[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

THE ELECTROLYSIS OF GRIGNARD SOLUTIONS[1]

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Introduction

The literature on the electrical properties of ether solutions is extremely scanty. It has been known for some time that certain ether solutions are slightly conductive, but the low specific inductive capacity of ether would seem to rate ether very low in the scale of ionizing solvents. Kondyrew,[2] whose work appeared while this work was in progress, has shown in a preliminary paper that the electrolysis of ethereal solutions of the Grignard reagent is possible, but made no effort to trace the course of the electrode reactions. Nelson and Evans[3] also made mention of the fact that ether solutions of the Grignard reagent are conductive. In this paper, work is reported which was undertaken to study the mechanism of the electrode reactions and, if possible, the manner of ionization. Further work on this problem is in progress at the present time.

Experimental Part

The Grignard reagents were prepared in the usual way, filtered and transferred to the electrolytic cell. The filtering apparatus consisted of a bell jar (Fig. 1), the ground-glass bottom of which was sealed with paraffin to the ground-glass bottom of an inverted desiccator lid. The stem of a funnel within the bell jar extended through a tight-fitting stopper in the opening in the desiccator lid and was attached by means of a rubber stopper to a long-stemmed Gooch filter tube. The stem of this tube extended into a large flask. After thorough drying, the various pieces were assembled as indicated in the diagram. Dried, compressed air was passed through the separatory funnel of the reaction flask and the Grignard solution forced over into the bell jar where it was filtered through filter paper, and collected in the flask A, which served as a reservoir. The solution was siphoned from this reservoir, through a long-stemmed Gooch filter tube, into the electrolytic cell. The stem of the filter tube was then sealed off, using a blast lamp. For a cell, a wide-necked flask of 500 cc. capacity was used. The wooden stopper used in the cell was made air-tight with water glass. The electrodes were platinum, about 5 cm. square and placed about 2 cm. apart. In the later experiments, a copper coulometer was connected in series. For source of current, a motor generator furnishing 110–130 v. was used. The current conducted

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[1] This paper was read in part at the National meeting of the American Chemical Society at Tulsa, Oklahoma, April, **1926**.

[2] Kondyrew, *Ber.*, **58**, 459 (1925).

[3] Nelson and Evans, THIS JOURNAL, **39**, 82 (1917).

by the Grignard solutions was of the order of 0.02 amp. In all cases magnesium began separating from the solution at the cathode within a few minutes after starting the electrolysis. In the case of the phenylmagnesium bromide, a very marked anodic luminescence was observed. In a dark room, the outlines of the anode could be distinctly seen at a distance of 4.5–6 meters.

In all cases samples of the unelectrolyzed solutions were analyzed. The concentration of Grignard reagent was determined by Gilman's titration method.[4] Phenol was determined gravimetrically as tribromophenol. Diphenyl, dibenzyl and benzyl alcohol were obtained by fractional distillation in a vacuum, and weighed directly.

When electrolysis had been continued as long as desired, the tube through which the Grignard solution entered the cell was removed, and a tube connecting the cell to a bell jar was inserted. This bell jar rested on the top of a desiccator. Within the bell jar was a flask carrying a funnel and filter paper. The solution in the electrolytic cell was forced, by means of pure compressed air, into the funnel within the bell jar, where filtration took place. The magnesium remaining in the electrolytic cell was washed with dry ether until free from the Grignard reagent, the washings being collected in the flask holding the original reaction solution. Portions of the washings were drawn off through the three-way stopcock B and tested for the Grignard reagent by Gilman's method.[5]

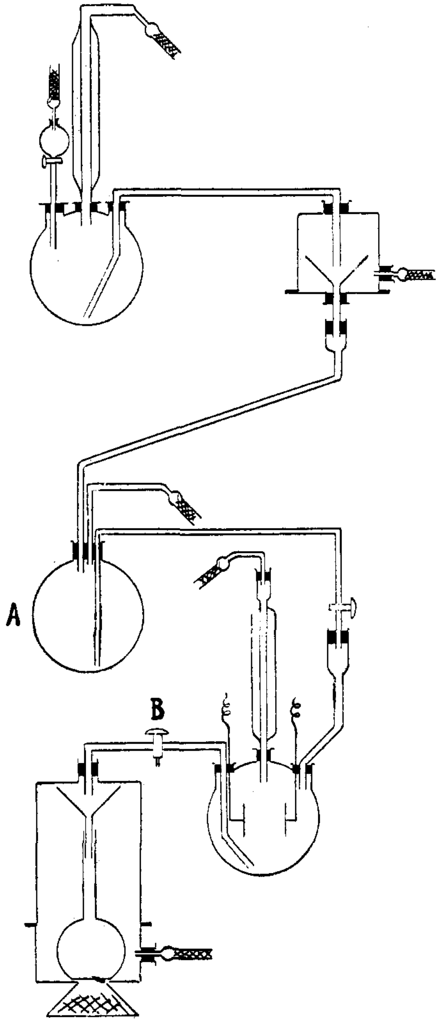

Fig. 1.

The magnesium obtained was found to be very reactive. With cold

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[4] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[5] Gilman, *ibid.*, **47**, 2002 (1925).

water it reacted with the evolution of a great deal of heat, forming magnesium hydroxide. Chlorobenzene in dry ether was found to react very readily indeed, forming phenylmagnesium chloride, while ethyl bromide in ether reacted with considerable violence.

In Expts. 7 and 8 the magnesium was determined by dissolving in nitric acid, making up to a known volume, and determining the magnesium gravimetrically from an aliquot portion. Absence of magnesium bromide was shown when tested with silver nitrate. In Expt. 6 the magnesium was determined by dissolving it in dry ether containing ethyl bromide, hydrolyzing an aliquot portion, and measuring the volume of ethane. In Expts. 1 to 5 the magnesium was determined by dissolving in an excess of standard sulfuric acid and titrating the excess of acid with standard alkali, using an aliquot portion of the acid solution.

In Expts. 2 to 8, inclusive, the reaction mixtures were hydrolyzed by pouring into chipped ice and water. In Expts. 5, 6, 7 and 8 the precipitated magnesium hydroxide was washed free from magnesium bromide and the two determined separately, the hydroxide gravimetrically and the bromide by titrating with silver nitrate. Upon hydrolysis there was obtained magnesium hydroxide and magnesium bromide in equivalent amounts from the unelectrolyzed Grignard reagent, plus magnesium bromide from the electrolysis. The amount of magnesium bromide formed by the electrolysis must then be the amount of magnesium bromide as determined by analysis, minus an amount equivalent to the magnesium hydroxide. The magnesium hydroxide was determined in Expts. 2, 3 and 4 by dissolving in standard sulfuric acid and titrating aliquot portions with standard alkali. Magnesium bromide was analyzed for in aliquot portions of the same solution by precipitation of the sulfate ion with a very slight excess of barium hydroxide solution (using phenolphthalein as an indicator), barely acidifying with 0.3 *N* sulfuric acid, and titrating with standard silver nitrate solution. The volume of the solution was such as to prevent the precipitation of the small amount of silver sulfate that would be formed. In Expt. 1, instead of hydrolyzing the whole ether solution and dissolving all of the magnesium hydroxide in standard acid, aliquot portions were hydrolyzed. Some of these portions were analyzed for magnesium hydroxide and some for halogen.

From the ether solutions left after hydrolysis, were obtained phenol and diphenyl in the case of phenylmagnesium bromide, and dibenzyl and benzyl alcohol in the case of benzylmagnesium chloride. In the electrolysis of the benzylmagnesium chloride, the magnesium chloride being quite insoluble in ether was found in the solution obtained on dissolving the magnesium. The results are briefly summarized in Table I. The weights of the hydrocarbons diphenyl and dibenzyl listed in Table I were obtained by subtracting the weight of the hydrocarbon formed in

Table I

Electrolysis of Phenylmagnesium Bromide and Benzylmagnesium Chloride

Expt. no.	Substance	Concn. of Grign., moles per liter	Products of electrolysis	Molecular quant.	Equiv. of electricity
1	$C_6H_5CH_2MgCl$	1.01	$C_6H_5CH_2CH_2C_6H_5$	0.0714	0.2677
			$MgCl_2$	.0791	
			Mg	.1304	
2	$C_6H_5CH_2MgCl$	.802	$C_6H_5CH_2CH_2C_6H_5$	.0769	.2864
			$MgCl_2$	.1348	
			Mg	.1412	
3	C_6H_5MgBr	1.548	$C_6H_5—C_6H_5$	?	.2294
			$MgBr_2$	.000	
			Mg	.074	
4	C_6H_5MgBr	1.70	$C_6H_5—C_6H_5$	?	.3213
			$MgBr_2$	?	
			Mg	.0654	
5	C_6H_5MgBr	1.73	$C_6H_5—C_6H_5$	.0324	
			$MgBr_2$	?	
			Mg	.107	
6	C_6H_5MgBr	1.00	$C_6H_5—C_6H_5$	.0266	
			$MgBr_2$	.044	
			Mg	.0414	
7	C_6H_5MgBr	1.43	$C_6H_5—C_6H_5$	?	
			$MgBr_2$	.000	
			Mg	.019	
8	C_6H_5MgBr	1.43	$C_6H_5—C_6H_5$	?	
			$MgBr_2$	.0000	
			Mg	.0218	

the synthesis of the Grignard reagent as indicated by analysis of unelectrolyzed Grignard, from the total weight of hydrocarbon obtained after electrolysis was complete. The amount of magnesium halide indicated in the table represents the total amount of the halide, minus an amount equivalent to the amount of hydrocarbon formed in the synthesis of the reagent.

In Expt. 8, a tantalum anode and a platinum cathode were used. In Expt. 4, the amount of phenol in the cell fell from 11.6 g. to 2.8 g. during the course of the electrolysis.

Discussion

As indicated by the analysis, the products of the electrolysis in the case of benzylmagnesium chloride were dibenzyl, magnesium chloride and magnesium. A very nearly quantitative yield of magnesium was obtained (based on the coulometer). On the same basis, the yield of dibenzyl was found to be somewhat greater than 50%. It seems likely, then, that the three substances are formed in equimolecular amounts. The experiments with phenylmagnesium bromide were not so satisfactory, the magnesium bromide being approximately the amount that would be formed during the synthesis of the Grignard reagent through the side reaction forming the hydrocarbon. Furthermore, the amount of magnesium obtained from phenylmagnesium bromide was very much less than that calculated, indicating the presence of side reactions. Regarding the nature of these side reactions, very little can be said as yet; however, it seems probable that the magnesium bromide in solution is responsible, since it is quite soluble in ether. The experiments with benzylmagnesium chloride also seem to bear this out, for the magnesium chloride produced is very much less soluble in ether than the bromide.

In these electrolyses, the magnesium was deposited on the cathode. In an earlier experiment with phenylmagnesium bromide, an oil was finally precipitated from the anode. This oil was identified as $MgBr_2$-$2C_2H_5$-O-C_2H_5. Apparently, then, the magnesium bromide is formed at the anode. The place of formation of the hydrocarbon is not definitely known, but it is presumably at the anode. The formation of that substance involves an oxidation (loss of electron) and in the case of phenylmagnesium bromide, electrolysis is accompanied by strong luminescence at the anode, suggestive of oxidation. Based on these considerations a possible mechanism of the reaction is indicated by the equations

$$\begin{array}{l}
\qquad\quad C_6H_5CH_2^- + Mg^{++} \\
\qquad\qquad\;\; \downarrow \; \uparrow \\
C_6H_5CH_2MgCl \rightleftharpoons C_6H_5^+CH_2^-Mg + Cl \\
Mg^{++} + 2\ominus \longrightarrow Mg^{+-} \text{ (cathode)} \\
Mg^{++} + 2Cl^- \longrightarrow MgCl_2 \\
C_6H_5CH_2^- \longrightarrow C_6H_5CH_2^+ + 2\ominus \text{ (anode)} \\
C_6H_5CH_2^- + C_6H_5CH_2^+ \longrightarrow C_6H_5CH_2\text{—}CH_2C_6H_5
\end{array}$$

With the low current densities used, it seems probable that Mg^{++} rather than $C_6H_5CH_2Mg^+$ would absorb the electrons at the cathode.

The anodic luminescence noted in the case of phenylmagnesium bromide was very marked. This luminescent property of Grignard reagents during oxidation with air has already been noted. It seems probable that this luminescent property is in both cases due to the transfer of electrons, as indicated by the equations

$$\begin{array}{ll}
C_6H_5^-\text{—}Mg^{++}\text{—}Br^- + O^{+-} & \longrightarrow C_6H_5^+\text{—}O^{--}\text{—}Mg^{++}\text{—}Br^- \\
C_6H_5^-\text{—}Mg^{++}\text{—}Br^- & \\
 & \longrightarrow C_6H_5^-\text{—}C_6H_5^+ + Mg^{+-} \\
C_6H_5^-\text{—}Mg^{++}\text{—}Br^- &
\end{array}$$

Summary

1. The electrolysis of phenylmagnesium bromide and benzylmagnesium chloride in ether solution has been carried out.

2. The products of reaction have been identified, and a possible mechanism of the reaction is suggested.

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