

UV-SPECTROSCOPIC STUDIES ON THE INTERACTION OF TRIETHYL ALUMINIUM WITH COBALT AND ALUMINIUM ACETYLACETONATES

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The $\text{Al}(\text{acac})_3/\text{Et}_2\text{Al}(\text{acac})$ ratio depends on the Al/Co and the solvent. The solvent contains $\text{Et}_2\text{Al}(\text{acac})$ as a dimer, which is stabilized in the presence of $\text{Co}(\text{O})$ and arenes. The role of $\text{Et}_2\text{Al}(\text{acac})$ dimer in the formation of active $\text{Co}(\text{O})$ complexes is discussed.

Показано, что соотношение $\text{Al}(\text{acac})_3/\text{Et}_2\text{Al}(\text{acac})$ зависит от Al/Co и природы растворителя. Установлено существование $(\text{Et}_2\text{Al}(\text{acac}))_2$ в растворе в форме димера и стабилизация его в присутствии $\text{Co}(\text{O})$ и аренов. Обсуждается роль димера $\text{Et}_2\text{Al}(\text{acac})$ в образовании активных комплексов $\text{Co}(\text{O})$.

Paramagnetic $\text{Co}(\text{O})$ complexes in catalytic $\text{Co}(\text{acac})_{2,3}$ systems, whose tentative composition and structure are discussed elsewhere /1, 2/, have been identified by the ESR method. Here we present results on the study of the interaction between $\text{Co}(\text{acac})_3$ and AlEt_3 . Figure 1 shows the UV spectra of initial compounds and supposed reaction products. The absorption bands in decalin significantly differ in positions and intensities, therefore, the concentration of each component in the reaction mixture can be determined.

The concentrations of $\text{Co}(\text{acac})_3$, $\text{Al}(\text{acac})_3$ and $\text{Et}_2\text{Al}(\text{acac})$ were determined from the absorption bands at $44,000\text{ cm}^{-1}$ (ν_1), $34,700\text{ cm}^{-1}$ (ν_3), $37,300\text{ cm}^{-1}$ (ν_4) and $32,500\text{ cm}^{-1}$ (ν_5), respectively.

At an Al/Co mole ratio of 2, the UV spectrum of the system exhibits decreasing intensities of the bands at $44,000\text{ cm}^{-1}$ (ν_1) and at $39,000\text{ cm}^{-1}$ (ν_2), assigned

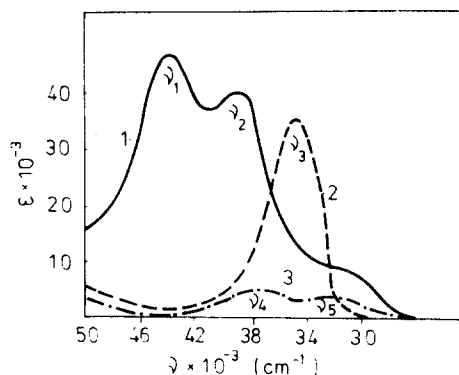


Fig. 1. UV spectra of acetylacetonate solutions in decalin. 1 - $\text{Co}(\text{acac})_3$ 2 - $\text{Al}(\text{acac})_3$, 3 - $\text{Et}_2\text{Al}(\text{acac})$. Spectroscopic studies were carried out at room temperature, at 10^{-3} Torr vacuum, in sealed vacuum glass systems connected with quartz cells ($d=0.01$ cm). UV spectra were taken on a Specord UV-Vis double-beam recording spectrophotometer

to $\text{Co}(\text{acac})_3$, and a gradual intensity growth of the band (ν_3) due to the formation of $\text{Al}(\text{acac})_3$. At a 3:1 ratio of the initial components, the reaction stops after 30 min with the formation of $\text{Al}(\text{acac})_3$ with almost quantitative yield. Compositions with Al:Co = 6 and 10, besides the band (ν_4) of $\text{Al}(\text{acac})_3$ the UV spectrum exhibits bands at $37,300\text{ cm}^{-1}$ (ν_4) and $32,500\text{ cm}^{-1}$ (ν_5), assigned to $\text{Et}_2\text{Al}(\text{acac})$. The ratio of $\text{Et}_2\text{Al}(\text{acac})$ and $\text{Al}(\text{acac})_3$ concentrations determined by a successive approximation method is 4:1. With a twenty-fold excess of AlEt_3 , the UV spectrum exhibits only the bands (ν_4) and (ν_5) of the quantitatively formed $\text{Et}_2\text{Al}(\text{acac})$. It should be noted that great excesses of AlEt_3 lead to gradually decreasing intensities of the (ν_4) and (ν_5) bands with time due to destruction of the acetylacetonate ligand upon the addition of AlEt_3 to its carbonyl group.

The transformation of the reaction products has been studied in more detail for the interaction between $\text{Al}(\text{acac})_3$ and AlEt_3 in decalin. With a threefold excess of AlEt_3 , no reaction proceeds, as the characteristics of the (ν_3) band, assigned to $\text{Al}(\text{acac})_3$, remain constant for 24 hrs after the beginning of interaction. At reagent

ratios of 6 and 10, only the bands (ν_4) and (ν_5) of $\text{Et}_2\text{Al}(\text{acac})$ are detected. Their intensities decrease with time due to the above decomposition. The rate of $\text{Et}_2\text{Al}(\text{acac})$ decomposition increases with increasing AlEt_3 content.

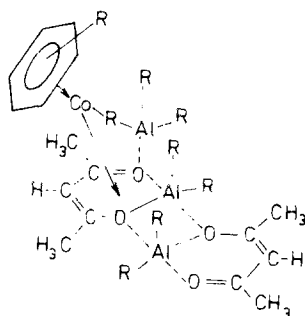
The ESR spectra of catalytic cobalt acetylacetonate systems show that paramagnetic complexes are formed during catalyst preparation in the arene medium /3/. Indeed, the presence of durene and toluene affects the reaction studied. At mole ratios of arene/Co = 2 and Al/Co = 3 the UV spectrum exhibits the $\text{Al}(\text{acac})_3$ and $\text{Et}_2\text{Al}(\text{acac})$ bands in a ratio of 1:5. With a ten-fold excess of AlEt_3 the spectrum shows only the (ν_4) and (ν_5) bands of $\text{Et}_2\text{Al}(\text{acac})$ which do not change with time.

The ratio of products from the reaction of $\text{Co}(\text{acac})_3$ with AlEt_3 is determined by the Al/Co mole ratio and the solvent. At a small excess of AlEt_3 , $\text{Al}(\text{acac})_3$ is formed, while a greater excess of AlEt_3 leads to the formation of $\text{Et}_2\text{Al}(\text{acac})$, whose proportion is increased and stabilized in the presence of arenes.

Cryoscopic studies show the existence of $\text{Et}_2\text{Al}(\text{acac})$ in benzene as a dimer. In contrast to $\text{Al}(\text{acac})_3$, two bands in the UV spectrum seem to be due to its existence in benzene and decalin as a dimer with parallel or almost parallel planes of the rings, whose π -systems can interact through the metal atom. The formation of a united π -electron system complicates the nature of electronic transitions as demonstrated by the UV spectrum of $\text{Co}(\text{acac})_3$ /4/.

The formation of Co(O) complexes with Li, Mg and Al organometallic compounds is reported elsewhere /3/. The results of the present study permit to detail the structure of the paramagnetic Co(O) complexes. Since during formation of the catalytic system, upon the addition of arene, $\text{Et}_2\text{Al}(\text{acac})$ is stabilized, it may be assumed to participate as one of the ligands stabilizing cobalt in an anomalously low oxidation state. In this connection it should be noted that the maximum paramagnetic Co(O) complex concentration and the most prolonged $\text{Et}_2\text{Al}(\text{acac})$ stabilization are observed at the same Al/Co ratio. Co(O) seems to be connected with acetylacetonate via its π -electron system. The experimental data imply the

following structure of the paramagnetic Co(O) complex formed in the catalytic $\text{AlEt}_3\text{-Co(acac)}_{2,3}$ systems in an arene medium:



This scheme is in agreement with available data on the influence of arene structure and of the alkyl groups of the Li, Mg and Al compound on the ESR parameters of the Co(O) complexes. The above model of Co(O) complexes permits a more unambiguous interpretation of bulk experimental data with respect to the properties of these catalysts in various catalytic transformations of unsaturated hydrocarbons.

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