

REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH VINYL CHLORIDE

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SUMMARY

The reactions of methylaluminium dichloride, dimethylaluminium chloride, and trimethylaluminium with vinyl chloride have been investigated. Of the methylaluminium compounds investigated, the dichloride reacted most readily. This reaction, carried out in n-heptane as solvent or without a solvent, produces chiefly cuprene and isobutane and a number of hydrocarbon and chlorohydrocarbon by-products. Dimethylaluminium chloride and trimethylaluminium react with vinyl chloride much less readily than methylaluminium dichloride; propylene and its oligomers are the major products. The mechanisms of the reactions of the individual methylaluminium compounds with vinyl chloride have been discussed on the basis of the experimental reaction data and NMR spectra. The decomposition of vinyl chloride by the Ziegler-Natta original and modified systems has been considered.

Our earlier investigations¹ were concerned with the reactions of methylaluminium compounds with methyl chloride, ethyl chloride, isopropyl chloride, and tert-butyl chloride, which were found to give aluminium chloride and saturated and unsaturated hydrocarbons.

The present paper deals with the reactions of methylaluminium dichloride, dimethylaluminium chloride, and trimethylaluminium with vinyl chloride which have not yet been reported in the literature. Razuvaev *et al.*² investigated the reactions of ethylaluminium compounds with vinyl chloride. They found that triethylaluminium fails to react with vinyl chloride at temperatures up to 60° at atmospheric pressure. Only at pressures of 7–9 atm and 60° does the reaction begin, with production of diethylaluminium chloride, ethane and acetylene; acetylene reacts with the unconverted triethylaluminium to yield diethyl-1-butenyl-1-aluminium.

A number of papers have also been published concerning polymerization of vinyl chloride in the presence of catalysts containing organoaluminium compounds^{3–12}. Ziegler-Natta unmodified catalysts became deactivated in the presence of vinyl chloride. Our investigations¹³ have shown that vinyl chloride does not react with titanium tetrachloride at room temperature. Razuvaev *et al.*² found that on the addition of a small amount of titanium trichloride to triethylaluminium (mole ratio Ti:Al = 1:25), vinyl chloride is vigorously decomposed with elimination of hydrogen chloride. The mode of reaction of the catalyst with vinyl chloride has not yet, however, been completely elucidated.

RESULTS

Methylaluminium dichloride reacted rapidly with vinyl chloride at room temperature to yield aluminium chloride, saturated and unsaturated hydrocarbons, and chlorohydrocarbons. Aluminium chloride, isobutane and cuprene are the major products. Methane, ethylene, acetylene, propane, propylene and its oligomers, and neopentane are obtained in smaller amounts. n-Butane, isobutylene, n-propyl and isopropyl chlorides, and higher hydrocarbons and chlorohydrocarbons (not identified) are produced in trace amounts. The reaction products released no methane on hydrolysis which testifies to the complete reaction of the aluminium-borne methyl groups.

When toluene is present in the reaction medium, a Friedel-Crafts reaction occurs as low as -75° giving aluminium chloride, methane and aromatic hydrocarbons (derivatives of benzene and anthracene).

A complex of methylaluminium dichloride with benzonitrile or ethyl ether does not react with vinyl chloride at room temperature.

Dimethylaluminium chloride reacts with vinyl chloride much less readily than methylaluminium dichloride. At 100° , propylene and its oligomers are the main products. The amount of isobutane and other products is less than in the reaction with the dichloride. The amount of methane released on hydrolysis of the reaction products indicated that only one-half of the methyl groups introduced in the form of dimethylaluminium chloride had reacted.

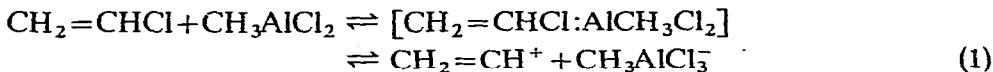
At 100° , trimethylaluminium reacts with vinyl chloride to give mainly propylene and its oligomers. Isobutane and the other products mentioned above are obtained in trace amounts. Hydrolysis of the reaction products released a smaller amount of methane than that corresponding to the methyl groups in trimethylaluminium.

NMR spectra of cyclohexane solutions of methylaluminium compounds with vinyl chloride were recorded at 6° . Chemical shifts of protons in the aluminium-borne methyl groups and in vinyl chloride were measured and NMR spectra of cyclohexane solutions of pure methylaluminium compounds and of vinyl chloride were recorded for comparison. For methylaluminium dichloride, dimethylaluminium chloride and trimethylaluminium at 6° , the chemical shifts are 89, 104 and 102 cps relative to cyclohexane, respectively. In the methylaluminium compound-vinyl chloride mixtures examined only a single signal of protons of the aluminium-borne methyl group was recorded. The chemical shift towards higher fields is changed by no more than 1 cps relative to the pure methylaluminium compound. Again, changes in the chemical shift of protons in vinyl chloride in the mixtures investigated do not exceed 1 cps towards lower fields relative to pure vinyl chloride.

DISCUSSION

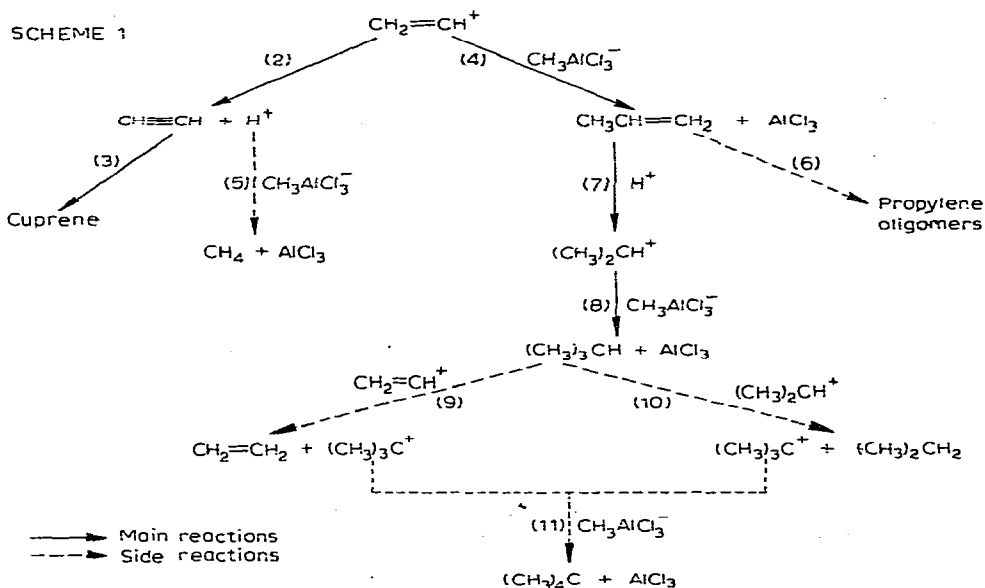
The NMR studies have shown vinyl chloride to form no stable donor-acceptor complexes with methylaluminium compounds. Nevertheless, the reactions of methylaluminium compounds with vinyl chloride may be assumed to begin by bringing the chlorine of the chloride nearer to the aluminium atom. As a result, a transitory donor-acceptor complex is formed which may enter into reactions.

As a Lewis-type strong acid, methylaluminium dichloride may split the complex into free ions (1):



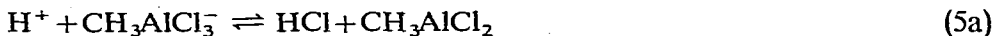
Similarly as with alkyl chlorides¹, the course of reaction (1) is related primarily to the acid strength of the methylaluminium compound and the stability of the resulting cation.

The reaction products are formed by further transformations of the ions formed. A simplified reaction sequence is presented in Scheme 1.

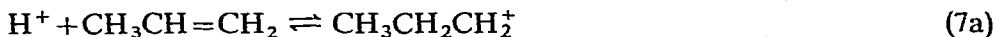


The cation, $\text{CH}_2=\text{CH}^+$, may stabilize itself by eliminating the proton to form acetylene (2), which in the reaction medium is polymerized chiefly to cuprene (3). The cation may also react with the anion, $\text{CH}_3\text{AlCl}_3^-$, to regenerate the reactants (1) or to give propylene and aluminium chloride (4).

The proton formed in reaction (2) may react with the anion, $\text{CH}_3\text{AlCl}_3^-$, to yield methane and aluminium chloride (5). Hydrogen chloride may be an intermediate product of this reaction; and further reacts with methylaluminium dichloride to give also methane and aluminium chloride (5a).



The proton may also react with the resulting propylene (reaction (4)) to give an isopropyl cation (7); a part of the propylene reacts to yield oligomers (6). In addition to the isopropyl cation, a n-propyl cation may also be formed (7a).



The inter-cation equilibrium is shifted towards the more stable, *i.e.*, isopropyl cation. This cation reacts with the anion, $\text{CH}_3\text{AlCl}_3^-$, to give isobutane (8), whereas

the n-propyl cation yields n-butane in trace amounts (8a).



Isobutane may react either with the vinyl (9) or with the isopropyl cation (10). Ethylene is the product in the former case, and propane in the latter case, and in either case a tert-butyl cation is formed. This cation reacts with the anion, $\text{CH}_3\text{AlCl}_3^-$, to give neopentane and aluminium chloride (11). Also, the tert-butyl cation may stabilize itself by eliminating the proton and forming (in trace amounts) isobutylene (11a).



Since cuprene and isobutane are the major products of the reaction of methylaluminium dichloride with vinyl chloride, it may be assumed that the vinyl cation stabilizes itself (2) or reacts with the anion (4) at a commensurable rate. The proton formed in the stabilization reaction (2) reacts primarily with propylene (7) and only slightly with the anion $\text{CH}_3\text{AlCl}_3^-$ as indicated by the small amount of methane in the products. Reactions (6), (9), (10), and (11) which give propylene oligomers, ethylene, propane, and neopentane, respectively, are also side reactions.

In addition to the main and side reactions presented in the scheme, a number of other reactions take place, which produce chlorohydrocarbons and higher hydrocarbons in trace amounts.

Of the chlorohydrocarbons identified, isopropyl chloride and n-propyl chloride may be produced (in trace amounts) by the reactions of the isopropyl cation or its isomer with the anion, $\text{CH}_3\text{AlCl}_3^-$ (8b, 8c):

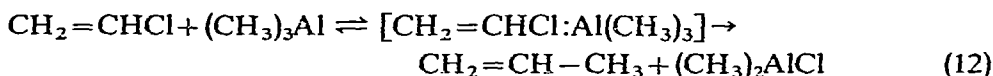


The equilibrium in reactions (8b) and (8c) is shifted to the left; nevertheless, both chlorides are found in slight amounts in the reaction products.

As already demonstrated¹, toluene or another aromatic hydrocarbon promotes ionic decomposition of alkyl chlorides in their reactions with organoaluminium compounds. In toluene as solvent, vinyl chloride reacts with methylaluminium dichloride at temperatures as low as -75° . The course of this reaction, involving production of aluminium chloride, methane and derivatives of benzene and anthracene, illustrates the ionic mechanism. This is also borne out by the fact that stable complexes of methylaluminium dichloride with benzonitrile or ethyl ether render the reaction with vinyl chloride unfeasible. Both benzonitrile and ethyl ether are stronger Lewis bases than vinyl chloride and therefore the formation of an intermediate complex of vinyl chloride with methylaluminium dichloride is unlikely. This renders reaction (1) and the formation of free ions, as well as further reactions thereof, impossible.

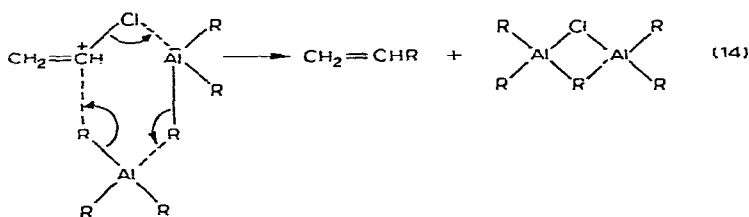
The reaction of trimethylaluminium and dimethylaluminium chloride with vinyl chloride is different from that of methylaluminium dichloride. In each of the reactions propylene and its oligomers are the main products. Isobutane, cuprene and other products formed in the reaction with the dichloride are, in the reaction of trimethylaluminium with vinyl chloride, produced in trace amounts only, or not at all. Also, the reaction temperature is much higher, indicating the lower reactivity of trimethylaluminium and dimethylaluminium chloride compared with that of methylaluminium dichloride.

The data obtained suggest that the mechanism of the reactions of trimethylaluminium and dimethylaluminium chloride with vinyl chloride is different from that of the reaction of methylaluminium dichloride. It appears likely that an intermediate complex now undergoes an intra- or intermolecular rearrangement (12).



The acid strength of the organoaluminium compound has a decisive effect on the course of the reaction (12). The stronger the acid, the easier the decomposition of the transitory complex into free ions, and the more difficult the rearrangement of the alkyl or aryl group from the aluminium atom to the positively charged carbon atom.

The mechanism of the rearrangement reaction was not investigated, but it appears to involve a transitory four-centre (13) or six-centre system (14) with electron transfer:



Dimethylaluminium chloride may react with vinyl chloride by the ionic mechanism (1) to a very slight extent, but the ionic reaction of trimethylaluminium is much less probable.

The present results and the data of Razuvaev *et al.*² show that trimethylaluminium and triethylaluminium do not react with vinyl chloride at temperatures up to 60°. Titanium tetrachloride does not react, either. On the other hand, typical Ziegler-Natta catalysts react readily with vinyl chloride and thus become deactivated. Trialkylaluminium, or dialkylaluminium chloride, alkylates titanium chlorides and, as a result, more chlorinated organoaluminium compounds are formed. As demonstrated in the present work, alkylaluminium dichloride decomposes vinyl chloride easily and is presumably responsible for the decomposition of vinyl chloride by Ziegler-Natta systems. The aluminium chloride resulting from the reaction of alkylaluminium dichloride with vinyl chloride may cause vinyl chloride to further decompose. As shown¹³, aluminium chloride reacts vigorously with vinyl chloride at room temperature to yield various products depending on whether the reaction is carried out in an aliphatic or aromatic solvent, or without a solvent.

In Ziegler-Natta systems modified by addition of alkylalkoxyaluminium, alkylalkenylaluminium or alkoxytitanium compounds, as well as Lewis bases as a third component of the catalyst, decomposition of vinyl chloride does not take place.

or occurs only with difficulty. Inhibition of this decomposition is either due to the weakly acidic character of the organoaluminium compounds added or to complexation of the resulting alkylaluminium dichloride by the Lewis base.

EXPERIMENTAL

1. Reactants

The methylaluminium compounds used in these investigations were prepared by conventional methods. Methylaluminium dichloride was purified by crystallization from *n*-heptane. Dimethylaluminium chloride and trimethylaluminium were distilled before use. Vinyl chloride (Chemical Works "Oświęcim", Oświęcim, Poland) was passed through a column containing potassium hydroxide and type-4A molecular sieves. Pure benzonitrile ("Xenon", Łódź, Poland) was dried over anhydrous magnesium sulphate, distilled in a nitrogen atmosphere, and stored over type-4A molecular sieves. Ethyl ether, *n*-heptane, toluene, and cyclohexane (pure-grade commercial reagents) were redistilled from sodium in a nitrogen atmosphere and stored over type-4A molecular sieves.

2. Apparatus and method

Reactions of methylaluminium compounds with vinyl chloride were carried out in *n*-heptane as solvent, or with no solvent, and in the case of methylaluminium dichloride, also in toluene as solvent. Reactions of methylaluminium dichloride with vinyl chloride in the presence of benzonitrile and ethyl ether were run in *n*-heptane; methylaluminium dichloride was complexed by the addition of an equimolecular amount of a Lewis base before the addition of vinyl chloride.

Each reaction was carried out in a nitrogen atmosphere, in a three-necked 30-ml stirred flask connected with a cold trap and a gas burette. Gaseous vinyl chloride was added in equimolecular amounts to the organoaluminium compound (with or without solvent) in the reactor flask at -75° . The reactor was then transferred into a thermostat and the temperature was progressively increased. The gaseous products not condensing in the cold trap (CH_4 and C_2 's) were collected in a gas burette. The products condensed in the trap were, after completion of the reaction, transferred to another gas burette. The products were hydrolyzed *in situ* with aqueous 10% hydrochloric acid; if the reaction was carried out without a solvent, *n*-heptane was added prior to hydrolysis. The gases liberated during hydrolysis were collected in a gas burette. If a sediment was precipitated as the result of the reaction, it was filtered off, washed with 10% hydrochloric acid and water, and then dried. The organic layer was separated from the water layer, washed with water, dried, and distilled.

The gaseous products formed in the reaction proper and during hydrolysis were analyzed by gas chromatography. The liquid products distilling, together with *n*-heptane, were analyzed on a Chrom II gas chromatograph. The liquid products not distilling up to the boiling point of *n*-heptane, and the solid products, were analyzed spectrophotometrically by the neat liquid and the potassium bromide-disk techniques, respectively, on a Zeiss UR-10 infrared spectrophotometer.

3. NMR studies

All the spectra were recorded on a Jeol Co. JNM-C-60H spectrometer with cyclohexane as internal standard.

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