

DISTORTION ISOMERISM IN FERROUS THIOUREA COMPLEXES—II(1)

THERMODYNAMICS AND KINETICS

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(Received 3 July 1978; received for publication 13 November 1978)

Abstract—Mössbauer spectroscopy as a function of temperature of $\text{Fe(II)(N,N'-dicyclohexylthiourea)}_6(\text{ClO}_4)_2$ (FeDCTU) shows the existence of two isomeric forms A and B which coexist in the temperature range $200 < T < 300$ K. The relative concentrations of A and B were studied as a function of time at different temperatures in the coexistence region. From the equilibrium constant as a function of temperature we obtain the following thermodynamic parameters: $\Delta H = -4520 \pm 120$ cal/mol and $\Delta S = 20.5 \pm 0.1$ e.u. The kinetics seem to follow an ordinary first order law but with an unusual temperature dependence of the rate constant k_1 . The results are discussed in terms of hydrogen bonded interactions between the perchlorate anions and the cyclohexylthiourea moieties.

INTRODUCTION

In a previous paper [1] we have reported Mössbauer studies showing the existence of two isomeric forms of $\text{Iron(II)(N,N'-dicyclohexylthiourea)}_6(\text{ClO}_4)_2$, hereafter FeDCTU. One of the isomeric forms, A, is stable below 170 K and has a quadrupole splitting $\Delta E_A = 3.31$ mm/s. Isomer B is the stable species at room temperature and above and is characterized by a quadrupole splitting $\Delta E_B = 1.32$ mm/s (see Fig. 1). Between 170 and 300 K both isomers are in thermal equilibrium (see Fig. 2). If, starting with an equilibrated mixture of A and B, the temperature is changed, the equilibration time for interconversion between the two isomers and reestablishment of equilibrium is of the order of several hours. In the present paper we report results of kinetic and thermodynamic studies on this FeDCTU isomer system. The relative concentrations of both isomers were obtained from the ratio of the areas of their Mössbauer spectra as a function of time and at different temperatures between 170 and 205 K.

Nature of the two isomeric forms. Mössbauer and IR spectra and magnetic susceptibility measurements reported previously [1] show that FeDCTU should be considered as a complex containing high spin iron(II) atoms coordinated through the sulphur atoms to six DCTU ligands. The absence of changes in the IR spectra or the isomer shift as a function of temperature and the essentially invariant magnetic moment rule out temperature dependent changes of the atoms in the first coordination sphere.

The magnitude of the quadrupole splitting ΔE is

related to the orbital degeneracy of the electronic ground state of the ferrous ion: the value for form A is typical of an orbital singlet ground state, while that for B is typical of an orbital doublet ground state [2, 3]. Spectra taken at different temperatures and in externally applied magnetic fields yielded the sign of the principal component of the

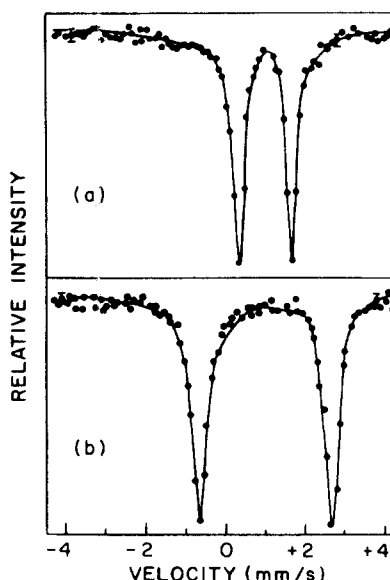


Fig. 1. Mössbauer spectra of FeDCTU at (a), 300 K and (b), 77 K.

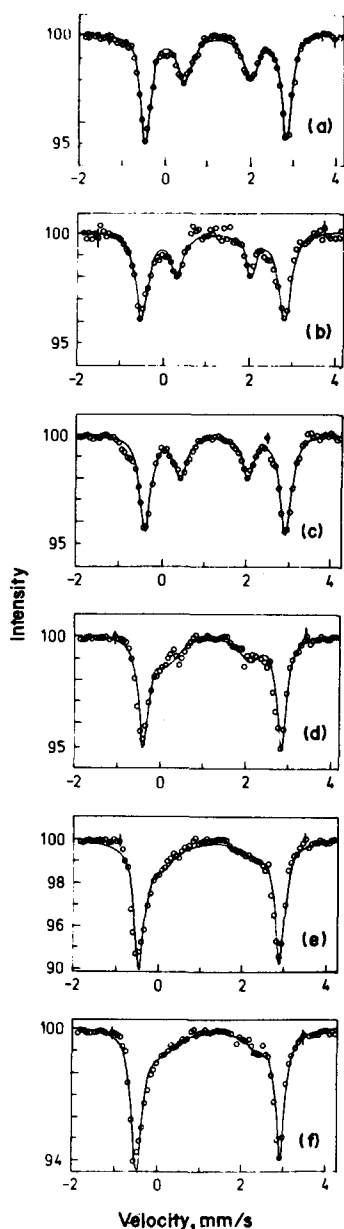


Fig. 2. Equilibrium Mössbauer spectra at (a), 205 K; (b), 195 K; (c), 190 K; (d), 180 K; (e), 175 K and (f), 170 K.

electric field gradient, V_{zz} . Form A was found to have negative V_{zz} whereas form B has positive V_{zz} [1].

We now consider the different situations that can arise in a hexacoordinated high-spin Fe(II) complex. The 5D term is split into 5E_g and 5T_g terms by an octahedral field, the latter lying lowest. If the site symmetry is lower than octahedral, the 5T_g term is split into a doublet and a singlet or three singlets. The first case corresponds to an axial distortion (trigonal or tetragonal) and the second case to a rhombic distortion. In the case of a tetragonal distortion along the z axis the 5T_g term is split into a singlet $|xy\rangle$ and a doublet $|xz\rangle, |yz\rangle$. V_{zz} is positive for the singlet term (oblate) and negative for the doublet (prolate). In the case of a trigonal distortion 5T_g splits into a singlet term with wavefunction $|t_{2g}^0\rangle = |z^2\rangle$, and a doublet with wavefunctions [4],

$$|t_{2g}^+\rangle = (2/3)^{1/2}|x^2 - y^2\rangle - (1/3)^{1/2}|xz\rangle$$

and

$$|t_{2g}^-\rangle = (2/3)^{1/2}|xy\rangle + (1/3)^{1/2}|yz\rangle.$$

In trigonal symmetry the singlet now has negative V_{zz} and the doublet positive V_{zz} . The latter doublet may be further split in accord with the Jahn-Teller effect, although Jahn-Teller distortion is usually small for t_{2g} configurations. In any event, V_{zz} remains positive.

Comparison with the experimental results cited above shows that the only consistent interpretation is in terms of a trigonally distorted octahedral environment for the Fe^{2+} in both (A) and (B). Furthermore, on the basis of simple crystal field theory it is possible to account for the transition (A) \rightarrow (B) as T increases in terms of a change in sign of the trigonal term in the crystal field expansion. A compression along the trigonal axis lowers the energy of $|t_{2g}^0\rangle$ relative to $|t_{2g}^+\rangle$ and $|t_{2g}^-\rangle$ while an elongation raises the energy of $|t_{2g}^0\rangle$ relative to $|t_{2g}^+\rangle$ and $|t_{2g}^-\rangle$. Thus (A) \rightarrow (B) corresponds to compression \rightarrow elongation with respect to the trigonal axis. Because this transformation does not involve major molecular rearrangements, but apparently only a change in the sign of the trigonal distortion, we propose to define it as a *distortion isomerism*. Similar distortion isomerism transformations have been studied previously in $Fe(H_2O)_6(ClO_4)_2$ by Dezi and Keszthelyi [5], Coey *et al.* [6], Reiff *et al.* [7], and Ouseph *et al.* [8].

Nature of the transformation. In the previous section we discussed the nature of the A and B individual species, i.e. the symmetry characteristics at the iron sites. We now address ourselves to the question of the nature of the transformation itself and of the interactions between A and B species, namely, whether A and B behave as independent chemical species and the A \rightarrow B transformation therefore follows the usual chemical kinetic and thermodynamic laws, or, whether there is a crystallographic phase transition between two solid species A and B. The latter conjecture implies some degree of cooperativity and interaction between sites.

Ouseph *et al.* [8] have interpreted their Mössbauer results in $Fe(H_2O)_6(ClO_4)_2$ in terms of a phase transition between two crystal forms. In the present case the fact that we find reproducible equilibrium ratios between the relative concentrations of the A and B forms of FeDCTU in different samples over a wide temperature range seems to rule out an interpretation based on a classical phase transition.

In order to elucidate the nature of the transition in FeDCTU, we have measured the equilibrium constants $K = [A]/[B]$ in the temperature range where both forms coexist, and have also studied the approach to equilibrium as a function of temperature. We have analyzed these data assuming the first hypothesis, that A and B behave as independent chemical species. As we show below, with this hypothesis we obtain reasonable results for the temperature dependence of the equilibrium values but not for the kinetic results. This implies some degree of cooperativity.

EXPERIMENTAL

FeDCTU was prepared as described by Yagupsky [9]; hot, concentrated methanol solutions of ferrous perchlorate and N,N' -dicyclohexylthiourea (DCTU) were mixed in stoichiometric proportions. When the mixture was allowed to cool a faintly yellowish precipitate was obtained. The precipitate was filtered and washed with cold ethanol and dried in vacuum. Elemental analyses are in agreement with the formula $Fe(DCTU)_6(ClO_4)_2$.

Mössbauer spectra were taken in a conventional constant acceleration spectrometer at several temperatures. A $6\text{ mC}^{57}\text{Co}$ in Pd source was used.

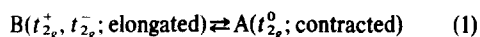
The experimental data were least squares computer fitted to a two-line or a four-line spectrum[10]. This program yields the "best" parameters for each line including the area under the line. When both A and B isomers are present the ratio of the areas of the A and B doublets is equal to the ratio of the relative concentrations of the isomers, assuming equal recoilless fractions for both forms at the same temperature.

RESULTS

The procedure for obtaining kinetic and thermodynamic data for the reaction $B \rightarrow A$, corresponding to the elongated \rightarrow compressed transformation of FeDCTU, is as follows. Starting with a sample in equilibrium at 300 K the temperature was rapidly lowered and consecutive Mössbauer spectra was recorded until the A/B ratio reached its new equilibrium value. The shortest period of counting time compatible with the statistical treatment of the data was found to be of the order of six hours. After each such period new counting was started. Figure 4 shows spectra taken at 205 K at different times after the temperature was lowered from 300 K. Thirty six hours after the temperature was changed the A/B ratio reached its equilibrium ratio. Figure 5 and Table 1 show the relative average concentration of A as a function of time for runs at different temperatures between 170 and 205 K. These data were obtained using a fresh sample for each run. Runs at the same temperature using different fresh samples gave reproducible results. Attempts to use the same sample for runs at different temperatures did not give reproducible kinetic results. Furthermore, attempts to follow the reaction $A \rightarrow B$ starting with samples equilibrated at 77 K (almost pure A) did not give reproducible 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.

The results of Table 1 show that the time necessary to reequilibrate the samples decreases as the temperature is decreased. Below 170 K the reaction is too fast to be studied by this technique: the reaction is more than 90% complete in 6 hr. Above 210 K the reaction is too slow. For $T > 230\text{ K}$ we could not detect any reaction from B to A. The temperature dependence of the kinetics of this isomerization (increase of reaction rate as temperature is lowered) is not like that of ordinary chemical reactions. Some tentative explanations will be offered below.

Thermodynamic quantities. From the data shown in Table 1 we can calculate the equilibrium constants for the transformation



$$K = \frac{[A]}{[B]} = \frac{N_A}{N_B} \quad (2)$$

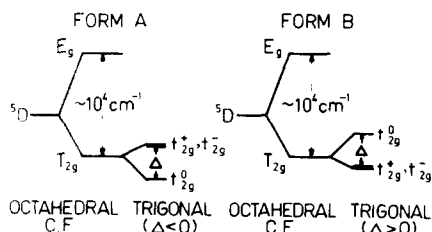


Fig. 3. Energy level diagrams for forms A and B of FeDCTU.

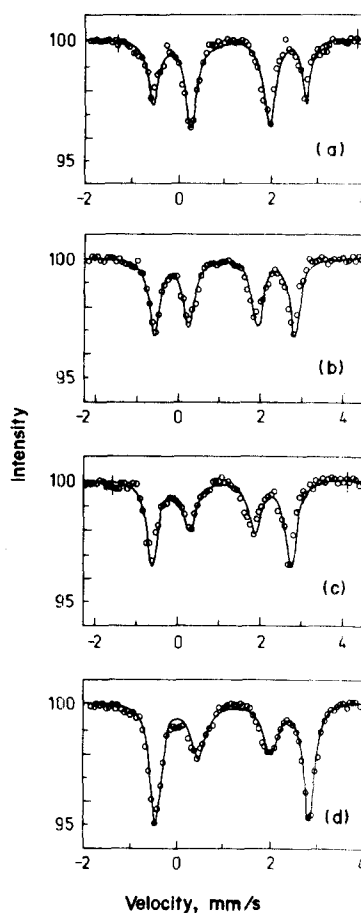


Fig. 4. Mössbauer spectra of FeDCTU at 205 K at different periods of time after rapid cooling from 300 K. (a), 0–9 hr; (b), 9–17 hr; (c), 17–24 hr and (d), 36–42.5 hr.

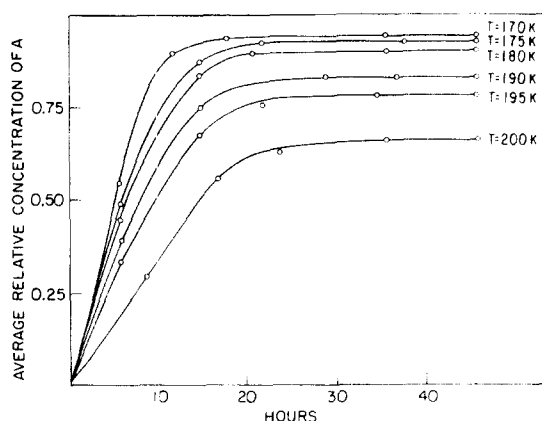


Fig. 5. Average relative concentration of isomer A as a function of time at different temperatures.

where N_A and N_B are the number of molecules of A and B respectively.

We show the calculated values of K in Table 2 for the temperature range of 170–205 K. (For the 298 K data, see below.) These data show that the reaction, as symbolized by eqn (1) is exothermic.

Figure 6 is a plot of $\ln K$ vs T^{-1} which shows a linear relation as in most ordinary chemical reactions. Therefore, using basic thermodynamic relations and a least squares treatment, we find the values of $\Delta\bar{H}$, $\Delta G(T)$,

Table 1. Relative average concentration of isomer A as a function of time at different temperatures as obtained from Mössbauer spectra†

| T = 200 K | | T = 195 K | | T = 190 K | | T = 180 K | | T = 175 K | | T = 170 K | |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] | $t_{(hr)}$ [A] |
| 9 | 0.30 | 6 | 0.34 | 6 | 0.40 | 6 | 0.47 | 6 | 0.50 | 6 | 0.55 |
| 17 | 0.56 | 15 | 0.68 | 15 | 0.755 | 15 | 0.84 | 15 | 0.875 | 12 | 0.90 |
| 24 | 0.63 | 22 | 0.76 | 21 | 0.82 | 21 | 0.895 | 22 | 0.925 | 18 | 0.94 |
| 36 | 0.66 | 28 | 0.78 | 29 | 0.83 | 28 | 0.90 | 29 | 0.93 | 26 | 0.95 |
| 42.5 | 0.66 | 35 | 0.78 | 37 | 0.83 | 36 | 0.90 | 38 | 0.93 | 36 | 0.95 |
| 53 | 0.67 | 45 | 0.78 | 43 | 0.83 | 42 | 0.90 | 45 | 0.93 | 42 | 0.95 |
| 62.5 | 0.65 | 52 | 0.78 | 51 | 0.835 | 49 | 0.90 | 60 | 0.93 | 49 | 0.95 |
| 74 | 0.66 | 63 | 0.78 | 59 | 0.83 | 58 | 0.90 | 75 | 0.93 | 62 | 0.95 |

†In all cases the initial concentration of A was negligible ($a = 0$). Relative concentration of B is $[B] = 1.00 - [A]$.

Table 2. Thermodynamic quantities for the reaction. B (elongated FeDCTU) \rightleftharpoons A (compressed FeDCTU)

| T(K) | K | $\Delta G(\text{cal/mol})$ | $\Delta S, \text{eu}(\text{cal})$ |
|------|--------|----------------------------|-----------------------------------|
| 298 | 0.0636 | +1630 | -20.5 |
| 205 | 1.94 | -270 | -20.6 |
| 195 | 3.55 | -490 | -20.5 |
| 190 | 4.88 | -600 | -20.5 |
| 180 | 9.00 | -785 | -20.6 |
| 175 | 13.3 | -900 | -20.5 |
| 170 | 19.0 | -995 | -20.5 |

$\Delta S(T)$ for the transformation. The value found for $\Delta \bar{H}$, is -4520 ± 120 cal/mol and can be equated to ΔH as the difference of specific heats of both species A and B should be very small or zero. As the volume change during transformation is very small, ΔH and ΔE are approximately equal.

In Table 2 we include corresponding values of the thermodynamic quantities for 298 K as found by extrapolation. Estimated error for these data is less than 5%. The values of $\Delta S(T)$ confirm our previous assumption that ΔC_p is nearly zero.

It is important to stress that this reaction is not of the usual type of reactants leading to some products, but a transformation which is discussed in terms of an equilibrium between two isomers whose structure is very closely related, probably only through an elongation-compression change with respect to the trigonal symmetry axis.

The difference in internal energy between both isomers is low, but enough to stabilize state A at low temperatures. The entropy difference is much more important and is responsible for the predominance of the B species at higher temperatures. Experimentally it is found that $K < 1.0$ for $T \gg 220$ K.

Kinetic parameters. The results shown in Fig. 4 seem to suggest a first-order reaction. Should this hypothesis be correct, as may be inferred from the results obtained below, we can write;

$$\frac{dx}{dt} = k_1 \times (b - x) - (k_1/K) \times (a + x) \quad (3)$$

where a and b are the initial relative concentrations of species A and B and $(a + x)$ the concentration of A at time t .

Equation (3) takes into account the reverse reaction,

which introduces the specific rate constant k_{-1} . Nevertheless as the studies of the reverse reaction, $A \rightarrow B$ did not produce reproducible kinetic results, we include the formally equivalent expression k_1/K (*vide infra*). We would like to emphasize that if only the direct reaction is considered, it is not possible to fit the experimental data with a first-order-rate law.

Substituting $k = x_e(b - x_e)$, eqn (3) can be written as:

$$\frac{dx}{dt} = k_1 \times \left\{ (b - x) - \frac{(b - x_e) \times (a + x)}{x_e} \right\} \quad (4)$$

where x_e is the relative concentration of A in the equilibrium state. Integration of eqn (4) leads to:

$$x = x_e' \times (1 - \exp(-k_1 \times b \times t/x_e)) \quad (5)$$

where $x_e' = (x_e/b) - a$.

To determine the specific reaction rate k_1 it is necessary to consider that the values of the relative concentrations for a time t obtained from Mössbauer spectra (Table 1 and Fig. 5) are the average of their instantaneous values in the period t_1 to t_2 corresponding to the beginning and end of the respective Mössbauer counting period. If we call \bar{x} the mean values of the relative concentration of A in this period, we have that

$$\bar{x} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} x_e' \left[1 - \exp\left(\frac{-k_1 \times b \times t}{x_e}\right) \right] dt. \quad (6)$$

Which yields

$$k_1 = - \frac{x_e x_e' [\exp(-k_1 b t_2/x_e) - \exp(-k_1 b t_1/x_e)]}{b(x_e - \bar{x})(t_2 - t_1)} \quad (7)$$

Equation (7) allows the calculation of k_1 by iteration for a given period $t_1 - t_2$. With these values it is possible to calculate the instantaneous relative concentrations for A and B at time t_2 using eqn (6). This is done for 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 on until the equilibrium concentrations are reached.

The nature of Mössbauer spectroscopy measurements is such that it is not possible to measure instantaneous concentration values. Nevertheless we can obtain them from the average values as shown above. In Table 3 we present the calculated values of k_1 and of the in-

Table 3. Kinetic parameters for the reaction $B \rightarrow A$ obtained from average relative concentrations

| $T(K) \bar{x}^\dagger$ | t_1 (hr) | t_2 (hr) | $k_1, 10^5 \text{ sec}^{-1}$ | $b(t_2)$ | |
|------------------------|---------------|---------------|------------------------------|-----------------------|--------|
| 205 | 0.30 | 0 | 9 | 2.78×10^{-5} | 0.51 |
| | 0.56 | 9 | 17 | 2.73 | 0.39‡ |
| | 0.63 | 17 | 24 | 2.83 | |
| 195 | 0.34 | 0 | 6 | 4.62 | 0.44 |
| | 0.68 | 6 | 15 | 4.51 | 0.25‡ |
| | 0.76 | 15 | 22 | 4.50 | |
| 190 | 0.40 | 0 | 6 | 5.76 | 0.36 |
| | 0.755 | 6 | 15 | 5.76 | 0.19‡ |
| | 0.82 | 15 | 21 | 5.84 | |
| 180 | 0.47 | 0 | 6 | 7.16 | 0.26 |
| | 0.84 | 6 | 15 | 6.93 | 0.11‡ |
| | 0.895 | 15 | 21 | 7.25 | |
| 175 | 0.50 | 0 | 6 | 7.79 | 0.223 |
| | 0.875 | 6 | 15 | 7.53 | 0.081‡ |
| | 0.925 | 15 | 22 | 7.39 | |
| 170 | 0.55 | 0 | 6 | 9.14 | 0.17 |
| | 0.90 | 6 | 12 | 9.19 | 0.065‡ |
| | 0.945 | 12 | 18 | 10.00 | |

† Average concentration of A in the period (t_1, t_2). Data from Table 1.

‡ Concentration values are close to equilibrium.

stantaneous concentration of B at the end of each counting period $b(t_2)$. These values were calculated from the average concentration values shown in Table 1, as outlined 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.

In Fig. 7 we have plotted the calculated instantaneous concentrations of A as a function of time, at different temperatures, obtained by the procedure outlined above. This plot is analogous to the one in Fig. 5 except that there we had plotted the experimental average concentrations of A. The rate constant k_1 was also calculated by least squares fitting of eqn (6) using all the experimental data for a given temperature and the calculated values of k_1 are given in Table 4.

The most striking fact is that the temperature dependence of k_1 does not follow Arrhenius' law: a plot of $\log k_1$ vs $1/T$ is not well represented by a single straight line. We tried several other functional relationships and have found that the best fit is given by

$$k_1 = p + \frac{m}{T} \quad (8)$$

(Fig. 8). Least squares fitting gave $m = 0.060 \pm 0.005 \text{ k/sec}$ and $p = -(2.62 \pm 0.02) \times 10^{-4} \text{ sec}^{-1}$. This relationship satisfies the boundary conditions

$$k_1(T \rightarrow 0) \rightarrow \infty.$$

$$k_1(T = 230) = 0.$$

The first condition is hypothetical but the later has been obtained experimentally as pointed out above.

As mentioned above we could not measure the rate

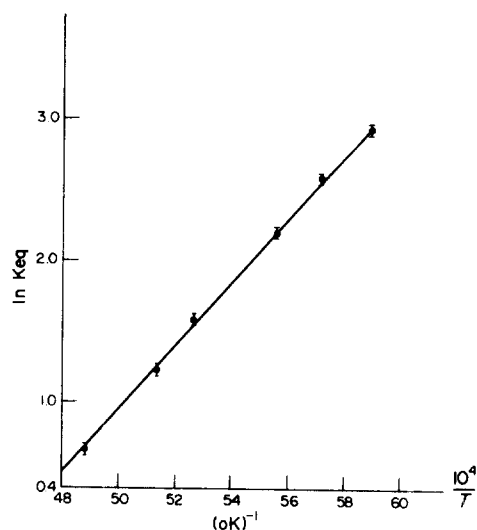


Fig. 6. Plot of logarithm of the equilibrium constant K as a function of T^{-1} for the isomerization equilibrium $B \rightleftharpoons A$.

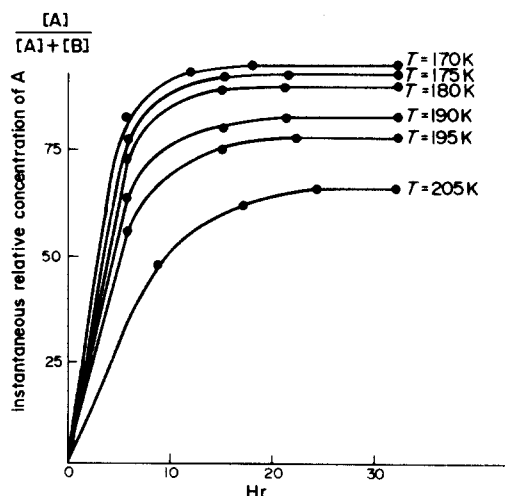


Fig. 7. Instantaneous relative concentration of A as a function of time for different temperatures. Instantaneous values are obtained from the average values plotted in Fig. 5 as described in the text.

Table 4. Kinetic parameters obtained by least squares fitting to eqn (6)

| $T(K)$ | $k_1(10^5)$ | $k_{-1}(10^5)^\dagger$ |
|--------|-------------|------------------------|
| 205 | 2.84 | 1.96 |
| 195 | 6.58 | 1.29 |
| 190 | 5.78 | 1.18 |
| 180 | 7.13 | 0.79 |
| 175 | 7.72 | 0.58 |
| 170 | 9.09 | 0.48 |

† k_{-1} was obtained from $k_{-1} = K/k_1$.

constant k_{-1} for the reverse reaction $A \rightarrow B$. However we can calculate k_{-1} at different temperatures using the relationship $k_{-1} = K/k_1$. Values of k_{-1} calculated in this way have been included in Table 4. Here we find a "normal" temperature dependence, but the fit to Arrhenius' law is also poor. The fact that k_{-1} increases with temperature is in qualitative agreement with our experimental results: although we could not obtain

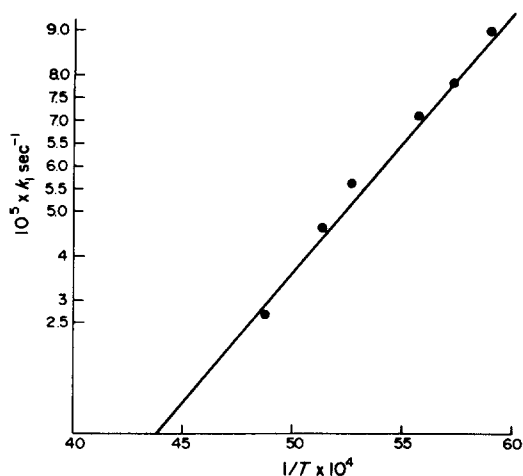


Fig. 8. Plot of the rate constant k_1 as a function of T^{-1} .

quantitative data for k_{-1} by warming samples of pure A we found that the equilibration time indeed decreases as temperature is raised.

DISCUSSION

We can think of two different mechanisms that could induce the $A \rightleftharpoons B$ transformation in FeDCTU: (a) changes in the hydrogen bonding between the perchlorate anions and the DCTU nitrogen atoms as temperature is changed, or (b) a thermal loosening of the packing of the twelve bulky cyclohexyl groups per molecule. In both cases the change would involve an increase in entropy and would be favored at higher temperatures as is indeed observed. Since similar distortion isomerism has also been found by Mössbauer spectroscopy in $\text{Fe}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ [5–8] we are more inclined to favor an explanation based on changes in hydrogen bonding.

Figgis *et al.* [11, 12] have reported structural and magnetic susceptibility studies on $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$ between 80 and 300 K that have some bearing on our results in FeDCTU and $\text{Fe}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$. They have found that Ti^{3+} lies at the center of an octahedron which is essentially regular within experimental error except for a 5° twist of one pair of opposite faces relative to each other about a three-fold axis. The angle of twist is found to be independent of temperature in the range studied. The magnetic anisotropy, however, changes sign at *ca.* 165 K and rises sharply in magnitude at lower temperatures. The temperature dependence of the principal magnetic moments is fitted by adjustment of electronic parameters including Δ , the splitting of the ${}^2T_{2g}$ term (compare with Fig. 3). Best fit between experimental and calculated data was obtained with $\Delta = -400 \text{ cm}^{-1}$. The negative value of Δ corresponds to an orbital doublet 2E ground state in accord with low temperature optical spectroscopy [14]. Figgis *et al.* [13] do not seem to believe that the relatively large value of Δ is due to the 5° twist but rather to crystallographically undetected compression or elongation along the three-fold axis. Although they have fitted the data with a constant value of Δ they argue that a better agreement could have been obtained with a temperature dependent Δ . X-Ray studies at 90 and 300 K [13] show little differences in the structure of $\text{Ti}(\text{urea})_6^{3+}$ but the O–Cl–O angles of ClO_4^- show significant differences, the angles at the higher temperature showing a larger departure from a regular

tetrahedral geometry. This structural difference is attributed to changes in hydrogen bonding between the perchlorate oxygen atoms with the urea nitrogen atoms. The results in $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$ also seem to lend support to an interpretation of the distortion isomerism in FeDCTU and $\text{Fe}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ based on changes in hydrogen bonding.

Mooy *et al.* [16] have studied the ESR of Cr^{3+} in $\text{Al}(\text{urea})_6(\text{ClO}_4)_3$ between 77 and 360 K. At 77 K they find there are six complexes per unit cell, differing in the orientation of their x axes. Above 77 K, the ESR spectrum is strongly temperature dependent, with the E parameter in the spin Hamiltonian going to zero at 295 K. Below 295 K both the D and E parameters in the spin Hamiltonian vary approximately as $(295 - T)^{0.5}$ (the D parameter also has a component which is linear in T above and below 295 K). The authors cite these observations as evidence for a second-order phase transition, possibly of an order–disorder type involving the occupancy of sites in the perchlorate tetrahedra. Above 295 K, there is rapid interconversion between the oxygen sites; below 295 K one site or the other is increasingly occupied leading to an ESR spectrum of lower symmetry.

Ouseph *et al.* [8] have measured the quadrupole splitting and isomer shift of $\text{Fe}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ as a function of temperature between 230 and 273 K. They find a transition from the room temperature form with $\Delta E = 3.2 \text{ mm/s}$ to a form with $\Delta E = 1.4 \text{ mm/s}$ at low temperatures. They report a transition which starts at 273 K when cooling the pure high temperature form. Both forms coexist in a 70 K temperature interval. When starting with the low temperature form and warming the transition range is shifted to 253 K. Taking into consideration the relatively narrow coexistence range between the two forms they describe the phenomenon as a phase transition. Chaudhuri [15] has found a sharp break in the magnetic anisotropy and magnetic susceptibility versus temperature curves of a series of $\text{M}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ compounds. In the case of $\text{Fe}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$, the reported temperature is $237 \pm 1 \text{ K}$. The magnetic results are also interpreted in terms of a phase transition from a pseudo-hexagonal structure at room temperature to a monoclinic one at low temperature. Even more complex transitions are observed in other substituted ferrous thiourea complexes [17].

It is difficult to reconcile the present results on FeDCTU as a phase transition of either first or second order. The existence of reproducible A/B (i.e. of an equilibrium constant for $A \rightleftharpoons B$ transformation) is not compatible with a heterogeneous phase equilibrium, but rather, implies that there are A and B sites within a single solid phase. On the other hand, the temperature dependence of the $B \rightarrow A$ kinetics is unlike that of ordinary homogeneous chemical reactions. It is difficult to rationalize the fact that the reaction rate for $B \rightarrow A$ increases as the temperature decreases on the basis of mechanisms based on isolated chemical species.

In some ways this temperature dependence of the kinetics is reminiscent of some solid state phase transformation and nucleation processes [18] where the reaction rate increases as the supercooling ΔT increases (i.e. as the temperature is lowered). In these cases there is a "driving force" related to the supercooling ΔT which accelerates the reaction as the temperature is lowered. In the present case we cannot speak of a supercooling or departure from equilibrium ΔT because at all the studied

temperatures there is an equilibrium state, but when B is cooled, the initial state is farthest from the final equilibrium ratio, the lower the temperature. If, as it seems, the B→A transformation involves a change of site symmetry which is related to changes in H-bonding to the tetrahedral ClO_4^- anions or perhaps some change involving order-disorder of the ClO_4^- anions, then the B→A transformation does not involve atomic migrations as other solid state reactions but simply some minor atomic displacements. In the temperature range where A and B coexist we can speak of neither a homogeneous system nor of a heterogeneous two-phase system, but rather a nonhomogeneous phase in which we cannot identify phase boundaries but where the microscopic structure is not constant everywhere. It is not surprising therefore that the reaction kinetics do not follow the classical laws since we are dealing with a system which is an intermediate between a reaction between isolated chemical species and a cooperative phase transition in the solid. Experiments under progress with similar systems and low temperature X-ray studies should clarify the situation further.

Acknowledgements—During the course of this work we have benefited from useful discussions with M. Passeggi, A. J. Pedrazza, D. F. de Pedrazza, R. Jordan, J. M. Friedt, W. M. Reiff and I. Deszi. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation (U.S.A.). E. F. wishes to acknowledge the support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil) and the Financiadora de Estudos e Projectos (Brazil). J. A. C. wishes to acknowledge the support of the Dirección de Investigaciones Científicas y Tecnológicas de la Univ. Técnica del Estado (Chile). R. L. wishes to acknowledge the support of the Forge Foundation, the Ford Foundation, Organization of American States, Petroleum Research Foundation, Research Corporation

and the Servicio de Desarrollo Científico y Creation Artística, Univ. de Chile (Chile).

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