric measurements has been described elsewhere.[13] The measurements were carried out as a series of titrations of a solution T into a solution S. Usually the solution S contained the central ion and T the ligand. In an attempt to perform some titrations where the central ion has been added to an unbuffered ligand solution hydrolysis of iron(III) immediately set in. Higher ligand concentrations could be reached without any hydrolysis if a ligand solution was added to solutions containing the metal and hydrogen ions as well as the ligand in various concentrations.

The heats of dilution have been determined by similar measurements but with only one of the reactants present. Every titration was carried out twice with a reproducibility within 0.07 J.
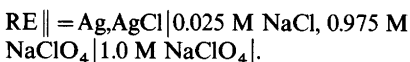
CAUTION. The acid vapour attacks the metallic parts of the measuring equipments forming corrosion products which even in minute amounts may cause violent explosions.

MEASUREMENTS AND RESULTS

Potentiometric measurements. The emfs of the following cells were measured.

$+$GE$|C_M$ M Fe(ClO$_4$)$_3$, C_H M HClO$_4$, C_L M NaN$_3$, NaClO$_4$ to $I=1$ M $\|$ RE$-$

where

RE$\|$ $=$ Ag,AgCl$|$0.025 M NaCl, 0.975 M NaClO$_4$$|$1.0 M NaClO$_4$$|$.

The emf of the above cell is given (in mV) at 25.0 °C by eqn. (3) where h is the free hydrogen ion

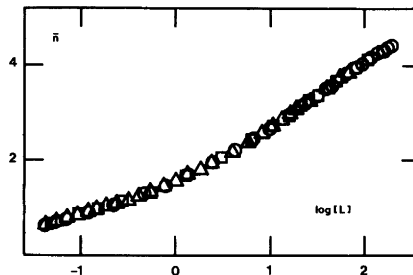$$E_H = E_H^\circ + 59.16 \log h + E_j \qquad (3)$$

Fig. 1. The complex formation function of the iron(III) azide system. Only half of the experimental points, chosen at random, have been plotted.
$\bigcirc$, $C_M = 15.00$ mM, $C_H = 201.1$ mM;
$\square$, $C_M = 20.00$ mM, $C_H = 207.6$ mM;
$\triangle$, $C_M = 30.00$ mM, $C_H = 277.3$ mM.

concentration, E_H° the cell constant and E_j the liquid junction potential.

Titrations have been performed with three different values of C_M, *i.e.* 15, 20 and 30 mM. In order to prevent the initial hydrolysis of Fe(III) ion the concentrations of acid were kept high for each series, *viz.* 201.1, 207.6 and 277.3 mM respectively. A free ligand ion concentration up to $\simeq 200$ mM was reached in the measurements.

The constants were evaluated both graphically[14] and numerically.[15] The methods gave concordant values. In the numerical calculations models including six and five, as well as four, mononuclear complexes have been tried. For a model containing six mononuclear complexes a value of $(4\pm1)\times10^{12}$ M^{-6} is found for β_6 with the acid constant

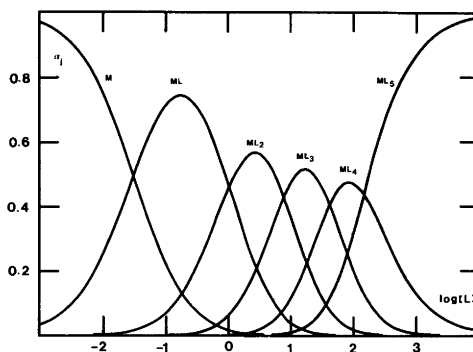*Fig. 2.* The distribution of iron(III) between the different complexes ML$_j$, at varying azide ion concentration, [L] (in mM).

Table 1. The overall formation constants and the values of ΔG_j°, ΔH_j° and ΔS_j° for the consecutive steps of the iron(III) azide system at 25.0 °C and $I = 1$ M. The errors given correspond to confidence limits on the 99.9 % level of significance.

j	$\beta_j (\mathrm{M}^{-j})$	$-\Delta G_j^\circ$ (kJ mol^{-1})	$-\Delta H_j^\circ$ (kJ mol^{-1})	ΔS_j° (J mol^{-1} K^{-1})
1	$(3.2 \pm 0.5) \times 10^4$	25.72 ± 0.39	12.8 ± 0.6	43.3 ± 2.4
2	$(3.0 \pm 0.4) \times 10^7$	17.0 ± 0.4	1 ± 1	54 ± 3
3	$(3.8 \pm 0.7) \times 10^9$	12.0 ± 0.6	7 ± 1	17 ± 4
4	$(9 \pm 1) \times 10^{10}$	7.9 ± 0.5	5 ± 2	11 ± 6
5	$(6 \pm 2) \times 10^{11}$	4.7 ± 0.9	20 ± 3	-51 ± 11

$K_a = 3.61 \times 10^{-5}$ M which has earlier been determined under the prevailing conditions.[10] However, when the value of K_a is increased to 3.70×10^{-5} M, the value of β_6 is decreased to $(1 \pm 2) \times 10^{12}$ M^{-6}. Thus, the sixth complex should be discarded. The value of β_6 depends very much on the value of K_a.

For a model including only five mononuclear complexes the numerical calculations were repeated for both a fixed K_a value of 3.61×10^{-5} M and the values of K_a varying within the limits of error. A better fit with the experimental data has been obtained in the latter case. For a value of $K_a = 3.76 \times 10^{-5}$ M the following estimates are obtained:

$$\beta_1 = (3.2 \pm 0.5) \times 10^4 \text{ M}^{-1}$$
$$\beta_2 = (3.0 \pm 0.4) \times 10^7 \text{ M}^{-2}$$
$$\beta_3 = (3.8 \pm 0.7) \times 10^9 \text{ M}^{-3}$$
$$\beta_4 = (9 \pm 1) \times 10^{10} \text{ M}^{-4}$$
$$\beta_5 = (6 \pm 2) \times 10^{11} \text{ M}^{-5}$$

The errors given correspond to confidence limits on the 99.9 % level of significance. Since with this set of constants a somewhat better fit to the calorimetric data is also achieved this set has been accepted as the "best" one.

The calculations were repeated for a model including only four mononuclear complexes which, however, gave a very poor fit of experimental data.

No systematic deviations could be seen between the three different titrations series used, Fig. 1, which shows that neither polynuclear nor acid complexes are formed in the range studied. The distribution of complexes is shown in Fig. 2.

Calorimetric measurements. Two different ligand solutions with $C_L = 100.0$ and 500.0 mM were added to iron(III) perchlorate solutions with different values of C_M and C_H. As a consequence, proton as well as iron(III) complexes are formed. In order to find the heat changes due to the formation of iron-(III) azide complexes, the values of ΔH_1° and K for

the formation of HN_3 must be known. These have been determined in an earlier investigation[10] and found to be $\Delta H_1^\circ = -12.76 \pm 0.09$ kJ.mol^{-1} and $K = (2.77 \pm 0.07) \times 10^4$ M$^{-1} = 1/K_a$.

The enthalpy changes were calculated by the least squares computer program "Letagrop Kalle".[16]

The results of this investigation are collected in Table 1.

DISCUSSION

The value of β_1 found here is slightly larger than the value of $(2.0 \pm 0.1) \times 10^4$ M^{-1} determined spectrophotometrically under the same conditions.[5] Considering the different experimental methods applied, the agreement is fairly good.

The entropy changes are all positive, except for the last step. The decrease of ΔS_j° is not regular, however. The most positive value is in fact found for the second step. The enthalpy changes are rather irregular. For the first, third and fourth steps the enthalpy and entropy changes contribute much the same to the overall stabilities. The second step is, on the other hand, wholly enthalpy stabilized.

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