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INTERACTION OF TRIETHYLALUMINIUM WITH ACETYLACETONATES OF TRANSITION METALS

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Summary

The reaction of $AlEt_3$ with acetylacetonates of Cr^{III}, Fe^{III}, Co^{III}, Ni^{II} and Pd^{II} in benzene and cyclohexane has been studied in a wide range of initial ratios of $AlEt_3/M(acac)_n$. Quantitative analysis of the reaction mixture, performed with the help of UV spectra, showed that acetylacetonate ligands were transferred from the transition metals to aluminium. A scheme involving stepwise substitution of ethyl radicals by acetylacetonate ligands on $AlEt_3$ with further formation of an $Al(acac)_3$-$Et_2Al(acac)$ mixture is proposed for $Al/M < n$ (M = Fe, Co, Ni). An increase of the Al/M ratio causes an increase of the $Et_2Al(acac)$ fraction. The only reaction product containing an acetylacetonate ligand is $Et_2Al(acac)$ at $Al/M = n$. $Cr(acac)_3$ and $Pd(acac)_2$ interact with $AlEt_3$ forming $Et_2Al(acac)$ at any initial ratio of Al/M. Stabilization of intermediate organo-nickel and -palladium compounds has been observed in the interaction of $AlEt_3$ with $Pd(acac)_2$ and $Ni(acac)_2$ in benzene, which inhibited the reaction rate considerably. Magnetochemical measurements showed that Fe^{III}, Co^{III}, Ni^{II} were reduced to the zerovalent state in their reaction with $AlEt_3$ $(Al/Mn \geqslant n)$. The content of the finely dispersed metal component is negligible small and the greater part of transition metal is present as M^0 complexes, where $Et_2Al(acac)$ formed in the reaction is the main stabilizing ligand.

Introduction

The catalytic systems of the Ziegler type based on acetylacetonates of transition metals, $M(acac)_n$, and aluminium alkyls have been intensively studied in the processes of hydrogenation, isomerization and oligo- and polymerization of unsaturated compounds. However, the mechanism of the interaction among the system components remains unclear in many aspects. The degree of reduction of transition metals is still the subject of discussion [1,2,3]. The quantitative and qualitative

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composition of the reaction products and their dependence on the initial $AlEt_3/M(acac)_n$ ratio have not been characterized.

Our paper presents an attempt to characterize the composition of the reaction products with the help of UV spectra and magnetochemical measurements. The results of earlier investigations have been summarized [4,5]. The general scheme of $AlEt_3$ interaction with acetylacetonates of transition metals, (Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}, and Pd^{II}), is discussed.

Results and discussion

The UV spectra of the initial acetylacetonates of transition metals and reaction products are given in Fig. 1. The positions and intensities of the absorption bands of these compounds differ considerably, which permits determination of the concentration of each component in the reaction mixture.

Fe(acac)$_3$-AlEt$_3$

Interaction in cyclohexane. The results are presented in Table 1. Consecutive decay of the intensity of the absorption bands of $Fe(acac)_3$ and the growth of the $Al(acac)_3$ absorption are observed in the spectrum of the reaction mixture for Al/Fe = 0.4. The spectra curves (Fig. 2a) pass through two isobestic points at 276 and 312 nm, which correspond to the equality of values of extinction coefficients of $Fe(acac)_3$ and $Al(acac)_3$. The quantitative analysis of spectra shows that rapid conversion of $Fe(acac)_3$ into $Al(acac)_3$ occurs and in an hour the greater part of the

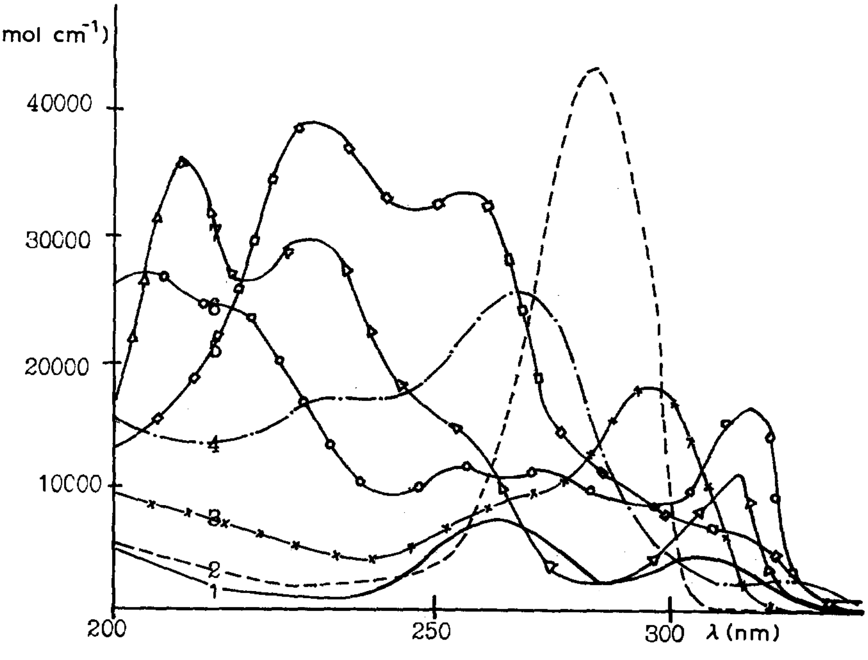

Fig. 1. UV spectra of acetylacetonates of transition metals and aluminium in cyclohexane: solutions of $Et_2Al(acac)$ (1), $Al(acac)_3$ (2), $Ni(acac)_2$ (3), $Fe(acac)_3$ (4), $Co(acac)_3$ (5), $Cr(acac)_3$ (6) and $Pd(acac)_2$ (7).

TABLE 1

$Fe(acac)_3$, $Et_2Al(acac)$ AND $Al(acac)_3$ CONCENTRATIONS IN THE INTERACTION OF $Fe(acac)_3$ WITH $AlEt_3$ IN CYCLOHEXANE

Al/Fe	Time (min)	$Fe(acac)_3$		$Et_2Al(acac)$		$Al(acac)_3$	
		$C \times 10^3$ (M)	% acac	$C \times 10^3$ (M)	% acac	$C \times 10^3$ (M)	% acac
0.4	0	0.28	100	–[a]	–	–	–
	3	0.23	81	–	–	0.03	10
	10	0.21	75	–	–	0.04	16
	20	0.20	71	–	–	0.06	20
	30	0.18	65	–	–	0.07	24
	40	0.17	61	–	–	0.08	28
	50	0.16	57	–	–	0.09	33
	60	0.16	55	–	–	0.10	35
	120	0.12	42	–	–	0.13	47
0.6	0	0.24	100	–	–	–	–
	4	0.18	74	0.07	10	0.03	13
	10	0.16	68	0.06	8	0.04	18
	30	0.13	53	0.05	7	0.08	34
	60	0.10	40	0.04	6	0.12	51
0.9	0	0.24	100	–	–	–	–
	3	0.07	30	0.19	26	0.08	33
	10	0.07	30	0.16	23	0.09	38
	30	0.07	30	0.14	19	0.11	44
	60	0.07	30	0.12	17	0.12	49
1.3	0	0.22	100	–	–	–	–
	3	–	–	0.24	36	0.10	45
	10	–	–	0.21	32	0.12	53
	30	–	–	0.18	28	0.13	61
	60	–	–	0.16	23	0.15	66
2	0	0.24	100	–	–	–	–
	3	–	–	0.39	55	0.07	28
	10	–	–	0.37	53	0.07	29
	30	–	–	0.35	49	0.08	32
	120	–	–	0.31	45	0.09	38
2.9	0	0.24	100	–	–	–	–
	3	–	–	0.44	67	0.05	23
	30	–	–	0.43	63	0.06	25
	90	–	–	0.40	57	0.07	28
	180	–	–	0.39	55	0.07	29
	24 h	–	–	0.34	49	0.07	31
12	0	0.30	100	–	–	–	–
	3	–	–	0.88	97	–	–
	60	–	–	0.77	85	–	–
	120	–	–	0.63	69	–	–
	180	–	–	0.56	62	–	–
	240	–	–	0.40	44	–	–
10[b]	0	0.58	100	–	–	–	–
	2	–	–	1.72	99	–	–
	60	–	–	1.56	90	–	–
	120	–	–	1.36	78	–	–
	240	–	–	0.98	56	–	–

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[a] Product not detected. [b] In benzene, % (acac for $Et_2Al(acac)$ is equal to $^3C(Et_2Al(acac))/C(Fe(acac)_3)_{init} \times 100\%$.

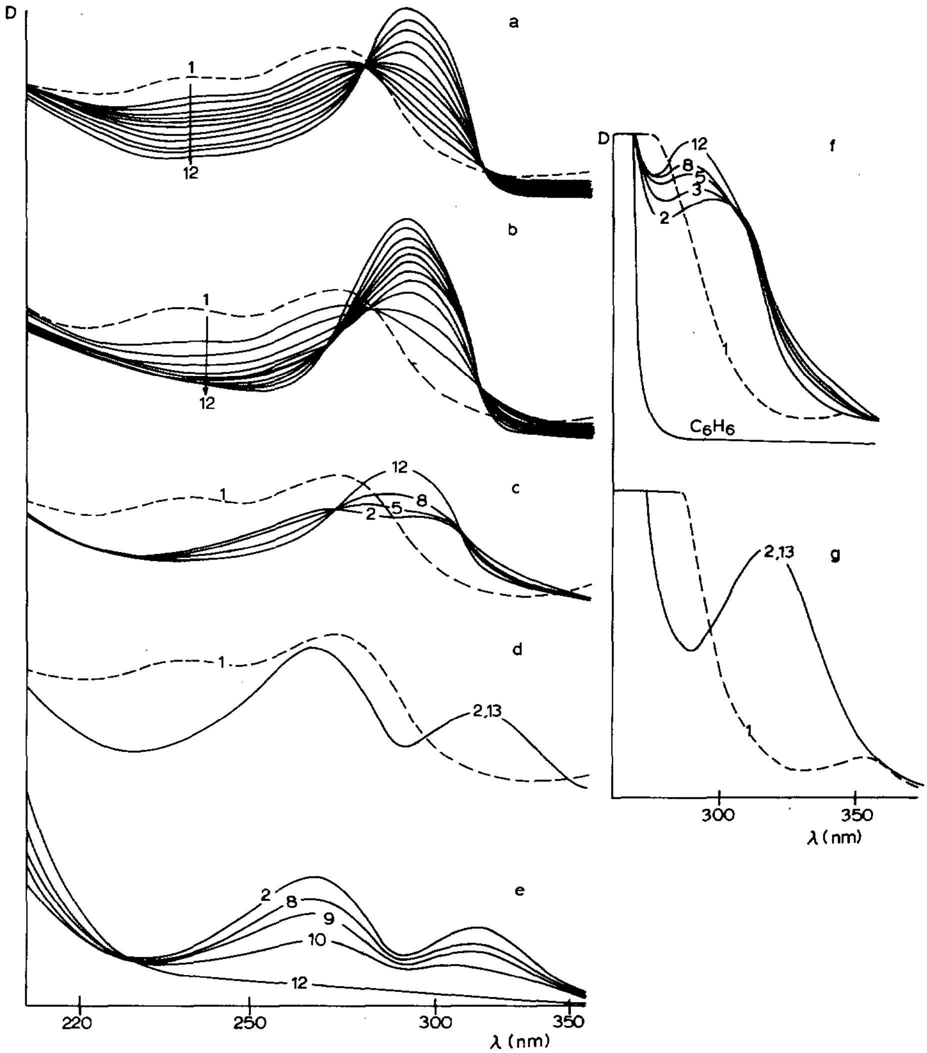


Fig. 2. Absorption spectra of Fe(acac)$_3$ (I) and the interaction of Fe(acac)$_3$ with AlEt$_3$ in cyclohexane at Al/Fe = 0.4 (a), 0.6 (b), 2 (c), 3 (d), 12 (e) and in benzene at Al/Fe = 2 (f), 3 (g) after 2 (2), 10 (3), 20 (4), 30 (5), 40 (6), 50 (7), 60 (8), 120 (9), 180 (10), 240 min (11), 24 hours (12) and 9 days (13).

acetylacetonate ligands is transferred from iron to aluminium. The concentration of unreacted Fe(acac)$_3$ is then lower and that of Al(acac)$_3$ somewhat higher than calculated in accordance with the supposition of direct conversion of Fe(acac)$_3$ into Al(acac)$_3$.

Tamai and Saito [1] proposed their scheme of stepwise reduction of a transition metal:

$$\mathrm{Co(acac)_3 \rightarrow Co(acac)_2 \rightarrow Co^0} \qquad (1)$$

In this case it can be also supposed that a part of the Fe(acac)$_3$ is converted into

$Fe(acac)_2$ and that the decomposition of three molecules of $Fe(acac)_3$ is needed to form one molecule of $Al(acac)_3$. This is the reason for the greater decrease of the $Fe(acac)_3$ concentration than expected from the simplified scheme of formation of $Al(acac)_3$. The $Fe(acac)_2$ spectrum contains an intense band in the region of 294 nm ($\epsilon = 1600$ 1 mol^{-1} cm^{-1}). The overlap of this band with the absorption band of $Al(acac)_3$ leads to the overestimated values of the concentration of the latter in calculations. The formation of $Fe(acac)_2$ can probably occur only at $Fe(acac)_3$ concentrations several times higher than that of $AlEt_3$ in the system, which in this particular case is 2.5.

Increase of the Al/Fe ratio up to 0.6 results in a change of the composition of the reaction products, which is confirmed by the appearance of the $Et_2Al(acac)$ absorption bands. For the first half hour the acetylacetonate ligand transfer from iron (+3) to aluminium takes place, and the spectral curves pass through the isobestic points at 276 and 312 nm. Then the conversion of formed $Et_2Al(acac)$ into $Al(acac)_3$ takes place and the spectral curves pass through 266 and 312 nm (Fig. 2b). As in the first case the formation of some $Fe(acac)_2$ as an intermediate can be supposed. Its interaction with $Et_2Al(acac)$ leads to an increase of the $Al(acac)_3$ concentration in the second stage of the reaction (Table 1).

At an initial ratio Al/Fe = 0.9 the reaction proceeds similarly. A decrease of the intensity of the $Fe(acac)_3$ absorption band is recorded three minutes after mixing the components, because of the formation of a $Al(acac)_3$ and $Et_3Al(acac)$ mixture. The comparison of the reaction rates of $Fe(acac)_3$ and $AlEt_3$ for the first 10 min at Al/Fe = 0.4 ($k = 6.7 \times 10^{-6}$ mol l^{-1} min^{-1}) and Al/Fe = 0.9 ($k = 1.7 \times 10^{-5}$ mol l^{-1} min^{-1}) show that the rate increases with the increase of the Et_3Al concentration in the system.

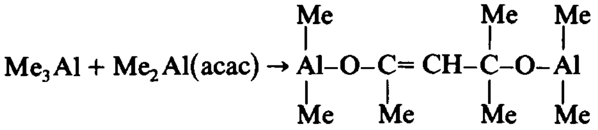
Increase of the Al/Fe ratio up to 1.3 leads to fast transfer of acac ligands from iron to aluminium. The $Et_2Al(acac)$ and $Al(acac)_3$ bands are observed in the reaction mixture spectrum 3 min after the beginning the reaction; the absorption of initial $Fe(acac)_3$ is not observed.

At Al/Fe = 2 and 2.9 ratios the fast transfer of acac ligands from iron to aluminium and the formation of two reaction products are also observed (Fig. 2c). The amount of $Et_2Al(acac)$ formed increases with increase of the $AlEt_3$ content in the system. Thus, after 24 hours of the reaction the $Et_2Al(acac)$ concentration is 1.5 and 4.7 times higher than that of $Al(acac)_3$ at Al/Fe = 2 and 2.9 ratios, respectively (Table 1).

A threefold excess of Et_3Al leads to a 100% yield of $Et_2Al(acac)$ ($C(Fe(acac)_3)$init. = 0.28×10^{-3} M, $C(Et_2Al(acac)) = 0.83 \times 10^{-3}$ M). The spectrum of the reaction mixture 9 days after the beginning of the interaction completely coincides with the spectrum of pure $Et_2Al(acac)$ (Fig. 2d).

An Al/Fe = 5.1 ration gives an analogous picture, but later the concentration of $Et_2Al(acac)$ formed decreases from 0.69×10^{-3} M (3 min) to 0.63×10^{-3} M (4 min), $C(Fe(acac)_3)$init. = 0.23×10^{-3} M.

A larger $AlEt_3$ excess (Al/Fe = 12) leads to a gradual decrease in intensity of the absorption bands of $Et_2Al(acac)$ and to their complete disappearance (Fig. 2e). The observed bands of $Et_2Al(acac)$ in the spectrum are assigned to π–π^* transitions in acac ligands [4], and the disappearance of these bands indicates the decomposition of the π system of the acac ligand in the interaction of $Et_2Al(acac)$ with $AlEt_3$. This confirms the scheme for aluminium alkyls interaction with $Alk_2Al(acac)$ as suggested by Kroll [6]:



$$Me_3Al + Me_2Al(acac) \rightarrow \underset{Me}{\overset{Me}{Al}}-O-\underset{Me}{C}=CH-\underset{Me}{\overset{Me}{C}}-O-\underset{Me}{\overset{Me}{Al}} \qquad (2)$$

Interaction in benzene. At $1 < Al/Fe < 3$ a mixture of $Al(acac)_3$ and $Et_2Al(acac)$ is formed, the proportion of the latter increasing with increase of the initial Al/Fe ratio. A quantitative estimation of the components of the reaction mixture cannot be made because of the strong absorption bands of benzene and overlap of absorption bands in the region free from benzene absorption (Fig. 2f).

At $Al/Fe < 1$ quantitative analysis is also impossible because of the strong overlap of the absorption bands of $Fe(acac)_3$, $Al(acac)_3$, and $Et_2Al(acac)$. The initial $Al/Fe = 3$ ratio provides a 100% yield of $Et_2Al(acac)$ ($C(Fe(acac)_3)$init. = 0.57×10^{-3} M, $C(Et_2Al(acac)) = 1.7 \times 10^{-3}$ M). The spectrum of the reaction mixture remains unchanged for several days and nights (Fig. 2g).

The rate of decomposition of $Et_2Al(acac)$ in the presence of excess $AlEt_3$ in the system ($Al/Fe > 3$) is comparable to that of the similar process in cyclohexane (Table 1).

$Ni(acac)_2$-$AlEt_3$

Interaction in cyclohexane. The results of the quantitative analysis of the reaction solution spectra are given in Table 2. At $Al/Ni = 0.5$ intensity decrease of the absorption bands at 310 nm and increase of absorption at 263 and 294 nm (Fig. 3a) are observed, which is explained by the removal of $Ni(acac)_2$ and the formation of $Al(acac)_3$ and some $Et_2Al(acac)$. The strong overlap of the bands hinders accurate calculation of $Et_2Al(acac)$ concentrations. Quantitative analysis of the two-component spectra shows gradual decay of the $Ni(acac)_2$ concentration down to 65% of the initial concentration and similtaneous formation of $Al(acac)_3$ in up to 25% yield during the first hour of the process. The total of acac ligands for the control points (2, 10, 30, 60 min) does not exceed 90%, the remaining 10% are assigned to the unaccounted $Et_2Al(acac)$. The spectrum recorded a day after the reaction started showed an additional 3% decrease of $Ni(acac)_2$ concentration, while the $Al(acac)_3$ concentration had increased by 14% (Table 2), which was in contradiction with the scheme involving direct conversion of $Ni(acac)_2$ into $Al(acac)_3$. Consequently, the formation of $Et_2Al(acac)$ may be supposed in the first stage of successive substitution of ethyl radicals in Et_3Al by acac ligands in the reaction of Et_3Al with both $Ni(acac)_2$ and $Fe(acac)_3$. Then the $Et_2Al(acac)$ formed could react with $Ni(acac)_2$ present in the reaction mixture, producing $EtAl(acac)_2$ and $Al(acac)_3$, the former instantly disproportionating into $Et_2Al(acac)$ and $Al(acac)_3$ [6]. The latter, a coordinatively saturated stable aluminium compound, does not participate in further conversion. $Et_2Al(acac)$ may react again, thus the main product of the reaction is $Al(acac)_3$ at $Al/Ni < 1$.

The formal scheme of the stepwise substitution of ethyl radicals in $AlEt_3$ for acac ligands is considered for the $Ni(acac)_2$ $AlEt_3$ system (see eq. 3).

At initial $Al/Ni = 0.7$ the spectra showed the simultaneous presence of three components: $Ni(acac)_2$, $Al(acac)_3$, $Et_2Al(acac)$. The concentration of initial $Ni(acac)_2$ decreased and that of $Al(acac)_3$ increased during the reaction. The relative

TABLE 2

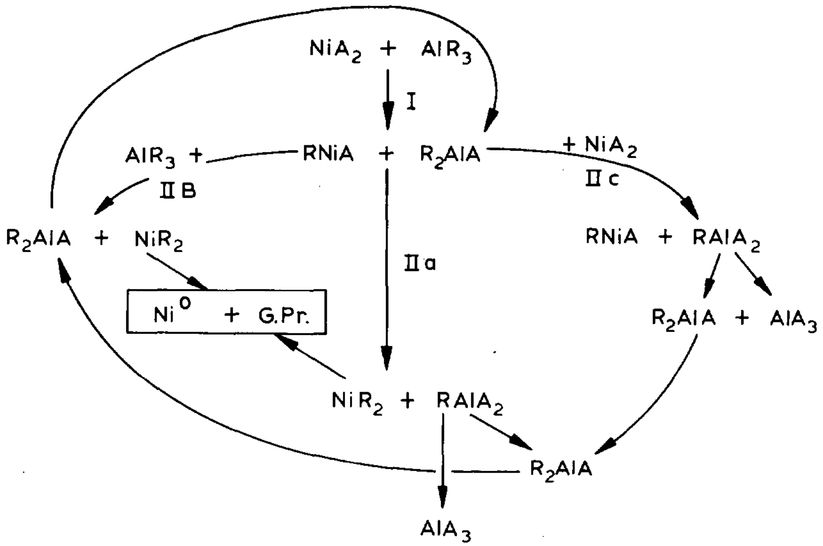
$Ni(acac)_2$, $Et_2Al(acac)$ AND $Al(acac)_3$ CONCENTRATIONS IN THE INTERACTION OF $Ni(acac)_2$ WITH $AlEt_3$ IN CYCLOHEXANE

Al/Ni	Time (min)	$Ni(acac)_2$		$Et_2Al(acac)$		$Al(acac)_3$	
		$C \times 10^3$ (M)	% acac	$C \times 10^3$, (M)	% acac	$C \times 10^3$ (M)	% acac
0.5	0	0.60	100	–[a]	–	–	–
	2	0.51	85	–	–	0.02	6
	10	0.47	78	–	–	0.05	12
	30	0.43	72	–	–	0.08	19
	60	0.39	65	–	–	0.10	25
	24h	0.37	62	–	–	0.16	39
0.7	0	0.62	100	–	–	–	–
	3	0.38	61	0.19	15	0.11	27
	10	0.35	56	0.21	17	0.14	32
	30	0.29	47	0.23	18	0.17	41
	60	0.27	44	0.21	17	0.19	47
	24h	0.21	33	0.18	15	0.25	60
1.3	0	0.47	100	–	–	–	–
	3	–	–	0.51	63	0.09	33
	10	–	–	0.51	63	0.09	33
	30	–	–	0.52	64	0.09	34
	24h	–	–	0.47	57	0.11	40
1.5	0	0.41	–	–	–	–	–
	3	–	–	0.55	68	0.08	31
	24h	–	–	0.51	62	0.10	36
1.8	0	0.62	100	–	–	–	–
	2	–	–	0.85	65	0.14	34
	60	–	–	0.96	77	0.12	28
3.0	0	0.33	100	–	–	–	–
	2	–	–	0.63	96	–	–
	10	–	–	0.61	93	–	–
	60	–	–	0.60	92	–	–
10.0	0	0.33	100	–	–	–	–
	2	–	–	0.47	72	–	–
	10	–	–	0.40	62	–	–
	30	–	–	0.31	48	–	–
	60	–	–	0.24	37	–	–
	24 h	–	–	0.07	11	–	–
15.0	0	0.33	100	–	–	–	–
	2	–	–	0.38	58	–	–
	10	–	–	0.25	39	–	–
	30	–	–	0.17	27	–	–
	60	–	–	0.11	17	–	–
	24 h	–	–	0.03	4	–	–

[a] Product not detected. % acac for $Et_2Al(acac) = (2C(Et_2(acac)/C(Ni(acac)_2)_{init}) \times 100\%$; % acac for $Al(acac)_3 = (1.5C(Al(acac)_3) \times 3/C(Ni(acac)_2)_{init.}) \times 100\%$.

constancy of the $Et_2Al(acac)$ concentration (Table 2) could be explained by its independence of the three processes in eq. 3.

Increase of the initial Al/Ni ratio to 1.3, 1.5 or 1.8 led to a faster transfer of acac ligands from nickel to aluminium. After 2–3 min the $Et_2Al(acac)$ and $Al(acac)_3$ absorption bands appeared in the spectrum of the mixture: the absorption bands of



(3)

where A is an acac ligand, R is an ethyl radical, and G.Pr. are gaseous products.

initial Ni(acac)$_2$ not being observed. The amount of Et$_2$Al(acac) among the reaction products grew with increase of the initial Al/Ni ratio (Table 2). Significant conversion of Et$_2$Al(acac) into Al(acac)$_3$, involving EtNi(acac) or Ni(acac)$_2$ according to eq. 3, did not occur (Fig. 3b, Table 2). This is probably connected with the absence of the above-mentioned Ni(acac)$_2$ at the required stage of the reaction and with the improbability of IIa and IIc routes (eq. 3).

A two-fold excess of Et$_3$Al results in a 100% yield of Et$_2$Al(acac) (C(Ni(acac)$_2$)init. = 0.62×10^{-3} M; C(Et$_2$Al(acac)) = 1.2×10^{-3} M). The spectrum of the mixture after three-days coincides completely with that of pure Et$_2$Al(acac) (Fig. 3c). According to eq. 3 the formation of only Et$_2$Al(acac) is conditioned by route IIb, which agrees with the higher AlEt$_3$ reactivity in comparison with Et$_2$Al(acac) [6].

Excess AlEt$_3$ (Al/Ni = 3, 10, 15) also results in instantaneous formation of Et$_2$Al(acac), which interacts with the AlEt$_3$ residue with cleavage of the acac ligand in accordance with the above scheme (Fig. 3d). The decomposition rate is proportional to the AlEt$_3$ concentration in the system (Table 2).

Interaction in benzene. It was not possible to analyze the reaction mixture quantitatively at Al/Ni < 2, because of the benzene absorption strong overlap of the absorption bands above 270 nm. Qualitative estimation of the spectra at Al/Ni = 1 suggests a gradual transition of acac ligands from nickel to aluminium with the formation of Et$_2$Al(acac) and Al(acac)$_3$, the amount of the latter increasing at the expense of the former (Fig. 3e).

At Al/Ni = 2.1 obvious signs of the reaction appear immediately after mixing the components: the green colour of the solution turns to dark brown. The spectrum of the reaction mixture recorded after 2 min shows a new absorption band at 290 nm, which cannot be assigned to any of the final products. Overlapping the Et$_2$Al(acac) absorption band (λ_{max} = 315 nm), it presents a broad band at 275–330 nm. Then during the following 2 hours a decrease of absorption in the region 285–295 nm is observed and a minimum is seen at 288 nm (Fig. 3f). The spectrum of the same

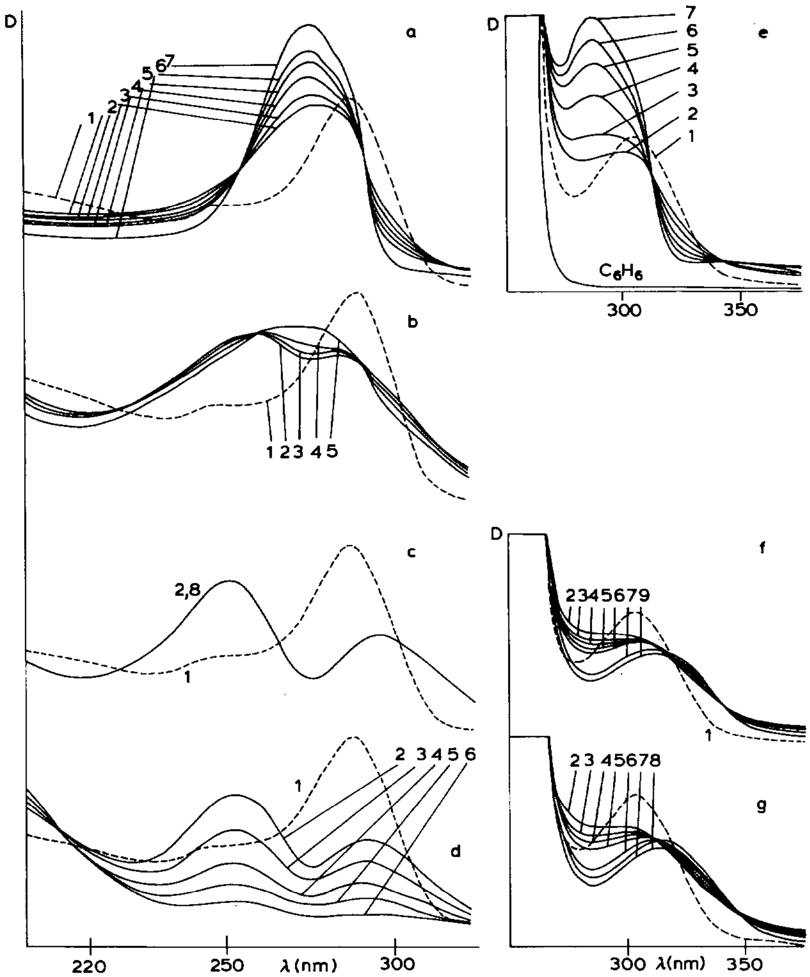


Fig. 3. Absorption spectra of $Ni(acac)_2$ (I) and the interaction of $Ni(acac)_2$ with $AlEt_3$ in cyclohexane at Al/Ni = 0.5 (a), 1.5 (b), 2 (c), 15 (d) and in benzene at Al/Ni = 1 (e), 2.1 (f), 5 (g) after 3 (2), 10 (3), 30 (4), 60 (5), 120 min (6), 24 hours (7), 3 days (8) and 12 days (9).

system 24 h later coincides in all parameters with that of pure $Et_2Al(acac)$ formed in 100% yield ($C(Ni(acac)_2)$init. = 0.6×10^{-3} *M*; $C(Et_2Al(acac)) = 1.2 \times 10^{-3}$ *M*). Thus the period conversion of $Ni(acac)_2$ into $Et_2Al(acac)$ in benzene is much longer than in cyclohexane. Over 12 days the spectrum in a hermetic system remains almost unchanged.

A similar picture is observed in the spectrum of the reaction mixture at Al/Ni = 5, though the process proceeds faster. Already after 2 hours the spectrum of the system is similar to that of pure $Et_2Al(acac)$ (Fig. 3g).

According to eq. 3 the additional absorption band ($\lambda_{max} = 290$ nm) can be assigned to the intermediate EtNi(acac) stabilized in benzene. To confirm this supposition a Ni^{II} compound with one acac group, $EtNiP(c\text{-}Hex)_3(acac)$, was chosen as a model. There is an absorption band in its UV spectra: $\lambda_{max} = 290$ nm,

$\epsilon = 12800$ l mol^{-1} cm^{-1}, which allows identification of the band observed in the Ni(acac)$_2$—AlEt$_3$ system as that of EtNi(acac).

The difference in the reaction rates of Ni(acac)$_2$ with AlEt$_3$ in cyclohexane and benzene agrees with the formation of different gaseous products in aromatic and saturated hydrocarbons [7]. When AlEt$_3$ interacts with Ni(acac)$_2$ in hexane, ethane and ethylene comprise 90% of the gaseous products. The total yield does not exceed 2 mol per g atom Ni, which agrees with eq. 3. The reaction in toluene leads to an increase in the proportion of alkene, and the total yield of gaseous products reaches 6 mol per g atom Ni at Al/Ni = 8. To our mind, this is connected with almost spontaneous substitution of acac ligands on Ni by ethyl radicals in saturated hydrocarbon solution, and ethane, ethylene and Ni^0 are formed from the decomposition of alkylnickel molecules. Benzene stabilizes intermediate Ni compounds, the reaction slows down and, since RNi(acac) is a catalyst of ethylene dimerization [8], it promotes the formation of a large amount of butenes. The interaction of intermediate Ni compounds with AlEt$_3$ results in greater conversion of the latter in benzene.

Co(acac)$_3$-AlEt$_3$

Interaction in cyclohexane. The results are presented in Table 3. At Al/Co = 0.5 a stepwise decrease of the intensity of Co(acac)$_3$ absorption bands is observed at 228 and 257 nm and then an increase in the region of 285 and 295 nm (Fig. 4a). Quantitative analysis of the spectra with the respect to the three components shows conversion of Co(acac)$_3$ into Et$_2$Al(acac) and Al(acac)$_3$. After 3 min the concentration of Et$_2$Al(acac) formed is 1.5 times higher than that of Al(acac)$_3$ and an hour later the latter is three times the former. Thus Et$_2$Al(acac) formed in the first stage interacts with Co(acac)$_3$ present in the reaction mixture to form Al(acac)$_3$. According to the scheme of stepwise substitution of ethyl radicals in AlEt$_3$ by acac ligands, EtCo(acac)$_2$, Co(acac)$_2$, EtCo(acac) and Et$_2$Co(acac) may be formed as intermediates containing acac ligands in the Co(acac)$_3$-AlEt$_3$ system. All the Co compounds can be the sources of acac ligands at Al/Co = 0.5.

A rapid decrease of the intensity of absorption bands of initial Co(acac)$_3$ is observed at Al/Co = 1.3, 2 and 2.5. The spectra recorded after 3–10 min shows the presence of two products in the system, Et$_2$Al(acac) and Al(acac)$_3$. The concentration of the former decreases at the expense of the latter. The proportion of Et$_2$Al(acac) among the reaction products increases with the increase of the initial Al/Co ratio (Table 3). The sources of acac ligands in this case may be acetylacetonates of Co^{II} and Co^{III}, since initial Co(acac)$_3$ is exhausted after 3–10 min (Table 3). Co(acac)$_2$ is a stable chemical compound, its absorption band ($\lambda_{max} = 292$ nm, $\epsilon = 16200$ l mol^{-1} cm^{-1}) [9] coincides and can be overlapped by the stronger band of Al(acac)$_3$: $\lambda_{max} = 288$ nm, $\epsilon = 43600$ l mol^{-1} cm^{-1}. The extinction coefficient (calc. per acac group) is equal to 14500 l mol^{-1} cm^{-1} and 8100 l mol^{-1} cm^{-1} for Al(acac)$_3$ and Co(acac)$_2$, respectively. Therefore we are making a mistake in the calculation of its concentration if we assign the absorption in the 285-295 nm region to Al(acac)$_3$ only. It is small at low contents of Co(acac)$_2$. The appearance of a new absorption band at 238 nm (Al/Co = 1.3, Fig. 4b), which cannot be assigned to any of the considered stable Co and Al compounds, suggests the presence of intermediate Co compounds after 3 min.

The ratio of Al/Co = 3.2 is characterized by the instantaneous formation of

TABLE 3

$Co(acac)_3$, $Et_2Al(acac)$ AND $Al(acac)_3$ CONCENTRATIONS IN THE INTERACTION OF $Co(acac)_3$ WITH $AlEt_3$ IN CYCLOHEXANE

Al/Co	Time (min)	$Co(acac)_3$		$Et_2Al(acac)$		$Al(acac)_3$	
		$C \times 10^3$ (M)	% acac	$C \times 10^3$, (M)	% acac	$C \times 10^3$, (M)	% acac
0.5	0	0.27	100	–[a]	–	–	–
	3	0.18	67	0.09	11	0.06	22
	10	0.17	63	0.06	7	0.08	29
	30	0.15	56	0.04	5	0.10	38
	60	0.15	56	0.03	4	0.11	41
	120	0.14	52	0.03	4	0.12	44
	24 h	0.12	44	0.05	6	0.13	48
1.3	0	0.22	100	–	–	–	–
	10	–	–	0.17	26	0.13	59
	30	–	–	0.16	24	0.14	64
	60	–	–	0.15	23	0.14	64
	120	–	–	0.13	20	0.15	68
	24 h	–	–	0.16	24	0.14	64
2.0	0	0.27	100	–	–	–	–
	3	–	–	0.50	62	0.07	26
	10	–	–	0.48	59	0.08	30
	30	–	–	0.41	51	0.10	37
	60	–	–	0.37	46	0.12	45
2.5	0	0.22	100	–	–	–	–
	2	–	–	0.44	67	0.06	27
	10	–	–	0.42	64	0.08	36
	30	–	–	0.40	61	0.08	36
	60	–	–	0.40	61	0.08	36
	24 h	–	–	0.38	58	0.09	41
10	0	0.26	100	–	–	–	–
	10	–	–	0.71	92	–	–
	60	–	–	0.62	80	–	–
	120	–	–	0.55	72	–	–
10[b]	0	1.14	100	–	–	–	–
	2	–	–	3.27	96	–	–
	10	–	–	2.97	87	–	–
	30	–	–	2.65	78	–	–
	60	–	–	2.24	66	–	–
	120	–	–	1.68	49	–	–
	24 h	–	–	0.24	7	–	–

[a] Product not detected. [b] In benzene.

$Et_2Al(acac)$ with 100% yield ($C(Co(acac)_3)$init. = 0.27×10^{-3} M; $C(Et_2Al(acac)) = 0.80 \times 10^{-3}$ M). The spectrum of the reaction mixture remains unchanged for several days.

At an increased initial Al/Co ratio up to 5 $Et_2Al(acac)$ is also formed, but its concentration in the system decreases ($C(Co(acac)_3)$init. = 0.21×10^{-3} M; $C(Et_2Al(acac)) = 0.62 \times 10^{-3}$ M). (3 min); $C(Et_2Al(acac)) = 0.55 \times 10^{-3}$ M (48 h). A larger excess of $AlEt_3$ results in faster decomposition of $Et_2Al(acac)$ (Table 3).

Interaction in benzene. A mixture of the substitution products, $Et_2Al(acac)$ and $Al(acac)_3$, is formed at $0 < Al/Co < 3$. The proportion of the former among the

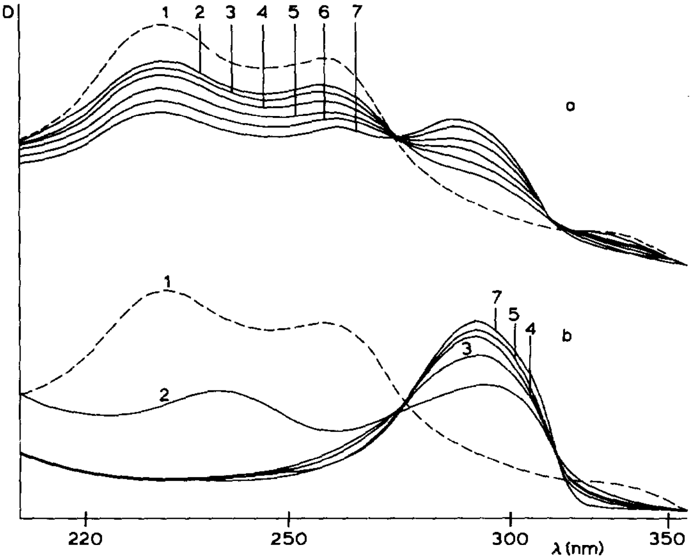


Fig. 4. Absorption spectra of $Co(acac)_3$ (I) and the interaction of $Co(acac)_3$ with $AlEt_3$ in cyclohexane at Al/Co = 0.5 (a), and 1.3 (b) after 3 (2), 10 (3), 30 (4), 60 (5), 120 min (6) and 24 hours (7).

reaction products increases with increasing $AlEt_3$ content in the system. At Al/Co = 3 $Et_2Al(acac)$ is produced in 100% yield ($C(Co(acac)_3)$init. $= 0.90 \times 10^{-3}$ *M*; $C(Et_2Al(acac)) = 2.7 \times 10^{-3}$ *M*). Excess $AlEt_3$ in the system (Al/Co > 3) leads to gradual decomposition of the $Et_2Al(acac)$ formed. The rate of $Et_2Al(acac)$ decomposition in benzene depends on the initial Al/Co ratio and is comparable with that in cyclohexane.

The interaction of $AlEt_3$ with Co^{II} and Co^{III} acetylacetonates has been studied by ESR spectroscopy. At Al/Co > 3 the formation of paramagnetic complexes of Co^0 was found in aromatic hydrocarbons, where $Et_2Al(acac)$ is considered to be one of the ligands, stabilizing Co in this anomalously low oxidation state [10].

The present work reports our magnetochemical investigations of the reaction products, carried out to characterize the state of metals in the $M(acac)_n$-$AlEt_3$ system at initial Al/M > *n*. After measurement of the magnetic susceptibility, χ at, in a magnetic field of 0–1 T at 4.2–295 K, we calculated metal contents for each system in the ferro-, dia- and paramagnetic states.

The ferromagnetic components in these states is temperature dependent and the samples are saturated at 4.2 K only. Such a behavior is characteristic of finely dispersed (up to 100 Å) super-paramagnetic particles. Quantitative analysis shows the proportion of the ferromagnetic component to not exceed 3–8% in all cases (Table 4).

The contents of the paramagnetic metal component and the corresponding value of the magnetic moment were determined for 4.2 K, i.e. under the condition of saturation. It was shown that for the system $Co(acac)_3$—$AlEt_3$ the proportion of finely dispersed Co^0 is 7–8% and the remaining 92% Co are assigned to the paramagnetic complexes. The value of the magnetic moment, μ_{eff}, is 1.66 B.M., i.e. close to the pure spin value for one uncoupled electron and is characteristic of both

TABLE 4

MAGNETIC STATE OF METAL IN PRODUCTS OF $M(acac)_n + AlEt_3$ INTERACTION

System	Al/M	State			
		Ferromagnetic (%)	Paramagnetic (%)	μ_{eff}	Diamagnetic (%)
$Co(acac)_3 + AlEt_3$	4	7–8	92	1.6 [a]	–
after 10 days in air	4	–	100	4.85	–
$Ni(acac)_2 + AlEt_3$	3.1	2.5–3	–		97
after 10 days in air	3.1	–	100	3.26	–
$Fe(acac)_3 + AlEt_3$	3.9	6–8	92	2.67 [a]	–

[a] The magnetic moment is calculated for $T = 4.2$ K. The difference between the total contents of metal and ferromagnetic fraction is taken for the paramagnetic component.

Co^0 and low spin Co^{II} complexes with d^9 and d^7 electron configurations, respectively.

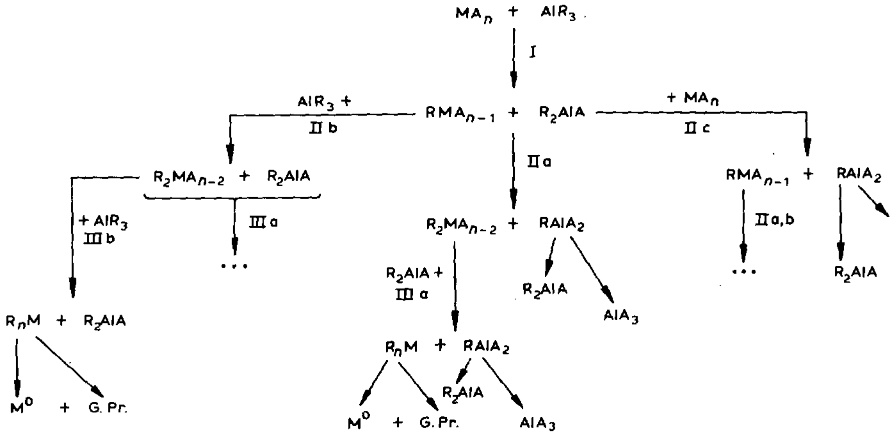
A considerable change in the magnetic properties of the sample is observed after it is exposed to air, the ferromagnetic component disappears completely, and the value of μ_{eff} decreases from 1.66 to 1.36 B.M. (after 2 days), and then it increases and reaches its final value of 4.85 B.M. after 10 days. According to ligand field theory, such a value of the magnetic moment is charactersitic of high spin Co^{II} complexes in a tetrahedral ligand field (d^7 configuration). Thus the results indicate oxidation of the reduced Co^0 in the air via diamagnetic Co^I state according to the scheme:

$$Co^0 \rightarrow Co^I \rightarrow Co^{II}$$

In the $Ni(acac)_2$-$AlEt_3$ system the contribution of the ferromagnetic component is 2–3% and the remaining 97% are assigned to diamagnetic complexes. Besides Ni^0 complexes with electronic configuration d^{10}, there may also be tetracoordinated square planar Ni(II) complexes. On autoxidation the sample becomes fully paramagnetic, which confirms the transition of diamagnetic Ni(0) complexes into paramagnetic ones with a magnetic moment of $\mu_{eff} = 3.23$ B.M., corresponding to Ni(II) in a tetrahedral ligand field. The ferromagnetic component also oxidizes completely. Similar results are obtained for the $Fe(acac)_3$—$AlEt_3$ system (Table 4).

The application of UV spectroscopy to the interaction of $AlEt_3$ with Fe^{III}, Co^{III} and Ni^{II} acetylacetonates allowed us to characterize quantitatively the composition of the reaction products, containing acac ligands on aluminium at different moments and in a wide range of initial Al/M ratios. It was then established that acac ligands were transfered from a transition metal to aluminium and a two-product mixture of $Al(acac)_3$ and $Et_2Al(acac)$ was formed. The proportion of the latter increased with increasing initial $AlEt_3/M(acac)_n$ ratio and reached 100% for $Al/M = n$. The reaction of $Ni(acac)_2$ with $AlEt_3$ in benzene showed stabilization of organonickel compounds and a considerable decrease of the reaction rate. $Et_2Al(acac)$ formed in the $M(acac)_n$—$AlEt_3$ system ($Al/M = n$) remained unchanged. At $Al/M > n$ the excess $AlEt_3$ interacted with $Et_2Al(acac)$ eliminating acetylacetonate. The rate of this process increases with increasing initial Al/M ratio.

The magnetic data showed that reduction of the transition metal to the zerovalent state occurred in the M(acac)$_n$—AlEt$_3$ system at Al/M $\geq n$, M^0 existing in the solution as complexes. Et$_2$Al(acac) was one of the ligands stabilizing the metal in anomalously the low oxidation state. The results were incorperated into a scheme for the stepwise substitution of ethyl radicals by acac ligands in AlEt$_3$, representing the interaction of AlEt$_3$ with Fe^{III}, Co^{III}, Ni^{II} acetylacetonates:



(4)

where M is Fe^{III}, Co^{III}, Ni^{II}, A is acac, R is Et and G.Pr. are gaseous products.

Cr(acac)$_3$-AlEt$_3$

The formation of two products of substitution, Et$_2$Al(acac) and Al(acac)$_3$, is expected in the reaction of Cr(acac)$_3$ and AlEt$_3$. However, the spectra of the reaction mixture showed a decrease in the intensities of the absorption bands of Cr(acac)$_3$ and an increase in the absorption of Et$_2$Al(acac) formed. The latter is the only product of substitution at all initial Al/Cr ratios. Careful analysis of the spectra in benzene and cyclohexane showed complete absence of any traces of Al(acac)$_3$-absorption bands (whose extinction coefficient was equal to 43600 l mol^{-1}cm^{-1} ($\lambda = 288$ nm)). The results of the quantitative analysis of spectra of the reaction mixture are listed in Table 5. These data show that for $0 < Al/Cr < 3$ the system is a mixture of Cr(acac)$_3$ and Et$_2$Al(acac). The degree of transfer of acac ligands from Cr to Al depends on the initial ratio of Al/Cr. Thus at Al/Cr = 1.4 Cr and Al have equal parts of the acac ligands by the end of the reaction (24 h) (Fig. 5a, Table 5). At Al/Cr = 3 complete transfer of acac ligands from the transition metal to aluminium is observed and Et$_2$Al(acac) is produced in 100% yield. Its spectrum remains unchanged for several days (Fig. 5b). Excess AlEt$_3$ (Al/Cr > 3) also results in Et$_2$Al(acac) formation, which decomposes under the action of unreacted AlEt$_3$ according to the above scheme. The decomposition rate is proportional to the AlEt$_3$ content in the system and does not depend on the choice of solvent (Table 5, Fig. 5c,d).

Sartory et al. [11] studied the interaction of AlEt$_3$ and Cr(acac)$_3$ in benzene under nitrogen and, taking into account the results of magnetic susceptibility measurements, they came to the conclusion that Cr^{III} was reduced to Cr^0 during the reaction (Al/Cr > 3). They could not identify the reaction products with IR and UV spectroscopy because of their extreme instability and the strong absorption of

TABLE 5

COMPOSITION CHANGES (% acac) IN THE INTERACTION OF $Cr(acac)_3$ WITH $AlEt_3$

Al/Cr	Time (min)	Cyclohexane		Benzene	
		$Cr(acac)_3$	$Et_2Al(acac)$	$Cr(acac)_3$	$Et_2Al(acac)$
0.6	0	100	–[a]	100	–
	3	86	1	88	15
	30	84	3	88	15
	24 h	80	13	88	15
1.4	0	100	–	100	–
	3	96	5	61	39
	30	84	19	53	51
	60	71	30	54	50
	24 h	54	47	54	49
2.4	0	100	–	100	–
	2	83	6	24	85
	30	62	31	21	83
	60	45	49	20	81
	24 h	13	79	21	80
3	0	100	–	100	–
	3	62	32	–	100
	30	40	57	–	100
	60	17	81	–	100
	24 h	2	94	–	–
10	0	100	–		
	2	–	94		
	30	–	91		
	60	–	86		
	24 h	–	76		
23	0			100	–
	2			–	97
	30			–	82
	60			–	72
	24 h			–	8
200	0	100	–		
	3	–	64		
	30	–	19		
	60	–	0		

[a] Product not detected. % acac for $Et_2Al(acac) = (3C(Et_2Al(acac))/C(Cr(acac)_3)_{init.})\times 100\%$. % acac for $Cr(acac)_3 = (C(Cr(acac)_3)/C(Cr(acac)_3)_{init.})\times 100\%$.

benzene (used as solvent) and suggested the following scheme for the reaction:

$$Cr(acac)_3 + 3AlEt_3 \rightarrow 3[C_2H_6, C_2H_4] + X \qquad (5)$$

where X contains Cr, Al and acac ligands. To study the mechanism in detail we determined the values of the reaction orders in each of the components in cyclohexane. The results are given in Table 6. The third order of the reaction in $AlEt_3$ and the first in $Cr(acac)_3$ presuppose primary formation of a $Cr(acac)_3$ complex with three molecules of $AlEt_3$. This results in complete exchange of acac ligands at Cr and ethyl radicals, already in the first stage of the reaction and explains the above observed absence of $Al(acac)_3$ among the reaction products at $0 < Al/Cr < 3$.

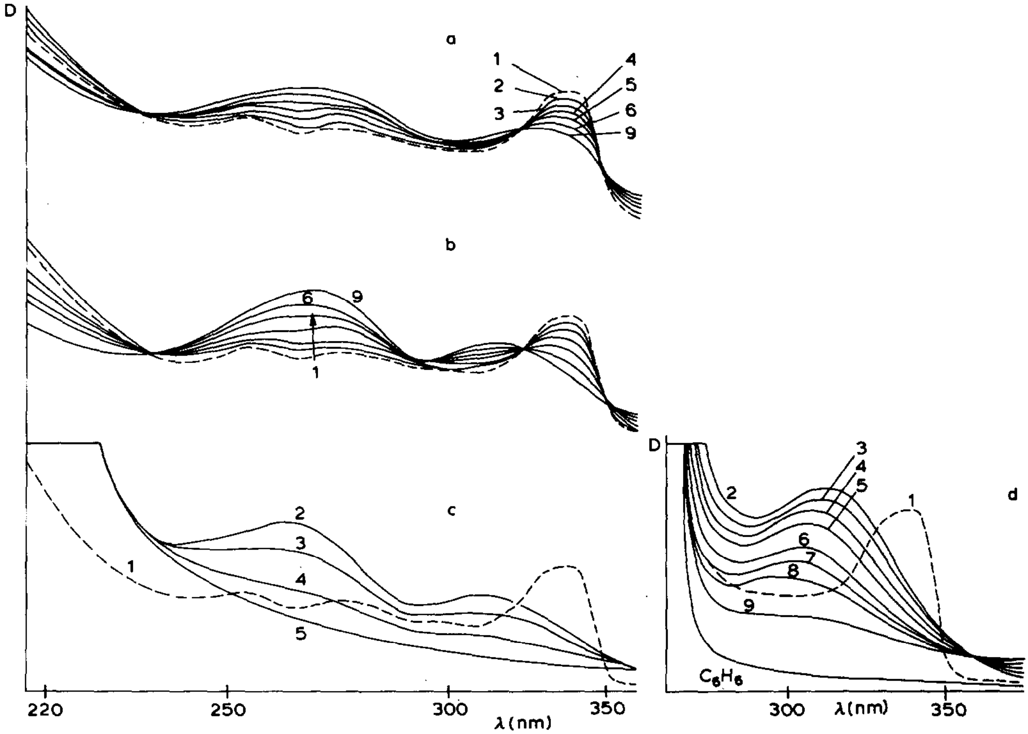


Fig. 5. Absorption spectra of $Cr(acac)_3$ (I) and the interaction of $Cr(acac)_3$ with $AlEt_3$ in cyclohexane at Al/Cr = 1.4 (a), 3 (b), 200 (c) and in benzene at Al/Cr = 23 (d) after 3 (2), 10 (3), 30 (4), 60 (5), 120 (6), 180 (7), 240 min (8) and 24 hours (9).

Hence, the reaction between $AlEt_3$ and $Cr(acac)_3$ can be written as follows:

$$\begin{array}{l} \mathrm{Cr(acac)_3 + 3AlEt_3 \rightarrow 3Et_2Al(acac) + \qquad CrEt_3} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \swarrow \quad \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{Cr^0 + 3[C_2H_6, C_2H_4]} \end{array} \tag{6}$$

The suggested mechanism clarifies the difference between the reaction rates in cyclohexane and benzene (Table 5). The molecules of $Cr(acac)_3$ in the solid state form associates in such a way that one of the three acetylacetonate rings is bonded to one of the three rings of another molecule due to Van der Waals interaction [12]. Cyclohexane is inert towards $Cr(acac)_3$ [13] and can retain dimeric associates.

TABLE 6

REACTION ORDERS FOR $Cr(acac)_3 + AlEt_3$ SYSTEM [a]

No.	n_c	n_t	r	S_0	m
1	3.15		0.980	0.246	4
2	2.81		0.988	0.168	4
3		1.04	0.911	0.134	19
4		0.977	0.993	0.030	9

[a] n_c = concentration order of the reaction in $AlEt_3$; n_t = time order of the reaction in $Cr(acac)_3$; r = correlation coefficient; S_0 = regression standard; m = number of measurements.

Simultaneous attack on the three acac ligands in a $Cr(acac)_3$ molecule is hindered and the reaction slows down (Fig. 5b, Table 5). Cryoscopic measurements on $Cr(acac)_3$ show it to be monomeric in benzene [12], which is connected with the formation of spherical complexes of $Cr(acac)_3$ with benzene, $Cr(acac)_3 \cdot 3C_6H_6$ [13], and allows the approach of three $AlEt_3$ molecules to the three acac ligands of the $Cr(acac)_3$ molecule; thus the reaction proceeds almost spontaneously (Table 5). Thus in the $Cr(acac)_3$-$AlEt_3$ system ($0 < Al/Cr < 200$) transfer of acac ligands from Cr to Al occurs with the formation of only the product of substitution, $Et_2Al(acac)$. This can be explained by the necessity of the preliminary formation of a $Cr(acac)_3$ complex with three $AlEt_3$ molecules and the subsequent simultaneous exchange of acac ligands. In the this case, as well as for Fe^{III}, Co^{III} and Ni^{II} acetylacetonate, Cr^0, formed in the decomposition of $CrEt_3$, is presumably held in solution by $Et_2Al(acac)$.

$Pd(acac)_2$-$AlEt_3$

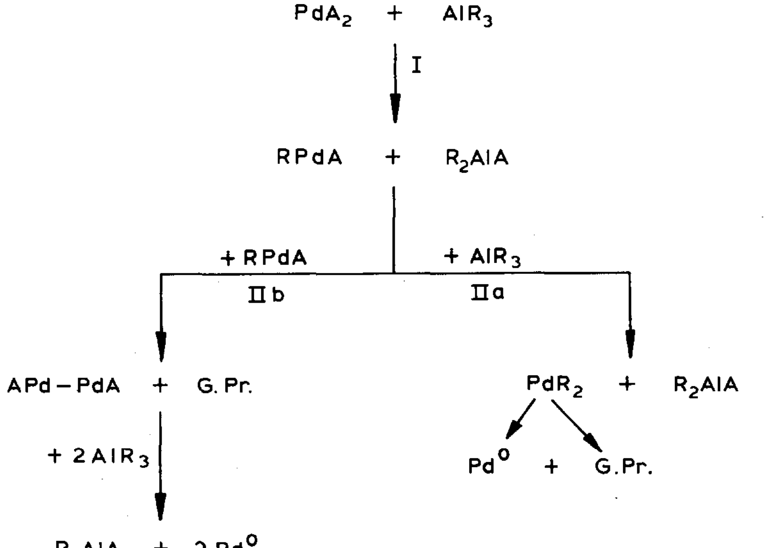
In the interaction of $Pd(acac)_2$ with $AlEt_3$ only one substitution product, $Et_2Al(acac)$, is formed at initial ratios of Al/Pd from 0.3 up to 600.

Interaction in cyclohexane. At $0 < Al/Pd < 2$ the spectrum of the reaction mixture shows a decrease of absorption in the region 200–250 nm and an increase of absorption at 260–310 nm, caused by the decay of $Pd(acac)_2$ and the formation of $Et_2Al(acac)$. The spectra show simultaneous presence of $Pd(acac)_2$ and $Et_2Al(acac)$ in the solution at $0 < Al/Pd < 2$ (Table 7). 2–3 min after mixing the components the conversion degree reaches 90–100% (Table 7).

At $Al/Pd = 2.1$ (after 2 min reaction) the spectrum of the system is the same as that of pure $Et_2Al(acac)$, which is formed with 100% yield: $C(Pd(acac)_2)\text{init.} = 0.29 \times 10^{-3}\ M$; $C(Et_2Al(acac)) = 0.58 \times 10^{-3}\ M$ (Fig. 6a).

Excess $AlEt_3$ ($Al/Pd = 6, 36, 600$) results in immediate formation of $Et_2Al(acac)$, which reacts with the $AlEt_3$ residue in a way similar to all the above systems. The rate of decomposition is proportional to the $AlEt_3$ concentration in the system (Table 7).

The absence of $Al(acac)_3$ among the reaction products suggests the following scheme:



(7)

TABLE 7

$Pd(acac)_2$ AND $Et_2Al(acac)$ CONCENTRATIONS IN THE INTERACTION OF $Pd(acac)_2$ WITH $AlEt_3$ IN CYCLOHEXANE

Al/Pd	Time (min)	$Pd(acac)_2$		$Et_2Al(acac)$	
		$C \times 10^3$ (M)	% acac	$C \times 10^3$ (M)	% acac
0.3	0	0.26	100	–	–
	3	0.22	86	0.09	17
	30	0.22	83	0.10	19
0.7	0	0.32	100	–	–
	3	0.22	67	0.14	21
	30	0.21	65	0.14	22
	60	0.21	65	0.14	22
1.0	0	0.29	100	–	–
	3	0.15	53	0.27	47
	30	0.15	53	0.27	47
1.5	0	0.32	100	–	–
	2	0.09	27	0.43	67
	30	0.08	25	0.45	70
1.8	0	0.29	100	–	–
	3	0.03	11	0.54	94
	30	0.02	9	0.53	92
6.0	0	0.32	100	–	–
	2	–	–	0.59	91
	10	–	–	0.57	90
	30	–	–	0.55	86
	60	–	–	0.52	81
	240	–	–	0.42	65
	24 h	–	–	0.35	54
36	0	0.32	100	–	–
	3	–	–	0.54	84
	10	–	–	0.46	71
	30	–	–	0.32	49
	60	–	–	0.19	30
	120	–	–	0.09	14
	180	–	–	0.07	12
600	0	0.30	100	–	–
	3	–	–	0.31	54
	10	–	–	0.26	45
	30	–	–	0.06	10
	60	–	–	–	–

where A is an acetylacetonate ligand, R is an ethyl radical and G.Pr. are gaseous products. The absence of interaction of $Et_2Al(acac)$ with $Pd(acac)_2$ (similarly to routes IIa and IIc in eq. 3) is probably conditioned by the high stability of the palladium–oxygen bond. The Pd–O bond is known to be much stronger than that of Ni–O [15].

Interaction in benzene. At Al/Pd = 1.5 a stepwise decrease of $Pd(acac)_2$ absorption is observed and a broad absorption band appears at 275–330 nm (Fig. 6b). This new band is similar to that in the $Ni(acac)_2$—$AlEt_3$ system (Al/Ni = 2.1) and can probably be assigned to the total absorption of EtPd(acac) and $Et_2Al(acac)$. The spectrum does not change during five days. Quantitative analysis of the products

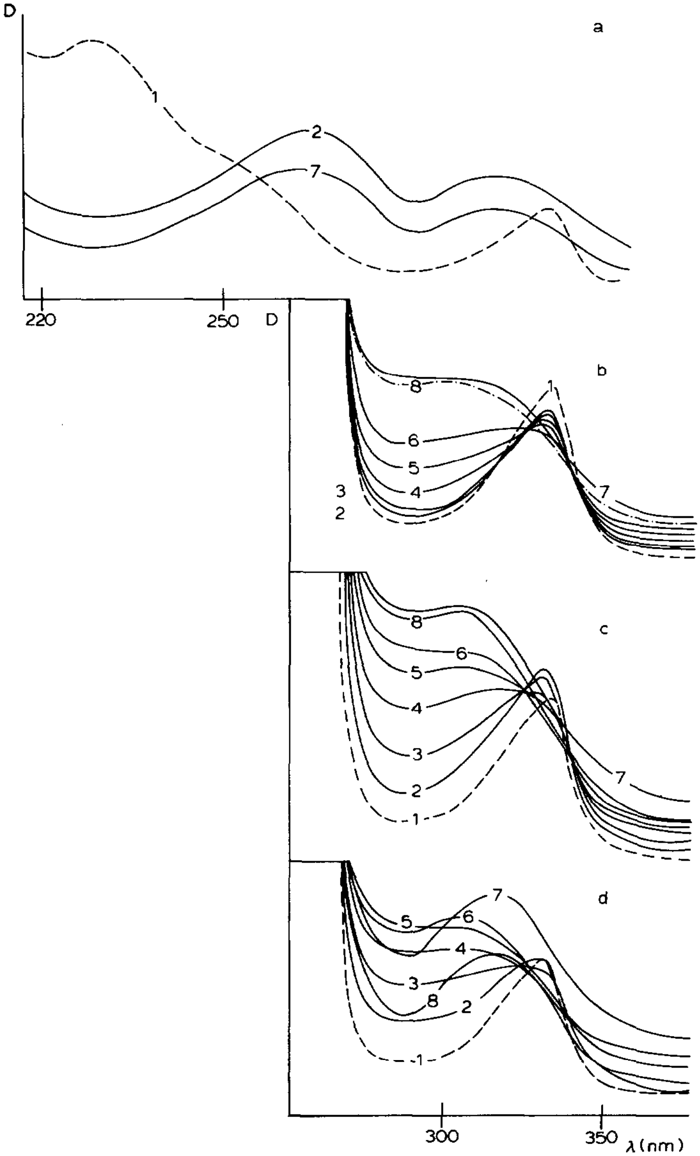
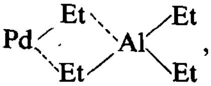


Fig. 6. Absorption spectra of $Pd(acac)_2$ (I) and the interaction of $Pd(acac)_2$ with $AlEt_3$ in cyclohexane at Al/Pd = 2.1 (a) and in benzene at Al/Pd = 1.5 (b), 2 (c), 3.7 (d), after 2 (2), 10 (3), 30 (4), 60 (5), 120 min (6), 24 hours (7) and 5 days (8).

after exposure to air and moisture shows the presence of unreacted $Pd(acac)_2$, comprising 25% of the initial concentration and in agreement with the initial Al/Pd ratio.

At Al/Pd = 2 a similar picture is observed but the absorption of initial $Pd(acac)_2$ decreases and the band corresponding to the formation of a new product increases much faster (Fig. 6c). In contrast to the reaction of $AlEt_3$ with $Ni(acac)_2$ (Al/Ni =

2.1) decomposition of the intermediate followed by $Et_2Al(acac)$ formation is not observed. Comparison of these data with the results of the reaction between $Pd(acac)_2$ and $AlEt_3$ in cyclohexane suggests the presence of complexes able to bond $AlEt_3$ and EtPd(acac) in benzene, which is the reason for the complete cessation of the reaction. This is why there are no signs of pure $Et_2Al(acac)$ in the spectrum. Taking into account the isoelectronic structures of Pd and Ni and the coincidence of the spectra of the reaction products, we suggest the following structure for the relatively stable intermediates in benzene:



, EtPd(acac), (acac)Pd-Pd(acac)

With excess $AlEt_3$ in the system (Al/Pd = 3.7), stage IIa proceeds faster. After 24 hours the spectrum of the system coincides with that of pure $Et_2Al(acac)$ (formed in 100% yield) (Fig. 6d). In this case the reaction proceeds due to the excess of unbound $AlEt_3$ present.

Experimental

Acetylacetonates of Cr^{III}, Fe^{III}, Co^{III}, Co^{II}, Ni^{II} and Pd^{II} were synthesized by general methods, recrystallized from benzene and sublimed under vacuum (10^{-3} Torr) just before reaction. $AlEt_3$ was distilled under low pressure, carefully degassed and poured into glass balls.

Solvents were purified according to standard techniques, dried with CaH_2 and sodium mirror, and degassed under vacuum.

UV spectra

UV spectra of cyclohexane and benzene, as solvents, were recorded between 200–360 nm and 260–450 nm, respectively (Specord UV-Vis spectrometer). Quartz cells ($\varnothing$ = 0.1 mm) were used for spectral investigations of the reactions under vacuum at 25°C. The concentrations were calculated from the maximum absorption for a single component and by the consecutive approaches procedure in the case of mixture components with overlapping absorption bands. The following analytical points were taken in the calculation of polycomponent systems: $Co(acac)_3$: 225 nm, $\epsilon = 39700$ l $mol^{-1}cm^{-1}$; $Ni(acac)_2$: 225 nm, $\epsilon = 5400$ l $mol^{-1}cm^{-1}$; $Cr(acac)_3$: 338 nm, $\epsilon = 16600$ l $mol^{-1}cm^{-1}$; $Pd(acac)_2$: 329 nm, $\epsilon = 11300$ l $mol^{-1}cm^{-1}$; $Al(acac)_3$: 288 nm, $\epsilon = 43600$ l $mol^{-1}cm^{-1}$; $Fe(acac)_3$: 234 nm, $\epsilon = 17500$ l $mol^{-1}cm^{-1}$; $Et_2Al(acac)$: 278 nm, $\epsilon = 4700$ l $mol^{-1}cm^{-1}$; 301 nm, $\epsilon = 3700$ l $mol^{-1}cm^{-1}$ and 333 nm, $\epsilon = 2750$ l $mol^{-1}cm^{-1}$ in the presence of $Al(acac)_3$.

The continuous absorption was taken in to account in the case of the $Pd(acac)_2$—$AlEt_3$ system. The background of the absorption was found to be independent of the wave length and to be constant for all spectral regions. Van 't Hoff's [16] method was used to obtain the reaction orders in $AlEt_3$ and $Cr(acac)_3$. The calculations of the reaction orders were made by the least-squares method. Coefficients of correlation (r) and regression standard (S_0) were used as statistical characteristics of regression.

Magnetic measurements

Solutions of metal acetylacetonates and $AlEt_3$ were prepared in glass balls under vacuum. Benzene was removed from the solution after one hour. The magnetic measurements were carried out in an inert atmosphere in quartz ampules. A small amount of helium was admitted to the ampule to act as a heat-transfer gas. The magnetic susceptibility was measured by Faraday's method in the range 4.2–293 K and in a field of 1–10 Kgauss. The magnetic moment was estimated from $\mu_{eff} = 2.84\sqrt{\chi_{at}T}$, where χ_{at} is the molar paramagnetic susceptibility. The content of a ferromagnetic metal (m) was estimated from the correlation: $m = \mu_f/\sigma$, where σ is the specific saturation [17]. μ_f is the magnetic moment of the ferromagnetic component, which was estimated from the slope of $\chi_{at} = f(1/H)$. The total contents of metal was determined on a atomic Saturn absorption spectrometer.

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