KINETICS OF THE GROUND STATE TRANSFORMATION IN Fe(II) \((N, N'-DICYCLOHEXYLTHIOUREA)_{6}(ClO_{4})_{2}\)

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Résumé. — Le complexe de Fe(II) à haut spin \((N, N'-dicyclohexylthiourea)_{6}(ClO_{4})_{2}\) existe sous deux formes qui ne diffèrent que par la distorsion de l'environnement octaédrique de l'ion Fe. Les caractéristiques thermodynamiques de la transformation de l'une à l'autre forme ont été déduites de l'étude Mössbauer. Nous décrivons aussi une méthode de détermination des paramètres cinétiques.

Abstract. — The high spin complex Fe(II) \((N, N'-dicyclohexylthiourea)_{6}(ClO_{4})_{2}\) exists in two forms which only differ in the distortion from octahedral symmetry of the environment of the Fe ion. Thermodynamic data for the transformation from one form to the other as obtained from Mössbauer spectroscopy are presented and a method to derive kinetic parameters is described.

1. Introduction. — In a previous paper [1] we have reported Mössbauer spectroscopy results of iron(II)\((N,N'-dicyclohexylthiourea)_{6}(ClO_{4})_{2}\) (hereafter FeDCTU), which show the existence of two isomers. At low temperatures \((T < 200 \text{ K})\) a form A with quadrupole splitting \(\Delta E = 3.31 \text{ mm/s}\) is stable. At and above room temperature a form B with \(\Delta E = 1.32 \text{ mm/s}\) is stable. For \(200 \text{ K} < T < 300 \text{ K}\) both forms are observed with the B/A ratio increasing with increasing temperature. Isomer shift and magnetic susceptibility results indicate that both forms of the molecule contain high spin ferrous iron. The values of \(\Delta E\) are typical for high spin Fe\(^{2+}\) with an orbital singlet and an orbital doublet ground state for A and B, respectively. Infrared spectra show that in both forms the iron is bound to the sulphur atoms of each of the six dicyclohexylthiourea ligands. Mössbauer spectra in external magnetic fields show that the sign of the principal component of the electric field gradient tensor is negative for form A and positive for form B and that the asymmetry parameter of the electric field gradient tensor is negligible in both forms. The only consistent interpretation of all the results outlined above is in terms of a trigonally
distorted octahedral coordination of the Fe$^{2+}$ for both isomers. In form A, the distortion is such that the ground state has $t^2_{2g}$ symmetry, while in form B the oblate ground state is an orbital doublet whose wavefunction are $|t^2_{2g}>$ and $|t^2_{g}>$. The foregoing suggest a low symmetry ligand field component ($\Delta$) of variable sign, going from a compression ($\Delta < 0$) along the trigonal axis at low temperature to an elongation ($\Delta > 0$) at higher temperatures. The origin of the transition is assigned as due to a subtle perturbation of the sulphur coordination environment, and two possibilities were suggested: a) a temperature dependence of the packing of the bulky cyclohexyl substituents in the thiourea ligands or, b) temperature dependence of perchlorate disorder and thus hydrogen bonding between the perchlorate anions and the thiourea anions. Since Fe(H$_2$O)$_6$(ClO$_4$)$_2$ has also been found [2] to show the same kind of isomeric transformation, it seems that alternative b) is more probable.

In this work we report a study of the kinetics of this transformation by Mössbauer spectroscopy. Previous Mössbauer studies concerning the kinetics of transformations have been made, particularly in metallurgy. (See for instance: GENIN J. M. et FLINN P. A. Trans. Met. Soc. AIME 242 (1968) 1419.) This study is possible because the time the system requires to reach equilibrium is of the order of several hours.

2. Experimental. — The compound was prepared as described in references [1] and [3] and elemental analysis was in agreement with the proposed formula. Spectra were taken in a conventional constant acceleration spectrometer at several temperatures using an approximately 6 mC Co$^{57}$ in Pd source. Temperature constancy was better than 0.1 °C over the whole run and reproducibility of the temperature better than 0.1 °C. When cooling down the sample the temperature overshoot below the required temperature was never more than 1 °C and for less than 3 min.

The results were analyzed with a least squares computer program [4]. Relative concentration of the high temperature species (B) and the low temperature species (A) were calculated from the areas of the fitted curves, as supplied by the computer program.

The procedure for collecting the raw data was as follows: for each set of runs a fresh sample was cooled down rapidly from room temperature to the desired temperature. As soon as this temperature was reached the counting was started for a period of time of at least six hours. When this period was over a new spectrum was started and so on up to reach equilibrium. The six hours period was the shortest compatible with the statistical treatment of data. A typical set of spectra is shown in figure 1. Different samples for each temperature run were used because if the same sample was used for all the required temperatures, kinetic results were no longer reproducible. Furthermore, attempts to follow the reaction A → B starting with samples equilibrated at 77 K (almost pure A) did not give reproducible

![Graphs and diagrams](image-url)
kinetic results either. Nevertheless in all cases the final equilibrium concentrations at each temperature were found to be independent of the thermal history of the sample.

3. Results. — Plots of relative concentration of form A as a function of time for several temperatures in the range 205 to 170 K are shown in figure 2. Below 170 K the transformation is more than 90 % complete in six hours. Therefore the fitted peak area results are not reliable enough. Above 205 K the transition is far too slow and therefore the measuring times are much longer if significant differences between two consecutive relative concentrations are to be found. Above 230 K we could not observe any transition from form B to A.

Two facts should be stressed from figure 2. First of all is that the transformation seems to be first order, as we will discuss below, and secondly the half-life of the reaction decreases with decreasing temperature. This is contrary to the temperature dependence of the rate of conventional chemical reactions.

From the data shown in figure 2 the equilibrium constants for the transformation $B \leftrightarrow A$ can be calculated, $K = [A]/[B] = N_A/N_B$, where $N_A$ and $N_B$ are the number of molecules of A and B respectively in equilibrium.

We collect the values of $K$ in table I for the temperature range of 170 to 205 K. (For the 298 K datum see below.) These data show that the reaction as symbolized above, is exothermic. Figure 3 is a plot of $\ln K$ vs. $T^{-1}$ which shows a linear relation as in ordinary chemical reactions. Therefore, using basic thermodynamic relations and a least squares treatment, we find the values of $\Delta H$, $\Delta G(T)$, $\Delta S(T)$ for the transformation. The value found for $\Delta H$ is $(-4.520 \pm 1.20)$ cal/mol and can be assimilated to $\Delta H^0$ as the difference of specific heat of both species A and B, should be very small or zero. As the volume change during transformation is very small, $\Delta H$ and $\Delta E$ are approximately equal. In table I we added the corresponding values of the thermodynamic parameters for 298 K as found by extrapolation. Uncertainty of these data is less than 5 %. The values of $\Delta S(T)$ confirm our previous assumption that $\Delta C_p$ is nearly zero. The difference in internal energy between both isomers is low, but enough to stabilize state A, whereas the entropy difference is much more important and responsible for the predominance of the B species at higher temperatures. Experimentally it was found that $K < 1.0$ for temperatures $T > 220$ K.

The results shown in figure 2 seem to suggest a first order reaction. Should this hypothesis be correct, as may be inferred from the results presented below, we may write:

$$\frac{dx}{dt} = k_1(b - x) - \left(\frac{k_1}{K}\right)(a + x)$$  \hspace{1cm} (1)
where \(a\) and \(b\) are the initial relative concentrations of species \(A\) and \(B\) and \((a + x)\) the concentration of \(A\) at time \(t\). This equation takes into account the reverse reaction, which introduces the specific rate constant \(k_{-1}\). Nevertheless as the studies of the reverse reaction, that is starting with isomer \(A\), did not produce reproducible kinetic results, we include the formally equivalent expression \(k_1/\mathcal{K}\).

To determine the specific rate constant of the reaction, \(k_1\), it is necessary to take into account that the values of the relative concentrations for a time \(t\) obtained from a Mössbauer spectrum are the mean values of their variation in the time interval \(t_1\), \(t_2\). If we call \(\bar{x}\) the mean values of the relative concentration of \(A\) in a period of time and \(x' = (x_0/b) - a\), where \(x_0\) is the relative concentration of \(A\) in the equilibrium state, integration of eq. (1) leads to

\[
k_1 = \frac{x_0 x'}{b (x' - \bar{x}) (t_2 - t_1)} [1 - \exp \left\{ -k_1 b (t_2 - t_1)/x' \right\}].
\]

Eq. (2) allows the calculation of \(k_1\) by iteration. With these values it is possible to calculate the instantaneous relative concentrations for \(A\) and \(B\) at the end of the first counting period and then with the instantaneous concentrations calculated for the end of the first period and the experimental average concentrations the procedure is repeated for the second period, and so no until the equilibrium concentrations are reached. In table II we show the kinetic parameters as calculated from the mean concentrations and of the instantaneous concentration of \(B\) at the end of each counting period, \(b(t_2)\). In table III we show data for \(k_1\) obtained as described above. The fact that there is good agreement between the values of \(k_1\) calculated from data for consecutive counting periods supports the assumption of a first order rate law.

The most striking fact of table III is that the temperature dependence of \(k_1\) does not follow Arrhenius' law. We have tried several functional relationships and the system is best described by the following analytical relation:

\[
k_1 = (m/T) + p.
\]

Best fit for eq. (3) is achieved with:

\[
m = (0.060 \pm 0.005) \text{ K/s},
\]

and

\[
p = (-2.62 \pm 0.02) \times 10^{-4} \text{ s}^{-1}.
\]

This relationship satisfies the boundary conditions

\[
k_1(T = 0) \rightarrow \infty,
\]

\[
k_1(T = 230) \rightarrow 0.
\]

The first is a hypothetical value but the latter has been obtained experimentally as pointed out above.

### Table II

<table>
<thead>
<tr>
<th>(T)</th>
<th>(x) (*)</th>
<th>(t_1) (hours)</th>
<th>(t_2) (hours)</th>
<th>(k_1) (b(t_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>0.30</td>
<td>0</td>
<td>9</td>
<td>2.78 (\pm) 0.51</td>
</tr>
<tr>
<td>195</td>
<td>0.34</td>
<td>0</td>
<td>6</td>
<td>4.62 (\pm) 0.44</td>
</tr>
<tr>
<td>190</td>
<td>0.40</td>
<td>0</td>
<td>6</td>
<td>5.76 (\pm) 0.36</td>
</tr>
<tr>
<td>180</td>
<td>0.47</td>
<td>0</td>
<td>6</td>
<td>7.16 (\pm) 0.26</td>
</tr>
<tr>
<td>175</td>
<td>0.50</td>
<td>0</td>
<td>6</td>
<td>7.79 (\pm) 0.223</td>
</tr>
<tr>
<td>170</td>
<td>0.55</td>
<td>0</td>
<td>6</td>
<td>7.39 (\pm) 0.081</td>
</tr>
<tr>
<td>150</td>
<td>0.90</td>
<td>6</td>
<td>12</td>
<td>9.19 (\pm) 0.065</td>
</tr>
<tr>
<td>145</td>
<td>0.945</td>
<td>12</td>
<td>18</td>
<td>9.12 (\pm) 0.025</td>
</tr>
</tbody>
</table>

(*) Average concentration of species \(A\) in the period \((t_1, t_2)\). Data plotted in figure 2. 
(**) Values close to equilibrium.

### Table III

<table>
<thead>
<tr>
<th>(T) K</th>
<th>(k_1 \times 10^5 \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>2.78 (\pm) 0.02</td>
</tr>
<tr>
<td>195</td>
<td>4.70 (\pm) 0.03</td>
</tr>
<tr>
<td>190</td>
<td>5.72 (\pm) 0.03</td>
</tr>
<tr>
<td>180</td>
<td>7.17 (\pm) 0.02</td>
</tr>
<tr>
<td>175</td>
<td>7.81 (\pm) 0.02</td>
</tr>
<tr>
<td>170</td>
<td>9.12 (\pm) 0.02</td>
</tr>
</tbody>
</table>

The first is a hypothetical value but the latter has been obtained experimentally as pointed out above.

**References**


b) **Déssi, I. and Keszthelyi, L., Solid State Commun. 4 (1966) 311;**

