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THE REACTIONS OF METHOXYALUMINIUM COMPOUNDS WITH ORGANOALUMINIUM COMPOUNDS

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Summary

The reactions of $Me_x(OMe)AlCl_{2-x}$ (where x = 1, 2, 0) with Me_yAlCl_{3-y} (y = 3, 2, 1) and Et_3Al have been investigated. They lead to the formation of aluminoxane systems $(>Al-O-Al<)_n$ with the evolution of alkanes and methyl chloride. The reaction mechanisms are discussed.

Introduction

. We have recently reported on the reactions of alkoxyaluminium dichlorides, $ROAlCl_2$, (where R = Me, Et, n-Pr, i-Pr, n-Bu, t-Bu) with methylaluminium dichloride [1]. We have observed that the reaction rate depended markedly on the bulk of the alkoxy group, to be more exact, on the degree of branching at the C—O carbon atom. The reactions lead to the formation of aluminoxanes with the evolution of saturated hydrocarbons. Olefins were also formed but underwent polymerization under the reaction conditions. Alkyl chlorides could have reacted with the organoaluminium compounds present and so were not observed in the gaseous products.

We have found that methoxyaluminum dichloride was the least reactive compound, probably because of its inability to stabilize the CH_3^+ cation by proton abstraction and olefin elimination.

It was interesting to find out how the methoxy compounds reacted and whether the mechanism proposed for alkoxyaluminium dichlorides is also valid in this case.

Results and discussion

We have studied the reactions of methoxyaluminium compounds $Me_x(OMe)AlCl_{2-x}$ (where x = 2, 1, 0) with various other organoaluminium compounds

Me_yAlCl_{3-y} (where $y = 3, 2, 1$) and Et_3Al. The reactions were carried out at ~140° C without solvent. They lead to the formation of aluminoxanes, simple and branched hydrocarbons and methyl chloride (the latter when either of the substances contained chlorine) (eq. 1).

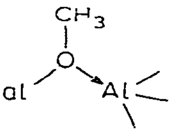
$$Me_x(OMe)AlCl_{2-x} + Me_yAlCl_{3-y} \rightarrow (>Al{-}O{-}Al<)_n + MeCl + \text{hydrocarbons}$$

$$(MeCl \text{ is formed when } x = 2 \text{ or } y \neq 0) \qquad ($$

Aluminoxanes have not been isolated in these reactions but their formation was proven by the IR and NMR studies.

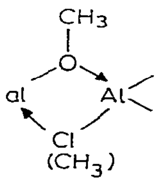
The IR spectra of the post reaction mixtures showed an absorption band at ~810 cm^{-1}, assigned to the vibrations of the Al—O—Al system [2]. The NMR spectra showed new signals in the region of τ 9.5—10.0. These signals could be assigned to the hydrocarbons formed in the reaction and/or to the protons of methyl groups in aluminoxanes. We have found earlier that the methyl group in mixed methylethylaluminoxanes gives rise to a signal at τ 9.94 [3]. The spectra of the post reaction mixtures changed after hydrolysis, some of the signals disappeared (Me—Al), others remained (hydrocarbons).

It seems reasonable to assume that these reactions, just like those of alkoxy aluminium dichlorides proceed with the formation of a complex between the methoxy compound and the other organoaluminium compound present (I,II).



(I)

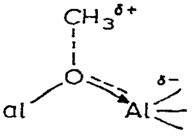
or



(II)

The charge distribution in such complex would depend strongly on the Lewis acidity of the organoaluminium compounds. It was found that the methoxy compound had no significant influence on the rate of the reaction, which suggests that the basicity of the oxygen is not an important factor in thi reaction. But the rate and the yield of the reactions depended markedly on the other organoaluminium compound present. The rate of the reactions decreased in the order of decreasing acidity of these compounds: $MeAlCl_2 >> Me_2AlCl > Me_3Al > Et_3Al$. $MeAlCl_2$ was the only compound that gave a 100% conversion the methoxy groups after 15 h.

The higher the Lewis acidity of these compounds, the greater electron-withdrawing effect from the oxygen, thus, the C—O bond would be more polarized (III).



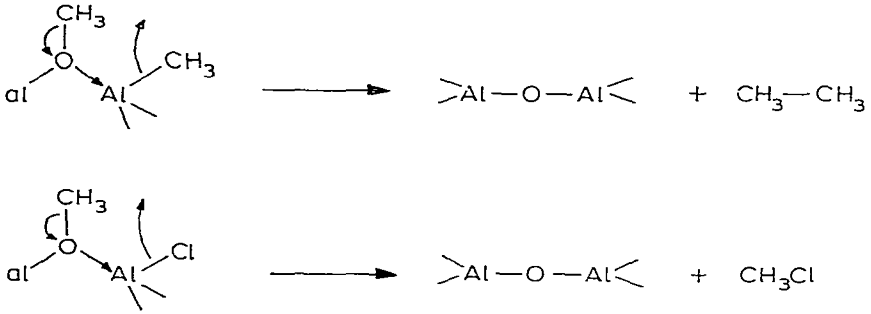
(III)

On the other hand, in such complex the negative charge on the Al substituents increases, which also facilitates the cleavage of the Al—Cl and Al—C bonds.

Thus the two following reactions may take place:

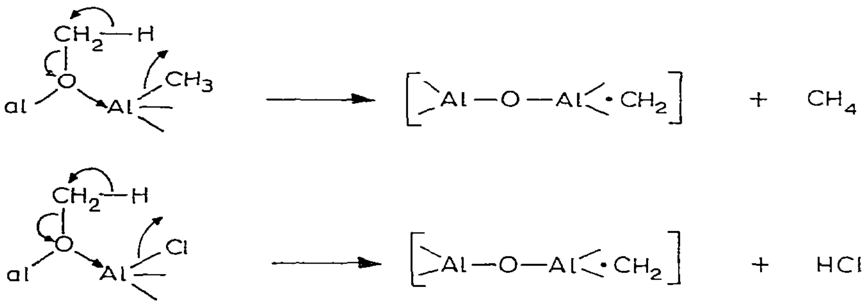
1. Rearrangement leading to the formation of ethane or methyl chloride and a corresponding aluminoxane system (Scheme 1).

SCHEME 1



2. Proton abstraction from the methoxy group yielding methane and also an aluminoxane (Scheme 2). We did not observe HCl in the gaseous products but it might have reacted further giving also methane (eq. 2). The formation of methane implies the formation of a carbenoid system which can react further leading to either insertion or polymerization products.

SCHEME 2



$$HCl + CH_3al \rightarrow Clal + CH_4 \qquad (2)$$

The composition of the gaseous products is given in Table 1. It can be seen that it also depends mainly on the other organoaluminium compound and less on the methoxyaluminium compound used. Me_3Al yields mainly methane, while Me_2AlCl and $MeAlCl_2$, besides methane, ethane and methyl chloride, also yield propane, isobutane, neopentane, 2,2-dimethylbutane and even higher alkanes which we have not identified.

When deuterated methoxy compounds, CD_3OAl, were used, CH_3D, CH_3CD_3 and CD_3Cl were formed, strongly supporting the proposed reaction schemes. The higher alkanes were also highly deuterated but the exact amount of deuterium in these compounds could not be established as the molecular ions were

TABLE 1

THE COMPOSITION OF THE MAIN GASEOUS PRODUCTS[a] IN REACTIONS OF $Me_x(OMe)AlCl_{2-x}$ (x = 2, 1, 0) WITH Me_yAlCl_{3-y} (y = 3, 2, 1)

Reaction	Yield[b] (%)	Methane	Ethane	Propane	Methyl chloride	i-Butane	neo-Pentane	2,2-Dimethyl butane
Me_2AlOMe + Me_3Al	4.6	100	—	—	—	—	—	—
+ Me_2AlCl	9.6	92.2	1.8	—	6.0	—	—	—
+ $MeAlCl_2$	100	36.3	46.9	—	7.3	4.5	5.0	—
$Me(OMe)AlCl$ + Me_3Al	5.5	94.7	2.5	—	2.8	—	—	—
+ Me_2AlCl	13.7	19.5	4.2	0.7	37.9	21.3	6.5	8.8
+ $MeAlCl_2$	100	1.6	74.0	0.7	22.3	0.4	0.5	—
$MeOAlCl_2$ + Me_3Al	7.4	89.8	—	—	10.2	—	—	—
+ Me_2AlCl	36.3	41.0	5.5	—	34.7	0.5	18.3	traces
+ $MeAlCl_2$	100	21.0	54.2	4.2	6.6	2.7	9.7	1.5

[a] Higher hydrocarbons were also found in the liquid phase. All data were calculated from GC analysis (in percent of peak area); Porapak Q, 80/100 Mesh, 6′/1/8″; *T*, 150°C; N_2, 25 ml/min; detector FID. [b] The conversion of the methoxy groups = $\frac{\text{gaseous products (mol)}}{\text{methoxy groups introduced (mol)}}$.

not present. What was significant though was the similarity of deuterium content in the C_4 fragmentation ions of neopentane and 2,2-dimethylbutane (Table 2). It implies that both compounds were formed according to the same mechanism, or that even neopentane could have been a precursor of 2,2-dimethylbutane. The higher alkanes could result from the carbene insertion to the C—H bond of the CH_3—Al group.

The reactions of diazomethane (a source of carbene) with organoaluminium compounds are well known. In these reactions the evolving carbene undergoes insertion into the Al—C bond in R_3Al [4,5], to the Al—X bond in chlorides, bromides and iodines [5,6,7,8], Al—H bond in hydrides [4] and Al—O bond in some more polarized alkoxy compounds, e.g. $Al(OCH_2CCl_3)_3$ [9]. In the presence of fluoro derivatives [8] and other alkoxy compounds e.g. $Al[OCH_2C(CH_3)_3]_3$ [9] the carbene undergoes polymerization. The halomethylderivatives Al—CH_2—X formed are unstable and give further reactions yielding higher alkylsubstituted organoaluminium compounds [6] (eq. 2).

$$\text{al—CH}_2\text{—X} + \text{al—CH}_3 \rightarrow \text{al—CH}_2\text{CH}_3 + \text{alX} \qquad (3)$$

The insertion into the Al—C bond leads to the formation of straight chain alkanes. But the reactions with diazomethane were carried out at low temperatures. On the other hand some cracking and isomerization reactions may take place under other reaction conditions (high temperatures, Al—O—Al systems formed).

While studying the reactions of alkoxyaluminium dichlorides with methylaluminium dichloride [1] we have observed an "initiation" time needed for the reactions to start vigorously. The same phenomenon was observed in these reactions though it was not so pronounced. Mole [11], who observed the same in his C-methylation reactions suggested that either aluminoxanes, or more probably hydroxyaluminium compounds, catalyze the reaction. We have carried out the reaction of Me_2AlOMe with Et_3Al in the presence of tetraethylaluminoxane, Et_4Al_2O, and without it. No influence of the aluminoxane on the reaction yield was observed.

It can be expected that methyl, or chlorine, exchange reactions should take place in the studied reaction mixtures. If they were fast, mixtures which would have equal amounts of methyl or chlorine groups should give the same NMR spectra and the same reaction products. This is not the case. The reactions lead to different gaseous products, the reactivity of the system is different and the NMR spectra of the mixtures also differ.

TABLE 2

MASS SPECTRA CHARACTERISTICS OF DEUTERATED HYDROCARBONS

	C_5	C_6		C_5	C_6
C_4H_9	8.2	8.7	$C_4H_4D_5$	5.9	0.9
$C_4H_8D_1$	2.3	6.2	$C_4H_3D_6$	33.5	30.1
$C_4H_7D_2$	4.2	12.5	$C_4H_2D_7$	0.8	
$C_4H_6D_3$	35.4	32.4	$C_4H_1D_8$	0.8	
$C_4H_5D_4$	3.9	8.8	C_4D_9	5.0	

Equimolar mixtures of $Me_2AlOMe/MeAlCl_2$ and of $Me(OMe)AlCl/Me_2AlCl$ gave very similar spectra though some of the signals differed in intensities (Fig. 1a, b). The same was observed in case of $MeOAlCl_2/Me_2AlCl$ and $Me(OMe)AlCl$-$MeAlCl_2$.

Me_3Al behaves somewhat differently. The equimolar mixture of $MeOAlCl_2/Me_3Al$ gave a completely different spectrum to that of $Me_2AlOMe/MeAlCl_2$ or $Me(OMe)AlCl/Me_2AlCl$ and $Me(OMe)AlCl/Me_3Al$ differed from Me_2AlOMe/Me_2AlCl (Fig. 1c, d).

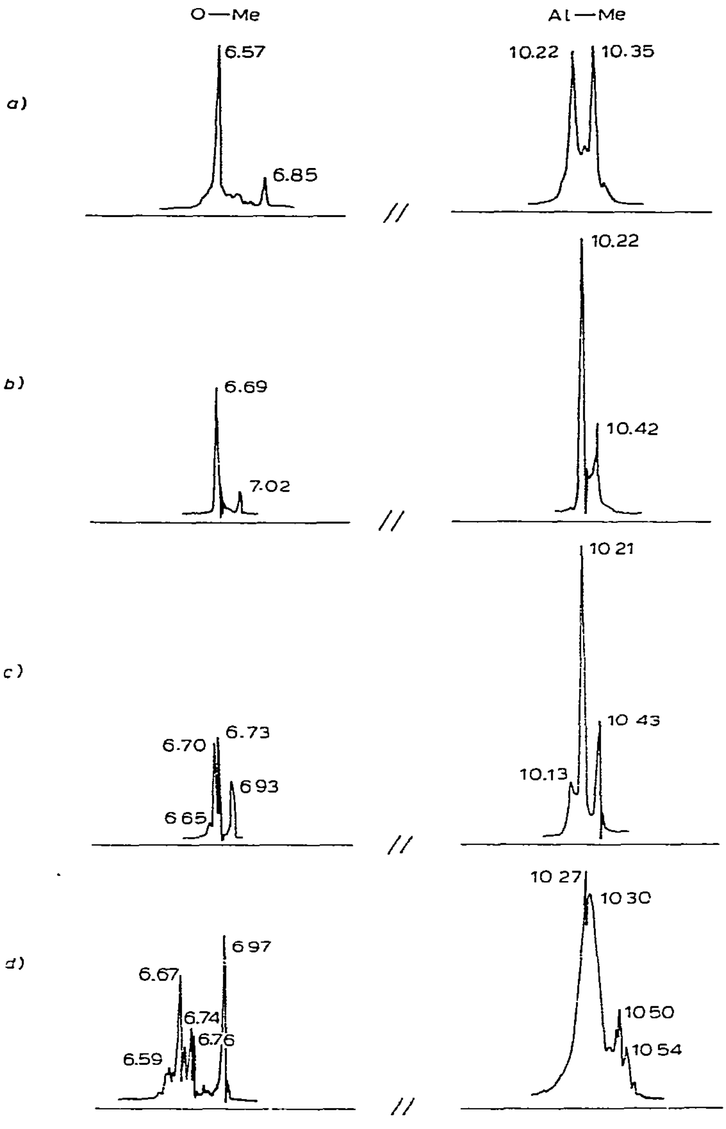


Fig. 1. The 100 MHz ^1H NMR spectra of equimolar mixtures of (*a*) Me_2AlOMe : $MeAlCl_2$, (*b*) Me/OMe/AlCl : Me_2AlCl, (*c*) $Me(OMe)AlCl$: Me_3Al, (*d*) Me_2AlOMe : Me_2AlCl, 270 Hz, room temp., toluene as a st dard (7.66 ppm).

The spectrum of the equimolar mixture of Me_3Al/Me_2AlOMe showed that no exchange reaction had taken place. The spectra of the studied systems also differed after the reaction.

The distillate obtained under normal pressure from an equimolar mixture of $Me_3Al/MeOAlCl_2$ contained methoxy groups as well as chlorine but there was 2.5 times more chlorine atoms than methoxy groups. The mixture of Et_3Al/Me(OMe)AlCl after prior heating was worked up under vacuum. The distillate contained methoxy groups and methyl groups but there was 5 times more methyl groups than methoxy groups. These experiments show clearly that to some extent both alkyl—alkyl and alkyl—chlorine exchange reactions do take place. The presence of methoxy groups in the distillates suggests that associates

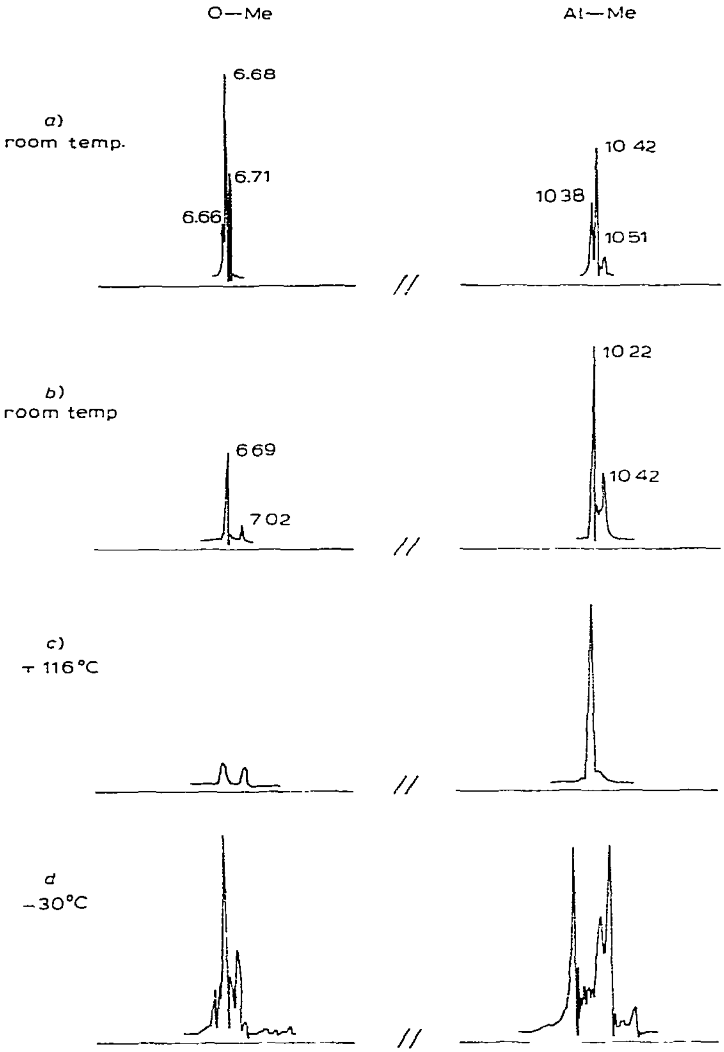


Fig. 2. The 100 MHz ^1H NMR spectra of (*a*) Me(OMe)AlCl, (*b*,*c*,*d*) equimolar mixture of Me(OMe)AlCl-Me_2AlCl. 1080 Hz, toluene as a standard (7.66 ppm).

through mixed bridges might have been formed. Such associates (II) might also be formed at high temperatures in the reaction mixtures.

As has been mentioned in our previous paper [1] associates through mixed bridges are known for many highly branched alkoxy compounds e.g. Me_2AlOt-Bu · $MeAlMe_2$ [12] and Me_2AlO-i-Pr · $BrAlMe_2$ [13], but they are not known for methoxycompounds, which have stronger bridges and are trimeric.

Some evidence for the existence of such mixed bridged species at higher temperatures can be found in the NMR spectra.

The mixture of Me_2AlCl/Me(OMe)AlCl gives a much more simple spectrum than the sum of both compounds (Fig. 2b). The spectrum does not change much upon heating. The signals broaden, the intensity of the signal at τ 7.02 increases and at 116° C two broad signals of O—Me groups of equal intensity are observed. When cooled to room temperature the mixture gives the same initial spectrum. When cooled further to —30° C the signal at τ 7.02 disappears and all signals of the individual compounds are observed. The spectra of pure Me(OMe)AlCl recorded at various temperatures were reported earlier [14] and showed none of the above changes. The intensity of the signal at τ 7.02 also depends on the ratio of Me_2AlCl/Me(OMe)AlCl. It is higher when more Me_2AlCl is present. It is quite possible that this signal corresponds to a methoxy group in an associate with mixed bridges, though no further proof for it could be obtained. Cryometrical measurements in benzene of this mixture gave an average molecular weight of both compounds, but one has to remember that the intensity of the τ 7.02 signal decreased with temperature. Ebuliometrical measurements in benzene could not be carried out because of the volatility of Me_2AlCl.

Conclusion

1. Exchange reactions take place but they are not fast and do not lead to full averaging of the studied systems.
2. The yield and the products of the reactions depended strongly on the methylaluminium compound and less on the methoxyaluminium compound used.
3. The yield of the reactions decreased in the order of decreasing acidity of the organoaluminium compounds: $MeAlCl_2 \gg Me_2AlCl > Me_3Al > Et_3Al$.
4. The reactions lead to the formation of aluminoxanes with the evolution of gases.
5. The gaseous products consist of the expected ethane and methyl chloride but also of methane and higher hydrocarbons.
6. A reaction scheme postulating the formation of a carbenoid system is proposed to explain the formation of methane and higher hydrocarbons.

Experimental

Compounds of the type Me_yAlCl_{3-y} (where y = 3, 2, 1) were obtained in our laboratory according to the literature [15] and purified by distillation. Et_3Al (Fluka) was distilled before use. Tetraethylaluminoxane was obtained in our laboratory according to a published procedure [16]. Compounds of the type

$Me_x(OMe)AlCl_{2-x}$ (where $x = 2, 1, 0$) were obtained by reactions of 30% solutions of organoaluminium compounds Me_yAlCl_{3-y} in hexane, with equimolar amounts of MeOH suspensed in hexane. The alcoholysis reactions were carried out at —10° C. The temperature was then raised to room temperature and the mixture was mixed vigorously for 2 h. The solvent was removed by vacuum distillation. Me_2AlOMe and Me(OMe)AlCl were purified correspondingly by distillation and sublimation at 60 and 90° C under pressure of the order of 10^{-4} mmHg. $MeOAlCl_2$ was crystallized from hexeane.

Reactions of $Me_x(OMe)AlCl_{2-x}$ with Me_yAlCl_{3-y}

Equimolar mixtures of the above compounds were heated at 135—140° C, for 45 h (only mixtures of $MeAlCl_2$ were heated for 15—25 h) without solvent. To the vessel was attached a condenser, though all mixtures were below their boiling points and distilled only when heated to 160—170° C. The condenser was connected to a gas burette through a U tube containing a drying agent. The amount of gas evolved was measured and from it the conversion of the methoxy groups calculated.

NMR spectra were measured on a INM-100-H(JEOL, Tokyo) spectrometer using 10% solutions in toluene or benzene. IR spectra were recorded over the range 400—1400 cm^{-1} on a Zeiss UR-10 instrument and a Perkin—Elmer Model 527 spectrometer. The gaseous products were analyzed by means of a Varian Model 2868 gas chromatograph and LKB 2891 mass spectrometer directly combined to PDP 11/05 computer, ionization energy was 70 eV (the samples were introduced via a GC column (2.7 m) filled with Porapak Q, 80—100 mesh).

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