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THE CONSTITUTION OF THE GRIGNARD REAGENT—III

THE REACTION BETWEEN R_2Mg AND MgX_2 IN TETRAHYDROFURAN

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Abstract—Dilute THF solutions (0·2–0·3M) of R_2Mg and MgX_2 (where R is Et or Ph and X is Cl or Br) react almost instantaneously in 1:1 mole ratio on mixing, with *absorption* of heat (heat was *evolved* in the corresponding reactions in ether). For the equimolar mixtures, conversions to product are lower than in ether and range from 39 to 58%. The equimolar mixtures are largely monomeric (i = 1·00–1·09), as are the reactants (i = 0·98–1·03). Monomeric reaction products can only be $(RMgX)_1$. Therefore the equimolar mixtures, whose i-factors are indistinguishable from those of the corresponding Grignard reagents, must consist largely of $(R_2Mg)_1$, $(MgX_2)_1$ and $(RMgX)_1$ existing in equilibrium. The system Et_2Mg–$MgCl_2$ also undergoes a secondary reaction with the formation of appreciable quantities of the species $(EtMg_2Cl_3)_1$. Equilibrium constants, free energy changes, and entropy changes are calculated. Entropy changes for the reactions are much larger than were observed in ether solution (for R = Et and X = Br, ΔS for $(R_2Mg)_1 + (MgX_2)_1 \rightarrow 2(RMgX)_1$ is 23·7 cal/deg). Heat of displacement measurements indicate that this large ΔS is associated with the loosening of THF molecules attached tightly to MgX_2 molecules. It is shown that the number of THF molecules attached to an $(MgBr_2)_1$ molecule in THF solution must exceed two and is probably at least four.

INTRODUCTION

STUDIES of the heat of mixing of solutions of R_2Mg and MgX_2, supplemented by molecular weight measurements, provide information about the equilibria existing among the various species present in the mixture and in the corresponding Grignard reagent. The results of such studies on four systems, with ether as the solvent, were reported[1,2] in the first two papers of the series. The present paper reports the results of similar studies on four systems in tetrahydrofuran (THF).

RESULTS AND DISCUSSION

The results of the thermochemical measurements are shown in Figs 1–3. Whereas the reactions studied were all *exothermic* in ether solution, they are all *endothermic* in THF solution. As in ether solution, the reaction accompanying each mixing is complete within one minute and probably sooner. Encircled points represent successive additions of R_2Mg to one mole of MgX_2. The total heat absorbed in kilocalories through a particular addition is plotted against the total moles of R_2Mg added. Square-enclosed points represent successive additions of MgX_2 to one mole of R_2Mg, the total heat absorbed through a particular addition being plotted against the total moles of MgX_2 added.

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[1] M. B. Smith and W. E. Becker, *Tetrahedron Letters* 3843 (1965).

[2] M. B. Smith and W. E. Becker, *Tetrahedron* **22**, 3027 (1966).

For each of the systems Et_2Mg–$MgBr_2$, Ph_2Mg–$MgBr_2$, and Ph_2Mg–$MgCl_2$, the data for the two series of mixing experiments are well represented by a single curve. This indicates that, as in ether solution, reaction occurs in 1 :1 mole ratio and in no other ratio. Unlike in ether solution, the near-linear portions of the curves at low mole ratios are very short. Since, in addition, the curves continue to rise well beyond 1·0 mole ratio, it is apparent that conversion to product is much lower than in ether solution. As shown in Table 1, ΔH's of reaction at 1 :1 mole ratio range from 3·23 kcal/mole reactant added for Et_2Mg–$MgBr_2$ down to 1·06 for Ph_2Mg–$MgCl_2$.

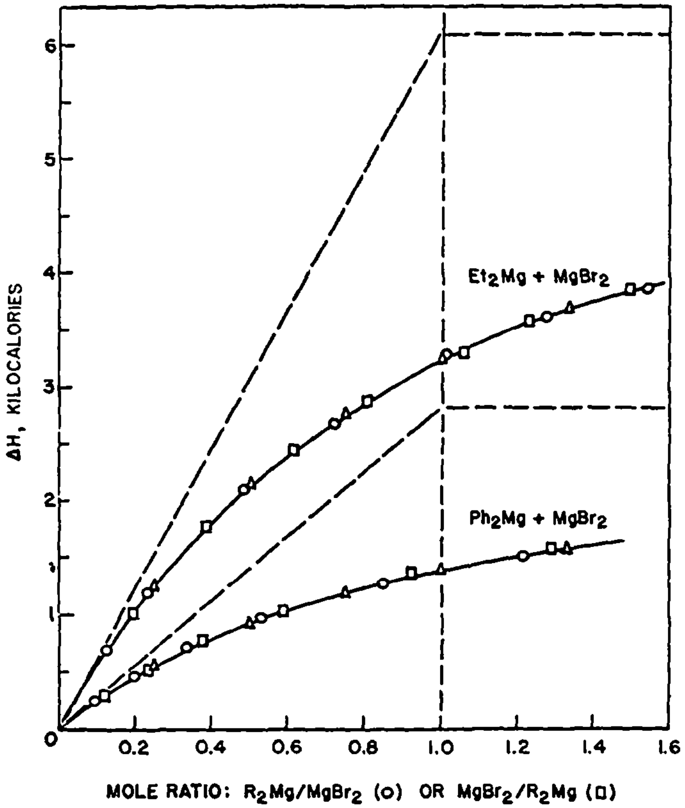

FIG. 1. Heat absorbed on mixing 0·2M R_2Mg with 0·2M $MgBr_2$, both in THF, at 25°. Encircled points represent successive additions of R_2Mg to one mole $MgBr_2$. Square-enclosed points refer to successive additions to $MgBr_2$ to one mole R_2Mg. Triangle-enclosed points were calculated from the equilibrium constant and the ΔH of reaction at 100% conversion.

To obtain the ΔH of reaction for a system at 100% conversion, $\Delta H/\Delta n$ was calculated for each addition, where ΔH is heat absorbed and Δn is the number of moles of R_2Mg (or MgX_2) added to a larger quantity of solution containing MgX_2 (or R_2Mg) and any R_2Mg (or MgX_2) from previous additions. The mean mole ratio for the addition was calculated as the average R_2Mg/MgX_2 (or MgX_2/R_2Mg) of the solution before and after the addition. The value of $\Delta H/\Delta n$ at zero mole ratio, equivalent to the ΔH of reaction at 100% conversion, was determined by extrapolation from a (nearly linear) plot of log ($\Delta H/\Delta n$) vs mean mole ratio. The values so obtained are listed in the fifth column of Table 1. Referring to Figs 1–3, the dashed line tangent to the curve for each system at zero mole ratio was drawn so as to intersect the 1·0 mole ratio ordinate at a value of ΔH equal to the ΔH of reaction at 100% conversion.

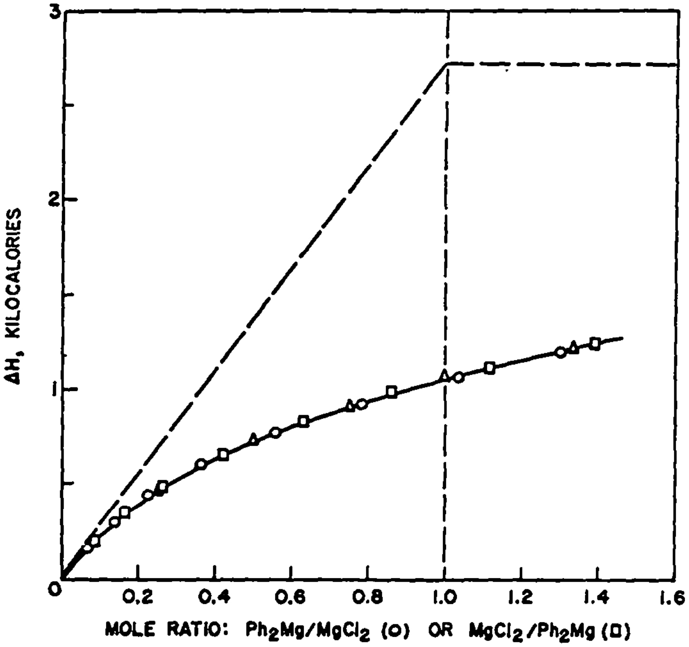

FIG 2 Heat absorbed on mixing 0·3M Ph_2Mg with 0·3M $MgCl_2$, both in THF, at 25 Encircled points represent successive additions of Ph_2Mg to one mole $MgCl_2$. Square-enclosed points refer to successive additions of $MgCl_2$ to one mole Ph_2Mg. Triangle-enclosed points were calculated from the equilibrium constant and the ΔH of reaction at 100% conversion.

Conversions at 1·0 mole ratio were calculated from the actual ΔH's of reaction at 1·0 mole ratio and from the corresponding ΔH's of reaction at 100% conversion. As shown in Table 1, these conversions range from 53% for Et_2Mg–$MgBr_2$ down to 39% for Ph_2Mg–$MgCl_2$. Evidently from 47 to 61% remains as unreacted $R_2Mg + MgX_2$ in equilibrium with product species.

The system Et_2Mg–$MgCl_2$ is unique among the systems studied thus far in that two distinct curves were obtained for the two series of mixing experiments (Fig. 3). This indicates that for this system, reaction does not occur only in 1:1 mole ratio. As will be developed in a later section, while the primary reaction does occur at 1:1 mole ratio, a secondary reaction, also endothermic, takes place at 3:1 mole ratio.

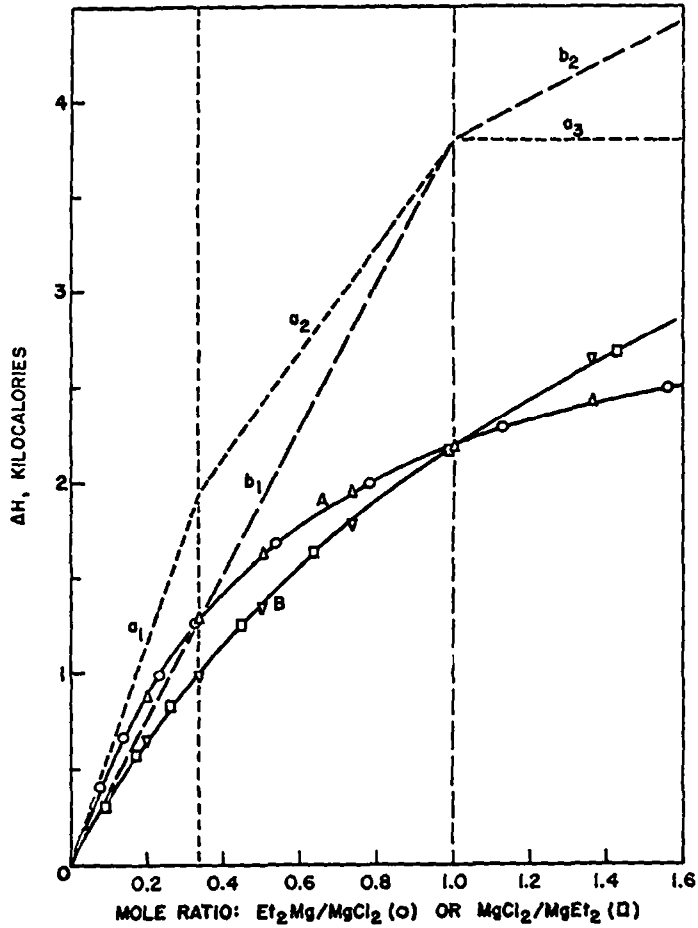

FIG. 3. Heat absorbed on mixing 0·3M Et_2Mg with 0·3M $MgCl_2$, both in THF, at 25°. In curve A, encircled points represent successive additions of Et_2Mg to one mole $MgCl_2$. Corresponding theoretical curve $a_1a_2a_3$ assumes following reactions at 100% conversion: a_1, $Et_2Mg + 3\,MgCl_2 \rightarrow 2\,EtMg_2Cl_3$; a_2, $Et_2Mg + EtMg_2Cl_3 \rightarrow 3\,EtMgCl$; a_3, No reaction (line a_3 extends indefinitely). In curve B, square-enclosed points refer to successive additions of $MgCl_2$ to Et_2Mg Corresponding theoretical curve $b_1b_2b_3$ assumes following reactions at 100% conversion: b_1, $MgCl_2 + Et_2Mg \rightarrow 2\,EtMgCl$; b_2, $MgCl_2 + EtMgCl \rightarrow EtMg_2Cl_3$ (line b_2 extends to $MgCl_2/MgEt_2 = 3{\cdot}0$ where $\Delta H = 5{\cdot}87$); b_3 No reaction (line b_3, not shown, is horizontal at $\Delta H = 5{\cdot}87$ and extends indefinitely from $MgCl_2/MgEt_2 = 3{\cdot}0$). Triangle-enclosed points were calculated from the equilibrium constant and the ΔH of reaction at 100% conversion

Since the two curves cross at 1:1 mole ratio, the same equilibrium mixture is obtained at this composition, regardless of the order of addition. Conversion at 1:1 mole ratio is close to that for the system Et_2Mg–$MgBr_2$ (Table 1).

Heats of dilution of the reactant and product solutions are small, all dilutions being slightly exothermic (Table 2). It follows that the heat of reaction between R_2Mg and MgX_2 per mole of either reactant converted varies only slightly with

TABLE 1. CONVERSIONS AT 1·0 MOLE RATIO FOR THE REACTION BETWEEN R_2Mg AND MgX_2 IN THF AT 25°

R	X	Molarity	ΔH at 1·0 mole ratio, kcal/mole R_2Mg Actual[a]	Theory[b]	% Conversion
Et	Br	0·2	3·23	6·10	53·0
Ph	Br	0·2	1·39	2·82	49·3
Ph	Cl	0·3	1·06	2·72	39·0
Et	Cl	0·3	2·19	3·80	57·6[c]

[a] Solid curve, Fig. 1, 2, or 3.

[b] Theoretical for 100% conversion (dashed line, Fig. 1, 2, or 3).

[c] Approximate only, since a portion of the observed heat absorbed is due to a secondary reaction (see text).

TABLE 2. HEATS OF DILUTION IN THF AT 25°

Compound	Molarity Initial	Final	−ΔH (diln.), kcal/mole
Et_2Mg	0·200	0·043	0·2
	0·300	0·067	0·2
Ph_2Mg	0·200	0·036	0·2
	0·300	0·056	0·2
$MgBr_2$	0·200	0·041	0·2
$MgCl_2$	0·300	0·058	0·3
$Et_2Mg + MgBr_2$	0·200	0·039	0·2
$Ph_2Mg + MgBr_2$	0·200	0·037	0·2
$Et_2Mg + MgCl_2$	0·300	0·061	0·3
$Ph_2Mg + MgCl_2$	0·300	0·053	0·3

concentration. The *i*-factors[3] for the different solutions, whether before or after dilution, do not differ significantly from unity (Table 3). Unlike in ether solution, therefore, the dilutions in THF solution are not accompanied by appreciable dissociation.

Before the mixing of equimolar quantities of R_2Mg and MgX_2, each reactant consists primarily of monomeric species, as shown by the *i*-factors (Table 3). The *i*-factors determined after reaction has occurred indicate that the resulting equilibrium mixture also contains mostly monomeric species. In view of the conversions obtained, these monomeric species consist of roughly equal amounts of monomeric reaction product and unreacted mixture. Since only small amounts of free ionic species are present[4], this monomeric reaction product must consist primarily of the species $(RMgX)_1$.

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[3] The *i*-factor (or association factor) is the ratio of solute mol wt to formula wt.

[4] For example, the degree of ionization of 0·2M EtMgBr (equimolar mixture in THF) was estimated as less than 0·2% from conductivity data obtained in this laboratory.

TABLE 3. ASSOCIATION FACTORS IN THF AT ABOUT 30°[a]

Compound	Molarity	i
Et_2Mg	0·159	0·99
	0·300	1·00
Ph_2Mg	0·200	1·01
	0·300	1·00
$MgCl_2$	0·150	1·01
	0·300	1·03
$MgBr_2$	0·100	0·98
	0·200	1·01
$Et_2Mg + MgCl_2$	0·100	1·05
	0·300	1·09
$(EtMgCl)_G$[b]	0·300	1·10
$Et_2Mg + MgBr_2$	0·200	1·02
$(EtMgBr)_G$	0·200	1·03
$Ph_2Mg + MgCl_2$	0·300	1·05
$(PhMgCl)_G$	0·300	1·04
$Ph_2Mg + MgBr_2$	0·200	1·00
$(PhMgBr)_G$	0·200	1·03

[a] The measurements were made at 200·0 mm Hg.

[b] The Grignard reagent formed from RX and Mg is represented by the expression $(RMgX)_G$.

The principal reaction occurring when equimolar quantities of R_2Mg and MgX_2, each in THF, are mixed is then:

$$(R_2Mg)_1 + (MgX_2)_1 \rightarrow 2(RMgX)_1$$

Possible mechanisms for this reaction in ether were discussed by Ashby and Smith.[5] These mechanisms, which apply equally well in THF, will not be discussed further here. Secondary processes, both accompanied by negligible heat effects, include physical mixing and some association of $(RMgX)_1$. The additional secondary process occurring in the system Et_2Mg–$MgCl_2$ is discussed in a later section.

Equilibrium constants and thermodynamic values for normal systems

For each of the three systems Et_2Mg–$MgBr_2$, Ph_2Mg–$MgBr_2$ and Ph_2Mg–$MgCl_2$, molar concentrations of $(R_2Mg)_1$, $(MgX_2)_1$ and $(RMgX)_1$ were calculated for the equimolar mixtures from the total molarity (0·2 or 0·3) and the percent conversion. Since the i-factors do not differ significantly from unity, the assumption was made that each system contains only monomeric species. Values of the equilibrium constant $K = [(RMgX)_1]^2/[(R_2Mg)_1][(MgX_2)_1]$ were calculated, activities being assumed equal to molar concentrations. These are listed in Table 4. Values of ΔH were calculated at several mole ratios from the equilibrium constant and the ΔH of reaction at 100% conversion (column 5, Table 1). These calculated values, plotted in Figures 1 and 2 as triangle-enclosed points, lie very close to the experimental curves. This gives additional confirmation to the existence of true equilibrium in

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[5] E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.* **86**, 4363 (1964).

these systems. Since the reaction between $(R_2Mg)_1$ and $(MgX_2)_1$ involves no change in the total number of molecules, percent conversion to $(RMgX)_1$ should be independent of concentration.

TABLE 4. EQUILIBRIUM CONSTANTS[a] FOR THE REACTION $(R_2Mg)_1 + (MgX_2)_1 \rightarrow 2\ (RMgX)_1$ IN THF at 25°

R	X	Molarity, M	% Conversion (1·0 mole ratio)	M[a] of $(RMgX)_1$	M[a] of $(R_2Mg)_1$ or $(MgX_2)_1$	K
Et	Br	0·200	53·0	0·1060	0·0470	5·09
Ph	Br	0·200	49·3	0·0985	0·05075	3·77
Ph	Cl	0·300	39·0	0·1175	0·09125	1·66

[a] Calculated on assumption that only monomeric species are present

Thermodynamic values for the reaction between R_2Mg and MgX_2 in THF solution are given in Table 5. Free energies were calculated from the K's using the relation $\Delta F = -RT \ln K$. Entropies were calculated from the equation $\Delta F = \Delta H - T\Delta S$. Whereas the entropy change for the reaction $(R_2Mg)_1 + (MgX_2)_1 \rightarrow 2\ (RMgX)_1$ was small in ether (0 ± 2 cal/deg. mole R_2Mg), it is large in THF, particularly for the system Et_2Mg–$MgBr_2$.

TABLE 5. THERMODYNAMIC VALUES FOR THE REACTION $(R_2Mg)_1 + (MgX_2)_1 \rightarrow 2\ (RMgX)_1$ IN THF at 25°

R	X	M	Per mole R_2Mg		
			$-\Delta F$, cal	ΔH, cal	ΔS, cal/deg
Et	Br	0·200	965	6100	23·7
Ph	Br	0·200	787	2820	12·1
Ph	Cl	0·300	300	2720	10·1

Heats of displacement of ether with THF

The large positive ΔS for the reaction between Et_2Mg and $MgBr_2$ in THF (as opposed to the small ΔS for the same reaction in ether) indicates that the reaction must be accompanied by a considerable overall loosening of solvent molecules attached to magnesium atoms. That is, the enthalpy of solvation of one or both reactant species must be considerably greater than that of the product species, $(EtMgBr)_1$. To confirm this, additional experiments were performed. Since it was not feasible to measure directly the heats of solvation of the unsolvated compounds, the heat of reaction of each compound, dissolved in ether, with a large excess of THF was determined. The results obtained, after applying suitable corrections, are summarized in the following equations:

$$(\mathrm{Et_2Mg}\cdot x_1\mathrm{Et_2O})_l + y_1\,\mathrm{THF} \rightarrow (\mathrm{Et_2Mg}\cdot y_1\mathrm{THF}) + x_1\mathrm{Et_2O} \qquad \Delta H(25^\circ) = -4{\cdot}6\,\mathrm{kcal}$$

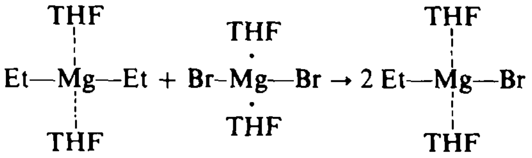
$$(\mathrm{MgBr_2}\cdot x_2\mathrm{Et_2O})_l + y_2\,\mathrm{THF} \rightarrow (\mathrm{MgBr_2}\cdot y_2\mathrm{THF})_l + x_2\mathrm{Et_2O} \qquad \Delta H(25^\circ) = -19{\cdot}1\,\mathrm{kcal}$$

$$(\mathrm{EtMgBr}\cdot x_3\mathrm{Et_2O})_l + y_3\,\mathrm{THF} \rightarrow (\mathrm{EtMgBr}\cdot y_3\mathrm{THF})_l + x_3\mathrm{Et_2O} \qquad \Delta H(25^\circ) = -7{\cdot}0\,\mathrm{kcal}$$

All reactions are exothermic, as expected, indicating that the magnesium atom of each species prefers THF, the stronger base, to ether. However, the degree of preference of THF over ether is far greater for $(\mathrm{MgBr_2})_l$, than for $(\mathrm{Et_2Mg})_l$ or $(\mathrm{EtMgBr})_l$.

These results indicate indirectly that the enthalpy of solvation with THF is far greater for the species $(\mathrm{MgBr_2})_l$ than for either of the other two species. Either the enthalpy per molecule of THF solvated is greater, or the number of THF molecules solvated per $(\mathrm{MgBr_2})_l$ molecule is greater, or both.

Solid dietherates have been prepared for a number of magnesium compounds including $\mathrm{Ph_2Mg}$,[6] $\mathrm{MgBr_2}$,[7,8] $\mathrm{MgI_2}$,[7] and Grignard reagents.[6,9] It has been suggested[6,8] that these compounds probably exist as the dietherates in ether solution. Heat-of-etheration measurements[10] indicate that this is true for $(\mathrm{PrMgI})_G$. The solid di-THF complex of at least one Grignard reagent, $(\mathrm{PhMgBr})_G$, has been prepared.[6] In the absence of data indicating otherwise, let it be assumed that the species $(\mathrm{Et_2Mg})_l$, $(\mathrm{MgBr_2})_l$ and $(\mathrm{EtMgBr})_l$ all exist as the di-THF complexes in THF solution. In this case the reaction between $(\mathrm{Et_2Mg})_l$ and $(\mathrm{MgBr_2})_l$ in THF may be represented schematically as follows:



$$\mathrm{Et{-}\overset{THF}{\underset{THF}{Mg}}{-}Et} + \mathrm{Br{-}\overset{THF}{\underset{THF}{Mg}}{-}Br} \rightarrow 2\,\mathrm{Et{-}\overset{THF}{\underset{THF}{Mg}}{-}Br}$$

Insofar as the solvent molecules are concerned, the net process is then roughly: 2THF (tightly held) → 2THF (loosely held). The entropy change per mole of THF for this process is about 23·7/2 or 11·8 cal/deg. This is close to the molar entropy of fusion of THF at 25° (estimated as 9–12 cal/deg). It would require that the THF molecules attached to $(\mathrm{MgBr_2})_l$ be "completely frozen" and that those attached to $(\mathrm{EtMgBr})_l$ be "completely melted". Since the THF molecules attached to $(\mathrm{EtMgBr})_l$ can only be "partially melted", the entropy change per mole of THF attached to $(\mathrm{MgBr_2})_l$ must be well below 11·8 cal/deg. It follows that the number of THF molecules attached to an $(\mathrm{MgBr_2})_l$ molecule must exceed two and is probably at least four. This conclusion is not changed if it is assumed that more than two THF molecules are attached to $(\mathrm{Et_2Mg})_l$ or $(\mathrm{EtMgBr})_l$ or both. This result is reasonable since

[6] G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.* **86**, 4825 (1964).

[7] B. N. Menschutkin, *Z. Anorg. Chem.* **49**, 34 (1906); *Ibid.* **62**, 395 (1909).

[8] W. E. Doering and C. R. Noller, *J. Am. Chem. Soc.* **61**, 3436 (1939).

[9] L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.* **86**, 5344 (1964).

[10] J. Lifschitz and O. E. Kalberer, *Z. Physik. Chem.* **102**, 393 (1922).

the solid complexes formed by magnesium halides with various ligands (for example, water, alcohols, amines and ketones) include many in which 6 ligand molecules are coordinated to each Mg atom, as well as those in which the number of ligand molecules per Mg atom is 4, 3, 2, or 1. It therefore seems likely that if $MgBr_2$ in THF consists of a single species, that species is $(MgBr_2 \cdot 4\ THF)_1$ or $(MgBr_2 \cdot 6\ THF)_1$.

Although these experiments provide information about the degree of solvation of $(MgBr_2)_1$, they neither prove nor disprove the correctness of the assumption that the species $(Et_2Mg)_1$ and $(EtMgBr)_1$ exist as the di-THF complexes in THF solution.

As indicated by the ΔS values, the amount of overall loosening of complexed THF molecules accompanying the reaction $(Ph_2Mg)_1 + (MgX_2)_1 \rightarrow 2(PhMgX)_1$, where X is Br or Cl, is considerably less than that for the reaction $(Et_2Mg)_1 + (MgBr_2)_1 \rightarrow 2(EtMgBr)_1$. Evidently the species $(PhMgBr)_1$ and $(PhMgCl)_1$ are more strongly solvated than the species $(EtMgBr)_1$.

The system Et_2Mg–$MgCl_2$

As developed earlier, the principal reaction occurring between Et_2Mg and $MgCl_2$ in THF is

$$(Et_2Mg)_1 + (MgCl_2)_1 \rightarrow 2(EtMgCl)_1. \qquad (1)$$

The existence of two distinct curves for the system (Fig. 3) indicates that a secondary reaction is taking place. Since curve A lies above curve B for mole ratios from 0 to 1, it is apparent that the secondary reaction (presumed to be endothermic like the primary reaction) is favored by having an excess of $MgCl_2$. Since, in addition, the vertical distance between the curves reaches a maximum at a mole ratio close to $\frac{1}{3}$, the reaction product is probably $(EtMg_2Cl_3)_1$, in which case the reaction can be represented as

$$(EtMgCl)_1 + (MgCl_2)_1 \rightarrow (EtMg_2Cl_3)_1 \qquad (2)$$

This reaction would be expected to be endothermic since, like the primary reaction, it involves the loosening of THF molecules attached tightly to $MgCl_2$ molecules. The possibility of the existence of the species $(EtMg_2Cl_3)_1$ in solution was suggested by Ashby and Becker[11] who obtained crystals of $EtMg_2Cl_3 \cdot THF$ by fractional crystallization of the Grignard reagent $(EtMgCl)_G$ from THF solution.

The ΔH for reaction (1) was evaluated by the method described earlier as 3·80 kcal/mole of Et_2Mg converted (end point of line b_1 at 1·0 mole ratio, Fig. 3). The ΔH for the reaction

$$\tfrac{1}{3}(Et_2Mg)_1 + (MgCl_2)_1 \rightarrow \tfrac{2}{3}(EtMg_2Cl_3)_1$$

was similarly determined as 1·957 kcal/mole of $MgCl_2$ converted (end point of line a_1 at $\frac{1}{3}$ mole ratio).

The ΔH for reaction (2) was calculated from these figures as $(\frac{3}{2})(1{\cdot}957) - (\frac{1}{2})(3{\cdot}80) =$ 1·035 kcal/mole of $MgCl_2$ converted. The equilibrium constants for reactions (1) and (2) were evaluated as 5·52 and 4·36, respectively, from the total molarity (0·3) and the thermochemical data. The assumption was made that only monomeric species are present (except for $(EtMg_2Cl_3)_1$ which is "dimeric" since it contains 2 Mg atoms).

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[11] E. C. Ashby and W. E. Becker, *J. Am. Chem. Soc.* **85**, 118 (1963).

Values of ΔH were calculated at several mole ratios from the equilibrium constants and the ΔH's at 100% conversion. These calculated values, plotted in Fig. 3 as triangle-enclosed points, lie close to the experimental curves. The proposed secondary reaction (Eq. 2) therefore accounts very satisfactorily for the two distinct curves obtained with this system.

Molar concentrations of the four species present in various mixtures of 0·3M Et_2Mg and 0·3M $MgCl_2$, calculated from the equilibrium constants, are listed in Table 6. As the $Et_2Mg/MgCl_2$ mole ratio is increased from $\frac{1}{3}$ to 1 to 3, the ratio of the molarity of $(EtMg_2Cl_3)_1$ in the mixture to that of $(EtMgCl_1)$ decreases from 0·520 to 0·195 to 0·054.

TABLE 6. COMPOSITIONS[a] OF MIXTURES OF 0·3M Et_2Mg WITH 0·3M $MgCl_2$ IN THF AT 25°

$Et_2Mg/MgCl_2$ mole ratio	Molarities				$\frac{(EtMg_2Cl_3)_1}{(EtMgCl)_1}$
	$(Et_2Mg)_1$	$(MgCl_2)_1$	$(EtMgCl)_1$	$(EtMg_2Cl_3)_1$	
0·333	0·0110	0·1176	0·0845	0·0434	0·520
0·735	0·0475	0·0604	0·1259	0·0331	0·253
1·000	0·0710	0·0452	0·1322	0·0258	0·195
1·362	0·0974	0·0326	0·1325	0·0188	0·142
3·000	0·1682	0·0124	0·1077	0·0058	0·054

[a] Calculated on the assumption that, except for $(EtMg_2Cl_3)_1$, only monomeric species are present.

Since the species $(EtMg_2Cl_3)_1$ is dimeric with respect to the magnesium atom, its presence in mixtures of Et_2Mg and $MgCl_2$ should lead to *i*-factors in excess of unity. To test this conclusion, *i*-factors were determined experimentally for 3 mixtures of 0·3M Et_2Mg with 0·3M $MgCl_2$. The results are compared in Table 7 with the corresponding values calculated from the compositions listed in Table 6. The agreement is satisfactory. The proposed secondary reaction is therefore consistent with molecular weight measurements.

TABLE 7. COMPARISON OF EXPERIMENTAL *i*-FACTORS WITH CALCULATED VALUES FOR MIXTURES OF 0·3M Et_2Mg WITH 0·3M $MgCl_2$

$Et_2Mg/MgCl_2$ mole ratio	*i*-Factors	
	Exptl	Calc[a]
(Pure $MgCl_2$)	1·03	1·00
$\frac{1}{3}$	1·15	1·17
1	1·09	1·09
3	1·04	1·02
(Pure Et_2Mg)	1·00	1·00

[a] Calculated on the assumption that, except for $(EtMg_2Cl_3)_1$, only monomeric species are present.

Since reaction (2) is accompanied by a decrease in the total number of molecules, the extent of the reaction increases with increasing concentration. Molar concentrations of the four species present in equimolar mixtures of Et_2Mg and $MgCl_2$ at various total Mg molarities, calculated from the equilibrium constants, are given in Table 8. As the total Mg molarity is increased from 0·01 to 2, the ratio of the molarity of $(EtMg_2Cl_3)_1$ in the mixture to that of $(EtMgCl)_1$ increases from 0·0101 to 0·597. As discussed in a later section, it is highly probable that equimolar mixtures of Et_2Mg and $MgCl_2$ are equivalent to the corresponding Grignard reagents $(EtMgCl)_G$. In this case, the compositions listed in Table 8 apply equally well to these Grignard reagents.

TABLE 8. COMPOSITIONS OF EQUIMOLAR MIXTURES[a] OF Et_2Mg AND $MgCl_2$ AT VARIOUS TOTAL Mg MOLARITIES

M (Total Mg)	Molarities				$\frac{(EtMg_2Cl_3)_1}{(EtMgCl)_1}$
	$(Et_2Mg)_1$	$(MgCl_2)_1$	$(EtMgCl)_1$	$(EtMg_2Cl_3)_1$	
0·0100	0·00230	0·00225	0·00535	0·000054	0·0101
0·0600	0·01388	0·01224	0·0306	0·00164	0·0536
0·3000	0·0710	0·0452	0·1322	0·0258	0·1951
1·000	0·2453	0·0955	0·360	0·1498	0·417
2·000	0·5060	0·1368	0·619	0·369	0·597

[a] Also, compositions of the corresponding Grignard reagents provided equivalence is assumed.

Thermodynamic values for the reactions occurring in the system are given in Table 9. The entropy change of 16·1 cal/deg for the first reaction, while large, is considerably less than the entropy change (23·7 cal/deg) for the corresponding reaction between Et_2Mg and $MgBr_2$. Evidently $MgCl_2$ holds complexed THF molecules less tightly than does $MgBr_2$. The third equation in Table 9 is obtained by combining the first two equations.

TABLE 9. THERMODYNAMIC VALUES FOR THE 0·3M SYSTEM $Et_2Mg—MgCl_2$ IN THF AT 25°

Reaction	K	$-\Delta F$, cal	ΔH, cal	ΔS, cal/deg
$(Et_2Mg)_1 + (MgCl_2)_1 \rightarrow 2(EtMgCl)_1$	5·52	1010	3800	16·1
$(EtMgCl)_1 + (MgCl_2)_1 \rightarrow (EtMg_2Cl_3)_1$	4·36	874	1035	6·4
$(Et_2Mg)_1 + 3(MgCl_2)_1 \rightarrow 2(EtMg_2Cl_3)_1$	105·0	2760	5870	28·9

Equivalence of Grignard reagent with equimolar mixture

For each of the four systems studied in THF, the *i*-factor for the Grignard reagent is indistinguishable from that of the corresponding equimolar mixture (Table 3). Because of this, and in view of arguments very similar to those presented in the second paper of the series,[2] it appears highly probable that, within the scope of these experiments, the Grignard reagent in THF is equivalent to the corresponding equimolar mixture (except for minor differences due to dissimilarities in the nature and amounts of impurities).

COMPARISON WITH LITERATURE RESULTS

Among earlier investigations concerned with reaction between R_2Mg and MgX_2 in THF are the infrared spectral studies of Salinger and Mosher.[12] For each of five Grignard reagents (MeMgCl, MeMgBr, EtMgCl, EtMgBr, and PhMgBr), the infrared spectrum of $(RMgX)_G$ was found to be identical to that of equimolar $R_2Mg + MgX_2$, while both differed from R_2Mg alone. It was concluded that R_2Mg and MgX_2 react rapidly in THF to give an equilibrium mixture containing the same species as the corresponding Grignard reagent. For $(MeMgCl)_G$ and $(MeMgBr)_G$, the position of the equilibrium did not change noticeably over a wide concentration range. It was therefore concluded that the reaction between Me_2Mg and MgX_2 must be unaccompanied by any change in the total number of molecules, hence the product species must be RMgX. The equilibrium constant $K = (MeMgX)^2/(Me_2Mg)(MgX_2)$ was estimated as 4·5 for X = Cl and 3·5 for X = Br.

Although circumstances did not permit the estimation of K values for the other systems, certainly these results and conclusions are in excellent agreement with the results of the present investigation.

Molecular association studies by Ashby and Becker[11] indicated that $(EtMgBr)_G$ and $(EtMgCl)_G$ are essentially monomeric in THF (0·1–0·3M). The Grignard reagent $(EtMgCl)_G$ was found to be identical to the corresponding equimolar mixture with respect to infrared spectra, conductance, and dipole moment. Crystals of $EtMg_2Cl_3 \cdot$ THF were produced by fractional crystallization of $(EtMgCl)_G$ from THF solution. This indicated that solutions of $(EtMgCl)_G$ in THF contain the species $(Et_2Mg)_1$, $(MgCl_2)_1$, $(EtMgCl)_1$, and possibly $(EtMg_2Cl_3)_1$. It was concluded that the Grignard reagent $(RMgX)_G$ in THF is best represented by the equilibrium $2(RMgX)_1 \rightleftarrows (R_2Mg)_1 + (MgX_2)_1$. These findings are all confirmed in the present investigation.

The molecular association studies of Vreugdenhil and Blomberg[13] indicated that Et_2Mg, $MgBr_2$, and $(EtMgBr)_G$ are all monomeric in dilute (10^{-3} to 10^{-2}M) THF. This agrees with the results of Ashby and Becker[11], as well as with those of the present investigation. On the other hand, measurements by Hashimoto, *et al*,[14] indicated that the *i*-factor for $(EtMgBr)_G$ in THF decreases in approximately linear fashion from 1·6 at M = 0·1 to 1·0 at M = 1·1, then remains at unity as the concentration is further increased. It appears likely that their results at the lower concentrations are in error, possibly due to contamination caused by exposure to oxygen or moisture.

Roos and Zeil[15] found that NMR spectra of Grignard compounds at various concentrations in THF were identical with the spectra of the corresponding equimolar mixtures. Bikales and Becker[16] found close agreement between the reaction rate of $(MeMgBr)_G$ with benzophenone in THF and that of the corresponding

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equimolar mixture. These results are in accord with the results of the present investigation.

We are planning similar studies in other solvents including dibutyl ether. We also plan to extend our studies in ether and THF to include $(MeMgX)_G$ and other Grignard compounds.

EXPERIMENTAL

All experimental details other than the preparation of materials are as described in the second paper of the series.[2]

Materials. THF was reagent-grade and was distilled over $NaAlH_4$ in a nitrogen atmosphere just prior to use. Domal high purity sublimed Mg granules (Dominion Magnesium Co. Ltd., Haley, Ont.) were used without purification.

Et_2Mg and Ph_2Mg were prepared by reacting R_2Hg with a large excess of magnesium in THF in a sealed tube at 100°. The products, shown to be free of R_2Hg by testing with dithizone, were standardized by hydrolyzing and titrating with standard acid.

$MgBr_2$ and $MgCl_2$ were prepared by reacting 1,2-$C_2H_4X_2$ with a slight excess of magnesium in THF. The products were shown to be free of unreacted 1,2-$C_2H_4X_2$ by VPC analysis. Grignard reagents were prepared in THF by conventional methods from magnesium and purified alkyl or aryl halide. The products were analyzed for halogen by the Volhard method and for Mg by Versene titration. The molarities calculated from the halogen and magnesium analyses agreed within 1%.

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