The Composition of Grignard Compounds. VI. The Nature of Association in Tetrahydrofuran and Diethyl Ether Solutions[1]

Frank W. Walker[2] and E. C. Ashby[3]

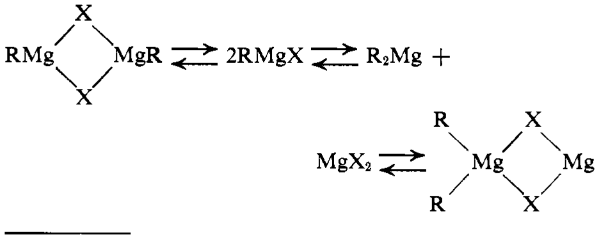
Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received September 15, 1968*

Abstract: Ebullioscopic data are presented for tetrahydrofuran and diethyl ether solutions of several Grignard and related magnesium compounds over a wide concentration range. Analysis of the data is accomplished by observing the change in association (i) with concentration and by consideration of the constancy of the equilibrium constants calculated for several possible descriptions of the associated system. The expected nonideality of the solutions studied was considered in the interpretation of the data. While all the compounds studied were found to be monomeric in tetrahydrofuran, the alkyl- and arylmagnesium bromides and iodides were found to be monomeric in diethyl ether only at low concentration (<0.1 m), exhibiting in general an increase in association with concentration. Interpretation of the data indicates that these compounds are associated in a polymeric fashion. In contrast the alkylmagnesium chlorides associate in diethyl ether to form stable dimers with the association insensitive to concentration changes. Comparison of the data for magnesium halides and dialkylmagnesium compounds in diethyl ether indicates that, except for the methyl compound, association is considerably stronger for the magnesium halides than for the dialkylmagnesium compounds. Thus, except for methylmagnesium halides, Grignard compounds associate with bridging mainly through the halogen atom. The methylmagnesium halides are exceptional since methyl bridging is strong enough in diethyl ether to permit association by bridging through either the methyl group or the halogen atom. Although the steric and electronic nature of the alkyl group has some effect on the association of Grignard compounds, the effect is generally small compared to the effect of halogen or solvent.

The Schlenk equilibrium (eq 1) is generally accepted as an adequate description of the basic composition

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

of Grignard compounds in polar solvents.[4] Solutions of magnesium compounds have been found to be monomeric either in dilute diethyl ether solution[5] or when complexed to solvents that are stronger Lewis bases than diethyl ether such as tetrahydrofuran[6] or tertiary amines.[7] However, results of recent molecular weight studies at higher concentrations in diethyl ether[5a,8] have been interpreted as indicating association of Grignard compounds to forms higher than the monomer (eq 2).



(2)

Clearly, many aspects of Grignard compound composition are not as yet resolved. For example, in tetrahydrofuran the number of compounds studied is quite small and therefore the general applicability of eq 1 for describing the degree of aggregation in tetrahydrofuran solutions as monomeric has not been clearly established. Even for the more commonly studied compounds (*e.g.*, ethylmagnesium bromide), there are conflicting reports on the degree of solute association in tetrahydrofuran.[6b,9]

Diethyl ether solutions have been examined in a little more detail. In diethyl ether, alkylmagnesium chlorides have been described as dimeric even at low concentrations[5a,10] while the alkyl- and arylmagnesium bromides and iodides are described as monomeric at low concentration (<0.1 m),[5] exhibiting increased association with concentration.[5a,8] However it is not known if the bromides and iodides associate in the same manner to some stable form (dimer, trimer, tetramer, polymer, etc.) or if the nature of the hydrocarbon portion of the Grignard compounds plays a major role in determining either the degree of association or the form the molecular aggregates assume in solution. Furthermore, it is not clear how the association occurs, whether by alkyl (aryl) bridges, halogen bridges, or a combination of the two.

Finally, deviations from ideal behavior (aside from that due to association of the solute) encountered in diethyl ether and tetrahydrofuran solutions must be considered and properly interpreted. Although the danger in attributing all of the increase in molecular weight to association without due regard for these deviations is well known,[11] this matter has received

---

[1] Initial communication of this work appeared in *J. Organometal. Chem.* (Amsterdam), 7, 17 (1967). This work was presented in part at the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1, 1967.

[2] Taken from a thesis submitted in partial fullfilment of the requirements for the degree of Doctor of Philosophy.

[3] To whom all inquiries should be sent.

[4] (a) E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967); (b) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966).

[5] (a) E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964); (b) A. D. Vreugdenhill and G. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).

[6] (a) M. B. Smith and W. E. Becker, *Tetrahedron*, **23**, 4215 (1967); (b) E. C. Ashby and W. E. Becker, *J. Am. Chem. Soc.*, **85**, 118 (1963); (c) A. D. Vreugdenhill and C. Blomberg, *Rec. Trav. Chim.*, **82**, 461 (1963).

[7] (a) E. C. Ashby, *J. Am. Chem. Soc.*, **87**, 2509 (1965); (b) G. E. Coates and J. A. Heslop, *J. Chem. Soc., A*, 26 (1966); (c) D. F. Evans and M. S. Khan, *ibid.*, 1648 (1967).

[8] (a) M. B. Smith and W. E. Becker, *Tetrahedron*, **22**, 3027 (1966); (b) W. Slough and A. R. Ubbelohde, *J. Chem. Soc.*, 108 (1955).

[9] H. Hashimoto, T. Nakano, and H. Ikada, *J. Org. Chem.*, **30**, 1234 (1965).

[10] G. M. Whitesides, F. Kaplan, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1112 (1962).

[11] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1950.

little attention in the past.[12] In an attempt to clarify these issues, a comprehensive ebullioscopic study of a series of Grignard and related compounds over a wide concentration range in tetrahydrofuran and diethyl ether has been made and the data have been evaluated with special emphasis concerning the ideality of the solutions studied.

Experimental Section

Diethyl ether was distilled from lithium aluminum hydride and tetrahydrofuran from sodium aluminum hydride, through a 2-ft packed column under dry oxygen-free nitrogen. The alkyl and aryl halides were dried over Na_2CO_3 prior to distillation through an 18-in. packed column under nitrogen. Ether-washed triply sublimed magnesium was employed in all of the preparations. The reaction systems were dried by flaming under vacuum and refilling with nitrogen; all preparations were then carried out under a nitrogen blanket. The reaction solutions were opened for sampling in a glove box equipped with a recirculating system that assured a dry and oxygen-free atmosphere.[13] All solutions were analyzed for magnesium by titration with EDTA; solutions of the Grignard compounds and magnesium halides were analyzed for halogen by the Volhard method.

Preparation of the Grignard Compounds. The Grignard compounds were prepared in 500-ml, round-bottomed, one-necked flasks containing a 10–100% excess of magnesium and a magnetic stirring bar. Gaseous halides were first passed through a tube of NaOH and drying agent (molecular seive 4 A) and then introduced into the reaction vessel through a side arm at the bottom of a Dry Ice condenser. The condenser was connected to the reaction vessel *via* a Claissen adapter with a parallel side arm which held an addition funnel containing 400 ml of ether. Liquid halides were added *via* an addition funnel which was connected to the reaction vessel by two Claissen adapters with parallel side arms. The other two arms held an addition funnel with 400 ml of ether and a water-cooled condenser.

The reactions were initiated by adding 50 ml of ether and a small portion of the halide. In each case the reaction started either spontaneously or after gentle warming; in no case was it necessary to add any kind of initiator. Enough halide was added in each case to prepare a 1 *M* solution. The products were concentrated by vacuum distilling the solvent at room temperature using a simple distillation apparatus with a Dry Ice–acetone-cooled receiver. The final solutions, which were *clear and colorless* (except for the arylmagnesium halides which were slightly colored), were not separated from the unreacted magnesium but were sampled directly from the reaction vessel. Samples of the solutions were hydrolyzed in ampoules containing either benzene or diethyl ether to trap the released hydrocarbons. The organic layers were analyzed by glpc and the yield of Grignard was consistently greater than 96%. The other material in solution consisted of a mixture of unreacted starting material and coupling product.

Preparation of the Dialkyl- and Diarylmagnesium Compounds. The preparation of these compounds has already been described;[14] the solutions were concentrated and sampled in the same manner as the Grignard compounds.

Preparation of the Magnesium Halides. The preparation of the magnesium halides has been described elsewhere.[14b] Studies with magnesium bromide prepared either by bromine addition to magnesium or by exchange between mercuric bromide and magnesium produced identical molecular weight data.

Ebullioscopic Determination of Molecular Weights. A complete description of the apparatus and its operation has been presented elsewhere.[15] The association studies were carried out in either diethyl ether or tetrahydrofuran at a pressure of 740.0 mm. No stem correction for the thermometer was made since only a small portion of the thermometer was exposed. The entire apparatus was wrapped with insulating material to avoid heat loss. No correction was made for 1–1.5% coupling products (R–R + MgX_2) present in some Grignard solutions.

Calculations. Equation 3 was derived from the Clapeyron–Clausius relationship with the assumption of an ideal but not necessarily a dilute solution. The terms are defined as

$$X_E = 1 - e^{-\Delta T_B M_1/1000K_B} \tag{3}$$

X_E, mol fraction of solute; ΔT_B, boiling point elevation; M_1, molecular weight of solvent; and K_B, the molal boiling point elevation constant (2.01 for diethyl ether at 740.0 mm; 2.20 for tetrahydrofuran at 740.0 mm). The use of this extended equation for the calculations was necessitated by the high solute concentrations which invalidate a number of dilute solution approximations[16] employed in the derivation of simpler relationships.

The results are calculated in terms of solute association expressed as an *i* value; the *i* value is defined as the molecular weight of a single solute species, which would give a boiling point equivalent to that observed experimentally, divided by a calculated formula weight. The relationship employed is shown by eq 4 and the additional terms include W_2, grams of solute; W_1, grams of solvent;

$$i = \frac{W_2M_1}{W_1M_2}\left(\frac{1}{e^{-\Delta T_B M_1/1000K_B} - 1}\right) \tag{4}$$

and M_2, the calculated formula weight of solute.

The computation of the formula weight of the solute (M_2) deserves further comment since there is the complicating feature of complexation between solute and solvent. This complexation in solution has been demonstrated in a number of ways, including the use of spectral techniques[17] and the use of optically active ethers.[18] While it is clear that the complexed solvent molecules should be included as an integral part of the formula weight,[4b] what is not known is the extent to which the solute molecules are solvated in solution. This becomes very important since the degree of solvation chosen in calculating the formula weight has a direct effect on the *i* values. If too little solvent is ascribed to the solute, the amount of free solvent (solvent molecules not complexed to solute molecules) is too high and the resulting *i* values will be lower than the correct values. Conversely, if too much solvent is included with the solute in computing the formula weight, the calculated value of *i* is higher than the correct value.

There is ample information available on the degree of complexation of solvent with solute *in the solid state*. The complexes with tetrahydrofuran, diethyl ether, and tertiary amines have been characterized[7,19] as monosolvates through hexasolvates; the degree of complexation apparently varies with the solvent and the identity of the magnesium compound. However, it is not clear that the degree of solvation *in solution* can be deduced from the extent of complexation in the solid state.

In the few instances where solvation data are available for solutions there is no agreement on the degree of solvation since similar magnesium compounds complexed with tetrahydrofuran have been characterized as both monoetherates[20] and dietherates.[21] Logically, one might suggest that the monomers are dietherates (tetracoordinate magnesium) and that association occurs with concurrent displacement of a solvent molecule by the bridging group to form monosolvated multimers (tetracoordinate magnesium). However, it is possible that dissolvated monomers (tetracoordinate magnesium) associate to dissolvated multimers if the magnesium atoms were pentacoordinate, as recently suggested[22] for dimethylmagnesium in its reaction with benzophenone.

Since the choice of the degree of solvation is somewhat arbitrary at this point, it is important to compare the results obtained when different formula weights are used. Figure 1 shows that the selec-

---

[12] H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

[13] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).

[14] (a) E. C. Ashby and F. W. Walker, *J. Org. Chem.*, **33**, 3821 (1968); (b) E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.* (Amsterdam), **14**, 1 (1968).

[15] F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, **45**, 654 (1968).

[16] For a detailed examination of this matter, see L. J. Sacks, *ibid.*, **45**, 183 (1968).

[17] (a) T. Holm, *Acta Chem. Scand.*, **19**, 1819 (1965); (b) R. M. Salinger and H. S. Mosher, *J. Am. Chem. Soc.*, **86**, 1782 (1964); (c) R. Hamelin and S. Hayes, *Compt. Rend.*, **252**, 1616 (1961).

[18] P. Vink, C. Blomberg, A. D. Vreugdenhill, and F. Bickelhaupt, *Tetrahedron Letters*, 6419 (1966).

[19] (a) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963); (b) G. D. Stucky and R. E. Rundle, *ibid.*, **86**, 4825 (1964); (c) L. J. Guggenberger and R. E. Rundle, *ibid.*, **86**, 5344 (1964); (d) J. Toney and G. D. Stucky, *Chem. Commun.*, 1168 (1967).

[20] (a) C. A. Hollingsworth, E. W. Smalley, and S. K. Podder, *Inorg. Chem.*, **3**, 222 (1964); (b) L. V. Guild, C. A. Hollingsworth, D. H. McDaniel, and S. K. Podder, *ibid.*, **1**, 921 (1962).

[21] T. Holm, *Acta Chem. Scand.*, **20**, 1139 (1966).

[22] H. O. House and J. E. Oliver, *J. Org. Chem.*, **33**, 929 (1968).

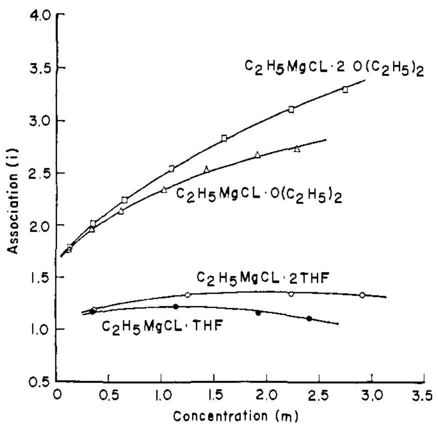


Figure 1. Demonstration of the effect of calculating association of Grignard compounds in diethyl ether and tetrahydrofuran based on mono- or disolvation.

tion of the formula weight of the solute has only a small influence on the *i* values in dilute solution, although the differences in the *i* value curves are magnified somewhat at higher concentrations. However, the relative positions of the *i* value curves for the various compounds are unchanged by the choice of formula weight. This observation, coupled with the insensitivity of the *i* value curves to the formula weight in dilute solution, means that the arguments, which are based on a comparison of the *i* value curves for the various compounds, are valid regardless of the degree of solvation. *Therefore, the formula weight of the solute as a monoetherate has been chosen for the computation of the i values.* It is felt that this is the best compromise since a monoetherate represents the minimum degree of solvation and therefore all of the compounds will be solvated at least to this extent.

Equilibrium constants were calculated from the association data by using equations derived[23] for model association systems.[24] The basic assumption made in deriving these equations is that the apparent molecular weight is solely a function of association of the solute without any contribution by deviations from ideality. Model I assumes a polymeric association with the same equilibrium constant for each step. Model II is based on the assumption of monomer in equilibrium with a single associated form; the data were analyzed for systems ranging from monomer:dimer ($n = 2$) through monomer:hexamer ($n = 6$).

Model I

$$\mathrm{A}_n + \mathrm{A}_1 \rightleftarrows \mathrm{A}_{n+1}$$

$$K_1 = \frac{X_\mathrm{S} - X_\mathrm{E}}{X_\mathrm{E}^2}$$

Model II

$$n\mathrm{A} \rightleftarrows \mathrm{A}_n$$

$$K_n = \frac{(X_\mathrm{S} - X_\mathrm{E})(n - 1)^{n-1}}{(nX_\mathrm{E} - X_\mathrm{S})^n}$$

The term X_S is the stoichiometric mole fraction of solute (based on the formula weight of the solute and the actual concentration in solution) and X_E, the experimental mole fraction, is given by eq 3. *All equilibrium constant calculations were made using both the monoetherate and the dietherate forms as the formula weight of solute* and were computed for the entire concentration range.

The assumption of ideal behavior inherent in the derivations means that the equilibrium constants calculated from the data in dilute solution will have greater validity than those calculated for the more concentrated solutions. Therefore, in addition to examining the consistency of the equilibrium constants calculated for all concentrations, particular attention was paid to the constancy of the values in the more dilute range. Generally it was found that if the equilibrium constants for a particular model were consistent in dilute solution, then they were reasonably consistent over-all and that model was chosen as the best description of the system.

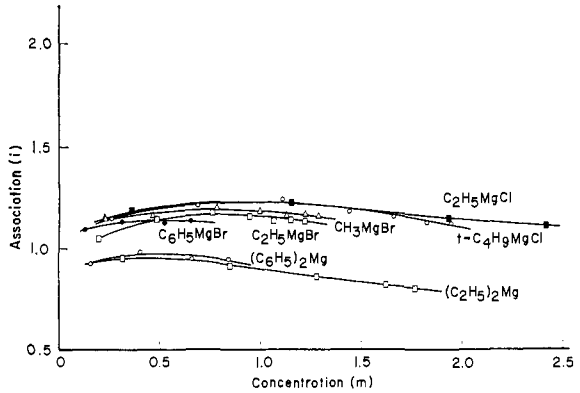


Figure 2. Association of several Grignard compounds in tetrahydrofuran.

Results and Discussion

Composition of Grignard Compounds in Tetrahydrofuran. Figure 2 shows the association expressed as an *i* value (apparent molecular weight divided by the formula weight) plotted against monoetherate solute concentration (molality) for selected Grignard and related compounds in tetrahydrofuran. The *i* value curves are clustered around the monomer value ($i = 1.0$) and display a small concentration-dependent line curvature. The lack of significant curvature argues against an equilibrium-type association since the *i* values would be expected to increase with concentration. Further, the *i* values for an equilibrium-type association would be expected to show a noticeable temperature effect. However, the *i* values reported here agree well with those reported at lower temperatures[6a] and a study of the same solution at two different temperatures[6b,c] failed to reveal any temperature effect. Although there appears to be no evidence for an equilibrium system of association, the solute could possibly form a stable multimer, *e.g.*, dimers, with the observed *i* values reflecting large negative deviations of the solutions from ideality; such behavior is not unreasonable for systems of this type.[11] However, dimer formation is not compatible with the fact that the *i* value curves all extrapolate with reasonable accuracy to an *i* value of 1. Since deviation from ideal behavior would be at a minimum at high dilution, an extrapolated *i* value of 2 would be expected for a solution of stable dimers. Finally, spectroscopic studies[18b] have been unable to find any evidence that magnesium compounds associate to any form in tetrahydrofuran solution. Therefore, all evidence clearly favors the interpretation that Grignard and related magnesium compounds are monomeric in tetrahydrofuran and that the observed slight departure of the *i* value curves from the ideal monomer value is due to deviation from ideal behavior.

Composition of Grignard Compounds in Diethyl Ether. a. Alkylmagnesium Chlorides. The *i* value curves for the alkylmagnesium chlorides in diethyl ether (Figure 3) extrapolate to an *i* value much greater than 1 at high dilution, a result unlike that observed in tetrahydrofuran. The fact that the *i* values do not

---

[23] The derivation of these relationships for use with vapor pressure osmometry data has been presented by E. E. Schrier, *J. Chem. Educ.*, 45, 176 (1968).

[24] (a) For examples of the use of similar models for studies with other systems, see P.O.P. Ts'o, I. S. Melvin, and A. C. Olson, *J. Am. Chem. Soc.*, **85**, 1289 (1963); (b) M. Davies and D. K. Thomas, *J. Phys. Chem.*, **60**, 763, 767 (1956).

Table I. Equilibrium Constants Calculated for *t*-Butylmagnesium Chloride in Diethyl Ether[a]

X_S	X_E	K_1	K_2	K_3	K_4	K_5	K_6
0.00725	0.00390	220.0	1.10×10^4	152.0×10^3	615.0×10^4	2.25×10^{-8}	4.38
0.0205	0.0104	93.2	9.57×10^4	32.7×10^3	45.5×10^4	518.0×10^4	13.2×10^6
0.0372	0.0184	55.4	13.6×10^4	12.8×10^3	9.59×10^4	60.6×10^4	5.87×10^{-2}
0.0575	0.0283	36.5	3.55×10^4	5.68×10^3	2.73×10^4	11.2×10^4	28.9×10^6
0.0750	0.0367	28.5	1.42×10^4	3.56×10^3	1.30×10^4	4.09×10^4	4.86×10^6
0.0819	0.0398	26.6	0.794×10^4	3.19×10^3	1.06×10^4	3.06×10^4	2.87×10^6
0.0963	0.0469	22.4	0.798×10^4	2.26×10^3	0.639×10^4	1.57×10^4	0.896×10^6
0.1113	0.0545	19.1	1.06×10^4	1.60×10^3	0.395×10^4	0.835×10^4	0.303×10^6
0.1238	0.0610	16.9	1.99×10^4	1.21×10^3	0.270×10^4	0.514×10^4	0.132×10^6

[a] K_1 = equilibrium constant for polymeric association model; K_2 = equilibrium constant for monomer $\rightleftarrows$ dimer model; K_3 = equilibrium constant for monomer $\rightleftarrows$ trimer model, etc.

extrapolate to a value near 1 is not compatible with an equilibrium-type association. Further, the extrapolated *i* value argues against solutions of monomers or stable trimers displaying deviations from ideality. The best conclusion is that the alkylmagnesium chlorides in diethyl ether are essentially completely dimerized over the entire concentration range.

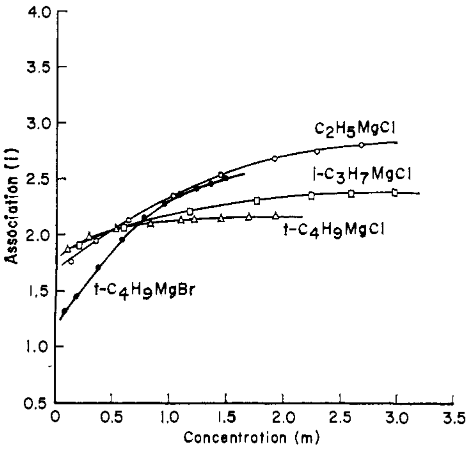


Figure 3. Association of alkylmagnesium chlorides in diethyl ether. Demonstration of importance of halogen *vs.* R group in determining the form of association in diethyl ether.

These conclusions are in harmony with the results obtained by calculating equilibrium constants with equations derived for model association systems. The data for all of the alkylmagnesium chlorides in diethyl ether were tested and were found to fit neither a polymeric association model (model I) nor a monomer: dimer through a monomer:hexamer model (model II with $n = 2$ through $n = 6$) as indicated by a wide variation in the equilibrium constants for each compound. The results of these calculations are shown for *t*-BuMgCl (Table I).

Finally the differences observed in the association curves at higher concentrations are probably a reflection of varying degrees of deviation from ideal behavior, rather than a real difference in the association phenomena. It is interesting to note that the *t*-butylmagnesium chloride solution appears to behave in a near-ideal manner since the *i* values lie nearest the ideal dimer value of 2. Although an argument might be made that the bulk of the *t*-butyl group is inhibiting the interactions responsible for deviations from Raoult's law, it seems more likely that the apparent ideal behavior of *t*-butylmagnesium chloride results from a fortuitous balancing of the various factors that influence deviations from ideal behavior.

b. Alkylmagnesium and Arylmagnesium Bromides and Iodides. Unlike the association curves for the alkylmagnesium chlorides in diethyl ether, the curves for several alkyl- and arylmagnesium bromides and iodides in diethyl ether (Figure 4) extrapolate to an *i* value of 1 at infinite dilution. Although this is reminiscent of the behavior of the tetrahydrofuran solutions (Figure 2), the *i* values for the diethyl ether solutions are noticeably larger even in dilute solution and continue to increase rapidly with concentration. This same type of behavior is observed for other magnesium compounds in diethyl ether, especially dimethylmagnesium and the magnesium halides (Figure 4). As noted earlier, this is the type of *i* value curve expected if the solute were either associated in a concentration-dependent equilibrium system or monomeric and displaying large deviations from ideal behavior. Although a decision on the importance of either factor would be very difficult based solely on the molecular weight data, a consideration of other data indicates that this type of *i* value curve is representative of a high degree of solute association.

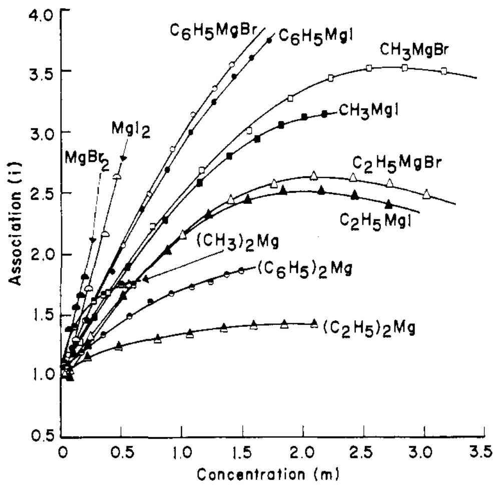


Figure 4. Association of several alkyl- and arylmagnesium bromides and iodides and related magnesium compounds in diethyl ether.

For example, it has been observed that the τ values for dimethylmagnesium in diethyl ether are concentration dependent[12,25] and this has been attributed to

---

(25) D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 5125 (1962).

Table II. Equilibrium Constants Calculated for the Polymeric Association (Model 1)

Compound[a]	K_1[b] (%)
CH_3MgBr	43.2 ± 6.7 (15.6)
CH_3MgI	41.0 ± 6.1 (14.9)
C_2H_5MgBr	23.6 ± 8.3 (35.2)
C_2H_5MgI	24.7 ± 6.4 (25.9)
C_6H_5MgBr	64.8 ± 15.8 (24.4)
C_6H_5MgI	63.7 ± 13.5 (21.2)

[a] Formula weight based on monoetherate. Values for dietherate show similar deviations. [b] Mole fraction scale. Uncertainties are standard deviation of the mean.

dissociation of polymeric dimethylmagnesium with dilution. A similar but less pronounced shift has been observed[25] on dilution of methylmagnesium iodide in diethyl ether. Perhaps the best spectroscopic evidence for association in diethyl ether is the presence of a concentration-dependent band in the infrared spectrum[17b] of a diethyl ether solution of dimethylmagnesium. The intensity of the band increases with concentration and has been ascribed to associated forms of dimethylmagnesium. This band is not present in tetrahydrofuran solutions. Although not as direct as the spectral evidence, heat of mixing data[6a,8a] have been interpreted in terms of Grignard compound association in diethyl ether.

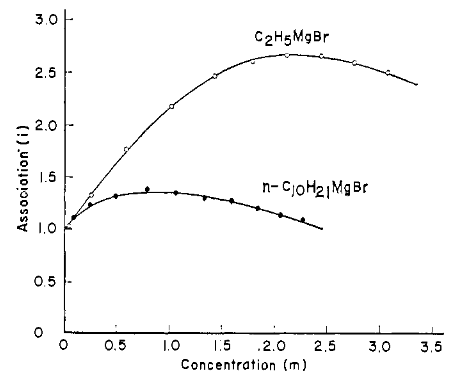


Figure 5. Association of ethylmagnesium bromide and *n*-decylmagnesium bromide in diethyl ether.

Table III. Equilibrium Constants Calculated for Methylmagnesium Bromide in Diethyl Ether[a]

K_S	X_E	K_1	K_2	K_3	K_4	K_5	K_6
0.0108	0.00830	36.2	74.0	3.55×10^3	8.90×10^4	14.6×10^5	0.326×10^7
0.0291	0.0173	39.5	392.0	3.99×10^3	4.12×10^4	3.04×10^5	2.95×10^{-2}
0.0526	0.0240	49.7	1330.0	15.8×10^3	7.29×10^4	3.30×10^5	14.6×10^7
0.0803	0.0310	51.3	147.0	97.0×10^3	12.2×10^4	3.40×10^5	7.96×10^7
0.1053	0.0371	49.5	70.6	1260.0×10^3	17.8×10^4	3.29×10^5	4.75×10^7
0.1254	0.0414	49.0	46.3	-1.98×10^{-2}	28.9×10^4	3.71×10^5	4.01×10^7
0.1442	0.0461	46.2	36.2	-1880.0×10^3	33.9×10^4	3.29×10^5	2.60×10^7
0.1613	0.0514	41.6	32.1	-1240.0×10^3	25.6×10^4	2.19×10^5	1.25×10^7
0.1766	0.0568	37.1	30.2	-1970.0×10^3	16.5×10^4	1.34×10^5	0.568×10^7
0.1926	0.0632	32.4	29.6	-19900.0×10^3	8.84×10^4	0.722×10^5	0.220×10^7

[a] K_1 = equilibrium constant for polymeric association model; K_2 = equilibrium constant for monomer $\rightleftarrows$ dimer model; K_3 = equilibrium constant for monomer $\rightleftarrows$ trimer model, etc.

Examination of the data in Figure 4 reveals that the *i* value curves are similar at low concentrations but, as the concentration is increased, a change from a positive to a negative slope is observed. This change in slope is not good evidence for the formation of a stable associated form in a monomer:dimer or monomer: trimer equilibrium since this would be indicated by flattening of the *i* value curve rather than by passage of the curve through a maximum. Instead, this curvature is best understood in terms of a high degree of solute–solvent interaction leading to negative deviation from Raoult's law. The decreasing *i* values at higher concentrations are expected if the solute and solvent molecules are interacting so as to reduce the amount of free solvent in solution. When it is realized that there are approximately seven molecules of solvent for every molecule of anhydrous solute in a 2.0 *m* ethereal solution, it is obvious that even a small interaction will cause a relatively large reduction in the percentage of free solvent. A comparison of the *i* values for a diethyl ether solution of *n*-decylmagnesium bromide (Figure 5) with those for ethylmagnesium bromide supports this conclusion. Although *n*-decylmagnesium bromide should exhibit approximately the same degree of association as ethylmagnesium bromide, the *i* values for the former are much smaller and the slope of the curve changes from positive to negative at a much lower concentration. This is in agreement with the trend observed in Figure 4, *i.e.*, the *i* values start decreasing at a lower concentration as the hydrocarbon chain is lengthened. From the data presented in Figure 1, it is clear that no reasonable increase in the amount of solvent ascribed to formal complexation with *n*-decylmagnesium bromide will cause a significant increase in the *i* values. Apparently, then, the negative deviations are best viewed as arising from some nonspecific interaction such as that due to van der Waal's forces between the solute and solvent molecules. Further evidence against the presence of a stable associated form in equilibrium with monomer is provided by the equilibrium constants calculated for model systems. Reasonably good agreement is obtained at all concentrations (Table II) for the polymeric association model (Model I) which is based on the formation of a series of multimers in solution. Table III shows in further detail the equilibrium constant data for a typical Grignard compound (methylmagnesium bromide) demonstrating the interpretation of the data as representing a polymeric association (K_1) as being superior to any other possibility.

The data may describe the formation of linear polymers (eq 5), the formation of transient cyclic dimers, trimers, etc. (eq 6), or a combination of linear and cyclic polymerization.

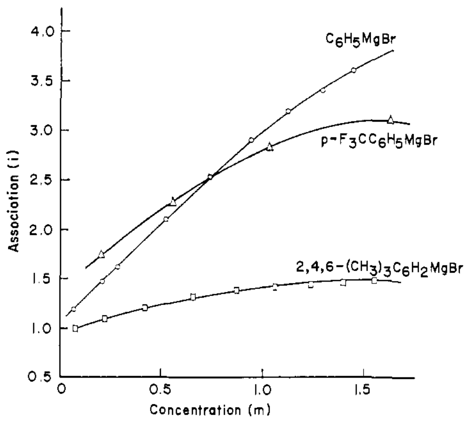
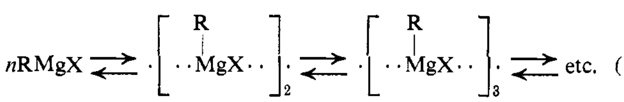
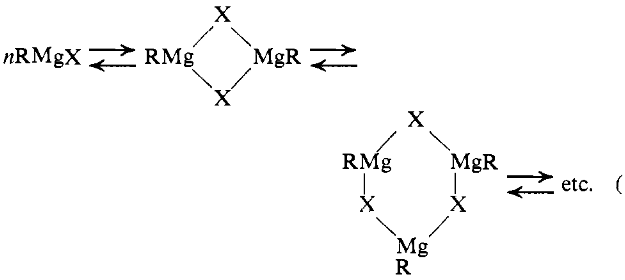


Figure 6. Demonstration of the effect of steric and electronic differences on association in diethyl ether.



$$n\mathrm{RMgX} \rightleftharpoons \cdot\left[\cdot\cdot\overset{\mathrm{R}}{\overset{|}{\mathrm{Mg}}}\mathrm{X}\cdot\cdot\right]_2\cdot \rightleftharpoons \cdot\left[\cdot\cdot\overset{\mathrm{R}}{\overset{|}{\mathrm{Mg}}}\mathrm{X}\cdot\cdot\right]_3\cdot \rightleftharpoons \text{etc.} \quad (5)$$



(6)

Although the formation of linear multimers (5) should have an entropy advantage over the formation of cyclic multimers (6), the cyclic association should have an enthalpy advantage over the linear association due to the formation of twice as many bridge bonds. A further complicating feature is introduced by the degree of solvation which could be different for the linear and cyclic association and thus produce unpredictable entropy and enthalpy differences. Therefore, it is not possible to distinguish between (5) and (6). Indeed, both linear and cyclic polymeric species may be present simultaneously.

Success in identifying the bridging group depends on the validity of comparing the *i* values for diethyl ether solutions of dissimilar compounds. Specifically, the magnesium halides, the magnesium alkyls (aryls), and the alkyl (aryl) Grignard compounds should differ considerably in polarity and the degree to which the *i* values reflect this difference must be considered. Information on polarity effects can be found in Figure 6 where it is seen that the *i* values for phenylmagnesium bromide and *p*-trifluoromethylphenylmagnesium bromide in diethyl ether are little changed although there is certain to be a large difference between the two compounds with respect to polarity. The difference between the *i* value curves is about the same as that observed with the other Grignard compounds (Figure 4) and the small depression of the *i* values for *p*-trifluoromethylphenylmagnesium bromide is probably similar to, but much smaller than, the effect observed with *n*-decylmagnesium bromide (Figure 5). That solute–solvent interactions can be increased by increasing the polarity of the solute is not surprising in a polar solvent such as diethyl ether.

Although the polarity differences apparently have little influence on the *i* values, it is evident from the data presented in Figure 5 that the *i* values are influenced by a change in the identity of the hydrocarbon portion of the solute molecule. Thus, while comparison of the *i* values for dimethyl- and diethylmagnesium (Figure 4) seems appropriate, a similar comparison with the data for diphenylmagnesium is difficult. A better understanding of the bridging abilities of the various groups is achieved by comparing the *i* values for a homologous series of magnesium compounds. Thus, the dilute solution data in Figure 4 for the methyl compounds and the magnesium halides indicate that the methylmagnesium halides associate by both methyl and halogen bridges. Similar comparisons of the *i* value curves for the magnesium halides with those for the phenyl compounds and the ethyl compounds (Figure 4) suggest that the phenylmagnesium halides and the ethylmagnesium halides associate mainly through the halogen atom. The superior bridging ability of the methyl group in organomagnesium compounds has been indicated by other evidence[26] and is well established in organoaluminum chemistry.

The association curve for mesitylmagnesium bromide[27] is shown in Figure 6. The very small *i* values, particularly in dilute solution, are clearly due to the bulk of the mesityl group effectively destroying the type of association observed for the unhindered phenylmagnesium bromide. Precisely what steric requirements are to be met before this occurs is not clear since the *i* values for *t*-butylmagnesium bromide (Figure 3) are a little larger than those for ethylmagnesium bromide. The differences between the *i* values for *t*-butylmagnesium bromide and *t*-butylmagnesium chloride indicate that the steric requirements play a small role in determining the form of the association since the *t*-butylmagnesium bromide curve shows all the characteristics found for the other bromides and iodides in diethyl ether rather than those of the dimeric chlorides.

Acknowledgment. Support of this research by the National Science Foundation, Grant GP-5297, is gratefully acknowledged.

---

[26] L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **89**, 1607 (1967).

[27] Previously it was reported[5a] that mesitylmagnesium bromide associates in diethyl ether solution to a higher degree than ethylmagnesium bromide. Although the reasons for this discrepancy are not known, the previously reported higher values are more questionable since oxygen contamination and magnesium bromide (produced as a by-product of coupling) are both known to increase the apparent molecular weights of these solutes.[28]

[28] A. D. Vreugdenhill and C. Blomberg, *Rec. Trav. Chim.*, **84**, 39 (1965).