SPECTROSCOPIC STUDIES
OF NON-TRANSITION
ORGANOMETALLIC COMPOUNDS

A Thesis
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by

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ABSTRACT

PART I of this thesis is concerned with the Raman and infrared spectra of some alkyl-zinc and alkyl-magnesium compounds.

Values of the zinc-carbon stretching frequencies for ZnR_2 (R = Me, Et) solutions in ethers (Et_2O, THF, DME) and complexes, ZnR_2L_2 (R = Me, Et; L_2 = py_2, dipy, TMED) are consistent with a bending of the C - Zn - C skeleton and a weakening of the Zn-C bond when the zinc dialkyl is in a co-ordinating environment.

The infrared spectra of 'RZnI' (R = Me, Et) solutions in ethers (THF, DME) and coincident Raman and infrared values of ν(Zn - C) for a diethyl ether solution of 'EtZnI', provide evidence for an RZnI monomer as the principal solution species. 'Mixed' ($R_2Zn + ZnX_2$) and normal ('RZnI') solutions both contain the same species. Infrared spectra of new complexes, $RZnIL_2$ (R = Me, Et; L_2 = py_2, dipy, TMED, DME) are given.

Raman spectra of Grignard reagents and $MgEt_2$ in Et_2O and THF are reported but no structural conclusions can be reached.

Calculations have been made using an XY_2 model.

PART II of this thesis is a study of mercury (199) - proton spin coupling in some aryl mercury compounds. The

Hg - H coupling constants vary in a similar manner to the analogous H - H parameters but are approximately 20 times larger. This similarity and the variation of Hg - H coupling in the series R_2Hg, RHgOAc which is explained by changes in the s-character of the mercury bonding orbital and the effective nuclear charge of the mercury atom, support a predominant Fermi contact mechanism for mercury (199) - proton coupling.

In the Supplement, ^{19}F n.m.r. parameters for some bis-(pentafluorophenyl)thallium(III) compounds are reported and the variation of Tl-F coupling correlated with the charge of the complex.

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5. INTRODUCTION

ABBREVIATIONS

Me	Methyl	Pe^n	n-Pentyl
Et	Ethyl	Pe^i	iso-Pentyl
Pr^n	n-Propyl	Vi	Vinyl
Pr^i	iso-Propyl	Ph	Phenyl
Bu^n	n-Butyl	p-Tol	p-Tolyl
Bu^i	iso-Butyl	OAc	Acetate

Et_2O	Diethyl Ether	MeOH	Methanol
THF	Tetrahydrofuran	Me_2CO	Acetone

DME	1,2-Dimethoxyethane
TMED	N,N,N',N'-Tetramethylethylenediamine
DMSO	Dimethyl Sulphoxide

py	Pyridine	dipy	Dipyridyl

o-phen	ortho-Phenanthroline

PART I

1. INTRODUCTION

1.1. General Survey.

The organometallic compounds of the Group II elements are of two main types, the dialkyls and diaryls MR_2, and compounds with the empirical formula 'RMX', where X = Cl, Br, I.(1) For the latter several formulations are possible (Fig 1). Either true RMX molecules or $R_2M + MX_2$ mixtures may exist with dimers or higher polymers formed using halogen bridges from RMX or $R_2M + MX_2$ units, with equilibria between any two or more species. Chemical and physical behaviour ranges from the numerous air and water stable mercury compounds to the few highly reactive calcium, strontium, and barium derivatives.

Ba Sr Ca Mg Be Zn Cd Hg

← more reactive less reactive →

Beryllium and cadmium compounds are similar to those of magnesium and zinc respectively but are less reactive.

Ethylzinc iodide and zinc diethyl were the first organometallic compounds prepared (2). Many organic syntheses were developed using zinc alkyls under carbon

FIG I Species and Equilibria possible for 'RMX' Systems

$$\begin{tikzcd}
 & (RMX)_n \arrow[d, shift right] & (R_2M:MX_2)_n \arrow[d, shift right] & \\
\mathrm{I} & 2\,RMX \arrow[u, shift right] \arrow[r, shift left] \arrow[d, shift right] \arrow[dr, shift left] & R_2M + MX_2 \arrow[l, shift left] \arrow[u, shift right] \arrow[d, shift right] \arrow[dl, shift left] & \mathrm{II} \\
\mathrm{III} & (RMX)_2 \arrow[u, shift right] \arrow[r, shift left] \arrow[ur, shift left] & R_2M:MX_2 \arrow[l, shift left] \arrow[u, shift right] \arrow[ul, shift left] & \mathrm{IV}
\end{tikzcd}$$

Grignard Jolibois

Formulae

dioxide until superseded by the more convenient Grignard reagents (1900). Pure zinc alkyls have been extensively studied but less is known of alkylzinc halides.

Magnesium alkyls were known some forty years before Grignard reagents (3) but less is known about them. Using diethyl ether, Grignard obtained solutions of organomagnesium halides (4) which quickly found a prominent role as reagents for a wide range of organic syntheses (5) but their constitution has remained controversial to the present day. The account of Kharasch and Reinmuth (6) is still the best survey of Grignard reagents but more recent work has been reviewed by Salinger (7), Ashby, and Hamelin (8).* Much of the terminology has originated with Grignard reagents and these are considered first, with the extensive work of the last decade emphasised, followed by the analogous zinc system.

1.2. Magnesium Alkyls.

Magnesium alkyls are highly reactive infusible solids, decomposing above 175°C, which are slightly soluble in hydrocarbons but readily soluble in ethers.

* Wakefield (183)

Table 1(a) Solubility of Magnesium Diethyl. $t = 20^{\circ}C$ (9)

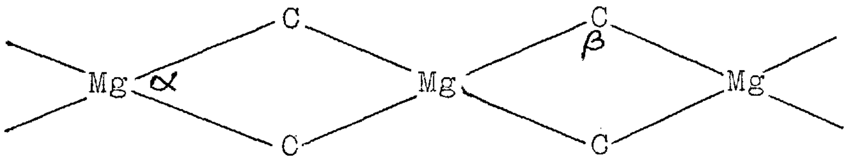
Solvent	Heptane	Benzene	Dioxan	Diethyl Ether
Solubility mole. l^{-1}.	0.0012	0.016		2.0

Table 1(b) Solubility (mole. l^{-1}.) of Magnesium Dialkyls in Hydrocarbons. $t = 20^{\circ}C$ (10)

	$MgEt_2$	$MgPr^n_2$	$MgPr^i_2$	$MgBu^n_2$
Heptane	0.0012	0.0032	0.0034	0.0030
Benzene	0.016	0.012	0.024	0.024

X-ray powder diagrams (11) show that like $BeMe_2$, $MgMe_2$ and $MgEt_2$ are long chain polymers with a near tetrahedral arrangement about the magnesium atom.

Table 2 Structural Parameters for Magnesium Dimethyl and Magnesium Diethyl. (11)



	d(Mg - Mg)	d(Mg - C)	d(C - C)	α	β
$MgEt_2$	2.67 ± 0.02 Å	2.26 Å	3.66 Å	108°	72°
$MgMe_2$	2.72 ± 0.02 Å	2.24 Å	3.51 Å	105°	75°

In ethers the alkyl bridges are broken and molecular weight results (Table 4) show the solutions contain monomers. Varying results have been reported due to oxygen contamination. Dioxan solutions prepared in vacuo contained monomers but under argon, degrees of association between 1 and 2 were found (12). In diethyl ether, monomers were present at low concentrations (43) but addition of oxygen gave a trimeric species. In dioxan, solvent-solute interaction occurs to give an unsymmetric species (Table 5a). Hollingsworth et al. by analysing the vapour above Et_2O solutions of magnesium dialkyls with THF as co-solvent found on average 1 mole THF complexed per MgR_2 and estimated equilibrium constants for the step-wise replacement reactions (13).

$$R_2Mg(Et_2O)_2 + THF \overset{K_1}{\rightleftharpoons} R_2Mg.THF.Et_2O + Et_2O$$

$$R_2Mg.THF.Et_2O + THF \overset{K_2}{\rightleftharpoons} R_2Mg(THF)_2 + Et_2O$$

$MgEt_2$,	$50 < K_1 < 130$,	$0 < K_2 < 20$
$MgPr^n_2$,	$90 < K_1 < 130$,	$0 < K_2 < 5$
$MgPr^i_2$,	$60 < K_1 < 170$,	$0 < K_2 < 15$

1.3. Zinc Alkyls

Zinc alkyls are volatile liquids with no evidence of association (14). The properties of zinc diethyl have been reviewed (15) for its use as a reaction medium.

X-ray diffraction (16) of crystalline zinc dimethyl showed linear molecules and the vibrational (17) and rotational (18) spectra of $ZnMe_2$ vapour are as expected for a linear structure. The zinc-methyl bond length is 1.93 ± 0.03 Å (16) or 1.929 ± 0.004 Å (18).

Table 3 Physical Properties of Zinc Alkyls (14)

ZnR_2	mpt. °C	bpt. °C/760 mm.	ΔH_{vap} cal. mole.$^{-1}$	$\Delta H_{vap}/T$ °K
$ZnMe_2$	-29.2	44	7,150	22.5
$ZnEt_2$	-30.0	117.6	9,605	24.6
$ZnPr^n{}_2$	-81 to -84	139.4	9,620	23.3
$ZnPr^i{}_2$	-57.7	201.1	10,260	21.7

The solutions contain monomers (Table 4) and dipole moment studies show that solvent-solute interaction occurs in dioxan while in hydrocarbons the molecules remain symmetric (Table 5). By studying the change in chemical shift (τ_{Me}) when dioxan, ethylene oxide, or DME are added to cyclohexane solutions of zinc dimethyl, equilibrium constants have been obtained for the complexing reaction (19).

$$ZnMe_2 + R_2O \rightleftarrows Me_2Zn.R_2O$$

Table 4 Molecular Weights (F.Pt. Depression) for Zinc and Magnesium Diethyl Solutions (20)

Solvent	Cyclohexane		Benzene		Dioxan	
MEt_2	mol. wt.	conc'n.	mol. wt.	conc'n.	mol. wt.	conc'n.
$ZnEt_2$	126 ± 2	0.16	123 ± 2	0.20	126 ± 2	0.18
123.5		0.49		0.50		0.50
$MgEt_2$	--	--	--	--	83 ± 2	0.146
82.5						0.30

concentration mole./1000 gm. solvent.

Table 5(a) Dipole Moments (Debyes) of $ZnEt_2$ and $MgEt_2$ Solutions, $t = 20^{\circ}C$ (21a)

	Heptane	Benzene	Dioxan
$ZnEt_2$	0.0	0.49	1.66
$MgEt_2$	-	–	4.8

Table 5(b) Dipole Moments (Debyes) of Zinc Alkyl Solutions $t = 20^{\circ}C$ (21b)

ZnR_2, R =	Me	Et	Pr^n	Pr^i	Bu^n	Bu^i	Pe^n	Pe^i
Heptane	0.4	0.0	0.1	0.2	0.0	0.0	0.0	0.0
Dioxan	1.82	1.66	1.66	1.73	1.70	1.63	1.54	1.64

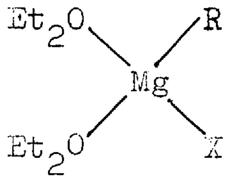
1.4. Grignard Reagents.

1.4.1. Introduction

Grignard reagents are prepared by interaction between alkyl, alkenyl or aryl halides (not fluorides) and magnesium in diethyl ether. Other ethers are useful, e.g. THF, for more difficult systems, while co-ordinating solvents such as tertiary amines and dimethyl sulphide (22) have also been used. Recently (23) hydrocarbon solutions of organomagnesium halides have been prepared but the simple 'RMgX' formula is not found in these systems which are thus not considered here.

1.4.2. Early Work.

From analytical and chemical data, Grignard proposed the formala RMgX (5). For the solid 'etherates', oxonium formulae were first suggested (24) but later, they were formulated as Werner complexes (25). Meisenheimer (26) was the first to propose a structure accepted today.



(I)

From the similarities of $MgEt_2$ and '$EtMgX$' systems and the association found in Grignard solutions, Jolibois (1912) advanced the formula, $Et_2Mg.MgX_2$ (IV) (27). The dimerisation of '$MeMgI$' in diethyl ether was later confirmed (28) but soon after with a wider range, it was found association varied from 1 to 2 with increasing concentration (29).

1.4.3. The Schlenk Equilibrium.

Schlenk and Schlenk (1929) discovered that by adding dioxan to a Grignard solution ($PhMgBr$ or $EtMgI$ in Et_2O) MgX_2 and $RMgX$ dioxanates were precipitated leaving MgR_2 in solution, and postulated two equilibria (30).

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

$$R_2Mg.MgX_2 \rightleftharpoons R_2Mg + MgX_2 \qquad (2)$$

Equation (1) was favoured as eight-fold dilution of a solution gave no change in the apparent equilibrium position. Equilibrium data for various systems were obtained by this method but Noller and White (31) showed these results to be illusory as the yield of magnesium dialkyl increased on leaving the solutions and precipitates in contact or on shaking together for 4-10 hours. Slow addition of dioxan over several days gave a 95% yield of MgR_2 (32).

Aston and Bernhard (33) used an extended equilibrium to consider Noller's results.

$$2\ RMgX \rightleftharpoons R_2Mg.MgX_2 \rightleftharpoons R_2Mg + MgX_2 \qquad (3)$$

Except MgR_2, all forms give insoluble dioxanates with slow equilibration between solid and solution species.

The increased solubility of magnesium halides in Grignard solutions has been studied for $MgBr_2$ + 'Bu^nMgBr' (34) and MgI_2 + 'MeMgI' (35) both in diethyl ether. For the latter, the results did not fit the Schlenk equilibria, but the data were accounted for by equation (4).

$$2\ MgI_2 + MeMgI \rightleftharpoons 2\ MgI_2.MeMgI \qquad (4)$$

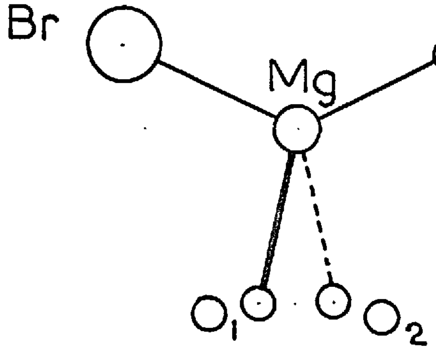
The solubility of $MgCl_2$ in an ether solution of $MgEt_2$ has been determined (36) with values of $MgCl_2/MgEt_2$ of 1.6 at -31°C and 1.1 at 15°C showing $EtMgCl.MgCl_2$ species are formed.

1.5. Grignard Reagents - The Last Decade (182)

1.5.1. X-ray Diffraction Results.

Definite formulae have only been assigned by X-ray diffraction studies. Rundle et al. have published the structures of $PhMgBr(Et_2O)_2$ (37) and $EtMgBr(Et_2O)_2$ (38)

FIG 2 Single-Crystal X-ray Results for Grignard Reagents



	$EtMgBr.2Et_2O$	$PhMgBr.2Et_2O$
d(Mg–Br)	2·48Å	2·44 Å
d(Mg–C)	2·16	~2·2
$d(Mg–O_1)$	2·03	2·01
$d(Mg–O_2)$	2·06	2·06

$\widehat{\mathrm{BrMgC}}$	124°	$\widehat{\mathrm{BrMgO_2}}$	110°
$\widehat{\mathrm{BrMgO_1}}$	104°	—	103°
$CMgO_2$	110°	closest	
next d(Mg–Br), 5·81Å		Mg–Mg ~6·1Å	
		Br–Br 6·1~6·4Å	

obtained by cooling solutions with $Et_2O:Mg > 2$. Both crystals consist of layers of ether molecules alternating with 'RMgBr' units. In each molecule, the magnesium atom is tetrahedrally surrounded by a carbon, a bromine, and two oxygen atoms with no evidence of any intermolecular bridges (Fig 2). Small bond lengths, especially Mg-O, show the molecules are strongly bound. Initial data for $MgPh_2(Et_2O)_2$ (37b) were consistent with a tetrahedral molecule. This evidence for solid state RMgX species is useful but must be extended to solutions with caution.

1.5.2. Molecular Weight Results.

Any scheme proposed for Grignard solutions must be consistent with reliable molecular weight data but only recently have such become available. Earlier discussion usually assumed dimers in diethyl ether solutions.

Results for diethyl ether solutions were reported by Slough and Ubbelohde (39) and Ashby and Smith (40). The former workers corrected the vapour pressure changes for the effect of side-reaction products,

$$Mg + 2\ RX \rightarrow MgX_2 + R_2,$$

but later workers have preferred to either minimise side-reactions or remove the products by recrystallisation. 'Catalytic' amounts of oxygen gave dramatic increases in association but no quantitative effects were reported (Table 6).

Table 6 Association in Diethyl Ether Solutions of Grignard Reagents

RMgX	Conc'n[c]	t°C	i[d]
EtMgCl[b]	0.086	35	1.87
	0.143		1.86
	0.192		1.92
$Pr^{i}MgCl$[b]	0.042	35	1.85
	0.080		1.90
	0.144		1.93
	0.201		2.00
	0.260		2.00
EtMgBr[b]	0.035	35	1.00
	0.102		1.04
	0.105		1.16
	0.200		1.26
	0.249		1.37
EtMgI[b]	0.055	35	1.00
	0.108		1.12
	0.158		1.27
	0.204		1.36
PhMgBr[a]	0.331	15.0	1.97
		20.0	1.77
PhMgBr[b]	0.042	35	1.07
	0.111		1.17
	0.179		1.31
	0.241		1.50
	0.326		1.71
p - Tol MgBr[a]	0.368	15.0	1.80
	0.566		2.03
		20.0	1.82
Mesityl MgBr[b]	0.059	35	1.06
	0.172		1.41
	0.275		1.77
MeMgI[b]	0.037	35	1.06
	0.084		1.17
	0.140		1.36
	0.245		1.59

a Tensimetry (39)

b Ebulliometry (40)

c Concentration mole. l^{-1}.

d i = Degree of Association = $\frac{\text{Observed Mol.Wt.}}{\text{Calculated Mol.Wt.}}$

A few association data for THF (41) and NEt_3 (42) solutions have been reported. A 2M solution of EtMgCl in THF had mol.wt. 65 (EtMgCl = 88.8) by ebulliometry showing it to essentially contain monomers.

Table 7 Association in Tetrahydrofuran Solutions of Grignard Reagents by Ebulliometry (41)

RMgX	Conc'n. mole.l^{-1}.	Degree of Association	
		760 mm., 66°C	200 mm., 30°C
EtMgBr	0.1-0.3	1.01	1.04
EtMgCl	0.1-0.3	1.11	1.01

Table 8 Association of Ethylmagnesium Bromide in Triethylamine by Ebulliometry at 150 mm. (42)

Conc'n. mole. l^{-1}.	0.086	0.148	0.198
Degree of Association	0.99	1.04	1.06

Not unexpectedly, association increases with concentration and decreases with rise in temperature. It also varies with solvent and halogen but the organic group has little effect. The existence of monomers where MgX_2 species would precipitate is strong evidence for the RMgX monomer.

A study of very dilute solutions manipulated with extreme care showed only monomers were present (43).

Table 9 Association in Very Dilute Solutions of Magnesium Compounds (43)

Diethyl Ether			Tetrahydrofuran			
Mg Comp'd	conc'n. mmole.l^{-1}	i	Mg Comp'd	conc'n. mmole.l^{-1}	i	
		at 27.3°C			at 27.3°C	at 37.3°C
EtMgBr	4.19	1.00	EtMgBr	8.67	1.00	1.00
	4.30	1.01		9.52	1.00	1.01
	6.71	1.01	$MgEt_2$	3.91	0.98	0.98
$MgEt_2$	2.50	0.99		3.90	1.00	1.00
	2.64	0.97				

The number of particles in solution was reduced by $^2/_3$ with the absorption of one oxygen atom per Mg-Et bond (44).

Hayes (45) reported tensimetric studies of Et_2O solutions of EtMgBr which agree with Ashby's data but direct comparison is not possible as different concentration units were used (mole-fraction). Vapour pressures above THF solutions were much lower than predicted even for monomeric species in solution.

1.5.3. Schlenk Equilibria Studies.

In general, the mixed and normal Grignard solutions are taken to be equivalent. Several experiments have been devised to show that R_2Mg and MgX_2 react and to prove the identity,

$$\underset{\text{Mixing}}{R_2Mg + MgX_2} \longrightarrow \text{Grignard} \longleftarrow \underset{\text{Normal}}{RX + Mg}$$

Dessy (1957) attempted to identify the Schlenk equilibrium (1) or (2) by a radiochemical method (46). $Mg^{*}Br_2$ (labelled with $^{28}Mg^{*}$) mixed with $MgEt_2$ or $MgPh_2$ in Et_2O was separated after 10 mins. or 36 hrs. by dioxan precipitation with only 4-10% exchange. Any RMgX species would cause 100% exchange and this confirmed equation (2). Mounting evidence (1963) for RMgX species in solution made Dessy consider a wider range of experiments (47). No obvious relation between practical techniques or purity of the magnesium source and the varying results can be made (Table 10). Mass-spectrometry was used to show complete exchange between $^{25}MgBr_2$ and 'EtMgBr' in Et_2O (48). No definite result is now inconsistent with the presence of RMgX species.

A linear dielectric constant change occurs when equimolar ether solutions of $MgBr_2$ and $MgEt_2$ are mixed (49). Two straight lines intersect where $MgBr_2$:$MgEt_2$ is 1, showing a 1:1 reaction has occurred. The dielectric constant at

Table 10 Radiochemical Study of the Exchange Reaction (47)

$$MgR_2 + {}^{28}Mg\ Br_2 \quad {}^{28}Mg\ R_2 + MgBr_2$$

R_2Mg	Prep'n[a]	^{28}Mg[b] source	$MgBr_2$[c] prep'n.	Solvent	Separ'n Method	Result
Et_2Mg	A	B	A	Et_2O	dioxan	No. Exch.
"	A	B + C	A	"	"	" "
"	A	B	A	"	electrolysis	" "
"	A	B	A	"	dioxan + electrolysis	Stat. " (^{25}Mg)
"	A	A	A	"	dioxan	Stat. Exch.
"	A	A	B	"	"	" "
"	A	A	B	THF	dipy	" "
Me_2Mg	B	A	B	"	"	" "
"	B	A	A	Et_2O	dioxan	" "
"	B	A	A	"	dipy	" "
Ph_2Mg	A	B	A	"	dioxan	No "

a) R_2Mg prepared by A. 'RMgX' + dioxan

B. R_2Hg + Mg

b) Mg source was A. Dow triply sublimed.

B. Dow atomised shot.

C. Grignard reagent grade turnings.

c) $MgBr_2$ prepared by A. Mg + Br_2.

B. Mg + $C_2H_4Br_2$.

this point is the same for an 'EtMgBr' solution of the same concentration. ('EtMgBr' and Et_2Mg + $MgCl_2$ solutions in THF had the same dipole moments (41)).

Smith and Becker (50) studied this reaction calorimetrically. Heat evolution on mixing is linear with moles added to 0.8:1 mole ratio with $\Delta H = 3.6$ kcal.mole $MgEt_2$. At 1:1 mole ratio, 8 mole % of ($MgEt_2$ + $MgBr_2$) is unchanged. This mixture (0.1M) has the same association as an 'EtMgBr' solution (0.1M), i = 1.04.

$$\begin{array}{lccc} & MgEt_2 + & MgBr_2 \rightleftharpoons & 2\ EtMgBr \\ \text{mole \%} & 4 & 4 & 92 \end{array}$$

Crystallisation techniques have been used to study mixtures and excess $MgBr_2$ or $MgEt_2$ can be removed in this way. Complete alkyl exchange occurred when 'EtMgBr' (^{14}C labelled) was mixed with $MgEt_2$ in Et_2O and then separated by crystallisation (51).

1.5.4. Nuclear Magnetic Resonance Results.

The application of nuclear magnetic resonance (n.m.r.) to Grignard reagents has proved disappointing. The chemical shifts (δ_R) for alkyl Grignard reagents and MgR_2 species are almost identical in both Et_2O (52) and THF (41) solutions, but a slight difference is reported for phenyl derivatives (37a). Mixtures of $MgEt_2$ + MgX_2 behaved as normal Grignard reagents (52b). Fast alkyl exchange (53), although hindered by co-ordinating solvents, averages the small chemical shifts found in these systems. As ^{19}F shifts are larger and phenyl exchange slower, 'C_6F_5MgX' solutions in Et_2O were found to contain both Grignard and Jolibois species (54). Fast exchange ($\tau \ll 0.01$ sec) accounts for the simple spectra of $R_2C{:}CH{\cdot}CH_2MgBr$ (R = H, Me) solutions; on cooling the single methyl line becomes a doublet (55). Detailed analysis of the changes $AA'BB' \rightarrow A_2B_2$ for $Me_3C.CH_2.CH_2.X$ (56) and $AA'X \rightarrow A_2X$ for $R.CH(Me){\cdot}CH_2MgBr$ (57) systems shows carbanion inversion responsible with an alkyl exchange mechanism indicated (56). From τ_{Me} for MeLi and MeMgI in Et_2O, the Mg-C bond was stated to have 21% ionic character (57) (99).

1.5.5. Solvent Effects in Grignard Solutions.

The need for co-ordinating solvents in Grignard reactions is well known. Solutions in hydrocarbons are easily prepared when 1 mole of THF (58) or NEt_3 (59) per Mg is added. Evaporation of 'EtMgBr' solutions gave precipitates with $MgBr_2$ in excess to the amount required by the formula 'EtMgBr', whose degree of solvation varied as,

$PhOMe > Pr^i{}_2O > Bu^n{}_2O < Et_2O \ll THF \sim NEt_3$, while

thermogravimetric studies gave a bond strength order of,

$Pr_2{}^iO \ll Bu_2{}^nO < Et_2O < THF$. (60)

The solution parameters are more difficult to estimate. From the variation of Et_2O and EtMgBr with concentration, $Mg{:}Et_2O$ was estimated to be 2 (52b). Hollingsworth (61) found, on average, 1 mole. THF complexed per magnesium in Et_2O solutions of 'RMgBr' with THF as co-solvent. The effect of solvent variation on reaction rates has been noted (62) while asymmetric Grignard syntheses are possible using optically active solvents (63).

1.6. Alkylzinc Halides

Only alkyl iodides can be used to prepare these compounds directly but unlike Grignard reagents, no solvent is necessary. Other halides and aryl derivatives are prepared by the 'mixing' reaction (64).

$$R_2Zn + ZnX_2 \longrightarrow 2\ RZnX$$

Dioxan precipitates the same compound, EtZnI.dioxan, from Et_2O solutions prepared by (a) Zn + EtI or (b) $ZnEt_2 + ZnI_2$ (64a), while formation of $ZnRR'$ species by the reaction of '$R'MgX$' with an 'RZnX' solution supports an RZnX species as Jolibois forms would give a mixture of zinc alkyls (64b).

Dessy found complete exchange when a mixture of $ZnEt_2$ and Zn^*Cl_2 (labelled with $^{65}Zn^*$) in THF was separated after 120 hours by dipyridyl. Since the mixture (0.1M) was monomeric, EtZnCl was present (65).

Abraham and Rolfe (66), found that Et_2O and THF solutions of 'EtZnI' gave the EtZnI.TMED complex as did 7 day-old mixtures of $Et_2Zn + ZnI_2$ in THF but ZnI_2.TMED was precipitated from a solution 2 hours old. Over a range of concentrations, B.Pt. elevation gave i = 1.2 for Et_2O and THF solutions showing EtZnI is the main solution species.

Both R_2Zn + RZnI species in ethereal solvents have very similar chemical shifts (52a) (66). Hydrocarbon solution results provide a possible explanation of this problem (67).

Table 11 Chemical Shifts for 'Ethylzinc' Solutions (67)

Compound	EtZnCl	EtZnBr	EtZnI	$ZnEt_2$
τ_{CH_2} (Toluene)	9.35	9.31	-	9.87
τ_{CH_2} (Et_2O)	9.78	9.72	9.65	9.79

Since tetrameric 'EtZnX' species exist in hydrocarbons, τ_{CH_2} varies with the change of co-ordination number rather than the replacement of Et by X.

1.7. Ionic Features of Organo-zinc and magnesium Solutions.

Abegg (68) suggested Grignard reagents react as R^-MgX^+, a concept still used today. Organo-zinc and magnesium solutions conduct electricity (69) but the small effect ($\Lambda \sim 10^{-5} - 10^{-6}$) is only detected using high frequency AC bridges and is increased considerably by traces of oxygen. The variation with species (RMgX $\gg$ $R_2Mg >$ R_2Zn), solvent ($C_6H_6 <$ diox $<$ $NEt_3 <$ Et_2O $<$ THF) and concentration (first increase, then decrease) shows that ion-pairs (aggregates at higher concentrations) carry the current. Normal 'EtMgBr' (Br/Et 1.10) and 'Et_2Mg + $MgBr_2$' (Br/Et 1.72, 1.07) solutions in ether show very similar conductivity behaviour (69b).

Evans (1934-42) studied the electrolysis of Grignard solutions extensively (70). Generally magnesium is discharged at the cathode and alkyl radicals at the anode, with a net gain of MgX_2 in solution. A magnesium gain near the anode shows it is present in both anions and cations. With solvated RMgX, R_2Mg, and MgX_2 species, Evans and Pearson (70b) suggested the scheme below.

Ionisation:

$$R_2Mg \rightleftharpoons RMg^+ + R^-$$

$$RMgX \rightleftharpoons RMg^+ + X^- \text{ or } MgX^+ + R^-$$

$$MgX_2 \rightleftharpoons MgX^+ + X^-$$

$$R^- + R_2Mg(RMgX \text{ or } MgX_2) \longrightarrow R_3Mg^-(R_2MgX^- \text{ or } RMgX_2^-)$$

Cathode Discharge

$$2\ MgX^+(RMg^+) + 2e^- \longrightarrow Mg + MgX_2(R_2Mg)$$

Anode Discharge

$$R_3Mg^-(R_2MgX^- \text{ or } RMgX_2^-) \longrightarrow R + R_2Mg(RMgX \text{ or } MgX_2) + e^-$$

$$2\ R \longrightarrow R_2 \text{ or } R_{+H} \text{ or } R_{-H} \text{ or reacts with solvent.}$$

From electrolysis results for $MgEt_2$ + Mg^*Br_2 ($^{28}Mg^*$) solutions, this scheme was simplified (71) but all radiochemical data now require reconsideration.

Evans did not consider Grignard solutions ionic but that the Mg-C bond had considerable ionic character. Carbanions probably exist transiently but a Grignard solution (MeMgI in Et_2O) was virtually unchanged after 30 years (72) in contrast to the ionic sodium alkyls which rapidly attack ether.

2. RESULTS AND DISCUSSION

2.1. Zinc Dialkyl Solutions and Complexes

The vibrational spectrum of zinc dimethyl has been well investigated by Raman (73) (74) and infra-red (17) (75) techninques and a complete analysis has been given (17). The few coincidences show the molecule has a centre of symmetry i.e. a linear C-Zn-C skeleton with free rotation of the methyl groups (75b). The zinc-carbon stretching frequencies are 504 cm^{-1}, symmetric, Raman active, polarised, and 615 cm^{-1}, asymmetric, infra-red active. The two methyl rocking frequencies occur in this region 707 cm^{-1} (infra-red) and 620 cm^{-1} (Raman). The C-Zn-C bending frequency is 144 cm^{-1}. Less is known for zinc diethyl (73) (76) but a part assignment of frequencies (77) shows the C-Zn-C skeleton is linear with probable free rotation. By analogy with zinc dimethyl, the intense Raman band at 476 cm^{-1} is assigned to the zinc-carbon symmetric stretch but weak bands at 533 and 579 cm^{-1} remain doubtful. Strong 564 cm^{-1} and weak 479 cm^{-1} bands observed with a hexane solution were assigned to asymmetric and symmetric zinc-carbon stretching modes respectively (78).

Raman data for zinc dimethyl and zinc diethyl solutions over the range 200-1,000 cm^{-1} are given in Tables 13 and 14, with data for the solvents used in Table 12.

The spectra are dominated by an extremely intense polarised band ca. 500 cm^{-1} which is assigned to the symmetric zinc-carbon stretch. Zinc dimethyl solutions have a strong band ca. 610 cm^{-1} assigned to the Raman active methyl rocking mode but zinc diethyl solutions have several weak bands in this region. They are most probably combination frequencies except the stronger band in the 570-590 cm^{-1} range which is assigned to the Raman active methylene rocking vibration. The remaining weak bands are most likely combination frequencies. Zinc diethyl spectra have two additional bands at 955 and 990 cm^{-1} assigned to ethyl group vibrations (86).

Table 12 Raman Spectra of the Solvents used. (cm^{-1}).

n-Hexane	323 m, 365 msp, 400 msp, 460 w, 750 w.
Diethyl Ether	438 s, 788 w, 842 vs, 918, vw, 930 s.
Tetrahydrofuran	282 vw, 912 vvs.
1,2-Dimethoxyethane	369 m, 828 msh, 850 s, 980 w.

Table 13 Raman Spectra of Zinc Dimethyl Solutions (cm^{-1})

Neat [a]	Hexane	Et_2O	THF	DME
Liquid	2.67M	2.67M	2.42M	3.03M
248 vw			254 vw	
	318 m		285 vw	
	373 msp	382 w	398 wsh	367 m
	400 wsp			
	450 w	441 msp	445 wsh	
488 w				
505* vvs	504* vvs	502* vvs	493* vvs	491* vvs
620 s	620 s	612 sbr	610 vs	603 s
	753 w	749 vw		
		791 w		
				820 wsh
		844 ssp		853 ssp
			915 vvs	
		930 m		983 w
*ρ =	0.32	0.27	0.29	0.34

a N.G. Pai (73)

Table 14 Raman Spectra of Zinc Diethyl Solutions (cm^{-1})

Neat Liquid[a]	Hexane 2.18M	Et_2O 2.85M	THF 3.02M	DME 2.91M
255 m	251 wm	253 w	251 w	247 vw
	320 wm			
	373 wmsp	382 w	381 vw	369 m
	406 wsp			
		441 msp		
476* vvs	475* vvs	472* vvs	469* vvs	465* vvs
533 w	538 vw			542 vw
	557 vw			
579 m	590 w	581 wbr	586 wbr	574 w
		636 vw	637 vw	636 vw
	750 w			
		795 w		
				826 wsh
		845 s	850 wsh	852 vs
		919 vw	915 vs	915 wsh
		933 m		
938 m		955 m	955 m	954 msp
990 m		990 m	994 m	990 m
*ρ =	0.32	0.32	0.37	0.27

[a] N.G. Pai (73)

Infra-red data (14-24μ) for zinc dimethyl and zinc diethyl solutions are given in Table 15, with assignments for the two strong bands observed (Fig 3). The additional weaker band ca. 490 cm^{-1} found for zinc dimethyl solutions is assigned to the symmetric zinc-carbon stretch, in good agreement with the Raman value.

Table 15 Infra-red Spectra (14-24μ) of Zinc Alkyl Solutions

(cm^{-1})

a) Diethyl Ether

$ZnEt_2$,	1.47M,	438 s	465 w	501 m	551 vs(b)	611 vs(c)
Solvent,		438 s		501 m		

b) Tetrahydrofuran

$ZnMe_2$,	1.72M,	487 m(a)	547 s(b)	579 v.w	623 sh	664 sbr(c)
$ZnEt_2$,	1.80M,		534 vs(b)		608 vs(c)	658 s
Solvent,						665 s

c) 1,2-Dimethoxyethane

$ZnMe_2$,	1.09M,	445 wbr	490 m(a)	515 sh	539 s	569 s	668 vs(c)
$ZnEt_2$,	1.04M,	445 wbr		513 w	539 s	569 w	608 vs(c)
Solvent,				513 w	539 s	568 w	

d) Dioxan

$ZnEt_2$,	1.55M,	437 m		546 vs(b)	604 vs(c)	611 vs
Solvent,		438 m	499 w			611 vs

Assignments.

(a) ν_{sym}(Zn - C) (b) ν_{asym}(Zn - C)

(c) $\delta_{CH_3(CH_2)}$ rock.

In recent years, complexes (ZnR_2L_2) with various ligands, in particular nitrogen donors, have been reported (79) (80) (81) which are much less reactive than the parent zinc dialkyl compounds. Infra-red data (14-24μ) for some of these complexes are given in Table 16, with assignments. Complex formation enables all four fundamentals in this region to be observed for zinc dimethyl systems but zinc diethyl spectra were less satisfactory as the bands were broad and not all the four fundamentals could be detected.

Table 16 Infra-red Spectra (14-24μ) of Zinc Alkyl Complexes

(cm^{-1})

a) ZnR_2py_2

R=Me	412w	419m	435w	462s(a)	514s(b)	595sh	614s(c)	639sbr	696s
R=Cl(82)		422						637	696

b) ZnR_2dipy

R=Me	412m	465m(a)	510s(b)	602m(c)	621ssp(c)	638sh	651s
R=Et			506sbr(b)		619ssp(c)	625sh	650m

c) $ZnR_2.TMED$

R = Me	458 sbr(a)	507 vsbr(b)	590 m(c)	638 sbr(c)
cf.(87)	453	510	610	645
R = Et	435 vsbr(a)	499 vsbr(b)	585 (c)	

Assignments

(a) $\nu_{sym}(Zn - C)$ (b) $\nu_{asym}(Zn - C)$

(c) $\delta_{CH_3(CH_2)}$ rock

The zinc-carbon stretching frequencies, Tables 17 and 18, show two distinct trends which provide information on the effect of co-ordinating environments on the zinc dialkyl structure.

Table 17 Zinc-Methyl Stretching Frequencies (cm^{-1})

	Pure $ZnMe_2$	$ZnMe_2$ Solutions				$ZnMe_2L_2$		
		C_6H_{14}	Et_2O	THF	DME	2 py	dipy	TMED
ν_{asym} (a)	615 (17)	-	-	547	*	514	510	507
ν_{sym} (b)	505 (73)	504	502	493	491	462	465	458
ν_{as}/ν_s	1.22	-	-	1.11		1.10	1.10	1.11
$\frac{1}{2}(\nu_{as} + \nu_s)$	559	-	-	520		488	488	483

Table 18 Zinc-Ethyl Stretching Frequencies (cm^{-1})

	Pure ZnEt$_2$	ZnEt$_2$ Solutions				ZnEt$_2$L$_2$		
		C_6H_{14}	Et$_2$O	THF	DME	2 py	dipy	TMED
ν_{asym} (a)	-	564 (78)	551	534	*	497	506	499
ν_{sym} (b)	476 (73)	475	472	469	465	440	*	435
ν_{as}/ν_{s}	-	1.19	1.17	1.14	-	1.13	-	1.15
$\frac{1}{2}(\nu_{as} + \nu_{s})$	-	525	511	502	-	468	-	467

*Band obscured by solvent or not observed

(a) I.R. data (b) Raman (soln.) or I.R. (complex) data

The ratio ν_{asym}/ν_{sym} is less when the zinc dialkyl is in a co-ordinating environment. The effect is marked for the zinc dimethyl system (ν_{asym}/ν_{sym} 1.22 1.10) and can only be attributed to bending of the C-Zn-C skeleton. Calculations with a simple XY$_2$ model suggest a value of 140°-120° for the C-Zn-C angle. The change is less marked and more varied for the zinc diethyl system and an intermediate value of ν_{asym}/ν_{sym} for the diethyl ether solution suggests a weaker complex is formed. The value of ν_{asym}(Zn - C) for the dioxan solution, 546 cm^{-1}, shows the frequency shift coincides with the dipole moment change noted previously (21).

If only Raman data had been collected the ZnR_2 molecules would be thought quasi-linear as no additional bands are detected with co-ordinating solvents and the symmetric stretching frequency is little altered by solvent change. However, the I.R. spectra show considerable changes and for the solids, both stretching frequencies are observed as expected for ZnR_2L_2 molecules with C_{2v} symmetry.

Disilyl ether, a more extreme case, obeys linear selection rules for both Raman and infra-red spectra (83a) but electron diffraction and the slight shift of ν_3(Si - O) on ^{18}O substitution show the molecule is bent with $\widehat{SiOSi} = 140^\circ$ (83b).

Both ν_{sym}(Zn - C) and ν_{asym}(Zn - C) frequencies decrease, the latter considerably, in co-ordinating environments. The average, $\frac{1}{2}(\nu_{sym} + \nu_{asym})$ is used here as the 'characteristic' zinc-carbon stretching frequency in these systems. The degree of ligand effect is in the order,

$$Et_2O < THF \sim DME \ll 2\ py \sim dipy \sim TMED,$$

which parallels the general trend in ligand donor ability. Calculations demonstrate that both an apparent increase of the mass of the central zinc atom with ligand attachment and decrease of the force-constant of the Zn-C bond are necessary to account for the change. Since different combinations of the two effects give similar changes, separate assessment of the two factors cannot be made. Values of ν_{asym}/ν_{sym} calculated using parameters appropriate for the 'characteristic' frequencies of the complexes usually differ from experimental results and more exact calculations for these systems would use a tetrahedral XY_2Z_2 model.

Changes in the zinc-carbon stretching frequencies run parallel with changes in the strength of the zinc-ligand bond. For ether molecules (Et_2O, THF, DME), the C-O-C deformation frequencies are lowered on co-ordination (84) (88) but no changes were noticed in this work. Since co-ordination does occur, the zinc-oxygen interaction is too weak to affect the C-O-C vibrations. The nitrogen complexes with lower ν(Zn - C) values are stronger bonded. Pyridine ring frequencies at 403, 601, and 700 cm^{-1} shift to 422, 637, 697 cm^{-1} in $ZnCl_2py_2$ (85). Strong bands at 419, 639, and 696 cm^{-1} for $ZnMe_2py_2$ show a strong Zn-N bond is formed.

2.2. Alkylzinc Iodide Solutions and Complexes

Infra-red data (14-24μ) are reported for alkylzinc iodide solutions, Table 19, Fig 3, and complexes, Table 20, Fig 4, with assignments for the two strong bands observed. The latter new unreactive compounds can be handled rapidly in dry air and usually decompose without melting when heated. Some, more concentrated ethylzinc iodide solutions

FIG 3 I.R. Spectrum of some Organo-zinc Solutions

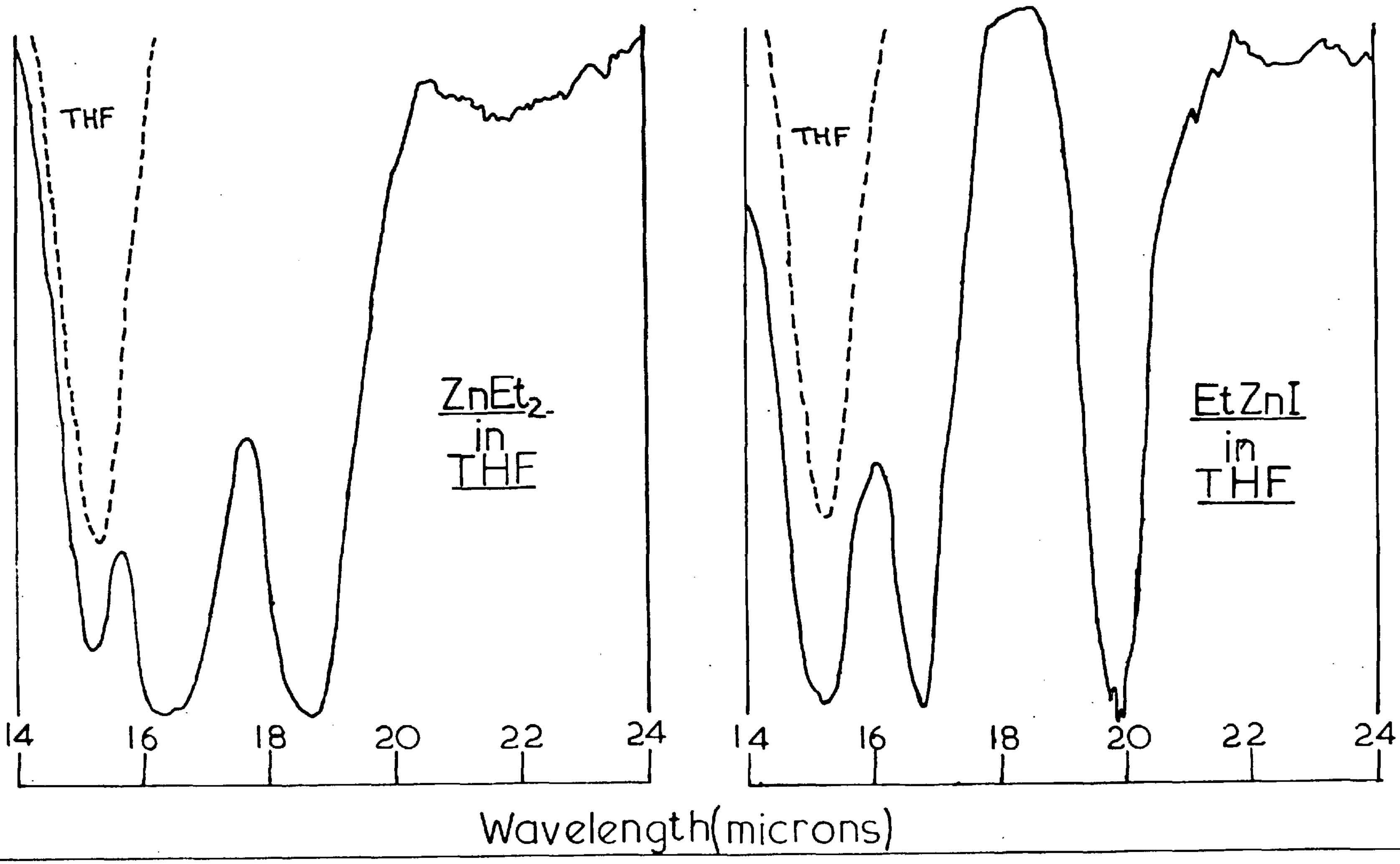
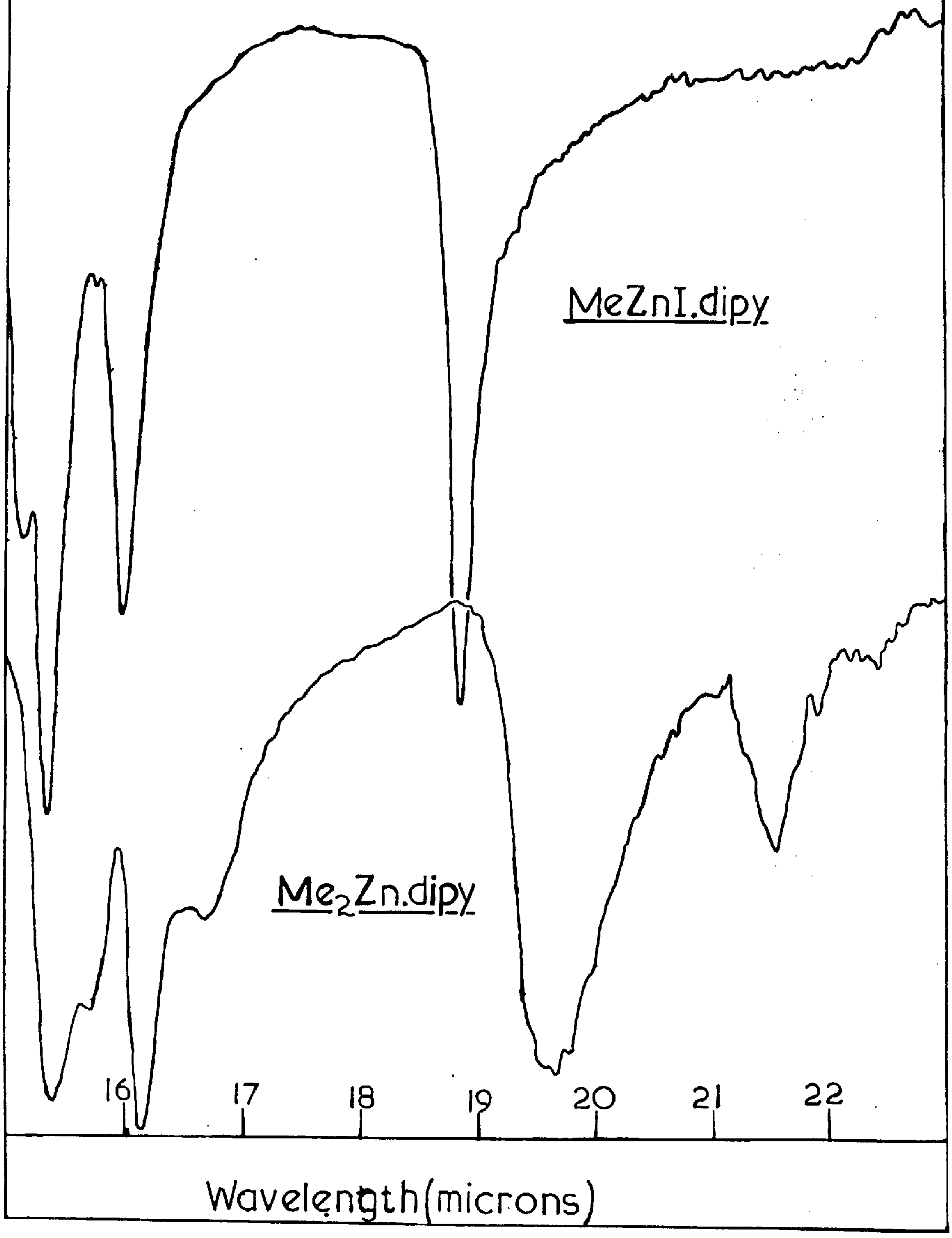


FIG 4 I.R. Spectrum of some Organo-zinc Complexes



were examined by Raman (200-1000 cm^{-1}) and infra-red (8-25μ) methods, Table 21. In the Raman spectrum, apart from solvent and ethyl group (951, 990) frequencies and the two bands assigned as above, a shoulder (473 cm^{-1}) due to a small amount of free zinc diethyl is observed.

Table 19 Infra-red Spectra (14-24μ) of Alkylzinc Iodide Solutions (cm^{-1})

a) Tetrahydrofuran

MeZnI,	2.83M,	530 s(a)	581 w	640 sbr(b)	668 sbr
EtZnI,	1.92M,	505 s(a)		600 s(b)	668 s
Solvent,					665 s

b) 1,2-Dimethoxyethane

MeZnI,	1.51M,	447mbr	494vw	514sh	523(a)	536vs	568w	654vs(b)
EtZnI,	1.61M,	445wbr	501vsbr (a)	511w		538vs	568w	607s(b)
Solvent,				513w		539vs	568w	

Table 20 Infra-red Spectra (14-24μ) of Alkylzinc Iodide Complexes (cm^{-1})

a) $RZnIpy_2$

R=Me	415m	423s	511s(a)	626vs(b)	636,640m	653wsp	678sh	695vs
R=Et	417m	425m	491mbr(a)	595m(b)	633,640m	651w	678sh	696vs
$ZnCl_2py_2$ (82)		422			637		696	

b) RZnIdipy

R = Me	410 s	533 vs(a)		630 s	638 vw	651 vs	662 w
R = Et		505 vs(a)	599 m(b)	633 m	638 sh	651 vs	

c) RZnI.TMED

R = Me	437 w	456 w	483 w	515 s(a)	586 vw	654 m(b)
R = Et	434 w	450 w	482 w	498 s(a)	585 w	603 m(b)

Assignments

(a) ν (Zn - C) (b) $\delta_{CH_3(CH_2)}$ rock.

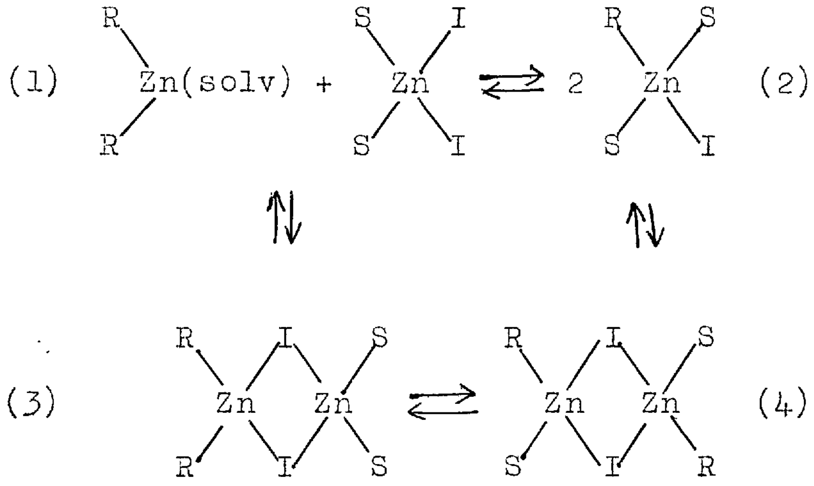
Table 21 Ethylzinc Iodide Solution Spectra (cm^{-1})

Diethyl Ether Solution 3.33M		THF Soln. 3.20M
Raman	Infra-red	Infra-red
374 vw		
396 vw		
	417 vw	
441 m	440 wbr	
473 sh		
511* vs (a)	510 s(a)	507 m(a)
	556 wbr	
581 vw		
611 w(b)	613 s(b)	605 m(b)
633 vw		663 m
781 wm	778 s	
	791 sh	
835 m	831 m	
844 vw	844 w	873 s
906 mbr	903 m	909 s
928 vw	917 w	943 sh
	932 w	
951 w	951 w	
989 m	996 m	
	1042 vs	1031 s
	1075 m	1056 s
	1109 vs	1176 w
	1149 s	

* ρ = 0.55

Similarly, the weak 556 cm^{-1} band in the infra-red spectrum may be due to free zinc diethyl present. The remaining bands are solvent or probable combination frequencies.

The possible solution species are,



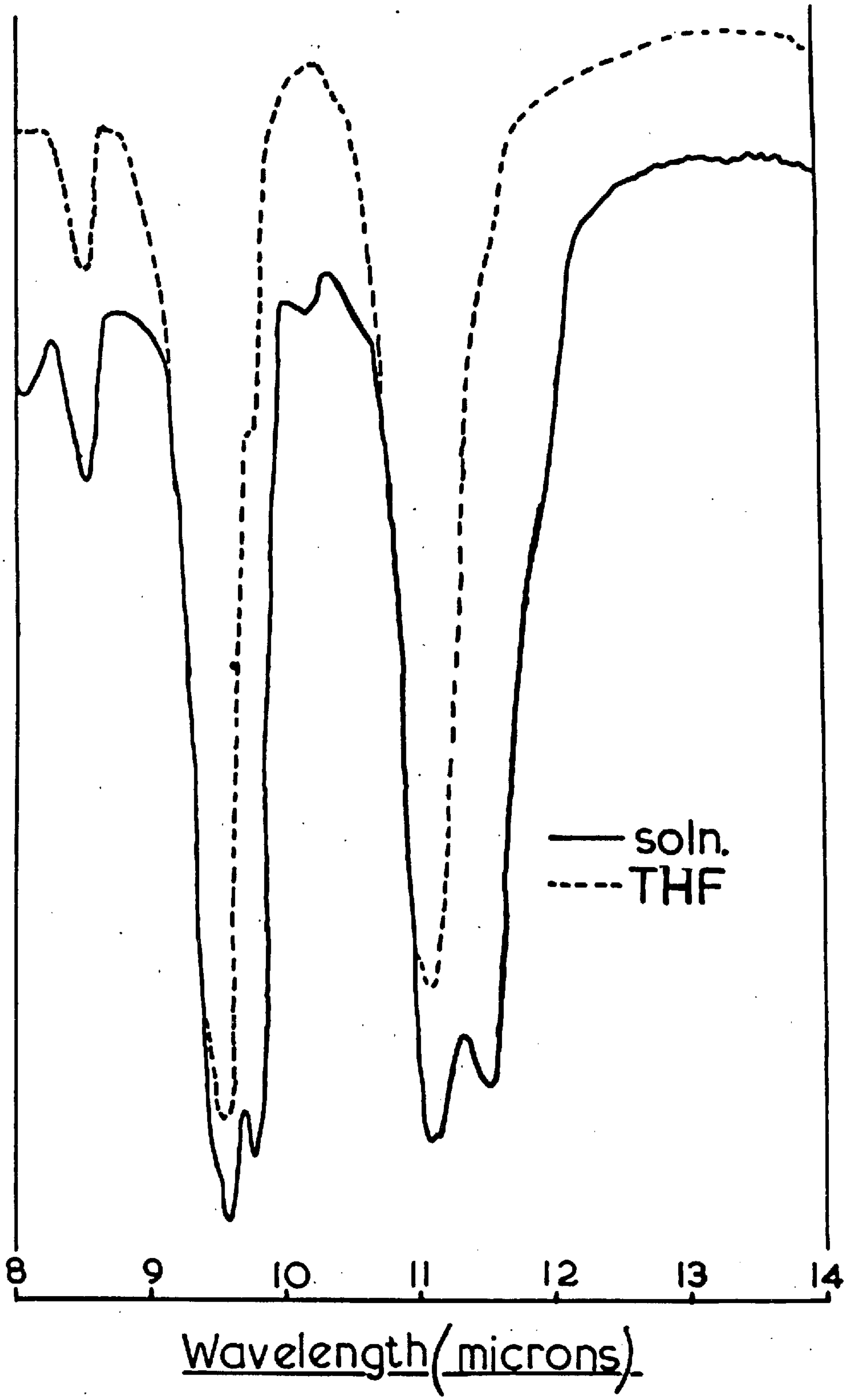
The simple mixture (1) is unlikely on chemical grounds but different infra-red data for R_2Zn and 'RZnI' systems eliminate it completely (Figs 3, 4). The solid complexes will have structure (2) but (3) and (4) are possible in solution. Structure (3), ZnR_2 complexed by I_2ZnS_2 requires distinct Raman and infra-red stretching frequencies. However, coincidence of the intense 511 ± 2 cm^{-1} Raman (= 0.55), and strong 510 ± 1 cm^{-1} infra-red bands in EtZnI ether solution spectra, assigned to (Zn - C) can only be accommodated by an RZnI structure, preferably monomeric. The sharp (Zn - C) band, 507 cm^{-1}, found for EtZnI in THF does not broaden or shift when the solution, 3.20M, is diluted to 0.49M and 0.26M. This suggests the same species for all concentrations and, as EtZnI in Et_2O or THF is monomeric over 'a range of concentrations' (66), that it is (2), $RZnIS_2$.

Table 22 Zinc-Carbon Stretching Frequencies (cm^{-1}) for RZnI Systems

Solvent or Ligand	RZnI Solutions			$RZnI.L_2$ Complexes			
	Et_2O	THF	DME	DME	2py	dipy	TMED
R = Me	-	530	523	527	511	533	515
R = Et	510	505	503	508	491	505	498

The smaller variation of ν(Zn - C) compared with ZnR_2 results shows the solution species and complexes to be similar. As before, co-ordinated pyridine bands (415, 422, 636, 640, and 695 cm^{-1}) for $MeZnIpy_2$ show strong Zn-N bonds are formed but, in contrast to the zinc diethyl systems, concentrated solutions of EtZnI in ether and THF have additional bands in the 8-14μ region which are known to indicate co-ordinated solvent molecules (84) (88) Table 23, Fig 5. The assignment of δ(C-O-C) frequencies for THF is straight forward, with shifts of 40-50 cm^{-1} on

FIG 5 I.R. Spectrum of an EtZnI–THF Sol'n.



co-ordination, but for Et_2O, since coupling occurs between δ(C-O-C) and ν(C-C) vibrations, the assignments are less certain (see Table 27).

Table 23 Solvent Frequencies (cm^{-1}) for EtZnI solutions (8-14μ)

Diethyl Ether

Solution	778s	791sh	831m	844w	903m	917w	932w	1042s	1075s	1109w
Solvent		792w		845m		917w	933m	1041m	1073m	1112s
$ZnCl_2(Et_2O)_2$ (88b)	780m		835m		900m			1030m	1090m	

Tetrahydrofuran

Solution	873 s	909 s	943 sh	1031 s	1056 s		1176 w
Solvent		909 s		1031 wsh		1087 s	1179 w
$ZnCl_2THF$	872 s		920 w	1022 s			1179 w
	δ_{sym}(C-O-C)				δ_{asym}(C-O-C)		

In the Raman spectrum of EtZnI in diethyl ether, the shoulder (473 cm^{-1}) due to free $ZnEt_2$ suggests that a Schlenk equilibrium may exist in this system. An estimate of the amount of free $ZnEt_2$ present was obtained using an ether band (840 cm^{-1}) as an internal intensity standard.

Calculation.

2.0 ml EtZnI solution weigh 2.719 gm.

By analysis, $[Zn] = 3.33M$, $[I] = 3.52M$.

Thus, by difference, $[Et_2O] = 7.31M$.

Now for standard $ZnEt_2/Et_2O$ solution with $[Et_2O]/[ZnEt_2] = 2.42$,

$$\frac{I_{Zn}}{I_S} = 3.58 = \frac{K[ZnEt_2]}{[Et_2O]},$$ where K is a constant.

Thus K = 3.58 x 2.42, for calibration.

For EtZnI solution,

$$\frac{I_{Zn}}{I_S} = \frac{47}{322} = \frac{K[ZnEt_2]}{7.31},$$

giving, $[ZnEt_2] = 0.12M$.

From mass-balance equations,

$[ZnI_2] = 0.31M$ and $[EtZnI] = 2.90M$.

The equilibrium present in this solution is,

$ZnEt_2 + ZnI_2 \rightleftharpoons 2\ EtZnI$, $K = 2.3 \times 10^2$.

mole % 3.6 9.3 87.1

These figures only give an order of magnitude but compare with the similar 'EtMgBr' equilibrium (50).

$MgEt_2 + MgBr_2 \rightleftharpoons 2\ EtMgBr$, $K = 5.7 \times 10^2$.

mole % 4 4 92

2.3. The 'Mixed' Solutions, $ZnR_2 + ZnX_2$.

The 'mixed' ($R_2Zn + ZnX_2$) and 'normal' ($Zn + RX$) solutions are usually considered identical but with hours or days necessary for complete exchange to occur. Thus Dessy (65) used contact times of 120 hours while Abrahams and Rolfe (66) stated that EtZnI.TMED was obtained from a 'mixed' solution after one week.

Infra-red data (14-24μ) are reported for the pure zinc alkyl solutions and also after the addition of solid zinc halide complex, Table 24. The identical spectra of 1:1 mixtures and RZnI solutions show that both solutions contain the same species. Further, spectra obtained 5-10 minutes and 18-20 hours after mixing were identical showing the reaction time is $\lesssim$ 5 min. With varying amounts of $ZnI_2(THF)_2$ added, the change from $ZnEt_2$ to EtZnI is clearly seen in the infra-red spectrum (Fig 6), as the 535 cm^{-1} band gradually disappears with the rise of the 507 cm^{-1} band of EtZnI. The stoichiometry of the mixing reaction is confirmed by the solubility of ZnI_2.DME in a DME solution of $ZnEt_2$ (1.04M). Addition of the equivalent amount of halide gives a solution 2.01M, while if 25% excess ZnI_2.DME is used, not all dissolves and this solution is 1.99M. Both solutions have identical spectra. Thus the reaction is, $ZnI_2 + ZnEt_2 \xrightarrow[DME]{} 2\ EtZnI$. This is in contrast to the analogous magnesium systems where 'insoluble' magnesium

Table 24 Infra-Red Spectra (14-24μ) of Solutions of $R_2Zn + ZnX_2$ (cm^{-1})

Tetrahydrofuran

$ZnEt_2$	1.06M,		535 s		610 s	660 s
+ $ZnCl_2$,	1.98M,	515 sbr		607 s		660 s
+ $ZnBr_2$,	2.06M,	511 s		606 s		668 s
+ ZnI_2,	2.14M,	507 s		605 s		668 s
EtZnI	1.92M,	505 s		600 s		668 s

$ZnMe_2$	1.72M,	487 m		547 s	579 w		664 sbr
+ $ZnCl_2$,	3.30M,		536 s		582 w	626 s	670 s
+ $ZnBr_2$,	3.71M,		531 s		584 w	638 s	670 s
+ ZnI_2,	3.20M,		528 s		580 w	638 s	668 s
EtZnI	2.83M,		530 s		518 w	638 s	668 s

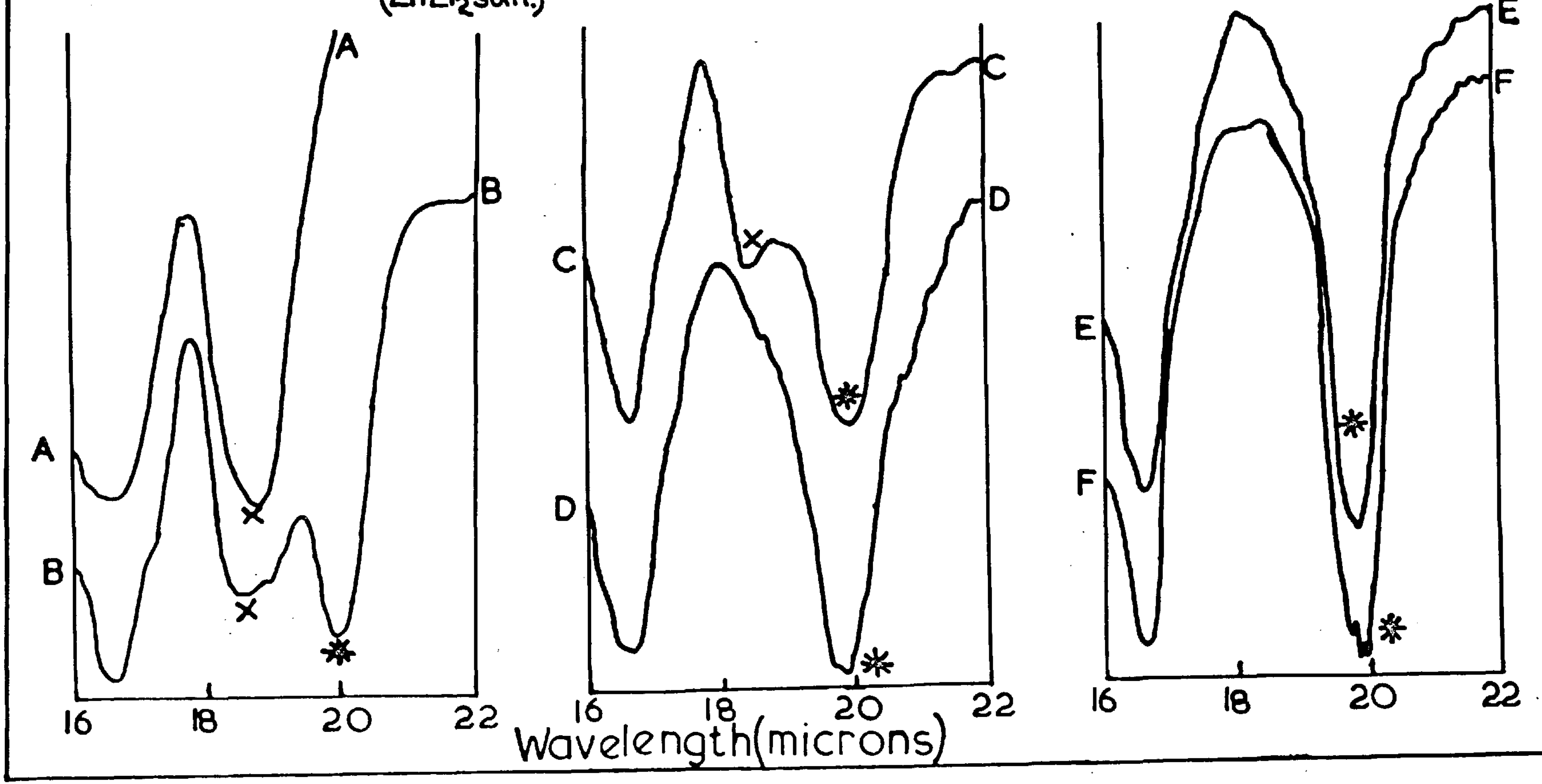
1,2-Dimethoxyethane

$ZnEt_2$	1.04M		512 sh	539 s	568 w		608 s
+ $ZnBr_2$	1.96M	506 s	511 w	543 s	568 w	609 s	
+ ZnI_2	2.01M	503 s	510 w	542 s	568 sh	607 s	
EtZnI	1.61M	501 s	510 w	539 s	568 sh	607 s	

FIG 6 Changes in the ν(Zn–C) Band for the Exchange Reaction,

$ZnEt_2 + ZnI_2 \xrightarrow{THF} 2EtZnI.$

Curve	A–A,	B–B,	C–C,	D–D,	E–E,	F–F.
Ratio [Zn]mixt./[Zn]orig. ($ZnEt_2$ soln.)	1·0,	1·35,	1·5,	1·65,	2·0,	EtZnI.



halides dissolve considerably in both magnesium dialkyl (36) and Grignard solutions.

2.4. Organo-magnesium Solutions.

Few studies have been reported of organo-magnesium compounds. Early infra-red work (89) (10,000-700 cm^{-1}) on Grignard reagents in ether showed two bands not found in the solvent spectrum which were later attributed to Mg-Br stretches (90). Recently (88) more extensive solution studies of the C-O-C deformation region of several ethers assigned these and other bands to solvent frequencies shifted by strong co-ordination. Skeletal frequencies have not been assigned except for magnesium-carbon vibrations (91). Previous Raman work was hindered by the fluorescence and cloudiness of the solutions examined (92) (88a).

Raman data (200-1000 cm^{-1}) for various solutions, 2-4M, are given in Table 25. The strong, sometimes broad, band ca. 500 cm^{-1} observed in each spectrum is assigned to a magnesium-carbon stretching vibration, Table 26. The infra-red frequencies (91) were obtained for dilute solutions 0.15-0.3M but were shown not to change over a 4 to 8-fold range of concentrations.

Table 25 Raman Spectra (200-1000 cm^{-1}) of Organo-magnesium Solutions (cm^{-1})

Diethyl Ether					Tetrahydrofuran		
Solvent	EtMgI	EtMgBr	$MgEt_2$	Pr^nMgCl	Solvent	EtMgBr	$MgEt_2$
238w	228s	239s		240m		246m	
	292vw	294vw		303w	282vw		
			367m				
372w				374w			
			412m			408wbr	413s
438vs	439w	440m	443m	435vs			
496w	486sbr	484sbr		489 ssp		492s	
	495sh		515sbr	498			521mbr
				550m		584vwbr	
				651w		678vwbr	
788vw	782vw	782m	787w	783m			
842s	836s	835m	839s	838vs			
				850w			
918sh	898m	904m		904w		890vs	
930m	923s	921s	919vs	934m	911vs	915vvs	917vvs
	972m		968m	968vs		964w	971w

Table 26 Magnesium-Carbon Stretching Frequencies (cm^{-1})

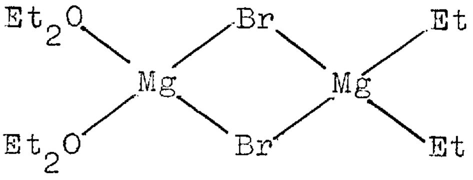
Diethyl Ether

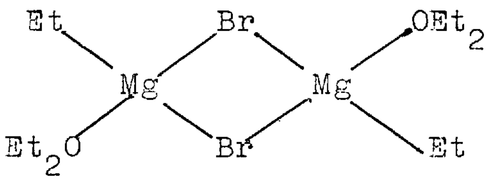
	$MgEt_2$	EtMgI	EtMgBr	Pr^nMgCl	$MgMe_2$	MeMgBr
Raman	515	486 495	484	489 494	-	-
infra-red (91)	512	-	508	-	525	520

Tetrahydrofuran

	EtMgBr	$MgEt_2$	MeMgCl	MeMgBr	$MgMe_2$
Raman	492	513	-	-	-
infra-red (91)	500	512	527	513	535

The infra-red and Raman values of the Mg-C stretching frequency are nearly identical for magnesium diethyl solutions, thus showing that the C-Mg-C angle is near tetrahedral as also indicated by X-ray results (37b). However, for Grignard solutions they do not coincide. The values for 'EtMgBr' in THF differ only by 8 cm^{-1} and the band at 492-500 cm^{-1} is assigned to the magnesium-carbon stretching mode of the monomeric EtMgBr species deduced from molecular weight measurements (41). For the diethyl ether solution, the difference is greater (24 cm^{-1}) but the data do not distinguish between the two dimeric structures which could occur at high concentrations (40).





The bands at 367 and 410 cm^{-1} observed for magnesium diethyl solutions can plausibly be assigned to magnesium-oxygen stretching modes but for Grignard solutions the bands at 230-240 and 290-300 cm^{-1} which are not much affected by change of halogen, appear rather low for such strongly bonded systems. No bands assignable to magnesium-halogen frequencies were observed. While Mg-Br-Mg or Mg-I-Mg bridge vibrations may be expected to lie below 200 cm^{-1}, the same does not apply to Mg-Cl-Mg or Mg-Br modes but these also could not be detected. Examination of EtMgBr and EtMgI solutions from 100-270 cm^{-1} with the mercury 'green' line only showed bands at 242 and 231 cm^{-1} respectively which had been observed previously.

No detailed assignment of diethyl ether has been published (93) (94) but the skeletal vibrations which are modified on complexing can be readily identified. Infra-red data (1150-700 cm^{-1}) for concentrated solutions of EtZnI and EtMgBr in diethyl ether are given in Table 27 (Fig 7) with an assignment following that of Jones and Wood. A previous study (88a) is incomplete. The Raman spectra show similar features in this region but in general the small shifts are not resolved.

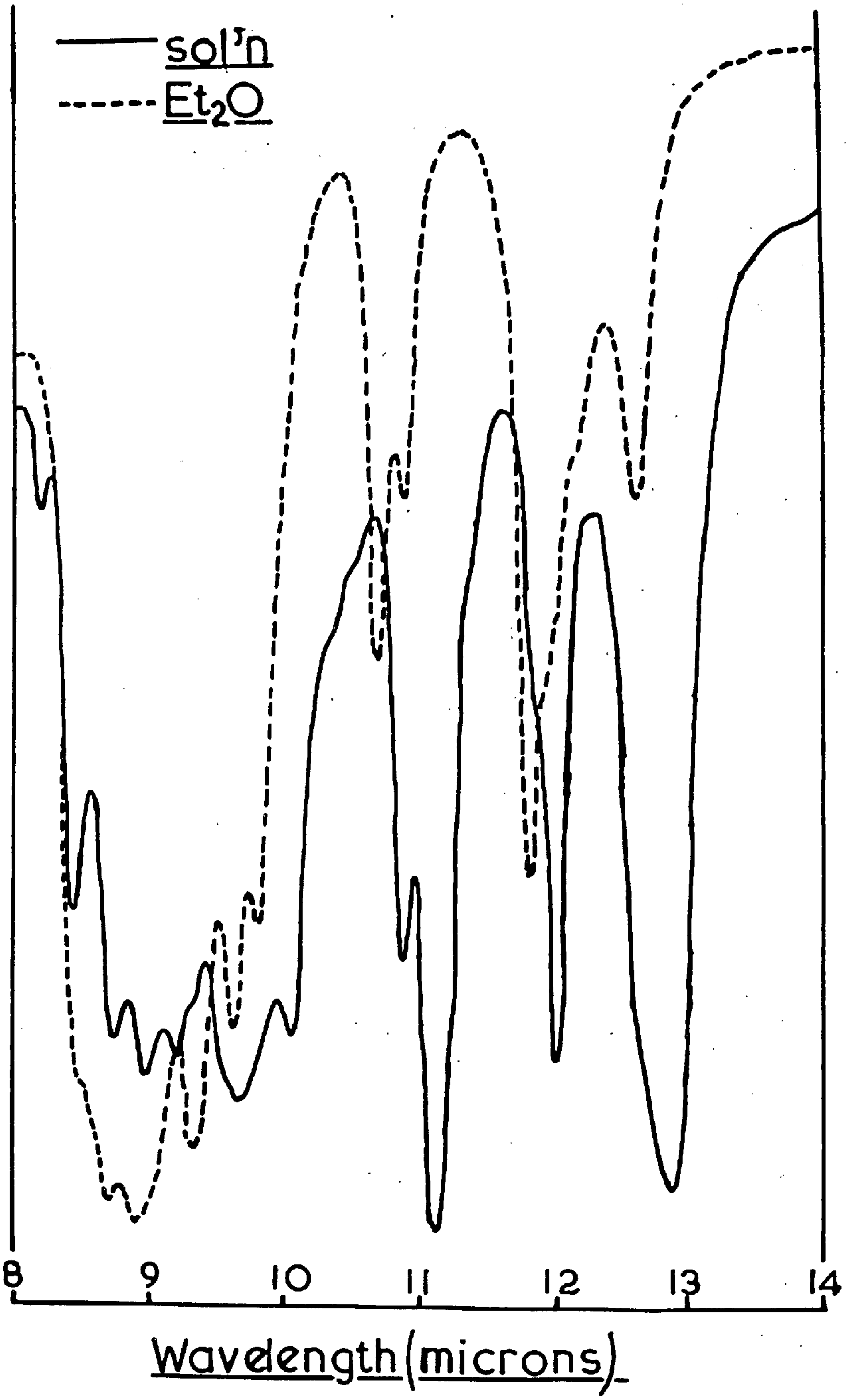
Table 27 Infra-red Spectra (1150-700 cm^{-1}) of Diethyl Ether Solutions of EtMgI and EtZnI (cm^{-1}).

Solvent	EtMgI	EtZnI	Assignment
1148 s	1148 m	1149 s	
1112 vs	1119 s	1109 vs	
1073 s	1090 w	1075 m	COC asym. stretch
1041 m			
	1037 s	1042 vs	
1022 m			
	998 w	996 m	EtMI$_2$, (ethyl group) vibrations
	950 sh	951 w	
933 m	931 s	932 w	COC sym. stretch
917 w		917 w	
	901 vs	903 m	
845 m	844 sh	844 w	C-C stretching vibrations
833 sh	836 s	831 m	
794 w	792 sh	791 sh	
	781 s	778 s	

Bands associated with co-ordinated Et$_2$O molecules are underlined.

Unlike the organo-zinc system where structural conclusions can be reached, the vibrational spectra of organo-magnesium compounds present no clear picture. In particular, the coincidence of ν_{asym}(Mg - C) and ν_{sym}(Mg - C) in magnesium diethyl spectra renders any study of the magnesium-carbon bands abortive if structural conclusions are desired. Thus, other physical techniques may be required if more certain information about the nature of Grignard solutions is to be obtained.

FIG 7 I.R. Spectrum of an EtMgI–Et_2O Sol'n.



3. EXPERIMENTAL.

3.1. General

Unless stated otherwise, all manipulations of these water and, in many cases, oxygen sensitive systems were carried out under dried 'oxygen-free' nitrogen. Whenever possible, solutions were handled in containers fitted with 'Suba-seals' and transferred using capillary tubing under differential nitrogen pressure. The neat zinc alkyls were handled using a conventional high-vacuum system fitted with a mercury diffusion pump. All solvents and liquid reagents were dried over Linde 3Å molecular sieves or where necessary, by distillation from sodium or lithium aluminium hydride.

Melting points were determined using a Kofler hot-stage block. Zinc analysis was by the conventional EDTA method; for solutions, a sample (1,0 or 2.0 ml) was withdrawn using a syringe and after hydrolysis with dilute nitric acid, titrated in the usual way.

3.2. Dimethylzinc and Diethylzinc. (14)

The zinc-copper couple containing 6-9% copper was prepared by adding clean brass filings (25 gm) to molten zinc (170 gm) and casting the alloy into bars. These were turned into fine shavings which were then stored in a stoppered bottle.

Dimethylzinc. (95) (19)

Methyl iodide (1 mole) with ethyl acetate (2 ml) was added to zinc turnings (140 gm. 8% Cu) and the mixture refluxed for 18-20 hours over a water bath at 60°C. The flask was then evacuated and after initial pumping to remove any methyl iodide remaining, the zinc dimethyl was distilled off by slowly raising the temperature of the oil-bath surrounding the flask to 190°C. The crude product was freed from methyl iodide by refluxing over excess zinc-copper turnings, the purity of the material being checked by its proton resonance spectrum. In most preparations, any methyl iodide was $\leq$0.5% of the zinc dimethyl.

Diethylzinc. (96)

Ethyl iodide (1 mole) with ethyl acetate (2 ml) was added to zinc turnings (140 gm, 8% Cu) in a flask fitted with a paraffin seal. After 18-24 hours a glassy solid formed and the flask was heated at 60°C for one hour to complete the reaction. The zinc diethyl was isolated as above for zinc dimethyl and its purity checked by the proton n.m.r. spectrum. If necessary, the crude material was refluxed over zinc-copper turnings until ethyl iodide was $\leq$ 0.5% of the zinc diethyl.

Both zinc dimethyl and zinc diethyl were stored in bulbs fitted with greaseless taps.

Dialkylzinc Complexes ZnR_2L_2.

These were prepared by literature methods either by distilling the dialkylzinc onto the ligand and removing the excess by pumping to dryness (87) (80) or by mixing solutions of the ligand and dialkyl zinc and filtering off the product (79) (80).

3.3. Alkylzinc Iodide Complexes.

A solution of ethylzinc iodide was prepared by slowly adding ethyl iodide (15.6 gm) to zinc-copper turnings (16 gm) in refluxing diethyl ether (40 ml). After four hours the solution was cooled and centrifuged, and then used below (conc'n. ca. 3.0 molar). A similar preparation using methyl iodide (14.2 ml) and tetrahydrofuran (50 ml) gave a methylzinc iodide solution, conc'n. ca. 2.5 molar.

Iodo(dipyridyl)methylzinc.

Dipyridyl (1.95 gm, 0.0125 mole) in iso-pentane (80 ml) was added to methylzinc iodide in tetrahydrofuran (0.0125 mole., 5 ml). The fine light-yellow precipitate was filtered off, washed with iso-pentane and dried in vacuo. Yield 75%, dec. $>$ 240°C (Found: Zn, 18.0%. $C_{11}H_{11}IN_2Zn$ requires Zn, 18.0%).

Iodo(dipyridyl)ethyl zinc.

A preparation analogous to that above using dipyridyl (2.35 gm, 0.015 mole) and a solution (5 ml) of ethylzinc iodide (0.015 mole) in diethyl ether gave an orange-yellow compound. Yield 73%, dec. 240°C (Found: Zn, 17.5%. $C_{12}H_{13}IN_2Zn$ requires Zn, 17.3%).

Iodo bis(pyridine)methyl zinc.

Pyridine (2.5 ml) in benzene (10 ml) was added to a tetrahydrofuran solution (5 ml) of methylzinc iodide (0.0125 mole). On adding hexane (60 ml) a white precipitate formed which was filtered off, washed with iso-pentane and dried in vacuo. Yield 85%, dec $>$ 110°C (Found: Zn, 18.05%. $C_{11}H_{13}IN_2Zn$ requires Zn, 17.9%).

Iodo bis(pyridine)ethyl zinc.

A similar preparation to above gave an off-white product precipitated from a light-yellow solution. Yield 72%, dec $>$ 100°C (Found: Zn, 17.5%. $C_{12}H_{15}IN_2Zn$ requires Zn, 17.2%).

Both pyridine complexes decomposed on standing, the 'ethyl' complex becoming brown within 2-3 days.

Iodo (1,2-dimethoxyethane)methyl zinc.

A solution (5 ml) of methylzinc iodide (0.0125 mole.) in tetrahydrofuran was mixed with 1,2-dimethoxyethane (20 ml) and tetrahydrofuran removed by distillation. Hexane (80 ml) was added and the white precipitate formed after cooling the mixture to $<$ 0°C was filtered off, washed with iso-pentane and dried in vacuo. Yield 57%, dec $>$ 60°C (Found: Zn, 22.2%. $C_5H_{13}IO_2Zn$ requires Zn, 22.0%).

Iodo (1,2-dimethoxyethane)ethylzinc.

A similar procedure to that above gave a white product which became brown if not dried as quickly as possible. The best preparation gave, yield 47%, dec > 60°C, (Found: Zn, 23.6%. $C_6H_{15}IO_2Zn$ requires Zn, 21.0%).

Iodo(N,N,N',N'-tetramethyl-1,2-diaminoethane)methylzinc.

Tetramethylethylene diamine (10 ml) was added to a tetrahydrofuran solution (5 ml) of methylzinc iodide, '5 (0.0125 mole) and the mixture diluted with hexane (80 ml). The precipitate was filtered off, washed with iso-pentane and dried in vacuo. The product was white needles, yield 80%, m. pt. 128°C (Found: Zn, 19.8%, $C_7H_{19}IN_2Zn$ requires Zn, 20.2%).

Iodo(N,N,N',N'-tetramethyl-1,2-diaminoethane)ethylzinc.

An analogous preparation to that above gave white needles, yield 77%, m. pt. 106-7°C (Found: Zn, 19.5%. $C_8H_{21}IN_2Zn$ requires Zn, 19.6%).

3.4. Zinc Halide Complexes.

Interest in zinc halide complexes has centred on those with nitrogen or phosphorus ligands (82) (97). In this work, several other complexes have been prepared and their ν(Zn - X) frequencies are given in Table 28.

Dichloro(tetrahydrofuran)zinc.

Zinc chloride (GPR) was recrystallised from tetrahydrofuran and the precipitate filtered off, washed with iso-pentane and dried in vacuo to constant weight. The product is white needles, m. pt. 98-100°C (Found: Zn, 31.2%. $C_4H_8Cl_2OZn$ requires Zn, 31.4%).

Table 28 Zinc-Halogen Stretching Frequencies (cm^{-1}) of some Zinc Halide-Ether Complexes.

ZnX_2.complex.	$ZnCl_2$.THF,	$ZnBr_2$.THF,	$ZnCl_2$.DME,	$ZnBr_2$.DME.
ν(Zn - X)	336, 248 ,	258 ,	326, 300 ,	238 .

Dibromo(tetrahydrofuran)zinc.

A procedure similar to above gave white needles, m. pt. 126-8°C, (Found: Zn, 22.05%. $C_4H_8Br_2OZn$ requires Zn, 22.0%).

Di-iodo bis(tetrahydrofuran)zinc.

Iodine (12.7 gm, 0.05 mole) in tetrahydrofuran (100 ml) was slowly added to zinc dust (5 gm) in refluxing tetrahydrofuran (30 ml). The mixture was refluxed for four hours to give a green-yellow solution which after filtering through paper, was poured into hexane (300 ml). The brown precipitate was filtered off, washed white with hexane (4 x 100 ml) and dried in vacuo to constant weight; m. pt. 108-110°C (ref. (98), 130°C) (Found: Zn, 14.1%. $C_8H_{16}I_2O_2Zn$ requires Zn, 14.1%).

Dichloro(1,2-dimethoxyethane)zinc.

Dichloro(tetrahydrofuran)zinc was dissolved in excess dimethoxyethane. After refluxing for 10 minutes, the solution was poured into hexane and the mixture cooled. The white precipitate was filtered off, and dried in vacuo; m. pt. 89-90°C (Found: Zn, 29.15%. $C_4H_{10}Cl_2O_2Zn$ requires Zn, 28.9%).

Dibromo(1,2-dimethoxyethane)zinc.

A preparation analogous to that above gave a white product; m. pt. 115-6°C (ref. (79a) 103-5°C) (Found: Zn, 21.0%. $C_4H_{10}Br_2O_2Zn$ requires Zn, 20.7%).

Di-iodo(1,2-dimethoxyethane)zinc.

The same procedure as above gave a brown precipitate which afforded a white product on washing with iso-pentane; m. pt. 150-1°C (Found: Zn, 16.1%. $C_4H_{10}I_2O_2Zn$ requires Zn, 16.0%).

3.5. Infra-red Spectral Studies.

Infra-red spectra were measured using a Grubb-Parsons Spectromaster instrument. The calibration was regularly checked by observing the spectrum of 1,2,4-trichlorobenzene and frequencies quoted are $\pm$ 1 cm^{-1} except for broad bands. Solid compounds were examined as Nujol mulls between potassium bromide plates but conventional solution cells proved useless for the highly reactive alkylzinc solutions studied here. For this purpose, a fixed-path length cell which could be dried and filled under nitrogen was made (Fig. 8a). Far infra-red spectra were measured using a Grubb-Parsons DM-2 instrument at University College, London.

Dialkylzinc Solutions.

Dialkylzinc solutions were prepared using a glass bulb fitted with a break-seal (Fig. 8b). The apparatus, attached to the vacuum-line at a, was pumped out for 2 hours and 'flamed' several times. The requisite quantities of dialkylzinc and solvent (thoroughly dried and degassed) sufficient to give a 1-2 molar solution (20-30 ml), were distilled into the bulb which was then sealed at b, the mixture being frozen in liquid nitrogen. The break-seal c was then broken while the volume under the Suba-seal was flushed out with a stream of nitrogen. Solutions prepared were of diethylzinc in diethyl ether, dioxan, tetrahydrofuran, and 1,2-dimethoxyethane and of dimethylzinc in the last two solvents.

Ethylzinc Iodide Solutions.

Zinc-copper turnings (3 gm) in a test-tube fitted with a Suba-seal and then flushed out with nitrogen, were treated with ethyl iodide (3.2 ml) containing a trace of ethyl acetate. The white solid formed after 18-20 hours was dissolved in tetrahydrofuran or 1,2-dimethoxyethane (10 ml). The solution was centrifuged and the clear supernatant

FIG 8a

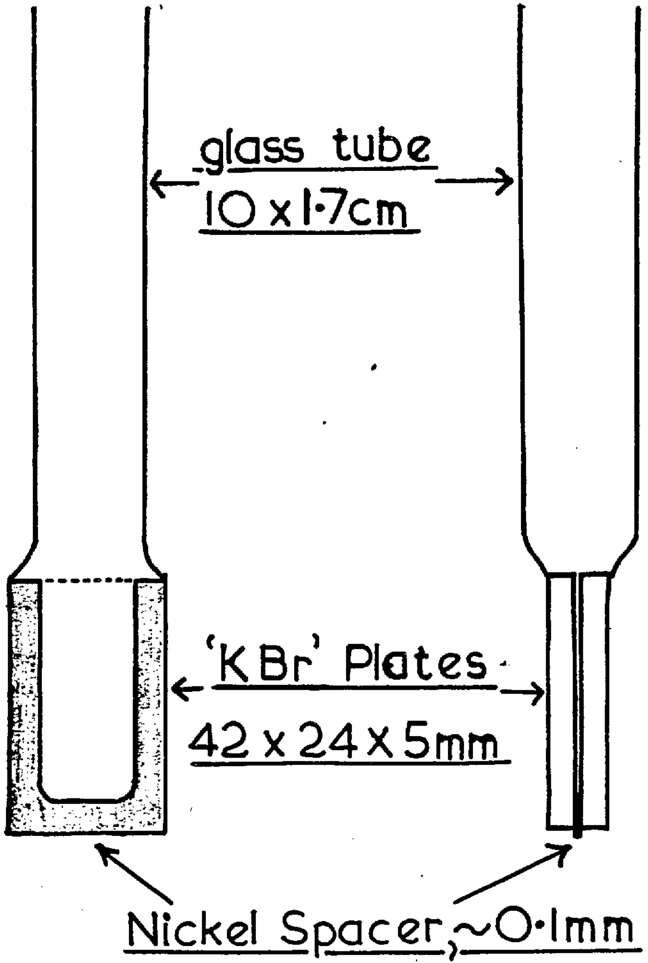
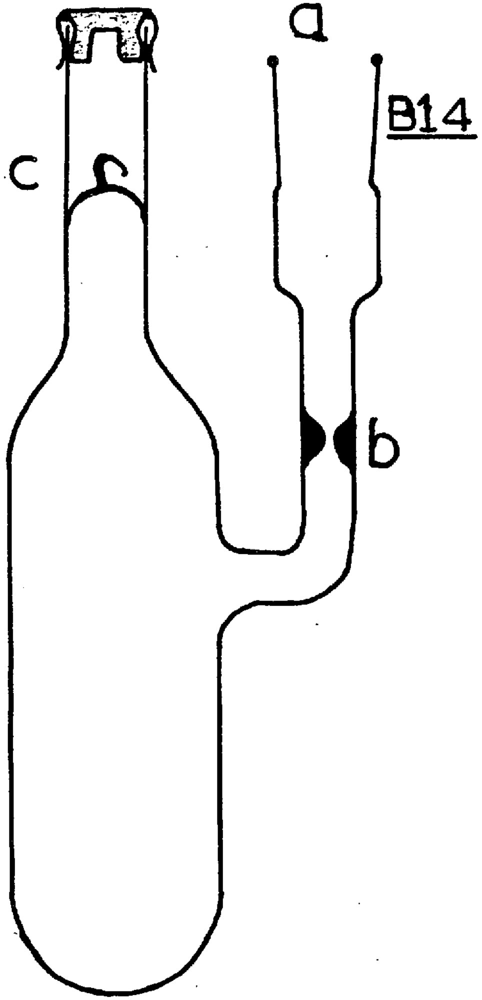

glass tube
10 x 1·7cm
'KBr' Plates
42 x 24 x 5mm
Nickel Spacer, ~0·1mm

FIG 8b


a
B14
c
b

liquid transferred to a storage vessel. The diethyl ether solution measured was that prepared below for Raman examination. The Raman tube was broken open in an atmosphere of carbon dioxide and the solution poured into a sample bottle which was then capped with a Suba-seal.

Methylzinc Iodide Solutions.

Tetrahydrofuran and 1,2-dimethoxyethane solutions were prepared. For the latter, methyl iodide (14.2 gm) in containing ethyl acetate (0.5 ml) was added to zinc-copper turnings (14 gm) in refluxing dimethoxyethane (60 ml). After 18 hours, the cooled solution was centrifuged and the clear liquid transferred to a flask closed with a Suba-seal. A solution in tetrahydrofuran (40 ml) was prepared by the same method.

Mixing Experiments.

A solution (5 ml) with a known concentration of diethylzinc or dimethylzinc was added to an equimolar quantity of the zinc halide complex in a sample bottle flushed out with nitrogen. After shaking clear solutions were usually obtained but in some cases, material remained undissolved and this was removed by centrifuging the mixture. The mixed solution obtained was re-analysed for zinc and, assuming only a small increase in volume occurred, the ratio $[\mathrm{Zn}]_{\mathrm{mixed}}/[\mathrm{Zn}]_{\mathrm{original}}$ was taken to indicate the amount of added zinc halide present.

The solution cell was filled with nitrogen by first evacuating it and then flushing with a stream of nitrogen, this being repeated several times. After use, the cell was washed out under nitrogen with the reaction solvent and then ether, and finally dried with a hot-air blower. The solvents used gradually dissolved the 'optical Araldite' which held various components together and the cell became unusable after 10-12 spectra had been measured.

3.6. Raman Spectral Studies.

The Raman effect has not become a general research technique like infra-red absorption spectrometry but the recent introduction of recording instruments has prompted renewed interest in this field (100). However, at present, the more complex procedure and the more restrictive sample criteria are likely to prevent the routine use of Raman spectrometry. For this work, as well as the usual restrictions on concentration and colour found with aqueous solutions, particular attention was also given to reducing cloudiness and fluorescence. This was done by carrying out all reactions in vacuo as moderately as possible. The Raman spectra were measured using a Cary 81 instrument at Kings College, London, and polarisation measurements were made using calibrated Polaroid filters. The calibration of the instrument was checked by either running over the exciting line or by observing the position of the intense polarised band of carbon tetrachloride at 459 cm^{-1}. Except for broad bands peak positions were ± 2 cm^{-1}.

Dialkylzinc Solutions.

Apparatus used is shown in Fig. 9a. The Raman tube, capacity 5-6 ml., was attached to a trap to prevent contamination of the solutions by silicone grease. Calibrated sealed tubing was used to make tap-bulbs and containers from which known volumes of liquid could be distilled. Solvents were degassed and dried over 3Å molecular sieves (hexane, diethyl ether) or lithium tetrahydroaluminate (tetrahydrofuran, dimethoxyethane). The Raman tube was pumped out for several hours and flamed several times. Known volumes of solvent and dialkylzinc sufficient to give solutions 2-3 molar in zinc, were distilled into the tube which was sealed with the mixture cooled in liquid nitrogen. On shaking to give a homogenous solution, no volume change was observed and thus the total volume was taken to be the sum of the volumes of the two constituents.

Ethylzinc Iodide-Diethyl Ether Solution.

Zinc-copper turnings (2 gm) and a magnet 'follower' were introduced into the reaction bulb of the apparatus shown in Fig. 9b, by a side-arm which was then sealed at a. The apparatus was attached to the vacuum line at A and pumped out overnight, being flamed several times. Ethyl iodide (3.06 gm) with a trace of ethyl acetate was then distilled onto the zinc turnings and the apparatus was sealed at b. After 1 day at room temperature, a clear, glassy solid had formed with no liquid remaining unreacted. The apparatus was pumped out at B for several hours and the break-seal c then broken. The solid product was pumped at room temperature to remove any unreacted ethyl iodide, then dissolved in diethyl ether (6 ml) and the apparatus sealed at d. The clear solution was filtered through the No 4 sintered glass plate into the Raman tube, which was then sealed at e with the solution cooled in ice-water.

Several attempts were made to carry out an equivalent preparation of a methylzinc iodide solution using various types of zinc-copper couple but all proved unsuccessful.

Ethylmagnesium Bromide-Diethyl Ether Solution.

The apparatus used is shown in Fig. 10a. Magnesium (0.72 gm) with a magnet 'follower' was introduced into the reaction bulb through a which was then sealed. The apparatus was pumped out overnight and flamed several times, the sintered glass plate being heated for a considerable time. Diethyl ether (5 ml), degassed and dried over 3Å molecular sieves, was distilled into the bulb. This was followed by a mixture of ethyl bromide (2.18 gm) in diethyl ether (1.0 ml) in several (ca. 10) portions. Reaction began immediately and was moderated by rapid stirring and cooling the reaction bulb in melting ice. The reaction was allowed to subside before further material was added and total addition required 1-1½ hours. The reaction mixture was allowed to warm to room temperature over a period of two hours and the apparatus was then sealed at b with the bulb cooled in liquid nitrogen. After leaving overnight, the solution was filtered into the Raman tube which was sealed at c while cooled in an ice-salt mixture.

Ethylmagnesium Iodide-Diethyl Ether Solution.

This was prepared in a like manner to the experiment above using ethyl iodide (3.12 gm). The reaction was slightly more vigorous but a nearly colourless solution was obtained.

n-Propylmagnesium Chloride-Diethyl Ether Solution.

This solution was obtained using n-propyl chloride (1.57 gm). The mixture was much less active than above and reaction only began after the bulb had been warmed with a hot-air blower. Once initiated, reaction was vigorous but a completely clear and colourless solution was produced which was viscous and could only be filtered by diluting the portion of the solution above the sintered glass plate, with diethyl ether distilled from the remainder of the solution.

Several preparations of a diethyl ether solution of methylmagnesium iodide were tried but even when the reaction mixture was cooled in dry-ice/alcohol at - 25°C reaction was too vigorous and a yellow solution was always obtained.

Ethylmagnesium Bromide-Tetrahydrofuran Solution.

This solution was prepared by the general procedure described above. Reaction was more vigorous than in the diethyl ether experiment, and when complete, a white precipitate had formed which was only dissolved by addition of further tetrahydrofuran (3 ml). After filtering into the Raman tube, the solution was concentrated to a 5-6 ml. volume and the Raman tube then sealed as usual.

The analogous procedure to obtain a tetrahydrofuran solution of ethylmagnesium iodide afforded at each attempt, a white or yellow solid which completely filled the reaction bulb and could not be dissolved.

Diethylmagnesium-Diethyl Ether Solution.

The apparatus used is shown in Fig. 10b. Diethylmercury (0.18 gm) in diethyl ether (2 ml) was poured onto the 3Å molecular sieves in bulb A which was then sealed at a. After two weeks, the ampoule was joined to the main apparatus B, after magnesium (1.0 gm) and a magnet 'follower' had been introduced into the reaction bulb. The apparatus was pumped out overnight and flamed several times. Ether (15 ml) previously dried and degassed, was distilled onto the magnesium and the apparatus sealed at b. The breakseal I was broken and most of the diethylmercury solution distilled into the reaction bulb. After removing A by sealing at c, the apparatus was left for 2 weeks. Then, after pumping at d for two hours, the break-seal II was broken, the solution evaporated to dryness and the residue pumped for 1 hour to remove any unreacted diethylmercury. Ether (6 ml) was then distilled onto the white solid and the apparatus sealed at e. The solution was filtered into the Raman tube which, cooled in an ice-salt mixture was sealed at f.

Diethylmagnesium-Tetrahydrofuran Solution.

This was prepared as described above. On evaporation of the initial solution, a thick syrup was obtained which did not solidify even after pumping for one hour.

FIG 9a

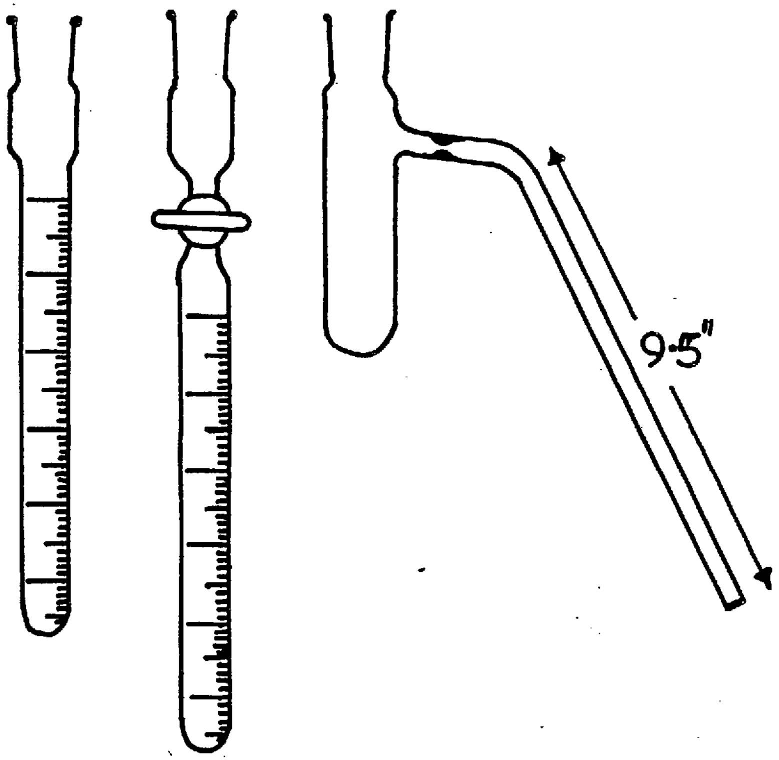


FIG 9b

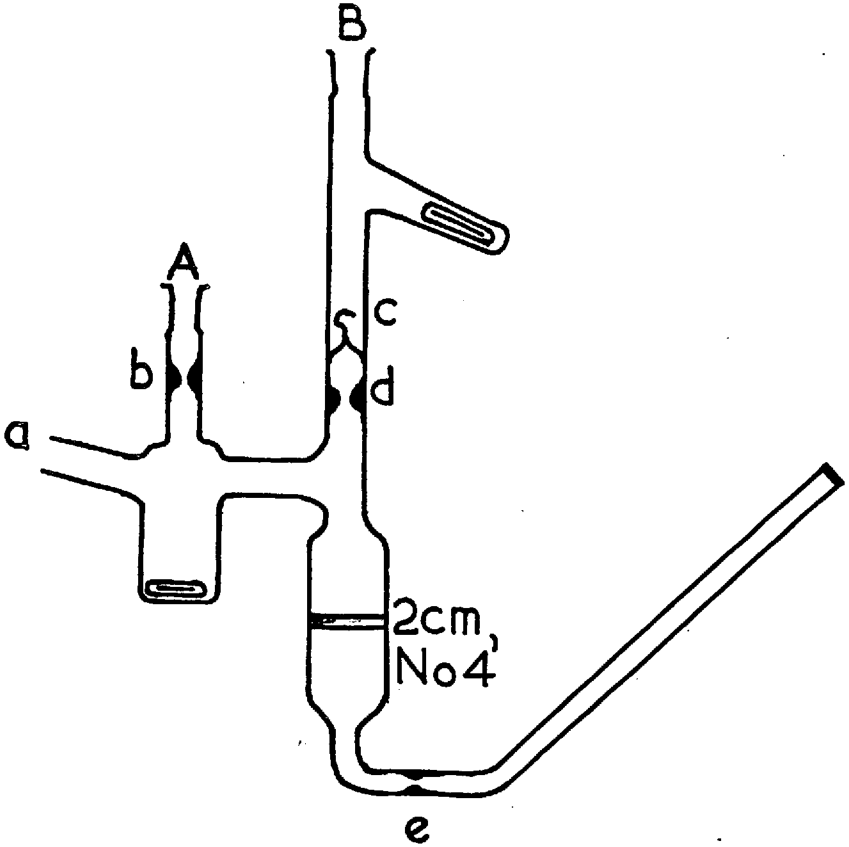


FIG 10a

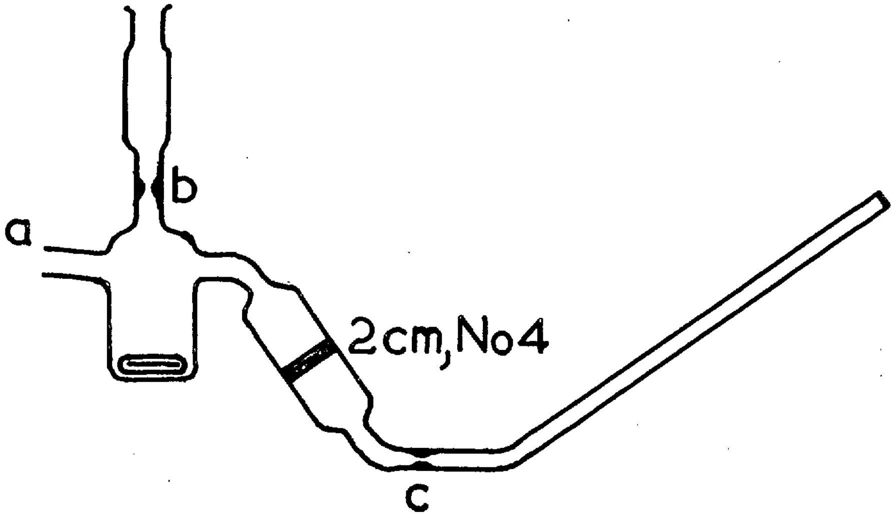
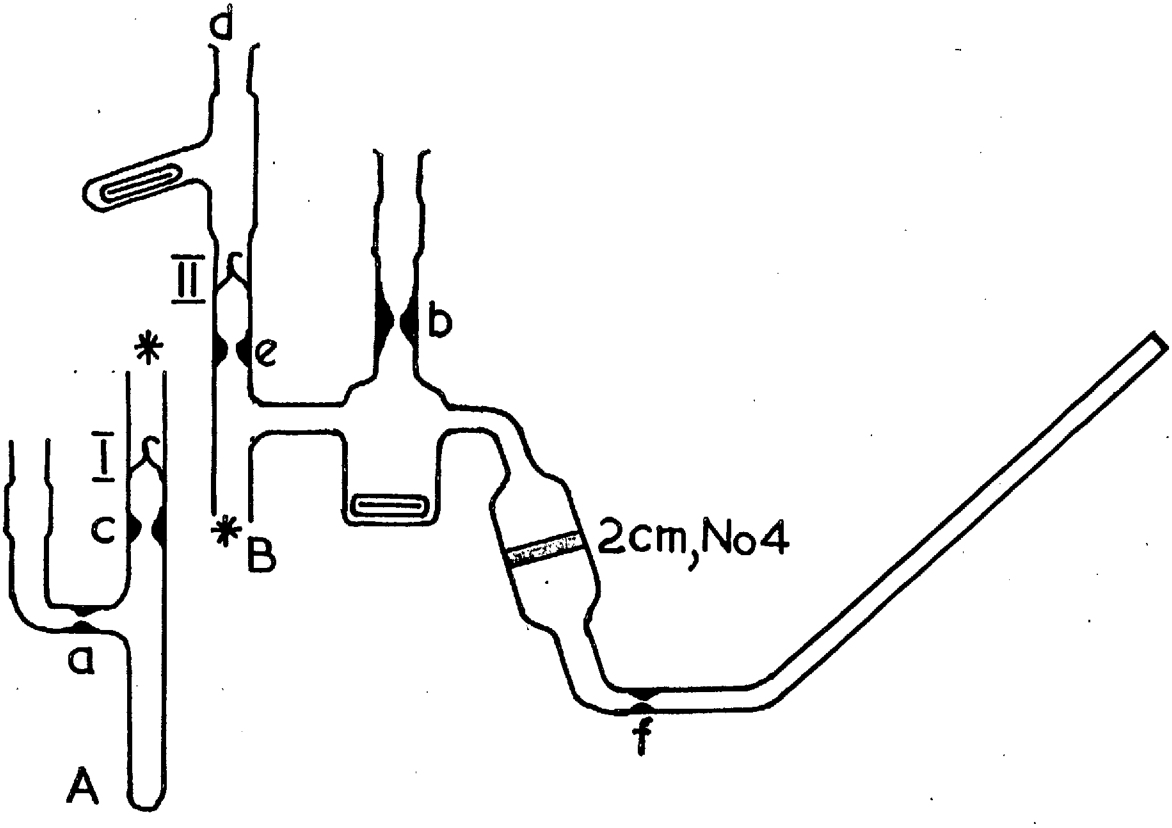
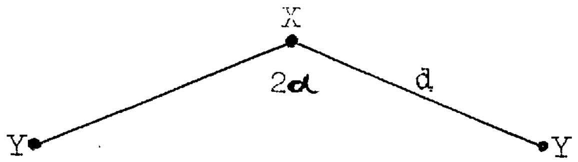


FIG 10b



4. CALCULATIONS USING AN XY_2 MODEL.

The equations for the normal frequencies of an XY_2 molecule derived using a valency-force field, have been given by Herzberg (101).



k_1 stretching force constant

k_δ bending " "

ν_1 symmetric stretch, ν_2 deformation, ν_3 asymmetric stretching frequencies.

For these calculations, the various constants were compounded to give $K_1 = k_1 A/4\pi^2 m_y$, where A is the factor needed to convert c/s to cm^{-1}., and for the bent molecule, it was assumed $k_\delta/d^2 = 0.1\ k_1$. In the general case, $\alpha \neq 90^\circ$, the equations are,

$$\nu_1^2 + \nu_2^2 = K_1\left\{1 + \frac{2\ m_y}{m_x}.\cos^2\alpha\right\} + 0.2\ K_1\left\{1 + \frac{2\ m_y}{m_x}.\sin^2\alpha\right\}$$

$$\nu_1^2\nu_2^2 = 0.2\ K_1^2\left\{1 + \frac{2\ m_y}{m_x}\right\}$$

$$\nu_3^2 = K_1\left\{1 + \frac{2\ m_y}{m_x}\sin^2\alpha\right\}$$

For a linear molecule, $\alpha = 90^{\circ}$, the equations become,

$$\nu_1^{2} = K_1$$

$$\nu_2^{2} = 0.2\ K_1\left\{1 + \frac{2\ m_y}{m_x}\right\}$$

$$\nu_3^{2} = K_1\left\{1 + \frac{2\ m_y}{m_x}\right\}$$

A value for K_1 was obtained using the Raman value of the symmetric stretching frequency of the linear molecule. For $ZnMe_2$, $\nu_1 = 504\ cm^{-1}$, $K_1 = (504)^2$. Using $m_x = Zn = 65$, $m_y = CH_3 = 15$, ν_3 (calc'd.) $= 609\ cm^{-1}$ which compares with a ν_3 (expt'l.) of $615\ cm^{-1}$.

A similar calculation for $ZnEt_2$ did not give such good agreement and only the $ZnMe_2$ case was studied further.

To simulate the observed Zn - C stretching frequencies, values of ν_1 and ν_3 were calculated for change in 2α, increase in m_x and decrease in K_1. Calculation of ν_3 is straightforward, but to avoid assuming a value of ν_2, the final quadratic equation in $(\nu_1^{2})^2$ was solved each time. The results for various combinations of these effects are given by Graphs A-F.

$\underline{2\alpha}$ This accounts for the bending of the molecule on co-ordination i.e. a change from sp to sp^2 or sp^3 hybridisation. The ratio ν_3/ν_1 becomes 1.0 when $2\alpha = 100^\circ - 90^\circ$, regardless of any other changes, but $\frac{1}{2}(\nu_1 + \nu_3)$ is nearly independent of angle change, giving support for the use of this quantity as a characteristic zinc-methyl stretching frequency.

$\underline{K_1}$ A decrease represents a weakening of the Zn-C bond on complex formation. This change can have no effect on ν_3/ν_1 but accounts for much of the variation in $\frac{1}{2}(\nu_3 + \nu_1)$.

$\underline{m_x}$ An increase in m_x takes account of the attachment of ligands to the central atom which will appear to increase its mass. Both ν_3/ν_1 and $\frac{1}{2}(\nu_3 + \nu_1)$ are affected by this change; if $m_x = \infty$ then $\nu_3/\nu_1 = 1$ for all values of 2α.

Dimethylzinc-Tetrahydrofuran Solution.

		ν_1 cm^{-1}.			ν_3 cm^{-1}.			$\frac{1}{2}(\nu_3 + \nu_1)$	ν_3/ν_1
m_x	x	140°	130°	120°	140°	130°	120°		
75	0.90	490	496	503	556	553	545	524	1.14-1.08
85	0.90	487	492	498	548	543	537	518	1.13-1.08
100	0.95	500	505	512	552	548	544	527	1.10-1.07
120	0.95	499	502	507	543	539	535	521	1.09-1.06
Expt'l.		493			547			520	1.11

Various combinations of m_x and x ($K_1 = x(504)^2$) give values ν_1, ν_3, $\frac{1}{2}(\nu_1 + \nu_3)$ and ν_3/ν_1 which agree well with the experimental results. The above calculations use several likely values for m_x and x and no specific choice can be made. A 'ligand mass' of 20-24 was used by Jones and Wood (94) in their calculations of frequencies for $AlCl_3L$ systems.

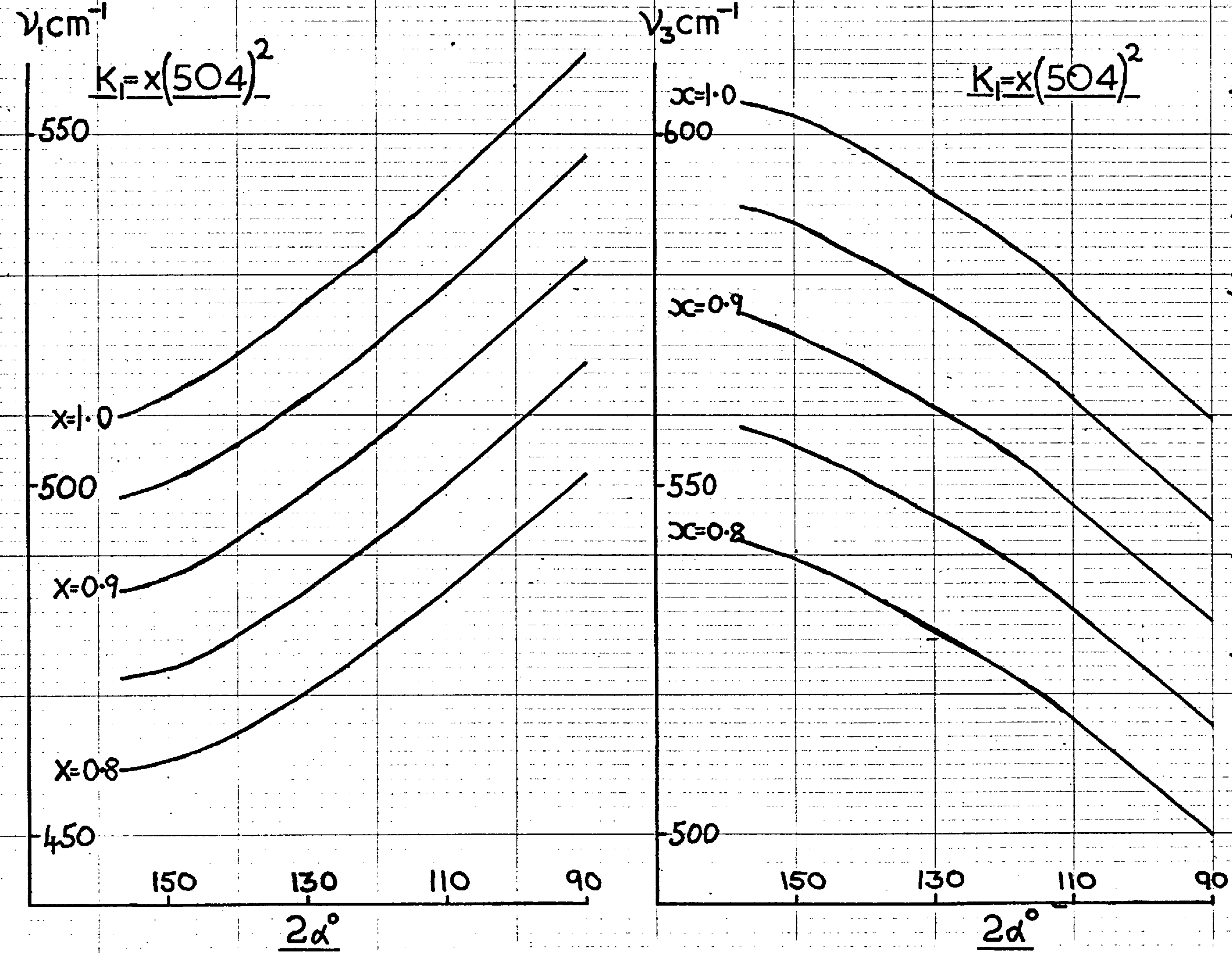
Dimethyl(dipyridyl)zinc.

X-ray studies of $ZnCl_2py_2$ (102) and $ZnCl_2$o-phen (103) afford values of ClZnCl of 126° and 115° respectively. Here, the C - Zn - C angle is given a value of 130°-110°.

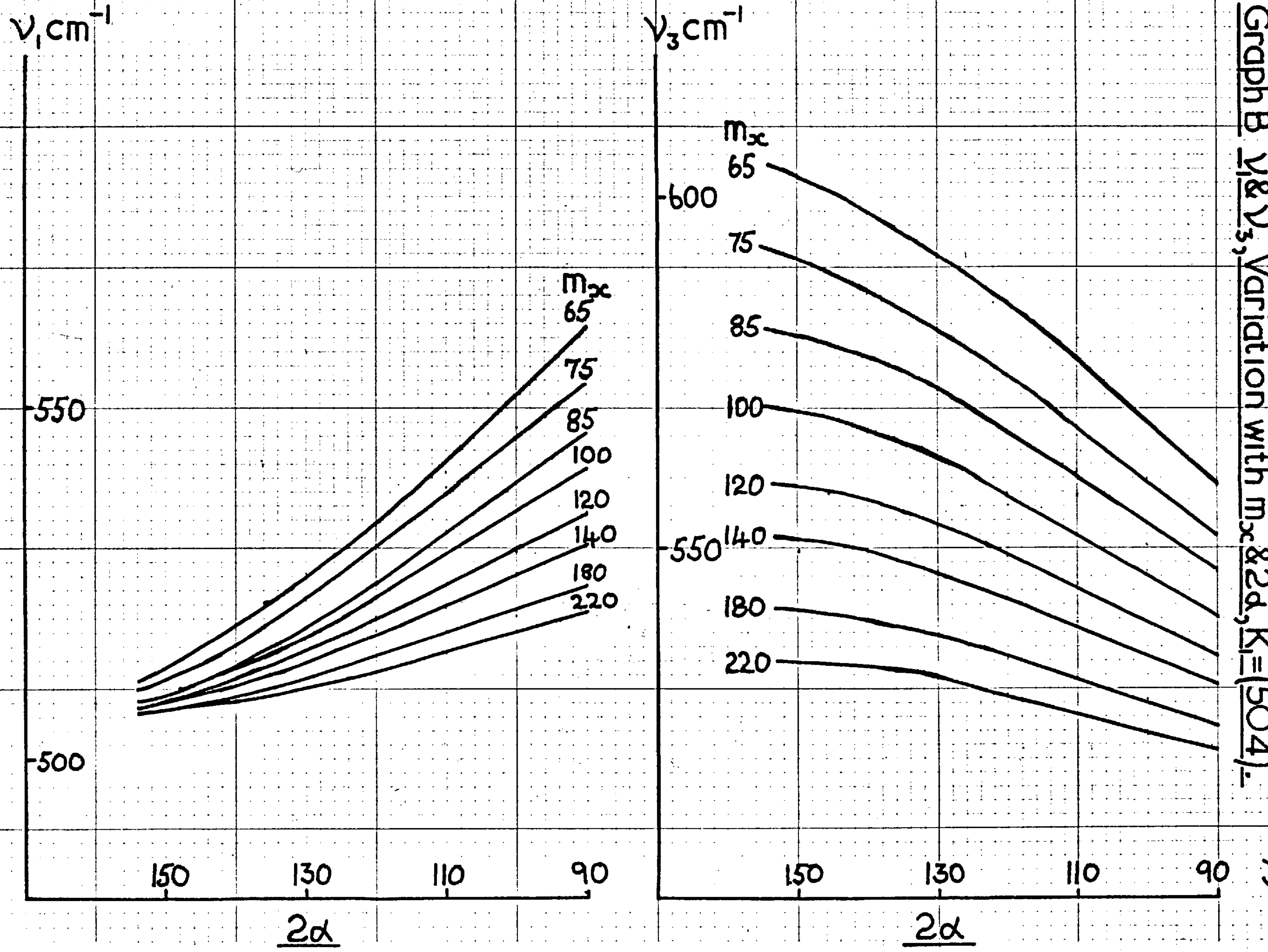
		ν_1 cm^{-1}.			ν_3 cm^{-1}.			$\frac{1}{2}(\nu_3 + \nu_1)$	ν_3/ν_1
m_x	x	130°	120°	110°	130°	120°	110°		
35	0.80	464	469	476	512	506	501	488	1.10-1.05
140	0.85	474	478	481	504	501	497	489	1.07-1.03
180	0.85	472	474	478	495	493	490	484	1.05-1.03
220	0.90	484	486	489	504	502	499	494	1.04-1.02
Expt'l.		465			510			488	1.10

Although calculated values of ν_1, ν_3, $\frac{1}{2}(\nu_1 + \nu_3)$ and ν_3/ν_1 can be obtained which are near the experimental results, the parameters necessary are somewhat less probable than in the previous example. The best fit requires a low force constant ($K_1 = 0.80(504)^2$), while other calculations use values of m_x which result in incorrect estimates of the ratio ν_3/ν_1.

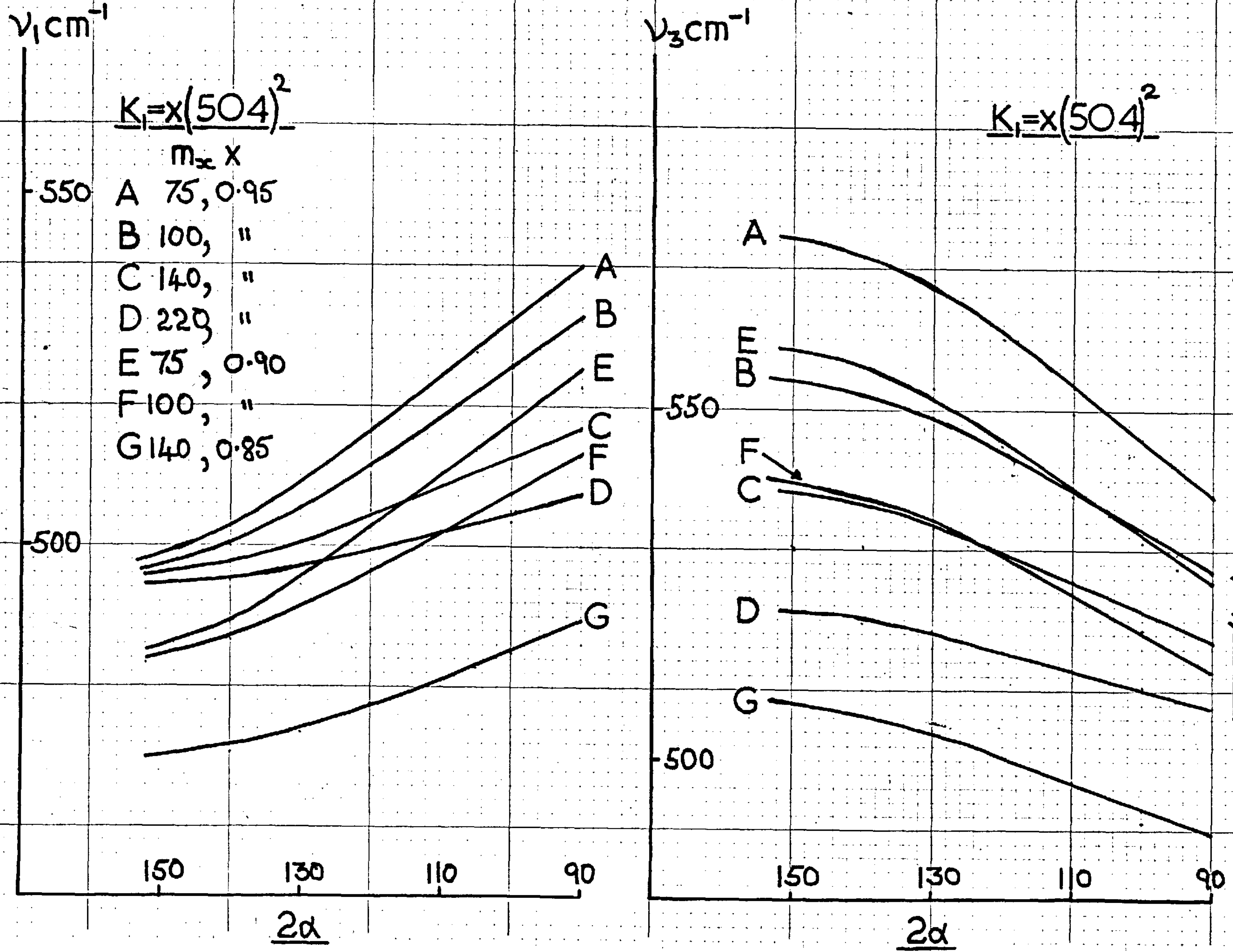
The agreement between the observed data and the values calculated using this approximate XY_2 model, for the $ZnMe_2$ - THF system supports the earlier suggestion that the Zn-O bond is weak and that no considerable interaction occurs between Zn-C and Zn-O vibrations. For $ZnMe_2$.dipy only general agreement is found and the approximation used will be unsuitable for a more strongly bonded system.



Graph A ν_1 & ν_3 Variation with K_1 & 2α, $m_x = 65$.

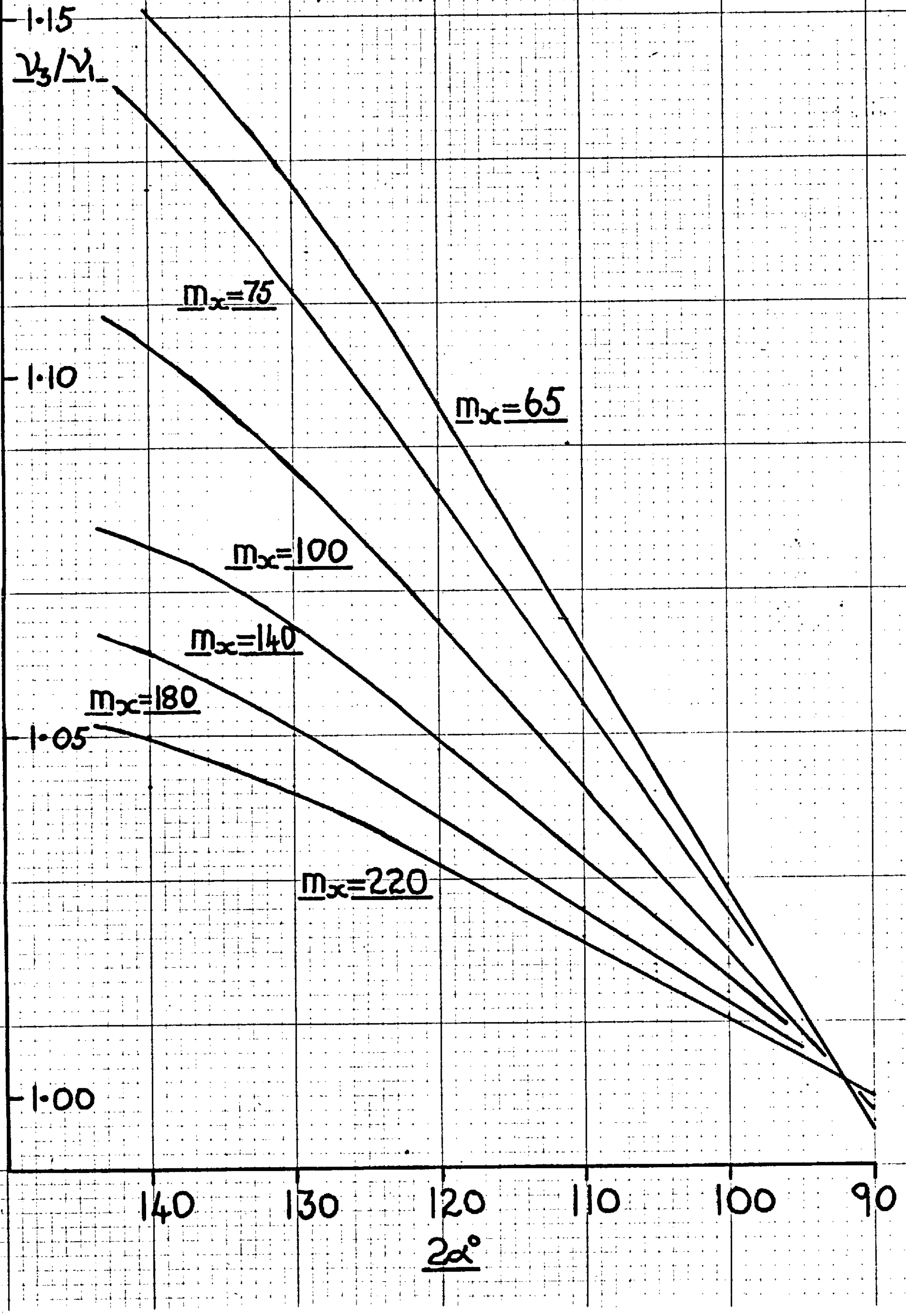


Graph B ν_1 & ν_3, Variation with m_x & 2α, $K_1 = (504)^2$

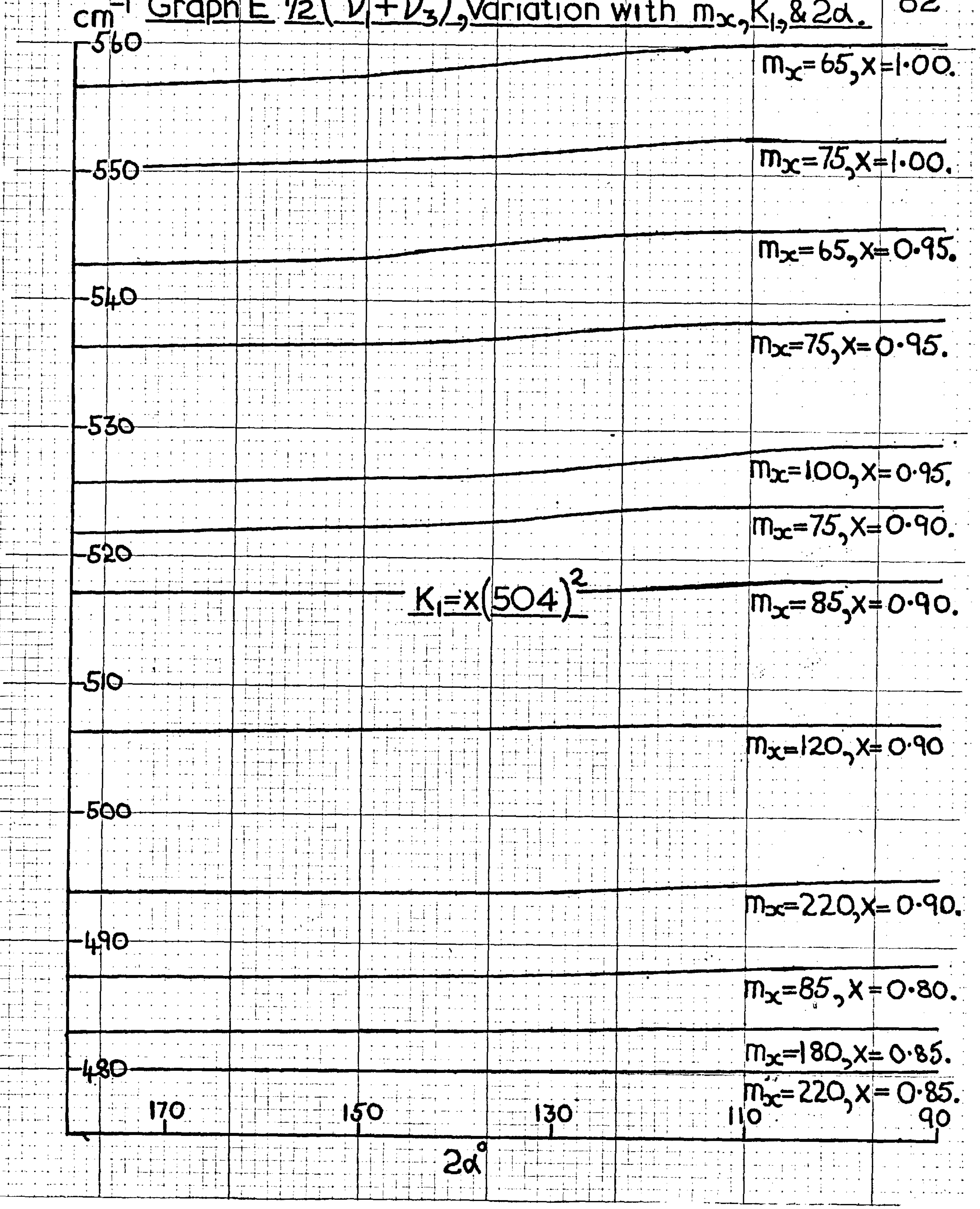


Graph C ν1 & ν3, Variation with mx, K1, & 2α.

Graph D Ratio, ν_3/ν_1, Variation with 2α & m_x.

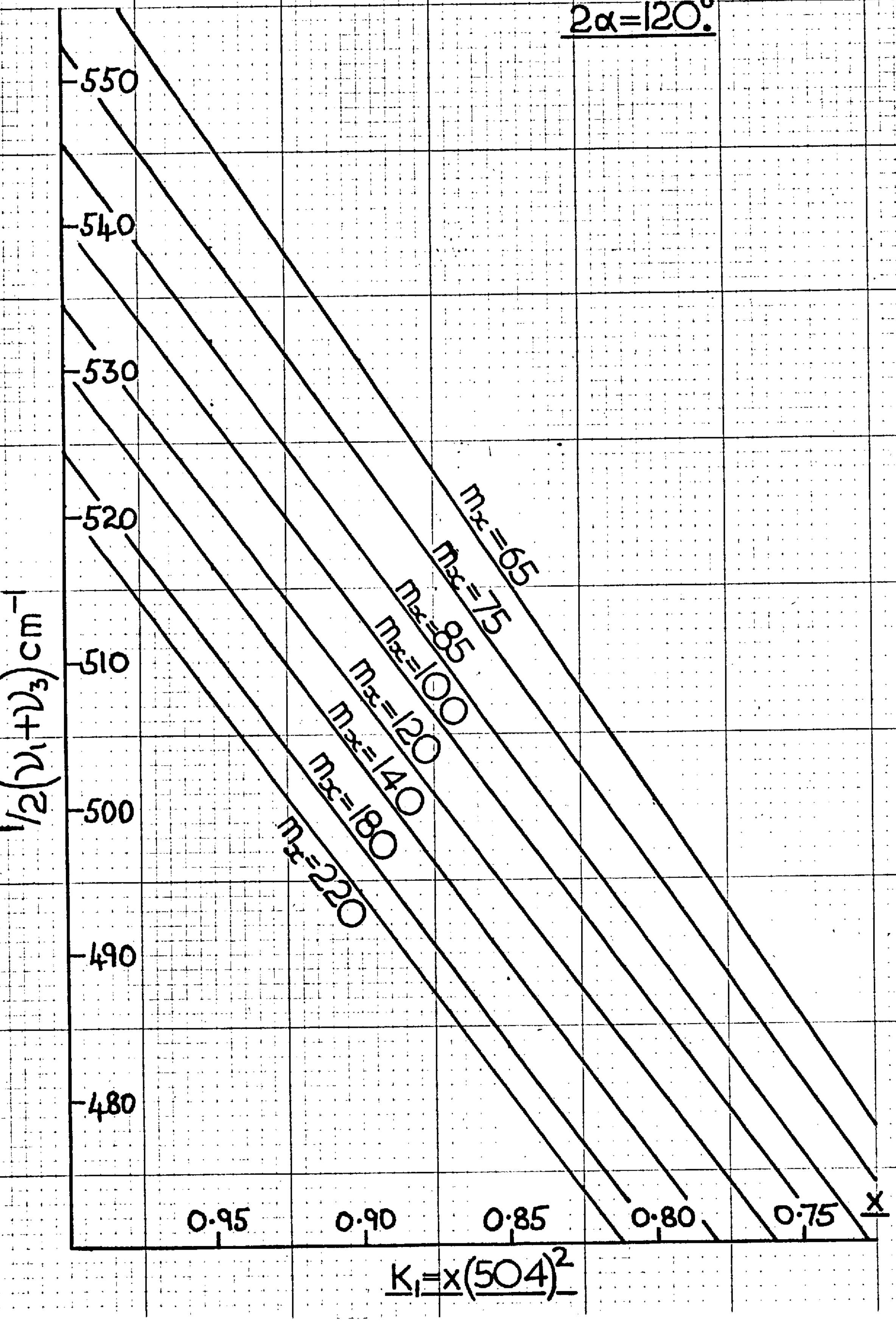


Graph E $\frac{1}{2}(\nu_1+\nu_3)$, Variation with m_x, K_1, & 2α.



Graph F $\frac{1}{2}(\nu_1+\nu_3)$, Variation with m_x & K_1

$2\alpha = 120°$

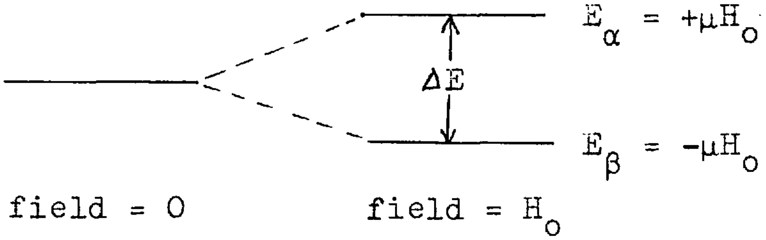


PART II

5. INTRODUCTION

5.1. General Concepts (104) (105)

A nucleus with a spin, $I > 0$, has a magnetic moment μ, and when placed in a magnetic field, H_o, its ground state is split into $(2I + 1)$ nuclear spin energy levels, $E = -\mu H_o, -(I - 1)/I.\mu H_o, -----, +(I - 1)/I.\mu H_o, +\mu H_o$. For nuclei with $I = \frac{1}{2}$, the two spin states are designated by $\alpha(I = +\frac{1}{2})$ and $\beta(I = -\frac{1}{2})$, and for the transition $\alpha \leftarrow \beta$, the frequency ν of the radiation required is given by,



$$\Delta E = h\nu = 2\mu H_o \tag{1}$$

Since the magnetic moment and nuclear angular momentum $(Ih/2\pi)$ act as parallel vectors, the two are combined, to give,

$$\mu = \gamma\,(Ih/2\pi), \tag{2}$$

where γ, the magnetogyric (or gyromagnetic) ratio is a constant for a particular nucleus. Hence, for nuclei with $I = \frac{1}{2}$,

$$\nu = \gamma H_o/2\pi. \tag{3}$$

The external magnetic field H_o, induces electron motion about the nucleus which thus experiences a secondary magnetic field proportional to but opposing the applied field. Thus,

$$H_{nucleus} = H_o(1 - \sigma), \tag{4}$$

where σ, the screening (or shielding) constant varies with the environment of the nucleus. Since the resonance frequency of a bare nucleus cannot normally be determined, relative chemical shifts are measured, common reference compounds being $Si(CH_3)_4$ or $(CH_3)_3COH$ (^1H spectra) and CF_3COOH or CCl_3F (^{19}F spectra). To avoid the dependence on H_o, the chemical shift is usually reported as the dimensionless parameter,

$$\delta = (H_{unk} - H_{ref})/H_{ref}. \times 10^6 \text{ p.p.m.} \tag{5}$$

Many molecules have n.m.r. spectra with fine structure due to interactions between magnetically non-equivalent nuclei. It was proposed (106) that the interaction which is independent of the applied field, is proportional to the product of the nuclear moments. The interaction energy, E_{AX}, between two such nuclei, A and X, is (107)

$$E_{AX} = h\ J_{AX}\ I_A\ I_X, \tag{6}$$

where J, the coupling constant measured in c/sec., is given by,

$$J_{AX} = K_{AX} \gamma_A \gamma_X\ h^2/4\pi^2, \tag{7}$$

where K_{AX} is dependent on the molecular system studied. For a set of n_A nuclei, type A, and n_X nuclei, type X, when $\delta_{AX} \ll J_{AX}$, the A signal has $2\ n_X\ I_X + 1$ components and the X signal $2\ n_A\ I_A + 1$ components. This is a 'first order' spectrum where the relative intensities within each group are given by the corresponding binomial coefficients. When $\delta_{AX} \sim J_{AX}$, more lines appear due to 'second order' splittings and analysis of the spectrum by inspection becomes impossible (108). By convention, the coupling is positive when the anti-parallel nuclear alignment is more stable than the parallel one.

5.2. The Proton Resonance Spectra of Organomercury Compounds

Many heavy metals have isotopes with spin $I = \frac{1}{2}$, and their alkyl and aryl derivatives have ^{1}H n.m.r. spectra which show large spin-spin splittings. Mercury has several isotopes but only one, ^{199}Hg ($I = \frac{1}{2}$, 16.86% abundant), produces large spin-spin splittings in the n.m.r. spectra of organomercury compounds, usually seen as 'satellites' by the side of the main peaks due to species containing the other mercury isotopes. Although not as convenient to study as the equivalent thallium systems, $^{203/205}Tl$ ($I = \frac{1}{2}$, 100% abundant) (109) (110), a large number of mercury compounds have been studied. The chemical shifts of these alkyls and aryls are as expected for the unsubstituted hydrocarbons.

5.3. The Mechanism of Spin Coupling

A successful theory for nuclear spin coupling was first developed by Ramsey (111). In the case of a molecular system undergoing multiple collisions in a magnetic field, the Hamiltonian for the nuclear spin interactions may be written as,

$$H = H_1 + H_2 + H_3. \qquad (8)$$

H_1 This is the nuclear spin-electron orbital term which is the Hamiltonian used in screening constant calculations. The magnitude of this coupling is related to the anisotropy of the screening constant, $\Delta\sigma = (\sigma_{\parallel} - \sigma_{\perp})$ (112). With $^{1}H - {}^{1}H$ coupling, $J^{(1)}$ is usually negligible, but for $^{1}H - {}^{19}F$ and $^{19}F - {}^{19}F$ coupling this mechanism can make a significant 'through space' contribution (112), but as most coupling constant calculations are only approximate, the small value of $J^{(1)}$ is usually ignored.

H_2 This is the nuclear spin - electron spin term which describes the classical dipole-dipole interactions between the nuclear and electron magnetic moments. Although for proton systems, this mechanism is unimportant since it depends on angular dependent atomic orbitals (e.g. p, d, f,), it can make a contribution to coupling between atoms which use these orbitals in bonding, e.g. fluorine-19 and carbon-13. (104).

H_3 This is a non-classical nuclear spin - electron spin interaction term first introduced by Fermi (113) to account for the hyperfine structure in S state atomic spectra. Since the interaction is proportional to the electron density at the nucleus, this 'Fermi contact' mechanism can only operate using electrons in bonding orbitals with some s character and as it is a two electron term, by the chemical bonds. For hydrogen with a 1s valency orbital, spin coupling occurs almost entirely by this mechanism.

The interaction energy, $E_{NN'}$, between two nuclei N and N' is given by (111),

$$\sum_{N \lessgtr N'} E_{NN'} = - \sum_{n \neq 0} (E_n - E_o)^{-1} \langle 0/H/n \rangle \langle n/H/0 \rangle \qquad (9)$$

where H is the Hamiltonian discussed above. The majority of calculations have used the average energy approximation (114) to obtain,

$$E_{NN'} = -\Delta E^{-1} \langle 0/H^2/0 \rangle , \qquad (10)$$

followed by evaluation of the integral over the ground state wave function. There is no unique way of estimating the mean singlet-triplet excitation energy and this is an important error in all coupling constant calculations.

Accurate wave functions are known for the hydrogen molecule and these were used by Ramsey to obtain for HD (111),

$$J_{HD}^{(3)} = 55.8/\Delta E \text{ c/sec.}, \qquad (11)$$

with similar expressions for $J^{(2)}$ and $J^{(1)}$. A value of 1.4 Rydberg for ΔE gave $J_{HD}^{(3)} = 40$ c/sec., $J_{HD}^{(2)} \sim 3$ c/sec. and $J_{HD}^{(1)} \lesssim 0.5$ c/sec. to give in total the observed coupling of 43.5 ± 1 c/sec. For all other systems, the ground state wave function must be approximated by molecular orbital (MO) or valence bond (VB) models.

The molecular orbital method was used by McConnell (115) and Gutowsky and Williams (116) for a general treatment of $^{1}H - ^{1}H$, $^{1}H - ^{19}F$, and $^{19}F - ^{19}F$ coupling constants. The method requires a large number of approximations but the Fermi contact term was shown to predominate. However, predictions that all coupling constants have the same sign with no attenuation with increasing distance are at odds with experiment. Recently, Pople and Santry (117) have shown that MO theory can lead to coupling constants of either sign if proper account is taken of the relative energy levels.

The valence bond approach, developed by Karplus (118)-(122) has proved more useful, particularly for $^{1}H-^{1}H$ interactions. Although $J^{(1)}$ and $J^{(2)}$ have been calculated by this approach (118), considerable effort is necessary, and attention has centred on the Fermi contact term. If the ground state wave function of the molecular system, $X \sim Y$, is represented by,

$$\psi_o = \sum_j c_j \psi_j, \qquad (12)$$

where C_j are the coefficients of the canonical structures Ψ_j, then the Fermi contact interaction between X and Y is given by,

$$J_{XY}^{(3)} = A(\Delta E^{-1})\,\gamma_X\gamma_Y\,\phi^2_X(0)\,\phi^2_Y(0)\,F, \tag{13}$$

where A is a numerical constant, $\phi^2_X(0)\left[\phi^2_Y(0)\right]$ is the density of the valency electron at the nucleus $X\left[Y\right]$ and F is a summation depending on the number and coefficients of the canonical forms used.

For protons, $\phi^2_H(0) = \Psi^2_{Is}(0)$, and the contact term becomes,

$$J_{HH}^{(3)} = \frac{1.395 \times 10^3 . F}{\Delta E(ev)}. \tag{14}$$

Using this equation, the VB method has been applied to H-C-H (119) (120) and H-C-C-H (121) (122) with some success but in certain cases the sign of the coupling constant predicted has been incorrect. However, most calculations support a 'through bond' Fermi contact mechanism for ^1H - ^1H coupling.

The few VB calculations for ^1H - ^{19}F and ^{19}F - ^{19}F systems (121) (123) have used the ^1H - ^1H formulae for the same structure with the assumptions that F is unchanged by the replacement of ^1H by ^{19}F and that $\phi^2_F(0) \sim 2\text{-}3\,\phi^2_H(0)$.

However, the wide variation of ^{1}H - ^{19}F and ^{19}F - ^{19}F coupling constants with molecular structure has led to the proposal that 'through space' contributions may be more important in these systems (124) (125) (165).

Measurement of directly bonded ^{13}C - ^{1}H coupling constants shows that,

$$J_{CH} = J_o\, a^2_c \tag{15}$$

where a^2_c is the s-character of the carbon hybrid orbital described by $\psi_c = a_c \phi_{2s} + b_c \phi_{2p}$ (126) (127) and that for substituted methanes an additive relation exists (128),

$$J_{CH}(CHXYZ) = J_{CH}(CH_3X) + J_{CH}(CH_3Y) + J_{CH}(CH_3Z) - 2\, J_{CH}(CH_4). \tag{16}$$

Both of these equations were later derived using a VB approximation (129) and support a Fermi contact mechanism. Coupling through two bonds, ^{13}C-C-H, is also linear with a^2_c (130) but ^{13}C-C-C-H constants present anomalies which suggest a 'through space' term may be important (131) (132) and that the use of $J_{^{13}C-H}$ to obtain a^2_c values (133) may be unjustified (134).

Although a large number of heavy metal-proton coupling constants have been reported (135), few theoretical studies have been published. The simple additivity rule (eqn. 16) does not describe $^{29}Si - ^{1}H$ coupling constant variations for substituted silanes (129) (136) and the use of J_{Sn-H} values to assign s-character values to the Sn-Me bond in various Me_nSnCl_{4-n} systems would appear to have been premature (137) (138). Similar deviations from the Malinowski additivity rule have been noted for $^{13}C - ^{19}F$, $^{29}Si - ^{1}H$ (139), $^{117/119}Sn - H$, $^{117/119}Sn - C - H$ (140) and $^{13}C - ^{1}H$ (141) coupling constants and an empirical equation has been devised,

$$J_{CH}(CHXYZ) = J_{CH}(CH_3X) + J_{CH}(CH_3Y) + J_{CH}(CH_3Z)$$

$$- 2\,J_{CH}(CH_4) + g_{XY} + g_{XZ} + g_{YZ}, \qquad (17)$$

where g_{XY} is an empirical 'interaction parameter' constant for X and Y and independent of Z. No derivation of this equation has yet been published.

The X - H coupling constants for several ethyl derivatives, C_2H_5X, have been reported but, unlike the equivalent H - H coupling constants, $J_{M-C-C-H} > J_{M-C-H}$, with opposite signs. This was first attributed to 'through space' (142), or π-electron system (143) terms, but Klose (144) showed, using the VB equations derived by Karplus for

H - H coupling, that both the magnitudes and signs of the M - H coupling constants could be predicted by the Fermi contact mechanism with an appropriate choice of the exchange integrals used in evaluating F. Several empirical correlations of coupling constants with atomic number have been suggested (145) (146) (147) which appear to provide support for the Fermi contact mechanism.

6. RESULTS AND DISCUSSION.

6.1. The Variation of the ^{199}Hg - H Coupling Constants in the Series, R_2Hg, RHgOAc.

Mercury (199) - proton coupling constants for a range of R_2Hg and RHgOAc species are given in Table 29. The uniform increase in the magnitude of the coupling constants is a general feature and, on the basis of the Fermi contact interaction, this can be rationalised as due to changes at the mercury atom.

The general expression (eqn. (13), page 91) for the Fermi contact term, in the case of ^{199}Hg - H coupling becomes,

$$J^{(3)}_{HgH} = A(\Delta E^{-1})\, \gamma_{Hg} \gamma_{H}\, \phi^2_{Hg}(0)\, \phi^2_{H}(0)\ F. \qquad (18)$$

Using 'hydrogen like' wave functions,

$$\phi^2_{Hg}(0) = a^2_{Hg.Hg}\phi^2_{6s}(0) = a^2_{Hg}(Z_{eff})^3 \cdot {}_{H}\phi^2_{6s}(0) \qquad (19)$$

where a^2_{Hg} is the s-character of the mercury bonding hybrid orbital, (0.5 and 1.0 for R_2Hg and RHg^+ respectively) and Z_{eff}, the effective nuclear charge, is calculated from $Z_{eff} = (Z_oZ)^{\frac{1}{2}}$ where for mercury, $Z = 80$, is the real nuclear charge and Z_o is the Slater screened nuclear charge (148).

Table 29 The Variation of ^{199}Hg - ^{1}H Coupling Constants (c/sec.) in the Series, R_2Hg, RHgOAc.

R	H position	$J(R_2Hg)$	J(RHgOAc)	J_{RHgOAc}/J_{R_2Hg}
Methyl	CH_3	101.4 (1) a	212.4 b	2.1
Ethyl	$-CH_2$	87.6 c	213.5 d	2.5
	$-CH_3$	115.2	296.9	
Phenyl	ortho	102.5 ± 1.3	202.5 ± 1.1	2.0
	meta	-	54 ± 2	
	para	-	16.2	
Mesityl	ortho-CH_3	9.4	21.4	2.3
	para-CH_3	-	11.7	
Vinyl	trans	295.5 (1) e	658 (3) g	2.2
	cis	159.6	331 } ± 2	
	gem	128.5	299	
neo--Pentyl	$-CH_2$	94.0 f	193.5 (2) f	2.2
	$-CH_3$	5.5	13.2	

a K.A. McLauchlan, D.H. Whiffen (150), b P.M. Ridout (151), c P.T. Narasimhan, M.T. Rogers (142), d R.K. Stapledon (152), e D.W. Moore, J.A. Happe (153), f G. Singh (154), g P.R. Wells, W. Kitching, R.F. Henzell (155).

Conditions Data are for $CHCl_3(CDCl_3)$ solutions except (1) neat liquid (2) dioxan solution (3) RHgCl in $CDCl_3$.

For Hg^{o}, $Z_o = 4.35$ and Hg^{+}, $Z_o = 4.70$. On this basis, assuming ΔE^{-1} and F remain constant, then,

$$\frac{J_{RHg^+}}{J_{R_2Hg}} = \frac{a^2_{RHg^+}\,(Z_{eff})^3_{Hg^+}}{a^2_{R_2Hg}\,(Z_{eff})^3_{Hg^o}} = 2.25. \tag{20}$$

The agreement between the theoretical and experimental values (Table 29) is good and seems to indicate that the predominant contribution to all the spin coupling constants is due to the Fermi contact term, particularly since the dipole-dipole term decreases with increasing s-character, becoming zero for pure s orbitals. However, this agreement must not be taken too far as, for example, the bonding orbital in RHgOAc will in no way approximate to the 6s orbital required for RHg^{+}, and also, possible changes in the exchange integrals contributing to F are neglected.

In a semi-empirical approach (149), Hatton, Schneider, and Siebrand wrote the Fermi contact contribution in terms of the optical hyperfine structure (hfs) constants, $\alpha_N \propto \phi^2_N(0)$. In the case of ^{199}Hg - H coupling,

$$J^{(3)}_{HgH} = h/2.\Delta E^{-1}.a^2_{Hg}.\eta^2\,\alpha_{Hg}\,\alpha_{H}, \tag{21}$$

where η is the MO 'bond order' between the nuclei Hg and H and a^2_{Hg} is the fractional s-character of the mercury hybrid orbital. Using, $\alpha_{Hg}(6s6p) = 1.5 \times 10^{10}$ c/sec. and

$\alpha_{Hg^+}(6s) = 4.05 \times 10^{10}$ c/sec., $J_{RHg^+}/J_{R_2Hg} = 5.4$. This is a more probable ratio for the change R_2Hg to RHg^+ but again indicates that the Fermi contact interaction is predominant for mercury (199) - proton coupling.

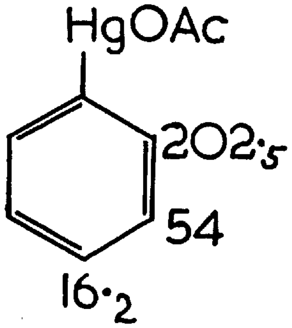
6.2. Arylmercuric Acetates

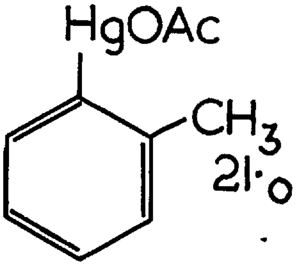
Mercury (199) - proton coupling constants for several arylmercuric acetates are given in Table 30. The mercury (199) - proton coupling constants decrease uniformly for the ring protons in the phenyl system but alternate for the methyl protons,of the tolyl derivatives. This behaviour is qualitatively similar to the thallium (205) - proton parameters in the iso-structural RTl^{2+} systems (110) but these are 5-8 times larger. If the Fermi contact term predominates then, assuming ΔE and F are the same, $J_{Tl^{2+}}/J_{Hg^+} = 4.4$, which is of the same order as the observed ratios but ^{199}Hg - H coupling constants show greater relative attenuation with the increase in the number of intervening bonds. This implies that F, which depends on a number of exchange integrals may not remain constant even for these very similar systems.

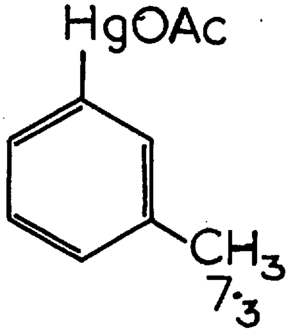
Further comparison can be made with the equivalent proton-proton parameters. In substituted benzenes, the ortho-, meta-, and para- ^1H - ^1H coupling constants decrease in the order 6 - 9, 1 - 3, and 0 - 1 c/sec. respectively

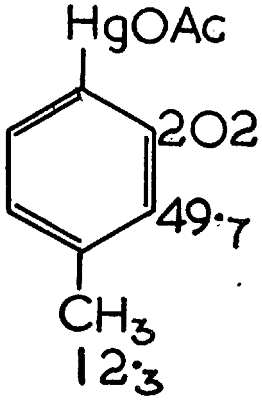
TABLE 30

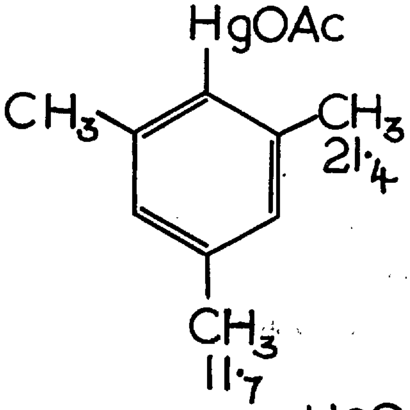
Mercury(199)–Proton Coupling Constants (c/sec.) for ArHgOAc Species in $CHCl_3$ ($CDCl_3$).

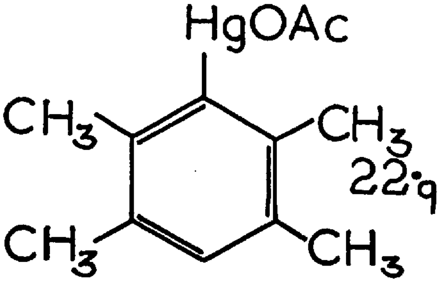


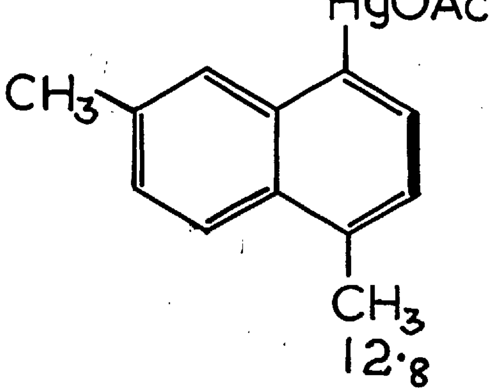












(156) (157), and similar values are obtained if the ^{199}Hg - H coupling constants for PhHgOAc are divided by $\sim$20. In mesitylene the ortho- and para- H - CH_3 couplings are 0.89 and 0.45 c/sec. respectively (158) which yields the ratio, $J_{HgH}/J_{HH} \sim 25$. Following Schneider and Buckingham (159), both the Fermi contact ($J^{(3)}$) and dipole-dipole ($J^{(2)}$) contributions to ^{199}Hg - ^{1}H coupling constants are given by,

$$J_{HgH} \propto \left(\frac{Z_{eff}}{n}\right)^3_{Hg} \left(\frac{Z_{eff}}{n}\right)^3_{H} \frac{\gamma_{Hg}\gamma_{H}}{\gamma^2_{H}} \qquad (22)$$

where n is the principal quantum number of the atom valency orbital (6s for Hg, 1s for H) and taking $J_{HH} \propto 1$. By this approach, $J_{HgH}/J_{HH} \sim 6$ which indicates that the increased mercury-proton coupling constants are in part due to the greater effective nuclear charge of mercury compared with hydrogen.

In unsaturated systems, the possibility exists of the nuclear spin interactions being transmitted by either the localised electron pairs of the σ-bond framework or the delocalised π-electron system. Hence J_{XY} may be written,

$$J_{XY} = J_{XY}(\sigma) + J_{XY}(\pi). \qquad (23)$$

McConnell (160) showed that for aromatic hydrocarbons,

$$J_{HH'}\ (\pi) = -AQ^2\Lambda_{NN'}\ ,$$

where A is a numerical constant, Q is the hyperfine interaction constant for the aromatic free radical and $\Lambda_{NN'}$ is an expression which describes the interaction between the π- electron spins on carbon atoms N and N' directly bonded to H and H' respectively. The calculated π-system contribution to the ring proton coupling constants, <0.5 c/sec., is small but for mesitylene, the calculated π-electron H - CH_3 coupling constants are in near agreement with the observed values of $J_{HH(CH_3)}$.

Karplus (161) obtained a similar expression for long range H - H coupling in olefines and acetylenes. Unlike alkane systems where $J(H - C - C \sim H') \sim 10J(CH_3 - C - C \sim H')$, in the unsaturated molecules, there is little attenuation of $J_{HH'}$ with the number of intervening bonds, i.e. $J(H - C = C \sim H') \sim J(CH_3 - C = C \sim H')$. Since $Q(H - \dot{C}) \simeq Q(CH_3 - \dot{C})$ but with opposite sign, Hoffman and Gronowitz (162) suggested that methyl substitution could be used to determine the magnitude of the π-electron contribution to the transmission of long range spin coupling as this would alter the sign but not the magnitude of $J_{HH}\ (\pi)$.

The application of this criterion to the phenylmercuric acetate system is shown in Table 31. The results suggest that like the corresponding H - H and Tl - H spin

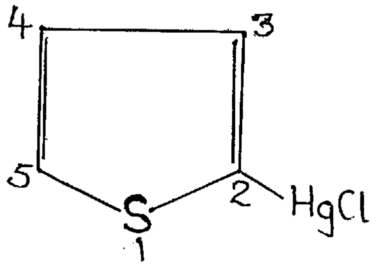
Table 31 The π - and σ - Contributions to ^{199}Hg - ^{1}H Coupling in Phenylmercuric Acetate.

H or CH_3 position	ortho	meta	para
J_{HgH}	202.5	54	16.2
J_{HgCH_3}	21.0	7.3	12.3
$\frac{J_{HgH}(\pi)}{J_{HgH}(total)}$ %	10	13.5	76
c.f. $\frac{J_{TlH}(\pi)}{J_{TlH}(total)}$ % *	10	14	50

* for $PhTl^{2+}$ (110).

interactions, the mercury coupling to the ortho- and meta-ring protons is transmitted mainly by the σ-electrons of the benzene ring. In contrast, transmission via the π-electrons is important for the para-position, more so than for the RTl^{2+} system. Similarly, although coupling through one more bond is involved, $J_{Hg-H}(p-CH_3) > J_{Hg-H}(m-CH_3)$ consistent with VB and MO calculations of π-electron contributions to H - H coupling in the benzene ring. For mesitylene (158), $J_{H-oCH_3} = 0.89$ c/sec., $J_{H-pCH_3} = 0.45$ c/sec. while $J_{CH_3-mCH_3} < 0.35$ c/sec. gives a calculated value of < 0.29 c/sec. for J_{H-mCH_3} in these systems. The σ-contribution to J_{H-H}(meta) is unusually large for a coupling through four bonds (156). Similarly, $J_{Hg-mH}(\sigma)$, ~ 47 c/sec., is greater than any Hg - γH coupling constant in alkylmercury derivatives. Although very conformation dependent, the largest value for $J_{Hg-\gamma H}$ is 22 c/sec. reported for sec-BuHgX compounds (163).

6.3. 2-Thienylmercuric Chloride-Dioxan.



The spectrum was assigned with the aid of the general H - H coupling constants (157) which are, $J_{23} = 4.9-5.8$ c/sec., $J_{24} = 1.2-1.7$ c/sec., $J_{34} = 3.4-4.3$ c/sec., and $J_{25} = 3.2-3.7$ c/sec.

Using the fine structure of the mercury (199) satellite peaks, the Hg - H coupling constants were found to be, $J_{Hg-3H} = 117.3$, $J_{Hg-4H} = 25.2$, and $J_{Hg-5H} = 69.2$ c/sec. As in the PhHgOAc system, the Hg - H coupling constants are approximately 20 times the corresponding H - H values, but greater relative attenuation with increasing number of bonds is found compared with Tl - H coupling constants in the $(2-C_4H_3S)_2Tl^+$ system. A detailed study of 3-furylmercuric chloride has been reported (164). Here the coupling constants are $J_{Hg-2H} = 40.4$, $J_{Hg-4H} = 74.9$, $J_{Hg-5H} = 27.9$ c/sec., which are also 20 times greater than the H - H couplings in substituted furans (157). Also the ratio of the 2,3 Hg - H coupling constants, $S-J_{Hg-H}/O-J_{Hg-H} = 2.9$, is similar to the ratio of the corresponding H - H coupling constants.

6.4. Discussion

The resemblance found between the variation patterns of Hg - H and H - H coupling constants, in particular the agreement observed in the relative behaviour of the aryl systems studied here, is a strong indication that similar spin interaction mechanisms operate in both cases, i.e. Hg - H coupling constants are dominated by the Fermi contact term. This is also supported by the agreement between the theoretical and experimental values of J_{RHgOAc}/J_{R_2Hg}.

Similar arguments have been used to show that Tl - H coupling occurs principally by the Fermi contact mechanism (110). If J_{Hg-H} values for RHgOAc compounds are divided by ~20, generally values are obtained similar to the equivalent H - H parameters in the unsubstituted hydrocarbons. Exceptions are the large values of J_{Hg-H} in C_2H_5HgOAc and $J_{Hg-gemH}$ in ViHgOAc, and an explanation like that proposed for the equivalent anomalous Tl - H coupling constants, may be also invoked in this case.

A feature of Hg - H and Tl - H coupling constants which is inconsistent with the Fermi contact mechanism, is that they increase when the compounds are studied dissolved in co-ordinating media. Examples of this effect are given in Tables 32-35.

Table 32 J_{Tl-H} values (c/sec.) for $(CH_3)_3Tl$ in various Solvents (110)

	CH_2Cl_2	Me_2O	Me_3N
$J_{Tl-H(CH_3)}$	251	270	270

Table 33 J_{Hg-H} values (c/sec.) for several CH_3HgX Compounds

	X =	OAc	Cl	Br	CN	SCN
$CHCl_3$	(152)	212.8	204.4	198.1	192.0	189.4
py	(149)	220.8	215.2	212.0	178.0	208.0

Table 34 J_{Tl-H} values^a (c/sec.) for $(CH_3)_2TlClO_4$ in various Solvents

	CH_3CN	D_2O	MeOH	py	Me_2CO	en	DMSO
$J_{Tl-H(CH_3)}$	412	413	414	416	420	427	442

Table 35 J_{Tl-H} values^a (c/sec.) for $(C_2H_5)_2TlClO_4$ in various Solvents

	CH_3CN	Me_2CO	py	MeOH	D_2O	DMSO	en
$J_{Tl-H(CH_2)}$	344	353	364	371	378	384	390
$J_{Tl-H(CH_3)}$	624	631	640	644	634	633	659

a (166) see also (167)

Increasing co-ordination, with changes from 'sp' to 'dsp' hybridisation schemes, should decrease the degree of s-character in the metal hybrid bonding orbital and with the Fermi contact mechanism, a fall in the M - H coupling constant value should occur. Alternatively, greater donation of electron density to the metal atom will lower its effective nuclear charge thus a decrease in both $J^{(2)}_{M-H}$ and $J^{(3)}_{M-H}$ should be noticed. Both of these predictions are inconsistent with the experimental trends.

In this work, the solvent used was chloroform and thus the mercury atom will be 2 co-ordinate with sp hybrids in R_2Hg species and with $>$ 50% s-character in the C-Hg bond opposite - OAc in RHgOAc compounds. Several complexes, RHgXL, have been reported but they are ionised in methanol and acetone solutions with a retention of 2 co-ordination in the RHgL $^+$ ion (168). Thus, even in co-ordinating solvents, the Hg-C bonds in RHgX compounds will probably have $>$ 50% s-character.

The co-ordination chemistry of thallium is less well known. Recently several $(Me_2TlL)ClO_4$ complexes (L is mono- or bidentate) have been prepared (166). No molecular weight solution measurements of the complexes have been reported and thus the degree of co-ordination of the thallium atom is uncertain. Tl - H coupling constants were given for systems where a linear C - Tl - C skeleton was indicated from infra-red and Raman results but this may be due to either sp or sp^3d hybridisation.

Therefore, while the general resemblances of the trends in Tl - H, and Hg - H coupling constants as compared with the equivalent H - H parameters, suggest a predominant Fermi contact term, the method of its operation with the more complex mercury and thallium atoms and the possible greater relative contributions of spin-orbital ($J^{(1)}$) and dipole-dipole ($J^{(2)}$) terms in these heavy-metal systems will remain subjects of controversy and investigation for some time to come.

7. EXPERIMENTAL

7.1. General

Analyses were by the Microanalytical Laboratory, Imperial College, and melting points were obtained using a Gallenkamp apparatus. Proton magnetic resonance spectra were measured on a Varian V4311 spectrometer at 56.45 Mc/sec., using concentrated (20-30%) or saturated solutions in chloroform (alcohol free) or deuterochloroform where appropriate. The main peaks were used for calibration and coupling constants are accurate to $\leqslant \pm$ 1.0 c/sec., but where a larger error is involved, it is quoted.

7.2. Preparations.

Arylmercuric Acetates were prepared by two methods.

(a) The appropriate hydrocarbon was mercurated using mercuric acetate (169). For example, mercuric acetate (8 gm) was dissolved in a mixture of mesitylene (32 ml) and glacial acetic acid (225 ml) containing 60% perchloric acid (4 ml). After two hours, the reaction was quenched with water (100 ml) and mesitylmercuric bromide precipitated by addition of a solution of potassium bromide (8 gm) in water (100 ml). The product was recrystallised from methanol. The acetate was obtained by shaking mesitylmercuric bromide (2.4 gm) with silver acetate (1 gm) in ethanol (50 ml) for

4 hours. The mixture was filtered and the residue obtained by evaporating the filtrate to dryness, was recrystallised from ethanol-water. The product was dried in vacuo over calcium chloride. Durylmercuric acetate was also prepared by this method.

(b) The appropriate arylboronic acid was reacted with mercuric acetate (170). For example, ortho-tolylboronic acid (3.3 gm) dissolved in methanol (100 ml), was mixed with mercuric acetate (ca. 8 gm) in water (50 ml), containing a trace of acetic acid. After boiling for 5 minutes, the mixture was cooled in ice. The precipitate was recrystallised from methanol-water and the product dried in vacuo over calcium chloride. Also prepared by this method were meta- and para-tolylmercuric acetates and a new compound, 4,7-dimethyl-α-naphthylmercuric acetate, yellow crystals from chloroform, m.pt. 168-170°C (Found, C, 40.5; H, 3.35; O, 7.6%. $C_{14}H_{14}HgO_2$ requires C, 40.5; H, 3.4; O, 7.7%).

Phenylmercuric acetate was the B.D.H. product.

Diarylmercury compounds were prepared from the arylmercuric acetate or bromide (171). For example, phenylmercuric acetate (10.1 gm), hydrazine hydrate (1.5 gm) and sodium carbonate (1.6 gm) were refluxed in ethanol (150 ml) for 6 hours. After cooling the reaction mixture to 0°C, the solid material was filtered off, and further yield obtained by evaporating the filtrate to small volume. The crude product was extracted with chloroform and the solutions obtained evaporated to dryness. The residue was recrystallised from benzene or chloroform. Mesitylmercuric bromide was used to prepare mercury dimesityl by a similar procedure.

2-Thienylmercuric Chloride (172)

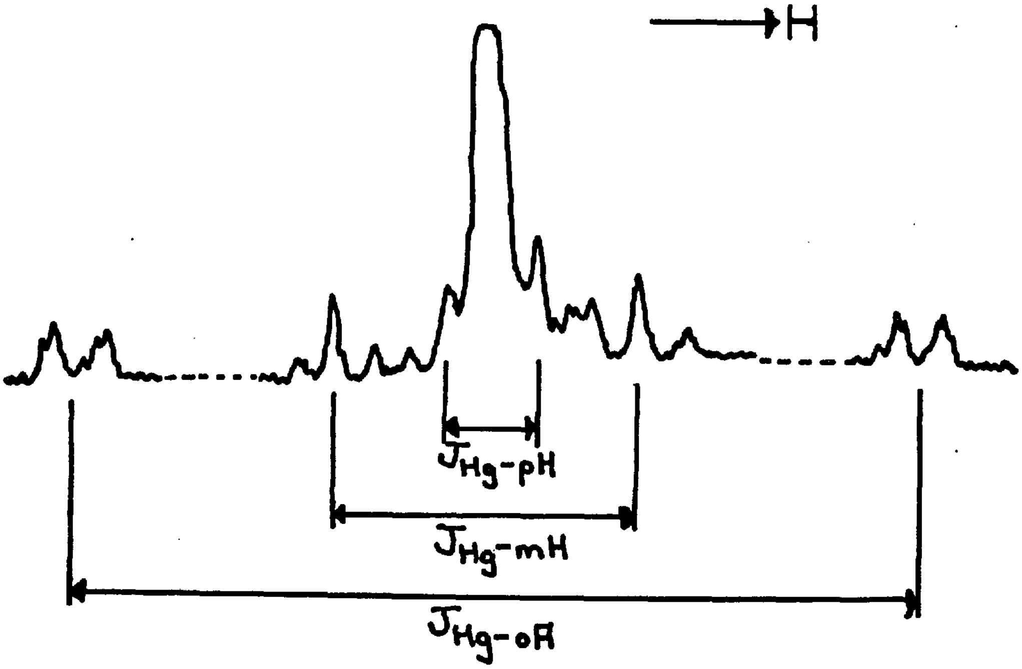
Mercuric chloride (13.6 gm) and sodium acetate (7.8 gm) were dissolved in boiling water (100 ml). The hot solution was added to thiophen (20 ml) in ethanol (100 ml) and on cooling, white plates were precipitated. These were filtered off, washed with alcohol and air-dried.

All attempts to prepare the corresponding acetate derivative by the methods outlined above, produced an infusible material which was insoluble in any common organic solvent. This was identified as 2,5-bis(acetoxymercuri)-thiophen (173).

The ^1H n.m.r. spectrum was obtained for a saturated solution of the chloride in dioxan.

FIG II $(C_6H_5)HgOAc-CDCl_3$

^1H n.m.r. Spectrum



'OAc' line is at higher field.

8. SUPPLEMENT

8.1. Preamble

Since the preparation of the Grignard reagent from bromopentafluorobenzene (174), many perfluorophenyl derivatives have been obtained. Several fluorine n.m.r. studies of these compounds have been reported (175). The chemical shifts vary considerably with the sole substituent including an ortho effect, where the difference, $\delta(\text{oF}) - \delta(\text{mF}, \text{pF})$, can be >30 p.p.m. for metal derivatives. Using the C_6F_5 group, (termed Ph_f), several four and five co-ordinate organothallium compounds have been prepared (176) (177) q.v. Although no clear picture of heavy metal-fluorine spin coupling has yet emerged, the availability of molecular weight and conductivity data for solutions of these compounds prompted a study of the ^{19}F n.m.r. spectra of these systems.

8.2. Results and Discussion

Spectra obtained were first order and were assigned by the fine structure and relative intensities of the bands. Chemical shift and thallium-fluorine coupling constant values are given in Table 36, with the relative signs of the coupling constants reported in Table 37. Values for $(C_6F_5)_2TlBr$ have been published (178) but no solvent was

Table 36

Chemical Shifts (p.p.m.) and Thallium-Fluorine Coupling Constants (c/sec.) for various Bis(pentafluorophenyl)thallium Systems.

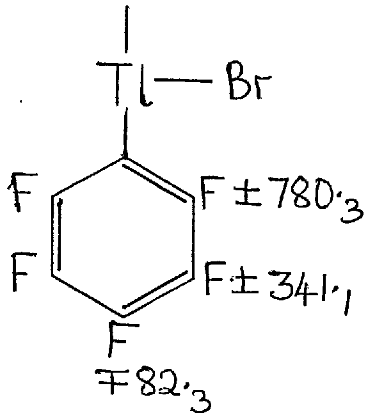
Compound and Solvent	δ p.p.m.*			J_{Tl-F} c/sec.		
	ortho	meta	para	ortho	meta	para
$(C_6F_5)_2TlBr$ /CH_3COCH_3	43.43	84.22	76.25	780.3	341.1	82.3
$(C_6F_5)_2TlBr$ /MeOH	42.51	84.31	76.79	802.2	340.4	82.4
$(C_6F_5)_2TlBr$ /py	40.70	81.31	74.08	768.3	341.2	80.0
$(C_6F_5)_2Tl$o:phenBr /CH_3COCH_3	43.25	83.26 ±0.06	76.88	876.2	386.1 ±7.3	87.1
$(C_6F_5)_2Tl$o:phenBr /C_6H_6	42.63	81.21	74.78	884.8	372.9	86.3

Compound and Solvent	δ p.p.m.*			J_{Tl-F} c/sec.		
	ortho	meta	para	ortho	meta	para
$Ph_4P\ (C_6F_5)_2TlBr_2$ /CH_3COCH_3	41.16	83.30	76.87	640.1	256.8	72.4
$Ph_{f2}TlNO_3$ /CH_3COCH_3	44.87	82.9 ±0.1	74.1 ±0.1	1009.3 ±5.6	428.8 ±15.1	92.9 ±13.6
$Ph_{f2}TlNO_3$ /MeOH	46.65	83.28	74.44	1031.1	446.5	96.2
$Ph_{f2}Tl$o-phen NO_3 /CH_3COCH_3	43.17	82.83	75.44	991.8	431.5	93.8
$Ph_{f2}Tl$o-phen NO_3 /MeOH	44.00	83.33	75.04	959.5	427.0	94.7

*Chemical Shift, δ p.p.m. upfield from CF_3COOH, external reference.

Table 37

Relative Signs of Tl - F Coupling Constants for $(C_6F_5)_2TlBr/CH_3COCH_3$.



apparently mentioned. All ortho-J_{FF} values were ca. 20 c/sec., in accordance with reported figures (179)-(181).

Like the analogous Tl - H parameters (110), the thallium - fluorine coupling constants decrease uniformly, ortho > meta > para. The same pattern is followed by ^1H - ^{19}F constants where $J_{oHF} \sim$ 8-10 c/sec., $J_{mHF} \sim$ 6-8 c/sec., and $J_{pHF} \sim$ 2-3 c/sec. (179)-(181), but the decrease is proportionately more pronounced in the thallium - fluorine case. The similarity of the two systems is further emphasised by the relative signs of the coupling constants. With both Tl - F and H - F systems, the ortho and meta coupling constants are both of opposite sign to the para coupling constant (180).

Thallium-fluorine coupling constants vary considerably in the range of compounds studied here. Small but significant differences in chemical shifts and coupling constants for pyridine, acetone, and methanol solutions of $(C_6F_5)_2TlBr$ indicate some interaction with the solvent occurs. As the solutions contained monomers and were non-conducting, and a crystalline $(C_6F_5)_2py_2TlBr$ complex had been isolated, Deacon postulated a five co-ordinate trigonal bipyramidal form, $(C_6F_5)_2S_2TlBr$ (S = Me_2CO, MeOH, py) with a linear C - Tl - C arrangement (176).

Similar small but significant variations for methanol and acetone solutions of $(C_6F_5)_2TlNO_3$ also occur. Dilute methanol solutions are conducting but this decreases with rise in concentration. Acetone solutions are non-conducting and contain monomers. However, the infrared spectrum of the solid nitrate indicates that the compound is ionic or that the NO_3^- group is only weakly co-ordinated to the thallium. Thus in concentrated solutions, an ion-pair form, $(C_6F_5)_2S_3Tl\ ^+NO_3^-$, or $(C_6F_5)_2S_2TlNO_3$ with a nearly ionic $Tl-ONO_2$ bond, may be equally possible.

Thallium-fluorine coupling constants for the anion,

$\left[(C_6F_5)_2TlBr_2\right]^-$, are much less than those for the neutral species, $(C_6F_5)_2TlBr$, both dissolved in acetone. In the solid state, the complex is four co-ordinate but assuming a Fermi contact term predominated, a similar solution species would not afford such low J_{TlF} values. Thus a solvated five co-ordinate species, $\left[(C_6F_5)_2STlBr_2\right]^-$ is postulated for the solution form.

Following the principles outlined above (page 95), if no changes in the degree of co-ordination occur, then coupling constants will vary only with $(Z_{eff})^3$, where $Z_{eff} = (ZZ_o)^{\frac{1}{2}}$. With thallium, Z = 81, and Z_o = 4.65, 5.00, and 5.35 for Tl^-, Tl^o, and Tl^+ respectively (148). If the overall charges on the complexes, $\left[(C_6F_5)_2TlX_2S\right]^-$, $\left[(C_6F_5)_2TlXS_2\right]^o$, and $\left[(C_6F_5)_2TlS_3\right]^+$, are taken to reside mainly on the central thallium atoms, the coupling constants will be in the ratios, 1.00:1.11:1.23. The average experimental ratios for the series, $\left[Ph_4P\right]\left[(C_6F_5)_5TlBr_2\right]$, $(C_6F_5)_2TlBr$, and $(C_6F_5)_2TlNO_3$ in acetone solutions, are 1.00:1.23:1.51. Although agreement between the observed and predicted trends supports an ionic nitrate species and a five co-ordinate form of the anion in solution, no information is gained on the mechanism of thallium-fluorine spin coupling as both $J^{(2)}$ and $J^{(3)}$ are proportional to $(Z_{eff})^3$ (159).

Thallium-fluorine coupling constants for

$(C_6F_5)_2$o-phenTlBr in acetone and benzene solutions are similar. Monomers are present in both solvents, and the same undissociated 5 co-ordinate species is considered to occur in both systems (176). The J_{TlF} values are 10% greater than those for $(C_6F_5)_2$TlBr in acetone. Increased coupling constants when a stronger donor is used as a ligand, have been noted previously (page 105), but, as in o-phen complexes $\widehat{NMN}$ is usually 90° or less, hybridisation changes may also be important.

With the nitrate system, when the ortho-phenanthroline complex is studied, a decreasein thallium-fluorine coupling constants is observed, the effect being larger for methanol solutions. Molecular weight and conductivity data for the solutions are similar to those obtained for $(C_6F_5)_2TlNO_3$. However, the infrared spectrum of solid $(C_6F_5)_2$o-phen $TlNO_3$ indicates definite co-ordination of the nitrate group occurs (176). Thus, the expected coupling constant increase for the ortho-phenanthroline complex may be countered by a decreased positive charge on the thallium due to the formation of a more covalent Tl - ONO_2 bond. This explanation must remain speculative until more is known of thallium -fluorine spin coupling.

In this work, concentrated solutions (10-20%) were used so as to obtain useful spectra with the instrument available. Further studies using suitable techniques e.g. C.A.T.

methods, of dilute solutions for which valid molecular weight and conductivity data can be obtained are obviously necessary before these and other n.m.r. phenomena can be understood.

8.3. Experimental

The majority of the compounds studied were provided by Dr. G.B. Deacon of University College and the remainder prepared by his procedures (176) from bis(pentafluorophenyl) thallium bromide also provided by Dr. Deacon. Fluorine (19) magnetic resonance spectra were measured using a Varian V4311 spectrometer at 56.45 Mc/sec., with trifluoroacetic acid as an external reference. Concentrated (10-20%) or saturated solutions were used. Chemical shifts and coupling constants are accurate to $\leqslant 0.05$ p.p.m. and $\leqslant 5$ c/sec. respectively but larger errors are quoted. Relative signs of the coupling constants were determined by double irradiation with the apparatus constructed by R.S. Milner.

I am grateful to Dr. G.B. Deacon for the gift of compounds and for many helpful and interesting discussions, and to Mr. R.S. Milner for his assistance with the double irradiation experiment.

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