KINETICS AND MECHANISM OF THE REACTIONS OF DIETHYLZINC WITH PHENOLS IN CYCLIC ETHERS

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Summary

Reactions of diethylzinc and phenols (phenol, 2-ethylphenol, 2-chlorophenol, 3-ethylphenol, 3-chlorophenol, 4-ethylphenol and 4-chlorophenol) have been carried out in tetrahydrofuran and 1,4-dioxane as solvents. Monomeric ethylzinc phenoxide has been found to be a product of the diethylzinc and phenol (1:1) reaction in 1,4-dioxane solution. Kinetic studies on the ethylzinc phenoxides and phenols reaction in tetrahydrofuran solution established the rate constants and the $S_{E}i$ mechanism of the reaction.
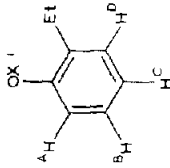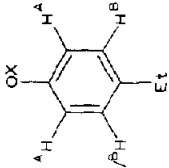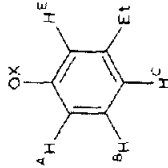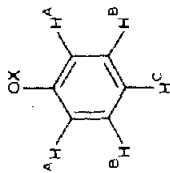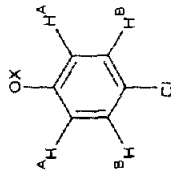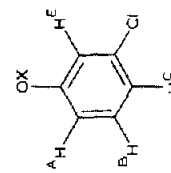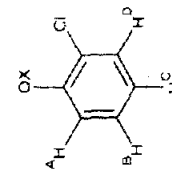
Introduction

In research on the organozinc catalysts for the copolymerization of carbon dioxide and oxiranes, produced from diethylzinc and trihydric phenols in 1,4-dioxane solution, the present authors noticed the lack of published data concerning the mechanism of the reaction between zinc dialkyls and phenol. Although the mechanisms of the acidolysis of organometallic compounds were reported by Abraham and Hill [1], and the association of alkylzinc alkoxides and phenoxides in non-polar solvents have been discussed [2–8], only scant information either on the association of alkylzinc phenoxides in donor solvents or on the direction of their attack on phenol was available. The comparison of the results obtained from kinetic studies on the reactions of zinc dialkyls with amines carried out in diisopropyl ether [9] or toluene [10] solution indicates the strong effect of the donor powder of the solvent on the mechanism of acidolysis of organozinc compounds.

The aim of this work was to establish the mechanism of the reaction of diethylzinc and phenol in cyclic ethers as solvent by means of kinetic studies, as well as the influence of phenol substituents on the reaction rate. The problem of the association of the diethylzinc and phenol reaction products was also a subject of our investigations.

TABLE 1

¹H NMR SPECTRA [a] OF PHENOLS AND THE PRODUCTS OF THE (1:1) REACTION OF ZnEt₂ AND PHENOLS

| Compound | X | Chemical shift (δ ppm) | | | | | | | | | |
| | | Aromatic | | | | | OH | Ethyl | | Ethylzinc | |
		H^A	H^B	H^C	H^D	H^E		CH_2	CH_3	CH_2	CH_3
	H	6.90	7.12	6.72	7.00	–	7.50	2.66	1.22	–	–
	ZnEt	6.82	7.08	6.72	7.00	–	–	2.80	1.32	0.37	1.25
	H	6.62	6.97	–	–	–	7.32	2.49	1.14	–	–
	ZnEt	6.70	6.85	–	–	–	–	2.53	1.19	0.46	1.34
	H	6.55	7.05	6.65	–	6.60	7.45	2.57	1.22	–	–
	ZnEt	6.52	7.05	6.70	–	6.67	–	2.49	1.14	0.48	1.34

Compound	X	H^A	H^B	H^C	H^D	H^E				CH_2	CH_3
OX, H^A, H^B, H^C (phenol)	H	6.68	7.15	6.72	–	–	7.47	–	–	–	–
	ZnEt	6.90	7.26	6.90	–	–	–	–	–	0.54	1.40
OX, H^A, H^B, Cl	H	6.70	7.18	–	–	–	7.73	–	–	–	–
	ZnEt	6.75	7.17	–	–	–	–	–	–	0.46	1.33
OX, H^E, Cl, H^A, H^B, H^C	H	6.65	7.12	6.85	–	6.80	7.97	–	–	–	–
	ZnEt	6.67	6.95	6.77	–	6.77	–	–	–	0.43	1.32
OX, Cl, H^D, H^A, H^B, H^C	H	6.90	7.15	6.82	7.32	–	7.92	–	–	–	–
	ZnEt	7.02	7.10	6.74	7.36	–	–	–	–	0.42	1.22

Results and discussion

The reaction of diethylzinc and phenol at a 1 : 2 mol ratio, carried out in donor solvents like tetrahydrofuran (THF) or 1,4-dioxane (DOX), proceeds in two stages with considerably different rates (eq. 1).

$$2\ PhOH + ZnEt_2 \xrightarrow[k_1]{-EtH} PhOZnEt + PhOH \xrightarrow[k_2]{-EtH} PhOZnOPh \qquad (1)$$
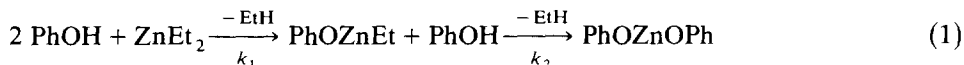
The course of the reaction conducted in THF at a temperature of $0°C$, monitored by measurement of the volume of ethane evolved within the reaction time, is illustrated by Fig. 1. The dependence of $V_\infty/(V - V_\infty)$ on the reaction time (V_∞ = total ethane volume evolved in the completed $ZnEt_2$ acidolysis), illustrated in Fig. 1 by two straight lines corresponding to the reaction stages, indicates that both reaction stages are second order and that the ratio of the stage rate constants is $k_1/k_2 \cong 25$.

As the course of reactions of $ZnEt_2$ and substituted phenols (2-ethylphenol, 2-chlorophenol, 3-ethylphenol, 3-chlorophenol, 4-ethylphenol and 4-chlorophenol) was found to be similar to that of unsubstituted phenol, the stages of the $ZnEt_2$/phenol (1 : 2) reaction were considered to consist of two separate reactions, $ZnEt_2$/phenol (1 : 1) and ethylzinc phenoxide/phenol (1 : 1).

The products of reactions of $ZnEt_2$ with some phenols (1 : 1) in DOX solution (eq. 2) were examined by means of ^1H NMR spectroscopy. Table 1 shows details of

$$ZnEt_2 + X-C_6H_4-OH \rightarrow EtH + X-C_6H_4-OZnEt \qquad (2)$$

($X = H$, o-Et, m-Et, p-Et, o-Cl, m-Cl, p-Cl)

the ^1H NMR spectra of the ethylzinc phenoxides formed by eq. 2 and of corresponding phenols. Their good resolution suggests that ethylzinc phenoxides are present in the solution as definate species, in contrast to the products formed in dialkylzinc/alcohol systems in non-polar solvents [2,4,5,7,8].

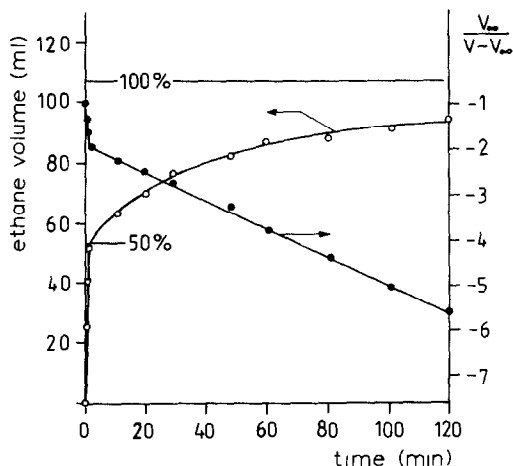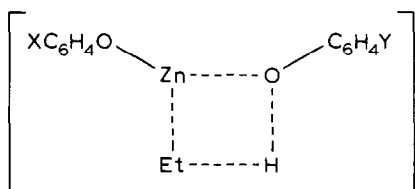The lack of association between ethylzinc phenoxide molecules in DOX solution

Fig. 1. Reaction of diethylzinc and phenol (1 : 2) in THF solution at $0°C$; volume of ethane evolved, and the negative inverse of the phenol mol fraction, as functions of the reaction time.

Additional confirmation of this conclusion was obtained by means of cryoscopic studies on the DOX solution of equimolar amounts of ethylzinc phenoxide and anisole. The molecular weight of the mixture was found to be 137; while that calculated for $C_2H_5ZnOC_6H_5 \cdot CH_3OC_6H_5$ is 289. Comparing the experimental value with the molecular weights of ethylzinc phenoxide (found, 181; calculated, 187) and anisole (calculated, 108) it was concluded that the mean value of the components molecular weights was given by the measurement, which indicated the lack of donor-acceptor complexation between ethylzinc phenoxide and anisole. It can be expected, similarly, that in the reaction between ethylzinc phenoxide and phenol the coordination of reactants does not occur, the more so as the basicity of the phenol oxygen is lower than that of anisole one.

The kinetic order of the reaction by eq. 3, and the effect of ethylzinc phenoxide substituents on the reaction rate, indicate an $S_E i$ mechanism. This type of the reaction mechanism involves formation of the four-centered transition state *:

The $S_E i$ mechanism explains the varied reactivities of phenols and ethylzinc phenoxides characteristic of the lack of a linear relationship between $\log(k_1/k_o)$ and the σ-constants of the substituents. It is apparent that substituents can cause different, and even opposite, effects onto each center of the transition state.

Experimental

Materials

Diethylzinc was synthetized from zinc powder and ethyl halides [13] and distilled under nitrogen before use. Phenols (commercial grade reagents) were purified by distillation under nitrogen. Solvents were purified according to known procedures.

Reaction of diethylzinc and phenol (1 : 2)

To a solution of $ZnEt_2$ (0.0025 mol in 5 cm³ of THF). previously saturated with ethane, was added rapidly under vigorous stirring at 0°C a solution of phenol (0.005 mol in 5 cm³ of THF) which had been previously saturated with ethane and cooled down to 0°C. The volume of ethane evolved (V) was measured in a gas-burette over the reaction time. The total ethane volume (V_∞) was determined by hydrolysis of the reaction mixture with a water solution of HCl. The mol fractions of unreacted phenol, $X_i = (V_\infty - V_i)/V_\infty$, after reaction times t_i, were calculated and the relationship between X and t was determined graphically.

Reaction of ethylzinc phenoxide and phenol (1 : 1)

The solution of ethylzinc phenoxide in THF was prepared by dropwise addition of a phenol solution (0.04 mol in 30 cm³ of THF) to the vigorously stirred solution of

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* Complexation by cyclic ethers is omitted.

TABLE 2

RATE CONSTANTS OF $X-C_6H_4-OZnEt/Y-C_6H_4-OH$ REACTIONS[a]

Y–C$_6$H$_4$–OH (σ)	X–C$_6$H$_4$–OZnEt (σ)		
	X = m–Cl (0.373)	X = H (0)	X = p–Et (−0.151)
		$10^4 k (s^{-1})$	
Y = o-Et	0.58	0.82	2.83
Y = p-Et (−0.151)	1.58	2.79	4.08
Y = m-Et (−0.07)	2.27	2.96	11.83
Y = H (0)	1.00	2.07	6.35
Y = p-Cl (0.227)	0.84	1.90	4.08
Y = m-Cl (0.373)	0.63	1.96	5.50
Y = o-Cl	0.99	1.80	9.55

[a] Reaction conditions: 5 mmol $X-C_6H_4-OZnEt$ and 0.5 mmol $Y-C_6H_4-OH$ in 10 cm^3 THF at 0°C. σ-constants according to ref. 12.

was shown by the cryoscopic investigation on the ZnEt$_2$/phenol (1 : 1) post-reaction mixture. The molecular weight of the reaction product was found to be 181; for $C_2H_5ZnOC_6H_5$ the calculated value is 187. This result indicates unequivocally that the ethylzinc phenoxide formed by eq. 2 exists in DOX solution as a monomer. Taking into account the known tendency of zinc atom to assume a tetrahedral bonding configuration, it would be expected that solvent molecules would occupy the other coordination positions. However, it could not be demonstrated by means of the method used. It should be noted that alkylzinc phenoxides were reported [4,11] to form tetrameric associates in benzene which could be transformed into dimeric ones by addition to the solution of an appropriate amount of a strong donor like pyridine. However, in the case of ethylzinc pentachlorophenoxide, whose oxygen is of lower basicity than that in ethylzinc phenoxide, a monomeric complex was obtained in benzene by coordination of two pyridine molecules at the zinc atom [11].

The kinetic studies on the reactions of ethylzinc phenoxides and phenols, in THF as solvent, according to eq. 3 were carried out using an excess of ethylzinc phenoxide in order to make the reaction a first-order.

$$X-C_6H_4-OZnEt + Y-C_6H_4-OH \rightarrow EtH + X-C_6H_4-OZnO-C_6H_4-Y \qquad (3)$$
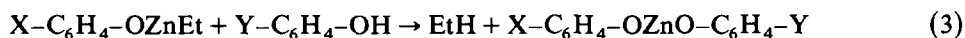
(X = H, m-Cl, p-Et;

Y = o-Et, m-Et, p-Et, H, o-Cl, m-Cl, p-Cl)

The calculated reaction rate constants are collected in Table 2. As can be seen from Table 2, ethylzinc phenoxide substituents affect the reaction rate much more strongly than those on the phenol. Introducing an ethyl group into the ethylzinc phenoxide ring increased its reactivity towards all of the phenols studied, while introducing a chlorine gave the opposite effect. The relationship between $\log(k_x/k_o)$ and the σ-constants of the ethylzinc phenoxide substituents [12] was not linear, although a decrease of value of the reaction rate constant with increase in the value of the corresponding σ-constants for the ethylzinc phenoxide substituents was observed. A statement to this effect excluded the possibility of an S_Ec mechanism for reaction by eq. 3.

ZnEt$_2$ (0.04 mol in 10 cm^3 of THF). Stirring was continued until the evolution of ethane was complete, and 5 cm^3 of the solution, containing about 0.0055 mol of ethylzinc phenoxide, was reacted with phenol (0.0005 mol in 5 cm^3 THF) at 0°C, according to the procedure described in the previous section. The reaction rate constant was calculated from the slope of the straight line obtained by plotting $\log((V_\infty - V)/V_\infty)$ vs. reaction time.

Reaction of diethylzinc and phenol (1 : 1)

A solution of phenol (0.01 mol in 10 cm^3 of DOX) was added dropwise to a vigorously stirred solution of ZnEt$_2$ (0.01 mol in 10 cm^3 of DOX). Stirring was continued until evolution of ethane was complete.

Analyses

^{1}H NMR spectra were recorded in a nitrogen atmosphere on 0.5 mol/dm^3 DOX solutions of the compounds at 25°C, relative to the solvent as an internal standard, using a JEOL C-100H spectrometer.

The cryoscopic measurements were made on the product of the (1 : 1) ZnEt$_2$/phenol reaction carried out in DOX solution. The product was not isolated from the solution which was diluted with DOX to a concentration of 2–5%. Actual ethylzinc phenoxide concentrations were calculated from the volume of ethane evolved by hydrolyzing the product after the measurement. A standard freezing point depression apparatus was used, modified so as to enable the measurements to be made in a nitrogen atmosphere. Cryoscopic constant was calculated from the calibration on DOX solutions of anisole in the concentrations range 0.1–0.5 mol/100 g DOX.

Acknowledgement

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