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THE CONSTITUTION OF THE GRIGNARD REAGENT - I. THE REACTION BETWEEN DIETHYL MAGNESIUM AND MAGNESIUM BROMIDE IN DIETHYL ETHER

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We wish to report that dilute ether solutions (0.1M) of diethylmagnesium and magnesium bromide react almost instantaneously in 1:1 mole ratio on mixing, with a heat evolution of 3.6 kcal/mole $(C_2H_5)_2Mg$, to give a monomeric product which can only be C_2H_5MgBr. The i-factor* for this product (1.04) is indistinguishable from the i-factor of 1.04 previously observed by Ashby and Smith (1) for the corresponding Grignard reagent $(C_2H_5MgBr)_G$**. Consequently, it must be concluded that in this system the following reaction is fast, with the equilibrium lying strongly to the right:

$$(C_2H_5)_2Mg + MgBr_2 \rightleftharpoons 2\ C_2H_5MgBr$$

Diethylmagnesium was prepared by reacting $(C_2H_5)_2Hg$ with a large excess of sublimed magnesium in ether in a sealed tube at 100°. The product, shown to be free of $(C_2H_5)_2Hg$ by testing with dithizone, was analyzed for Mg content by hydrolyzing and titrating with standard acid. Magnesium bromide

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* The i-factor (or association factor) is the ratio of the solute molecular weight to the formula weight.

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

was prepared in ether by reacting ethylene bromide with a slight excess of sublimed magnesium. The product was analyzed for Br by the Volhard method. The ether used in the preparations and in dilution to 0.1M was freshly distilled from $LiAlH_4$.

In the first series of experiments, measured portions of 0.1M $MgBr_2$* were added successively to a larger quantity of 0.1M $(C_2H_5)_2Mg$ in a calorimeter, the temperature rise for each addition being measured with a platinum resistance thermometer. The second series was similar to the first except that 0.1M $(C_2H_5)_2Mg$ was added stepwise to a larger quantity of 0.1M $MgBr_2$. The reaction accompanying each mixing was complete within one minute and probably sooner. The heat of dilution of one volume of either solution with four volumes of ether was found to be almost negligible (less than 0.3 kcal/mole in magnitude).

The results for the two series of experiments are shown in Figures 1 and 2. Each curve is practically linear up to about 0.7:1 mole ratio, indicating a high degree of conversion in the presence of a sufficient excess of either reactant. The average heat of reaction, calculated from the slopes of these lines, is $\Delta H = 3.6$ kcal/mole $(C_2H_5)_2Mg$ reacted. 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 clearly

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* A small measured amount of $(C_2H_5)_2Mg$ was added to the $MgBr_2$ ahead of time to ensure dryness.

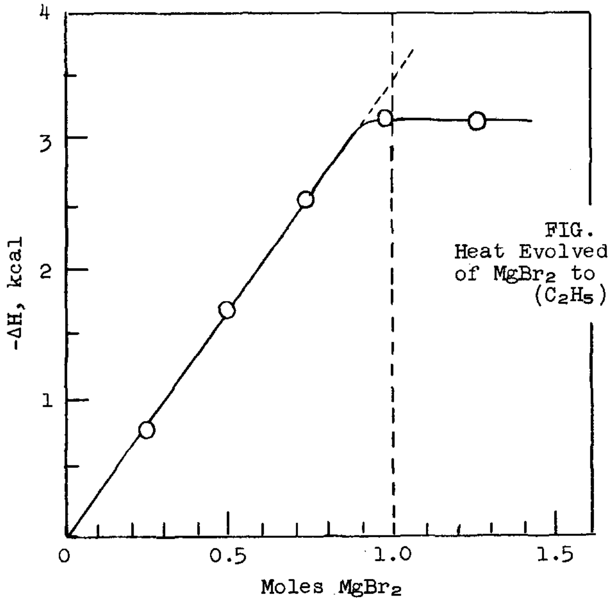

FIG. 1
Heat Evolved on Addition of $MgBr_2$ to One Mole of $(C_2H_5)_2Mg$

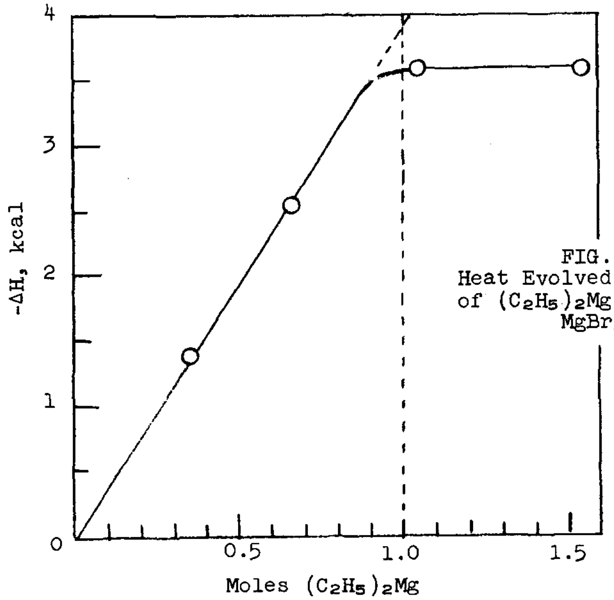

FIG. 2
Heat Evolved on Addition of $(C_2H_5)_2Mg$ to One Mole $MgBr_2$

that reaction occurs at 1:1 mole ratio and at no other ratio. It is calculated from the data that for the equimolar mixture, about 92 wt. % of the reactants is converted into product, while about 8 wt. % remains as unreacted $(C_2H_5)_2Mg$ and $MgBr_2$ in equilibrium with the product species. The ebullioscopic i-factor of 1.04 for the mixture indicates that it consists essentially of monomeric species. Since the amounts of ionic species present are very small*, the only possible monomeric reaction product of $(C_2H_5)_2Mg$ and $MgBr_2$ is C_2H_5MgBr. It follows that the principal species present in the equimolar mixture is the monomeric species C_2H_5MgBr. Mechanisms for the reaction of R_2Mg with MgX_2 to form 2 RMgX were discussed by Ashby and Smith (1).

As far as we know, the thermochemical technique has not been employed previously in studying reactions of the type R_2Mg (in an ether) plus MgX_2 (in an ether). As shown by the present study, this technique is capable of yielding valuable information in this field such as detection of reaction between R_2Mg and MgX_2; measurement of rate, heat, and extent of reaction; determination of stoichiometric ratios; identification of product species; and, under certain conditions, evaluation of equilibrium constants. Of earlier investigations relating to reaction between R_2Mg and MgX_2 in dilute solution, the infrared spectral studies of Salinger and Mosher (2) are particularly noteworthy. For several Grignard reagents

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* The degree of ionization of the equimolar mixture is estimated as less than 0.01% from the conductivity data of Vreugdenhil and Blomberg (4).

in THF, the infrared spectrum was identical to that of the corresponding equimolar mixture, while both were noticeably different from the spectrum of R_2Mg alone. It was shown that the spectra could be interpreted in terms of the equilibrium, $R_2Mg + MgX_2 \rightleftharpoons 2\ RMgX$. For the same Grignard reagents in ether, however, this technique was unsuccessful since the spectra of the Grignard reagents were hardly distinguishable from those of the corresponding R_2Mg compounds. A few investigators have provided evidence of reaction between $(C_2H_5)_2Mg$ and $MgBr_2$ in dilute ether solution by the measurement of certain physical properties of the reactants and of their mixtures. These include Dessy (3) [dielectric constants] and Vreugdenhil and Blomberg (4) [electrical conductivities]. Such studies, while very revealing, do not yield quantitative information such as is obtainable by the thermochemical technique.

We are conducting similar studies with Grignard reagents in which the R-group, the halogen, the solvent, and the concentration are varied.

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