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ETHYLZINC HYDROXIDE AS AN INTERMEDIATE IN THE REACTION OF DIETHYLZINC WITH WATER

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Summary

The diethylzinc/water (1/1 mol) reaction in 1,4-dioxane as solvent has been studied by applying the cryoscopic method for molecular weight determinations to the products formed in the reaction solution. An ethylzinc hydroxide dimer was found to be formed as an intermediate in the reaction system during fast ethane elimination. Monomeric ethylzinc[tri(oxyzinc)] hydroxide was found to be the main product of the subsequent reaction of this intermediate, with further ethane elimination. A mechanism for the latter reaction, involving the formation of a transient ethylzinc hydroxide tetrameric species, is proposed.

The reaction pathway in the diethylzinc/water (2/1 mol) system is also discussed. The formation of ethylzinc[tri(oxyzinc)] hydroxide, as in the 1/1 system, followed by the subsequent reaction of this compound with diethylzinc gave further ethane elimination and lead to ethylzinc[tri(oxyzinc)] ethylzinc oxide as the main product, is the proposed route in this case.

In contrast to diethylzinc, which is too weak a Lewis acid to react with the ethylzinc hydroxide dimer, trimethylaluminium was found to undergo reaction with it in 1,4-dioxane solution, with fast methane and ethane elimination.

Introduction

Current interest in the products of reaction of diethylzinc with water is derived from their use as catalysts. The usefulness of such reaction products, especially those obtained at a 1/1 mol ratio of reactants, has been shown for the polymerization of epoxides [1] and the copolymerization of epoxides and carbon dioxide [2].

The diethylzinc/water (1/1 mol) reaction has been studied by several authors [3–8]. It was concluded [5] that the reaction product results from the initial formation of ethylzinc hydroxide, according to eq. 1, followed by the condensation of this intermediate according to eq. 2.

$$Et_2Zn + H_2O \rightarrow EtZnOH + EtH \qquad (1)$$

$$(EtZnOH)_n \rightarrow Et(ZnO)_nH + (n-1)EtH \qquad (2)$$

Ethylzinc hydroxide, formed relatively fast according to eq. 1, was suggested [5] to undergo auto-association prior to the ethane elimination reaction expressed by eq. 2. The reaction according to eq. 2 would be expected to complete the product formation process in the diethylzinc/water (1/1 mol) system in the ideal case. However, the real system was found [4–7] to involve, to some extent, the formation of by-products, which were responsible for the colloidal nature and the heterogeneity of the system. Thus, the final product was formulated as $[\mathrm{Et(ZnO)}_l\mathrm{ZnEt}]_\alpha \cdot [\mathrm{Et(ZnO)}_m\mathrm{H}]_\beta \cdot [\mathrm{HO(ZnO)}_n\mathrm{H}]_\gamma$, where l, m, n, α, β and $\gamma = 0, 1, 2, \ldots$ [5].

As a part of a research programme on the nature of ethylzinc–oxygen compounds as catalysts for the carbon dioxide-oxirane copolymerization [9] we are currently investigating their ability to form auto-associates in donor solvents. In the course of our studies we have applied a cryoscopic method for molecular weight determination to the diethylzinc/water (1/1 mol) reaction system with 1,4-dioxane as solvent. Determinations of the molecular weight of ethylzinc hydroxide and of the product obtained by the ethane elimination from this intermediate, have been thought to give key data for the elucidation of the reaction mechanism and the structure of the products. Consideration of the ethane elimination in the condensation of ethylzinc hydroxide, but not in its reaction with diethylzinc, and the determination of the ethylzinc hydroxide reactivity towards trimethylaluminium, a relatively strong Lewis acid, also seemed to give relevant information about the nature of ethylzinc hydroxide.

Experimental

Materials

Diethylzinc, prepared by the method described previously [10], and trimethylaluminium (Alfa Products, Ventron) were distilled under reduced pressure before use. Distilled water was de-oxygenated by use of the freeze-degassing technique, and stored under nitrogen. 1,4-Dioxane (POCh reagent grade) was dried by heating over calcium hydride and lithium aluminium hydride and then by distillation in a nitrogen atmosphere.

Reaction of diethylzinc with water

To 10 cm^3 of a diethylzinc solution * (0.5 $\mathrm{mol/dm}^3$, in 1,4-dioxane), previously cooled to 15°C, 10 cm^3 of a solution of water (0.5 $\mathrm{mol/dm}^3$, in 1,4-dioxane), was added dropwise with vigorous stirring. When the addition of the water solution was complete and the amount of the gas evolved had reached a predetermined value (the gas volume was measured by a gas burette), a sample of the clear colourless reaction solution was taken for ^{1}H NMR studies. An equivalent amount of this solution was then transferred to a cooled standard freezing point depression apparatus and subjected to a measurement immediately in order to reduce the possibility of decomposition of the ethylzinc hydroxide obtained. In order to check the amount of ethylzinc groups present, the solution was hydrolyzed and the gas volume was measured by a gas burette connected with the apparatus.

^{1}H NMR spectra of ethylzinc hydroxide solutions were recorded on a Tesla BS 487C 80 MHz spectrometer at room temperature. The tube containing the sample

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* Formation of a complex between diethylzinc and 1,4-dioxane has been reported [11].

was immersed in a dry ice-methanol bath, to stop the decomposition reaction, prior to making the measurement.

Decomposition reaction of ethylzinc hydroxide

The ethylzinc hydroxide solution (0.25 mol/dm^3, in 1,4-dioxane) was left to react in the cryoscopic cell kept at ambient temperature. When the amount of gas evolved had reached a predetermined value, the standard freezing point of the resulting yellow solution was measured *. In order to determine the ethyl groups still remaining in the reaction product, the solution was hydrolyzed and the volume of gas evolved was measured.

Reaction of ethylzinc hydroxide with trimethylaluminium

To 10 cm^3 of an ethylzinc hydroxide solution (0.5 mol/dm^3, in 1,4-dioxane), obtained in a similar manner to that described above and then freeze-degassed, 5 cm^3 of trimethylaluminium solution ** (1.0 mol/dm^3, in 1,4-dioxane) was added dropwise with vigorous stirring at 15°C. The amount of gas evolved during the reaction was measured in a gas burette. The remaining clear, colourless solution was hydrolyzed by the addition of 5 cm^3 of a water solution (1.0 mol/dm^3, in 1,4-dioxane).

The composition of the gas evolved was determined on a Chrom-4 gas chromatograph using a column packed with Poropac Q.

Results

The amounts of ethane evolved during the diethylzinc/water (1/1 mol) reaction and during the subsequent hydrolysis of the product of this reaction were practically the same, which indicates completion of the reaction course leading to ethylzinc hydroxide. The molecular weight of the ethylzinc hydroxide formed was found to be 230 (compared with 223 calculated for $(C_2H_6OZn)_2$) at the freezing temperature of the 1,4-dioxane solution. The ^{1}H NMR spectrum recorded on such a solution at room temperature exhibited a broad signal (the fine structure was not visible) at δ 0.22, a much sharper triplet at δ 1.26, and a sharp singlet at δ 6.19 ppm. These signals are assigned to the resonances of the ethylzinc hydroxide methylene, methyl, and hydroxyl protons, respectively. A sharp singlet at δ 0.84 ppm from the ethane protons was also present in the spectrum.

The molecular weight of the product formed in solution by the ethylzinc hydroxide decomposition reaction when 75% of the ethane had evolved, was found to be 359 (cf. that calculated for $C_2H_6O_4Zn_4$ is 356) at the freezing temperature of the 1,4-dioxane solution. When 50% of the ethyl groups of ethylzinc hydroxide had been released as ethane the apparent molecular weight was 283 (the mean value for the 1/1 mixture, $(C_2H_6OZn)_2/C_2H_6O_4Zn_4$ is 289.5). Subsequent hydrolysis of the reaction mixture showed that the amount of ethane liberated corresponded to the amount of ethylzinc groups actually present in the solution.

When trimethylaluminium was added to the ethylzinc hydroxide solution, practically instantaneous gas evolution occurred. The amount of the gas, consisting of methane and ethane, corresponded to the amount of active hydrogen in the ethylzinc hydroxide. The gas evolution during the subsequent hydrolysis of the product,

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* A weight loss of the sample was considered for the molecular weight determination.

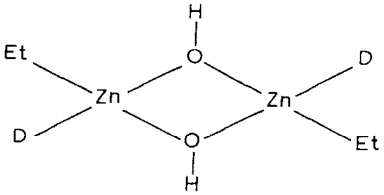
** Formation of a complex between trimethylaluminium and 1,4-dioxane was reported [12].

occurred in a two-step manner, similar to that during the diethylzinc/water (1/1 mol) reaction.

Discussion

From the cryoscopic data it seems that the ethylzinc hydroxide formed in the diethylzinc/water (1/1 mol) reaction involves formation of dimeric species in the 1,4-dioxane solution. It seems worthwhile to note that ethylzinc phenoxide, the oxygen atom of which has a weaker donating capacity than that of ethylzinc hydroxide, has been found recently [13] to be a monomer in 1,4-dioxane solution, whereas in benzene solution it formed tetrameric species [14], similar to methylzinc phenoxide [15]. On the other hand, methylzinc methoxide, with an oxygen atom of a stronger donating capacity than that in ethylzinc hydroxide, was reported [15] to exist as a tetramer even in stronger donor solvents than 1,4-dioxane, such as pyridine.

It seems that the ethylzinc hydroxide dimer can be complexed with 1,4-dioxane (D) in the solution being investigated, otherwise it would possess coordinatively unsaturated zinc atoms:



The analogous dimeric methyl- and ethyl-zinc phenoxide complexes with pyridine in the benzene solution have been described previously [14,15]. However, the complexing of the ethylzinc hydroxide dimer with 1,4-dioxane seems to be rather weak. This is suggested by a comparison of the ^{1}H NMR spectra recorded on the solution being studied and on the benzene solution of the diethylzinc/water reaction products containing a relatively low zinc–oxygen bond mol fraction [6]. Only slight differences between the chemical shifts of the equivalent ethyl group protons can be observed, which indicates relatively weak interactions between 1,4-dioxane and ethylzinc hydroxide.

Considering the results of cryoscopic studies on the solution containing the product of the ethylzinc hydroxide decomposition reaction after ethane elimination, one may conclude that this product contains mainly four zincoxy units in the molecule with one ethyl group bounded to the zinc atom and one hydrogen atom bounded to the oxygen atom. It should be noted that the mol ratio of ethylzinc to zincoxy units of 1/4 was also found [6] in the case of the diethylzinc/water (1/1 mol) reaction product obtained in benzene.

In view of the results obtained, and taking into account a known [14] tendency for tetrahedral bonding configurations around zinc and oxygen atoms in organozinc-oxygen compounds, a pathway for the reaction studied can be proposed as given in eq. 3 *.

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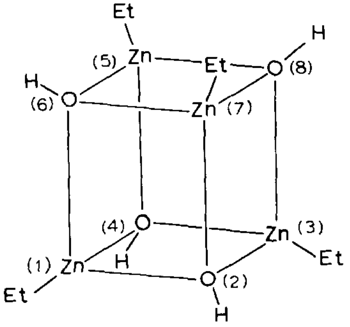
* Possible complexing of zinc compounds with 1,4-dioxane is omitted in the formulae.

$$2\,(\mathrm{EtZnOH})_2 \rightleftharpoons (\mathrm{EtZnOH})_4 \xrightarrow{-\mathrm{EtH}} \mathrm{EtZn(OZn)(HOZnEt)_2OH}$$

$$\xrightarrow{-\mathrm{EtH}} \mathrm{EtZn(OZn)_2(HOZnEt)OH} \xrightarrow{-\mathrm{EtH}} \mathrm{EtZn(OZn)_3OH} \qquad (3)$$

The complexing of the ethylzinc hydroxide dimer with 1,4-dioxane is not strong enough to prevent the hydroxyl oxygen, being of a moderate donating capacity, from dislodgement of 1,4-dioxane from the complex by forming two coordinate bonds with zinc atoms. Coordinative saturation of the oxygen atoms would then be attained by intermolecular coordination of two dimer molecules. Thus, the ethylzinc hydroxide tetramer, containing a Zn_4O_4 with a slightly distorted cubic structure with alternatingly placed zinc and oxygen atoms at the corners, analogous to that of the methylzinc methoxide tetramer [16], can probably be formed as a transient species in the reaction system:

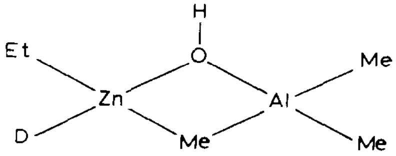


Such tetrameric species with the tetrahedral bonding configuration around zinc and oxygen atoms, are then thought to undergo ethane elimination (the oxygen bounded hydrogen atoms in the tetramer should be more labile than in the dimer). This reaction can be accompanied by complexing of the product with 1,4-dioxane to allow the zinc atom to be four-coordinated. In the literature [4], the possibility of forming the ethylzinc hydroxide dimer which might eliminate ethane intramolecularly was considered. This proposal, however, also tried to explain the zinc oxide formation, which was believed to take place to some extent in the diethylzinc/water system. Nevertheless, the possibility of ethane elimination from the dimeric species yielding ethylzinc(oxyzinc) hydroxide, which could then complex to the next molecule of the unreacted dimer should be mentioned and taken into consideration.

After one ethane molecule is eliminated, further reaction most probably involves the relatively fast elimination of ethane, consecutively, from the O(4)–Zn(5) and O(6)–Zn(7) bonds of the distorted Zn_4O_4 cube which leads to a remarkably stable product, ethylzinc[tri(oxyzinc)] hydroxide. The hydrogen atom and the ethyl group in the product are bonded to the O(8) and Zn(1) atoms on the diagonal line of the distorted Zn_4O_4 cube. Thus, the ethylzinc[tri(oxyzinc)] hydroxide molecule seems to have a structure similar to that of the chair form of the Zn_3O_3 ring, where the oxygen face is bonded with the ethylzinc group and the zinc face with the hydroxyl group. This probably makes the further elimination of ethane from the product rather difficult, since no direct interaction between these groups occurs in the molecule. The proposed reaction course leading to ethylzinc[tri(oxyzinc)] hydroxide seems to be more plausible, especially when considering the apparent molecular weight of 283, which was found when half of the ethyl groups of ethylzinc hydroxide had been released as ethane in the studied system. This result can be interpreted as a mean value between the molecular weight of the monomeric ethylzinc[tri(oxyzinc)] hydroxide formed and the unreacted dimeric ethylzinc hydroxide, both being present in the solution in equimolar amounts. If the reaction pathway involved the ethylzinc(oxyzinc) hydroxide dimer as the product when half of the ethyl groups had been eliminated as ethane from the ethylzinc hydroxide, the molecular weight found would then be 386.

Kinetic studies on the diethylzinc/water reaction in 1,2-dimethoxyethane revealed [4] a decrease in the logarithmic value of the ethane elimination rate at the point corresponding to the end of the reaction postulated to proceed by eq. 3, which may strongly support the mechanism proposed in this work. Thus, further ethane elimination, which proceeds rather slowly, can be then postulated, analogously to the literature suggestions [7,8], to result from intermolecular condensation of the product of the reaction expressed by eq. 3, i.e. ethylzinc[tri(oxyzinc)] hydroxide. It should be mentioned that the reported values of n, denoting the number of zincoxy units per ethylzinc group in the diethylzinc/water reaction products similar to $Et(ZnO)_nH$, were relatively small when 1,4-dioxane or benzene was used as the reaction medium (e.g. $n = 3.2$ after 0.5 h or $n = 5$ after 96 h reaction at 25°C, respectively) [7] and very big when n-heptane was used [5].

The reaction of ethylzinc hydroxide with trimethylaluminium at a 1/1 mol ratio involves most probably formation of the analogous complex, the degree of association of which could not, however, be determined at the freezing point of the 1,4-dioxane solution:



The complex, in which the hydrogen atom at the bridging oxygen atom should be more acidic than in the ethylzinc hydroxide dimer, can easily undergo an alkane elimination reaction by releasing the alkyl (methyl and ethyl) group from both the metal atoms, aluminium and zinc, in an amount corresponding to that of the active hydrogen. Ethane elimination, due to the participation of the analogous complex between ethylzinc hydroxide and diethylzinc (a relatively weak Lewis acid) in the diethylzinc/water (2/1 mol) reaction system [17], does not seem probable. However, the formation of ethylzinc[tri(oxyzinc)] hydroxide, as in the 1/1 system, followed by the subsequent reaction of this compound with diethylzinc, leading to further ethane elimination to give ethylzinc[tri(oxyzinc)] ethylzinc oxide as the main product, seems to be more probable in this case. The ethylzinc to zincoxy units mol ratio of 1/2 in ethylzinc[tri(oxyzinc)] ethylzinc oxide is in agreement with that reported for the diethylzinc/water (2/1 mol) reaction product obtained in 1,4-dioxane [5] and benzene [6].

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