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$\eta^3:\eta^1 \rightleftarrows \eta^2$-TAUTOMERISM IN CARBONYLIRON COMPLEXES. THERMODYNAMIC CHARACTERISTICS

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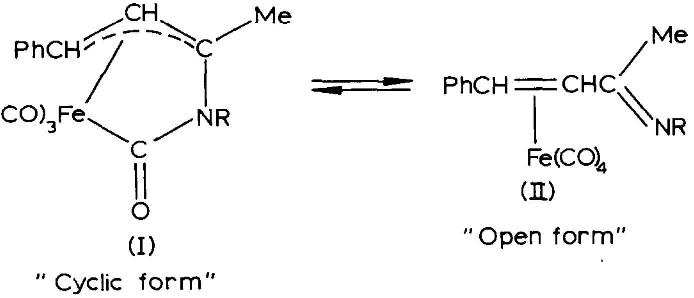
Summary

The thermodynamic characteristics of the equilibrium between the chelate tricarbonylmethyl-π-allyl-σ-R-carbamoyliron complex (R = $c\text{-}C_6H_{11}$) and its π-olefinic isomer in hexane and in hexane/dichloromethane were determined. The observed values fit fairly well with the thermodynamic scale of tautomerism and allow a quantitative conclusion on the influence of solvent, temperature and polarity on the relative stabilities of the tautomeric forms to be reached.

Introduction

We earlier discovered that the tricarbonyl-σ-[*N*-(1-methyl-3-phenyl-1-3-η-allyl)-*N*-R-carbamoyl]iron complexes (I, where R = Me, i-Pr, $c\text{-}C_6H_{11}$, CH_2Ph) isomerize reversibly in solutions to tetracarbonyl(1-R-2-methyl-4-phenyl-3-4-η-1-azadiene)iron complexes (II) [1].



The equilibrium position depends on the polarity of the solvent and is shifted towards I in more polar solvents. In the solid state, the complexes were isolated only in form I. For a stringent assignment of this reversible isomerization to tautomerism, it was necessary to determine the thermodynamic parameters. The purpose of the

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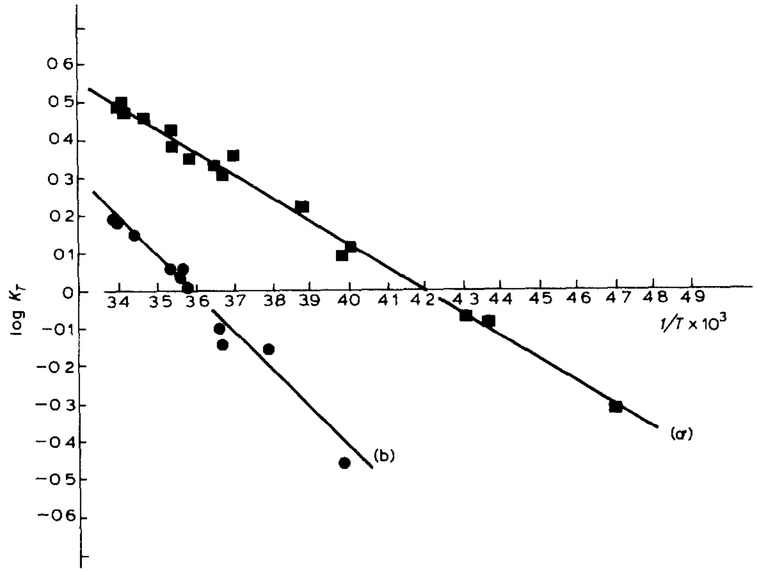


Fig. 1. Plot of log K_T vs. $1/T$ for the tautomeric equilibrium I $\rightleftharpoons$ II, for R = c-C_6H_4, (a) in hexane and (b) in hexane/CH_2Cl_2 (96/4).

present paper was to investigate the temperature dependence of the equilibrium constant, K_T, and to calculate the changes in enthalpy (ΔH), entropy (ΔS) and free energy ($\Delta G°$) for the isomerization I $\rightleftarrows$ II, for R = c-C_6H_{11}.

Results and discussion

The equilibrium constants, K_T, were determined by the IR spectroscopy (see Experimental). The measurements were carried out in hexane and in hexane/CH_2Cl_2 (96/4, v/v) in the temperature range −60–22°C. The temperature dependence of K_T is presented in Fig. 1. The correlation coefficient for the plot of log K_T vs. $1/T$, processed by the least-squares method, is 0.99 for solutions in hexane and 0.98 for solutions in hexane/CH_2Cl_2. The values of ΔH and ΔS for the conversion of the cyclic form I into the open olefinic form II, and the difference in the free energies of these two forms, $\Delta G°$, were calculated from the temperature dependence of K_T. The thermodynamic equilibrium parameters are given in Table 1.

TABLE 1

THERMODYNAMIC PARAMETERS OF EQUILIBRIUM [a]

Solvent	ΔH (kJ/mol)	ΔS (J/mol)	$\Delta G°$ (kJ/mol)		
			295 K	250 K	210 K
Hexane	11.8	49.5	−28	−0.6	1.4
Hexane/CH_2Cl_2 (96/4)	20.3	72.8	−1.2	2.1	–

[a] Errors in the determination of ΔH, ΔS and $\Delta G°$ comprise ~10%.

The free energy change ($\Delta G°$) characterizes the relative stability of the two tautomeric forms. From the data obtained, it follows that the olefinic form II is more stable in both solvents at room temperature, whereas the chelate form I is more stable in hexane below −35°C and in hexane/CH_2Cl_2 below −6°C. Such a rise in the stability of the chelate form and an increase in its relative quantity in the mixture with decreasing temperature correspond to the endothermal conversion of I into II ($\Delta H > 0$), and are probably due to a decrease in the role of the entropy factors $T\Delta S$ at low temperature. It should be noted that the conversion of cyclic form I into open form II may be regarded as a rare case in chemical reactions when $\Delta H > 0$ and hinders the course of the reaction, but ΔS is also positive and so great that $T\Delta S$ is larger than the value of ΔH at ordinary temperatures.

The entropy growth of the system in the conversion of I into II is apparently accounted for by the transition from a rigid chelate molecule to a more mobile molecule with an open chain.

The difference in the free energies, $\Delta G°$, decreases in a more polar solvent and is, in all probability, due to the better solvation of the chelate form I compared with the open form II. The enthalpy and entropy of conversion of I into II increase simultaneously.

We also estimated the low limit of the rate constants for the conversion of I into II, and calculated the free energy of activation, $\Delta G^{\neq}$, corresponding to it, using the Eiring equation. According to the IR spectra, an equilibrium mixture exists in the solution immediately after dissolution of complex I. Therefore, we may assume that equilibrium is established in less than 5 min. Assuming that this time corresponds, at least, to the period of semiconversion for the monomolecular reaction, we have:

$$t_{1/2} < 300\ \text{s};\ t_{1/2} = \frac{0.693}{k} \quad \text{or } k > 2.3 \times 10^{-3}\ \text{s}^{-1}$$

$$k = x\frac{kT}{h}e^{-\frac{\Delta G^{\neq}}{RT}} \qquad \Delta G^{\neq} < 90\ \text{kJ/mol}$$

The thermodynamic and kinetic parameters of the equilibrium under study fit fairly well with the corresponding tautomerism scale [2], while the equilibrium itself may be related to a novel case of ring-chain valent tautomerism in organometallic compounds of the transition metals. Its peculiarity lies in the fact that at the same time as the closing and opening of the chelate ring, a change in the metal–ligand bond ($\eta^2 \rightleftarrows \eta^3$) occurs. There is scant information available concerning similar cases of ring-chain dynamic isomerism in π-complexes of the transition metals [3].

Experimental

IR measurements were made on a Specord 75-IR grating spectrophotometer using a compensation recorder (K-201) with an integrator for direct obtention of the integrated absorption band intensities. The bands of the totally-symmetrical CO vibrations at 2068 cm^{-1} for the cyclic form I and at 2085 cm^{-1} for the open form II were used as the "working" bands. These bands do not overlap each other or other CO bands. The high intensity of these bands makes it possible to work with dissolved solutions ($\sim 10^{-3}$ mol l^{-1}). The optical densities of the "working" bands ranged from 0.2 to 0.8. The scan rate was 40 cm^{-1}/min and the spectral slit width was ~ 3 cm^{-1}.

To study the temperature dependence, the sample cell was placed in the cryostat provided with the apparatus of the instruments. It was cooled with liquid nitrogen vapour.

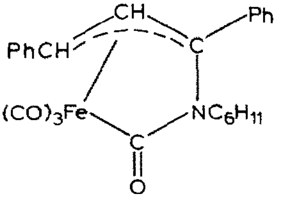
For measurements below room temperature, dry argon was sprayed against the cell windows to prevent condensation. The temperature in the cell was measured with an iron-constantan thermocouple with an accuracy ±1°C. The integrated intensity (A) was obtained for each sample and each temperature as the average of three measurements. The intensity measurements were performed twice: when the temperature was decreased and again increased; the reproducibility of the relative changes in the optical density of the corresponding bands was observed.

The equilibrium constant, K_T, was calculated from the following equations:

$$K_T = \frac{C_{II}}{C_I} = \frac{A_{II} A_I^\circ}{A_I A_{II}^\circ}, \; A = c\, d\, A^\circ$$

where C_I and C_{II} are the concentrations of forms I and II in mol l^{-1}, A_I and A_{II} are the integrated band intensities of forms I and II in cm^{-1}, A_I° and A_{II}° are the absolute integrated intensities of the corresponding forms in l mol^{-1} cm^{-2}, and d is the absorption thickness in cm.

A_I° was assumed to be equal to A° for the model compound III; the IR spectrum of III revealed only one chelate structure independent of the solvent polarity.



III

A_{II}° was calculated from the formula $A_{II}/(C - C_I)$, where C is the total concentration of both forms calculated on the basis of compound weights and dissolution.

Special experiments have shown that the Buger–Lambert–Beer rule holds for the concentration range studied. For the model compound III, it was also shown that the absolute integrated intensity, A°, is practically independent of temperature. Therefore it is assumed that the values of A_I° and A_{II}°, or their ratio A_I°/A_{II}°, also remain constant with varying temperature.

While recording the spectra (~ 2 h), slight decomposition of the complexes was observed, which had hardly any influence on the precision of the determination of the equilibrium constant because the concentration of each form was determined independently.

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