experiment about half of the $N_2H_3{}^+$ formed underwent oxidation by reaction 11, reactions 10 and 12 or reactions 10, 14 and 15.

The above mechanism thus serves to explain the effects of pH on i_l/C and on n. Since an increase of the initial hydrazine concentration leads to a proportional increase of the diimide concentration at every instant during an electrolysis, and since, as above, this causes the rate of the dimerization to increase more rapidly than the rate of the further oxidation, it obviously also serves to explain the effects of the initial concentration of hydrazine. It thus provides a simple and consistent description of the phenomena observed over a wide range of experimental conditions.

It remains to be said only that the effect of chloride ion in decreasing the n-values obtained in strongly acidic solutions must reflect a decrease of the activation energy required for the dimerization of N_2H^+ brought about by the presence of chloride. Reactions 16 and 17 serve to account for this effect.

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# Exchange of Methyl Groups in Organometallic Compounds[1]

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Rapid, intermolecular exchange of methyl groups in solutions of trimethylaluminum and dimethylcadmium and in solutions of dimethylzinc and dimethylcadmium has been demonstrated by nuclear magnetic resonance. For trimethylaluminum and dimethylcadmium dissolved in benzene, an upper limit of the average lifetime of a methyl group before exchange was estimated. For solutions of dimethylzinc and dimethylcadmium in five solvents, the average pre-exchange lifetimes, reaction orders and rate constants were determined. For the dimethylzinc–dimethylmercury and the dimethylcadmium–dimethylmercury system, lower limits of the pre-exchange lifetimes were calculated.

Introduction

The bridge structure of trimethyl aluminum probably exists in benzene solutions[2] and in the

$$(CH_3)_2Al \underset{\underset{CH_3}{\diagdown\diagup}}{\overset{\overset{CH_3}{\diagup\diagdown}}{}} Al(CH_3)_2$$
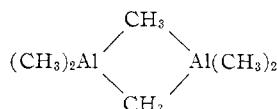
gas phase[3] and is definitely present in the solid state as shown by X-ray techniques.[4] To investigate the existence of the bridge structure in the liquid phase, the proton magnetic resonance spectrum was obtained. Only one sharp peak in the spectrum was observed and is consistent with the bridge structure only if the methyl groups change environments often. Recently,[5] two peaks were found at low temperatures in cyclopentane solution and were attributed to two magnetically different types of protons. The nuclear magnetic resonance (n.m.r.) spectrum of trimethylaluminum at room temperature can be accounted for by either an intermolecular or an intramolecular exchange process. Also, exchange of methyl groups has been demonstrated for systems containing methylaluminum chlorides.[6] This paper discusses the investigation of intermolecular exchange in several systems of organometallic compounds. This investigation of relatively simple organometallic compounds also was prompted by observations of the n.m.r. spectra of Grignard reagents and of organolithium compounds.

(1) For the previous paper in this series, see Tetrahedron Letters, 27, 25 (1960).

(2) K. S. Pitzer and H. S. Gutowsky, J. Am. Chem. Soc., 68, 2204 (1946).

(3) A. W. Laubengayer and W. F. Gilliam, ibid., 63, 477 (1941).

(4) P. H. Lewis and R. E. Rundle, J. Chem. Phys., 21, 986 (1953).

(5) N. Muller and D. E. Pritchard, J. Am. Chem. Soc., 82, 248 (1960).

(6) S. Brownstein, B. C. Smith, G. Erlich and A. W. Laubengayer, ibid., 82, 1000 (1960).

Experimental

Preparation of Compounds and Solutions.—Dimethylmercury was prepared by the method of Gilman and Brown.[7]

Trimethylaluminum was prepared by refluxing dimethylmercury with three times the stoichiometric quantity of aluminum in a nitrogen atmosphere. About one-third of the aluminum was foil and the remainder thin turnings. The product was removed by vacuum distillation from the reaction flask to a mercury-sealed storage container. The melting point was 14.5–15.0° (reported[2] m.p. 15°).

Dimethylzinc was obtained from the reaction of dimethylmercury and 20 mesh granular zinc. The reactants were maintained at the reflux temperature of dimethylmercury by distilling from time to time the accumulated product, b.p. 45–46°, through a 25 cm. Vigreux column. By this procedure 35 g. of dimethylmercury was converted into dimethylzinc in 48 hr.

Dimethylcadmium was prepared by the reaction of cadmium dichloride and methylmagnesium iodide[8] and purified by high-vacuum techniques. The product melted at 3.5–5.0° (reported[8] 4.5°). The n.m.r. spectrum of this product, and of each of the above products, consisted of only one peak and indicated the absence of any other hydrogen-containing compound.

Approximately 0.5 molar methylmagnesium iodide in diethyl ether was prepared from methyl iodide and magnesium turnings.

Approximately 0.5 molar methyllithium in diethyl ether was obtained from the reaction of methyl iodide and lithium shot.

The solvents were dried (benzene and cyclohexane over sodium, nitrobenzene over phosphoric anhydride, ether over sodium and pyridine over potassium hydroxide and then over phosphoric anhydride) and fractionally distilled. Also, benzene was fractionally crystallized twice.

The 5 mm. o.d. Pyrex sample tubes for n.m.r. spectra were filled with a long, 1.5-mm. o.d. capillary tube containing the reference and with a pure organometallic compound or solution to a height of 11 cm. The volumes of the metal alkyls were measured at 25° in a calibrated capillary tube. For concentrations greater than 1 M, the metal alkyl was transferred directly to the sample tube by high vacuum techniques. For concentrations less than 1 M, the metal alkyl was vacuum distilled into a 30-ml. flask containing 25 ml. of solvent and then an aliquot of the stirred solution transferred to the n.m.r. tube. The maximum concentra-

(7) H. Gilman and R. E. Brown, ibid., 52, 3314 (1930).

(8) H. Gilman and J. F. Nelson, Rec. trav. chim., 55, 518 (1936).

tion error was about 4%, and the error for most samples was much less.

N.m.r. Measurements.—All n.m.r. spectra were observed at 25.0 ± 1.5° and at 40.0 mc. with a Varian Associates High-resolution Spectrometer equipped with a flux stabilizer and an air turbine spinner. Chemical shifts were measured by the side-band technique. The reference and the precision of chemical shift measurements are indicated with each set of data. Relaxation times were determined from line widths which were measured by graphical interpolation with a precision of ±25%.

Results and Discussion

I.   The Trimethylaluminum–Dimethylcadmium System.—In an investigation of the possibility of intermolecular exchange, solutions of dimethylcadmium and trimethylaluminum were prepared and their n.m.r. spectra observed. Each n.m.r. spectrum consisted of only a single peak and, in view of the difference of chemical shifts of the pure compounds, indicated intermolecular exchange of methyl groups. The chemical shifts expressed in cycles per second (c./sec.) at magnetic fields above the external reference, benzene and the concentrations expressed in parentheses as fractions of the methyl groups belonging to trimethylaluminum are: 250.0 ± 0.5(0), 255.7 ± 0.5(0.21), 264.3 ± 0.5(0.49), 275.5 ± 0.5(0.89) and 279.5 ± 0.5(1). A plot of the chemical shift of these peaks as a function of the fraction of methyl groups on trimethylaluminum is fitted very closely by a straight line. This linear relation supports the hypothesis that the magnetic equivalence of the protons in solutions of dimethylcadmium and trimethylaluminum is due to exchange, since magnetic equivalence of the protons for other reasons would not give, in general, a linear function of the mole fraction of one component.

For protons exchanging between two sites, equation 1[9] can be used to estimate

$$\tau_A \leqq \frac{\sqrt{2}}{\pi(\nu_A - \nu_B)} \tag{1}$$

an upper limit for the average time τ_A that a proton remains on a site before exchange. The chemical shift separation of n.m.r. peaks from protons on the two sites is $(\nu_A - \nu_B)$ c./sec. in the absence of exchange, is less for slow rates of exchange and disappears for average lifetimes equal to or less than $\sqrt{2}/\pi(\nu_A - \nu_B)$. Equation 1 is applicable only for a small radio-frequency field H_1, equal mole fractions of the protons on the two sites and chemical shifts which are large relative to the reciprocal of the transverse relaxation time, T_2.

The following three solutions were prepared and their n.m.r. spectra observed: (A) 0.062 M trimethylaluminum in benzene, (B) 0.097 M dimethylcadmium in benzene and (C) 0.062 M trimethylaluminum and 0.097 M dimethylcadmium in benzene. The difference between the chemical shift of trimethylaluminum (A), relative to the solvent, and the chemical shift of dimethylcadmium (B), relative to the solvent, was 5 c./sec. Only one peak corresponding to methyl protons was observed for solution C, which contained equal mole fractions of methyl groups on aluminum and cadmium. The relaxation times of the methyl protons in solutions A and B were approximately 0.3 sec.

(9) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

The upper limit of the average lifetime of a methyl group bonded to a given metal atom in solution C of trimethylaluminum and dimethylcadmium was calculated with equation 1 and is 0.09 sec. If the exchange of methyl groups is assumed to be a second-order process, the lower limit of the rate constant can be calculated. The lower limit of this rate constant is estimated at 6 × 10^1 l. mole^{-1} sec.$^{-1}$.

II.   The Dimethylzinc–Dimethylcadmium System.—An investigation of the dimethylzinc–dimethylcadmium system was made to ascertain whether rapid exchange of methyl groups is unique to systems containing trimethylaluminum or is more general. The n.m.r. spectra of dimethylzinc–dimethylcadmium solutions containing the mole fractions 0, 0.071, 0.122, 0.530, 0.818 and 1.00 of dimethylzinc consisted of only a single rather broad peak for each solution. The chemical shifts of these peaks relative to benzene (external reference) were 250.0 ± 0.5, 251.5 ± 1.0, 252.5 ± 1.0, 263.0 ± 1.0, 270.5 ± 1.0, 274.0 ± 1.0, respectively. A plot of these data revealed a linear variation of chemical shift with concentration, and thus rapid exchange of methyl groups in this system is established.

Unlike dilute solutions of trimethylaluminum and dimethylcadmium in organic solvents, moderately dilute, ∼0.1 M, solutions of dimethylzinc and dimethylcadmium exhibit two methyl absorption peaks in their n.m.r. spectra. The average lifetime of methyl groups before exchange was estimated by the equations of Gutowsky.[9] These equations relate τ_A to the extent to which the resonance lines merge due to exchange.

For estimation of exchange rates, two assumptions were necessary. First, the approximation was made that the effect of exchange of methyl groups bonded to the cadmium isotopes of mass numbers 111 and 113 with the methyl groups bonded to zinc is small, and therefore the system can be treated as if there were two components of equal concentrations. (Equal mole fractions of dimethylzinc and dimethylcadmium always were used.) The proton magnetic resonance spectrum of dimethylcadmium consists of one large peak due to methyl groups bonded to the 112 ($I = 0$) isotope of cadmium and of two doublets due to methyl groups bonded to the 111($I = {}^1/_2$) and 113 ($I = {}^1/_2$) isotopes of cadmium. The spin–spin coupling constants $J_{\text{111Cd-1H}}$ and $J_{\text{113Cd-1H}}$ are approximately 60 c./sec. and differ by about 2 c./sec. Exchange of methyl groups between these different isotopes would produce a broadening of peaks and a shorter apparent relaxation time. To treat the exchange process rigorously, it would be necessary to consider the exchange of methyl groups on the different isotopes of cadmium with the methyl groups on zinc and also the exchange of methyl groups between the different isotopes of cadmium. Such a treatment would be extremely cumbersome at best.

The second assumption is that the mean of the observed transverse relaxation times T_2 may be assigned to both components. The present method is strictly applicable only if the relaxation times of

Table I

Data and Results for Exchange of Methyl Groups in Solutions of Dimethylzinc and Dimethylcadmium

Solvent	$[(CH_3)_2Zn]$,[a] mole/l.	$\delta\omega_e$, rad./sec.	$\delta\omega$, rad./sec.	τ_A, sec.	n	$k_{apparent}$, (mole/ l.)$^{1-n}$ sec.$^{-1}$	k_{n-2} (l./mole sec.)	τ_A (1 M), sec.
Nitrobenzene	0.247	21.6 ± 1.0	27.5	0.260 ± 0.097		8.9	15.6	
	.375	20.6	29.0	.199 ± .058		9.1	13.4	
	.492	18.7	30.0	.168 ± .044	1.6	9.1	12.1	0.11
	.619	17.7	31.3	.148 ± .033		9.0	10.9	
Pyridine	.18₅	19.0 ± 1.5	22.5	.473 ± .263		11.4	11.4	
	.24₀	17.3	22.6	.342 ± .151	2.0	12.2	12.2	.09
	.30₅	15.6	22.7	.282 ± .106		11.6	11.6	
	.38₅[b]	0	22.9	.18[b]				
Ether	.545	38.4 ± 1.0	39.2	.836 ± .646				
	.685	37.4	39.6	.351 ± .186	[d]	[d]	[d]	> .09
	.833	36.5	39.8	.273 ± .125				
	1.00[b]	0	39.7	.09[b]				
Benzene	0.79	26.6 ± 1.0	30.5 ± 1.0	.231 ± .057		5.2	5.5	
	1.35	22.6	32.4	.137 ± .015	1.8	5.7	5.4	.19[e]
	2.23	17.8	34.4	.106 ± .008		5.0	4.2	
	3.02[b]	0	34.7	.09[b]				
Cyclohexane	2.36	30.3 ± 1.0	39.6 ± 1.0	.124 ± .015		5.7	3.4	
	2.80	29.8	39.6	.121 ± .015	1.4	5.5	3.0	.18[e]
	3.40	29.0	40.8	.108 ± .010		5.7	2.7	

[a] Concentrations of $(CH_3)_2Zn$ and $(CH_3)_2Cd$ are equal. [b] At these concentrations the resonance components were merged. The data were treated as if merging had occurred at the precise concentrations listed. This treatment tends to give τ_A values that are too large and therefore, these τ_A values were not used in the computation of the apparent order and of τ_A (1 M). [c] The errors for τ_A were estimated by assuming the maximum indicated errors for $\delta\omega_e$ and $\delta\omega$ and an error of 25% in T_2. [d] Not calculated due to the large uncertainty in the value of τ_A. [e] These values slightly differ from those in ref. 1 due to a different correction for the effect of bulk magnetic susceptibility.

both components are the same or if $(T_2)^{-1}$ is small compared with $\delta\omega$, the separation in radians/sec. of peaks in the absence of exchange. The relaxation time of dimethylzinc in benzene and in cyclohexane is approximately 0.4 sec. and in diethyl ether, pyridine and nitrobenzene is approximately 0.25 sec. The relaxation times for dimethylcadmium are 0.3 sec. in benzene and in cyclohexane and 0.05 second in diethyl ether, pyridine and nitrobenzene. In benzene and cyclohexane solutions, the relaxation times of the two components are approximately equal and $(T_2)^{-1}$ is small compared to $\delta\omega$. In diethyl ether solutions, $(T_2)^{-1}$ is small compared to $\delta\omega$. However, in pyridine and nitrobenzene, the relaxation times of the two components are not equal and $(T_2)^{-1}$ is not small compared to $\delta\omega$. Since the relaxation times of the protons of dimethylzinc change, in comparison with the protons of dimethylcadmium, relatively little from solvent to solvent, the apparent decrease in the relaxation times of protons of dimethylcadmium in diethyl ether, pyridine and nitrobenzene may be due to an exchange of methyls between different isotopes of cadmium. Alternatively, the broadening in these three donor solvents may be due to the formation of short-lived complexes. Although the above approximations introduce some error, a fairly accurate estimate of the mean lifetimes before exchange probably can be made.

Solutions containing equimolar quantities, stated in Table I, of dimethylzinc and dimethylcadmium in benzene, cyclohexane, diethyl ether, pyridine and nitrobenzene were prepared. The experimentally observed separations $\delta\omega_e$ of the resonance components are presented in column 3 of Table I. Solutions of dimethylzinc or of dimethylcadmium at approximately the same concentrations as the samples containing both were prepared, and the

chemical shifts of the methyl protons relative to suitable references were measured and are presented in c./sec. in Table II. The separations $\delta\omega$ in the absence of exchange were obtained by graphical interpolation of the data in Table II and are given in column 4 of Table I. Corrections for the effect of bulk magnetic susceptibility were made.

The mean lifetimes τ_A of a methyl group before exchange were calculated[9] from the above data and are presented in column 5 of Table I.

If the rate expression has the simple form,

$$-\frac{d[(CH_3)_2Zn]}{dt} = k[(CH_3)_2Zn]^{n_1}[(CH_3)_2Cd]^{n_2} \quad (2)$$

the kinetic order, $n = n_1 + n_2$, of the reaction can be obtained from the slope of a plot of log τ_A as a function of log $[(CH_3)_2Zn]$. The plots for each solvent were linear over the range of concentrations investigated and led to the values of n listed in column 6 of Table I. Apparent order rate constants, presented in column 7 of Table I, were estimated from equation 3. Also, second-order

$$k_{apparent} = \frac{1}{\tau_A[(CH_3)_2Zn]^{n-1}} \quad (3)$$

rate constants were calculated and are tabulated in column 7 of Table I. For the comparison of pre-exchange lifetimes of methyl groups at concentrations of $1M$ in different solvents, the mean lifetimes $\tau_A(1\ M)$ were calculated from the apparent order and the apparent-order rate constant and appear in the final column of Table I.

The average of the apparent orders, excluding that for diethyl ether solutions, is 1.7 with a maximum deviation of 0.3. The order is not absolutely established in view of the approximations involved in the calculations; and, therefore, no detailed mechanistic speculations are presented. However,

Table II

Chemical Shifts of $(CH_3)_2Zn$ and $(CH_3)_2Cd$ in Various Solvents

Solvent	Reference	$(CH_3)_2Zn$ % by volume	δ,[b] c./sec.	$(CH_3)_2Cd$ % by volume	δ,[b] c./sec.
Cyclohexane	Benzene	33.3	285.0 ± 0.2	33.3	272.5 ± 0.2
		20.1	286.9	20.4	276.5
		14.4	287.2	15.7	279.2
Benzene	Cyclohexane	19.0	91.9 ± .2	20.2	83.2 ± 0.2
		11.2	95.6	10.1	89.5
		1.56	99.7	2.07	95.2
Diethyl ether	Benzene	19.8	298.2 ± .5	21.5	287.7 ± 1.0[a]
		15.5	299.0	18.2	289.7
		9.9	301.2	9.8	292.2
Pyridine	Cyclohexane	8.3	84.3 ± .5	5.6	80.4 ± 1.0[a]
		3.0	85.4	3.0	81.7
		1.95	85.8	2.0	81.7
		0.95	85.9	1.10	82.3
Nitrobenzene	Cyclohexane	4.26	99.5 ± .5	3.21	94.9 ± 1.0[a]
		2.96	99.9	2.07	95.4
		1.95	100.0	1.01	96.0

[a] Broad peaks. [b] The chemical shifts are upfield from the references.

it is established that the effect of the solvent is small. There is no correlation of the dielectric constant, which was varied from 2.0 for pure cyclohexane to 36.1 for pure nitrobenzene, with the rate of exchange; and, therefore, the rate-determining step is not primarily ionic. The rate of exchange increases slightly with increasing donor ability of the solvent and thus the activated complex may be stabilized by coördination. The strong coördination of pyridine to dimethylzinc is shown by the sharpening of the resonance components of the α-protons in solutions of dimethylzinc in pyridine and by the isolation of a solid pyridine-dimethylzinc complex in this research. Since the existence of an appreciable concentration of the dimer of dimethylcadmium in rapid equilibrium with the monomer could cause the anomalously high boiling point $((CH_3)_2Zn:46°, (CH_3)_2Cd:105.5°$ and $(CH_3)_2Hg:92°)$[10] and the line broadening mentioned earlier, the apparent molecular weight of dimethylcadmium in benzene was investigated. Cryoscopic measurements in dilute benzene indicated a molecular weight of approximately 141 compared with the calculated value of 142.5 for the monomeric species. In view of the apparent molecular weight and a Trouton constant of 22.3,[11] the extent of association is probably slight. The existence of stable methyl bridges in several compounds, including derivatives of platinum, aluminum and beryllium, suggests that the intermediate in the intermolecular exchange process may involve a bridging methyl group.

III. The Dimethylzinc-Dimethylmercury and the Dimethylcadmium-Dimethylmercury Systems.

(10) E. Krause and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, pp. 115, 124, and 173.

(11) C. H. Bamford, D. L. Levi and D. M. Newitt, J. Chem. Soc., 40, 468 (1946).

—The possibility of intermolecular exchange of methyl groups in these systems was investigated. An equimolar solution of dimethylzinc and dimethylmercury exhibited two resonance components with the sharpness and a separation comparable to that estimated, from the pure compounds, for no exchange. A similar observation was made with the dimethylcadmium-dimethylmercury system. The mean lifetime of a methyl group before exchange must be greater than $10\sqrt{2}/\pi\ (\nu_A - \nu_B)$, or 0.08 sec. for the former and 0.14 sec. for the latter system.[12] The small magnitudes of these lower limits of τ_A are a consequence of $\delta\omega$ being relatively large, compared with $\delta\omega$ for the dimethylzinc-dimethylcadmium system; and τ_A for the dimethylmercury solutions may be much larger than the stated lower limits.

IV. Methylmagnesium Iodide and Methyllithium.—The n.m.r. spectrum of methylmagnesium iodide in diethyl ether consisted of a single rather broad peak. The exact nature of Grignard reagents is unknown and they are generally considered to be very complex. In view of the lability of methyl groups in other organometallic systems, the presence of this broad peak is indicative of an exchange process between different components. The n.m.r. spectrum of methyllithium under comparable conditions consisted of a single sharp line. Investigations of mixtures of Grignard reagents and organolithium compounds now are planned.

(12) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 64.