

Journal of Organometallic Chemistry, 153 (1978) 281–288
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REACTIONS OF ALKOXYALUMINIUM DICHLORIDES WITH METHYLALUMINIUM DICHLORIDE

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(Received January 26th, 1978)

Summary

Reactions of alkoxyaluminium compounds of the type ROAlCl_2 ($\text{R} = \text{Me}$, Et , $n\text{-Pr}$, $i\text{-Pr}$, $n\text{-Bu}$, $t\text{-Bu}$) with MeAlCl_2 were investigated. They proceed with the evolution of gases and the formation of aluminoxane systems $\text{Al}-\text{O}-\text{Al}$. The reaction products were identified by GC, IR and MS. The reaction mechanism is discussed. The influence of the type of OR group on the reactivity of alkoxyaluminium compounds was observed.

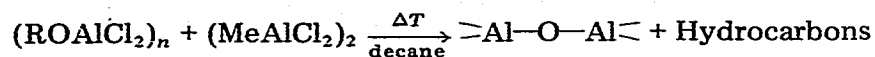
Introduction

The formation of alkoxyaluminium compounds as intermediate products in the alkylation reactions of aldehydes, ketones, esters etc. has been postulated in the literature for a long time. Mole [1,2,3] studied the methylation reaction using an excess of Me_3Al . He observed a further methylation of the alkoxyaluminium intermediates formed resulting in fully methylated hydrocarbons. He [1] also used a mixture of Me_3Al and Me_2AlCl and stated that the reaction then occurred rather more easily, but that the olefin elimination predominated.

In this paper we present the results of our study concerning the direct reaction between alkoxyaluminium dichlorides and methylaluminium dichloride.

Results and discussion

We have investigated the reactions of various alkoxyaluminium dichlorides with methylaluminium dichloride at elevated temperatures in a decane solution. The molar ratio of the compounds was 1 : 1.



$\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, i\text{-Pr}, n\text{-Bu}, t\text{-Bu}$

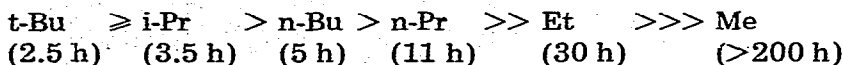
TABLE 1
THE DEPENDANCE OF THE REACTION TEMPERATURE ON THE KIND OF ALKOXY GROUP IN
THE REACTIONS OF $ROAlCl_2$ WITH $MeAlCl_2$ ^a

Alkoxy group	Initial reaction temperature ^b (°C)	Final reaction temperature ^c (°C)
t-butoxy	65	173
n-butoxy	150	173
i-propoxy	120	173
n-propoxy	165	173
ethoxy	185	185
methoxy	190	190

^a In all cases the conversion of the alkoxy group was over 90%. ^b The temperature at which rapid evolution of gases begins. ^c The rate of heating was 4°C/min.

The reactions begin violently after a certain time (much smaller for the branched alkoxy compounds) and a considerable amount of gas is evolved instantaneously. Simultaneously a yellow solid product (aluminoxane) is precipitated.

In order to determine the reactivity toward $MeAlCl_2$ of the alkoxy compounds studied, the reactions were carried out in two ways. In the first one, the temperature was raised continuously to 173°C ($R = n\text{-Pr, } i\text{-Pr, } n\text{-Bu, } t\text{-Bu}$) or higher ($R = \text{Me, Et}$) and the temperature at which a fast evolution of gases occurred was noted (Table 1). In the second one all reactions were carried out at 100°C and the time to when no further evolution of gases was observed was measured. From these data the following order of the reactivity of the alkoxy compounds could be established:

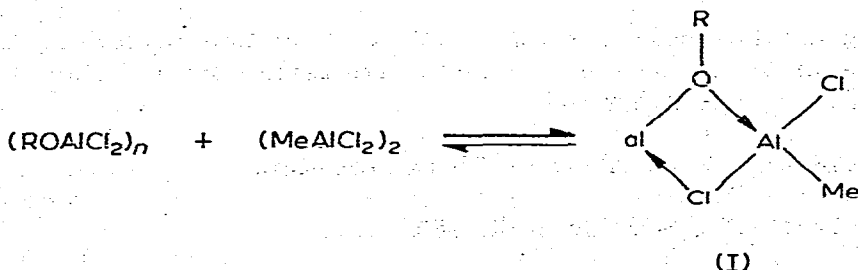


As one can see, methoxyaluminium dichloride is the least reactive. It also gives somewhat different gaseous products than the other alkoxyaluminium dichlorides. For this reason the reaction of the methoxy compounds is not discussed further in this paper.

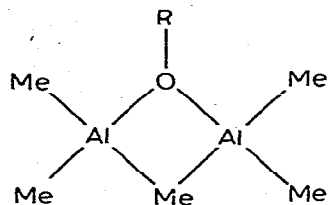
The above order shows that the more branched the alkoxy group, the more stable is the R^+ cation, and the easier the reaction proceeds. This suggests that the formation of a carbocation from the OR group must play a significant role in the reaction mechanism.

The following reaction scheme seems to be the most probable one:

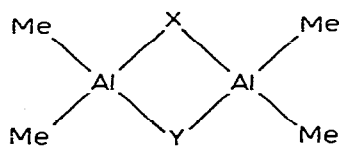
(i) In the first step of the reaction the alkoxyaluminium dichloride forms a complex with methylaluminium dichloride of type I:



This suggestion is partly proven by the formation of hemialkoxides (a) in the methylation reactions of aldehydes and ketones by Me_3Al [4], and further by the formation of similar mixed bridged species (b) in the mixtures of Me_2AlX and Me_2AlY [5–8].



(a)



(b)

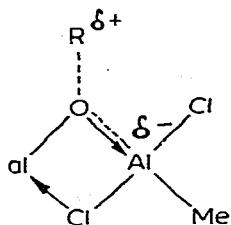
ref. 5: X = Cl, Br, PhCC ;

Y = Me, Br, PhCC, Ph, OPr

ref. 6,8: X = OCMe(Ph)₂ ; Y = Me

ref. 7,8: X = Me ; Y = NPh₂

(ii) The charge distribution in the intermediate I formed leads to the weakening of the C–O bond.



The carbocation R^+ formed may undergo several different reactions leading to different gaseous products (Table 2). These reactions can be grouped as fol-

TABLE 2

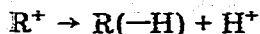
GASEOUS PRODUCTS FORMED IN THE REACTIONS OF ROAlCl_2 WITH MeAlCl_2 (100°C, decane solution)^a

Alkoxy group	Methane (%)	Ethane (%)	Propane (%)	i-Butane (%)	Neopentane (%)	i-Pentane (%)	2,2-Dimethylbutane (%)
t-butoxy	9.45	0.06	0.19	49.72	24.51	14.93	1.14
i-propoxy	10.71	0.02	47.36	28.85	1.25	11.01	0.80
ethoxy	10.54	17.24	2.92	42.84	0.89	20.65	4.93

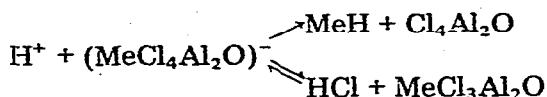
^a 2-Methylpentane and 3-methylpentane were also present. All data were calculated from GC analysis (in percentage of peak area); Porapak Q, 80/100 mesh, 6' x 1/8", temp. 150°C, N₂ 25 ml/min, detector FID.

lows:

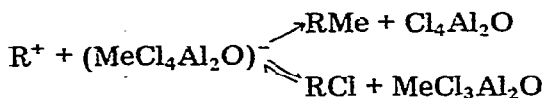
(1) stabilization by elimination of a proton followed by the formation of a corresponding olefin.



The proton reacts with the anion to give methane.



(2) direct reaction with the anion to yield the corresponding alkane or alkyl chloride.



(3) isomerization yielding an isomer R'^+ , which will further react similarly as cation R^+ .

(4) Reactions with alkanes RMe or $R'Me$ involving abstraction from them of the hydride anion.



The new carbocations may also undergo the same reactions. From the gaseous products shown in Table 2 one can easily see that nearly all products of the above reactions are present. For example $t\text{-BuOAlCl}_2$ yields methane (1), i -butane (4), neopentane (2), isopentane (3, 4) and higher hydrocarbons. The higher hydrocarbons are formed in subsequent reactions (4), (2), (4) etc.



The absence of alkyl chlorides can be easily explained by their great reactivity toward the organoaluminium compounds present. According to our earlier studies t -butyl chloride and i -propyl chloride react with $MeAlCl_2$ even at -78°C and with ethyl chloride at $+50^\circ\text{C}$ [9]. The reactions of alkyl chlorides also proceed with carbocation formation and thus would yield the same products.

Olefins formed in reaction (1) may easily undergo a partial or complete polymerization on the active organoaluminium catalysts present. It was found that the reaction mixture darkened on further heating after the yellow precipitate had formed, and that the precipitate changed to a very viscous dark brown liquid. The IR spectra of this product formed in reactions of $t\text{-BuOAlCl}_2$, $i\text{-PrOAlCl}_2$ and EtOAlCl_2 are shown in Fig. 1. The IR spectrum of polyethylene is given for comparison. One can see that there is little difference between these spectra. The band at 1600 cm^{-1} can be assigned to the vibrations of residual $\text{C}=\text{C}$ bonds present. The strong band of polyethylene at $\sim 730\text{ cm}^{-1}$ overlaps a very strong band of CH_2Cl_2 , thus it may not be observed in the spectra II and III. In spectrum I, which was taken in toluene, a broad band in this region is observed. The band at 800 cm^{-1} is assigned in the literature to the vibrations of the $\text{Al}-\text{O}-\text{Al}$ system in aluminoxanes [10]. No strong band due to $\text{C}-\text{O}$ vibrations in the

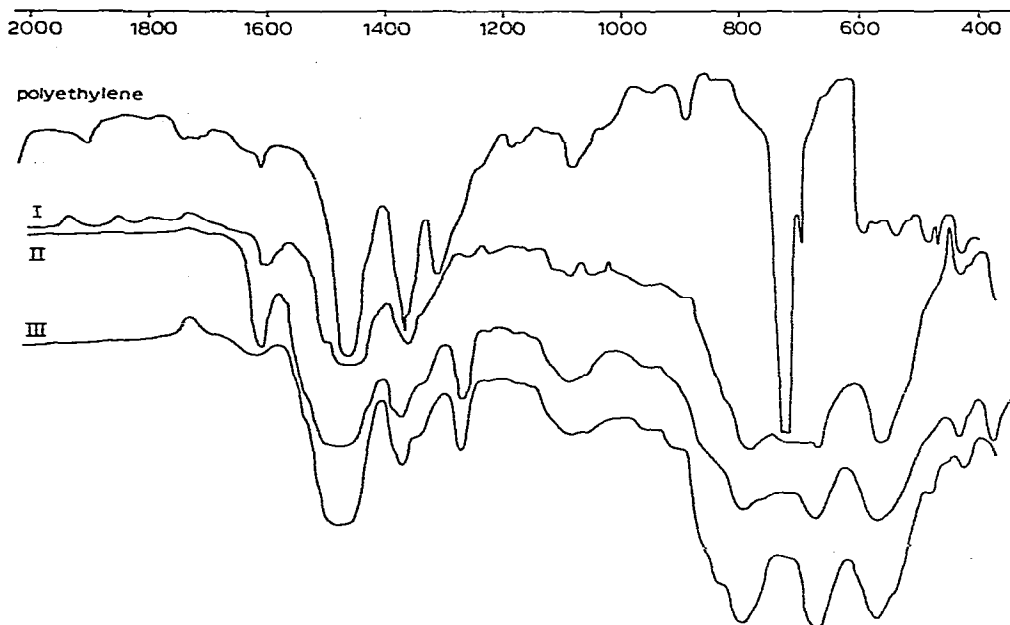


Fig. 1. The comparison of IR spectra of polyethylene and reaction products of: I, $\text{EtOAlCl}_2 + \text{MeAlCl}_2$ (in toluene); II, $i\text{-PrOAlCl}_2 + \text{MeAlCl}_2$ (in CH_2Cl_2); III, $t\text{-BuOAlCl}_2 + \text{MeAlCl}_2$ (in CH_2Cl_2).

region of $900\text{--}1100\text{ cm}^{-1}$ is observed. This is in good agreement with the amount of gases evolved.

The precipitate formed at the beginning was found to be insoluble in such solvents as benzene, toluene, chlorobenzene, chloroform and diethyl ether. It did not distill nor sublime at $40^\circ\text{C}/10^{-4}\text{ mmHg}$ but decomposed at $140^\circ\text{C}/10^{-1}\text{ mmHg}$. The analysis showed that it did not contain any alkoxy groups and only 5.3 weight % of methyl groups. The precipitate was partly soluble in wet benzonitrile. The liquid over the precipitate was decanted and worked up under vacuum. The distillate contained pure benzonitrile. The IR spectrum of the residual precipitate showed characteristic absorption bands at 800 cm^{-1} (Al—O—Al) and at 2273 cm^{-1} ($\text{C}\equiv\text{N}$). The $\nu(\text{C}\equiv\text{N})$ band is shifted about $+43\text{ cm}^{-1}$ and indicates that all benzonitrile is complexed. The elementary analysis indicated that the molar ratio of aluminoxane to benzonitrile is 1 : 1.4.

We have previously studied the reaction of the controlled hydrolysis of benzonitrile complexes of methyl aluminium compounds [11]. It was found that the aluminoxane complexes thus obtained do not exhibit stoichiometry, e.g. $\text{Cl}_4\text{Al}_2\text{O}$ forms a complex with 1.86 moles of PhCN while $\text{Me}_4\text{Al}_2\text{O}$ with 0.98 moles of PhCN.

The analysis data of our complex compared with those calculated for $\text{Cl}_4\text{Al}_2\text{O} \cdot 1.4\text{ PhCN}$ and $\text{MeCl}_3\text{Al}_2\text{O} \cdot 1.4\text{ PhCN}$ are given in Table 3. The results indicate that the residual precipitate is a mixture of $\text{Cl}_4\text{Al}_2\text{O}$ and $\text{MeCl}_3\text{Al}_2\text{O}$ complexed with benzonitrile. The aluminoxanes formed under the reaction conditions must have highly polymeric structures, and that is the reason for their insolubility in donor solvents.

TABLE 3
ANALYSIS DATA

Complex	Analysis (%)				
	Al	Cl	C	H	N
Found for the obtained complex	14.10	34.60	34.61	3.12	5.20
Calcd. for $\text{Cl}_4\text{Al}_2\text{O} \cdot 1.4 \text{ PhCN}$	15.10	39.80	33.03	1.97	5.50
Calcd. for $\text{MeCl}_3\text{Al}_2\text{O} \cdot 1.4 \text{ PhCN}$	16.10	31.60	35.04	2.08	5.08

As we have earlier mentioned the reactions of alkoxyaluminium dichlorides with methylaluminium dichloride are characterized by a certain "initiation time" after which they start violently. Mole [1] observed the same phenomena in his studies and stated the reactions to be autocatalytic. According to him alumin-oxanes, or more probably hydroxyaluminium compounds, may act as catalysts. In our case their formation occurs more easily and the reactions proceeded faster and under milder conditions.

Mole [1] observed that when the mixture of Me_3Al and Me_2AlCl was used, not the C-methylation reaction but the olefin elimination reaction predominated. Both these reactions seem to occur at the same level in the processes we have studied.

We have also carried out the reaction of $t\text{-BuOAlMe}_2$ with Me_3Al (in the molar ratio 1 : 1) at 100°C for 240 h without any solvent. The gaseous products consisted of methane (67%), isobutylene (29%) and neopentane (3%). Mole [1] performed the same reaction in benzene at 120°C and found neopentane to be the main product. The difference in the reaction course may be due to the presence of the solvent. It seems that the reactions of alkoxy compounds may lead to different products depending on the reaction conditions. MeOAlCl_2 did not react with MeAlCl_2 in decane at 140°C even when heated for more than 200 h. The same compounds began to react at the same temperature after 10 h when no solvent was present.

The reactions of various methoxyaluminium compounds with methylaluminium compounds are being investigated and will be discussed in a following paper.

Experimental

All the experiments were carried out in a purified nitrogen atmosphere.

Methylaluminium dichloride was obtained in our laboratory according to the method previously described [12] and purified by distillation.

Decane, benzene and toluene were distilled from solutions containing blue ketyl ($\text{K} + \text{Ph}_2\text{CO}$). Diethyl ether was distilled first from sulphuric acid and then from LiAlH_4 . Benzonitrile was distilled twice, and fractions of b.p. $190\text{--}191^\circ\text{C}$ were collected. Dichlorobenzene and chloroform were distilled from P_2O_5 .

Methylene dichloride was distilled from molecular sieves (5 Å).

Methyl alcohol was distilled from magnesium methylate. The other alcohols: ethyl, n-propyl, i-propyl, n-butyl and t-butyl, were distilled from corresponding sodium alcoholates.

The gaseous products were analyzed by means of a Varian model 2868 gas chromatograph and LKB 2891 mass spectrometer. The IR spectra were recorded on a Perkin-Elmer model 577 spectrometer.

The reactions of ROAlCl₂ with MeAlCl₂

To a reaction vessel equipped with a stirrer and a condenser, containing 70 ml of 15% solution of MeAlCl₂ in decane, 0.5 mol of alcohol was added slowly at 0°C. When all the alcohol had been added, the temperature was raised to room temperature. When no further evolution of gases was observed, the solution was cooled and the reaction vessel was carefully evacuated and filled again with nitrogen. This was done in order to remove methane formed in the alcoholysis.

A. The "temperature dependence" experiment. The reactor was then placed in a thermostat and heated gradually, 4°C/min, and the evolution of gases was observed. The t-BuOAlCl₂, n-BuOAlCl₂, n-PrOAlCl₂ and i-PrOAlCl₂ systems were heated up to 173°C, though they reacted below this temperature. EtOAlCl₂ begins to react at 185°C and was heated at that temperature for 7 h till no further evolution of gases was observed. MeOAlCl₂ reacted only at 190°C and was heated for 33 h.

B. The "time dependance" experiment. The reactor was placed in a thermostat at 100°C. The gaseous products were collected in a gas burette. The time to reach the point where no further evolution of gases was observed was noted. t-BuOAlCl₂, 2.5 h; n-BuOAlCl₂, 5 h; i-PrOAlCl₂, 3.5 h; n-PrOAlCl₂, 11 h; EtOAlCl₂, 30 h; MeOAlCl₂, >200 h.

Analyses

Weighed samples were decomposed with n-hexanol and then with diluted nitric acid. The volume of gases resulting from the methyl groups bonded to aluminium was measured. Aluminium and chlorine were determined from the solutions after hydrolysis, complexometrically and argentometrically respectively. Benzonitrile was determined chromatographically from the toluene layer, after hydrolysis, by the internal standard method. Carbon, nitrogen and hydrogen were determined by elemental analysis.

Acknowledgements

We would like to express our gratitude to Dr. E. Baranowska for recording and analysing the mass spectra. We also thank the Polish Academy of Sciences for financial support.

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