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COMPLEX CATALYST STUDIES OF ZIEGLER—NATTA TYPE

I. A STUDY OF THE IRON STEARATE REACTION WITH ALKYLALUMINIUM IN SOLVENTS WITH THE HELP OF THE MÖSSBAUER EFFECT AND IR SPECTROSCOPY

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Summary

The usual reaction of alkylaluminium addition to the end carbonyl groups of the stearate ligand takes place with $Al(C_2N_5)_3 : Fe(C_{17}N_{35}COO)_3 \leqslant 2$, maintaining the dimer structure of the original iron stearate. The reaction is not significantly complicated by redox reactions.

The study of complex organometallic catalysts of the Ziegler—Natta type is a rather difficult task because the composition of the complexes is considerably altered by varying the ratio of the compounds, nature of the solvent and preparation conditions. Furthermore, considerable complications are caused by redox reactions proceeding in the system. In spite of intensive investigations into these catalysts, judgements concerning the nature of active complexes and the mechanism of their formation have up to the present time, been debatable and often contradictory.

In the present paper, the reaction of iron stearate with triethyl aluminium was studied with the help of the Mössbauer effect. The product obtained was a catalyst of the Ziegler—Natta type, used in hydrogenation reactions. The reaction with iron stearate ($Fe(St)_3$) dissolved in heptane was studied using IR and Mössbauer spectroscopy simultaneously.

Experimental

Iron stearate ($Fe(St)_3$) and triethyl aluminium were prepared in toluene and heptane at 20°C, at molar ratios of Al : Fe = 1—10, in accordance with the procedure described in the literature [1]. Gamma resonance spectra (GR spectra)

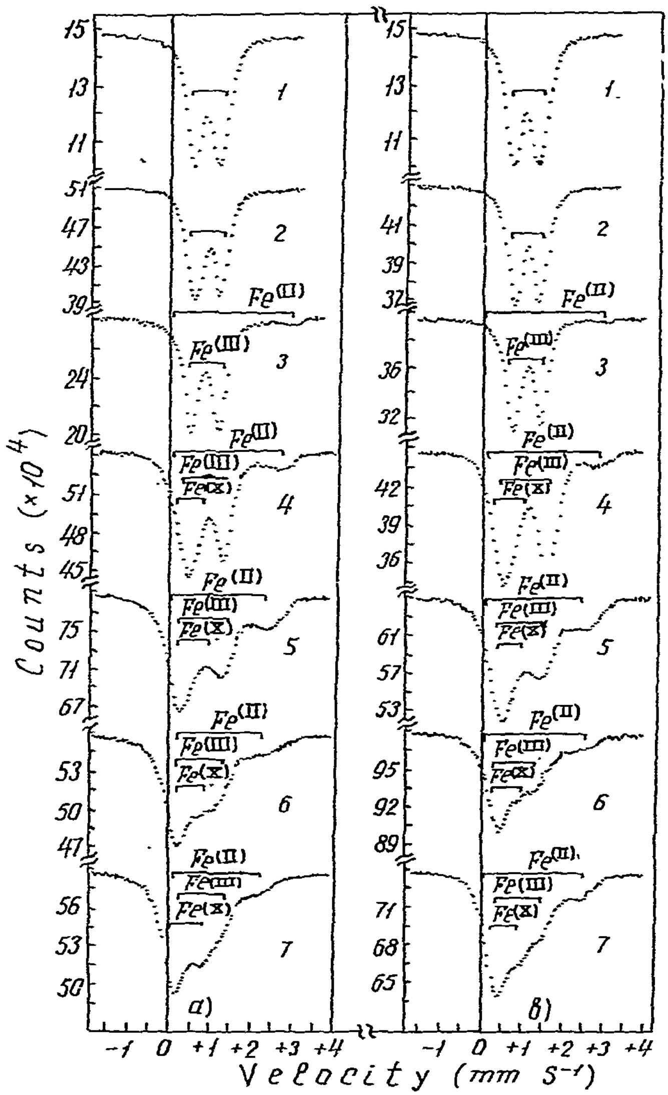


Fig. 1. Mössbauer spectra of the $Fe(St)_3$ + $Al(C_2H_5)_3$ system (a) in toluene and (b) heptane with changing Al : Fe. 1, Original $Fe(St)_3$; 2, $Fe(St)_3$ in solvent; 3, Al : Fe = 2; 4, Al : Fe = 4; 5, Al : Fe = 6; 6, Al : Fe = 8; 7, Al : Fe = 10.

of samples quickly frozen in liquid nitrogen were taken in a regime of constant accelerating ^{57}Co source at room temperature, in Cr, with 50 mCi activity. For GR spectroscopy, $Fe(St)_3$ was prepared with a 30% enrichment by ^{57}Fe. Mössbauer apparatus has been described in the literature [2]. GR spectra (Fig. 1) were processed on the BESM-4M by the "least squares" method. Error in the determination of halfwidth, Γ, quadrupole splitting, ΔE_Q, and isomeric shift, δE_I, is ± 0.02 mm s^{-1}. All the results are cited with respect to sodium nitroprussiate. Catalytic complex samples for GR and IR spectroscopy were prepared in an argon atmosphere.

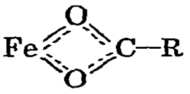
Results and discussion

Physical and chemical properties of stearates of the *d*-group of the Period IV transition metals, Fe(St)$_3$ in particular, have been studied [3—5].

Data from X-ray analysis and magnetic susceptibility measurements suggested that these compounds existed as metal—metal bonded dimers. The formation of the metal—metal bond is a result of the promotion effect caused by transition of atomic *nd*-electrons to the π-molecular orbital of the stearic acid carbonyl group and by formation of a quasi cyclic aromatic [4]. We have carried out the X-ray analysis of the iron stearate used and have measured its magnetic susceptibility at room temperature. The results are close to the literature values [5].

The Mössbauer spectrum of Fe(St)$_3$ presents a doublet which indicates a considerable deviation from the cubic in the symmetry of the environment of the iron atom [6]. The probability of the recoil-free process for iron stearate decreases to 8.5 with an increase in temperature from 80° to 295°K. Such a sharp decrease in f' is a result of a low Debye temperature [8].

In the region of absorption due to carbonyl bond valence vibration, the IR spectrum of the original iron stearate gives two absorption bands at 1580 and 1740 cm^{-1} (Fig. 2). The first of them characterizes carbonyl group vibrations in



the chelate ring, the more intensive second is associated with vibrations of the free —C=O group.

δE_I and ΔE_Q of Fe(St)$_3$ are typical for a high-spin iron(III) state [7] and indicate that the promotional effect and, consequently, the formation of the quasi cyclic aromatic with the metal—metal bond, do not lead to a considerable change in the ligand field.

The parameters of the GR spectra of Fe(St)$_3$, measured in solvents and without them, are similar (Table 1). The observed asymmetry in peak halfwidths is, probably, due to solvent solvation [8]. Large asymmetry in toluene may be associated with its high coordination ability when compared with heptane.

The IR spectrum of the iron stearate, measured in heptane, exhibited the same absorption bands as in the original Fe(St)$_3$, however the intensity of the 1740 cm^{-1} band is increased considerably while the 1580 cm^{-1} band is decreased (Fig. 2). The solvation probably impedes the donation of *d*-electrons to the carbonyl π-bond.

With the introduction of alkyl aluminium in both solvents systems, at

TABLE 1

GR-PARAMETERS OF THE ORIGINAL IRON STEARATE (mm sec^{-1})

Fe(St)$_3$	δE_I	ΔE_Q	Γ_1	Γ_2
Without solvent	0.79	0.67	0.50	0.50
In heptane	0.80	0.64	0.46	0.42
In toluene	0.81	0.65	0.52	0.37

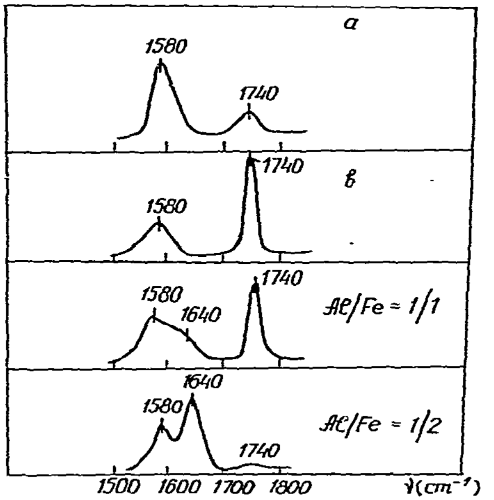


Fig. 2. IR spectra of (a) original Fe(St)$_3$ and (b) dissolved in heptane. Spectrum on introduction of triethyl aluminium.

Al : Fe = 1—2; the GR spectrum represents a superimposition of doublets, the parameters of which identify the high-spin state of a three-valent iron, iron(III), which at Al : Fe > 2 is considerably different from the original iron stearate and the high-spin state of a two-valent iron, iron(II). The third state has GR parameters which lie in the Dunkan-Golding diagram in the region corresponding to low-spin states of the three- and two-valent iron (Fig. 3a, b). This form of iron is further designated as iron(X).

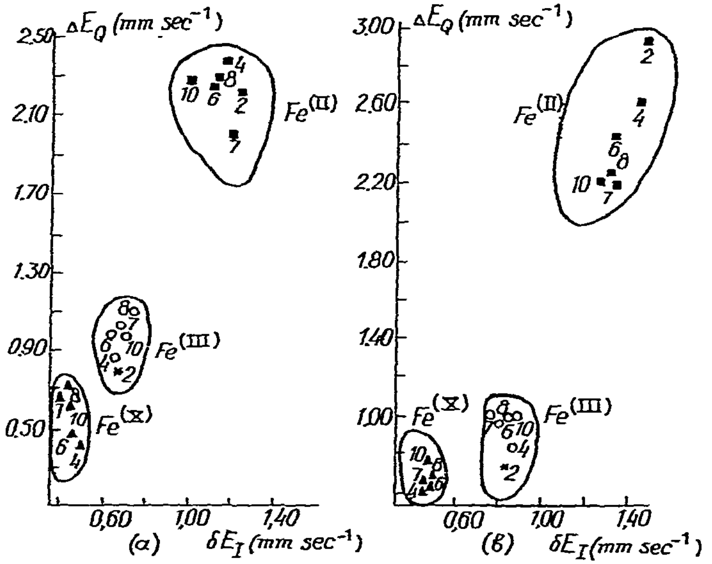


Fig. 3. Dunkan-Golding diagram. Solvent is (a) heptane (b) toluene. Numbers of the points correspond to the value of Al : Fe.

By analyzing the results obtained from GR and IR spectroscopy we may conventionally single out three stages in formation of the catalytically active system:

1. Iron stearate interaction with AlR_3 causes no considerable change in the electron density in the iron(III) nucleus and no alteration in its nearest environment, when compared to $Fe(St)_3$ ($Al : Fe \leqslant 2$).

2. Partial reduction of $iron^{III}$ to $iron^{II}$ ($2 \leqslant Al : Fe \leqslant 4$).

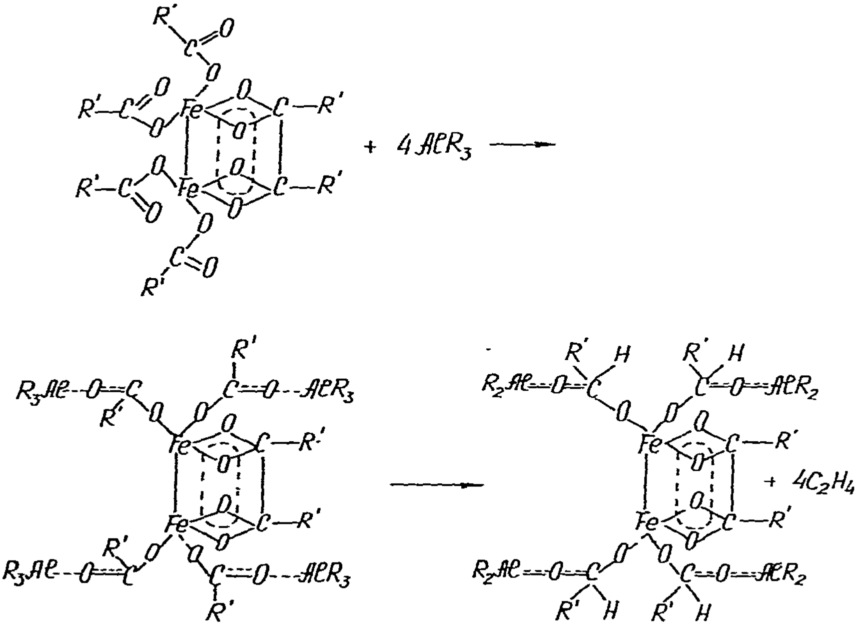
3. Formation of the compound characterised by its GR spectrum as $iron^{X}$ ($Al : Fe > 4$).

The present communication describes only the first stage of the formation of the active system, when the process of interaction of the compounds is only negligably complicated by redox reactions.

The first stage, the introduction of AlR_3 into the solution until $Al : Fe = 2$, causes only a small widening of the GR spectrum observed for iron stearate in solvents, with no considerable change in its parameters. The emergence of an additional low-intensity doublet is due to $iron^{II}$ formation (Fig. 1a, spectrum 3; Fig. 1b, spectrum 3).

From the IR spectrum it follows that with the introduction of alkyl aluminium into the $Fe(St)_3$ solution until $Al : Fe = 2$ (Fig. 2) decreases the concentration of free carbonyl groups. Halfwidth of the absorption band at 1580 cm^{-1} decreases almost to zero and a new maximum at 1640 cm^{-1} appears, the intensity of which increases with the amount of AlR_3. Similar changes in the IR spectrum are, probably, due to AlR_3 interaction with an unshared pair of carbonyl group electrons. This process (Scheme 1) may be accompanied by liberation of gaseous products due to loss of one of the alkyl groups (I), or there may

SCHEME 1



(I) ($R = C_2H_5$, $R' = C_{17}H_{35}$) (II) be no liberation if the reaction takes place between the unshared pair of oxygen electrons and the alkyl aluminium acceptor orbital (I).

This stage in the formation is in no doubt. It has been noted in various versions by many researchers though the details have not been elucidated. Usually, addition of an organometallic compound to oxygen directly bonded to a transition metal is suggested [9]. Such an interpretation is debatable, and in the case of stearates of the Group IV transition metals, it is completely wrong. For the latter, as shown in the literature [3—5] and analyzed above, bonding of a carboxylate type with only one acidic residue of the stearic acid is observed. Two other ligands are bonded only through oxygen and have free carbonyl groups.

Structural degeneration of stearate causes participation of all the three acidic residues in the quasi aromatic cyclic π-bond. As a consequence, in the original $Fe(St)_3$ the absorption at 1580 cm^{-1}, the extinction coefficient of which is usually several times higher than that for free carbonyl groups, is low in intensity and broadened. With the introduction of AlR_3, blocking the free carbonyl groups, the structural degeneration is removed. The latter causes an increase in the absorption intensity at 1580 cm^{-1} with simultaneous narrowing. Further, absorption at 1640 cm^{-1} occurs which should be associated with valence vibrations of $C{=}O$ participating in the interaction with alkyl aluminium. The insignificant changes in the GR spectrum at $Al : Fe \leqslant 2$ compared with $Fe(St)_3$, is due to alkyl aliminium addition to free carbonyl groups exerting only an indirect influence on iron (Scheme 1).

Appearance in the solution of only small amounts of iron(II) is due to a deviation of the process from stoichiometry. Thus, at $Al : Fe \leqslant 2$, the normal reaction of alkyl aluminium addition to end carbonyl groups of a stearate ligand occurs. The above reaction leads to removal of the three-fold degeneracy of the iron stearate structure and to quasi aromatic cyclic destabilization which determines the site of attack for subsequent alkyl aluminium molecules.

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