higher than the corresponding value in water (*e.g.*, acetylactone, 8.95[15]; 2-thenoyltrifluoroacetone, 6.38[16]; dimedone, 5.22[17]). Values reported for pK_a in 75 vol. % dioxane–25 vol. % water are somewhat higher than those obtained by us in methanol and ethanol: acetylacetone, 12.70[18]; benzoylacetone, 12.85[18]; dibenzoylmethane, 13.75[18]; 2-thenoyltrifluoroacetone, 8.64[19] and 9.1[18]; and dimedone, 10.16.[17] The values in water and the dioxane–water mixture are not inconsistent with ours when one considers the differences in basic character of the media and the varying dielectric constants—water, *ca.* 78; dioxane–water mixture, *ca.* 15; methanol, *ca.* 33; and ethanol, *ca.* 24.

The pK values for the dissociation of the complexes of alkali metal ions with the anions of the β-diketones generally follow the expected trend relative to metal ion size. Except for dimedone, for any particular β-diketone anion there is a substantial decrease in stability of the complex with increasing size of the alkali metal ion. It is interesting to note that for dimedone there is little difference between the stabilities of the lithium and sodium complexes in methanol or between the same complexes in ethanol. A possible explanation for this fact lies in the structural inability of the anion of dimedone to function as a chelating agent; the pK values of the complexes formed therefore reflect weak nonchelating interactions of the strongly solvated lithium ion and of the more weakly solvated sodium ion with the anion of the diketone.

Examination of the data of Table I shows that for the diketones which can act as chelating agents (all except dimedone) there is no clear correlation between the pK_a values of the ketones and the dissociation constants of the complexes in either solvent. However, all pK values in ethanol are higher than those for corresponding complexes in methanol. This fact is consistent with the lower dielectric constant of ethanol.

In conclusion, although the values reported by Fernelius and Van Uitert[2] for the stability constants of the complexes of alkali metal ions with the anion of dibenzoylmethane in 75% dioxane–25% water originally seemed high relative to the large water content of the mixture, our studies in anhydrous methanol and ethanol indicate that their values are reasonable if no preferential solvation effects by water molecules were operative in their medium.

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Nuclear Magnetic Resonance Studies on Exchange Reactions of Group III Alkyl Addition Compounds[1]

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Received July 29, 1965

The exchange reaction which takes place between trimethylgallium and the trimethylgallium–trimethylamine addition compound has been studied by n.m.r. spectroscopy. The reaction has been shown to proceed through a dissociation step followed by recombination.

$$\mathrm{Ga(C_3H)_3 \cdot N(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ga(CH_3)_3 + N(CH_3)_3}$$

The over-all activation energy for this exchange is 23 kcal./mole. Preliminary investigations have also been carried out on the systems trimethylgallium, trimethylgallium–trimethylphosphine and trimethylgallium, trimethylgallium–dimethyl ether.

There has been growing interest in the exchange reactions of group III alkyls and their addition compounds. A number of studies have been reported on the self-exchange of alkyl groups on aluminum,[3-5] gallium,[6] and thallium.[7] The reports on aluminum have been quantitative with respect to the rate of the exchange reaction and a mechanism has been proposed; however, the other studies have been much more limited in scope. Work has also been reported

[1] Presented in part by J. B. DeRoos, M. T. Emerson, and J. P. Oliver at the 148th National Meeting of the American Chemical Society, Aug. 1964, Abstracts, p. O-21; and by J. B. DeRoos and J. P. Oliver at the 149th National Meeting of the American Chemical Society, April 1965, Abstracts, p. M96.

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on the exchange of addition compounds, particularly those of boron. Several reports in the literature show that compounds such as $(CH_3)_3B\cdot O(CH_3)_2$[8,9] and $F_3B\cdot O(CH_3)_2$ undergo rapid exchange with excess base[10-12] while other workers have observed that $RBH_2\cdot N(CH_3)_3$ and $(n\text{-}Bu)_3P$ undergo relatively slow exchange[13] which may be studied by conventional techniques. The present study extends quantitative measurements on the rate of exchange reactions to alkylgallium addition compounds and provides for the first time clear evidence for a dissociation exchange process.

This is to be contrasted with other studies on exchange reactions of organometallic systems such as the self-exchange of $Al_2(CH_3)_6$, which has been shown to proceed through a low-energy (10 ± 5 kcal./mole) nondissociative process,[4] and other metal–alkyl exchanges which appear to proceed through bimolecular displacement reactions.[3,14] It should also be pointed out that in similar n.m.r. studies, other group III derivatives indicate slow or no exchange and show in the case of $Ga(CH_3)_3$ that this material is monomeric. This has been confirmed by molecular weight measurements.[15]

The second type of experiment which must be considered is best illustrated by the work on boron trifluoride–base systems.[8,10,11] In these studies it has been shown that several different paths for exchange exist and are operative under different conditions. One of these may be described by the equation

$$F_3B\cdot\text{base (1)} + \text{base (2)} \rightleftharpoons F_3B\cdot\text{base (2)} + \text{base (1)} \quad (1)$$

where the free base is in large excess. The activation energy for this type of process is less than the dissociation energy for the addition compound in question. Another path is described by the bimolecular reaction

$$F_3B^*\cdot\text{base (1)} + F_3B\cdot\text{base (2)} \rightleftharpoons F_3B^*\cdot\text{base (2)} + F_3B\cdot\text{base (1)} \quad (2)$$

This path takes precedence when there is little or no free base present and again proceeds with an activation energy less than that required for the dissociation of the complex. A third possible mechanism for the exchange is for the addition compound to undergo a dissociation followed by a rapid recombination step

$$F_3B\cdot\text{base (1)} \xrightarrow{\text{slow}} F_3B + \text{base (1)} \quad (3)$$

$$F_3B + \text{base (2)} \xrightarrow{\text{fast}} F_3B\cdot\text{base (2)} \quad (4)$$

The latter reaction path has been ruled out in most instances because the dissociation energies for the group III addition compounds are greater than the reported activation energies for the exchange processes. However, recent evidence indicates that it must be considered as well as the other more complex processes.[11] Brownstein[10] reports the only study of BF_3–base systems where excess acid is present. His results show the activation energy for the process is much less than the dissociation energy for the addition compound, thus indicating that a bimolecular displacement reaction is occurring in this system.

These studies provide some preliminary information on the course of exchange reactions of group III alkyl derivatives and of their addition compounds. Clearly, they do not allow predictions to be made concerning the course of any particular reaction nor do they provide a clear understanding of the detailed mechanism. Thus, considerably more work must be undertaken to illucidate the course of these exchange reactions.

The present work provides a kinetic study on a previously unreported system $Ga(CH_3)_3 + Ga(CH_3)_3\cdot$base and shows that when the base present is trimethylamine the reaction proceeds by a path described by eq. 3 and 4, unlike the previously reported example in which excess Lewis acid was present.

Experimental

Trimethylgallium was prepared by the reaction of $Hg(CH_3)_2$ with gallium metal by essentially the same procedure described by Dennis.[16] It was found that a catalyst, either mercuric chloride or mercurous chloride, had to be added to the $Hg(CH_3)_2$ in order to make the metal exchange proceed at a reasonable rate with refluxing $Hg(CH_3)_2$. The crude product was purified by preparative scale gas chromatography using a closed system similar to that previously described.[17] Good separation of $Hg(CH_3)_2$ from $Ga(CH_3)_3$ was obtained with a minimum of decomposition when a 3-ft. column packed with Teflon coated with 5% silicone oil was operated at room temperature. The pressure drop across the column was approximately 200 mm. Trimethylamine and dimethyl ether were purchased from the Matheson Co., while cyclopentane was obtained from Matheson Coleman and Bell. Each of these materials was dried over sodium metal and distilled before use. Freon 11 (CCl_3F) was obtained from the Matheson Co. and dried over magnesium perchlorate before use. Trimethylphosphine was prepared by the reaction of PBr_3 with methyl Grignard reagent and purified by trap to trap distillation in the vacuum system. The purity was then determined by n.m.r. spectroscopy, which indicated that no other materials were present.

All of the materials described above were transferred to the high vacuum system following purification and were stored in Dry Ice–acetone baths until used for sample preparation. All samples were prepared on the high vacuum system using standard techniques. The $Ga(CH_3)_3$, base ($O(CH_3)_2$, $N(CH_3)_3$, or $P(CH_3)_3$), and cyclopentane used as an internal standard were measured as gases in a precalibrated volume and then condensed directly into the n.m.r. sample tube. The Freon 11 was measured in a calibrated pipet also attached to the vacuum system and then transferred by distillation to the n.m.r. tube. The sample was sealed off and stored in liquid nitrogen until the n.m.r. studies were made.

All n.m.r. studies were carried out using a Varian D.P. 60 spectrometer equipped with a modified Varian low-temperature probe.[18] The temperature in the insert was controlled to ±0.3° at temperatures between −20 and +50° and to ±1° below −20°.

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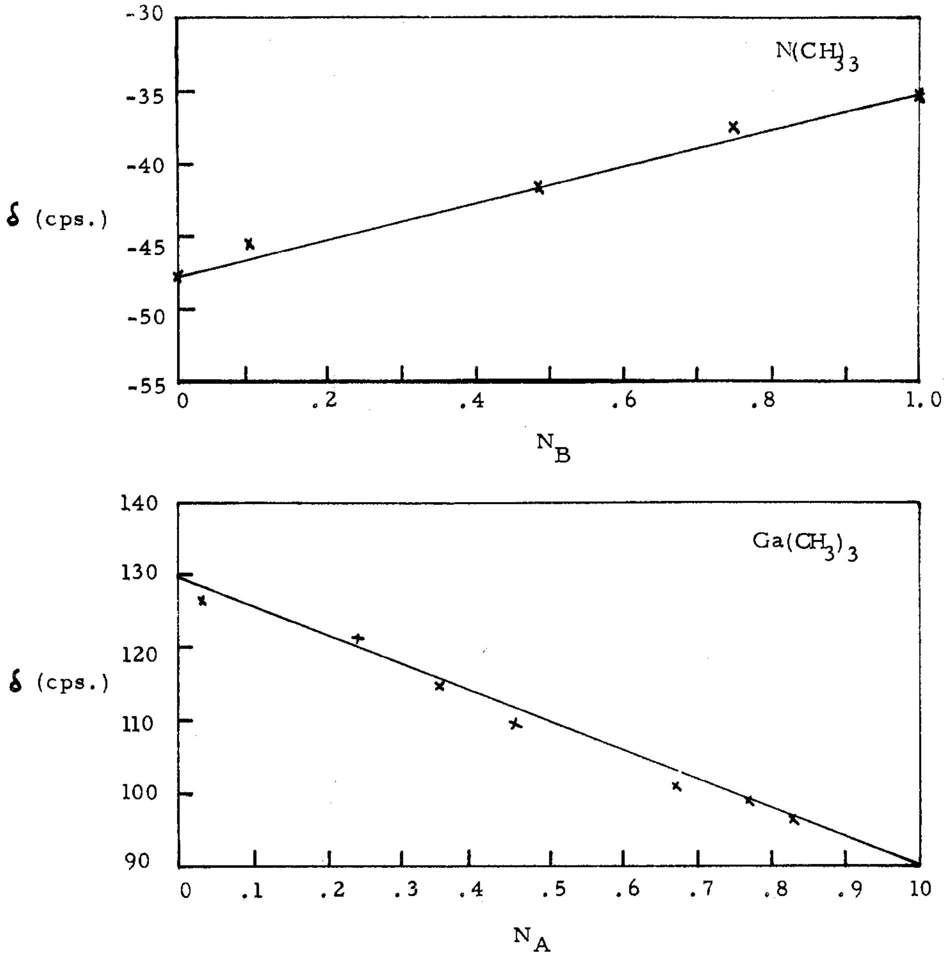

Figure 1.—The dependence of the chemical shift of $Ga(CH_3)_3$ and $N(CH_3)_3$ on concentration of either excess $Ga(CH_3)_3$ or $N(CH_3)_3$.

The temperature in the insert immediately next to the sample was continuously monitored by a thermocouple circuit to ensure reasonable temperature stability.

The spectra were calibrated by linear interpolation between audiofrequency side bands of cyclopentane, which was used as an internal standard in all cases. All reported values are the average of five or more traces of the spectrum. The line widths reported were determined by the same technique, with the measurements representing the width at half-height of the line. Errors for line-width measurements vary considerably depending on concentration, temperature, and other factors such as spectrometer noise. In general, errors for lines with $\nu_{1/2} < 10$ c.p.s. are between 0 and 0.5 c.p.s.; for lines with $\nu_{1/2} > 10$ c.p.s. the average error is from 0.5 to 1.5 c.p.s. with the error increasing rapidly with increasing line widths.

Results and Discussion

The exchange reactions which occur in the system $Ga(CH_3)_3$–$N(CH_3)_3$ have been investigated over a wide range of concentration and temperature in order to determine the conditions under which quantitative data can best be obtained for the rate of the exchange reaction. Limited studies have also been carried out with the systems $Ga(CH_3)_3$–$P(CH_3)_3$ and $Ga(CH_3)_3$–$O(CH_3)_2$.

Prior to the kinetic studies it was determined that the chemical shifts of $Ga(CH_3)_3$ and of $Ga(CH_3)_3 \cdot N(CH_3)_3$ were independent of concentration, within the limits of error (±0.2 c.p.s.) of the measurement of line position in either Freon 11 or in cyclopentane between 5 and 100% concentration. It was also shown that the chemical shift of free $Ga(CH_3)_3$ was independent of temperature between 80 and −40°.

In all cases the quantitative kinetic data were obtained by n.m.r. line-broadening techniques. The concentration dependence data were collected at a temperature such that conditions of slow exchange exist (11°), that is, the lifetimes of trimethylgallium (τ_A) and the trimethylgallium adduct (τ_{AB}) are large compared to the reciprocal of the difference between the chemical shifts of the two species ($(\delta_A - \delta_{AB})^{-1}$).[19]

Proof that rapid chemical exchange occurs between $Ga(CH_3)_3$ and $Ga(CH_3)_3 \cdot N(CH_3)_3$ and between $N(CH_3)_3$ and $Ga(CH_3)_3 \cdot N(CH_3)_3$ at 30° can readily be ascertained from Figure 1, which shows the linear dependence of the chemical shift of the single resonance line for $Ga(CH_3)_3$ and $N(CH_3)_3$ on concentration.

Low-temperature studies on the samples which contain excess base show no significant line broadening. This can be seen in Table I. These results clearly indicate that the exchange

$$N^*(CH_3)_3 + Ga(CH_3)_3 \cdot N(CH_3)_3 \rightleftharpoons Ga(CH_3)_3N^*(CH_3)_3 + N(CH_3)_3 \quad (5)$$

is very rapid and proceeds through a low-energy pathway, probably through a bimolecular collision which is

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TABLE I

THE TEMPERATURE DEPENDENCE OF $\nu_{1/2}$ FOR $N(CH_3)_3$ IN THE $Ga(CH_3)_3 \cdot N(CH_3)_3$ SYSTEM WITH EXCESS $N(CH_3)_3$ PRESENT

°C.	$\delta(CH_3)_3$, c.p.s.	$\nu_{1/2}$, c.p.s.
+27	38.2	0.79
+8	38.8	0.71
−30	38.0	0.62
−80	38.0	Narrow[a]

[a] The line width was not measured but observed on the oscilloscope and compared with the internal standard.

controlled by the rate of diffusion of the molecules in solution. This process appears to be analogous to those examples of BF_3 where a large excess of base was present.[11] Current instrumentation available in this laboratory does not allow this reaction to be studied at sufficiently low temperatures to confirm this postulated mechanism.

Variable temperature studies on the n.m.r. line width ($\nu_{1/2}$) on samples which contain excess $Ga(CH_3)_3$ in the presence of $Ga(CH_3)_3 \cdot N(CH_3)_3$ show that $\nu_{1/2}$ decreases with increasing temperature and increases with lower temperature. On cooling the sample to approximately 0° two resonance lines appear, one located at 89.8 c.p.s. (1.495 p.p.m.) above cyclopentane, attributed to free $Ga(CH)_3$, and the other at 129.7 c.p.s. (2.161 p.p.m.) upfield from cyclopentane, arising from the $Ga(CH_3)_3$ present in the addition compound. This can be seen in Table II, which shows the temperature dependence of the line width $\nu_{1/2}$ for the single line above room temperature and for the two lines observed below room temperature.

TABLE II

THE TEMPERATURE DEPENDENCE OF THE LINE WIDTH $\nu_{1/2}$ FOR THE $Ga(CH_3)_3$–$Ga(CH_3)_3 \cdot N(CH_3)_3$ SYSTEM

°C.	$\nu_{1/2}$ $Ga(CH_3)_3$, c.p.s.	$\nu_{1/2}$ $Ga(CH_3)_3 \cdot N(CH_3)_3$, c.p.s.
5.3	1.90	2.97
6.8	1.73	3.31
8.6	2.41	4.02
10.6	2.21	4.80
12.8	2.80	6.54
15.0	4.46	9.62
18.6	5.87	16.70
22.2	8.69	...
24.0	10.67	...
26.3	15.16	...
29	29[a]	
38	25.2	
42	8.32	
60	1.49	
73	.78	

[a] At 29° the two signals from $Ga(CH_3)_3$ and $Ga(CH_3)_3 \cdot N(CH_3)_3$ merge into a single resonance absorption.

TABLE III

CONCENTRATION DEPENDENCE OF THE LIFETIMES AND RATE CONSTANTS FOR THE EXCHANGE $Ga(CH_3)_3$ + $Ga(CH_3)_3 \cdot N(CH_3)_3$

A,[a] M	AB,[a] M	$1/\tau_A$, sec.$^{-1}$	$1/\tau_{AB}$, sec.$^{-1}$ [b]	$(1/\tau_A)/(AB/A)$[b]
0.022	0.606	...	14.83	...
0.036	0.720	...	16.90	...
0.068	0.214	52.21	18.79	16.6
0.242	0.447	26.26	13.16	13.3
0.280	0.342	17.78	15.39	12.4
0.406	0.196	7.70	16.18	14.5
0.472	0.772	20.39	13.07	18.1
0.492	0.240	8.83	16.15	14.2
0.786	0.244	5.78	15.36	18.2
1.040	0.240	6.09	16.78	...

[a] A is $Ga(CH_3)_3$; AB is $Ga(CH_3)_3 \cdot N(CH_3)_3$. [b] $1/\tau_{AB}$ and $(1/\tau_A)/(AB/A)$ are equal to k_2K_e for the treatment given in this paper.

The concentration dependence of the lifetimes of $Ga(CH_3)_3$ (τ_A) and of $Ga(CH_3)_3 \cdot N(CH_3)_3$ (τ_{AB}) were studied at 11° for this reaction and are seen in Table III. Under these conditions the lifetime, τ, is related to the line width by the expression

$$\frac{1}{\tau} = \pi(\nu_{1/2} - \nu_{1/2}{}^0) \tag{6}$$

where $\nu_{1/2}$ is the measured line width and $\nu_{1/2}{}^0$ is the line width for the species undergoing no observable exchange. It is clear that the lifetime of $Ga(CH_3)_3 \cdot N(CH_3)_3$, τ_{AB}, is independent of concentration within the limits of error, while the lifetime of $Ga(CH_3)_3$, τ_A, is concentration dependent.

Under these conditions, a simple bimolecular process similar to that postulated for the exchange with excess $N(CH_3)_3$ is ruled out since the lifetime for the disappearance of $Ga(CH_3)_3 \cdot N(CH_3)_3$ is concentration independent, indicating that this reaction proceeds through a first-order process. An alternate mechanism which leads to a rate expression consistent with the experimentally determined lifetimes is given by the equation

$$Ga(CH_3)_3 \cdot N(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ga(CH_3)_3 + N(CH_3)_3 \tag{7}$$

The rate of disappearance of $Ga(CH_3)_3$ is then given by

$$\frac{-d\,[Ga(CH_3)_3]}{dt} = k_2[Ga(CH_3)_3]\,[N(CH_3)_3] \tag{8}$$

or expressed in terms of lifetime

$$\frac{1}{\tau_A} = \frac{\dfrac{-d\,[Ga(CH_3)_3]}{dt}}{[Ga(CH_3)_3]} = k_2[N(CH_3)_3] \tag{9}$$

then, upon substitution of the proper form of the equilibrium constant for $[N(CH_3)_3]$

$$K_e = \frac{[Ga(CH_3)_3]\,[N(CH_3)_3]}{[Ga(CH_3)_3 \cdot N(CH_3)_3]} \tag{10}$$

one obtains

$$\frac{1}{\tau_A} = k_2K_e\,\frac{[Ga(CH_3)_3 \cdot N(CH_3)_3]}{[Ga(CH_3)_3]} \tag{11}$$

This gives a concentration dependence for τ_A which may be tested by plotting $1/\tau_A$ *vs.* $[Ga(CH_3)_3 \cdot N(CH_3)_3]/[Ga(CH_3)_3]$. The results of this are seen in Figure 2. The slope of this line is equal to K_ek_2 and is 15.9.

An expression based on eq. 7 may be derived in a similar manner for the lifetime of $Ga(CH_3)_3 \cdot N(CH_3)_3$, τ_{AB}, and takes the form

$$\frac{1}{\tau_{AB}} = k_2K_e = k_1 \tag{12}$$

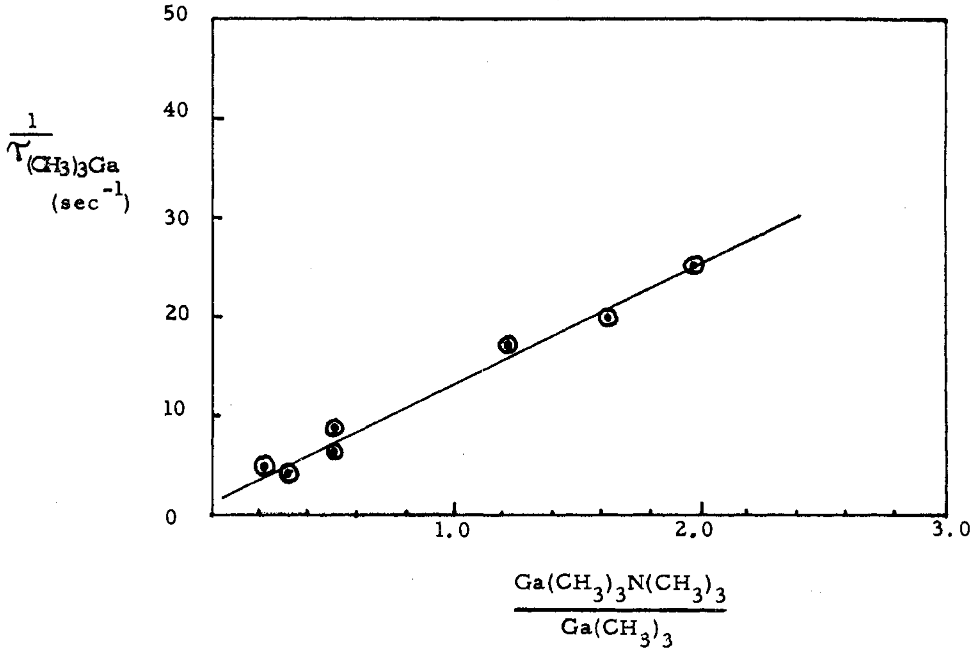

Figure 2.—A test of the rate expression, $1/\tau_A$ *vs.* the concentration ratio $[Ga(CH_3)_3 \cdot N(CH_3)_3]/[Ga(CH_3)_3]$. The slope of the line is equal to $K_e k_2$ sec.$^{-1}$ (15.9 sec.$^{-1}$).

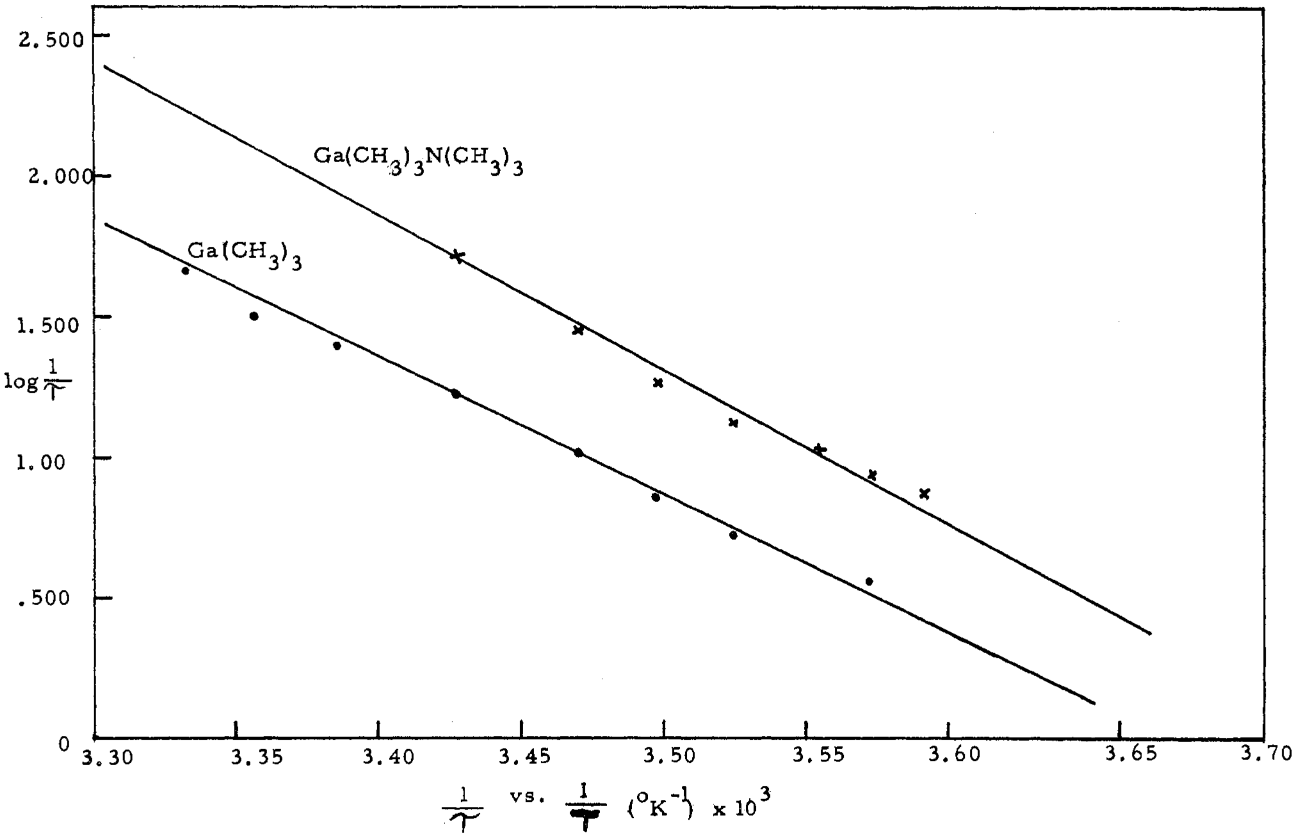

Figure 3.—The least-squares plot for activation energy, $1/\tau$ *vs.* $1/T$ (°K.$^{-1}$). A is obtained from $Ga(CH_3)_3$ (ΔE = 22.3 kcal./mole) while B is from $Ga(CH_3)_3 \cdot N(CH_3)_3$ (ΔE = 25.3 kcal./mole).

which is independent of the concentration. Values for $1/\tau_{AB}$ for samples having different concentrations are given in Table III. The average value for these is 15.7, which is in excellent agreement with the value obtained from Figure 3.

The possibility that several additional reactions such as those given by eq. 2 and 5 occur was considered but discarded, since any significant contribution by these paths would alter the concentration dependence of τ_A and τ_{AB}.

The one remaining feature of this reaction which must be dealt with is the activation energy for the exchange processs. Figure 3 is a plot of log $1/\tau$ *vs.* $1/T$ (°K.$^{-1}$) for $Ga(CH_3)_3$ and $Ga(CH_3)_3 \cdot N(CH_3)_3$, from which the activation energy may be calculated. The data for $Ga(CH_3)_3$ gave a value of 22.3 kcal./mole, while those for $Ga(CH_3)_3 \cdot N(CH_3)_3$ yield a value of 25.3 kcal./mole. This is reasonable agreement for the two measurements of the activation energy. Since this is slightly larger than the reported dissociation energy for $Ga(CH_3)_3 \cdot N(CH_3)_3$ (21 kcal./mole)[20] all of the data are in agreement with the proposed dissociation mechanism for the exchange reaction when excess $Ga(CH_3)_3$ is present.

Table IV

Chemical Shifts and Coupling Constants for $Ga(CH_3)_3$ Addition Compounds

Compound	δ_A, p.p.m.[a]	δ_B, p.p.m.[a]	J_{XH}, c.p.s.	$J_{XH'}$, c.p.s.
$N(CH_3)_3$		−0.589		
$P(CH_3)_3$		0.592	2.68	
$O(CH_3)_2$		−1.678		
$Ga(CH_3)_3$	1.495			
$Ga(CH_3)_3 \cdot N(CH_3)_3$	2.161	−0.797		
$Ga(CH_3)_3 \cdot P(CH_3)_3$	2.085	0.360	6.07	8.44
$Ga(CH_3)_3 \cdot O(CH_3)_2$	2.047	−1.881		

[a] Chemical shifts are given in p.p.m. relative to cyclopentane, which was used as an internal reference.

Preliminary investigations have been carried out on two other systems, $Ga(CH_3)_3 \cdot O(CH_3)_2$ and $Ga(CH_3)_3 \cdot P(CH_3)_3$, which are at least in qualitative agreement with the exchange process postulated above. In the $Ga(CH_3)_3 \cdot O(CH_3)_2$ case, the exchange process could not be slowed sufficiently to allow the reaction to be followed by line broadening when either excess $O(CH_3)_2$ or $Ga(CH_3)_3$ was present. Thus, it is not possible to establish a mechanism for this exchange; however, the rate of this reaction is in line with the low dissociation energy of $Ga(CH_3)_3 \cdot O(CH_3)_2$ (9 kcal./mole).[21] For the $Ga(CH_3)_3 \cdot P(CH_3)_3$ case, line broadening could be observed below 0° and three sharp resonance lines were observed at −50°, as seen in Figure 4. The line at 90 c.p.s. (1.5 p.p.m.) is again attributed to free $Ga(CH_3)_3$, while the two lines upfield are from the $Ga(CH_3)_3$ in the $Ga(CH_3)_3 \cdot P(CH_3)_3$. The splitting of the protons in this case is due to long-range coupling between the protons and phosphorus. The fact that this exchange process proceeds at a rate intermediate between that for $Ga(CH_3)_3 \cdot N(CH_3)_3$ and $Ga(CH_3)_3 \cdot O(CH_3)_2$ is in agreement with the known dissociation energy for $Ga(CH_3)_3 \cdot P(CH_3)_3$ (18 kcal./mole),[21] which lies intermediate between the dissociation energies for the other adducts. This reaction is now under further investigation and a detailed mechanism will be given later.

All of the chemical shifts for the addition compounds and the P–H coupling constant for the phosphine adduct are collected in Table IV for convenience.

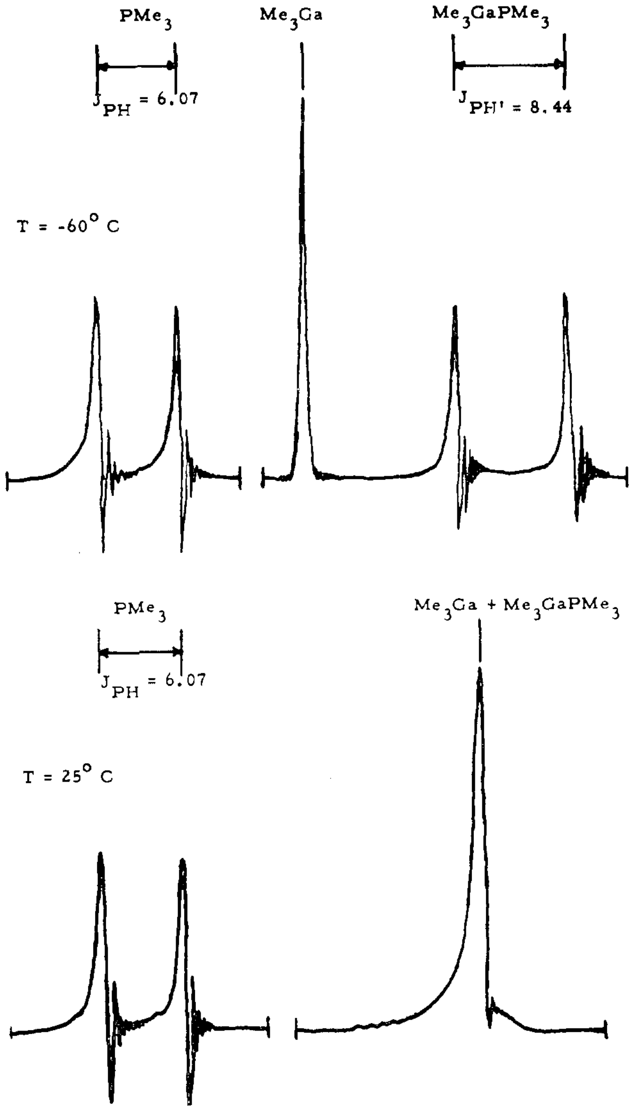

Figure 4.—The n.m.r. spectrum of $Ga(CH_3)_3 \cdot P(CH_3)_3$ with excess $Ga(CH_3)_3$ at 27 and −50°.

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