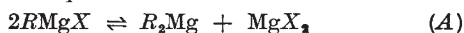


Composition of the Grignard Reagent

In 1912 Jolibois¹ suggested that the formula of the Grignard reagent was $R_2Mg \cdot MgX_2$, and since that time there have been several controversial papers dealing with experimental evidence for and against this idea. The work of W. Schlenk and W. Schlenk, jun.^{2,3}, in which the halogen was entirely precipitated from ether solutions of the Grignard reagent with dioxane, leaving dialkylmagnesium, led them to favour a slow equilibrium in the reaction

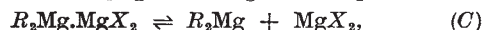


as the best explanation of the results obtained. This idea of the composition of the Grignard reagent has been popularly held ever since, in spite of many reasons for doubting how anything so simple can fit all the complex results obtained—for example, those of Noller and White⁴, in which dialkylmagnesium returned to the solution on further shaking the precipitate with the solution after precipitation.

The results of Noller and White are perfectly understandable on the basis of the slow equilibrium of $RMgX$ and a complex of R_2Mg with MgX_2 , never being obtained,



and the postulate that there is practically no free dialkylmagnesium in the ordinary Grignard solution. (Incidentally, the ease with which dialkylmagnesium solutions catch fire as compared with those of the Grignard reagent is difficult to account for on any other basis.) Any solution containing $R_2Mg \cdot MgX_2$ will be in equilibrium with a small but finite amount of R_2Mg according to the equation



requiring that

$$\frac{(R_2Mg)(MgX_2)}{(R_2Mg \cdot MgX_2)} = K_1 \quad (1)$$

As soon as a solution becomes saturated with respect to $R_2Mg \cdot MgX_2$, the concentration of this complex is constant and

$$(R_2Mg)(MgX_2) = K_2 \quad (2)$$

When dioxane is added to the solution, both compounds in equation (B) are precipitated, and only after sufficient dioxane has been added to make the solution saturated with respect to MgX_2 (present in only small concentrations) can the R_2Mg , originally present as $R_2Mg \cdot MgX_2$, return to the solution, as will then be required to satisfy equation (1). In fact, equation (2) requires a fixed concentration of R_2Mg for a given ratio of dioxane to ether when MgX_2 starts to be precipitated. The $RMgX$, of course, stays in the precipitate.

We have been able to demonstrate that a solution of methylmagnesium iodide in di-*n*-butyl ether contains no free dimethylmagnesium by some extremely simple and conclusive experiments.

Brugger⁵ found that such solutions reacted with acetone in di-*n*-butyl ether very rapidly (half-life about 7×10^{-3} sec. at 27°) according to a reaction independent of the acetone concentration and dependent on the first power of the total Grignard concentration. Exactly the same rate ($k_1 \approx 100$ sec.⁻¹ at 27°) was obtained with ethyl acetate.

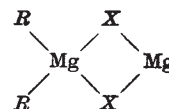
Recently, we have carried out similar experiments with solutions of dimethylmagnesium prepared by precipitation from diethyl ether with dioxane, and

transferred to di-*n*-butyl ether by distilling the dioxane and ethyl ether away, using a good fractionating column, under an atmosphere of nitrogen after adding di-*n*-butyl ether. The rate was found at 27° to be about fifty times that observed by Brugger. In this experiment, the final constant temperature down the tube of the rapid-rate apparatus⁶ corresponded approximately with the total heat (48.4 k.cal.) determined in our laboratory^{7,8} on the basis that only one methyl group reacted per mole of dimethylmagnesium; whereas, in Brugger's experiments, it varied from 25 to 40 per cent of the rise expected from the heat determined in this laboratory calculated on the basis of all being CH_3MgI , but 50–80 per cent on the basis of all being $(CH_3)_2Mg$, with only one methyl group reacting.

Quite clearly there can be no appreciable amount of free dimethylmagnesium in the di-*n*-butyl ether solution of the Grignard reagent, and the slower rate of reaction in this case is either due to the rate of dissociation of $(CH_3)_2Mg \cdot MgI_2$, or, less likely, the slow rate of dissociation of $CH_3MgI [(C_4H_9)_{12}O]$.

This last conclusion is made necessary because the total heat liberated when methyl magnesium iodide reacted with acetone in the rapid-rate apparatus, at the point down the tube where the temperature became constant, is only a fraction of the measured heat of the reaction. This fact indicates that one of these species must react very slowly. Assuming that the rate of the $(CH_3)_2Mg \cdot MgI_2$ dissociation determines the rate, Brugger's results point to more than 50 per cent of the Grignard solution existing as $(CH_3)_2Mg \cdot MgI_2$, or the other assumption to more than 60 per cent. Further experiments are in progress.

The conclusion that the Grignard reagent has the formula



has been made previously by Evans and Lee⁹ from experiments on electrolysis and transference.

J. G. ASTON
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¹ Jolibois, *C.R. Acad. Sci., Paris*, **155**, 353 (1912).

² Schlenk, W., and Schlenk, W., jun., *Ber.*, **62**, 920 (1929).

³ Schlenk, W., jun., *Ber.*, **64B**, 734 (1931).

⁴ Noller, C. R., and White, W. R., *J. Amer. Chem. Soc.*, **59**, 1354 (1937).

⁵ Brugger, J. E., M.S. Thesis, Penn. State College (1946).

⁶ This apparatus was essentially like that of La Mer and Reed (*J. Amer. Chem. Soc.*, **52**, 3098; 1930), with the fraction which had reacted down the tube measured by the temperature-rise indicated by suitably placed thermocouples.

⁷ Aston, J. G., and Bernhard, S. A. (to be published).

⁸ Aston, J. G., and Kennedy, R. M. (to be published).

⁹ Evans, W. V., and Lee, F. H., *J. Amer. Chem. Soc.*, **56**, 654 (1934).

Polarographic Behaviour of Acetone

In supporting electrolytes generally used in polarography, for example, in solutions of potassium, lithium or ammonium salts or lithium hydroxide or in buffer solutions, no polarographic reduction wave of acetone can be observed. Only if electrolytes of tetra-alkylammonium are used can a reduction wave at a half-wave potential of about -2.1 V. (from