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COMPLEX CATALYST STUDIES OF ZIEGLER—NATTA TYPE

II. OXIDATION—REDUCTION REACTION IN THE IRON STEARATE—TRIETHYLALUMINIUM SYSTEM

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Summary

At molar ratios of $\leqslant 2$ $Al(C_2H_5)_3 : \leqslant 4$ $Fe(C_{17}H_{35}COO)_3$ complexes containing iron(III) and iron(II) are formed as a result of redox transformations. With an increase in Al : Fe, multinuclear associated systems result, in which iron(III) and iron(II) are bound to alkylaluminium. A further increase in concentration of AlR_3 leads to only an increase in the size of associates due to alkylaluminium coordination.

In the present work carried out according to the procedure described in the previous paper [9], reaction of iron stearate with triethylaluminium at $Al : Fe > 2$ was studied with the help of the Mössbauer effect and IR spectroscopy. Earlier [1] we singled out three stages of formation of a catalytically active system.

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

2. Patial iron(III) reduction to iron(II). ($\leqslant 2$ Al : $\leqslant 4$ Fe).

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

At molar ratio $Al : Fe \leqslant 2$, alkyl aluminium addition to the end carbonyl groups of iron stearate takes place. Introduction of subsequently more triethylaluminium to give $Al : Fe > 2$, leads to further interaction of components which is accompanied by redox transformations.

An Al : Fe increase is characterized by a sharp alteration in the Mössbauer spectrum. Firstly, the appearance of iron(II) in considerable amounts (Figs. 1c and 2c), the concentration of which gradually increases until Al : Fe = 6—7, in both solvents.

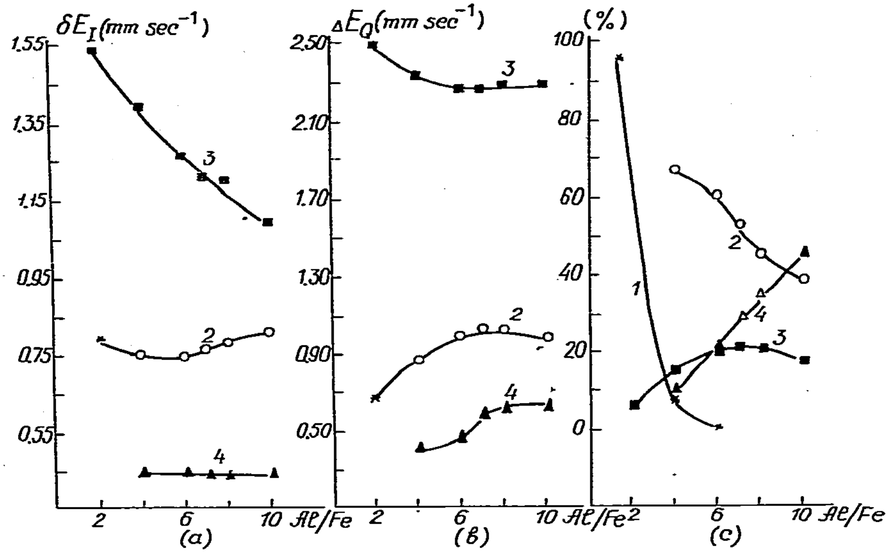


Fig. 1. Dependence of Mössbauer parameter (a, b) and relative content of iron form (c) on Al/Fe. The solvent is heptane. 1, According to GR parameters, the iron form not differing from original ($Fe(St)_3$; 2, Fe^{III}; 3, Fe^{II}; 4, FeX.

The presence of iron(II) in the solution may be accounted for by an intraspheric reduction of the central atom by alkylation due to alkylaluminium, which was earlier bound to free carbonyl groups, and by decomposition of the alkylmetal formed. At the same time, however, there should be no consider-

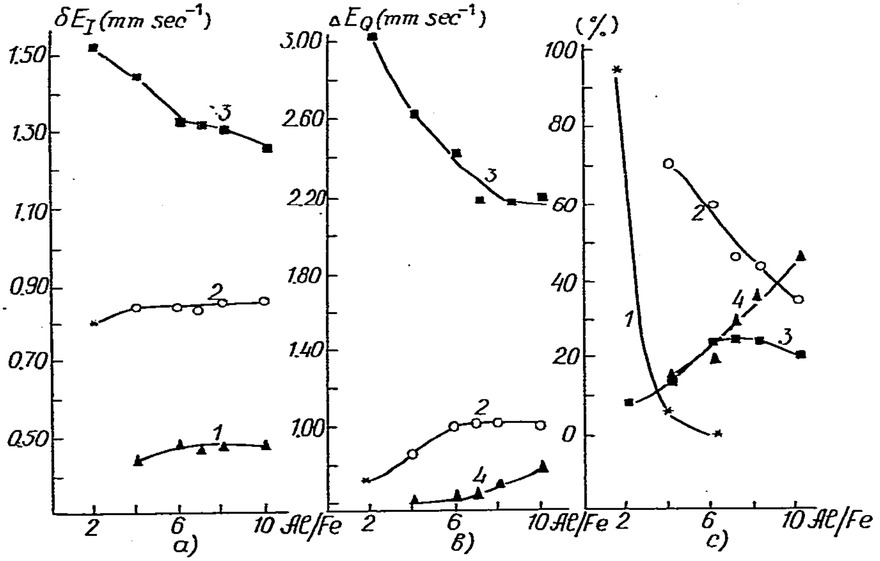
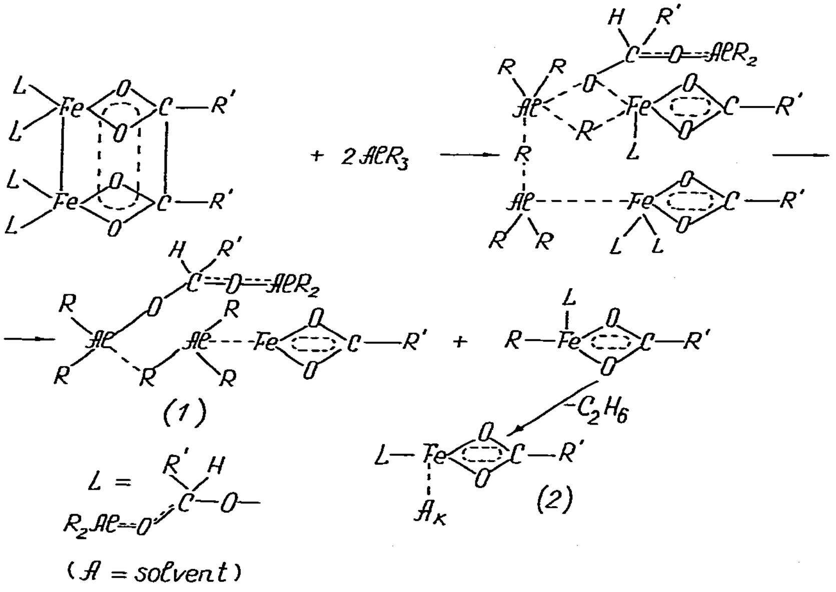


Fig. 2. Dependence of Mössbauer parameters (a, b) and relative content of iron form (c) on Al/Fe. The solvent is toluene. 1, Iron form not differing from $Fe(St)_3$ according to GR parameters; 2, Fe^{III}; 3, Fe^{II}; 4, Fe^{X}.

able alteration in the Mössbauer parameters of iron(III) not participating in the redox process, which is in fact not observed. In the range of Al : Fe values from 2 to 4 there occurs a considerable increase in ΔE_Q in both solvents (Figs. 1b and 2b). (At Al : Fe = 2 the parameters for iron(III) are almost identical to those Fe(St)$_3$ [1].) The changes in δE_I are not so definite but with a further increase in Al : Fe it is possible to say that these values do not remain constant (Figs. 1a, 2a). Furthermore, the nature of the change in δE_I in toluene and heptane is different. Difficulties also occur in interpreting the fact that the amount of the reduced iron form, iron(II), does not exceed 20—25% even at higher Al : Fe ratios.

Taking into consideration all this evidence, we may suggest that reduction of iron(III), which is carried out by addition of AlR$_3$, introduced when the ratio Al : Fe was above 1 : 2, proceeds according to Scheme 1, e.g., with the

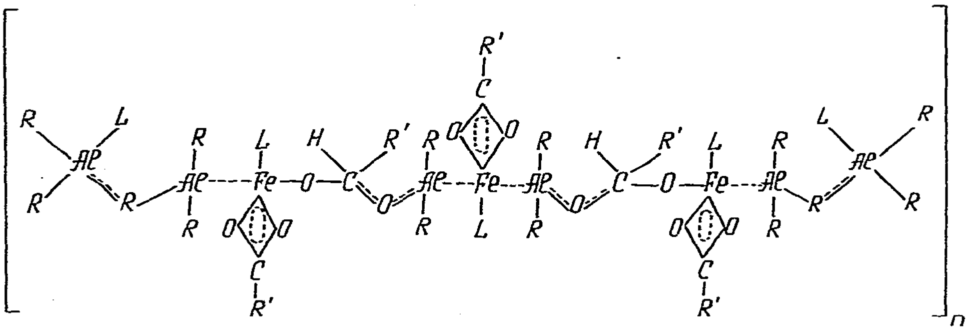
SCHEME 1.



complex II given in the previous paper [1]: Mössbauer parameters of iron(III) change as a result of influence of the alkylaluminium, which is bound to it (I). As follows from Scheme 1, iron(III) at this stage is considerably different from that when Al : Fe = 2. In fact, here iron(III) is a new alkylated form or iron.

The destruction of alkylaluminium releases a vacant π-orbital to which any donor molecule can be added, iron(II) in particular. The latter can also interact with alkylaluminium bound with free carbonyl groups by displacing the alkyl substituent.

The formation of similar multinuclear, associated systems (II) determines, at the third stage of catalyst formation, the emergence in the GR spectrum of the iron form differing from iron(II) and iron(III) and designated as iron(X). Furthermore, the iron(III) form, close in GR parameters to the original Fe(St)$_3$, almost disappears (Figs. 1c and 2c). The decrease in the IR spectrum of the absorption band corresponding to vibrations of a free carbonyl group occurs



(II)

much faster. Thus, at Al : Fe = 2 the 1740 cm^{-1} band disappears almost completely [1].

For both solvents, the concentration of the complex corresponding to iron(X) increases with an increase of the Al : Fe ratio. (Figs. 1 and 2). In the IR spectrum the absorption observed earlier at 1640 cm^{-1} is transferred to the longer wavelength as a result of weakening the $C=O$ bond due to the interaction of aluminium with iron(II) (Fig. 3). A decrease of the δE_I value in both solvents, corresponding to iron(II), with an increase in the Al : Fe ratio (Figs. 1a, 2a), may serve as confirmation of the presence of such an interaction. δE_I decrease occurs due to the contribution of s-electrons to the electron density at the iron(II) nucleus, which may be caused by some displacement of d-electrons from the nucleus and, consequently, by a decrease of their screening effect. d-Electron displacement may be observed in the formation of the dative bond between iron(II) and aluminium by a vacant alkylaluminium π-orbital (II).

It should be noted that with an increase in the Al : Fe ratio, not only does the concentration of a new iron form, iron(X) increase, but the system becomes more stable with some decrease in catalytic activity. Such facts, as

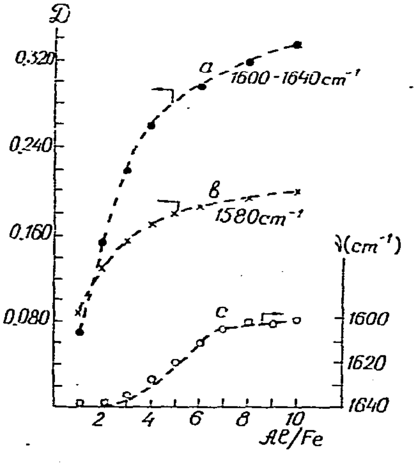


Fig. 3. The change of intensity (a, b) and band positions (c) at valent vibrations of CO groups in $Fe(St)_3$ on introduction of $Al(C_2H_5)_3$. The solvent is heptane.

well as the character of the changes in GR parameters for iron(II), iron(III) and iron(X) are, probably, determined by the sizes of associates. Thus, for example, the supply of new alkyl aluminium portions to iron(II) may account for a decrease of δE_I and ΔE_Q in both solvent systems, with an increase in the Al : Fe ratio. With a decrease of coordination saturation of iron(II), the decrease in δE_I and ΔE_Q is retarded.

The nature of the change in ΔE_Q for iron(III) in toluene and heptane indicates, on the basis of Scheme I and II, that alkylation occurs with subsequent formation and growth of associates. The symmetry of the iron(III) environment is deteriorated until Al : Fe ~ 7 after which it barely changes. Such behaviour of ΔE_Q is also associated with retardation of growth of associates.

Change in δE_I interaction character with the Al : Fe ratio in toluene and heptane is caused by a difference in the coordination ability of the solvents which is considerably higher for the former. Confirmation is provided by the sharper and greater decrease in δE_I (increase of electron density from *s*-electrons at the nucleus as a result of decrease of the screening effect from *d*-electrons) at the iron(II) nucleus in the case of heptane (Fig. 1a). In toluene, changes are not so great and proceed more smoothly. Also, the higher ΔE_Q value at Al : Fe = 2 was obtained in toluene, and with an increase in the Al : Fe ratio up to ~7 there occurs a rapid decrease in the ΔE_Q value. At Al : Fe ~ 7, ΔE_Q values in toluene and heptane become almost identical. The facts given above indicate that at Al : Fe ratios lower than 6—7 displacement of toluene occurs from iron(III) and iron(II) coordination spheres interacting by π-electrons.

The increase in δE_I and ΔE_Q in both solvents with the increase in the ratio Al : Fe may be explained by deterioration of the symmetry of the iron(X) environment with an increase in association without an appreciable change in electron density at its nuclei. Changes in ΔE_Q do not occur above Al : Fe ~ 7—8 which, as has been stated above, is associated with coordination saturation and retardation in the size of associates.

Addition of excess AlR_3 increases the acceptor ability of the active complex. The oxidation—reduction process in the system, from GR spectroscopy data (see relative iron(II) amount) appears suppressed at Al : Fe ~ 8. This is obvious from Scheme II because in this complex iron(III) appears to be blocked by alkylaluminium and can participate in the oxidation—reduction process only by cleavage of the available bonds. Such a situation is made possible when introducing the unsaturated compound into the system.

Thus, iron stearate interaction with AlR_3 at Al : Fe $\leqslant$ 4 leads to the formation of complexes with iron(III) and iron(II). With a further increase in Al : Fe, associated systems are formed containing iron(III) and iron(II) bound to each other by an alkylaluminium. Subsequent introduction of alkylaluminium into the system leads only to an increase in the size of associates.

References

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