TABLE II

SOME REPRESENTATIVE SPREADING PRESSURE VALUES

Unimolecular film	Spreading material	Spreading pressure, dynes/cm.	Harkins' spreading coefficients,[3] dynes/cm.
Palmitic acid	Nitrobenzene	3.6	3.76
Stearic acid		3.7	
Tristearin		3.6	
Palmitic acid	Toluene	8.7	6.84
Stearic acid		8.5	
Tristearin		8.4	
Palmitic acid	Benzene	9.5	8.94
Stearic acid		9.4	
Tristearin		9.4	
Palmitic acid	Anisole	11.6	11.76
Stearic acid		11.7	
Tristearin		11.3	
Palmitic acid	Diethyl carbonate	32.7	33.63
Stearic acid		32.7	
Tristearin		32.3	
Palmitic acid	Isoamyl chloride	14.6	33.88
Stearic acid		15.8	
Tristearin		..	

These values were obtained at temperatures between 20 and 25°. Within this range there was no noticeable change of spreading pressures with temperature.

Whereas the determination of spreading coefficients by Harkins' method requires three measurements of interfacial tension, in which four measurements of density are involved, this method requires only one measurement which is quickly carried out with a film pressure balance and a very small quantity of spreading material.

While the precision of a single reading is of the order of ±0.02 dyne/cm., the accuracy of the spreading pressures as indicated by the reproducibility of results is probably not greater than ±0.1 dyne/cm.

There are probably two principal sources of error:

1. The unimolecular film when under pressure can probably dissolve into the drop of the spreading liquid and thereby cause a decrease in area and a decrease in the observed pressure. This is possibly the explanation of the low values obtained with isoamyl chloride.
2. Vapors from the drop of applied liquid may be adsorbed into the film of stearic acid and cause it to expand so as to exert an abnormally high pressure.

Studies are now in progress on the accuracy of the determination of the spreading pressures of other pure organic liquids as well as on the behavior of binary mixtures of various compositions.

Summary

A method has been developed for the measurement of spreading pressures by means of a film pressure balance and a small quantity of the spreading liquid put on a unimolecular film.

Spreading pressures of nitrobenzene, toluene, benzene, anisole, diethyl carbonate, and isoamyl chloride on unimolecular films of palmitic acid, stearic acid, and tristearin have been measured by this method.

LINCOLN, NEB. RECEIVED FEBRUARY 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Equilibrium Composition of *n*-Butylmagnesium Chloride Solutions in Ethyl Ether

BY C. R. NOLLER AND D. C. RANEY

It is well-known that solutions of Grignard reagents prepared from alkyl chlorides will deposit magnesium chloride on standing.[1] This presumably is due to the insolubility of the magnesium chloride etherate in ether and the existence of equilibrium 1.

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

No quantitative determination of the solubility of anhydrous magnesium chloride in ether appears to have been reported but we have found it to be approximately 0.001 mole per 1000 g. of solution. With this marked insolubility one might predict that equilibrium 1 would be shifted completely to the right and that only dialkylmagnesium would remain in solution. That the magnesium chloride does not precipitate immediately was explained by Schlenk and Schlenk as due to the formation of metastable supersaturated solutions.

The work which we wish to report shows that in the case of Grignard solutions prepared from *n*-butyl chloride in ethyl ether, magnesium chloride does not completely precipitate under conditions

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[1] Schlenk and Schlenk, Jr., *Ber.*, **62**, 920 (1929); Cope, THIS JOURNAL, **57**, 2238 (1935).

which should exclude the possibility of supersaturation. If these solutions are shaken with finely powdered anhydrous magnesium chloride and the clear supernatant liquid analyzed for halide ion and active Grignard reagent from time to time, the halogen content decreases at first but becomes constant for a given Grignard concentration after fifty to one hundred and fifty hours. The same results are obtained when the solutions are shaken without the addition of magnesium chloride although equilibrium is attained more slowly. These values at equilibrium are given in columns A and B of Table I. It can be seen at once that while the equivalents of halogen are always less than the equivalents of active Grignard reagent, the amount of magnesium chloride preciptated is relatively small, varying from about three equivalent per cent. for a concentration of 0.4 equivalent of active Grignard reagent per 1000 g. of solution to about ten equivalent per cent. for 1.8 equivalents per 1000 g. of solution.

TABLE I

EQUILIBRIUM COMPOSITION OF *n*-BUTYLMAGNESIUM CHLORIDE SOLUTIONS

A Total C_4H_9	B Total Cl^-	C $K(1) \times 10^3$
1.849	1.665	0.034
1.651	1.496	.035
1.629	1.485	.033
1.216	1.130	.035
0.947	0.894	.035
.711	.681	.035
.612	.586	.041
.602	.577	.041
.394	.383	.038

It seems to us that there are two possible explanations for these results. One would be based on the assumption that the solubility of magnesium chloride etherate is the same in the Grignard solutions as in pure ether; that is, that the concentration of magnesium chloride is at all times approximately 0.001 mole per 1000 g. of solution. If this were the case the rest of the halogen must be in solution as *n*-butylmagnesium chloride. Making this assumption one can calculate the equilibrium constant for reaction 1 for the different concentrations. It is seen from column C that a fairly satisfactory constant is obtained, the average value being 0.036×10^{-3}. If one calculates from this the amount of dibutylmagnesium that would be present if no magnesium chloride precipitated, one arrives at the value of approximately 1.2% of the active Grignard reagent in the form of dibutylmagnesium. This is in sharp contrast to the value of 88% obtained by precipitation of the halogen containing compounds with dioxane.[2] It should be mentioned that the data do not give a satisfactory equilibrium constant if reaction 2 is postulated.

$$R_2Mg_2X_2 \rightleftarrows R_2Mg + MgX_2 \qquad (2)$$

Since the data in Table I were obtained,[3] it has been found that magnesium bromide is much more soluble in the Grignard solution from *n*-butyl bromide than in pure ether and that the Grignard reagent is more soluble in liquid magnesium bromide dietherate than in an ether solution of magnesium bromide.[4] Accordingly one can assume that the magnesium chloride does not precipitate because its solubility is greatly increased by the presence of butylmagnesium chloride and dibutylmagnesium. If one accepts the results of dioxane precipitation, namely, 88% of the active Grignard reagent in the form of dibutylmagnesium, the solubility of the magnesium chloride would have to be increased from practically nothing to approximately one mole for every mole of dibutylmagnesium present.

A better idea of the way in which the amount of magnesium chloride precipitated varies with the Grignard concentration can be obtained by plotting the difference between column A and column B against column A. These values are shown in Fig. 1 by the small circles which are found to fall close to the curve which represents the values calculated from the average equilibrium constant 0.036×10^{-3}. This of course does not prove that the first explanation of the solubility of magnesium chloride is correct but merely is another way of indicating that the data are in good agreement with this explanation. It does not seem to us likely, however, that with all Grignard reagents the effect on the solubility would always be such that satisfactory equilibrium constants for reaction 1 would be obtained. It is hoped that we shall be able in the near future to extend these investigations to other Grignard reagents, particularly those from methyl and tertiary butyl chlorides which according to dioxane precipitation have a much lower dialkyl magnesium content and from benzyl chloride which is known to pre-

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(2) For work on the reliability of this method and references to previous papers on precipitation with dioxane, see Noller and White, THIS JOURNAL, **59**, 1354 (1937), and Cope, *ibid.*, **60**, 2215 (1938).

(3) First presented at the Milwaukee meeting of the American Chemical Society, September, 1938.

(4) Doering and Noller, THIS JOURNAL, **61**, 3436 (1939).

cipitate considerable quantities of magnesium chloride.

Experimental

An approximately 2 *N* solution of Grignard reagent in ethyl ether was prepared in the usual manner from *n*-butyl chloride and pure magnesium turnings[5] without the use of catalysts.

Anhydrous magnesium chloride was prepared by grinding together one mole of magnesium chloride hexahydrate and three moles of ammonium chloride. Thirty grams of this mixture was placed in the closed end of a Pyrex tube having a right-angled bend and slowly heated to drive off as much water as possible before the ammonium chloride began to decompose and then more strongly to drive off the ammonium chloride. Finally the full heat of a blast lamp was applied until the mass fused at a red heat. After cooling, the end of the tube was broken and the lump of anhydrous magnesium chloride placed in a covered weighing bottle which was kept in a desiccator over phosphorus pentoxide.

The tubes in which the Grignard solutions were brought to equilibrium were standard 100-cc. Pyrex centrifuge tubes to the open end of which had been sealed stopcocks of 3 mm. bore. The tubes were swept out with nitrogen and from 1–2 g. of finely powdered anhydrous magnesium chloride added. This was accomplished by placing the magnesium chloride in a narrow glass tube which was then attached to the stopcock by means of a short length of rubber tubing. On opening the stopcock the magnesium chloride could be shaken into the tube. The desired amount of the stock solution of Grignard reagent was added by means of specially designed pipets, the stem of which could pass through the bore of the stopcock. Ether was added until the reaction tubes were approximately three-quarters full and the tubes fastened to a mechanical device for turning them end over end.

After shaking for the desired length of time the tubes were centrifuged until the liquid was water clear. The stopcock was opened momentarily to bring the contents to atmospheric pressure and the tube weighed to the nearest milligram. Approximately 5-cc. samples were withdrawn with special wash-out pipets and the tubes weighed again to give the weight of the sample. The active Grignard reagent was determined by decomposing with water and titrating the magnesium hydroxide with standard sulfuric acid and the halide ion determined on the same sample by the standard Volhard titration. By this procedure duplicate determinations checked within 0.1–0.2%. It was found that equilibrium was reached in from fifty to one hundred and fifty hours of shaking. The results for various concentrations of active Grignard reagent are tabulated in Table I.

For determining the solubility of anhydrous magnesium chloride in pure ether, the powdered material was shaken with absolute ether until equilibrium was reached. It was found that the chloride content of the solution as determined by Volhard titration corresponded to 0.001 mole of magnesium chloride per 1000 g. of solution.

Dioxane precipitation indicated that the dibutylmagnesium content of a 1.1 *N* Grignard solution from butyl chloride was 88.6%.

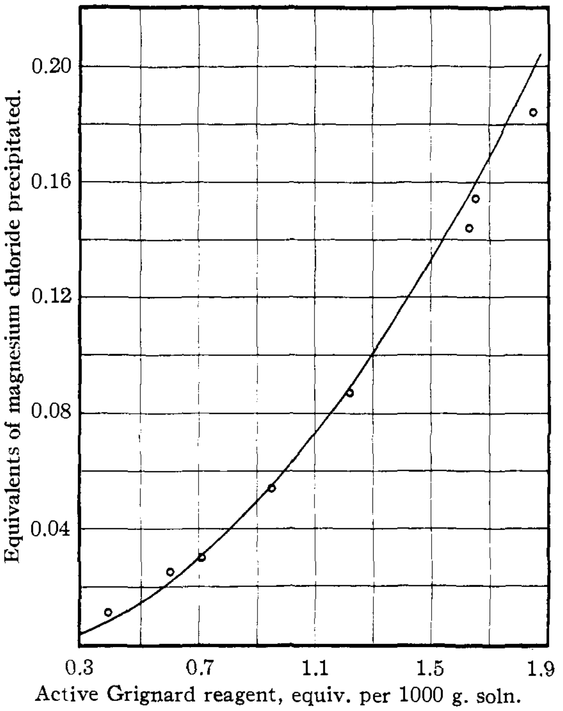

Fig. 1.—Relation of magnesium chloride precipitated to concentration of active Grignard reagent. Circles give experimental values; solid curve represents calculated values for $K = 0.036 \times 10^{-3}$.

Summary

A determination of the equilibrium composition of the Grignard solution from *n*-butyl chloride at concentrations ranging from 0.4 to 1.8 equivalents per 1000 g. of solution shows that in spite of the low solubility of magnesium chloride etherate in ether, only from 3–10% of the halogen originally present precipitates as magnesium chloride. Dioxane precipitation indicates that at least 88% of the halogen should be present as magnesium chloride in solution. Either dioxane precipitation does not give a correct picture of the composition of Grignard solutions and the reagent is almost entirely in the form of *n*-butylmagnesium chloride with about 1% dissociation into dibutylmagnesium and magnesium chloride or the solubility of magnesium chloride is increased from practically nothing to the extent of approximately one mole per mole of dibutylmagnesium.

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RECEIVED MAY 7, 1940

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[5] Aluminum Company of America, No. 651 ingot.