

NUCLEAR MAGNETIC RESONANCE STUDIES OF
EXCHANGE REACTIONS BETWEEN
ORGANOLITHIUM AND ORGANOMERCURY COMPOUNDS

by G82

STANLEY DEAN HALL

B.A., Sterling College 1967

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

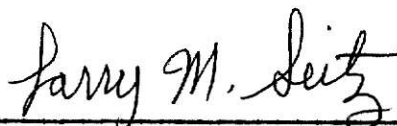
MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1970

Approved by:



Major Professor

LD
2668
T4
1970
H35
C.2

ii

TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iv
I. INTRODUCTION AND HISTORICAL BACKGROUND	1
II. EXPERIMENTAL	6
A. Manipulation of Air Sensitive Compounds	6
B. Reagents and Solvents	10
C. Preparation of NMR Samples	12
D. NMR and Gas Chromatography	15
E. Analysis of NMR Data	16
III. RESULTS AND DISCUSSION	18
A. Methyllithium-Dimethylmercury Exchange in Diethylether	18
Observations	18
Mechanisms of Exchange	25
B. Methyllithium-Dimethylmercury Exchange in THF	37
Observations	37
Mechanisms of Exchange	40
C. Methyllithium-Dimethylmercury Exchange in DME	45
Reaction of CH_3Li with DME	45
NMR of DME	46
$\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ Exchange in DME	49
IV. SUMMARY OF $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ EXCHANGE	55
V. DIMETHYLMERCURY SELF EXCHANGE	62
ACKNOWLEDGEMENTS	77
LITERATURE CITED	78
APPENDIX	80

LIST OF TABLES

Table 1.	Methylithium Linewidth as a Function of Li/Hg in Ether at $+36^{\circ}\text{C}$	25
Table 2.	Methylithium Linewidth as a Function of Li/Hg in THF at -18°C	40
Table 3.	Methylithium Linewidth as a Function of Li/Hg in DME at -78°C	53

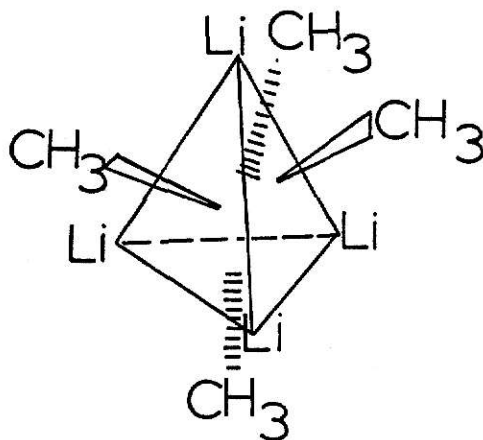
LIST OF FIGURES

Figure 1.	Schematic Drawing of Dry Box and Continuous Flow Atmosphere Purification System	8
Figure 2.	Drawing of Specially Modified 5mm NMR Tube Used in Sealing off Samples from the Atmosphere	14
Figure 3.	Methyl lithium Linewidth as a Function of Temperature in Ether, THF, and DME	20
Figure 4.	Temperature Dependence of Proton NMR Spectra of $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ Exchange in Diethylether	23
Figure 5.	Temperature Dependence of Proton NMR Spectra of $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ Exchange in THF	39
Figure 6.	Concentration Dependence of Methyl lithium Linewidth in THF at -18°C	43
Figure 7.	Proton NMR Spectrum of $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ in DME at $+34^\circ\text{C}$	48
Figure 8.	Temperature Dependence of Proton NMR Spectra of $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ Exchange in DME	52
Figure 9.	Solvent Dependence of NMR Spectra for Methyl Group Exchange between CH_3Li and $(\text{CH}_3)_2\text{Hg}$	57
Figure 10.	$\log 1/\tau_{\text{CH}_3\text{Li}}$ as a Function of $1/T(^{\circ}\text{K})$ for Ether, THF, and DME	59
Figure 11.	Proton NMR of the $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ System in THF and DME at low temperature	64
Figure 12.	Temperature Dependence of Proton NMR Spectra of $\text{C}_6\text{H}_5\text{HgCH}_3/(\text{CH}_3)_2\text{Hg}$ System in Ether and THF	67
Figure 13.	Theoretical ^1H -NMR Spectra for ^{199}Hg - ^{200}Hg Methyl Group Exchange	70
Figure 14.	$\log 1/\tau_{\Lambda}$ as a Function of $1/T(^{\circ}\text{K})$ for ^{199}Hg - ^{200}Hg Methyl Group Exchange in Ether	74

I. INTRODUCTION AND HISTORICAL BACKGROUND

Within the past ten years, chemists have come to realize the significance of nuclear magnetic resonance spectroscopy, especially in application to kinetics problems. NMR lends itself well to the study of rapid reactions and exchanges. The field of organolithium chemistry has been studied extensively using NMR to obtain exchange rate and activation energy parameters, as well as deducing exchange mechanisms.

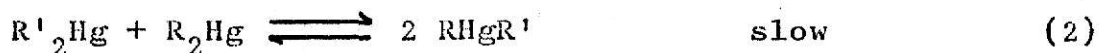
Methyl lithium has been shown to be a tetramer in the solid state (1), and in diethylether and THF using colligative property measurements (2). Seitz and Brown (3) used ^7Li NMR at low temperatures to verify the tetramer structure of a mixed $\text{C}_2\text{H}_5\text{Li}$ and CH_3Li species. The structure is thought to consist of lithium atoms at the corners of a regular tetrahedron. Surrounding the tetrahedron are methyl groups, each with an unfilled sp^3 hybrid orbital directed towards a face of the tetrahedron. Thus, a four center, two electron bond is formed with each methyl group and three lithium atoms.



McKeever, et al. (4), have verified this tetramer structure by noting ^7Li - ^{13}C scalar coupling in the ^7Li magnetic resonance spectrum. However, Brown, et al. (5), have noted that the metal-metal bond order between lithium atoms may be zero, due to the absence of observable ^7Li - ^6Li scalar spin-spin coupling at low temperature.

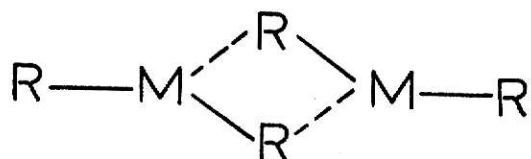
Ordinarily, alkyl group exchange where an alkyl mercury compound is involved is slow. For example, Dessy, et al. (6), observed no exchange between $(\text{CH}_3)_2\text{M}$ and $(\text{CD}_3)_2\text{Hg}$, (where $\text{M}=\text{Zn}$, Cd , or Hg), after eight days at room temperature. Comparably, other Group II dialkyls exchange very rapidly at room temperature. It has been shown that $(\text{CH}_3)_2\text{Cd}$ exchanges methyl groups rapidly with both $(\text{CH}_3)_2\text{Zn}$ and $(\text{CH}_3)_2\text{Mg}$. Also, it has been shown that $(\text{CH}_3)_2\text{Zn}$ exchanges rapidly with $(\text{CH}_3)_2\text{Mg}$, even at -103°C in diethyl ether (7). However, all three of the above mentioned Group II dialkyls exchange rather slowly with $(\text{CH}_3)_2\text{Hg}$ (8).

It may also be noted that with each of the Group II metals, heteroalkyl exchange is rapid, while it is slow with R_2Hg (9).



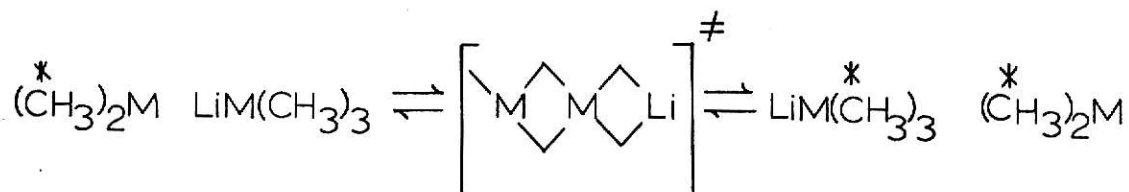
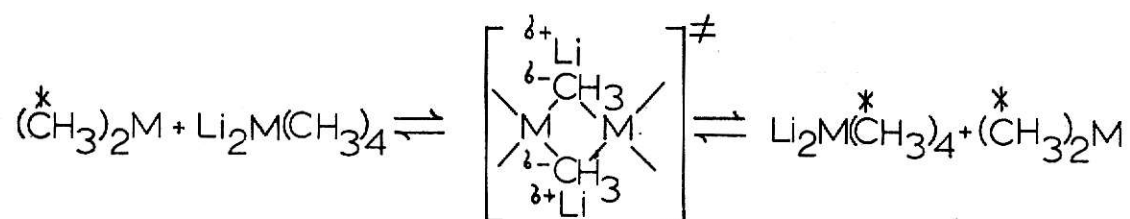
The apparent inertness of dialkyl mercury compounds arises from two factors (6). First, the size of the mercury atom is large enough to prevent the metal-metal approach necessary in the transition state for exchange to occur. Secondly, the ds hybridization used by the mercury atom may prevent distortion of the 180° bond angle necessary for the second order alkyl-bridged

transition state to occur as depicted below.

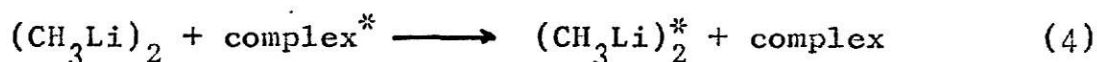


It might be noted that alkyl group exchange occurs rapidly among Group III trialkyl compounds, i.e., where the size of the metal allows, presumably because the trialkyl compounds are already close to the proper orientation needed for the alkyl-bridged transition state.

In addition to exchanging rapidly among themselves, $(\text{CH}_3)_2\text{M}$ ($\text{M}=\text{Mg}$, Zn or Cd) compounds rapidly exchange methyl groups with complexes of the type $\text{Li}_2\text{M}(\text{CH}_3)_4$ or $\text{LiM}(\text{CH}_3)_3$ in diethyl ether and THF (10,11). These exchange reactions are very facile even at temperatures below -70°C and the mechanisms are considered to be as follows:



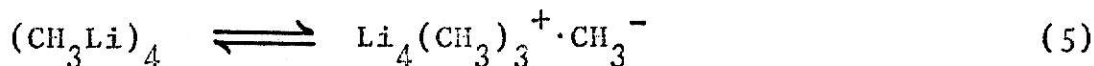
Methyl lithium also exchanges methyl groups and lithium atoms with the complexes $\text{Li}_3\text{M}(\text{CH}_3)_3$, $\text{Li}_2\text{M}(\text{CH}_3)_4$ or $\text{LiM}(\text{CH}_3)_3$ although this is considerably less facile than the $(\text{CH}_3)_2\text{M}$ -complex exchange discussed above. For the systems studied so far, methyl lithium-complex exchange has been considered to occur by way of a methyl lithium tetramer to dimer dissociation step followed by exchange of dimer with the complex.



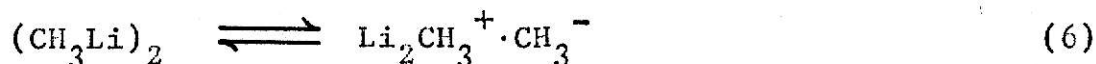
In a study of lithium exchange between methyl lithium and $\text{LiB}(\text{CH}_3)_4$ [also $\text{LiAl}(\text{CH}_3)_4$], Williams and Brown (12) proposed the above mechanism with the tetramer-dimer step (3) being rate determining and having an activation energy of 11.2 ± 1.0 kcal mole⁻¹. Since methyl group and lithium exchange between methyl lithium and complex in the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{M}$ systems appears to be concurrent, and with the activation energy about the same as that found by Williams and Brown for the $\text{CH}_3\text{Li}-\text{LiB}(\text{CH}_3)_4$ system, it has been presumed that a mechanism represented by steps (3) and (4) is operative.

Witanowski and Roberts (13) have suggested the inversion of neohexyllithium in diethylether involves a dissociation-recombination step. The nature of the dissociation step is not certain, but since the inversion is much slower and has a higher activation energy (15 ± 2.0 kcal mole⁻¹) than the methyl lithium complex exchanges described above, it appears it is different from (3). Presuming neohexyllithium is tetrameric in ether, the step could be of the form $\text{R}_4\text{Li}_4 \rightleftharpoons \text{Li}_4\text{R}_3^+\text{R}^-$, in which the ionic species

is considered to be a contact ion pair. With this in mind, it would appear reasonable to consider that methyllithium could dissociate ionically from either the tetramer or dimer.



and/or



Toppet, et al. (14), have observed slow methyl group exchange between $(\text{C}_2\text{H}_5)_2\text{Li}$ and $(\text{C}_2\text{H}_5)_2\text{Hg}$ in benzene, but noted an acceleration of rate upon addition of small amounts of THF. Exchange of methyl groups has also been reported between CH_3Li and $(\text{CH}_3)_2\text{Hg}$ in diethylether (15). Since the tendency for complex formation between mercury alkyls and methyllithium is relatively low (16), and the methyl group exchange much slower than with Zn, Mg, or Cd dialkyls, the $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ system seems to be a good system for obtaining information about the rate determining step for the exchange process. The object of this work is to determine the nature of the rate determining step, its activation energy and its response to a change in solvent.

II. EXPERIMENTAL

A. Manipulation of Air Sensitive Compounds

Since most of the compounds dealt with were either air sensitive or toxic, all manipulations were carried out in an inert atmosphere glove box. The box was purchased from Vacuum Atmospheres Corporation. Argon was used as the inert gas and was kept rigorously free of air and water by circulation through manganese (II) oxide and molecular sieve columns, as depicted in Figure 1. The argon first passed through a 4A molecular sieve column to remove water, then through a 13x molecular sieve column to remove organic solvents and any residual water, and finally through a column filled with vermiculite coated with manganese (II) oxide to remove oxygen. The oxygen removal column was placed last in the chain to prevent slow poisoning of the MnO by organic solvents. It was generally necessary to regenerate the oxygen removal columns much more frequently than the molecular sieve columns; and therefore, these columns were placed in parallel so that one could be regenerated while the other was being used.

All of these columns were attached to a 7/8" o.d. copper tubing manifold by using a short piece of 1" i.d. rubber tubing on each end. In order to regenerate, it was necessary to isolate the column involved from the box so that it could be evacuated. This was accomplished by using a clamp on the rubber tubing which connects the column to the copper tubing manifold. The molecular sieves were regenerated by heating (310°C. for 4A, 220°C. for 13x) in a vacuum for a period of at least six hours. The vacuum for

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH ILLEGIBLE
PAGE NUMBERS
THAT ARE CUT OFF
OR MISSING.**

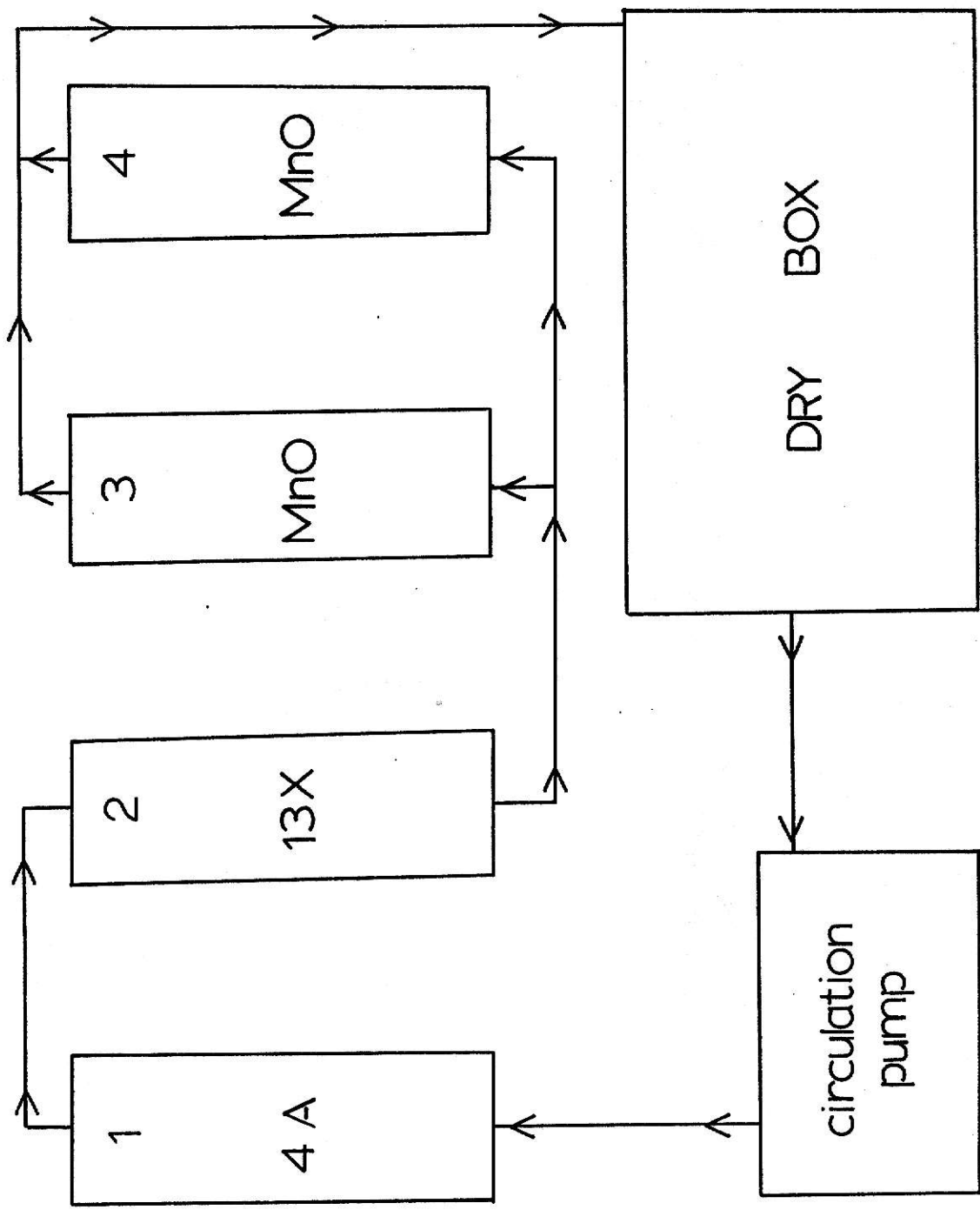
**THIS IS AS
RECEIVED FROM
THE CUSTOMER.**

Explanation of Figure 1

Schematic Drawing of Dry Box and Continuous
Flow Atmosphere Purification System.

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

**THIS IS AS
RECEIVED FROM
CUSTOMER.**



regeneration of all the columns was supplied by a Model 1400 Welch pump connected to a trap cooled with dry ice or liquid nitrogen. Heat was provided by 20 gauge nichrome wire, or large commercial heating tape, wrapped around the column and controlled by a variac. To retain the heat, each column was jacketed with a heavy asbestos liner (steam pipe cover obtained from the Kansas State University physical plant).

The MnO columns for oxygen removal were prepared according to a procedure suggested by Brown, et al. (17). The columns were filled with vermiculite coated with about 500g. $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, evacuated and very slowly heated to 380°C . This temperature was maintained until all the oxalate had decomposed to manganese (II) oxide, a bright green solid. When the columns had returned to room temperature, the argon atmosphere was allowed to pass through. As the columns removed oxygen from the argon atmosphere, the color of the manganese oxide turned from bright green to dark brown, apparently due to a higher oxide of manganese approaching the composition Mn_2O_3 . Regeneration was accomplished by the following procedure. First the column was evacuated and heated to about 380°C ., at which temperature the vacuum was shut off and hydrogen gas passed through until the green color was restored. Then the hydrogen was shut off and allowed to cool to room temperature while being evacuated.

Work in the dry box was infrequent, depending upon the outcome of previous samples, time available, and general readiness of the box. However, during regular use one would go in and out of the box approximately five times per day. This along with diffusion through the butyl rubber gloves was the largest outside

contaminant of the box atmosphere. Under these conditions, regeneration of the purification columns was necessary about every third day. Under moderate use, the columns stayed charged as much as a week before regeneration was necessary. In order to lessen oxygen contamination, all glassware was taken into the box slightly warmed from the oven.

B. Reagents and Solvents

Reagent grade anhydrous diethylether was purchased from the Allied Chemical Co.

1,2-Dimethoxyethane (analytical reagent grade) was purchased from the Mallinckrodt Chemical Works, as well as analytical grade tetrahydrofuran.

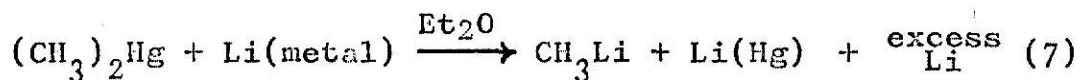
The distillation of solvents was carried out in an argon or nitrogen filled distillation apparatus within the hood. The distilling flask was warmed with a heating mantle; and the receiver was cooled with dry ice. The water free solvents were sealed with $\text{\$}$ stoppers which were taped down with Scotch No. 33 plastic tape and then taken into the dry box. No difficulty was encountered with explosion of the solvents under vacuum in the port chamber.

99.99% pure lithium metal was purchased from Gallard-Schlesinger Manufacturing Corporation. The lithium was stored within the inert dry box atmosphere continually to avoid oxidation.

All solvents used were dried over sodium metal and distilled from lithium aluminum hydride, then taken immediately into the dry box and used within two or three days.

The dimethylmercury used was purchased from Eastman Organic Chemical Company. Because of the high volatility and toxicity of $(\text{CH}_3)_2\text{Hg}$, each 25g. bottle was opened inside the inert atmosphere dry box and stored there in a sealed container until used.

Methylolithium was prepared by adding excess lithium metal to measured amounts of dimethylmercury in diethylether, Et_2O .



Concentrations of methylolithium were determined by titration of hydrolysed aliquot samples with standardized hydrochloric acid, or KHP using phenolphthalien as an indicator. The concentrations made were usually 1M. In a typical preparation, one would put 30 ml. of diethylether and 1 ml. dimethylmercury in a 50 ml. § joint Erlenmeyer flask with a magnetic stirring bar. Small pieces of lithium metal were added slowly until the lithium metal continued to float and remained shiny, signifying that the reaction was complete. The process usually took about one hour. Thirty ml. of diethylether was used instead of twenty-five ml. to allow for evaporation during the process. Occasionally small pieces of broken glass were added to the reaction mixture to keep the surface of the lithium metal clean and available for reaction. Upon completion of the reaction, the $\text{Li}(\text{Hg})$ amalgam and excess lithium were filtered off and the methylolithium was ready for sample preparation.

A special procedure was followed to minimize the reaction of methylolithium with THF and DME. Solutions of methylolithium in these solvents were prepared by first preparing methylolithium in diethylether, as described above, and then pumping off the ether

and redissolving in the new solvent. It was found that in order for the methyllithium to redissolve readily in the new solvent, it should not be dried under vacuum for more than an hour. Once the methyllithium was dissolved in THF and DME, the methyllithium-dimethylmercury mixtures were prepared, placed in NMR tubes, sealed off and placed in dry ice as rapidly as possible.

Concentrations of the dimethylmercury were prepared by using volumetric pipettes and a 25 ml. volumetric flask. The dimethylmercury concentration was usually made about 0.5M.

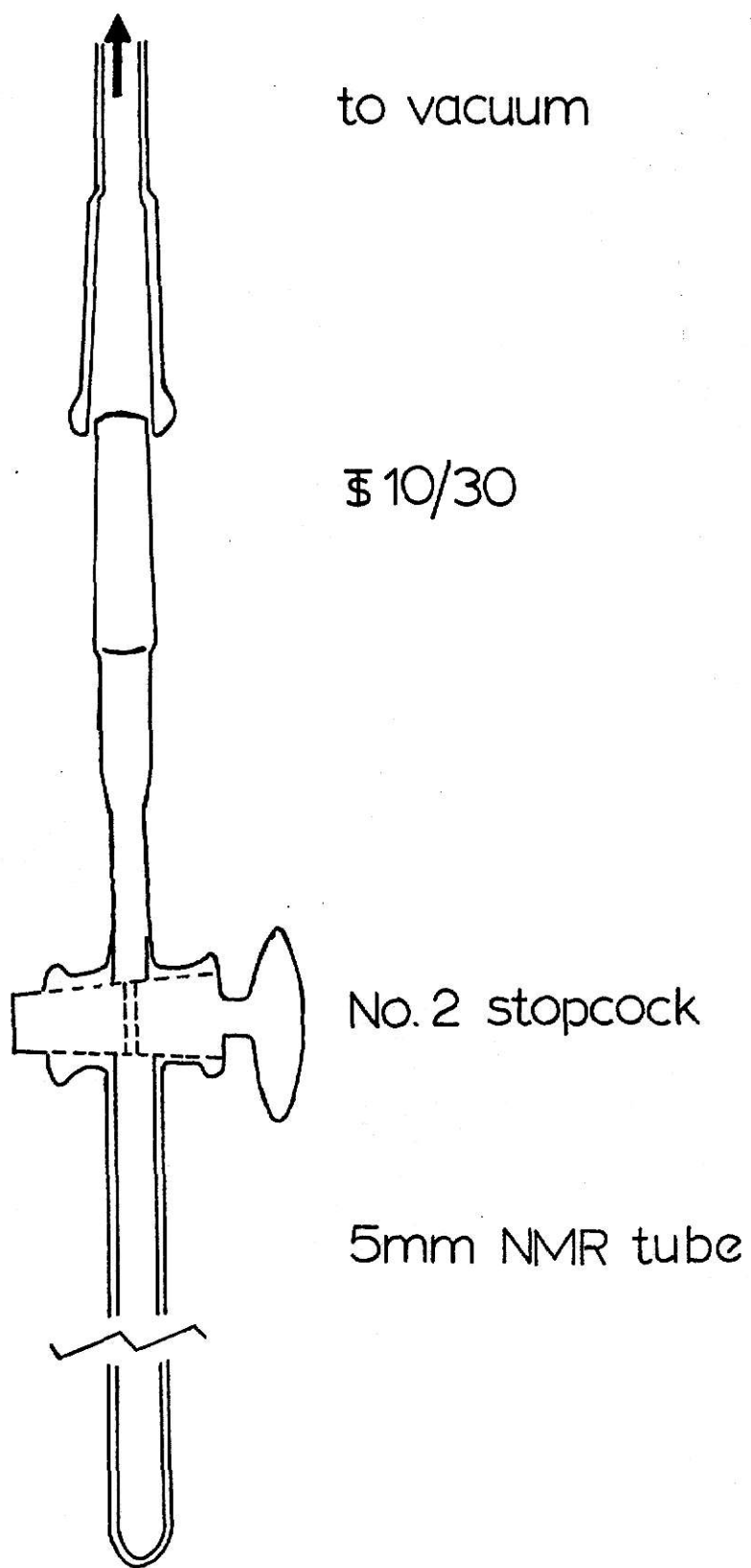
C. Preparation of NMR Samples

After the concentrations of methyllithium and dimethylmercury had been determined, mixed samples of these two compounds were prepared in 25 ml. Erlenmeyer flasks, using the appropriate volumetric pipettes. A certain number of milliliters of each were used depending upon the molar ratio desired and the concentrations of the reactants.

Specially prepared NMR tubes were used for the NMR samples. The tubes were prepared by attaching a #2 stopcock to the open end of a 5 mm o.d. NMR tube. On the other end of this stopcock was affixed a standard taper 10/30 male joint (Figure 2). These labeled tubes were taken into the dry box and filled with the appropriate mixed sample, using 30 ml. Multifit syringes equipped with 6" long hypodermic needles. The long needle was required in order to reach the bottom of the NMR tube. Thereafter, the stopcocks were greased and closed, taken from the dry box, and fitted to a female 10/30 joint attached to a vacuum pump. The sample

Explanation of Figure 2

Drawing of Specially Modified 5 mm NMR Tube
used in Sealing off Samples from the Atmosphere.



was then frozen in liquid nitrogen and the stopcock opened.

The sides of the NMR tube were fused together just below the stopcock thus sealing off its contents. The labeled tube was then warmed to room temperature and stored in dry ice until NMR spectra could be taken. The entire process, beginning with preparation of the methyllithium was done as rapidly as possible to avoid reaction of methyllithium with the solvent. It was most important that all equipment remained clean and dry throughout the process.

D. NMR and Gas Chromatography

NMR spectra were recorded on a Varian Associates A-60 nuclear magnetic resonance spectrometer, equipped with standard Varian Associates variable temperature accessories. The temperature was measured before and after each spectrum was recorded by a copper-constantan thermocouple within a standard size NMR tube inserted into the probe of the NMR. The thermocouple was connected to a Leeds and Northrup millivolt potentiometer. Temperature measurements were found to be accurate to within $\pm 1^{\circ}\text{C}$. by this method.

The resolution was readjusted at each temperature using the Y gradient to insure accurate recording of the spectra. A 250 second sweep time was used most frequently and the R.F. field was kept as low as possible to avoid saturation of the signal.

The spectrometer was calibrated at each temperature using the sideband technique. At each temperature the recorder response was found to be 1% low, i.e., 5.00 Hz was actually 4.95 Hz from this technique.

Gas chromatographic analyses were made using an F and M model 700 dual column instrument packed with SE-30.

E. Analysis of NMR Data

Information about the kinetics of exchange processes can be obtained from NMR data in a number of ways (18). Principally two methods were used in this work: measurement of full linewidths at half height (hereafter simply referred to as linewidth) in the region of slow exchange, and calculation of an overall line shape as a function of τ , where $1/\tau = 1/\tau_A + 1/\tau_B + 1/\tau_C$ for a three site system ($\tau_{A,B,or C}$ = mean lifetime of a particular methyl group on that indicated site). The former was used as a measure of the methyllithium-dimethylmercury exchange and the latter as a measure of the dimethylmercury self exchange.

In the region of slow exchange, the mean lifetime of an exchanging group at site i, τ_i was related to the linewidth, $\Delta_{1/2}$, by the expression $1/\tau_i = \pi(\Delta_{1/2} - \Delta_{1/2}^0)$, (8) where $\Delta_{1/2}^0$ represents the linewidth of site i in the absence of exchange.

A Fortran computer program was used to calculate theoretical three-site exchange spectra for the dimethylmercury self exchange (19)*.

Activation energies were obtained from the temperature dependence of the NMR spectra. According to the Arrhenius

* Ref. 19 is an example system upon which the multi-site exchange program written by Whitesides was also used.

equation,

$$k = Ae^{-E_a/RT}$$

a plot of $\ln k$ vs. $1/T(^{\circ}\text{K})$ would give a slope equivalent to $-E_a/RT$. Since $1/\tau \propto k$, $\ln 1/\tau$ vs. $1/T(^{\circ}\text{K})$ gave a straight line of slope $-E_a/RT$. The best straight line fit was determined by the method of least squares.

III. RESULTS AND DISCUSSION

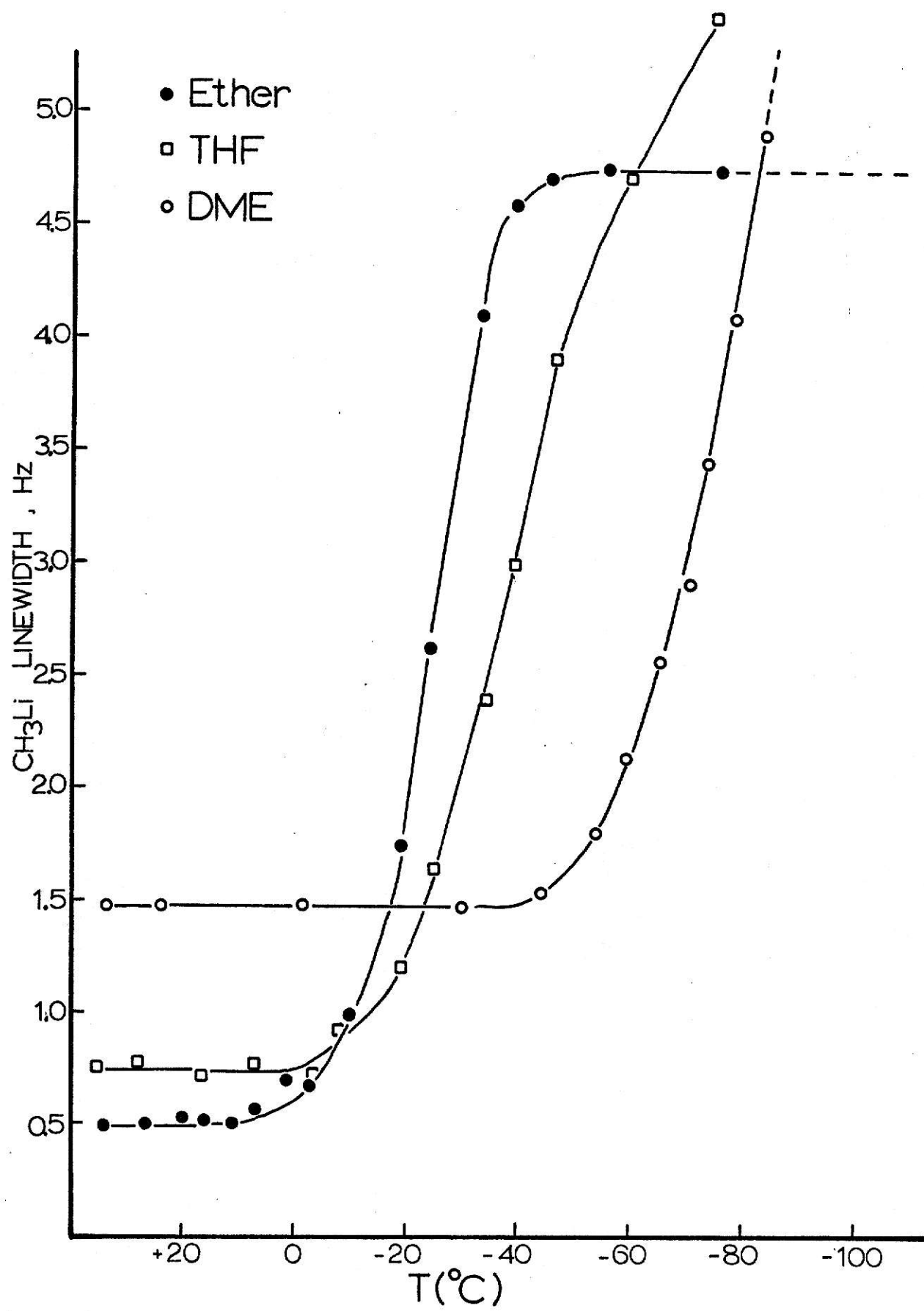
A. Methyl lithium-Dimethylmercury Exchange in DiethyletherObservations

At probe temperature, the proton NMR spectrum of methyl lithium in diethylether consists of a single resonance located 3.08 ppm upfield from the ether triplet. The linewidth at 36°C is 0.50 Hz. As the temperature is lowered, the linewidth begins to broaden and continues to do so until it reaches 5.00 Hz at -60°C, then remains constant as the temperature is lowered further (Figure 3). The broadening is due to a combination of methyl group exchange between methyllithium tetramers and ${}^7\text{Li}-{}^1\text{H}$ coupling. When the exchange is rapid, as at 36°C, ${}^7\text{Li}-{}^1\text{H}$ coupling is absent. As the exchange becomes slower, ${}^7\text{Li}-{}^1\text{H}$ coupling becomes apparent and broadening of the methyllithium linewidth occurs. It was suggested by Seitz and Brown (3) that the broadening is actually ten lines resulting from the proton of a methyl group coupling with three equivalent lithium atoms on one face of the tetramer. The coupling constant is small; and hence, a single broad line results.

The proton spectrum of dimethylmercury in diethylether consists of a single resonance at 0.87 ppm upfield from the ether triplet due to the methyl groups bonded to ${}^{200}\text{Hg}$, ($I=0$), at all temperatures studied. Also, at all temperatures of interest the linewidth is 0.98 Hz. At 51.5 Hz on each side of the mercury-200 methyl resonance, satellite resonances occur which are due to ${}^{199}\text{Hg}-{}^1\text{H}$ coupling (${}^{199}\text{Hg}$, $I=\frac{1}{2}$, 16.93% natural abundance). The intensity of each of these peaks is 8.45% of the total

Explanation of Figure 3

Methylolithium Linewidth as a Function of Temperature
in Ether, THF and DME.



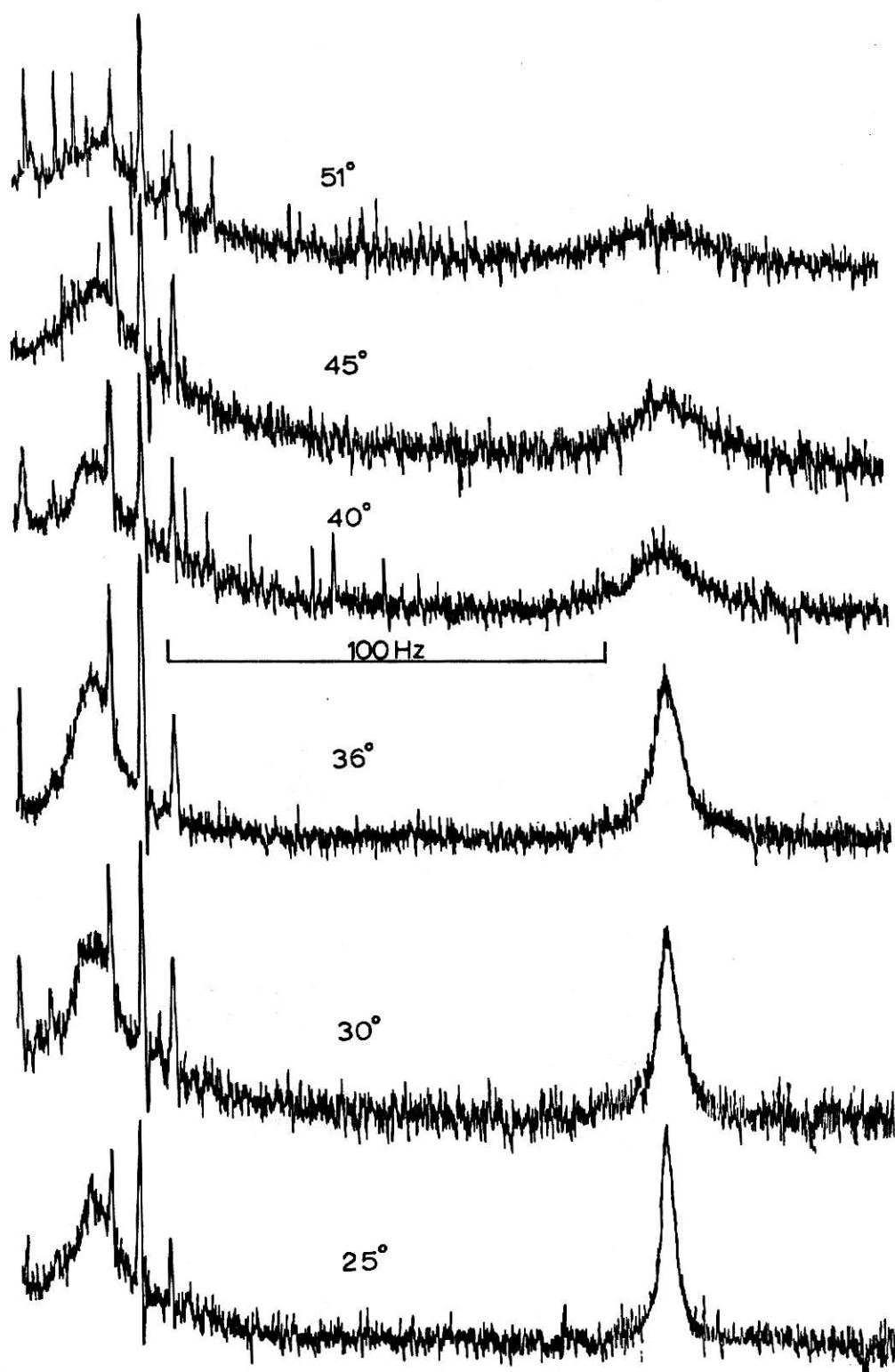
dimethylmercury peak areas. The measured coupling constant for $^{199}\text{Hg}-^1\text{H}$ is 103 Hz.

From Figure 4, one can see that the probe temperature (36°C) spectrum of a mixed methyllithium-dimethylmercury sample in diethylether consists of two broad peaks separated by approximately 133 Hz. The broadness is due to a relatively slow methyl group exchange between methyllithium and dimethylmercury. The upfield peak was assigned to methyllithium and the downfield peak assigned to dimethylmercury. The triplet superimposed on the dimethylmercury peak arises from $^{13}\text{C}-^1\text{H}$ coupling in the solvent, and is a satellite group to the larger ether triplet further downfield. As the temperature is raised above 36°C , the two resonances begin to coalesce. At 51°C the two peaks are still discernible; however, the depth of the valley between them has decreased greatly. As the temperature is decreased below 36°C , the two resonances begin to separate and sharpen. At 6°C the peaks appear to be completely separated. The separation at this point is 133 Hz.

Linewidths of each peak were recorded and measured over the temperature range 55°C to -34°C . The linewidth of dimethylmercury is assumed to be affected by three factors: (1) Phasing difficulty due to the larger ether triplet being in close proximity to the dimethylmercury peak made it difficult to draw a meaningful baseline; (2) The $^{13}\text{C}-\text{H}$ triplet superimposed on the dimethylmercury peak would act to increase the normal linewidth; (3) The dimethylmercury self exchange discussed in Section V contributes to the linewidth. Therefore, the activation energy

Explanation of Figure 4

Temperature Dependence of Proton NMR Spectra of
 $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ Exchange in Diethylether.
Li/Hg = 1.23



for methyl group exchange between methyllithium and dimethylmercury was obtained from measurements of the methyllithium linewidth at various temperatures. A $1/\tau_{\text{CH}_3\text{Li}}$ was calculated at each temperature using equation (8) explained in the experimental section. An Arrhenius plot of $\log 1/\tau_{\text{CH}_3\text{Li}}$ vs. $1/T(^{\circ}\text{K})$ is shown in Figure 10. The activation energy was calculated from the slope of the line as $16.4 \pm 2.0 \text{ kcal mole}^{-1}$. The main disadvantage to using $\log 1/\tau_{\text{CH}_3\text{Li}}$ in this plot instead of $\log 1/\tau_{\text{T}}$, where $\tau_{\text{T}} = \tau_{\text{A}}\tau_{\text{B}}/(\tau_{\text{A}} + \tau_{\text{B}})$ as determined from a complete line shape analysis, is that the temperature range over which usable data could be obtained is shortened. Using $1/\tau_{\text{CH}_3\text{Li}}$, one had to cease measurements as soon as the methyllithium linewidth became large enough to overlap the dimethylmercury peak. By using a complete line shape analysis, it is possible to measure the linewidth of the single peak observed even after coalescence has occurred.

Upon examination of Table 1., one can see that the methyllithium linewidth is relatively independent of Li/Hg. This can be more readily seen upon comparison of the same data in THF where methyllithium linewidth does vary with Li/Hg, and the data obtained by Brown (20) for the $\text{Ga}(\text{CH}_3)_3 \cdot \text{NC}_5\text{H}_5 / (\text{CH}_3)_3\text{Ga}$ system where the linewidth is also a function of concentration. Sections I and II of Table 1 must be considered separately. They cannot be combined because the two sets of data were obtained at slightly different temperatures. The important aspect to notice is that the linewidth is independent of Li/Hg in each set.

The slight increase in linewidth with increase in Li/Hg in Section I, Table 1 is within experimental error and may be coincidental.

Table 1.
Methyl lithium Linewidth as a Function of Li/Hg
in Ether at 36°C.

		Li/Hg	$\Delta_{\frac{1}{2}\text{CH}_3\text{Li}}$ (Hz)	$1/\tau_{\text{CH}_3\text{Li}}$ (sec ⁻¹)
I.	A.	6.17	5.9	17.1
	B.	3.70	7.9	23.3
	C.	1.23	8.3	24.4
	D.	0.61	8.4	24.9
	E.	0.31	9.4	28.0
II.	F.	2.83	8.8	26.1
	G.	1.89	11.5	34.6
	H.	0.94	11.0	33.1
	I.	0.47	12.0	36.1
	J.	0.31	10.5	31.2
	K.	0.94	9.3	27.7

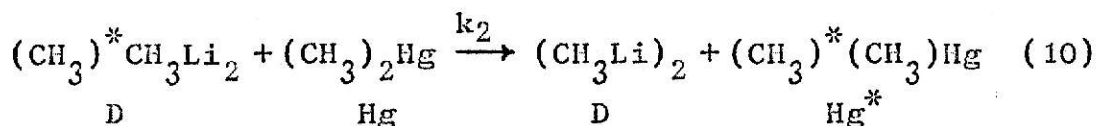
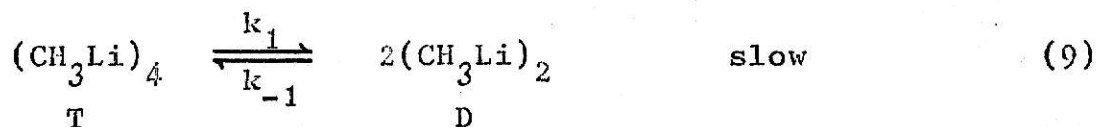
Section II reveals no such similar pattern. Sample A exhibits an unusually small linewidth in view of the others in Section I. This deviation is outside experimental error and is probably due to a breakdown of the mechanistic model at higher Li/Hg ratio. Sample K is a double dilution of H; one can see that the methyl lithium linewidth changes only 1.71 Hz, which is well within experimental error of ± 2 Hz, and probably due to an increase of signal to noise ratio upon dilution.

Mechanisms of Exchange

There appear to be five different mechanisms that deserve consideration as possible pathways for methyl group exchange

between methyllithium and dimethylmercury. The first of those five is as follows:

CASE I



Case I consists of a slow tetramer to dimer dissociative step which is rate determining followed by reaction of the dimer with dimethylmercury to exchange methyl groups. Applying the steady state approximation to the dimer:

$$\frac{d(\text{D})}{dt} = 0 = 2k_1(\text{T}) - 2k_{-1}(\text{D})^2 - k_2(\text{D})(\text{Hg}) \quad (11)$$

from which,

$$(\text{D}) = 2k_1(\text{T})/2k_{-1}(\text{D}) + k_2(\text{Hg}) \quad (12)$$

The rate of formation of exchanged products, Hg^* is:

$$\frac{d(\text{Hg}^*)}{dt} = k_2(\text{D})(\text{Hg}) \quad (13)$$

Upon substitution of (D), Expression (13) becomes:

$$\frac{d(\text{Hg}^*)}{dt} = \frac{2k_1k_2(\text{T})(\text{Hg})}{2k_{-1}(\text{D}) + k_2(\text{Hg})} \quad (14)$$

If one assumes that the reaction of the dimer with dimethylmercury is much faster than recombination of two dimers to form a tetramer, then $2k_{-1}(\text{D}) \ll k_2(\text{Hg})$, and Expression (14) becomes

$$\frac{d(\text{Hg}^*)}{dt} = 2k_1(\text{T}) \quad (15)$$

from which $1/\tau_{\text{CH}_3\text{Li}}$ is:

$$\frac{1}{\tau_{\text{CH}_3\text{Li}}} = \frac{1}{4} \frac{1}{(T)} \cdot \frac{d(\text{Hg}^*)}{dt} = \frac{1}{2}k_1 \quad (16)$$

Therefore, $1/\tau_{\text{CH}_3\text{Li}}$ is predicted to be independent of Li/Hg from expression (16).

It becomes obvious that the exchange mechanism of Case I is not operative in diethylether. Although the methyllithium linewidth is not a function of Li/Hg as the mechanism predicts, the activation energy is too high, and the exchange rate too slow, for tetramer to dimer dissociation to be the rate determining step. An activation energy of 16.4 ± 2.0 kcal mole⁻¹ is significantly different from the 11.2 ± 1.0 kcal mole⁻¹ Williams and Brown (12) measured for the same process in the $\text{CH}_3\text{Li-LiB}(\text{CH}_3)_4$ system, indicating that whatever the rate determining step, it does not appear to be a tetramer to dimer dissociation.

However, if the reverse is true, *i.e.*, $k_2(\text{Hg}) \ll k_{-1}(\text{D})$, the second step is rate determining while the tetramer to dimer dissociation is rapid. The kinetic expressions then become:

$$\frac{d(\text{Hg}^*)}{dt} = 2k_1k_2(T)(\text{Hg})/2k_{-1}(\text{D}) \quad (17)$$

From equation (9):

$$K_{\text{eq}} = (\text{D})^2/(\text{T}) \quad (18)$$

$$\text{, or } (\text{D}) = K_{\text{eq}}^{\frac{1}{2}}(\text{T})^{\frac{1}{2}} \quad (19)$$

$$\text{, and } \frac{d(\text{Hg}^*)}{dt} = \frac{k_1k_2(T)(\text{Hg})}{k_{-1}K_{\text{eq}}^{\frac{1}{2}}(\text{T})^{\frac{1}{2}}} \quad (20)$$

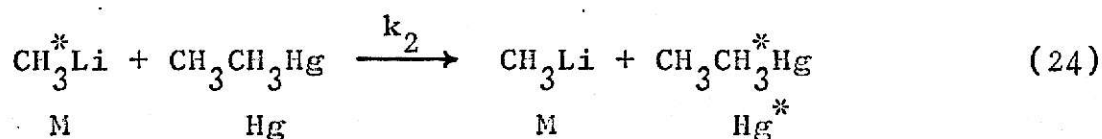
From Expression (20):

$$1/\tau_{\text{CH}_3\text{Li}} = 1/4(\text{T}) \cdot d(\text{Hg}^*)/dt \quad (21)$$

$$1/\tau_{\text{CH}_3\text{Li}} = k_1 k_2 (\text{Hg}) / 4k_{-1} K_{\text{eq}}^{1/2} (\text{T})^{1/2} \quad (22)$$

This assumption predicts $1/\tau_{\text{CH}_3\text{Li}}$ to be a function of $(\text{Hg})/(\text{T})^{1/2}$, which is not consistent with the data. The fact that neither assumption in this case seems to fit suggests that a methyllithium species more reactive than dimer towards $(\text{CH}_3)_2\text{Hg}$ must be involved to account for the observed exchange. The methyllithium species, although more reactive, must be produced more slowly since the methyllithium-dimethylmercury exchange is slower than tetramer to dimer dissociation. Some suggestions for that species appear in the following cases.

CASE II



Case II consists of a complete tetramer dissociative process directly to the monomer. The dissociation is the rate determining step after which exchange of methyl groups occurs between the monomer and dimethylmercury. Use of the steady state theory for the monomer yields:

$$\frac{d(\text{M})}{dt} = 0 = 4k_1(\text{T}) - 4k_{-1}(\text{M})^4 - k_2(\text{M})(\text{Hg}) \quad (25)$$

and upon rearrangement:

$$(\text{M}) = 4k_1(\text{T})/4k_{-1}(\text{M})^3 + k_2(\text{Hg}) \quad (26)$$

The rate of formation of exchanged products is:

$$\frac{d(\text{Hg}^*)}{dt} = k_2(\text{M})(\text{Hg}) \quad (27)$$

which, after substitution of Expression (26) yields:

$$\frac{d(\text{Hg}^*)}{dt} = 4k_1k_2(\text{T})(\text{Hg})/4k_{-1}(\text{M})^3 + k_2(\text{Hg}) \quad (28)$$

However, if $4k_{-1}(\text{M})^3 \ll k_2(\text{Hg})$, i.e., the exchange of the monomer with dimethylmercury is more rapid than their recombination to form a tetramer:

$$\frac{d(\text{Hg}^*)}{dt} = 4k_1(\text{T}) \quad (29)$$

, and

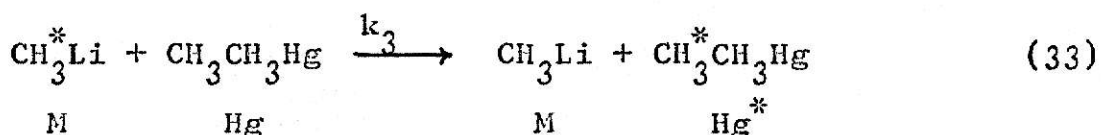
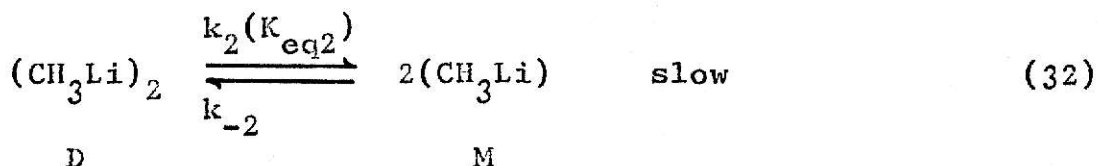
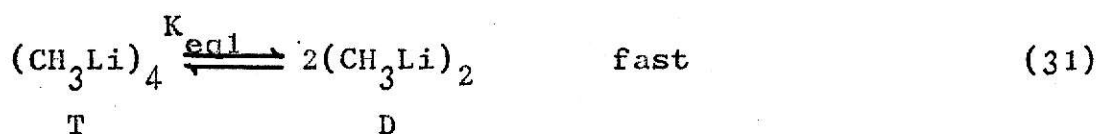
$$1/\tau_{\text{CH}_3\text{Li}} = \frac{1}{4} \left(\frac{1}{\text{T}} \right) \cdot \frac{d(\text{Hg}^*)}{dt} = \frac{1}{4}k_1 \quad (30)$$

From the results of Expression (30), this mechanism cannot be eliminated. The kinetics predicts that $1/\tau_{\text{CH}_3\text{Li}}$ will be independent of Li/Hg, which is what was observed. If $k_{-1}(\text{M})^3 \gg k_2(\text{Hg})$, this would predict a Li/Hg dependence for $1/\tau_{\text{CH}_3\text{Li}}$ which was not observed.

Studies of other systems suggest that direct breakdown to monomer, e.g., $(\text{RLi})_n \rightleftharpoons n\text{RLi}$, may occur. Waack and Doran (21) have shown in their study of methyllithium with 1,1-diphenylethylene in THF that the reaction was $\frac{1}{4}$ order in methyllithium indicating a rate determining step consisting of tetramer to monomer dissociation. Many others (22,23) have also reported fractional reaction orders for alkyl lithium compounds upon reaction with olefins as the initiation step for anionic polymerization. This mechanism must be considered even though

Brown (24) has criticized the fractional reaction orders obtained by Bywater and Worsfold (25) and insists that this type of mechanism is energetically not feasible. However, it must be kept in mind that Brown's arguments are primarily based on reactions in hydrocarbon solvents. In donor solvents, solvation of the monomer could favor this reaction.

CASE III



Case III, a three step process, consists of a rapid tetramer to dimer dissociation followed by a slower dimer to monomer breakdown. The monomer then reacts rapidly with the dimethylmercury to exchange methyl groups. By applying the steady state assumption to the monomer and rearranging the result one obtains:

$$\frac{d(\text{M})}{dt} = 0 = 2k_2(\text{D}) - 2k_{-2}(\text{M})^2 - k_3(\text{M})(\text{Hg}) \quad (34)$$

$$(\text{M}) = 2k_2(\text{D})/2k_{-2}(\text{M}) + k_3(\text{Hg}) \quad (35)$$

The rate of formation of exchanged products is:

$$\frac{d(\text{Hg}^*)}{dt} = k_3(\text{M})(\text{Hg}) = 2k_2k_3(\text{D})(\text{Hg})/2k_{-2}(\text{M}) + k_3(\text{Hg}) \quad (36)$$

If $2k_{-2}(M) \ll k_3(Hg)$ then,

$$\frac{d(Hg^*)}{dt} = 2k_2(D) \quad (37)$$

and substitution of expression (35) yields:

$$d(Hg^*)/dt = 2k_2K_{eq}^{1/2}(T)^{1/2} \quad (38)$$

from which:

$$1/\tau_{CH_3Li} = \frac{1}{2}k_2K_{eq}^{1/2} \times 1/(T)^{1/2} \quad (39)$$

From expression (39), $1/\tau_{CH_3Li}$ is predicted to be a linear function of $1/(T)^{1/2}$ with a slope of $\frac{1}{2}k_2K_{eq}^{1/2}$ and an intercept of zero. A plot of $1/\tau_{CH_3Li}$ vs. $1/(T)^{1/2}$ yields a straight line independent of (T) with a nonzero intercept. Clearly this assumption must not be operative. If $2k_{-2} \gg k_3(Hg)$ then,

$$d(Hg^*)/dt = k_2k_3(D)(Hg)/k_{-2}(M) \quad (40)$$

Using the expressions:

$$(D) = K_{eq1}^{1/2}(T)^{1/2} \quad (41)$$

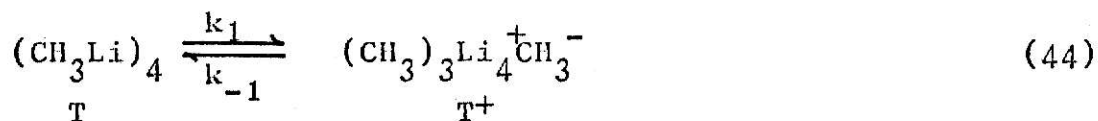
$$(M) = (D)^{1/2}K_{eq2}^{1/2} \quad (42)$$

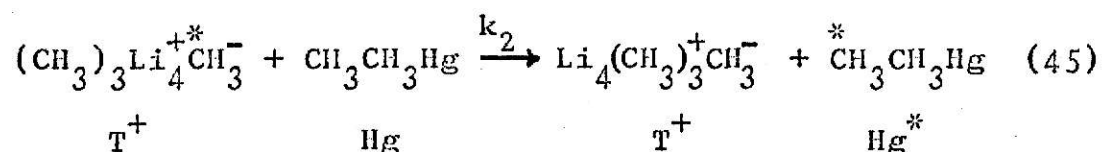
, then

$$1/\tau_{CH_3Li} = K_{eq1}^{1/4}K_{eq2}^{1/2}k_3(Hg)/(T)^{3/4} \quad (43)$$

Again $1/\tau_{CH_3Li}$ is predicted to be dependent upon Li/Hg which was not what was observed. This mechanism may be considered unlikely on these bases.

CASE IV





Case IV is essentially a dissociation of the tetramer to a contact ion pair. The methide ion, now more available for reaction is exchanged directly with dimethylmercury. A contact ion pair is suggested rather than a free methide ion, because if the latter were involved one would expect methyllithium to react with ether much more rapidly than it actually does. A contact ion pair suggests that the methide ion does not actually separate from the tetramer, rather a polarization of charge occurs at a specific time to put appreciable negative charge on one methyl group. Application of the steady state approximation to the contact ion pair yields:

$$\frac{d(\text{T}^+)}{dt} = 0 = k_1(\text{T}) - k_{-1}(\text{T}^+) - k_2(\text{T}^+)(\text{Hg}) \quad (46)$$

$$(\text{T}^+) = k_1(\text{T})/k_{-1} + k_2(\text{Hg}) \quad (47)$$

The rate of formation of exchanged products is:

$$\frac{d(\text{Hg}^*)}{dt} = k_2(\text{T}^+)(\text{Hg}) \quad (48)$$

$$= k_1k_2(\text{T})(\text{Hg})/k_{-1} + k_2(\text{Hg}) \quad (49)$$

If $k_{-1} \ll k_2(\text{Hg})$, then

$$\frac{d(\text{Hg}^*)}{dt} = k_1(\text{T}) \quad (50)$$

, and

$$1/\tau_{\text{CH}_3\text{Li}} = k_1/4 \quad (51)$$

; however, if $k_{-1} \gg k_2(\text{Hg})$,

$$\frac{d(\text{Hg}^*)}{dt} = \frac{k_1 k_2(\text{T})(\text{Hg})}{k_{-1}} \quad (52)$$

, and

$$1/\tau_{\text{CH}_3\text{Li}} = \frac{k_1 k_2(\text{Hg})}{k_{-1}} \quad (53)$$

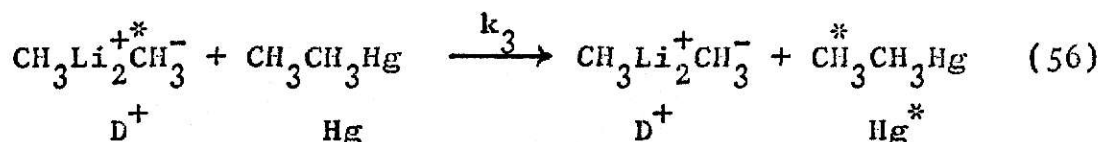
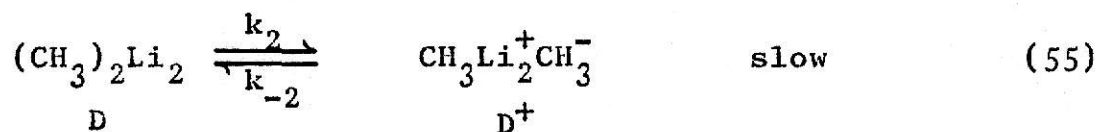
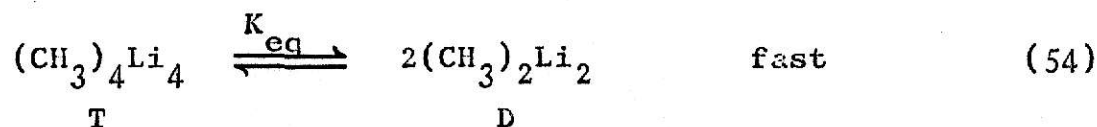
$1/\tau_{\text{CH}_3\text{Li}}$ has already been shown to be independent of Li/Hg; therefore, the assumption that $k_{-1} \gg k_2(\text{Hg})$ cannot be true.

However, the assumption $k_{-1} \ll k_2(\text{Hg})$ leads to the expression

$1/\tau_{\text{CH}_3\text{Li}} = \frac{1}{4}k_1$, which predicts $1/\tau_{\text{CH}_3\text{Li}}$ to be independent of Li/Hg. Thus, for mechanism IV to be operative, the reverse of equation (44) must be appreciably slower than the forward reaction of equation (45).

Witanowski and Roberts (13) have measured the inversion rate of neohexyllithium, believed to be a dissociation-recombination mechanism. This would apparently occur by way of an ionic dissociation pathway. Their measured activation energy was 15 kcal mole⁻¹. From this value it does not seem unreasonable to expect the homolytic dissociation (contact ion pair formation) to occur from either the tetramer or the dimer with a measured activation energy of 16.4 ± 2.0 kcal mole⁻¹. This, coupled with the fact that $1/\tau_{\text{CH}_3\text{Li}} \neq f(\text{Li}/\text{Hg})$, as predicted, lead the author to favor the homolytic dissociation over the previous cases.

CASE V



Case V is similar to Cases III and IV. It involves a rapid pre-equilibrium step consisting of tetramer to dimer dissociation and a following slower step which produces a contact ion pair from the dimer. The dimeric contact ion pair then exchanges methyl groups directly with dimethylmercury.

Application of the steady state approximation to the dimeric contact ion pair and treatment in a similar fashion as Case III yields:

$$\frac{d(\text{Hg}^*)}{dt} = \frac{2k_2k_3K_{\text{eq}}^{\frac{1}{2}}(\text{T})^{\frac{1}{2}}(\text{Hg})}{k_{-2} + k_3(\text{Hg})} \quad (57)$$

If one assumes $k_{-2} \ll k_3(\text{Hg})$, then

$$1/\tau_{\text{CH}_3\text{Li}} = 1/4(\text{T}) \cdot d(\text{Hg}^*)/dt = k_2K_{\text{eq}}^{\frac{1}{2}}/2(\text{T})^{\frac{1}{2}} \quad (58)$$

, and $1/\tau_{\text{CH}_3\text{Li}}$ is predicted to be dependent upon $1/(\text{T})^{\frac{1}{2}}$.

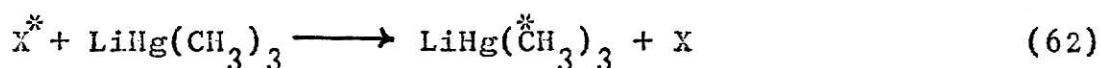
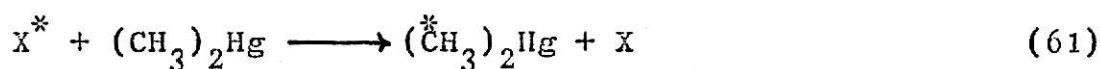
However, if $k_{-2} \gg k_3(\text{Hg})$ then,

$$1/\tau_{\text{CH}_3\text{Li}} = \frac{k_2k_3K_{\text{eq}}^{\frac{1}{2}}(\text{Hg})}{2k_{-2}(\text{T})^{\frac{1}{2}}} \quad (59)$$

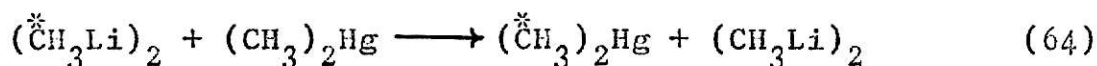
One can see immediately that the latter assumption predicts

$1/T$ CH_3Li to be dependent upon Li/Hg , and the former upon $1/(T)^{\frac{1}{2}}$. Neither of these relations was found to be true and therefore, Case V can be said to not contribute significantly to the exchange kinetics observed.

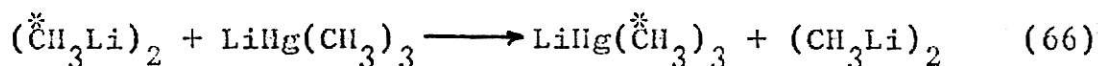
In ether, as THF, the possibility of exchange occurring through $\text{LiHg}(\text{CH}_3)_3$ (62) is present as well as exchange of the tetrameric dissociation species, X, directly with $(\text{CH}_3)_2\text{Hg}$, (61).



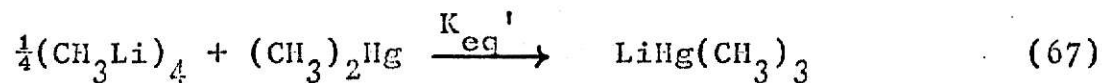
Although the complex was not observed in the NMR it may be present in low concentration. Therefore, step (62) involving the complex, $\text{LiHg}(\text{CH}_3)_3$, would have to have a large rate constant. It must also be noted that the kinetic expressions would be the same whether species X reacts with the complex or with dimethylmercury. For example, Case I, pg. 26,



Substituting $\text{LiHg}(\text{CH}_3)_3$ for $(\text{CH}_3)_2\text{Hg}$ gives:



Since complex must be formed directly from methyllithium and dimethylmercury as in equation (67):



(C) = $K_{\text{eq}}'(\text{Hg})(\text{T})^{\frac{1}{4}}$, and the modified kinetic expression for Case I becomes:

$$1/\tau_{\text{CH}_3\text{Li}} = K_{\text{eq}}^{\frac{1}{2}} K_{\text{eq}}' k_2(\text{Hg})/(\text{T})^{\frac{1}{4}} \quad (68)$$

, where $k_2(\text{complex}) \ll k_{-1}(\text{D})$.

For these reasons it is believed that only the reaction of any species X with dimethylmercury itself is important, keeping in mind the possibility of exchange with $\text{LiHg}(\text{CH}_3)_3$ may be occurring.

B. Methyl lithium-Dimethylmercury Exchange in THF

Observations

Methyl lithium, in the absence of dimethylmercury exhibits a single resonance at 12.12 τ in THF at 36°C. The linewidth at this temperature is 0.75 Hz. As the temperature is lowered the linewidth remains 0.75 Hz until at 0°, the peak begins to broaden. At -70° the linewidth is 5.5 Hz (Figure 3), and unlike the methyl lithium linewidth in ether, has not leveled off, but continues to broaden. From the shape of the THF curve in Figure 3, it appears the linewidth is approaching a constant value at low temperature by the slight inflexion point at approximately -60°. Unfortunately, data at temperatures lower than -70° were unattainable.

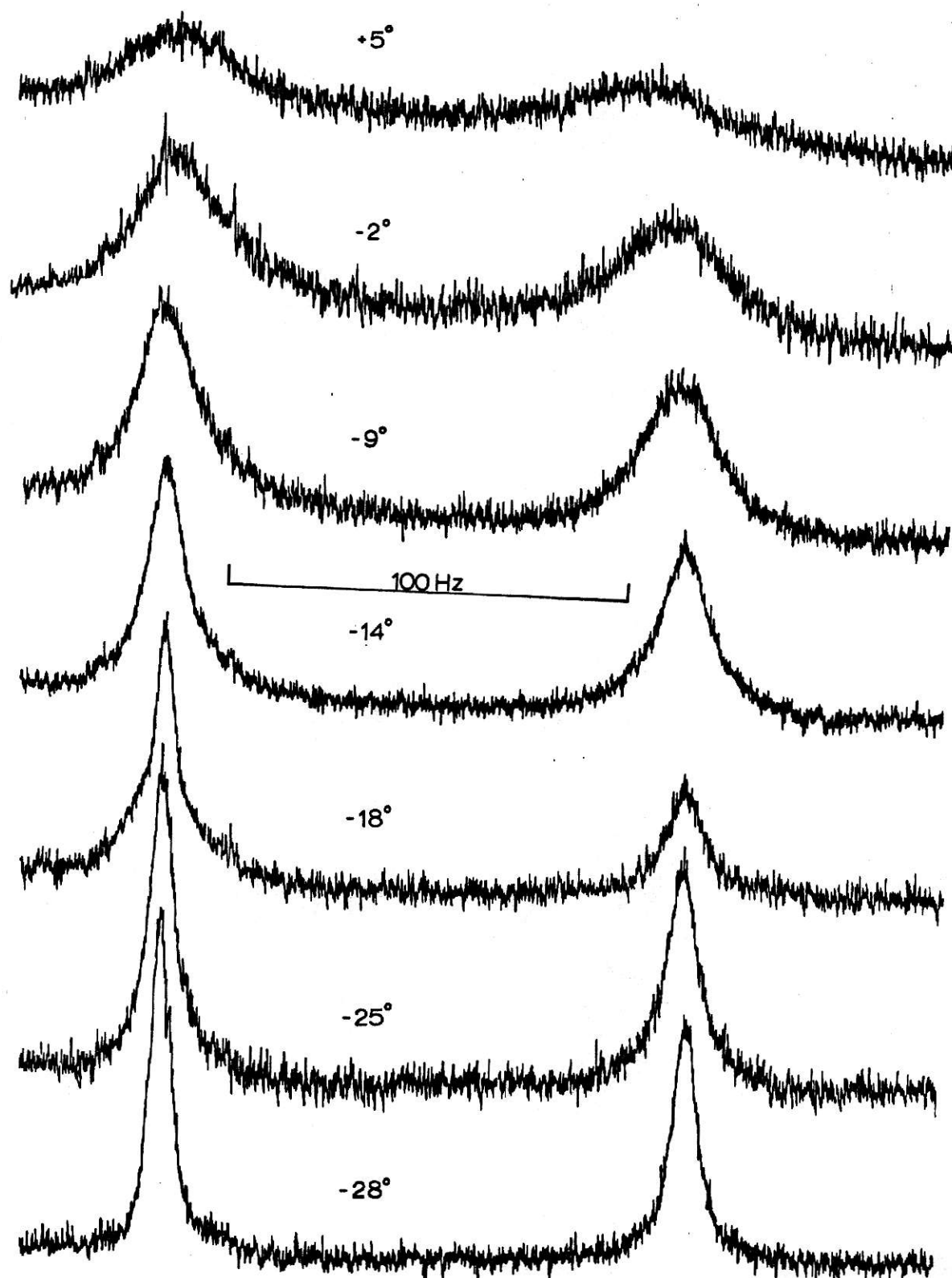
Similar to ether, the broadening is due to ^7Li -proton coupling in the tetrameric structure, see Section III A, page 18.

The dimethylmercury resonance appears as a singlet at 10.29 τ of linewidth 0.98 Hz at all temperatures studied. Scalar ^1H - ^{199}Hg coupling was, as in ether, observed at all temperatures between 36° and -70° with a coupling constant of 103 Hz.

Rapid methyl group exchange is indicated in methyl lithium-dimethylmercury mixtures in THF by a single broad NMR resonance at probe temperature (36°C.). As the temperature is lowered, the broad resonance begins to separate into two clearly discernible peaks at -18°C, due to the individual methyl groups of dimethylmercury and methyl lithium, as depicted in Figure 5. At -44°, the exchange appears completely stopped with the distance between the two peaks being 133 Hz.

Explanation of Figure 5

Temperature Dependence of Proton NMR Spectra of
 $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ Exchange in Tetrahydrofuran.
Li/Hg = 1.65



The methyl group exchange data presented in Figure 10 were obtained from the methyllithium linewidth in the temperature region where the spectrum was quite sensitive, *i.e.*, near the coalescence point of the methyllithium and dimethylmercury resonances. As was the case in ether, dimethylmercury self exchange is occurring rapidly at this point. Therefore, the dimethylmercury linewidth is not a true measure of its exchange with methyllithium alone. The activation energy was calculated from the slope of the THF line in Figure 10 to be 9.2 ± 2.0 kcal mole⁻¹.

Concentration dependent data were recorded in the slow exchange region, *i.e.*, -18°C for a variety of Li-Hg ratios. The methyllithium linewidth was found to be inversely proportional to Li/Hg at this temperature as recorded in Table 2.

Table 2.
Methyllithium Linewidth as a Function of Li/Hg
in THF at -18°C.

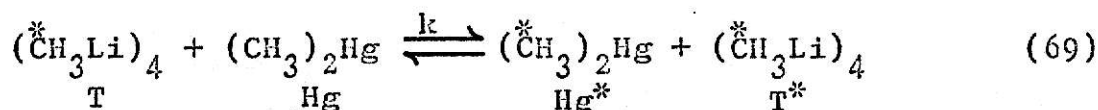
	Li/Hg	$\Delta_{\frac{1}{2}\text{CH}_3\text{Li}}(\text{Hz})$	$1/\tau_{\text{CH}_3\text{Li}}, \text{sec}^{-1}$
A.	4.20	7.0	17.3
B.	3.10	9.5	25.2
C.	2.30	11.5	31.4
D.	1.54	12.0	33.1
E.	0.76	16.5	47.2
F.	0.40	17.0	48.7

Mechanisms of Exchange

It appears that $1/\tau_{\text{CH}_3\text{Li}}$ is a linear function of (Hg) or any multiple of (Hg), such as: $(\text{Hg})/(\text{T})^{\frac{1}{4}}$, $(\text{Hg})/(\text{T})^{\frac{1}{2}}$, $(\text{Hg})(\text{T})^{\frac{1}{4}}$,

or $(\text{Hg})(\text{T})^{\frac{1}{4}} + (\text{Hg})/(\text{T})^{\frac{1}{4}}$. An example of this linear dependency is presented in Figure 6. However, $1/\tau_{\text{CH}_3\text{Li}}$ is not a linear function of $1/(\text{T})^{\frac{1}{2}}$ or (T) .

Certainly, the simplest mechanism consistent with the data obtained is direct reaction of the methyllithium tetramer with dimethylmercury:



The rate of formation of exchanged products is :

$$d(\text{Hg}^*)/dt = k(\text{T})(\text{Hg}) \quad (70)$$

From which:

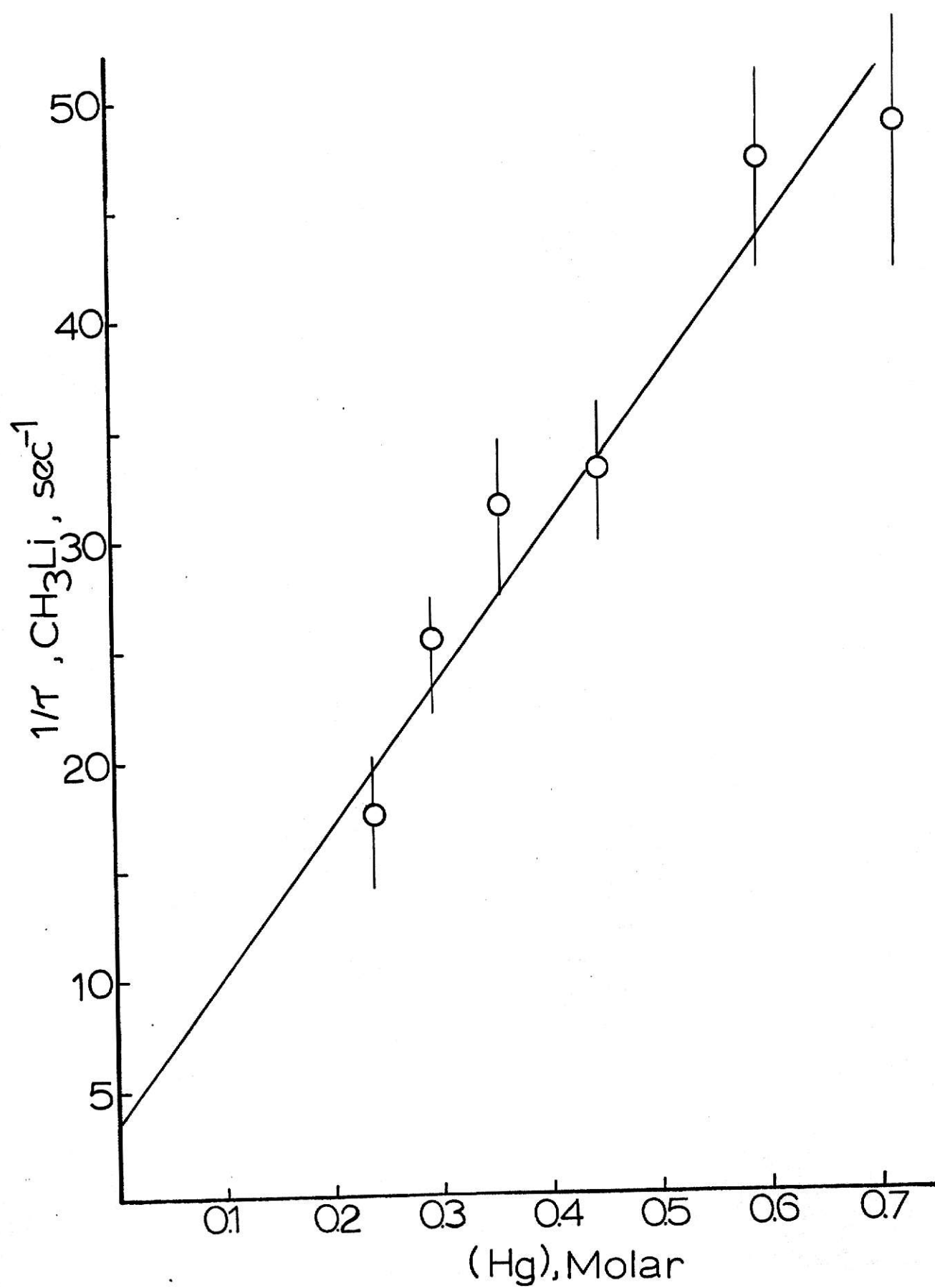
$$1/\tau_{\text{CH}_3\text{Li}} = 1/4(\text{T}) \cdot d(\text{Hg}^*)/dt = k(\text{Hg}) \quad (71)$$

Clearly, this mechanism cannot be eliminated as a possibility since it predicts $1/\tau_{\text{CH}_3\text{Li}}$ to be a linear function of (Hg) , as was observed. Furthermore, a plot of $1/\tau_{\text{CH}_3\text{Li}}$ vs. (Hg) would be predicted to have a slope of k and a zero intercept. Within the margin of experimental error, Figure 6 meets these requirements.

However, the concentration data obtained does not permit one to uniquely define the mechanism of exchange in THF. From the results presented above, one can make several observations. Since $1/\tau_{\text{CH}_3\text{Li}}$ is linearly dependent upon (Hg) , a tetrameric dissociation process cannot be the sole rate determining step. Therefore, Cases I, II, and IV in Section III A cannot be solely operative in THF when the reaction of the active species with dimethylmercury occurs more rapidly than the tetrameric dissociation.

Explanation of Figure 6

Concentration Dependence of Methylolithium
Linewidth in THF at -18°C .



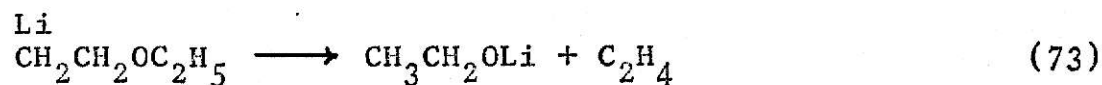
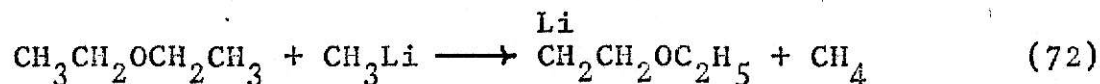
It appears that some of the assumptions made for this exchange in ether are no longer true in THF. The data indicate that any one of the five mechanisms proposed for ether could be occurring in THF if the proper assumptions are made to allow $1/\tau_{\text{CH}_3\text{Li}}$ to be a function of (Hg) or some multiple thereof. In each of the five cases in Section III A, the methyllithium linewidth is predicted to be a function of (Hg) if one assumes that reaction of the active exchange species with dimethylmercury is comparable to or slower in rate than any tetrameric dissociation.

It is not unreasonable to consider the possibility of two different mechanisms proceeding simultaneously at comparable rates, although one of these two mechanisms must be concentration dependent. The other, whose kinetic expression could be independent of Li/Hg would represent the intercept on the ordinate of a linear plot of $1/\tau_{\text{CH}_3\text{Li}}$ vs. (Hg). Furthermore, since $1/\tau_{\text{CH}_3\text{Li}}$ is not a linear function of $1/(T)^{\frac{1}{2}}$, any mechanism requiring this to be true cannot be solely operative. For example, cases III and V, where $2k_{-2}(M) \ll k_3(\text{Hg})$ and $k_{-2} \ll k_3(\text{Hg})$ respectively. This also suggests that these cases cannot be involved, i.e., are not occurring to any large extent, simultaneously with another mechanism.

C. Methyl lithium-Dimethylmercury Exchange in
1,2-Dimethoxyethane

Reaction of Methyl lithium with DME

Methyl lithium is known to react with the β -proton of diethylether to form ethylene, methane, and lithium ethoxide (27,28).

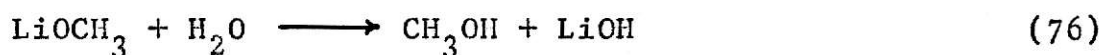
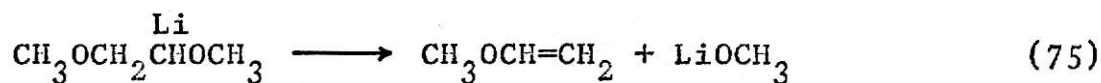
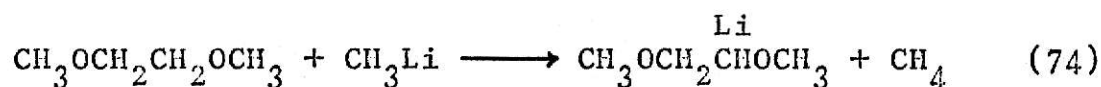


The reaction is quite slow and is not a problem at all if the samples are stored at dry ice temperature.

Methyl lithium attacks the α -proton of THF at room temperature (29). The reaction takes place faster than the reaction with diethylether; however, it can still be avoided by storing the samples at low temperature. Before preparing mixed samples of methyl lithium-dimethylmercury in DME, it was necessary to determine how and to what extent methyl lithium reacts with DME, since this reaction is fast enough to be troublesome.

Upon standing at room temperature for a short period of time a solution of methyl lithium in DME forms a white gelatinous precipitate. The NMR spectrum of this solution shows a resonance for methyl lithium at 12.01 τ and a resonance presumably due to LiOCH_3 133 Hz downfield from methyl lithium. As time progressed, the LiOCH_3 peak increased in intensity, while the methyl lithium peak simultaneously decreased.

Hydrolyzed portions of the precipitate and supernatant liquid were distilled and analyzed by gas chromatography. Matching retention times verified the presence of CH_3OH , the suspected reaction product. On this basis the proposed mechanism of reaction is:



The methylvinylether produced was undetected. It presumably evaporated rapidly after hydrolysis occurred.

The reaction of methyllithium with DME occurs more rapidly than with ether or THF; however, again extensive reaction can be avoided if the samples are prepared and stored at dry ice temperature as quickly as possible.

NMR of DME

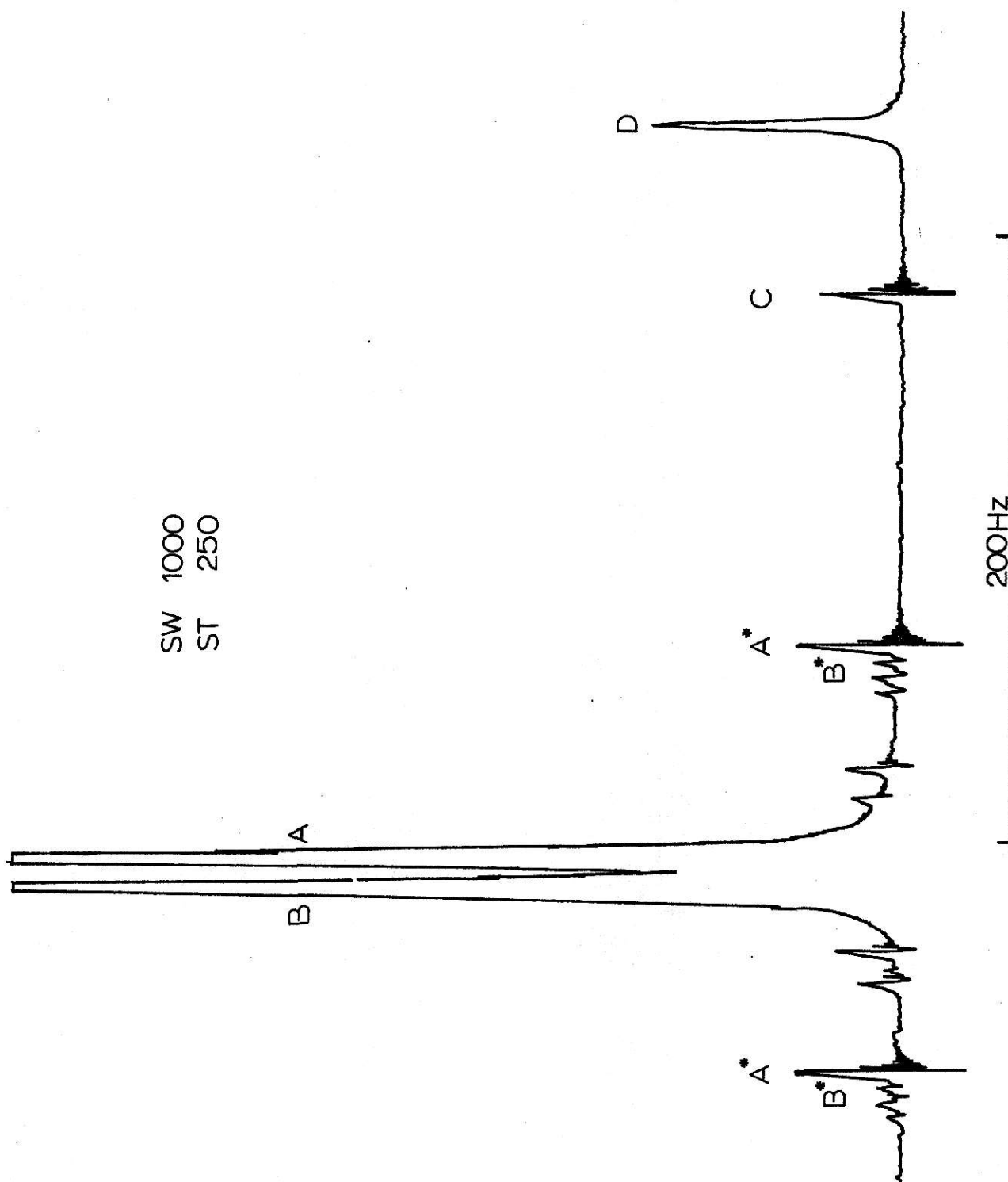
DME produces a first order NMR spectrum which consists of two singlets, one at 6.69τ of intensity three assigned to the methyl protons and another at 6.09τ assigned to the methylene protons (Figure 7). In addition, the methyl proton resonance exhibits $^{13}\text{C}-^1\text{H}$ singlet satellite peaks 70 Hz on each side. The methylene proton peak also exhibits $^{13}\text{C}-^1\text{H}$ satellite triplets 70 Hz on each side. The triplet satellites arise in the following manner: a doublet is produced from $^{13}\text{C}-^1\text{H}_{(1)}$ coupling (140 Hz) in a methylene group, then each member of this doublet

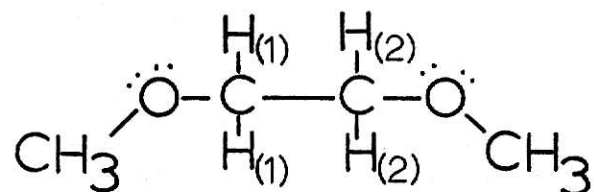
Explanation of Figure 7

Proton NMR Spectrum of $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ in DME at 34°C .

KEY

- A - methyl proton resonance from DME
- A* - ^{13}C -H satellite peaks from A
- B - methylene proton resonance from DME
- B* - ^{13}C -H satellite triplets from B
- C - proton resonance from LiOCH_3
- D - sharp resonance due to methyl groups rapidly exchanging from CH_3Li to $(\text{CH}_3)_2\text{Hg}$





is further split (5 Hz) by the two protons, $H_{(2)}$, on the adjacent methylene. Thus, it was possible to see 1H - 1H coupling indirectly through the carbon-13 proton coupling.

Methyl lithium-Dimethylmercury Exchange in DME

The proton NMR spectrum of methyl lithium in DME in the absence of exchange with dimethylmercury consists of a singlet of linewidth 1.42 Hz at 36°C 5.30 ppm upfield from the DME methyl resonance. As the temperature is lowered, the linewidth begins to broaden at -30°C and continues to do so until at -80°C the linewidth is 5.0 Hz (Figure 3).

Increased viscosity at the lower temperatures could be a contributing factor in the broadening; but the fact that the linewidth pattern for DME solutions is similar to ether and THF, and the fact that the resonances due to DME itself remains relatively sharp, suggests that the contribution from viscosity effects is small. Therefore, it appears that the broadening, as in ether and THF, can be ascribed to 7Li - 1H coupling as intermolecular exchange slows at lower temperature. In contrast to ether and THF, the association of methyl lithium in DME is not known. It would appear likely, however, that dissociation of a

methyl lithium aggregate, either tetramer or dimer, is involved in the intermolecular exchange. In any case, the exchange is considerably faster in DME than THF or ether.

The dimethylmercury resonance in DME appears 3.45 ppm upfield from the methyl DME resonance, with ^{199}Hg - ^1H singlet satellite peaks 52 Hz on each side of the resonance of methyl groups bonded to ^{200}Hg . The linewidth in the absence of exchange with methyl lithium remained 0.98 Hz over the temperature range from -78°C to 34°C .

The proton spectrum of a mixed sample of dimethylmercury and methyl lithium in DME consists of a single sharp resonance at 36°C . Its chemical shift is between that of methyl lithium and dimethylmercury in the absence of exchange and depends upon Li/Hg in the following manner:

$$\delta = f_{\text{CH}_3\text{Li}} \delta_{\text{CH}_3\text{Li}} + f_{(\text{CH}_3)_2\text{Hg}} \delta_{(\text{CH}_3)_2\text{Hg}}$$

, where

f = mole fraction of methyl groups

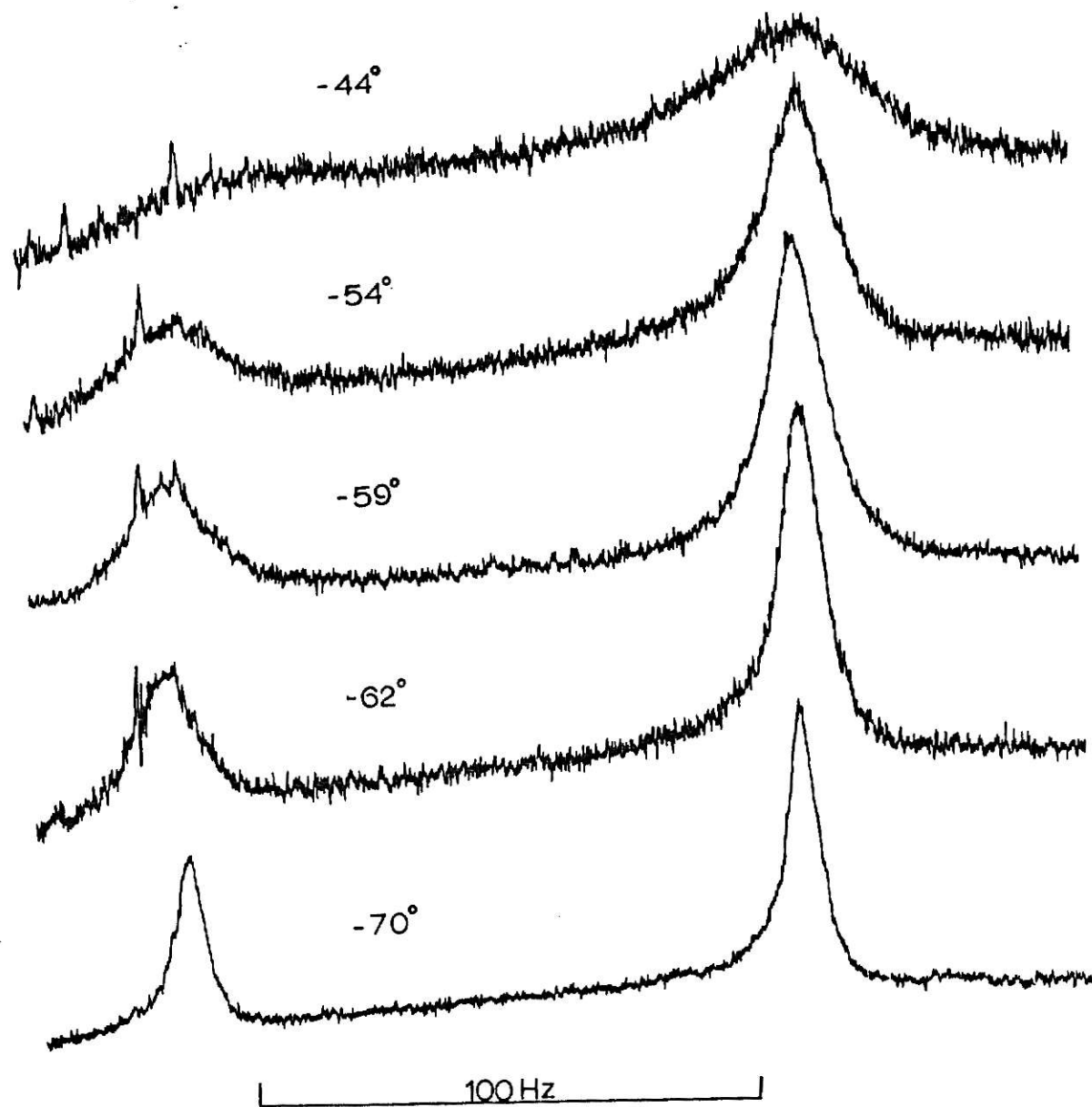
δ = chemical shift in the absence of exchange.

As the temperature is lowered to -40° , the single resonance begins to separate into two broad peaks, until, at -78°C two separate resonances are well defined (Figure 8). Clearly, methyl lithium-dimethylmercury methyl group exchange is occurring.

Methyl lithium linewidths were recorded and measured over the temperature range -78°C to -44°C . $1/\tau_{\text{CH}_3\text{Li}}$ was calculated at each temperature as described in the experimental section

Explanation of Figure 8

Temperature Dependence of Proton NMR Spectra of
 $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ Exchange in 1,2-Dimethoxyethane.
Li/Hg = 3.38



and the activation energy obtained from the slope of the Arrhenius plot shown in Figure 10. The activation energy for methyl group exchange in DME was 6.8 ± 2.0 kcal mole⁻¹; and the exchange is more rapid in DME than in either ether or THF.

Although no attempt was made to obtain extensive concentration dependent data, it was noted that $1/\tau_{\text{CH}_3\text{Li}}$ does depend upon Li/Hg. Spectra of solutions having various Li/Hg ratios were recorded at -78°C, at which temperature the methyllithium resonance is still significantly broadened by exchange with dimethylmercury. The data, Table 3, indicate that as Li/Hg decreases, the methyllithium linewidth increases.

Table 3.

Methyllithium Linewidth as a Function of Li/Hg
in DME at -78°C

	Li/Hg	$\Delta_{\frac{1}{2}\text{CH}_3\text{Li}}$ (Hz)	$1/\tau_{\text{CH}_3\text{Li}}^*$ (sec ⁻¹)
A.	5.06	5.1	3.3
B.	3.38	6.3	7.1
C.	1.69	10.1	19.0

* $\Delta_{\frac{1}{2}\text{CH}_3\text{Li}}^0$ @ -78°C = 4.06 Hz

Since the association of methyllithium in DME is not known, it is not possible to propose a detailed exchange mechanism. About the only conclusion one can make is that whatever the mechanism, it does not appear that methyllithium aggregate dissociation is rate determining, since this would require $\tau_{\text{CH}_3\text{Li}}$ to be independent of Li/Hg.

At -62°C , $\tau_{\text{CH}_3\text{Li}}$ for the methyllithium-dimethylmercury exchange in DME is 0.043. For comparison, $\tau_{\text{CH}_3\text{Li}}$ for ^7Li exchange in the $\text{CH}_3\text{Li-LiB}(\text{CH}_3)_4$ system, where it is known that the rate determining step is tetramer-dimer dissociation, at -62°C is 0.212. Thus, it appears that the methyl group exchange between methyllithium and dimethylmercury in DME is approximately five times faster than the ^7Li exchange between LiCH_3 and $\text{LiB}(\text{CH}_3)_4$ at -62°C .

IV. SUMMARY OF METHYLLITHIUM-DIMETHYLMERCURY EXCHANGE

Clearly, the rate of methyl group exchange between methyllithium and dimethylmercury is greatest in DME followed by THF, then diethylether. From Figure 9, one can see that the dimethylmercury linewidth, due to exchange with methyllithium is broad in DME even at -60°C . The same peak in THF is still broad, but much sharper than in DME. The dimethylmercury resonance at -60° in ether has sharpened to the same extent that it is at probe temperature in the absence of methyllithium, indicating very slow exchange at this temperature with methyllithium.

One can obtain an accurate comparison of the relative rates of exchange at a particular temperature by observing $1/\tau_{\text{CH}_3\text{Li}}$ in each solvent. $1/\tau_{\text{CH}_3\text{Li}}$ is directly proportional to the rate constant. From Figure 10 at 9°C , or $1/T(^{\circ}\text{K}) = 3.55 \times 10^{-3}$, the relative rates of exchange are approximately 1000:100:1.

The activation energies for exchange in each solvent were obtained from the slopes of the Arrhenius plots in Figure 10. In ether, THF, and DME the activation energies are 16.4 ± 2.0 , 9.2 ± 2.0 , and 6.8 ± 2.0 kcal mole $^{-1}$ respectively.

The methyllithium linewidth was found to be independent of Li/Hg in ether, but linearly dependent upon concentration in THF and DME.

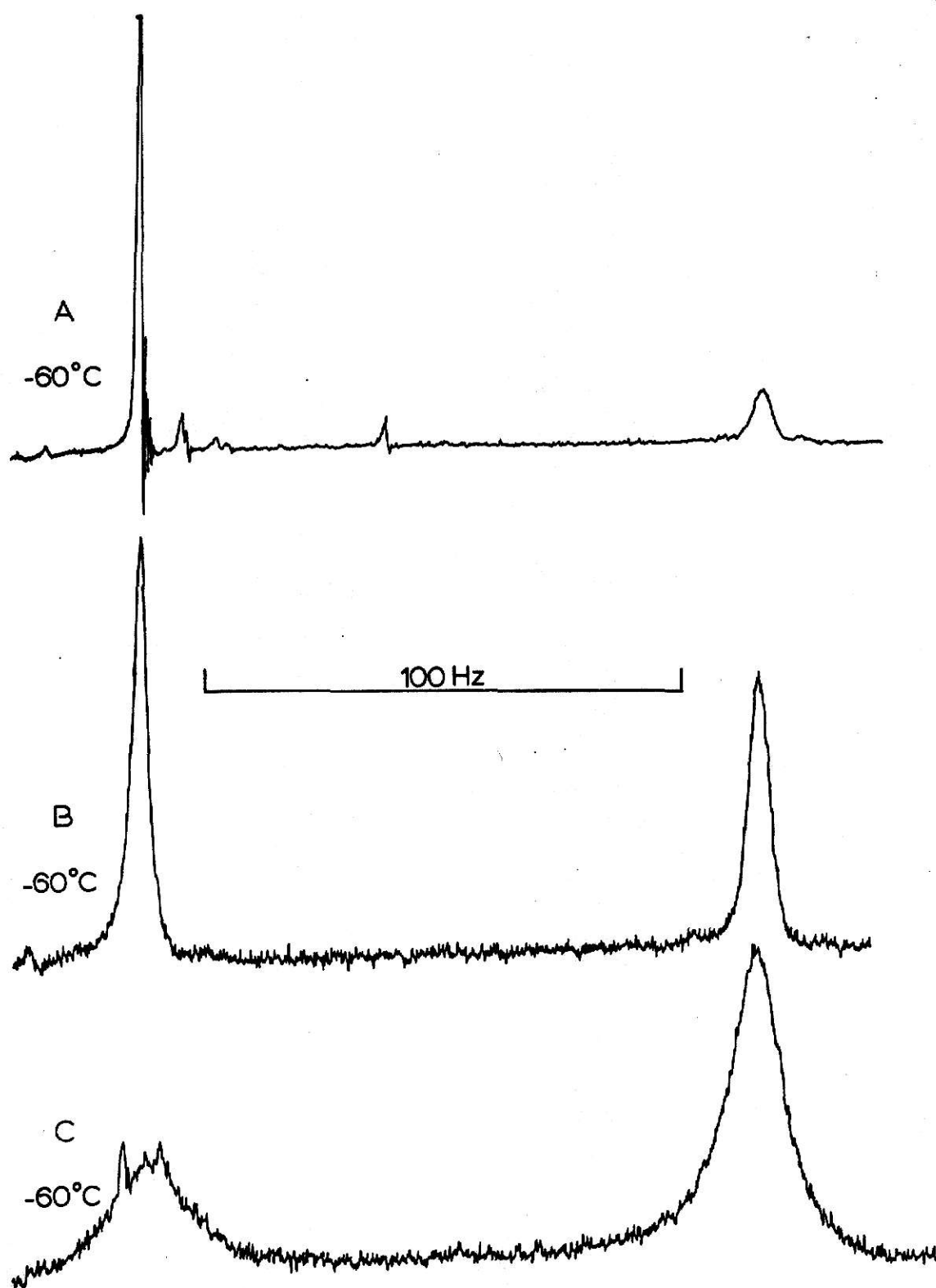
Several mechanisms for methyl group exchange were proposed in diethylether including: (1) a tetramer to dimer dissociation which is rate determining, (2) dissociation of the methyllithium tetramer into a contact ion pair which also would be rate

Explanation of Figure 9

Solvent Dependence of NMR Spectra for Methyl Group
Exchange Between CH_3Li and $(\text{CH}_3)_2\text{Hg}$.

- A - Diethylether
- B - Tetrahydrofuran
- C - 1,2-Dimethoxyethane

Note: ^{199}Hg - ^{200}Hg methyl group exchange in Ether has
apparently ceased at -60°C , while it appears to
proceed rapidly in THF and DME at this temperature.

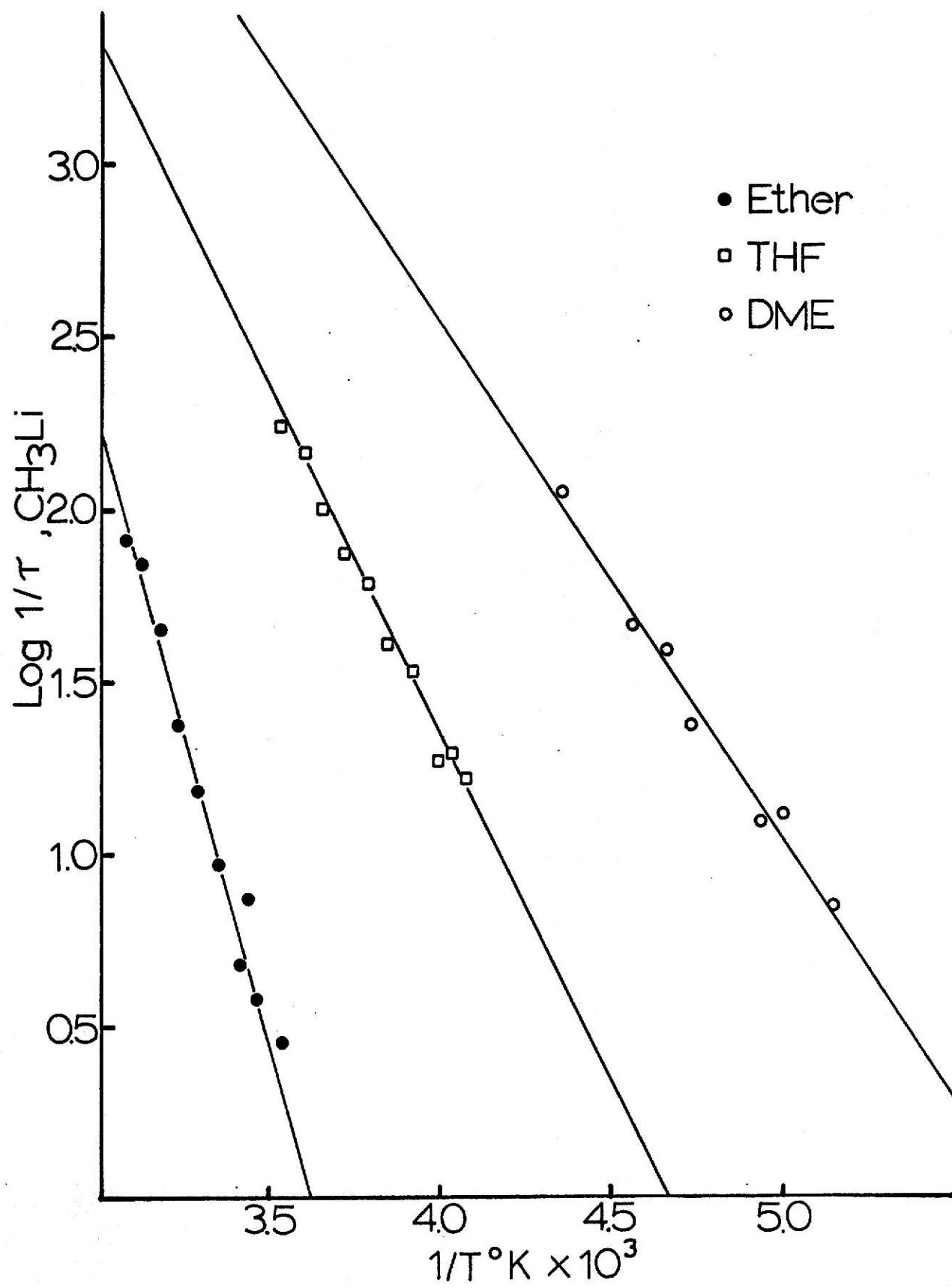


Explanation of Figure 10

Log $1/\tau_{\text{CH}_3\text{Li}}$ as a Function of $1/T(^{\circ}\text{K})$ for Ether, THF and DME.

Note: E_a was calculated from the slope of each line:

$$\begin{aligned} E_a(\text{ether}) &= 16.4 \pm 2.0 \text{ kcal mole}^{-1} \\ E_a(\text{THF}) &= 9.2 \pm 2.0 \text{ kcal mole}^{-1} \\ E_a(\text{DME}) &= 6.8 \pm 2.0 \text{ kcal mole}^{-1} \end{aligned}$$



determining, (3) dissociation of the tetramer directly to the monomer species, and also (4) dissociation of the tetramer to the dimer, then to the monomer with the dimer-monomer step being rate limiting. Although no single mechanism could be verified, the tetramer to contact ion pair possibility was most likely in light of the magnitude of the activation energy and the energetic unfeasibility of the tetramer to monomer dissociation process. The formation of any complex species, such as $\text{LiHg}(\text{CH}_3)_3$ was not directly observed, probably due to its low concentration and consequently its insignificance in the rate limiting step.

In THF, it was again difficult to assign a unique mechanism for exchange. $1/\tau_{\text{CH}_3\text{Li}}$ appeared to be a linear function of (Hg) which suggests that any mechanism, if operating solely, cannot have tetrameric dissociation as the rate determining step. This would require that $1/\tau_{\text{CH}_3\text{Li}}$ be independent of Li/Hg . The simplest mechanism consistent with the data is the direct reaction between tetramer and dimethylmercury.

No extensive concentration dependent data were obtained in DME; however, preliminary results indicate $1/\tau_{\text{CH}_3\text{Li}}$ to be linearly dependent upon Li/Hg . Exchange mechanisms are particularly difficult to assign in DME, since the association of methyllithium is not known in this solvent as it is in ether and THF. Once again the indication is that the rate determining step is not a tetrameric dissociation.

Comparison of τ values at -62°C for the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ system in DME and the $\text{CH}_3\text{Li}-\text{LiB}(\text{CH}_3)_4$ system in ether indicate the exchange is five times faster in DME than the ^7Li exchange

in ether, where the rate determining step is known to be tetrameric dissociation to the dimer.

V. DIMETHYLMERCURY SELF EXCHANGE

The proton spectrum of dimethylmercury in THF, ether or DME consists of three sharp lines at $+36^{\circ}\text{C}$; one intense line due to methyl groups bonded to mercury isotopes of spin zero and two satellite lines due to methyl groups bonded to mercury-199 of spin $\frac{1}{2}$ (16.92% natural abundance). The two satellites are separated by 103 Hz in each solvent.

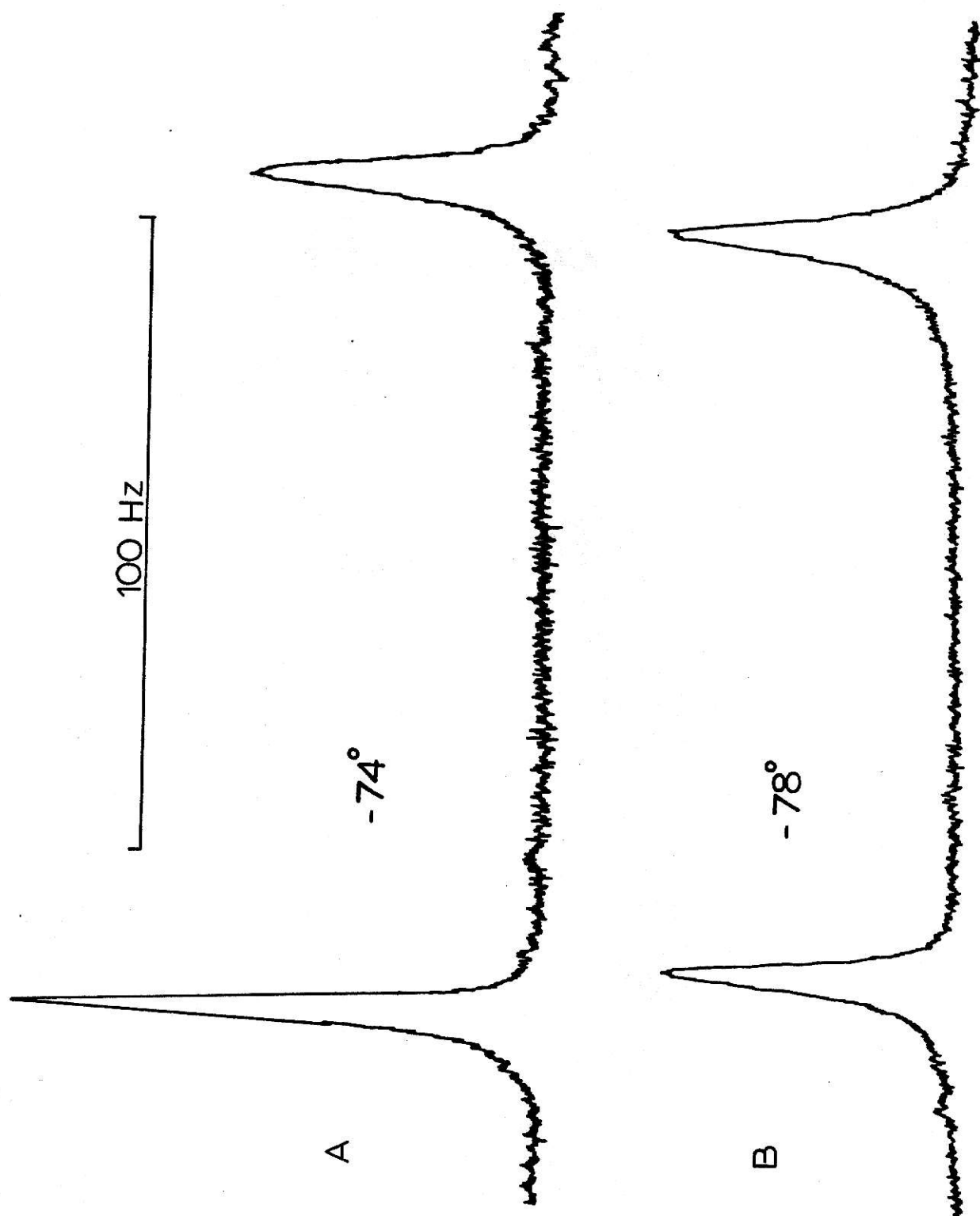
Proton spectra of ether solutions (Figure 4) containing dimethylmercury and methyllithium show two broad resonances at $+36^{\circ}\text{C}$, a result of methyl group exchange between these two compounds. When the temperature is lowered to about $+6^{\circ}\text{C}$, the methyllithium resonance becomes very sharp with the linewidth being essentially the same as that for methyllithium alone in ether indicating that exchange between methyllithium and dimethylmercury has become slow on the NMR time scale. At this same temperature, however, the dimethylmercury resonance remained broad; and it was not until about -60°C was reached that the satellite lines approached the sharpness observed for dimethylmercury alone at $+36^{\circ}\text{C}$ (15). Thus, a rather facile exchange of methyl groups between molecules of dimethylmercury is apparent.

The same general pattern of temperature dependence is observed with THF solutions, but it appears that the exchange reactions are faster in THF than in ether. At -74°C in THF (Figure 11), the dimethylmercury resonance is still broad and the satellite lines cannot be seen; the spectrum appears similar to that for ether solutions at about -10°C .

Explanation of Figure 11

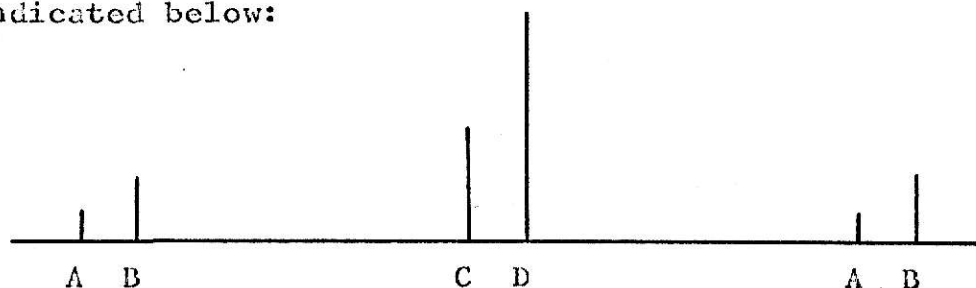
Proton NMR of the $\text{CH}_3\text{Li}/(\text{CH}_3)_2\text{Hg}$ System
in A-THF and in B-DME.

Note: The ^1H - ^{199}Hg satellite peaks are not discernible
in either solvent at these temperatures.



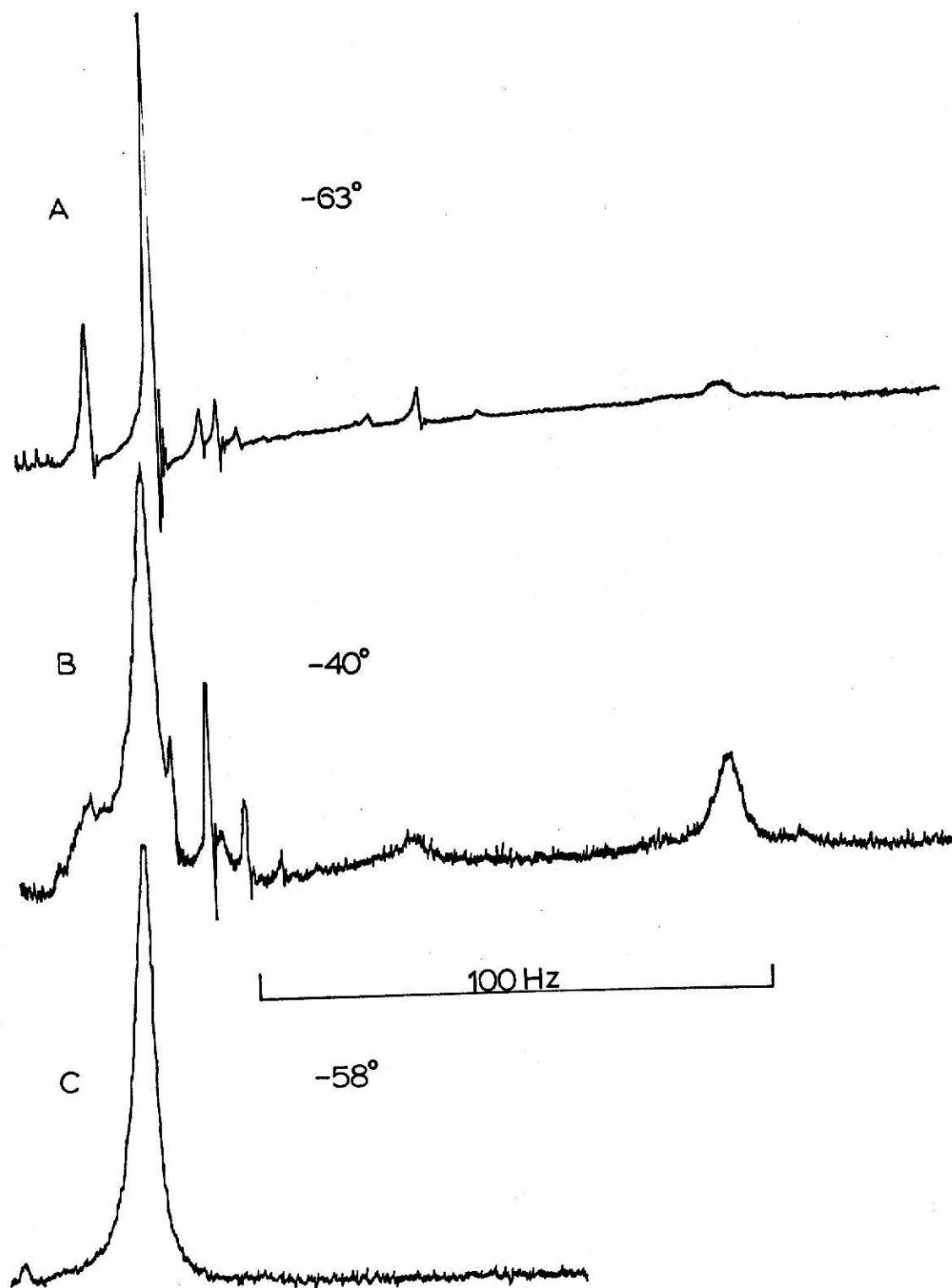
While it is clear that methyl lithium-dimethylmercury exchange is faster in DME than in THF (see section IV), it was not possible from the information available to discern the relative rates of the dimethylmercury self-exchange in these two solvents. At -78°C in DME (Figure 11), the satellite lines were not observed; so it appeared that the dimethylmercury self-exchange is at least as fast in DME as in THF.

Additional evidence was obtained for exchange of methyl groups from one Hg atom to another by observing that $(\text{CH}_3)_2\text{Hg}$ exchanges methyl groups with $\text{C}_6\text{H}_5\text{HgCH}_3$ in diethylether. $\text{C}_6\text{H}_5\text{HgCH}_3$ arises as a result of combining $\text{C}_6\text{H}_5\text{Li}$ and $(\text{CH}_3)_2\text{Hg}$ in diethylether. From Figure 12 it is clear that no exchange is occurring between $\text{C}_6\text{H}_5\text{HgCH}_3$ and $(\text{CH}_3)_2\text{Hg}$ at -60°C ; however, as the temperature is raised to -40° coalescence of these peaks begins to occur. Even the ^{199}Hg satellite peaks reflect this coalescence, and hence, exchange of methyl groups. The same system in THF (Figure 12C) exhibits a single broad resonance at -58° indicating rapid methyl group exchange between $\text{C}_6\text{H}_5\text{HgCH}_3$ and $(\text{CH}_3)_2\text{Hg}$ at this temperature. As with dimethylmercury self exchange, it appears to be more rapid in THF than in ether. The $\text{C}_6\text{H}_5\text{HgCH}_3/(\text{CH}_3)_2\text{Hg}$ system actually represents a six-site exchange system as $\text{CH}_3^{200}\text{HgC}_6\text{H}_5$ not only exchanges with $(\text{CH}_3)_2^{200}\text{Hg}$, but also with $\text{C}_6\text{H}_5^{199}\text{HgCH}_3$ and $(\text{CH}_3)_2^{199}\text{Hg}$ as indicated below:

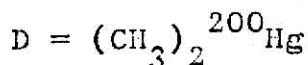
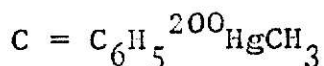
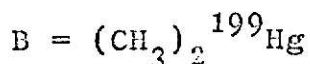
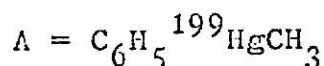


Explanation of Figure 12

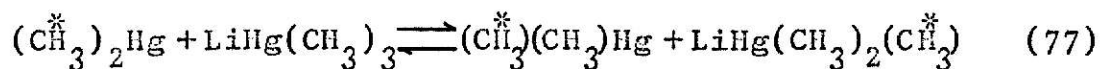
Temperature Dependence of Proton NMR Spectra of
 $\text{C}_6\text{H}_5\text{HgCH}_3/(\text{CH}_3)_2\text{Hg}$ in: A,B-Diethylether
and C- THF.



, where



In contrast to the corresponding cadmium (11), zinc (10), magnesium (10), and beryllium (26) systems in ether, no mixed complex was observed in the NMR spectra of $CH_3Li/(CH_3)_2Hg$ system in ether, THF or DME. However, it appeared that a minute amount of complex, possibly $LiHg(CH_3)_3$, was present which served to facilitate the dimethylmercury self-exchange. The exchange could occur through a reaction of the type:



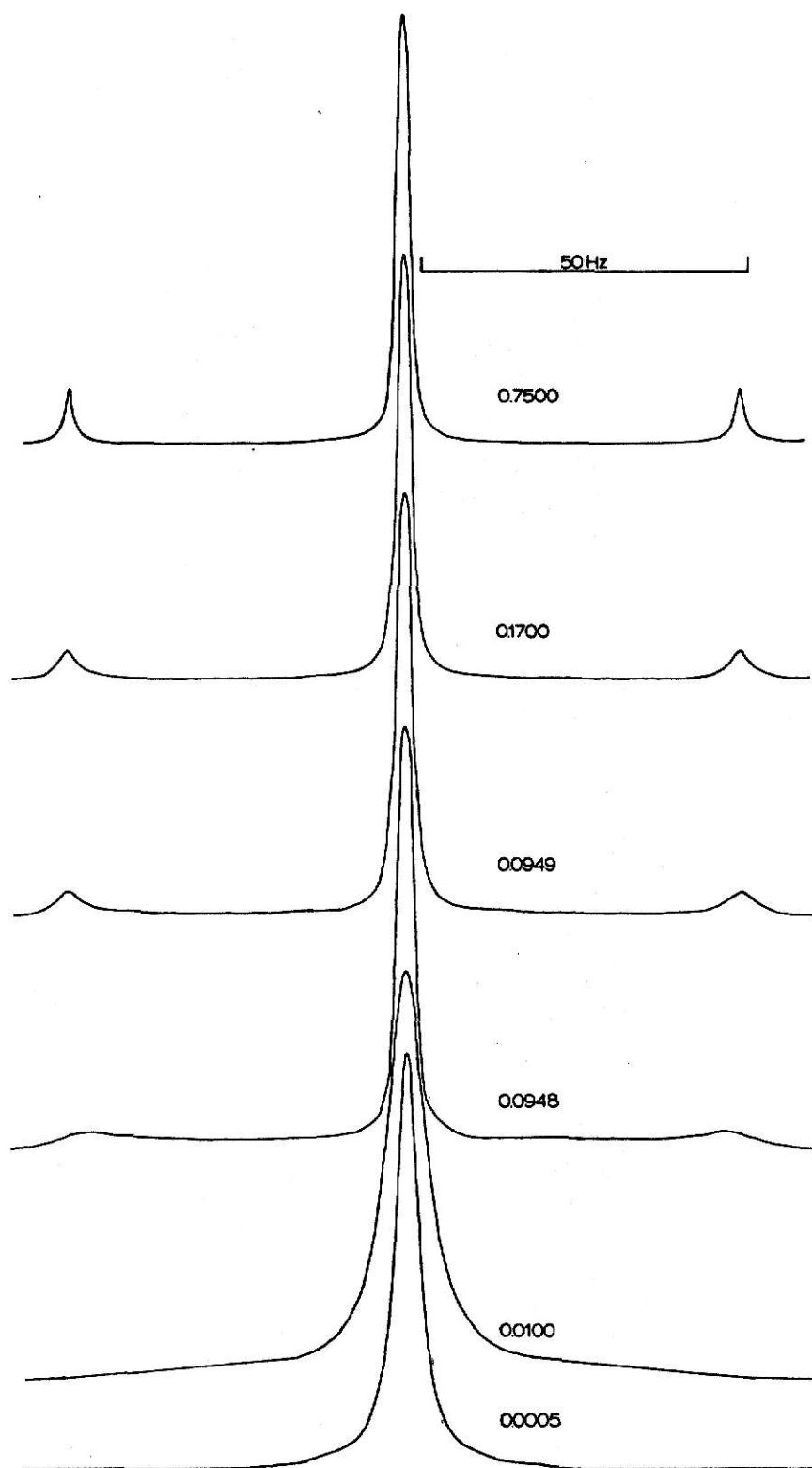
Similar exchanges in the magnesium, zinc, and cadmium systems in ether, are known to be very rapid. It is notable that ordinary Lewis bases, such as ethers, amines and other basic solvents, do not bring about rapid dimethylmercury self-exchange; whereas, the apparent formation of an "ate" complex does.

Theoretical NMR spectra, shown in Figure 13, were calculated using the three site exchange computer program, explained in the Appendix. The τ value given for each spectrum in Figure 13 represents the lifetime of a methyl group on ^{199}Hg , τ_A . The overall correlation time, τ^* , for the system is

Explanation of Figure 13

Theoretical ^1H -NMR Spectra for ^{199}Hg - ^{200}Hg Methyl
Group Exchange

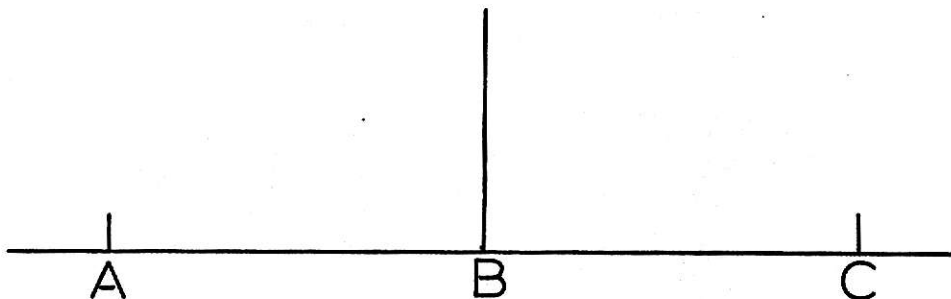
Note: The indicated τ values are for the lifetime
of a methyl group on ^{199}Hg . See Fig. 14 for
an estimated E_a for this exchange.



given by:

$$1/\tau^* = \frac{1}{\tau_A} + \frac{1}{\tau_B} + \frac{1}{\tau_C} \quad (78)$$

,where τ_A , τ_B , and τ_C represent the lifetime of a methyl group on the respective sites as illustrated below.



One may obtain $1/\tau^*$ as a function of τ_A by using the relationships:

$$\tau_A = \tau_C \quad (79)$$

$$P_A = \tau_A/2 \tau_A + \tau_B \quad (80)$$

,where $P_A = 0.0846$ and represents the population of site A.

Accordingly,

$$1/\tau^* = 2/\tau_A + 1/9.82 \tau_A \quad (81)$$

The rate constant for reaction (77) must surely be second order. In order to obtain this second order constant, one would have to know (1) τ for the complex species and (2) the concentration of the complex species. Since the NMR sees only CH_3Li and $(\text{CH}_3)_2\text{Hg}$ and no detectable complex at any temperature,

τ complex was not obtainable, nor was the concentration of the complex. The three site exchange computer program gives only information on the lifetime of methyl groups on dimethylmercury. Therefore, only a first order rate constant representing exchange of methyl groups to and from dimethylmercury can be obtained from the calculated spectra. At the disappearance of the satellites (Figure 13), $\tau_A = 0.0948$, the first order rate constant from Expression (82), using Expression (81)

$$1/\tau^* = k_1 \quad (82)$$

was calculated to be 25.7 sec^{-1} . This corresponds to a temperature of -38°C in ether. In THF and DME, satellite lines were not observed at temperatures as low as -74°C and -78°C , respectively, which means that k_1 in these solvents must be greater than 25.7 sec^{-1} and could be as high as 2000. Considering that sharp satellite lines are observed, $k_1 > 1.3$, at 36°C when methyl lithium is not present, it is obvious methyl lithium causes a very great enhancement of the self exchange rate. For THF and DME, it appears the rate is enhanced by a factor as high as 10^6 .

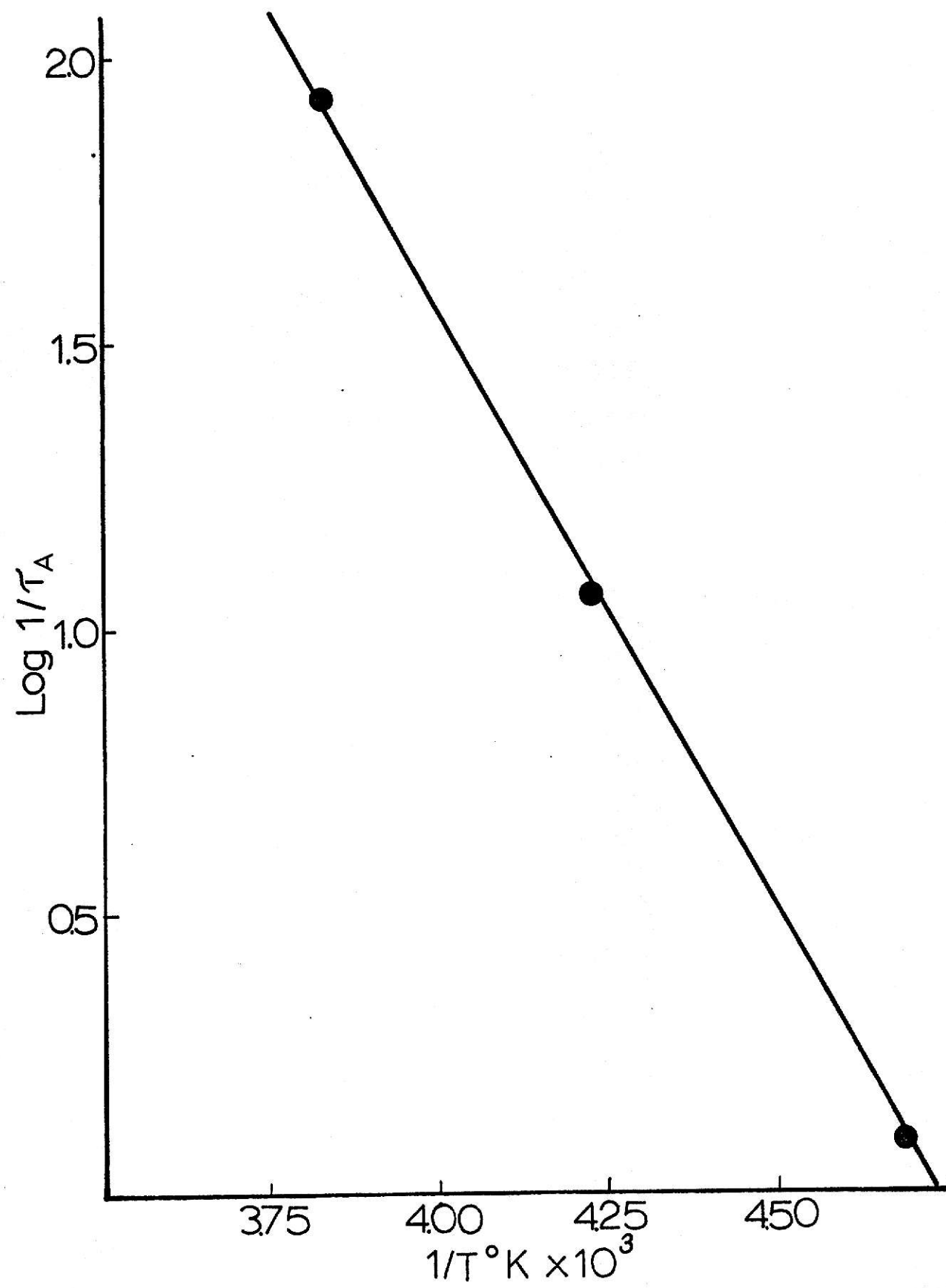
The theoretical spectra were compared with the experimental spectra obtained over a temperature range from -60°C to 0°C in diethylether. Precise comparisons were difficult due to the differences in size of the three peaks. However, a rough estimate of the activation energy from an Arrhenius plot of $\log 1/\tau_A$ vs. $1/T(^{\circ}\text{K})$ yielded a value of $9.1 \pm 2.0 \text{ kcal mole}^{-1}$ (Figure 14).

Explanation of Figure 14

Log $1/\tau_A$ as a Function of $1/T(^{\circ}\text{K})$ for ^{200}Hg - ^{199}Hg
Methyl Group Exchange in Diethylether.

$$E_a = 9.1 \pm 2.0 \text{ kcal mole}^{-1}$$

Note: This plot was obtained through comparison of experimental spectra at various temperatures with calculated spectra in Fig. 13.



This low E_a was not unreasonable in light of the fact that an E_a of 6.0 ± 0.5 kcal mole⁻¹ for $Tl(CH_3)_3$ methyl group exchange has been reported (30).

Dimethylmercury self exchange occurs simultaneously with $CH_3Li-(CH_3)_2Hg$ exchange in all three solvents. To obtain an estimate of the relative rates of exchange of these two processes in ether, a temperature was chosen at which the methyllithium peak is broadened due to exchange with dimethylmercury and the dimethylmercury peak is broadened as a result of both self-exchange and exchange with methyllithium. A temperature of +16°C seemed to be most appropriate. The linewidth of dimethylmercury results from self exchange (exchange between ^{200}Hg and ^{199}Hg) and exchange with methyllithium, as represented by the following equation.

$$1/\tau_{(CH_3)_2Hg_{total}} = 1/\tau_{self\ exchange} + 1/\tau_{exchange\ with\ CH_3Li} \quad (83)$$

The $1/\tau$ representing exchange with methyllithium can be obtained from the relationship:

$$P_{CH_3Li} = \frac{\tau_{CH_3Li}}{\tau_{CH_3Li} + \tau_{(CH_3)_2Hg}} \quad (84)$$

For the sample employed, $Li/Hg = 1.24$, so the population of the methyllithium peak, P_{CH_3Li} , is 0.553. At 16°C, the linewidth of the methyllithium peak yields $\tau_{CH_3Li} = 0.266$. Substitution of these quantities into (84), one obtains:

$$1/\tau_{exchange\ with\ CH_3Li} = 2.3\ sec^{-1}$$

The total $1/\tau$ for dimethylmercury is obtained from the line-width of the dimethylmercury peak. At $+16^{\circ}\text{C}$, $1/\tau_{\text{total}} = 26.4 \text{ sec}^{-1}$. Equation (83) can then be employed to calculate $1/\tau$ representing dimethylmercury self exchange.

$$1/\tau_{\text{self exchange}} = 26.4 \text{ sec}^{-1} - 2.3 \text{ sec}^{-1} = 24.1 \text{ sec}^{-1}$$

Comparison of the values 24.1 and 2.3 indicate that at $+16^{\circ}\text{C}$, dimethylmercury self exchange occurs more than ten times faster than methyl lithium-dimethylmercury exchange at 16°C in diethylether. A similar comparison with THF and DME solutions is not possible.

ACKNOWLEDGEMENTS

Clearly, a thesis of this size could not have been completed without the aid of several persons. Deepest gratitude is expressed to Dr. L.M. Seitz for his careful guidance and understanding throughout my graduate program.

Financial support in the form of a traineeship with funds provided by the National Aeronautics and Space Administration is gratefully acknowledged.

Thanks is also expressed to Mr. B.F. Little, without whose helpful discussions and moral encouragement this degree would not have been attained.

To my wife, Gail, special gratitude is expressed for her encouragement and unselfish sacrifices in this venture. She happily shouldered the unenviable task of typing the preliminary copies of the manuscript, and helped with many of the figures.

My parents, Mr. and Mrs. D.D. Hall, deserve a word of appreciation for the value they placed on a formal education. My parents have served as outstanding examples of moral character and wisdom throughout the most distressing situations.

LITERATURE CITED

1. E. Weiss and E.A.C. Lucken, J. Organometal. Chem., 2, 197 (1964).
2. P. West and R. Waack, J. Am. Chem. Soc., 89, 4395 (1967).
3. L.M. Seitz and T.L. Brown, J. Am. Chem. Soc., 88, 2174 (1966).
4. L.D. McKeever, R. Waack, M.A. Doran and E.B. Baker, J. Am. Chem. Soc., 90, 3244 (1968).
5. T.L. Brown, L.M. Seitz and B.Y. Kimura, J. Am. Chem. Soc., 90, 3245 (1968).
6. R.E. Dessy, F. Kaplan, G.R. Coe and R.M. Salinger, J. Am. Chem. Soc., 85, 1191 (1963).
7. L.M. Seitz and T.L. Brown, J. Am. Chem. Soc., 88, 4140 (1966).
8. C.R. McCoy and A.L. Allred, J. Am. Chem. Soc., 84, 912 (1962).
9. B.J. Wakefield, Adv. Inorg. and Radiochem., 11, 341 (1968).
10. L.M. Seitz and T.L. Brown, J. Am. Chem. Soc.: 88, 4140 (1966); 89, 1602 (1967); 89, 1607 (1967).
11. L.M. Seitz and B.F. Little, J. Organometal. Chem., 18, 227 (1969).
12. K.C. Williams and T.L. Brown, J. Am. Chem. Soc., 88, 4134 (1966).
13. M. Witanowski and J.D. Roberts, J. Am. Chem. Soc., 88, 737 (1966).
14. S. Toppet, G. Slincks and G. Smets, J. Organometal. Chem., (Amsterdam), 9, 205 (1967).
15. L.M. Seitz and S.D. Hall, J. Organometal. Chem., 15, P7 (1968).
16. G. Wittig, Ann., 571, 167 (1951).
17. T.L. Brown, D.W. Dickerhoof, D.A. Bafus and G.L. Morgan, Rev. Sci. Instr., 33 491 (1962).
18. C.S. Johnson, Jr., Advan. Magnetic Resonance, 1, 33 (1965).

19. G.M. Whitesides and J.S. Fleming, J. Am. Chem. Soc., 89, 2855 (1967).
20. T.L. Brown, Acc. Chem. Res., 1, 23 (1968).
21. R. Waack and M.A. Doran, J. Am. Chem. Soc., 91, 2456 (1969).
22. R. Waack and M.A. Doran, J. Org. Chem., 32, 3395 (1967).
23. R.A.H. Casling, A.G. Evans, and N.H. Rees, J. Chem. Soc., B 519 (1966).
24. T.L. Brown, J. Organometal. Chem., 5, 191 (1966).
25. S. Bywater and D. Worsfold, J. Organometal. Chem., 10, 1 (1968).
26. L.M. Seitz and B.F. Little, personal communication.
27. R.L. Burwell, Jr., Chem. Rev., 54, 615 (1954).
28. R.L. Letsinger and D.F. Pollart, J. Am. Chem. Soc., 78, 6079 (1956).
29. H. Gilman and B.J. Gaj, J. Am. Chem. Soc., 22, 1165 (1957).
30. G.E. Coates, M.L.H. Green and K. Wade, "Organometallic Compounds", 1, 365 (1967).

APPENDIX

A Fortran computer program was used for computation of theoretical spectra of a three-site exchange system. This program calculates line shapes for spin systems composed of spin $\frac{1}{2}$ nuclei undergoing exchange between magnetically non-equivalent sites. The fundamental mathematical operation performed by the program is the solution of equation (85),

$$I(\omega) \propto \left[\begin{pmatrix} I_1, I_2, I_3, \dots \end{pmatrix} \begin{pmatrix} -\alpha_1 - K_{11}/\tau & K_{12}/\tau & K_{13}/\tau \\ K_{21}/\tau & -\alpha_2 - K_{22}/\tau & K_{23}/\tau \\ K_{31}/\tau & K_{32}/\tau & -\alpha_3 - K_{33}/\tau \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}^{-1} \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \end{pmatrix} \right] \quad (85)$$

, where

$I(\omega)$ = intensity of the spectrum at frequency ω

I_k = intensity of line k

$\alpha_k = i(\omega_k - \omega) + 1/T_{2k}$

K_{ij} are matrix elements of the kinetic exchange matrix K which specifies the exchange scheme. τ is the pre-exchange lifetime. Here ω_k is the frequency at which the intensity is being calculated, and T_{2k} is the relaxation time characterizing the k^{th} line.

The basic input parameters consist of identity cards followed by the first data card consisting of \$\$\$\$EXCH. The second data card contains:

cols 1 - 9: problem no.
cols 10-14: no. of peaks
cols 14-19: sweep width of program
cols 25-30: beginning computation frequency

Subsequent cards are TAU cards with the value of TAU beginning in column 10. Following the TAU cards is an ENDTAU card (columns 1 through 6) signifying the last of the TAU values to be read. Subsequent to ENDTAU are the exchange matrix cards, each with one row of the matrix punched on it, the first number beginning in column 1, the others following in any orderly properly spaced alignment. The end of the data cards is signified by a \$\$\$\$STOP card, and the end of the program by a /* card.

NUCLEAR MAGNETIC RESONANCE STUDIES OF
EXCHANGE REACTIONS BETWEEN
ORGANOLITHIUM AND ORGANOMERCURY COMPOUNDS

by

STANLEY DEAN HALL

B.A., Sterling College, 1967

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

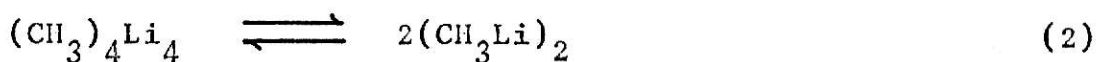
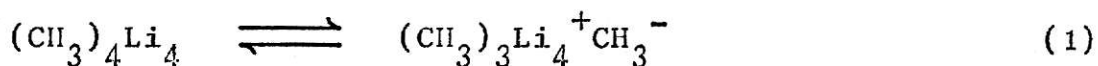
KANSAS STATE UNIVERSITY
Manhattan, Kansas

1970

The tendency for complex formation between mercury alkyls and methyllithium is relatively low, and the methyl group exchange much slower than with Zn, Mg or Cd dialkyls. Therefore, the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ system seemed to be a good system for obtaining activation parameters and other information about the rate determining step for the exchange process.

A study of the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ methyl group exchange by NMR in diethylether, tetrahydrofuran, and 1,2-Dimethoxyethane yielded activation energies of 16.4 ± 2.0 , 9.2 ± 2.0 , and 6.8 ± 2.0 kcal mole⁻¹ respectively. From an Arrhenius plot of $\log 1/\tau_{\text{CH}_3\text{Li}}$ versus $1/T(^{\circ}\text{K})$ at 6°C , the rate of methyl group exchange was observed to be $\text{DME} > \text{THF} > \text{Ether}$, in the approximate ratio of 1,000:100:1.

In diethylether the mechanism appeared to be a dissociation of the CH_3Li tetrameric aggregate into a contact ion pair species which appeared to be the rate determining step (1), and subsequent reaction with $(\text{CH}_3)_2\text{Hg}$. It was noted that tetramer to dimer dissociation (2) was probably not the rate determining step as it was in the $\text{CH}_3\text{Li}-\text{LiB}(\text{CH}_3)_4$ system studied by Williams and Brown, principally because of the higher activation energy and slower exchange rate obtained for the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ system.



In THF, the mechanism of exchange is doubtful; however since $1/\tau_{\text{CH}_3\text{Li}}$ is a linear function of $[(\text{CH}_3)_2\text{Hg}]$, the simple

second order reaction of methyllithium tetramer with dimethylmercury is suggested. This observation also suggests that if a methyllithium tetrameric dissociation mechanism is solely operative, the dissociation is not the rate determining step.

In DME, $1/\tau_{\text{CH}_3\text{Li}}$ again appears to be dependent upon Li/Hg; and although extensive rate data were not obtained, it appeared that the rate determining step is not methyllithium dissociation.

It was also observed that methyllithium facilitates methyl group exchange between ^{199}Hg and ^{200}Hg , which was directly observed in ether and measured, with the aid of a complete three-site line shape analysis from a Fortran computer program, to proceed with an estimated activation energy of approximately $9.0 \text{ kcal mole}^{-1}$. ^{199}Hg - ^{200}Hg exchange occurs approximately ten times faster in ether than the methyl group exchange between CH_3Li and $(\text{CH}_3)_2\text{Hg}$ at 16°C . The exchange is more rapid in THF and DME; but no comparison of these two solvents was obtainable. This exchange process suggests the presence of the complex species, $\text{LiHg}(\text{CH}_3)_3$, through which methyl group exchange is thought to occur in the following manner:

