Journal of Organometallic Chemistry, 201 (1980) 89—96
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ALUMINOXANES WITH ACETYLACETONATE SUBSTITUENTS *

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(Received April 14th, 1980)

Summary

The reaction of tetraalkylaluminoxanes (R_4Al_2O; R = Me, Et and i-Bu) with acetylacetone (acacH) has been studied at various molar ratios. The acetylacetonate substituents were found to have a destabilizing effect on the stability of the aluminoxanes. The stability of these compounds decreases in the order: $R_4Al_2O > R_3acacAl_2O > R_2(acac)_2Al_2O \gg (acac)_4Al_2O$.

Aluminoxanes with acetylacetonate substituents undergo disproportionation, yielding aluminium trisacetylacetonate. The alkyl group also has an effect on the stability of alkylacetylacetonatoaluminoxanes, which decreases in the order i-Bu > Et > Me.

Introduction

Many active catalytic systems are obtained from the reaction of transition metal acetylacetonates with alkylaluminium compounds. The reaction of alkylaluminium compounds with cobalt acetylacetonates proceeds through the transfer of the acetylacetonate groups from cobalt to aluminium yielding aluminium dialkylacetylacetonate or aluminium trisacetylacetonate depending on the molar ratio of the reactants [1,2].

Active catalytic systems are also obtained from the reactions of cobalt acetylacetonates with aluminoxanes [3]. Aluminoxanes containing one or more acetylacetonate substituents are expected to be formed from these reactions by transfer of acetylacetonate groups from cobalt to aluminium. The formation of such compounds has been proposed in the literature [4,5], but their synthesis and properties have not been studied.

The purpose of this work was to study the course of the reaction of tetraalkylaluminoxanes with acetylacetone and to determine the stability and properties of aluminoxanes with acetylacetone substituents.

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

Results

Reactions of tetramethylaluminoxane with acetylacetone

The reaction of the ether complex of tetramethylaluminoxane, $[(Me_4Al_2O \cdot B)_2$; B = diethyl ether (Et_2O) or 1,2-dimethoxyethane (DME)], with acetylacetone (acacH) was carried out in an excess of Et_2O or DME as solvents, within the temperature range —70° C to room temperature, for the molar ratios $(Me_4Al_2O \cdot B)_2$: acacH = 1 : 2; 1 : 4 and 1 : 8. Depending on the molar ratio of the reactants, one, two or four moles of methane evolve with respect to one mole of tetramethylaluminoxane.

Aluminium trisacetylacetonate, [Al(acac)$_3$], and a mixture of aluminoxane oligomers containing both acetylacetonate and alkyl substituents are the other reaction products, formed irrespective of the molar ratio of the reactants (eq. 1).

$$[(CH_3)_4Al_2O \cdot B]_2 + n\ \mathrm{acacH} \rightarrow n\ CH_4 + m\mathrm{Al(acac)_3} + \text{oligomers} \qquad (1)$$

Aluminium trisacetylacetonate precipitates from the reaction mixture as a finely crystalline solid. The rate of its formation increases with an increase of the acetylacetone : aluminoxane molar ratio. The reaction in a NMR tube and comparison of the spectra recorded at different temperature (from —70° C to room temperature) (Fig. 1) indicates the following reaction course:

The substitution of the first acetylacetonate group in the aluminoxane proceeds at —70° C (eq. 2).

$$[(CH_3)_4Al_2O \cdot \mathrm{DME}]_2 + 2\ \mathrm{acacH} \xrightarrow[\mathrm{DME}]{-70^\circ C} 2\ CH_4 + 2/n\ [(CH_3)_3\mathrm{acac}Al_2O]_n \qquad (2)$$

Trimethylacetylacetonatoaluminoxane formed from reaction 2 is stable in solution up to about 0° C. At this temperature the signals assigned to the protons of methyl and methine groups of aluminium trisacetylacetonate (δ 1.87 and 5.38 ppm; Fig. 1) appear. The intensity of these signals increases with rising temperature (to room temperature) and at the same time the intensity of signals assigned to the trimethylacetylacetonatoaluminoxane protons decreases. In the spectrum recorded after a few days broadening of the signals is observed, which indicates the presence of oligomers in the reaction mixture (eq. 3).

$$[(CH_3)_3\mathrm{acac}Al_2O]_n \xrightarrow[\mathrm{DME}]{0^\circ C} m\ \mathrm{Al(acac)_3} + \text{oligomers} \qquad (3)$$

Changing the molar ratio of the reactants to $(Me_4Al_2O \cdot \mathrm{DME})_2$: acacH = 1 : 4 shows that substitution of the second acetylacetonate group in the aluminoxane takes place at about —40° C (eq. 4).

$$[(CH_3)_3\mathrm{acac}Al_2O]_n + n\ \mathrm{acacH} \xrightarrow[\mathrm{DME}]{-40^\circ C} n\ CH_4 + n/m\ [(CH_3)_2(\mathrm{acac})_2Al_2O]_m \qquad (4)$$

Dimethyldiacetylacetonatoaluminoxane formed in reaction 4 decomposes at

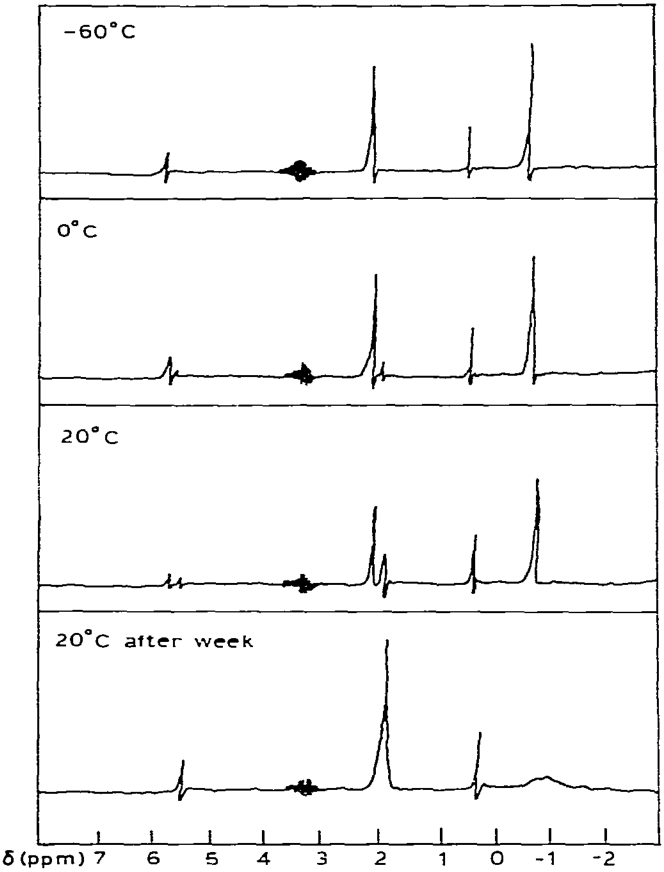


Fig. 1. The PMR spectra of the reaction at Me_4Al_2O : acacH = 1 : 1 carried out in NMR tube. Assignment of the signals: 2.02 and 5.68, protons of the acetylacetonate group in $Me_3acacAl_2O$; —0.82, protons of the methyl groups bonded to aluminium; 1.87 and 5.38, protons of $Al(acac)_3$; 0.26 protons of methane.

about —15°C, forming aluminium trisacetylacetonate and a mixture of oligomers (eq. 5).

$$[(CH_3)_2(acac)_2Al_2O]_n \xrightarrow[DME]{-15°C} m\ Al(acac)_3 + \text{oligomers} \qquad (5)$$

For a $(Me_4Al_2O \cdot DME)_2$: acacH molar ratio of 1 : 8 the formation of aluminoxanes with three or four acetylacetonate substituents is not observed. Aluminium trisacetylacetonate precipitates readily on mixing the reactants at low temperature.

Reactions of tetraethylaluminoxane with acetylacetone

The reactions of tetraethylaluminoxane with acetylacetone were carried out for equimolar ratio of the reactants, in diethyl ether or dimethyloxyethane as solvents, within the temperature range of —70° C to —20° C. During the reaction ethane was evolved (one mole of ethane per one mole of acetylacetone). The product isolated by distilling of the solvent under reduced pressure at —20° C is an oily, colourless, slightly opalescent liquid, which was identified as triethylacetylacetonatoaluminoxane (eq. 6).

$$[(C_2H_5)_4Al_2O]_3 + 3\ \text{acacH} \xrightarrow[Et_2O]{-70^\circ C} 3\ C_2H_6 + 3/2\ [(C_2H_5)_3\text{acac}Al_2O]_2 \qquad (6)$$

Triethylacetylacetonatoaluminoxane is stable at low temperature. At room temperature it slowly disproportionates, yielding aluminium trisacetylacetonate and oligomers (eq. 7). Cryoscopic molecular weight determinations in benzene suggests a dimeric structure for triethylacetylacetonatoaluminoxane (calcd. 512, found 460).

$$[(C_2H_5)_3\text{acac}Al_2O]_2 \xrightarrow[Et_2O]{\text{room temp.}} n\ Al(\text{acac})_3 + \text{oligomers} \qquad (7)$$

Attempts to isolate the product of the reaction carried out for the molar ratio Et_4Al_2O : acacH = 1 : 2 were not successful. Low temperature NMR studies showed that diethyldiacetylacetonatoaluminoxane is more stable than its methyl analogue.

Synthesis of triisobutylacetylacetonatoaluminoxane

The reactions of tetraisobutylaluminoxane with acetylacetone were carried out at temperatures from —70° C to room temperature, in diethyl ether as a solvent. Triisobutylacetylacetonatoaluminoxane, formed in the reaction with an equimolar ratio of the substrates, is stable in the solution at room temperature (eq. 8). The compound obtained in this reaction, however, always contains

$$(\text{i-Bu}_4Al_2O)_n + n\ \text{acacH} \xrightarrow[Et_2O]{} n\ \text{i-BuH} + n/m\ (\text{i-Bu}_3\text{acac}Al_2O)_m \qquad (8)$$

impurities (aluminium trisacetylacetonate and aluminoxane oligomers). This is probably due to the fact that it is impossible to obtain the initial tetraisobutylaluminoxane in a pure state by the controlled hydrolysis of triisobutylaluminium. Pure triisobutylacetylacetonatoaluminoxane may be obtained in a two step reaction (eq. 9, 10):

$$\text{i-Bu}_2\text{Alacac} + H_2O \xrightarrow[Et_2O \text{ or DME}]{-40^\circ C} [\text{i-BuacacAlOH}] + \text{i-BuH} \qquad (9)$$

$$[\text{i-BuacacAlOH}] + \text{i-Bu}_3Al \xrightarrow[Et_2O \text{ or DME}]{-40^\circ C} \text{i-Bu}_3\text{acac}Al_2O + \text{i-BuH} \qquad (10)$$

The high selectivity of this method suggests that isobutylhydroxyaluminium acetylacetonate formed in reaction 9 reacts much faster with triisobutylaluminium than with the second molecule of isobutylhydroxyaluminium acetylacetonate. For complete conversion of aluminium diisobutylacetylacetonate sufficient reaction time (3—4 hours) is essential.

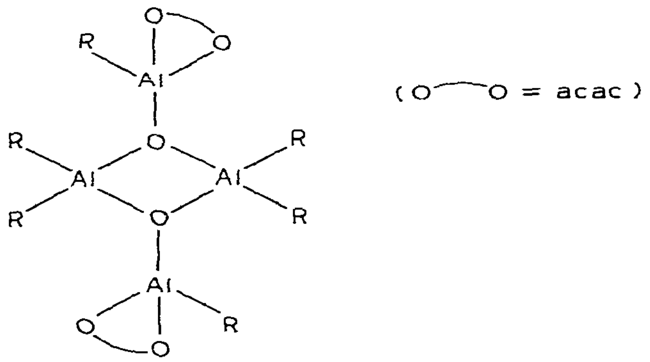
Triisobutylacetylacetonatoaluminoxane is a thick, slightly opalescent, colourless liquid, readily soluble in organic solvents (Et_2O, DME, benzene, toluence, etc.).

Discussion

The above studies show that both the number of acetylacetonate substituents and kind of alkyl radical have an effect on the stability of alkylacetylacetonatoaluminoxanes. An increase in the number of acetylacetonate substituents in the aluminoxane causes a decrease of its stability, suggested by its quicker decomposition with the formation of aluminium trisacetylacetonate and aluminoxane oligomers. Thus, the stability of aluminoxanes with acetylacetonate substituents decreases in the following order:

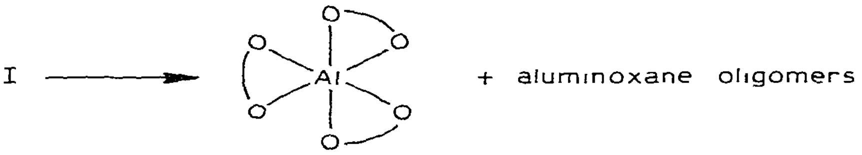
$R_3acacAl_2O > R_2(acac)_2Al_2O \gg (acac)_4Al_2O$.

From cryoscopic measurements it appears that trialkylacetylacetonatoaluminoxane is a dimer and the following structure can be proposed:



I

Trialkylacetylacetonatoaluminoxane (I) readily disproportionates to aluminium trisacetylacetonate (II) (eq. 11).



(11)

(II)

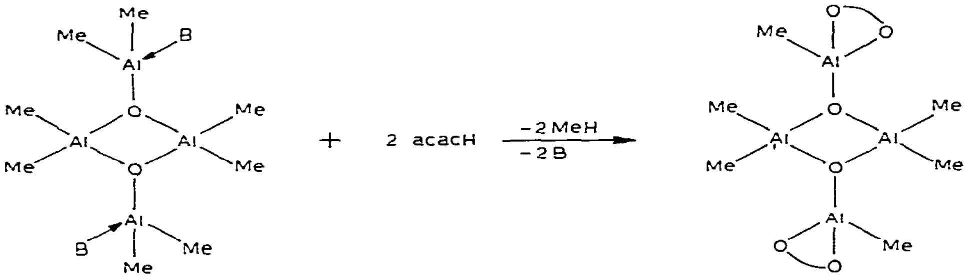
It is well known that the most stable aluminium compounds are those in which aluminium is six-coordinate and is surrounded by strong electron donating atoms, eg. oxygen in aluminium trisacetylacetonate. Thus the driving force for the disproportionation of alkylacetylacetonatoaluminoxanes is the change of the coordination number of aluminium from four in compound I to six in compound II and an increase in the number of coordinating oxygen atoms from three to six.

$$2\,Me_2Alacac + H_2O \rightarrow 2\,MeH + n\,Al(acac)_3 + \text{oligomers} \qquad (12)$$

Similar reactions were observed previously for the hydrolysis of aluminium dimethylacetylacetonate (eq. 12) [6], and the disproportionation of aluminium dimethylacetylacetonate in the presence of pyridine (eq. 13) [7].

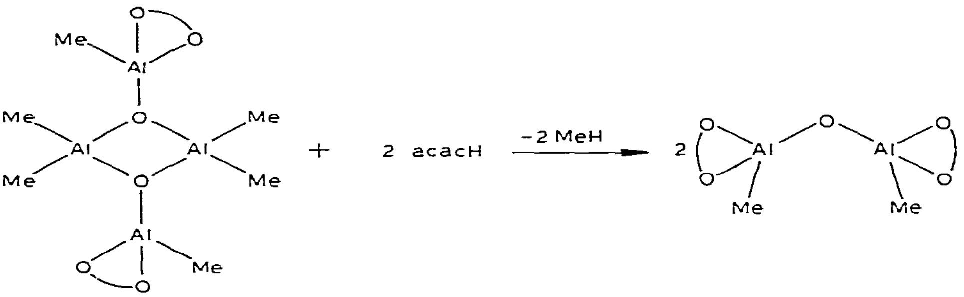
$$2\,Me_2Alacac + 2\,py \rightarrow Al(acac)_3 + 2\,Me_3Al \cdot py \qquad (13)$$

The possibility of maintaining an associated structure for trialkylacetylacetonatoaluminoxanes may be an additional reason for their higher stability compared to dialkylacetylacetonatoaluminoxanes (eq. 14).



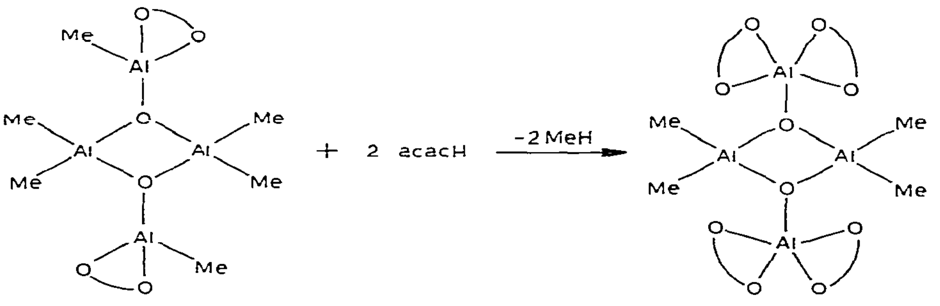
(14)

The introduction of a second acetylacetonate group probably causes the dissociation of the molecule (eq. 15).



(15)

Retention of the associated structure in the above reaction seems to be less probable as this would give five-coordinate aluminium atoms (eq. 16).



(16)

As the trialkylacetylacetonatoaluminoxane molecule contains one acetylacetonate group, the formation of aluminium trisacetylacetonate demands an intermolecular transfer of acetylacetonate groups. An enlargement of the alkyl group, due to steric hindrances, makes the intermolecular exchange of the groups more difficult, resulting in a decreased rate of disproportionation of the trialkylacetylacetonatoaluminoxanes and hence in their increased stability in the order:

$Me_3acacAl_2O < Et_3acacAl_2O < i\text{-}Bu_3acacAl_2O$.

Experimental

Solvents and reactants

Diethyl ether (Pronit, ERG, Poland), 1,2-dimethoxyethane (Fluka) and acetylacetone (Veb. Laborchemie Apolda) were dried, and then distilled and stored under nitrogen before use. Tetramethylaluminoxane [8], tetraethylaluminoxane [9] and aluminium diisobutylacetylacetonate [10] were obtained by methods described in the literature. All the reactions were carried out under dry, deoxygenated nitrogen.

Reactions of tetramethylaluminoxanes with acetylacetone

To 2.535 g (12 mmol) of an ether complex of tetramethylaluminoxane in 30 cm^3 of diethyl ether, 1.243 g (12 mmol) of acetylacetone in 15 cm^3 of ether was slowly added dropwise at —70° C. The reaction mixture was slowly heated up to room temperature. The precipitate was filtered off and identified as aluminium trisacetylacetonate. Concentration of the filtrate caused the further precipitation of aluminium trisacetylacetonate. Attempts to isolate the reaction product by distilling off the solvent under reduced pressure at —20° C caused its decomposition and the precipitation of $Al(acac)_3$.

Reactions of tetramethylaluminoxane with acetylacetone in a NMR tube

The ether complex of tetramethylaluminoxane and acetylacetone in dimethoxyethane were introduced into a NMR tube placed in liquid nitrogen. The tube was then sealed and the NMR spectra of the reaction mixture were recorded during the gradual increase of temperature from —70° C up to room temperature.

Reactions of tetraethylaluminoxane with acetylacetone

These reactions were carried out analogously to the reactions of tetramethylaluminoxane within the temperature range from —70° C to —20° C. The solvent was distilled off under reduced pressure at —20° C. The residue was an oily, colourless, slightly opalescent liquid, which was identified as triethylacetylacetonatoaluminoxanes: found: Al, 22.0, $C_{11}H_{22}Al_2O_3$ calcd.: Al, 21.09%. NMR spectrum in DME (δ, ppm): 5.68, (1 H), singlet; 2.08, (6 H), singlet: 0.96, (9 H), triplet: —0.12, (6 H), quartet. The product was stable at low temperature. At room temperature it underwent slow decomposition with the formation of $Al(acac)_3$.

Synthesis of triisobutylacetylacetonatoaluminoxane

To 2.195 g (9 mmol) of aluminium diisobutylacetylacetonate in 20 cm^3 of Et_2O, 0.16 g (9 mmol) of water in 30 cm^3 of Et_2O was slowly added at —40° C. The reactants were stirred for 3 to 4 h at —40° C, and then 1.811 g (9 mmol) of triisobutylaluminium in 16 cm^3 of Et_2O was introduced dropwise at —40° C. The reaction mixture was slowly heated till room temperature, and then the solvent was distilled off under reduced pressure.

The residue was a thick, colourless, slightly opalescent liquid, which was identified as trisobutylacetylacetonatoaluminoxane: found: Al, 15.50, $C_{17}H_{34}Al_2O_3$ calcd.: Al, 15.28%. ^{1}H NMR spectrum in DME (δ ppm): 5.58, (1 H), singlet; 2.11, singlet overlapping a multiplet, (total 9 H); 0.99, (18 H) doublet; —0.11, (6 H) doublet. The product was stable at room temperature.

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