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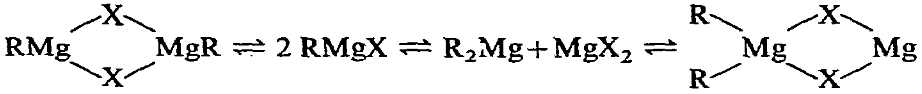
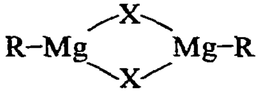
Composition of Grignard compounds
III. Nature of association in diethyl ether

Since 1963 the composition of Grignard compounds in ether solvents has been clarified considerably[1-7]. There appears to be general agreement that the composition of Grignard compounds in diethyl ether solution is best represented by the Schlenk equilibrium expanded to include dimeric species[8].

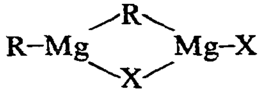


Recently Hashimoto and coworkers[9] have reported results which appear to confuse the evolving picture of Grignard compound composition in solution. These workers reported that C_2H_5MgBr in diethyl ether is associated in solution past the dimer stage ($i = 2.4$ at 1.0 *M*) and then decreases in association below the dimer stage with an increase in concentration ($i = 1.6$ at 2.0 *M*). Also they report that C_2H_5MgBr in tetrahydrofuran is associated at low concentration ($i = 1.6$ at 0.1 *M*) and then decreases in association to a monomer only at high concentration ($i = 1.0$ at 1.2 *M*). It does not seem reasonable that association phenomena should decrease with an increase in concentration and indeed we maintain that this is not the case.

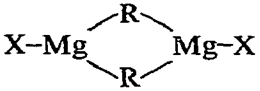
At the time that this work appeared we also were studying the association of Grignard compounds at high concentration in an attempt to learn more about the type of bridging that exists in associated Grignard compounds. For example, if 2 molecules of the RMgX species associate to a dimer in solution, the resulting structure can be represented by (A), (B), or (C). Although structure (A) should be the most stable, there exists no evidence anywhere to substantiate such a choice



(A)



(B)



(C)

Likewise association of the R_2Mg and MgX_2 species can be described by means of a double halogen bridge, a double alkyl bridge or a mixed alkylhalogen bridge species. Recently, however, it has been shown[6,7] that RMgX is by far the most predominant species in diethyl ether solution for typical alkylmagnesium halides.

The data (Fig. 1) shows quite clearly that association of magnesium through the halogen in $MgBr_2$ and MgI_2 ($MgCl_2$ is insoluble in diethyl ether) is much stronger than through the alkyl group as in $(C_2H_5)_2Mg$ or $(CH_3)_2Mg$*. Since methyl and ethyl are optimum bridging groups, and dimethylmagnesium and diethylmagnesium are only weakly associated in diethyl ether, it would appear that association of the Grignard compounds is predominantly through the halogen. The association of all of the compounds studied can be explained purely on inductive grounds, *i.e.*, association is proportional to the positive character of the magnesium atom.

The association of some Grignard compounds past the dimer stage points out

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* The molecular weight measurements were made by a method previously described[3].

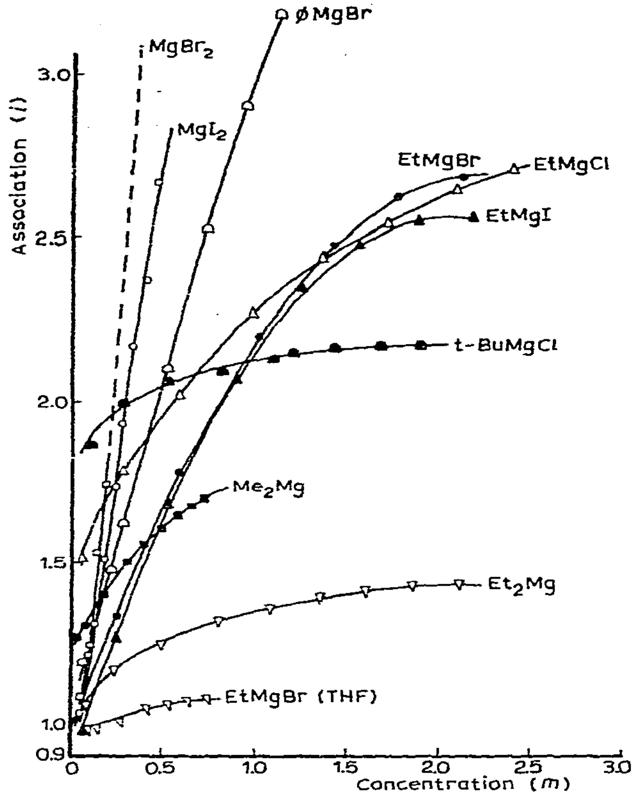
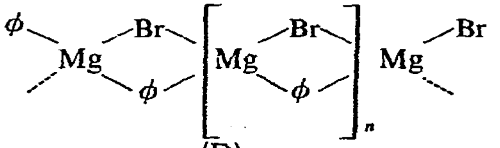
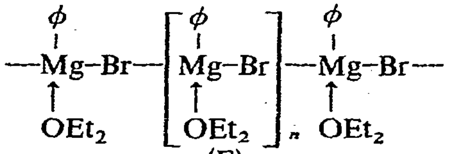


Fig. 1. Association studies in diethyl ether.

the need to consider the possibility that different Grignard compounds are associated differently. For example, it appears that C_6H_5MgBr is linearly associated whereas the ethyl Grignard compounds appear to be either linearly associated (curvature due to deviation from ideality at high concentration) or are trimeric. On the other hand t-butylmagnesium chloride appears to level off in association at the dimer stage.

The representation of associated molecules of C_6H_5MgBr does not appear to be tenable on the basis of structure (A) since association of this type would predict gross curvature of the association line at $i=2$ due to the change in the nature of the bonding which must take place at this point. Structures (D) and (E) are compatible with the type of association exhibited by C_6H_5MgBr.


(D)


(E)

On the basis that solid magnesium halides and Grignard compounds hold one molecule of ether tightly per magnesium atom, structure E is preferred.

In contrast to the report of Hashimoto[9] our results confirm our earlier report[1] that ethylmagnesium bromide is monomeric in tetrahydrofuran showing only a low degree of association at high concentration. The anomalies exhibited in the data of Hashimoto could be due to any of several problems which make measurements on such sensitive systems very difficult.

The decrease in association with concentration reported by Hashimoto in diethyl ether is undoubtedly due to the high concentration studied and hence non-ideality of the system. Their observation of a decrease in association with an increase in concentration was made between 1 and 2 M concentration which is significantly higher than the highest concentration used in our studies (2 $M \cong 3$ m). Calculations show that there are only three to four molecules of solvent present for every molecule of Grignard compound in the concentration range that the drecrease in association was observed.

There is some concern in evaluating ebullioscopic data at high concentrations. The accuracy of the data, of course, depends on the ideality of the solutions involved. In calculating the data, equation (1) compensates for non-dilute solutions.

$$i = \frac{\mathrm{W_G M_E}}{\mathrm{W_E M_G}} \left[\frac{1}{1 - \mathrm{e}^{\frac{-\Delta T_\mathrm{B} \mathrm{M_E}}{1000\, K_\mathrm{B}}}} - 1 \right] \tag{1}$$

$\mathrm{W_G}$ = weight of solute; $\mathrm{M_G}$ = formula weight of solute (calculated as a monoetherate); $\mathrm{W_E}$ = weight of solvent; $\mathrm{M_E}$ = molecular weight of solvent; ΔT_B = boiling point elevation; K_B = molal boiling point elevation constant.

Deviations of the solutions from ideality should not be great at low concentration, however at the higher concentrations, curvature of association lines could be due to a deviation of the solutions from ideality. We are continuing these studies in an attempt to define the nature of the association bonding of Grignard compounds at high concentration with respect to the halogen and the organic substituent. We are also attempting to determine the validity of such determinations at high concentrations by studying line curvature at high concentration for solid hydrocarbon compounds and long straight chain Grignard and dialkylmagnesium compounds.

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