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THE CONSTITUTION OF THE GRIGNARD REAGENT—II

THE REACTION BETWEEN R_2Mg AND MgX_2 IN ETHER

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Abstract—Dilute ether solutions (0·1–0·3M) of R_2Mg and MgX_2 (where R is C_2H_5 or C_6H_5 and X is Br or I) react almost instantaneously in 1:1 mole ratio on mixing, with evolution of heat (2·0–4·9 kcal/mole of either reactant converted). For the equimolar mixture, conversion to product is high (82–98%). At 0·1M concentration, the product is largely monomeric (i = 1·04–1·14). This monomeric product, by far the principal species in the mixture, can only be $(RMgX)_1$. At 0·3M concentration, the mixture contains both $(RMgX)_1$ and associated RMgX molecules. The i-factor for the equimolar mixture is indistinguishable from that of the corresponding Grignard reagent at every concentration studied. Consequently, it must be concluded that, for the systems studied, the following reaction is fast, with the equilibrium lying strongly to the right:

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

The equilibrium constant, free energy change, and entropy change are calculated for this reaction for each system. Entropy changes are small in magnitude (about 0 ± 2 e.u./mole R_2Mg). Heat of dilution measurements indicate that the heat of association of $(MgX_2)_1$, and also that of $(RMgX)_1$, is small.

THE problem of establishing the precise nature of the Grignard reagent in ether solution has received considerable attention in the last few years. Molecular weight measurements[1,2] have shown that a number of Grignard reagents (bromides and iodides) are essentially monomeric at low concentrations (up to at least 0·1M). As stated by Ashby and Smith[1] among others, these monomeric species may consist of $(RMgX)_1$, $(R_2Mg)_1 + (MgX_2)_1$, or an equilibrium mixture of these. The purpose of the present study was to investigate the existence of such an equilibrium and, if it exists, to determine its position. The method selected was the measurement of the heat of mixing of R_2Mg and MgX_2, each in dilute ether solution. Preliminary data on the system $(C_2H_5)_2Mg + MgBr_2$ were reported earlier.[3] More accurate data on this system are reported here as well as data on three additional systems.

RESULTS

The four systems studied in ether solution include the 0·1M systems

$$(C_2H_5)_2Mg—MgBr_2 \quad \text{and} \quad (C_6H_5)_2Mg—MgBr_2$$

and the 0·3M systems $(C_2H_5)_2Mg—MgI_2$ and $(C_6H_5)_2Mg—MgI_2$. For each system, two series of thermochemical experiments were performed. In the first series, measured portions of 0·1M (or 0·3M) R_2Mg were added successively to a larger quantity

[1] E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.* **86**, 4363 (1964).
[2] A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).
[3] M. B. Smith and W. E. Becker, *Tetrahedron Letters* 3843 (1965).

of 0·1M (or 0·3M) MgX_2 in a calorimeter, the temperature rise for each addition determined, and the heat evolution calculated in kcal/mole MgX_2. Each circled point in Figs. 1 and 2 corresponds to a particular addition of R_2Mg and represents the total heat evolved through that addition plotted against total moles R_2Mg added. The second series was similar to the first except that MgX_2 was added stepwise to a larger quantity of R_2Mg. Each square-enclosed point in Figs. 1 and 2 represents the total

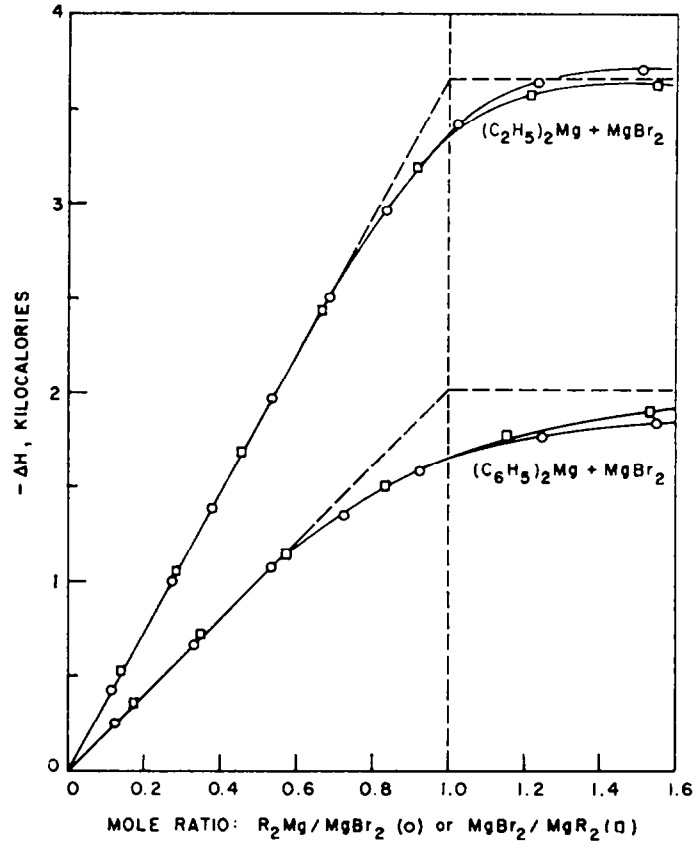

FIG. 1. Heat evolved on mixing 0·1M R_2Mg with 0·1M $MgBr_2$, both in ether, at 25°. Encircled points represent successive additions of R_2Mg to 1 mole $MgBr_2$. Square-enclosed points refer to successive additions of $MgBr_2$ to 1 mole R_2Mg.

heat evolved in kcal/mole R_2Mg plotted against total moles MgX_2 added. The reaction accompanying each mixing was complete within one minute and probably sooner (as shown by temperature–time curves).

For each of the four systems, the data for the two series of mixing experiments are well represented by a single curve up to at least 0·7:1 mole ratio. The slight separation which occurs as 1:1 mole ratio is approached is presumably due to experimental error. In addition, each curve is linear (within experimental error) up to at least 0·5:1 mole ratio, indicating almost complete conversion in the presence of a sufficient excess of either reactant. The slope of each curve decreases as 1:1 mole ratio is approached, showing that conversion to product is here incomplete.

When either reactant is present in excess, further addition of that reactant is accompanied by a negligible amount of reaction. These results indicate conclusively that for each system reaction occurs in 1:1 mole ratio and in no other ratio. As shown in

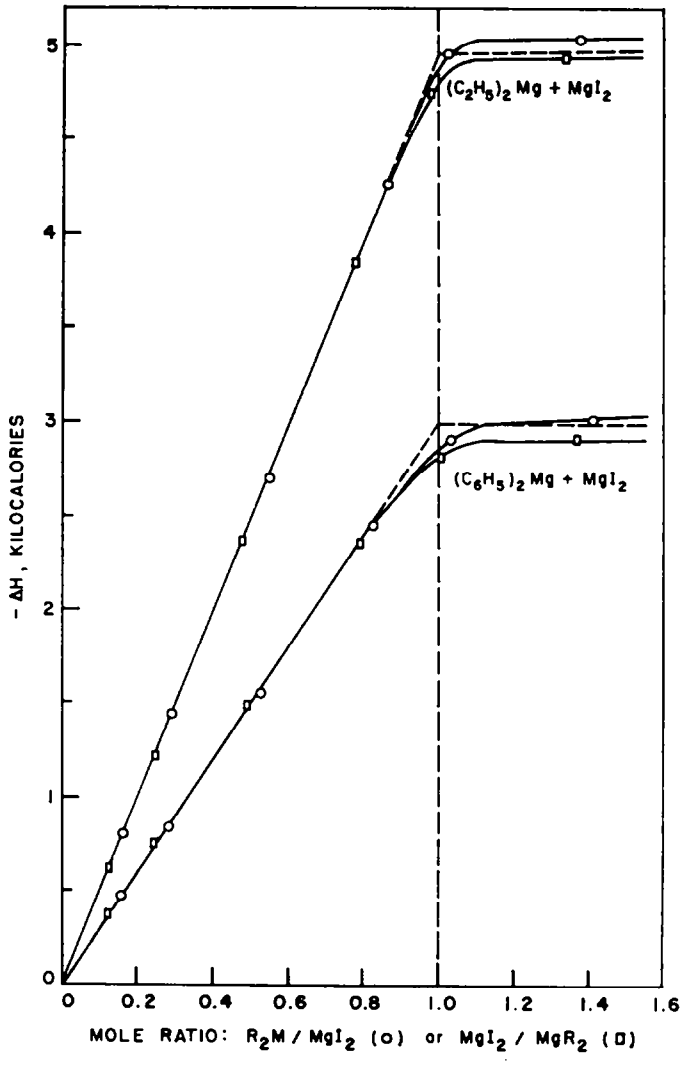

FIG. 2. Heat evolved on mixing 0·3M R_2Mg with 0·3M MgI_2, both in ether, at 25°. Encircled points represent successive additions of R_2Mg to 1 mole MgI_2. Square-enclosed points refer to successive additions of MgI_2 to 1 mole R_2Mg.

Table 1, heats of reaction ($-\Delta H$) at 1:1 mole ratio range from 4·86 kcal/mole reactant added for $(C_2H_5)_2Mg—MgI_2$ down to 1·66 for $(C_6H_5)_2Mg—MgBr_2$. Conversions at 1:1 mole ratio, calculated from these heats and from the corresponding heats at 100% conversion (dashed lines), range from 98% for $(C_2H_5)_2Mg—MgI_2$ down to 82% for $(C_6H_5)_2Mg—MgBr_2$. Evidently from 2 to 18% remains as unreacted $R_2Mg + MgX_2$ in equilibrium with product species.

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

R	X	Molarity	$-\Delta H$ at 1·0 mole ratio, kcal/mole R_2Mg Actual[a]	Theory[b]	% Conversion
C_2H_5	Br	0·1	3·34	3·64	91·8
C_6H_5	Br	0·1	1·66	2·02	82·2
C_2H_5	I	0·3	4·86	4·94	98·4
C_6H_5	I	0·3	2·83	2·99	94·6

[a] Average for the two solid curves, Fig. 1 or Fig. 2.
[b] Theoretical for 100% conversion (dashed line, Fig. 1 or Fig. 2).

TABLE 2. HEATS OF DILUTION IN ETHER

Compound	Molarity Initial	Final	Association factor,[a] i Initial	Final	ΔH (diln.), kcal/mole
$(C_2H_5)_2Mg$	0·100	0·020	1·01	1·00	−0·2
	0·300	0·059	1·18	1·00	−0·3
$(C_6H_5)_2Mg$	0·300	0·060	1·18	1·00	+0·1
$MgBr_2$	0·100	0·021	1·40	1·09	+0·3
	0·126	0·030	1·62	1·10	+0·4
MgI_2	0·300	0·059	2·72	1·14	+0·3
$(C_2H_5)_2Mg + MgBr_2$	0·100	0·019	1·04	1·00	0·0
$(C_2H_5MgBr)_G$	0·496	0·103	1·96	1·04	−0·2
$(C_2H_5)_2Mg + MgI_2$	0·300	0·061	1·62	1·01	0·0
$(C_6H_5)_2Mg + MgBr_2$	0·100	0·018	1·12	1·01	+0·2
$(C_6H_5)_2Mg + MgI_2$	0·300	0·061	1·75	1·06	+0·2
$(C_6H_5MgI)_G$	0·386	0·077	2·02	1·08	+0·2

[a] Taken from Fig. 3 or Fig. 4.

Heats of dilution of the reactant and product solutions are small (Table 2). It follows that the heat of the reaction between R_2Mg and MgX_2 per mole of either reactant converted varies only slightly with concentration. For example, application of the heats of dilution indicates that ΔH for the reaction of $(C_6H_5)_2Mg$ with MgI_2 is the same (−2·99 kcal/mole $(C_6H_5)_2Mg$ converted) at M = 0·06 as at M = 0·3. Values of $-\Delta H$ calculated for the four systems in dilute solution are included in Table 4. Many of the dilutions, including those of the Grignard reagents 0·496M $(C_2H_5MgBr)_G$[4] and 0·386M $(C_6H_5MgI)_G$, are accompanied by considerable dissociation, as shown by large decreases in i-factor.[5] In these instances, the measured heat is the sum of the heat of dilution and the heat of dissociation. However, the measured heats are also small when the decreases in i-factor are small (for example, in tetrahydrofuran solution[6]). It is therefore concluded that while the heat of dilution and the heat of dissociation may tend to cancel one another, both are relatively small for each of these substances.

[4] The Grignard reagent formed from RX and Mg is represented by the expression $(RMgX)_G$.
[5] The i-factor (or association factor) is the ratio of solute molecular weight to formula weight.
[6] Forthcoming publication.

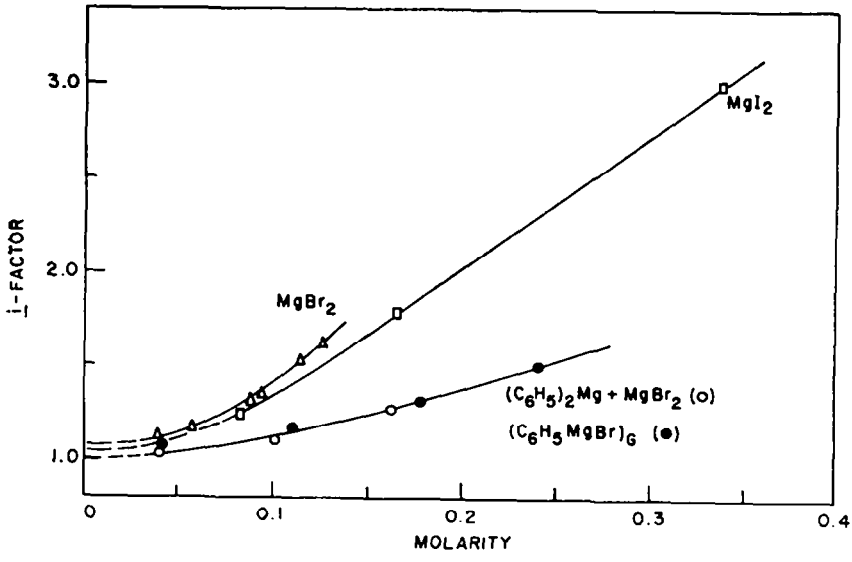

FIG. 3. Association factors for Mg compounds in ether at 35°. Values for $(C_6H_5MgBr)_G$ were taken from Ref. 1. Other values were determined experimentally as part of this investigation.

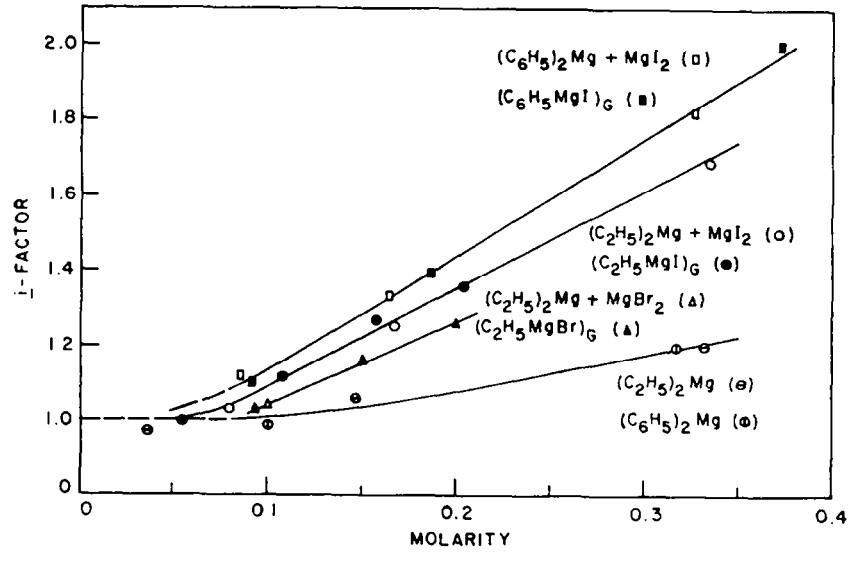

FIG. 4. Association factors for Mg compounds in ether at 35°. Values for $(C_2H_5MgBr)_G$ and $(C_2H_5MgI)_G$ were taken from Ref. 1. Other values were determined experimentally as part of this investigation.

Reactions at 0·1M *concentration*

On physical mixing (prior to reaction) of equal volumes of 0·1M R_2Mg (where R is C_2H_5 or C_6H_5) and 0·1M $MgBr_2$, the concentration of each reactant drops to 0·05M. The *i*-factors for 0·05M R_2Mg (1·00 when R is either C_2H_5 or C_6H_5, Fig. 4) and 0·05M $MgBr_2$ (1·15, Fig. 3) indicate that each reactant consists primarily of monomeric species. The *i*-factors determined after reaction has occurred (1·04 when R is C_2H_5 and

1·12 when R is C_6H_5) indicate that the reaction product also contains mostly monomeric species. In view of the high conversions, these monomeric species consist largely of monomeric reaction product together with a relatively small quantity of unreacted mixture. Since the amounts of ionic species present are very small,[7] the only possible monomeric reaction product of R_2Mg and $MgBr_2$ is $(RMgBr)_1$. *It follows that the principal species present in the* 0·1M *equimolar mixture is the monomeric species* $(RMgBr)_1$.

The principal reaction occurring when equal volumes of 0·1M R_2Mg and 0·1M $MgBr_2$ are mixed is then:

$$(R_2Mg)_1 + (MgBr_2)_1 \rightarrow 2(RMgBr)_1$$

Possible mechanisms for this reaction were discussed by Ashby and Smith[1] and will not be discussed further here. Secondary processes, all accompanied by negligible heat effects as discussed previously, include physical mixing, dissociation of most of the associated $MgBr_2$ into monomer, and association of a portion of the $(RMgBr)_1$.

Reactions at 0·3M *concentration*

On physical mixing (prior to reaction) of equal volumes of 0·3M R_2Mg (where R is C_2H_5 or C_6H_5) and 0·3M MgI_2, the concentration of each reactant drops to 0·15M. The *i*-factor for 0·15M R_2Mg (1·04 when R is either C_2H_5 or C_6H_5) shows that it is primarily monomeric. The *i*-factor for 0·15M MgI_2 (1·68), however, indicates that it contains substantial amounts of both monomeric and associated material. The *i*-factors determined after reaction has occurred (1·62 when R is C_2H_5 and 1·74 when R is C_6H_5) indicate that the reaction product also contains considerable quantities of both monomeric and associated materials. In view of the high conversions obtained, only a small portion of the monomeric species present in the reacted mixture is unreacted $(R_2Mg)_1 + (MgI_2)_1$. The major portion of these monomeric species is therefore monomeric reaction product which can only be $(RMgI)_1$.

As at 0·1M concentration, the principal reaction occurring at 0·3M concentration may be regarded as the following:

$$(R_2Mg)_1 + (MgI_2)_1 \rightarrow 2(RMgI)_1$$

Secondary processes, again accompanied by negligible heat effects, include physical mixing, extensive dissociation of associated MgI_2 into monomer, some dissociation of associated R_2Mg into monomer, and extensive association of $(RMgI)_1$.

Equilibrium constants

Degrees of polymerization (values of *m* and *n*) for the associated molecules $(RMgX)_m$ and $(MgX_2)_n$ are not known. It is not improbable that mixtures of dimeric, trimeric, and higher forms exist and that the average degree of polymerization increases with concentration. Certainly 0·35M MgI_2 ($i = 3·07$) contains a substantial amount of species that are at least trimeric. On the other hand, 0·1M MgI_2 ($i = 1·34$)

[7] For example, the degrees of ionization of both the 0·1M equimolar mixture $(C_2H_5)_2Mg + MgBr_2$ and the 0·1M Grignard reagent $(C_2H_5MgBr)_0$ were estimated as less than 0·01% from the conductivity data of Vreugdenhil and Blomberg.[8]

[8] A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.* **83**, 1096 (1964).

may contain only monomeric and dimeric species. If values are assumed for m and n in the reacted mixture $R_2Mg + MgX_2$, one can calculate the molar concentrations of $(R_2Mg)_1$, $(MgX_2)_1$ and $(RMgX)_1$ from the total molarity (0·1 or 0·3), the percent conversion, the i-factor for the mixture and the i-factor for MgX_2 at the final concentration. One can then calculate the equilibrium constant $K = [(RMgX)_1]^2/[(R_2Mg)_1][(MgX_2)_1]$, activities being assumed equal to molar concentrations.

Since the i-factors for MgX_2 at the final concentration did not exceed 1·07, the value of n was taken as 2 (that is, MgX_2 was assumed to be a mixture of monomer and dimer only). Values of K calculated for $m = 2$ and $m = 3$ are given in Table 3.[9] For each of the two systems studied at 0·1M concentration, the two values of K do not differ significantly. The equilibrium constants for these systems are therefore well established. For each system studied at 0·3M concentration, however, the two values of K differ markedly. For these systems, therefore, the equilibrium constants are uncertain. One can only say with certainty that they exceed 630 and 14·6, respectively. Values of the percent of the monomeric species that are present as $(RMgX)_1$ are also given in Table 3. Since the reaction between R_2Mg and MgX_2

TABLE 3. EQUILIBRIUM CONSTANTS FOR THE REACTION
$R_2Mg + MgX_2 \rightarrow 2RMgX$

R	X	Molarity M	i	For $(RMgX)_m$ = Dimer M of $(RMgX)_1$	% Monomer as $(RMgX)_1$	K
C_2H_5	Br	0·100	1·04	0·0846	91·7	480
C_6H_5	Br	0·100	1·12	0·0618	78·7	55
C_2H_5	I	0·300	1·62	0·0653	92·6	630
C_6H_5	I	0·300	1·74	0·0294	65·6	14·6

R	X	Molarity M	i	For $(RMgX)_m$ = Trimer M of $(RMgX)_1$	% Monomer as $(RMgX)_1$	K
C_2H_5	Br	0·100	1·04	0·0864	91·7	484
C_6H_5	Br	0·100	1·12	0·0670	79·7	62
C_2H_5	I	0·300	1·62	0·123	95·9	2230
C_6H_5	I	0·300	1·74	0·0932	85·9	146

involves no change in the total number of molecules, % monomer as $(RMgX)_1$ should be independent of the concentration. Thus, at any concentration, the monomeric species contained in the equimolar mixture $(C_2H_5)_2Mg + MgBr_2$ should consist of 91·7% $(C_2H_5MgBr)_1$ and 8·3% unreacted $[(C_2H_5)_2Mg]_1 + (MgBr_2)_1$.

Thermodynamic values

Thermodynamic values for the reaction between R_2Mg and MgX_2 in dilute ether solution are given in Table 4. The values of K used for the first two systems are those derived with $m = 2$ (K's based on $m = 3$ or higher would give similar results). The values of K used for the last two systems are based on $m = 3$ (this is a "best guess" since the actual "average m" may be 2, 3, or higher). Free energies were

[9] In taking $m = 3$, it is assumed that the associated RMgX molecules are all trimers. This is equivalent to assuming that some of the associated molecules are dimeric, some trimeric, some tetrameric, etc., and that the (suitably weighted) average degree of polymerization is three.

TABLE 4. THERMODYNAMIC VALUES FOR THE REACTION $R_2Mg + MgX_2 \rightarrow 2RMgX$ IN DILUTE ETHER SOLUTION

R	X	M	K	Per mole R_2Mg $-\Delta F$, cal	$-\Delta H$, cal	ΔS, e.u.
C_2H_5	Br	0·02	480	3660	3740	−0·3
C_6H_5	Br	0·02	55	2370	2020	+1·2
C_2H_5	I	0·06	2230[a]	4570[a]	4940	−1·2[a]
C_6H_5	I	0·06	146[a]	2960[a]	2990	−0·1[a]

[a] These uncertain values are based on the assumption that the average degree of polymerization of associated RMgX molecules is three.

calculated from the K's using the relation $\Delta F = -RT \ln K$ since the reaction involves no change in the total number of molecules. Entropy changes were calculated from the equation $\Delta F = \Delta H - T\Delta S$. Although the ΔS values for the last two systems are rather uncertain, the results justify the conclusion that, in ether, the entropy change for the reaction $(R_2Mg)_1 + (MgX_2)_1 \rightarrow 2(RMgX)_1$ is small in magnitude (about 0 ± 2 cal/deg mole R_2Mg). In tetrahydrofuran, the entropy change for the reaction is markedly different.[6]

Equivalence of Grignard reagent with equimolar mixture

For each of the four systems, the *i*-factor for the Grignard reagent is indistinguishable from that of the corresponding equimolar mixture at every concentration studied (Figs. 3 and 4). It therefore seems highly probable that, within the scope of these experiments, the Grignard reagent is essentially equivalent[10] to the corresponding equimolar mixture. Thus at 0·1M concentration, the *i*-factor for each Grignard reagent indicates that it contains primarily monomeric species. These monomeric species may consist only of unreacted $(R_2Mg)_1 + (MgX_2)_1$ or $(RMgX)_1$ or both (since ionic species can be present in only very small concentrations[7]). It has been shown that in the equimolar mixture, the amounts of these species are governed by the following equilibrium which lies strongly to the right:

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

Since this same equilibrium would be expected to apply in the case of the Grignard reagent, the monomeric species existing in the latter must have the same composition as those existing in the equimolar mixture. Associated species existing in the Grignard reagent would also be expected to have the same composition as those in the equimolar mixture since, in each case, the associated species are in equilibrium with the same monomeric species. The reversible nature of this aggregate formation was confirmed by the careful conductivity measurements of Vreugdenhil and Blomberg.[8] The argument is similar at 0·3M concentration except that the quantities of associated species are much higher so that monomeric species do not necessarily predominate.

DISCUSSION

Earlier investigations concerned with reaction between R_2Mg and MgX_2 in ether include the IR spectral studies of Salinger and Mosher.[11] The IR spectrum of $(C_6H_5MgI)_G$ was found to be identical to that of equimolar $(C_6H_5)_2Mg + MgI_2$, while both were noticeably different from $(C_6H_5)_2Mg$ alone. It was concluded that

[10] Except, of course, for minor differences due to dissimilarities in nature and amounts of impurities.

the following reaction is fast, with the equilibrium lying strongly to the right:

$$(C_6H_5)_2Mg + MgI_2 \rightleftarrows 2C_6H_5MgI$$

The identity of the spectra of the Grignard reagent and the equimolar mixture was shown to support the conclusion that the same species exist in both solutions. Similarly, Roos and Zeil[12] found that NMR spectra of Grignard compounds at various concentrations in ether were identical with the spectra of the corresponding equimolar mixtures. Dessy[13] concluded from dielectric constant measurements that $(C_2H_5)_2Mg$ reacts rapidly with $MgBr_2$ in 1:1 mole ratio. At each of the concentrations (0·25 and 0·50M), the dielectric constant value for $(C_2H_5MgBr)_G$ was identical with that measured for the corresponding equimolar mixture and higher than the sum calculated from the values for the individual components. Wotiz *et al.*[14] found that, in reactivity toward hexyne-1, 1M $(C_2H_5MgBr)_G$ behaved identically with the corresponding equimolar mixture. These results all agree with the results of the present investigation, as well as with conclusions drawn by Ashby and Smith.[1]

Vreugdenhil and Blomberg[2] reported association factors of $1·00 \pm 0·02$ for $(C_2H_5MgBr)_G$ and 1·05–1·06 for $(C_2H_5)_2Mg + MgBr_2$ at concentrations of 10^{-3} to 10^{-2}M in ether. An *i*-factor of 1·06 should have been obtained for the equimolar mixture if only physical mixing occurred. If these small differences in *i*-value are considered significant, the data indicate that little, if any, reaction occurred between $(C_2H_5)_2Mg$ and $MgBr_2$ and that the equimolar mixture was not equivalent to the Grignard reagent at these low concentrations. In a later paper,[8] these authors reported electrical conductivities of $(C_2H_5MgBr)_G$, $(C_2H_5)_2Mg$, and $(C_2H_5)_2Mg + MgBr_2$ for the range 0·05–3·0M and $MgBr_2$ up to 0·074M. Extreme precautions were taken to prevent contamination with oxygen and moisture during all stages of the work. Of the materials tested, $MgBr_2$ was by far the most conductive and $(C_2H_5)_2Mg$ by far the least, with $(C_2H_5MgBr)_G$ and $(C_2H_5)_2Mg + MgBr_2$ intermediate in conductivity. These results show clearly that the concentration of $MgBr_2$ in the mixture $(C_2H_5)_2Mg + MgBr_2$ was very small, hence that extensive reaction occurred at every concentration tested. This conclusion conflicts with the indication from the *i*-values, although applying to a higher concentration range, and is consistent with the results of the present investigation. In plots of molar conductance vs. concentration, the curve for the Grignard reagent has nearly the same shape as the curve for the corresponding mixture and lies somewhat below it. The considerable resemblance of the curves over the entire concentration range of 0·05–3M would seem to indicate that $(C_2H_5MgBr)_G$ is probably equivalent to $(C_2H_5)_2Mg + MgBr_2$. The authors concluded that the observed difference in conductivity between Grignard reagent and corresponding mixture was significant up to 0·4M but not from 0·4M to 3·0M.

We are conducting similar studies in other solvents including tetrahydrofuran.

EXPERIMENTAL

Materials. Precautions were taken to minimize exposure of all materials to O_2 and moisture. Raw materials and prepared solutions were stored in a dry N_2 box and the containers opened only inside the box. Some of the preparative reactions were conducted inside the box, others outside under dry N_2. Solutions were transferred into the dry, N_2-purged calorimeter with hypodermic syringes. The transfer of solutions into the dry, N_2-filled mol. wt. apparatus was made inside the box.

[11] R. M. Salinger and H. S. Mosher, *J. Amer. Chem. Soc.* **86**, 1782 (1964).
[12] H. Roos and W. Zeil, *Ber. Bunsenges. Physik. Chem.* **67**, 28 (1963).
[13] R. E. Dessy, *J. Org. Chem.* **25**, 2260 (1960).
[14] J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *J. Org. Chem.* **21**, 1063 (1956).

Diethyl ether was reagent-grade and was distilled over LAH in N_2 atmos. just prior to use. Domal high purity sublimed Mg granules (Dominion Magnesium Co., Ltd., Haley, Ont.) were used without purification.

Et_2Mg and diphenyl-Mg were prepared by reacting R_2Hg with a large excess of Mg in ether in a sealed tube at 100°. The products, shown to be free of R_2Hg by testing with dithizone, were analysed for Mg content by hydrolysing and titrating with standard acid. Separate portions of each solution were diluted to 0·100M and to 0·300M.

$MgBr_2$ was prepared by reacting ethylene bromide with a slight excess of Mg in ether. MgI_2 was prepared by adding elemental I_2 in small increments to Mg in ether. Grignard reagents were prepared in ether by conventional methods from Mg and purified alkyl or aryl halide. The products were analysed for halogen by the Volhard method and for Mg by Versene titration. With the exception of $(C_6H_5MgI)_O$, which contained 3·5% excess MgI_2, the molarities calculated from the halogen and magnesium analyses agreed within 1%.

Thermochemical measurements. The calorimeter consisted of a 180-ml, 3·4-cm (inside diameter) clear borosilicate glass Dewar fitted with a rubber stopper. A 10-ml bulb for the inner liquid had a capillary side-arm leading from the bottom of the bulb to just above the outer liquid surface. The neck of the bulb extended through a Teflon sleeve mounted in the stopper to a point somewhat above the stopper. A short piece of rubber tubing around the bulb neck and stretched over the top of the sleeve provided a tight seal and yet allowed the bulb to be moved up or down as needed. A length of rubber tubing led from the top of the bulb neck to a hypodermic syringe. The N_2-filled syringe was used to control the level of the inner liquid in the side-arm and later to discharge the liquid into the outer liquid. Temps were read to the nearest 0·001° with a Pt resistance thermometer (mounted tightly in the stopper) in conjunction with a G-2 Mueller Bridge and a Leeds and Northrup 9834 Electronic Null Detector. Stirring was magnetic using a Teflon-covered bar. A slight positive N_2 pressure was applied to the Dewar through a hypodermic needle which penetrated the stopper. The Dewar and a glass shell surrounding it (except at the top) were mounted in a larger beaker filled with water maintained at the desired temp (this minimized the effects of drafts and changes in room temp). The heat capacity of the calorimeter was evaluated by cooling it to a steady temp somewhat below ambient, introducing a measured quantity of n-undecane[15] at a known temp near ambient, and measuring the equilibrium temp. A plot was made of calorimeter heat capacity (corrected to 25°) vs. liquid volume.

Prior to an experiment, the clean apparatus was heated and allowed to cool under a N_2 flush. With the bulb in a raised position, about 35 ml of outer liquid was introduced into the bottom of the calorimeter with a syringe. The wt. of liquid was determined by weighing the syringe before and after the addition. The desired volume of inner liquid (up to 10 ml) was similarly transferred to the bulb and its wt. determined. The rubber tube, plugged during sample addition, was re-connected to the bulb neck and the liquid level in the side-arm adjusted with the syringe. The bulb was lowered until the opening of the side-arm was just above the level of the outer liquid and stirring was begun. When thermal equilibrium had been achieved (rate of temp change 0·002° per min or less), the inner liquid was forced out of the bulb with the syringe and allowed to mix with the outer liquid. The temp rise (or fall) for the experiment was determined from a temp–time plot. The heat liberated (or absorbed) was calculated from the temp change, the heat capacity of the calorimeter, and the heat capacity of the final solution (taken as the heat capacity of an equal volume of pure ether), and a "blank correction" applied. The "blank correction" (made necessary because of vaporization of ether during the emptying of the bulb) was measured by repeating the experiment using the final solution as both inner and outer liquid. When the volume of liquid reached the maximum desired for effective stirring (usually about 55 ml) during a series of additions of inner liquid, a portion of the solution (usually about 10 ml) was withdrawn and weighed before making the next addition.

Molecular weight determinations. Mol. wts were determined ebullioscopically in a closed system at 760·0 mm with a standard Cottrell b.p. apparatus modified to accommodate a Pt resistance thermometer. The condenser, which was cooled with ice-water, was connected through a manifold to a Wallace-Tiernan precision manometer, a surge tank, a source of dry N_2, and a vacuum pump.

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[15] The specific heat of n-undecane was taken from: H. L. Finke, M. E. Gross, G. Waddington and H. M. Huffman, *J. Am. Chem. Soc.* **76**, 333 (1954).