1018. *Organozinc Compounds. Part I. Proton Magnetic Resonance Spectra of Some Etherates of Dimethyl- and Diphenyl-zinc*

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Proton magnetic resonance spectra of solutions of dimethyl- and diphenylzinc containing severally ethylene oxide, dioxan, and 1,2-dimethoxyethane are described. Equilibrium constants and heats of formation are reported for the dimethylzinc etherates.

THE products from the reaction of dialkylzincs with water,[1-3] alcohols,[1,2,4,5] and other species [2] have been used as catalysts for the polymerisation of epoxides, but despite kinetic and infrared-spectroscopic studies of the hydrolysis [6,7] and alcoholysis [4,7] reactions, and an investigation [8] of the polymerisation of propylene oxide by the diethylzinc–water system, little is known about their structure and mode of action. The present Series reports the results of proton magnetic resonance spectroscopic and other studies of these and related systems.

An examination of etherates was undertaken because similarly co-ordinated species may be present in the products of hydrolysis and alcoholysis of dialkylzincs, and because the catalysts for the polymerisation of epoxides are frequently prepared *in situ*, often with dioxan as solvent. Dimethyl- and diphenyl-zinc were chosen because it was hoped that

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[1] J. Furukawa, T. Tsuruta, R. Sakata, T. Saegusa, and A. Kawasaki, *Makromol. Chem.*, 1959, **32**, 90.

[2] K. T. Garty, T. B. Gibb, and R. A. Clendinning, *J. Polymer Sci., Part A, General Papers*, 1963, **1**, 85.

[3] N. S. Chu and C. C. Price, *J. Polymer Sci., Part A, General Papers*, 1963, **1**, 1105.

[4] M. Ishimori and T. Tsuruta, *Makromol. Chem.*, 1963, **64**, 190.

[5] T. Tsuruta, S. Inoue, N. Yoshida, and J. Furukawa, *Makromol. Chem.*, 1962, **55**, 230; S. Inoue, T. Tsuruta, and J. Furukawa, *ibid.*, 1962, **53**, 215.

[6] R. Sakata, T. Tsuruta, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, 1960, **40**, 64.

[7] R. J. Herold, S. L. Aggarwal, and V. Neff, *Canad. J. Chem.*, 1963, **41**, 1368.

[8] C. Booth, W. C. E. Higginson, and E. Powell, *Polymer*, 1964, **5**, 479.

the spectra of the reaction products from the former would be simple and readily amenable to quantitative study, whilst those from the latter would be more complex but of a type from which information concerning the environment of the phenyl groups could be obtained by examination of the spin–spin coupling patterns of the aromatic protons.

Dimethylzinc forms both mono- and di-etherates,[9,10] suggesting that in the 1 : 1 complexes with monoethers 3-co-ordinate zinc may be quite stable, although dimeric structures involving 4-co-ordinate zinc are possible. The co-ordinate bonding is relatively weak, since the etherates dissociate in solution, more so in benzene than in cyclohexane. The etherates of diarylzincs [11,12] are more stable, particularly when diethers are used, and when the aromatic rings carry electron-accepting substituents.

Benzene solutions of dimethylzinc containing either ethylene oxide, dioxan, or 1,2-dimethoxyethane gave proton magnetic resonance spectra in which the lines due to dimethylzinc moved to higher field, and those due to the ethers moved to lower field, as the concentration of the ether was increased. However, although these shifts are in the directions expected [13] for systems involving equilibria between dimethylzinc and its etherates, those of the ether resonances could be closely matched by varying the concentration in benzene of this solute alone; for benzene solutions of dimethylzinc the shift was of smaller magnitude, and in the opposite sense from that observed in the presence of ethers. These solute–solvent interactions [14] rendered the calculation of equilibrium constants unreliable, but for solutions in cyclohexane the chemical shift of either solute alone was almost independent of concentration, and equilibrium constants could therefore be obtained. In all cases sharp single lines were observed for the methyl and methylene resonances, implying a rapid exchange between complexed and uncomplexed species. The equilibrium constants were calculated from the chemical shift of the dimethylzinc resonance, assuming (*a*) that the observed value is the weighted arithmetic mean [15] of those for the complexed and uncomplexed species, and (*b*) that the major equilibrium involved was that between dimethylzinc and its monoetherate. The latter is probably true for ethylene oxide and dioxan, from which 1 : 1 complexes have been isolated,[9,10] but it may not be so for 1,2-dimethoxyethane, from which only a dietherate has been obtained [10] at temperatures above 0°. The results are summarised in Table 1, and thermodynamic functions calculated from these figures for the formation of the complexes are given in Table 2. The low value for the heat of formation of the dioxan complex may be attributed to the energy of conversion of dioxan from a chair to the boat conformation required for a monomeric monoetherate involving 4-co-ordinate zinc. Similarly, conversion of 1,2-dimethoxyethane to the totally eclipsed form could account for the difference between the heats of formation of the ethylene oxide and 1,2-dimethoxyethane complexes. Within experimental error, entropy changes are the same for ethylene oxide and 1,2-dimethoxyethane, but very much smaller for dioxan.

Since diphenylzinc and some of its etherates are sparingly soluble in cyclohexane at 40°, most of the measurements were made for solutions in hexadeuterobenzene. The proton magnetic resonance spectrum of diphenylzinc in cyclohexane at 80° contains at least twenty lines, of which twelve are readily resolved, between τ 2·46 and 2·88, indicating that the aromatic protons are not equivalent, but only a singlet, at τ 2·73, was observed for solutions in hexadeuterobenzene, suggesting that in the latter solvent there may be rapid exchange between free and solvated molecules of diphenylzinc, a view which is supported

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[9] K.-H. Thiele, *Z. anorg. Chem.*, 1962, **319**, 183.

[10] K.-H. Thiele, *Z. anorg. Chem.*, 1963, **322**, 71.

[11] N. I. Sheverdina, L. V. Abramova, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **128**, 320.

[12] J. G. Noltes and J. W. G. van den Hurk, *J. Organometallic Chem.*, 1961, **1**, 377.

[13] Cf. R. Waak and M. A. Doran, *J. Amer. Chem. Soc.*, 1963, **85**, 4042.

[14] F. Hein, A. Schleede, and H. Kallmeyer, *Z. anorg. Chem.*, 1961, **311**, 260; cf. W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.

[15] J. A. Pople, W. G. Schneider, and H. J. Bernstein, " High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, ch. 10, p. 218.

TABLE 1

τ Values and equilibrium constants, $K = [Me_2Zn, ether]/[Me_2Zn][ether]$, for cyclohexane solutions of dimethylzinc and ethers

Ether (mole l.$^{-1}$)	Me_2Zn (mole l.$^{-1}$)	τ_{MeZn} (at 40°)	K (at 40°)	τ_{MeZn} (at 60°)	K (at 60°)	τ_{MeZn} (at 80°)	K (at 80°)
Ethylene oxide			(*a*)		(*b*)		(*c*)
0	1·72	10·50	—	10·53	—	10·56	—
1·34	1·72	10·60	0·34	10·59	0·14	10·59	0·06
2·20	1·72	10·65	0·35	10·63	0·15	10·62	0·07
4·90	1·72	10·73	0·31	10·70	0·15	10·68	0·07
7·70	1·72	10·78	0·31	10·75	0·14	10·72	0·07
15·30	1·72	10·85	0·35	10·83	0·14	10·81	0·07
Dioxan			(*d*)				(*e*)
0	1·40	10·50	—			10·53	—
0·77	1·40	10·57	0·45			10·58	0·34
1·47	1·40	10·64	0·62			10·61	0·30
2·90	1·40	10·70	0·52			10·68	0·40
5·60	1·40	10·77	0·57			10·73	0·36
1,2-*Dimethoxyethane*			(*f*)		(*g*)		(*h*)
0	1·40	10·51	—	10·53	—	10·56	—
0·74	1·40	10·62	1·18	10·61	0·50	10·58	—
1·60	1·40	10·72	1·36	10·69	0·62	10·65	0·23
3·20	1·40	10·79	1·14	10·76	0·52	10·74	0·32
5·60	1·40	10·83	0·96	10·82	0·53	10·80	0·32
6·60	1·40	10·84	1·00	10·85	0·64	10·81	0·30

The figures in the first two columns refer, respectively, to the total (complexed and free) concentrations of ether and zinc compound. The first figure of each set in the columns headed τ_{MeZn} is for free dimethylzinc, the remaining figures being for the mixtures. Values of τ_{MeZn} for the undissociated complex, required for the calculation [15] of the equilibrium constants, were obtained by extrapolation of a plot of $[Me_2Zn]/[ether]$ *vs.* τ_{MeZn} to $[Me_2Zn]/[ether] = 0$, and were as follows, the letters corresponding with those in the columns headed K: (*a*) 10·92, (*b*) 10·98, (*c*) 11·04, (*d*) 10·88, (*e*) 10·85, (*f*) 10·90, (*g*) 10·94, (*h*) 10·96.

TABLE 2

Thermodynamic functions for the equilibrium $Me_2Zn + ether \rightleftharpoons Me_2Zn, ether$

Ether	ΔG°_{313} (kcal. mole^{-1})	ΔH° (kcal. mole^{-1})	ΔS°_{313} (cal. mole^{-1} deg.$^{-1}$)
Ethylene oxide	0·7	−9·1	−31
Dioxan	0·4	−2·4	−9
1,2-Dimethoxyethane	−0·1	−7·2	−23

The error in ΔH° is estimated to be ±10%.

by dipole-moment measurements,[16] which indicate the presence of solute–solvent complexes. The spectrum of pure diphenylzinc measured at 120° is also a singlet, although of greater half-band-width than that observed for the hexadeuterobenzene solution, suggesting that an exchange process, possibly involving the aromatic π-electron system, may also occur in the melt.

Addition of 0·3 mole l.$^{-1}$ of dioxan to a solution containing 0·6 mole l.$^{-1}$ of diphenylzinc in hexadeuterobenzene caused the resonance due to the aromatic protons to become broader and to show fine-structure, whilst addition of 0·6 mole l.$^{-1}$ resulted in the appearance of two distinct groups of bands with centres of gravity at, respectively, τ 2·45 and 2·67, and intensities in the ratio 2 : 3. Further increases in the concentration of dioxan caused little change in fine-structure and no change in the ratio of intensities, but the group at lower field moved progressively downfield until, at 10 mole l.$^{-1}$ of dioxan, the form of the spectrum was almost identical with that of a 0·7 mole l.$^{-1}$ solution of diphenylzinc in dioxan, for which a quartet and a septet centred at, respectively, τ 2·40 and 2·80 were observed. The constancy of the ratio of the intensities of the two multiplets

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[16] W. Strohmeier, *Z. Elektrochem.*, 1956, **60**, 58.

establishes that they do not individually arise from complexed and uncomplexed diphenylzinc. The group at lower field is attributed to the *ortho*-protons since the aromatic region of the spectrum of di-*m*-tolylzinc in dioxan also consists of two multiplets (τ 2·63, quartet, and τ 3·00, quintet), but with intensities in the ratio 1 : 1. Attempts to use the separation between the multiplets as a quantitative measure of the equilibrium position were unsuccessful.

The spectra of mixtures of diphenylzinc and dioxan in hexadeuterobenzene were almost unchanged when measured at 60° instead of at 40°, suggesting, in agreement with its other physical properties,[11] that the dioxan complex is fairly strong. However, the facts that only a single resonance was observed for the dioxan even when more than one equivalent was present, and that the multiplets due to the aromatic protons moved further apart as the proportion of dioxan was increased, suggest the occurrence of an exchange process. A hexadeuterobenzene solution prepared from the solid dioxanate showed aromatic and methylene proton resonances in the ratio 5 : 4, confirming the presence of equal numbers of diphenylzinc and dioxan residues. Comparison [17] of the vapour pressure of benzene solutions of the dioxanate with that of pure benzene at the same temperature indicated that the dioxanate was monomeric and almost undissociated at 0·33 mole l.$^{-1}$, but approximately 30% dissociated at 0·11 mole l.$^{-1}$.

Almost identical patterns were observed for the aromatic proton resonances when 1,2-dimethoxyethane or ethylene oxide was used instead of dioxan. Removal, at 20°/10^{-4} mm., of the excess of solvent from a solution of diphenylzinc in 1,2-dimethoxyethane left a solid 1 : 1 complex [12] which in hexadeuterobenzene gave a spectrum analogous to that observed for the dioxanate, but, when similarly treated, a solution of ethylene oxide afforded largely diphenylzinc. However, removal of the ethylene oxide at −78°/10^{-4} mm. for varying lengths of time in all cases left a solid which in hexadeuterobenzene gave a spectrum identical with that obtained for a solution of similar concentration prepared from a mixture of diphenylzinc and ethylene oxide in the molar ratio 1 : 2, indicating the existence of a dietherate.

EXPERIMENTAL

Zinc Compounds.—Dimethylzinc was prepared from methyl iodide using a procedure similar to that described [18] for diethylzinc, except that the initial mixture was stirred and refluxed for 24 hr., and then distilled at normal pressure, the distillate being collected on a fresh zinc–copper couple with which it was refluxed for a further 24 hr. The crude dimethylzinc was removed by distillation, and its vapour repeatedly passed through a finely divided zinc–copper couple at 150° until the methyl iodide content, determined by gas–liquid chromatography on a Celite–silicone oil column and by proton magnetic resonance spectroscopy, was $<0·5\%$. It then had b. p. 44°/770 mm., and d_4^{20} 1·33 g./c.c. determined by comparative integration of the proton magnetic resonances given by a mixture of it with equal volumes of cyclohexane and benzene (cf. lit.,[19] 1·386 at 10·5°).

Diphenylzinc was prepared [20] from phenyl-lithium and zinc chloride, and purified by bulb-to-bulb fractional distillation at 135—170° (bath)/10^{-5} mm., the main fraction having m. p. 107—108° (lit.,[20] 106—107°) and, as a liquid, d_4^{110} 1·34 g./c.c. Di-*m*-tolyzinc was prepared analogously from *m*-tolyl-lithium, distilled at 180° (bath)/10^{-4} mm., and crystallised *in vacuo* twice from cyclohexane and then from cyclohexane–pentane. It had m. p. 75—76°.

Preparation of Samples.—Solutions were prepared using normal Pyrex glass vacuum-line techniques with pressures $\not> 10^{-4}$ mm. measured when the samples were cooled in liquid nitrogen. Benzene was purified by fractional freezing, cyclohexane by washing with concentrated sulphuric acid, and dioxan and 1,2-dimethoxyethane by refluxing with sodium. These compounds, ethylene oxide, and hexadeuterobenzene (Koch Light Laboratories Ltd.)

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[17] Cf. G. W. Thomson, " Technique of Organic Chemistry," ed. A. Weissberger, Interscience, New York, 1959, vol. I, p. 451.

[18] C. R. Noller, *Org. Synth.*, Coll. Vol. II, 1963, p. 184.

[19] E. Frankland and B. F. Duppa, *Annalen*, 1864, **130**, 119.

[20] G. Wittig, F. J. Meyer, and G. Lange, *Annalen*, 1951, **571**, 167.

were checked for purity by gas–liquid chromatography, and then individually distilled on to calcium oxide (freshly ignited and cooled in a desiccator) contained in vessels connected *via* taps to the vacuum system, and degassed by the freeze-pump-thaw method. They were stored under their own vapour pressure at room temperature, except for ethylene oxide which was kept at 0°. Samples were removed and checked for water content by addition of dimethylzinc: those which gave turbid solutions were further dried.

Dimethylzinc attacks normal tap greases, and its container was therefore isolated from the rest of the apparatus by a Springham greaseless tap (L. Springham & Co. Ltd., Harlow) fitted with a " Viton A" pad. Glass hemispherical break-seals were used instead of taps on parts of the apparatus through which diphenyl- and di-*m*-tolyl-zinc were distilled, since temperatures above 100° were required. Solvents and solutes were distilled from their storage vessels into calibrated capillary tubes until the required volume, measured at 20° except for ethylene oxide (10°) and the diarylzincs (110°), had been collected; they were then distilled into the spectrometer sample tubes, which were subsequently sealed. The concentration of ethylene oxide in the samples was checked by comparison of the intensity of its proton magnetic resonance absorption with that of the dimethylzinc.

Spectra.—These were measured with a Varian A-60 spectrometer at 60 Mc./sec. for solutions contained in sample tubes of 4 mm. internal diameter, tetramethylsilane being used as an internal standard except for solutions in cyclohexane, for which the solvent resonance (τ 8·55) relative to internal tetramethylsilane) was used.

Diphenylzinc: (*a*) Saturated solution in cyclohexane at 80°, τ 2·47, 2·54, 2·57, 2·60, 2·62, 2·63, 2·68, 2·72, 2·77, 2·80, 2·82, 2·87, with relative peak heights 1·0 : 1·8 : 2·0 : 2·8 : 2·3 : 3·3 : 1·7 : 2·2 : 7·2 : 3·4 : 5·0 : 2·8, but at least 10 more lines could be detected by scale expansion; (*b*) 0·3 mole l.$^{-1}$ in C_6D_6 at 40°, singlet, τ 2·73; (*c*) 0·7 mole l.$^{-1}$ in dioxan at 40°, low-field group τ 2·33, 2·38, 2·43, 2·47, high-field group τ 2·68, 2·71, 2·77, 2·80, 2·84, 2·89, with relative peak heights of 1·0 : 1·7 : 2·2 : 1·8 : 1·1 : 1·0 : 2·0 : 1·8 : 4·0 : 2·2; (*d*) 1·2 mole l.$^{-1}$ in 1,2-dimethoxyethane at 40°, low-field group τ 2·36, 2·43, 2·48, 2·51, high-field group τ 2·74, 2·78, 2·83, 2·86, 2·89, 2·94, with relative peak heights 1·0 : 2·0 : 2·2 : 1·8 : 1·1 : 1·0 : 2·0 : 1·5 : 4·0 : 3·0; (*e*) 0·8 mole l.$^{-1}$ in ethylene oxide at 40°, low-field group τ 2·29, 2·34, 2·40, 2·44, high-field group τ 2·63, 2·69, 2·72, 2·75, 2·79, 2·81, with relative peak heights 1·0 : 1·9 : 2·2 : 1·8 : 2·3 : 1·1 : 2·4 : 1·7 : 4·0 : 3·0; these solutions gradually became more viscous due to polymerisation of the ethylene oxide.

Solutions in hexadeuterobenzene of the residues obtained by removal of the solvent, finally at 20°/10^{-4} mm., from solutions of diphenylzinc in dioxan and in 1,2-dimethoxyethane gave spectra which in each case were consistent with the presence of a 1 : 1 complex, and identical with those obtained for solutions of similar concentration prepared directly from the reactants. For ethylene oxide, the solvent was removed at −78° from three separate solutions, the residues being pumped at −78°/10^{-4} mm. for, respectively, 9, 20, and 46 hr., and then dissolved in hexadeuterobenzene: integration of the spectra of these solutions gave values of, respectively, 2·3, 2·1, and 1·9 for the quotient [ethylene oxide]/[Ph_2Zn].

Di-*m*-tolylzinc, 0·8 mole l.$^{-1}$ in dioxan at 40°, had low-field group τ 2·55, 2·59, 2·66, 2·70, high-field group τ 2·80, 2·86, 2·91, 3·02, 3·12 with relative peak heights 6·3 : 6·5 : 2·8 : 3·3 : 2·0 : 1·6 : 5·3 : 7·0 : 1·0, τ_{Me} 7·74; integrated intensities: low-field group : high-field group : methyl = 2 : 2 : 3.

Molecular Weights.—These were determined with a tensimeter, employing the following modifications of the method [17] previously described. Using the vacuum-line technique a known weight of diphenylzinc and an excess of dioxan were distilled into a cylindrical round-bottomed ampoule of about 8 c.c. capacity fitted with a side-arm carrying a hemispherical glass break-seal, and the mixture, after being allowed to warm to room temperature, was stirred magnetically until a clear solution was obtained. The excess of dioxan was removed at 0—10° by distillation into a cold trap, and the solid residue was then pumped at 20° until the pressure in the system was $<10^{-4}$ mm. A known volume of benzene was distilled in, the ampoule was sealed, and the side-arm was then fused to the upper part of one limb of a thoroughly degreased differential mercury manometer with vertical arms of 14·5 mm. internal diameter and 50 mm. length over the region where measurements of the mercury levels were to be taken. A second ampoule, also fitted with a break-seal, containing a similar volume of benzene distilled from the same stock was fused to the upper part of the other arm of the manometer, alongside the first ampoule. Both arms of the manometer above the measuring region were joined by the horizontal arm of an inverted T-piece, the vertical arm being connected *via* a constriction to the pumping system; the limbs below the measuring region were connected by the horizontal arm of a second T-piece, the vertical arm passing into a reservoir containing distilled mercury. The space above the mercury in the reservoir was connected *via* a tap to the pumping system. The arms of the manometer and the space above the mercury in the reservoir were pumped out until a pressure of $\not> 10^{-4}$ mm. had been attained, and the constriction above the manometer limbs was sealed, the tap on the reservoir was closed, and the apparatus was removed from the pumping system; the mercury in the vertical arm of the lower T-piece was at this stage below the junction with the horizontal arm. The ampoules only were immersed in a small water thermostat which operated over the range 20—50°, and the whole assembly was transferred to an air thermostat set at a temperature 5° above that of the thermostat containing the ampoules, in order to prevent condensation of benzene in the limbs of the manometer. The break-seals were broken, and air was then cautiously admitted *via* the tap to the space above the mercury in the reservoir until mercury had risen above the lower T-junction and to a suitable level in the wide arms of the manometer; the tap was then closed. The difference between the mercury levels in the manometer was periodically measured with a cathetometer until equilibrium, as judged by the constancy of the difference, had been reached. For measurements at different temperatures, the level of the mercury in the manometer was adjusted by removal of air from, or admittance of air to, the space above the mercury in the reservoir.

The following results are typical: for $(Ph_2Zn, dioxan)_n$ at 0·33, 0·20, and 0·11 mole $l.^{-1}$ in benzene, $n = 0{\cdot}99$, 0·87, and 0·70 at 20°, and $n = 1{\cdot}11$, 0·92, and 0·73 at 40°, respectively. The slightly higher complexity at 40° is probably due to experimental error.

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