Equilibrium in the Methanolysis of Dimethylzinc

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Abstract: When a solution of dimethylzinc in a hydrocarbon solvent is treated with various proportions of methanol, methane is evolved and it is shown from the interpretation of proton nuclear magnetic resonance (nmr) spectra that three molecular species are in equilibrium with each other in the resulting solutions. These species are $(CH_3)_2Zn$, the bird-cage molecule $(CH_3)_4Zn_4(OCH_3)_4$, and what is believed to be a double bird-cage molecule $(CH_3)_4Zn_7(OCH_3)_8$. This latter compound has been isolated in crystalline form. When the ratio of methanol to dimethylzinc is greater than 8:7 (corresponding to the latter compound), polymeric dimethoxyzinc is seen to precipitate. Addition of trimethylamine, pyridine, or other strongly complexing ligands to solutions of methoxymethylzinc causes an increase in the relative amount of dissolved $(CH_3)_6Zn_7(OCH_3)_8$ due to removal of free $(CH_3)_2Zn$ by complex formation. The appropriate equilibrium constants are evaluated and the observed rapid rates for exchange of methyl groups are discussed.

Although there has been considerable recent work[2] in the organic chemistry of zinc, the important role of equilibrium control in determining the kinds and amounts of reaction products has not been sufficiently emphasized. Therefore, we decided to apply the nuclear magnetic resonance (nmr) techniques which have proved so fruitful in our laboratory to the study of a relatively simple zinc system which hopefully would be representative of this chemistry. About the time we started the laboratory work, a paper[3] describing a similar experimental approach appeared; but, since it only reported qualitative findings on limited compositions, we proceeded. Fortunately we were able to isolate a new compound in this work and to define the controlling equilibrium constant and obtain its value.

Experimental Details

The dimethylzinc was purchased as a heptane solution from Orgmet, Hampstead, N. H., and was used without further purification since it exhibited a sharp single-peak nmr spectrum, the same as that obtained on a sample from another source. Amorphous dimethoxyzinc was prepared by adding a slight excess of methanol to the solution of dimethylzinc at −70°, gradually warming to cause evolution of methane, and finally boiling before filtering off the resulting precipitated product. It was then heated for 8 hr at 100° under a vacuum of 10^{-3} mm. Methoxymethylzinc, $(CH_3)_4Zn_4(OCH_3)_4$, was not made according to the original preparation[4] but was crystallized from a solution having a considerable excess of dimethylzinc ($R = 1.5$; see next paragraph for definition of R), as recommended in the literature.[3] When dissolved in benzene at temperatures near 0°, this compound exhibited a sharp nmr peak in the CH_3O region of the proton nmr spectrum and another sharp peak of equal area in the CH_3Zn region, with no other resonances in evidence. Only freshly prepared samples were employed since on standing there is some loss of $(CH_3)_2Zn$.

The proton nmr measurements were made on a Varian A56-60 spectrometer equipped with a V-6040 temperature controller. All referencing was done to tetramethylsilane, and peak areas were measured by the cut-and-weigh technique. In this work, we attempted to vary systematically the temperature, solvent concentration, and the proportion of methoxyl groups to the methyl groups bonded to the zinc (after the methane had been eliminated when methanol was allowed to react with dimethylzinc). This proportion is characterized in this paper in terms of the composition ratio R which equals the ratio of total CH_3Zn to total Zn and ranges from 0 for the dimethoxyzinc to 1 for the methoxymethylzinc to 2 for the dimethylzinc composition. The first series of samples studied was obtained by adding various proportions of methanol to the dimethylzinc thereby displacing a Zn–methyl group (as methane) by a methoxyl group until the methanol was exhausted. However, much of the quantitative work was done by combining various proportions of crystalline[5] $(CH_3)_4Zn_4(OCH_3)_4$ either with amorphous $[(CH_3O)_2Zn]_n$ or with dimethylzinc. In all cases, benzene was employed as the added solvent and the samples were sealed in 5-mm precision nmr tubes.

Preparation of Crystalline $(CH_3)_6Zn_7(OCH_3)_8$. Dimethoxyzinc (13.0 g) was suspended in 250 ml of absolute benzene in a 500-ml flask provided with a reflux condenser and a drying tube containing KOH. After addition of 7.0 g of dimethylzinc in 40 ml of heptane, the mixture was heated to 80° for 20 min under a slight nitrogen pressure. After cooling, the small excess of dimethoxyzinc, which is essential for obtaining a clean product not contaminated by $(CH_3)_4Zn_4(OCH_3)_4$, was removed by vacuum suction through a sintered-glass filter. Crystallization was effected by concentrating the resulting clear solution to 50 ml under vacuum at 5°. The resulting small crystals were redissolved by heating to 80° under a slight nitrogen pressure. The clear, colorless 1–5-mm crystals precipitated upon slow cooling were separated by vacuum suction and recrystallized twice from absolute benzene. Final removal of the solvent was carried out at 5° under a 3×10^{-3} mm vacuum for 48 hr (yield, 18.8 g crude product = *ca.* 95%). The compound is sensitive to air and moisture and must be handled in dry solvents under dry nitrogen.

Analysis. C and H analyses were carried out according to the modified Ingram method. Instantaneous combustion of the weighed sample was achieved in an O_2 atmosphere at 1000°, the gases were passed over cobalt oxide at 750° and then over Ag wire, and finally H_2O and CO_2 were absorbed and determined gravimetrically. The Zn analysis was done in a NH_4Cl-buffered aqueous ammonia solution using 0.05 M Na_2EDTA. Erio T was used as the endpoint indicator.

Base hydrolysis must be used in preparing samples for Zn analysis since acid hydrolysis leads to the evolution of appreciable amounts of dimethylzinc. Hydrolyzable methyl groups were determined volumetrically by the amount of methane evolved on base hydrolysis. *Anal.* Calcd for $(CH_3)_6Zn_7(OCH_3)_8$: Zn, 57.48; C, 21.12; H, 5.32; CH_3Zn, 11.33. Found: Zn, 57.49; C, 20.87; H, 5.19; CH_3Zn by hydrolysis, 11.29. The observed molecular weights by cryoscopy were 730, 940, 680, 754, and 670, with 796 corresponding to $(CH_3)_6Zn_7(OCH_3)_8$. Large cryoscopic values can probably be attributed to some hydrolysis, with or without precipitation of dimethoxyzinc, and small values to some form of dissociation. A melting point of 255–257° was observed in a sealed tube with simultaneous evolution of a gas (presumably dimethylzinc), followed by sublimation of two different kinds of crystals and opacification of the melt.

Results and Interpretation

Nmr Assignments. Only methyl-group resonances are seen in the nmr spectra and these are divided into

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[1] Postdoctoral fellow from Heidelberg University, 1966–1967.

[2] G. E. Coates, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **28**, 3 (1967).

[3] G. Allen, J. M. Bruce, D. W. Farren, and F. G. Hutchinson, *J. Chem. Soc., B*, 799 (1966).

[4] G. E. Coates and D. Ridley, *ibid.*, 1870 (1965).

[5] H. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, 194 (1966).

two regions: a downfield one in the range of -3.3 to -3.5 ppm corresponding to the CH_3O groups, and an upfield one at $+0.4$ to $+0.7$ ppm corresponding to CH_3Zn groups. At elevated temperatures (60–80°), three resonances are observed in the downfield region, whereas the resonances in the upfield region are all coalesced to a single line. At lower temperatures (<20°), three resonances are observed in the upfield region. This means that there are a total of six nmr peaks which we shall label[6] *A* through *F*, starting with the most downfield one. Chemical shifts of resonances *B* at -3.43 ppm and *C* at -3.36 ppm change less than 0.05 ppm with temperature in the range of -5 to $+80°$ and vary even less with dilution in the range from 4.7 to 12.2 wt % of total Zn compounds in benzene. However, the shift of peak *A* is quite temperature dependent, ranging from -3.35 ppm at $-5°$ up to -3.48 ppm at $+80°$, so that at a temperature of $+40°$ the *A* and *B* peak are superimposed, and at $-5°$ the *A* and *C* peaks are superimposed. Peak *F* is assigned to dimethylzinc and, for a pure heptane solution, it appears as a sharp resonance at $+0.49$ ppm, independent of temperature. Even at temperatures as low as 0°, this peak broadens greatly with increasing amounts of methoxyl groups so that the exact shift cannot be precisely determined, but it is seen to be in the range of $+0.4$ to $+0.7$ ppm. At low temperatures, the chemical shifts of resonances *D* ($+0.40$ ppm) and *E* ($+0.43$ ppm) vary only slightly with over-all concentration and composition.

Upon varying the value of the ratio of total zinc-bonded methyl groups to total zinc, $R = CH_3Zn/Zn$, the areas of the various peaks are seen to change, with the A:B:E area ratio always being 3:1:3 and the C:D ratio being 1:1, within experimental error. Furthermore, the area of resonance *F* is a maximum at $R = 2$ and gradually diminishes as the *R* value is lowered, whereas the areas of peaks *C* and *D* are found to maximize at $R =$ *ca.* 1.0 and resonances *A*, *B*, and *E* become the only peaks in the spectrum at *R* values of 0.857 and lower. At $R \geq 0.857$, the solution is clear, but, as the *R* value is decreased, there is increasing precipitation of a polymer having a composition approximating dimethoxyzinc until at $R = 0$ all the zinc is precipitated.

It is obvious from the above that resonance *F* corresponds to dimethylzinc, resonances *C* and *D* correspond to methoxymethylzinc, and resonances *A*, *B*, and *E* correspond to a compound which has the empirical formula $3(CH_3)_2Zn \cdot 4(CH_3O)_2Zn$, while the compound $(CH_3O)_2Zn$ is too insoluble to give any detectable proton resonance.

Reaction Rates. Resonances *A*, *B*, and *C* in the nmr spectra are always sharp, having a width at half-height of 0.5–0.7 cps in the temperature range of -5 to $+80°$ for any ratio of starting ingredients or concentration up to the maximum employed of 12.2 wt % of total Zn compounds. On the other hand, peaks *D*, *E*, and *F* always seem to be broad and, indeed, exhibit coalescence into a single peak above room temperature. This broadness and coalescence indicate that the methyl groups bonded to the zinc undergo rapid exchange. Although in pure solution the resonance for dimethylzinc is no more broad than that of the reference tetramethylsilane, its width is always several times that of peaks *D* and *E*, with peak *D* also being somewhat more broad than peak *E*. For example, at a benzene concentration of 12.2 wt % of zinc-containing species at 0°, the width at half-height of peak *F* is *ca.* 9.0 cps, whereas it is 1.7 and 1.3 cps for *D* and *E*, respectively. We interpret this to mean that the rate of exchange of zinc-bonded methyl groups between dimethylzinc and the compound $(CH_3)_4Zn_4(OCH_3)_4$ is faster than the rate between dimethylzinc and the compound which has the empirical formula $3(CH_3)_2Zn \cdot 4(CH_3O)_2Zn$, with essentially no direct exchange between the two methoxyl-containing compounds. On the assumption of a second-order rate process (since there is narrowing of the peak width with increasing dilution), the rate constants for these exchanges at 0° are estimated to be *ca.* 15 and *ca.* 12 l./(mole sec), respectively, with activation energies around 7 kcal/mole.

In the reaction between dimethylzinc and methanol, the initial replacement of zinc methyls by methoxyl groups is an extremely rapid process, with sufficiently fast formation of methane gas at room temperature to cause hissing. However, by the time that an average of one methoxyl group is substituted for a methyl group, the rate becomes much slower, with completion times being of the order of magnitude of a few minutes at room temperature. For $R < 0.857$, dimethoxyzinc is found to precipitate, and boiling for a few minutes is necessary to remove the last traces of methane formed from the reaction with methanol.

For the precipitate-free solutions corresponding to $0.857 \leq R \leq 2.0$, equilibrium seems to be reached in *ca.* 2 days at room temperature since the same nmr pattern is found within this time for a given *R* value obtained from any mixture of different *R* values, whether or not the solutions thus combined represented pure compounds or mixtures in themselves. Such equilibration is exemplified by Figure 1 in which the decomposition of pure methoxymethylzinc into the mixture corresponding to its stoichiometric composition ($R = 1$) is compared with the rate of reaction of the two other ingredients in this mixture, dimethylzinc and the compound having the empirical formula $3(CH_3)_2Zn \cdot 4(CH_3O)_2Zn$. Since the same composition is reached from the two extremes, Figure 1 is a proof of the attainment of an equilibrium between the three soluble species present in this system. It should be noted that once equilibrium is reached, the nmr pattern corresponding to a given temperature and concentration was not found to change owing to thermal cycling or storage of the solution in sealed nmr tubes for many months.

Equilibrium in Solution. The equilibrium equation may be written as follows, where the compound $3(CH_3)_2Zn \cdot 4(CH_3O)_2Zn$ is assumed to be monomeric in accord with the molecular weight measurements on solutions of its crystals (see Experimental Details).

$$2(CH_3)_4Zn_4(OCH_3)_4 = (CH_3)_2Zn + (CH_3)_6Zn_7(OCH_3)_8 \qquad (1)$$

The corresponding equilibrium constant is

$$K_s = \frac{[(CH_3)_2Zn][(CH_3)_6Zn_7(OCH_3)_8]}{[(CH_3)_4Zn_4(OCH_3)_4]^2} \qquad (2)$$

Values of this constant were calculated from peaks *A*, *B*, and *C* in the nmr spectrum using the over-all material balance (given by the *R* value). From data on 11 dif-

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(6) In the labeling scheme used by Allen, Bruce, Farren, and Hutchinson,[8] their *a* equals our *A* + *B*, and their *b* = *C*, *c* = *D*, *d* = *E*, *e* = *F*, *f* = *B*, while they did not observe resonance *F* because it shows up only at temperatures lower than were employed in their investigation.

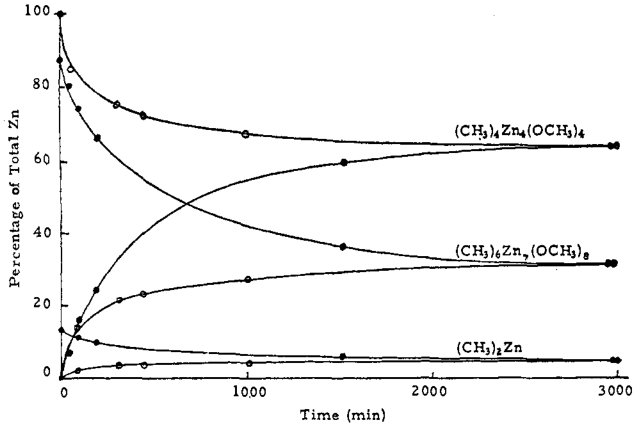


Figure 1. Reaction-rate curves at 25° for the decomposition of methoxymethylzinc (open circles) and for the reaction (black circles) of dimethylzinc with the compound $(CH_3)_6Zn_7(OCH_3)_8$ to give the same equilibrium mixture.

ferent preparations, the weighted value of K_s at 60° was found to be 0.076 with a standard deviation, σ, of 0.016. In addition, data for an R value of 1.00 at four different concentrations ranging from 4.7 to 12.1 wt % of the total zinc-containing compounds were obtained at 20, 40, and 80°. From these data, the following constants were obtained: $K_s = 0.068$ for 20°, with $\sigma = 0.008$; 0.088 at 40°, with $\sigma = 0.006$; and 0.076 at 80°, with $\sigma = 0.013$. These results show that there is no systematic change in the equilibrium of eq 1 with either dilution or temperature so that for this reaction ΔH is estimated to be smaller than *ca.* 1 kcal/mole.

In Figure 2, experimental points obtained at 60° are compared with the theoretical curves calculated for the average value of 0.076 and another value of 0.066 for K_s. The agreement between the experimental points and the theoretical curves is good and shows that there is no need to assume other than unity values for the activity coefficients to fit the data within the experimental error.

It appears from the good fit in Figure 2 between the experimental data and the curves calculated from the equilibrium constant, K_s, that eq 1 accounts for all of the detectable compounds. Thus if we wish to estimate the entropy based only on rearrangement of atoms in the reaction corresponding to eq 1, only the three compounds involved therein must be considered. This entropy is calculated, $\Delta S = R \ln (K_s)_{\text{random}}$, from the random equilibrium constant which is estimated on the sorting of $CH_3Zn_{1/2}$ groups with $(CH_3O)_4(CH_3Zn)_3Zn_{1/2}$ broken-ended cages. If the first of these groups is symbolized by α and the second by β, eq 1 reduces to the form $2\alpha\beta \rightleftarrows \alpha\alpha + \beta\beta$. Normally the random equilibrium constant for such an equation would equal $^1/_4$, but, because the bird-cage compound, $(CH_3)_4Zn_4(OCH_3)_4$, exhibits fourfold degeneracy with respect to the splitting off of a $CH_3Zn_{1/2}$, the random equilibrium constant corresponding to eq 1 is equal to 4. The corresponding entropy of eq 1 due to the rearrangement of atoms is 2.75 eu, whereas the observed entropy is -5.11 eu. It is tempting to ascribe the difference of -8 eu to some kind of molecular association involving the low-lying empty orbitals of the dimethylzinc. However, this can only account for a small part of the -8 eu unless the dimethylzinc is involved in a macromolecular agglomerate. It is more probable that the major part of the observed entropy difference is due to changes in the vibrational modes when going from the reactants to the products, even though there is no change in the number of vibrational degrees of freedom. For example, in the case of hydrocarbons, torsional vibration corresponds to *ca.* 4 eu, bending to *ca.* 2 eu, and stretching to *ca.* 1 eu. Presumably the ΔH terms involved in such vibrational changes cancel out.

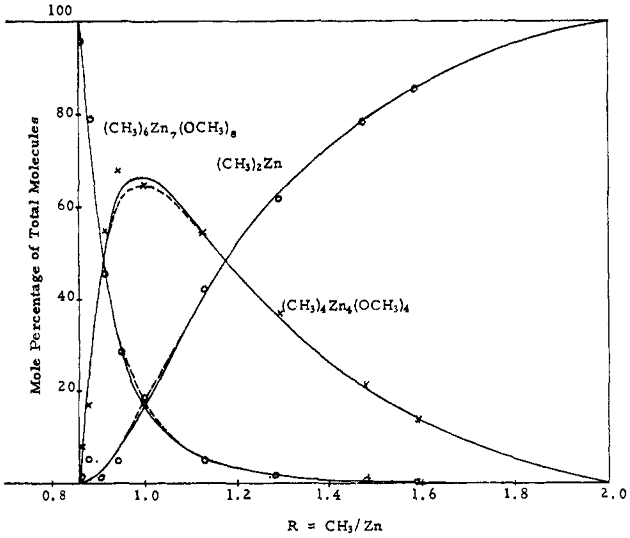
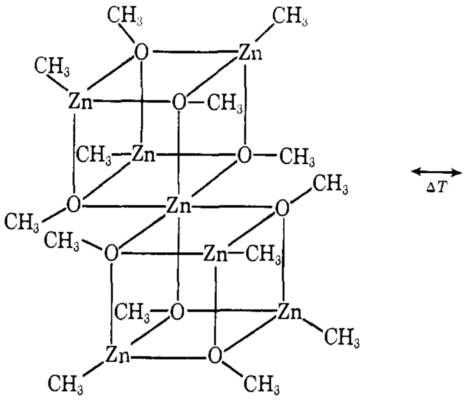


Figure 2. Equilibrium diagram at 60° for the completely soluble part of the system ranging from dimethylzinc to dimethoxyzinc. The solid lines correspond to $K_s = 0.066$ and the dotted ones to $K_s = 0.076$.

Postulated Structure of $3(CH_3)_2Zn \cdot 4(CH_3O)_2Zn$. The elemental analysis and cryoscopic molecular weight as well as the constancy of the equilibrium constants of eq 2 all support the formulation of the newly isolated compound described herein as $(CH_3)_6Zn_7(OCH_3)_8$. In analogy with methoxymethylzinc,[4,5] it seems reasonable to assume that all of the unshared electron pairs of the oxygens in this compound are coordinated to zinc atoms so that each oxygen exhibits the approximate geometry of sp^3 hybridization. Based on this postulate, a reasonable structure for the compound is presented as structure I. This structure should exhibit a single CH_3Zn peak of relative area 3 (resonance E) and two resonances in the CH_3O region of the nmr spectrum, with relative areas of 3 (resonance A) corresponding to the oxygen adjacent to the hexacoordinate zinc and one (resonance B) corresponding to the oxygens at the far corners of the cubes. The fact that the chemical shift of resonance A varies with temperature, whereas those of resonances B and E do not, seems to be in accord with the postulated structure on the assumption that there is a temperature dependence for the degree of hexa- *vs.* tetracoordination of the central zinc atom. The tetracoordinate situation is represented by structure II. This postulated hexatetra equilibrium is obviously rapid and must surely involve all six of the oxygen atoms shown bonded to the central zinc in structure I.

Complexing of Dimethylzinc. Since exclusive of solvation the zinc in dimethylzinc exhibits a coordination number of 2, one would expect that addition of complexing agents such as a trialkylamine would shift



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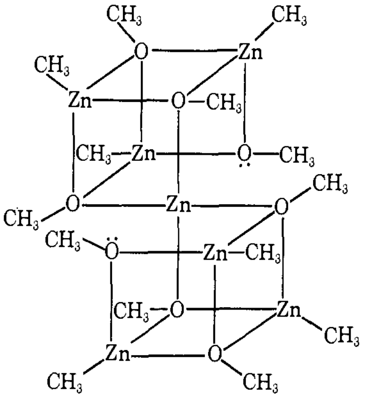

II

the equilibrium of eq 1 because of a diminution of the free dimethylzinc according to the following reaction in which X stands for the complexing agent.

$$(CH_3)_2ZnX_2 \rightleftharpoons (CH_3)_2Zn + 2X \qquad (3)$$

$$K_c = [(CH_3)_2Zn][X]^2/[(CH_3)_2ZnX_2] \qquad (4)$$

Values for the equilibrium constants of eq 4 for dissociation of the dimethylzinc complex can readily be evaluated by adding different amounts of the complexing agent to a solution of methoxymethylzinc and evaluating, from the nmr spectra, the concentrations of the compounds involved in eq 3. For trimethylamine as the complexing agent, when going upfield in the nmr spectrum obtained at a sample temperature of 10°, the CH_3O region of the spectrum appears first, with peak *B* followed by a doublet peak corresponding to near coalescence of resonances *A* and *C*. Then there is a single peak in the CH_3N region, followed by one to three peaks (depending on the over-all composition and concentration) in the CH_3Zn region. From these assignments, it is apparent that the area of the downfield peak is proportional to $2[(CH_3)_6Zn_7(OCH_3)_8]$; the next peak to $6[(CH_3)_6Zn_7(OCH_3)_8] + 4[(CH_3)_4Zn_4(OCH_3)_4]$; the CH_3N peak to $3[X] + 6[(CH_3)_2ZnX_2]$; and the CH_3Zn resonance(s) to $6[(CH_3)_6Zn_7(OCH_3)_8] + 4[(CH_3)_4Zn_4(OCH_3)_4] + 2[(CH_3)_2Zn] + 2[(CH_3)_2ZnX_2]$. From relationships of this type, the total Zn concentration, and $K_s = 0.076$, values of K_c were calculated for several different complexing agents. At 0°, K_c equals *ca.* 1×10^{-4} for pyridine, and it is *ca.* 5×10^{-2} for trimethylphosphine, but for triphenylphosphine, the amount of complexed Zn was too small to measure in the five runs carried out on this system ($K_c >$ *ca.* 1). For trimethylamine at 10°, $K_c =$ *ca.* 10^{-5}, with all values of K_c being in units of (moles/l.)^2.

Although the necessity of taking the difference between relatively large numbers in the mathematical operations does not make this a particularly good way of studying equilibrium constants for eq 4, it is interesting to note that the calculated values of K_c for a given system generally remained within a tenfold range and did not vary systematically with a 20-fold variation in the proportion of added ligand. Use of *p*-dimethylaminopyridine as a ligand led to nmr spectra which looked different from the ones obtained with the other ligands (probably because of the presence of several complexes). Although we did not attempt a quantitative interpretation of these spectra, it was clear that the equilibrium of eq 1 was again being shifted by addition of this substituted pyridine.

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