The Electrolysis of n-Propylmagnesium Bromide and Isopropylmagnesium Bromide in Ethyl Ether

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The electrolysis of methylmagnesium halides in ether solution has been studied for both ethyl and n-butyl ether.[1,2] The electrolysis of ethylmagnesium halides in ethyl ether also has been studied.[3] The products of these electrolyses indicated that the solvent had played an important role, and a mechanism was postulated[2] for the reaction between the free radical and the ether.

The present work is a continuation of the investigation in ethyl ether using n-propyl and isopropylmagnesium bromides as electrolytes. A comparison of the products of the electrolysis studies so far is shown in Table I.

TABLE I

COMPARISON OF THE PRODUCTS OF ELECTROLYSIS OF METHYL, ETHYL AND PROPYL GRIGNARD REAGENTS

Grignard reagent and ether	Gaseous products	Liquid products
Ethylmagnesium iodide	Ethane	
Ethyl	Ethylene	
	Hydrogen	
Propylmagnesium	Propane	Hexane
bromide	Propylene	n-Propyl alc.
Ethyl	Ethylene	Ethyl alc.
	Hydrogen	s-Amyl alc.
	Oxygen	
	Carbon dioxide	
Isopropylmagnesium	Propane	Isopropyl alc.
bromide	Propylene	Ethyl alc.
Ethyl	Ethylene	2,3-Dimethyl-
	Hydrogen	butane
	Oxygen	
	Carbon dioxide	
Methylmagnesium	Ethane	n-Butyl alc.
iodide	Methane	s-Amyl alc.
n-Butyl	Butane	
	Butylene	
	Oxygen	
	Hydrogen	
	Carbon dioxide	
Methylmagnesium	Ethane	Ethyl alc.
bromide	Methane	Isopropyl alc.
Ethyl	Ethylene	
	Hydrogen	
	Oxygen	
	Carbon dioxide	

(1) Evans and Field, THIS JOURNAL, 58, 720 (1936).
(2) Evans and Field, ibid., 58, 2284 (1936).
(3) Evans and Lee, ibid., 56, 654 (1934).

Experimental

The apparatus and procedure were the same as previously described.[2] Platinum electrodes for both the anode and the cathode were used throughout the experiment.

n-Propylmagnesium Bromide.—Propane and propylene were the main gaseous products of the electrolysis, but small amounts of carbon dioxide, hydrogen and oxygen were also found. These last constituents have been present as products of all of the electrolyses. They have always occurred in small erratic amounts irrespective of the current density.

Propane and propylene occurred in approximately equivalent amounts, and their relation was found to be independent of the current density. The analysis of the gaseous products was made by the absorption method. To make sure that the composition of the gas did not vary with change in current density, at each change the apparatus was run for from four to five hours to make sure that any change in gas would have ample time to manifest itself.[4] The results of the analyses of the gaseous products with change in current density are tabulated in Table II. At the completion of the electrolysis, the remaining

TABLE II

GASEOUS PRODUCTS OF THE ELECTROLYSIS OF n-PROPYL-MAGNESIUM BROMIDE IN ETHYL ETHER

Order taken	Efficiency 91% Amp./ sq. dm.	Orig. normality 1.99				Final normality 1.24		
		CO₂	C₂H₄	O₂	H₂	CO	C₃H₆	C₃H₈
1	1.64	0.3	1.3	2.1	1.0	0.3	45.4	47.0
2	1.48	.8	1.3	1.5	1.0	.3	47.0	47.6
3	1.08	.8	1.5	1.5	1.7	.8	46.7	46.3
4	1.08	.6	1.9	1.3	1.6	.3	47.2	46.4
5	0.80	.6	1.4	1.7	1.7	.1	48.0	46.3
6	.80	1.0	1.3	1.7	1.9	.8	45.5	45.9
7	.96	0.4	1.3	1.0	1.3	.3	47.0	48.0

solution was hydrolyzed in an atmosphere of nitrogen and fractionally distilled using a Davis column. The liquid products remaining after the removal of the ethyl ether were extremely difficult to separate completely by fractionation, and so only approximations can be made as to quantities present. From 9 to 10 cc. of n-hexane was isolated and identified, as was 2 to 3 cc. of ethyl alcohol, some n-propyl alcohol and a trace of s-amyl alcohol. It had been reported previously that no hexane was formed.[3] This has been shown to be in error. The alcohols were identified by 3,5-dinitrobenzoate derivatives. Practically no high boiling products were obtained, indicating that very little polymerization took place.

The efficiency of the electrolysis determined on the change in Grignard concentration (by titration) was 91%. Since all the propyls liberated did not form gaseous prod-

(4) Each Grignard compound was electrolyzed for a total of about 100 consecutive hours.

ucts, and since it was impossible to determine accurately the amount of coupling, it is impossible to calculate the efficiency of the electrolysis on this basis. It can be shown, however, that a rough calculation on the basis of the propyl radicals liberated using the data available indicates that the efficiency is in the range given by the titration method.

Isopropylmagnesium Bromide.—When this electrolysis was carried out, it was noted that a different type of magnesium seemed to plate out. The magnesium deposited in "strings" and stuck to the electrode so tightly that the agitation due to the boiling of the solvent ether was not sufficient to free it from the electrode. Consequently, unless watched continuously, the magnesium plated across the two electrodes and caused a type of short circuit that caused difficulty, especially in determining the efficiency. The electrodes were cleaned from time to time by shaking the cell or by dismantling and scraping. The efficiency was determined to be between 90 and 100%. Samples of the gas given off at various current densities were analyzed by the absorption method. The results are tabulated in Table III.

TABLE III

GASEOUS PRODUCTS OF THE ELECTROLYSIS OF ISOPROPYL-
MAGNESIUM BROMIDE IN ETHYL ETHER

Order taken	Efficiency 90–100% Amp./ sq. dm.	Orig. normality 1.61				Final normality 0.58		
		CO_2	C_2H_4	O_2	H_2	CO	C_3H_6	C_3H_8
1	0.88	0.6	1.5	1.5	1.3	0.9	47.6	46.5
2	.88	.4	1.2	1.0	1.0	.2	47.3	49.0
3	1.60	.0	0.8	1.7	1.7	.2	53.6	42.0
4	1.60	.0	.6	1.2	1.2	.2	52.0	45.0
5	1.28	.4	.2	1.4	3.7	.3	52.1	41.3
6	1.20	.5	.5	1.4	2.5	.9	51.7	42.6

On analysis of the liquid products it was found that only a minute fraction of the isopropyl radicals liberated had coupled. On fractionation, an impure fraction was obtained (0.5 cc.) that had the boiling point of 2,3-dimethylbutane but the refractive index was low. The lowering of the index undoubtedly was due to the presence of some ethyl ether. Approximately 0.5 cc. of ethyl alcohol was obtained, as was about 0.5 cc. of isopropyl alcohol. These were identified by 3,5-dinitrobenzoate derivatives. No secondary alcohol was found. This does not mean that it was not present, however, because there was so little high boiling material that it could not be fractionated, and since there are no common derivatives of methyl isopropylcarbinol, it could not be extracted in this manner.
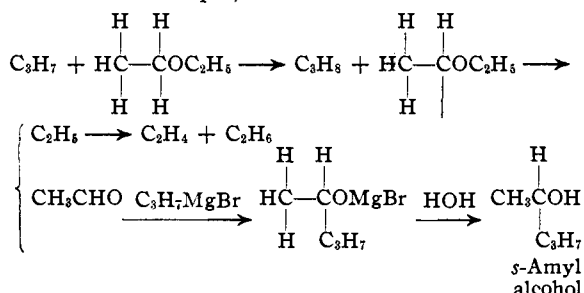
An interesting observation is the tendency to couple. A trace of butane has been reported[5] as a product of the electrolysis of ethylmagnesium halides. n-Propyl radicals seem to have approximately a fifty-fifty tendency to couple as shown by the amount of hexane found and the amount of gas liberated. This would indicate that the butyl radical should show very marked tendency to couple, and this is the case.[6] As soon as branched chain compounds are used the tendency to couple is greatly reduced, apparently, since the isopropyl radical forms propane and propylene and little 2,3-dimethylbutane. This
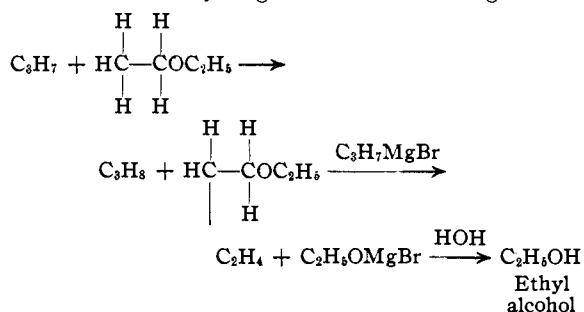
(5) Plump and Hammett, unpublished article.
(6) Data in forthcoming paper from this Laboratory.

probably will be brought out more clearly when the various butylmagnesium halides are studied.[6]

Reaction with Ethers.—The theory already postulated[2] explains all of the liquid products except the n-propyl and the isopropyl alcohols. These may be explained easily by the reaction of the Grignard compound with the oxygen from the electrolysis. Using this theory to explain the formation of the liquid products, the course of the reaction would be (using n-propylmagnesium bromide as an example)

$$C_3H_7 + H\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}\text{—}C\overset{H}{\underset{H}{\overset{|}{\underset{|}{}}}}OC_2H_5 \longrightarrow C_3H_8 + H\overset{H}{\underset{|}{\overset{|}{C}}}\text{—}C\overset{H}{\underset{|}{\overset{|}{}}}OC_2H_5 \longrightarrow$$

$$\begin{cases} C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \\ \\ CH_3CHO \xrightarrow{\ C_3H_7MgBr\ } H\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}\text{—}C\overset{H}{\underset{C_3H_7}{\overset{|}{\underset{|}{}}}}OMgBr \xrightarrow{\ HOH\ } CH_3\overset{H}{\underset{C_3H_7}{\overset{|}{\underset{|}{}}}}COH \\ \\ \quad \text{s-Amyl alcohol} \end{cases}$$

and with the β hydrogen of the ether we get

$$C_3H_7 + H\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}\text{—}C\overset{H}{\underset{H}{\overset{|}{\underset{|}{}}}}OC_2H_5 \longrightarrow$$

$$C_3H_8 + H\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}\text{—}C\overset{H}{\underset{}{\overset{|}{}}}OC_2H_5 \xrightarrow{\ C_3H_7MgBr\ }$$

$$C_2H_4 + C_2H_5OMgBr \xrightarrow{\ HOH\ } C_2H_5OH$$
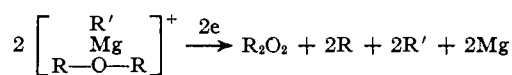$$\text{Ethyl alcohol}$$

This theory explains the important liquid products, but it does not indicate any possible source of the oxygen and trace of carbon dioxide that have been reported. A little different approach seems to offer possibilities.

If the ionization of the Grignard compound is as already postulated

$$2RMgX \longrightarrow RMgX_2^- + RMg^+$$

it is reasonable to suppose that the RMg^+ ion might form some type of oxonium ion similar to $\begin{bmatrix} R' \\ Mg \\ R\text{—}O\text{—}R \end{bmatrix}^+$. If this complex radical were to be discharged at the cathode, a series of decompositions undoubtedly would take place, and it is possible that one of the products might be a peroxide. The reaction would then be as follows

$$2\begin{bmatrix} R' \\ Mg \\ R\text{—}O\text{—}R \end{bmatrix}^+ \xrightarrow{\ 2e\ } R_2O_2 + 2R + 2R' + 2Mg$$

The peroxide formed could immediately decompose to give oxygen, or it could oxidize the

ether to give an ether peroxide. This ether peroxide has been shown by Clover[7] to decompose to give carbon dioxide, ethyl alcohol, methane and acetaldehyde. The oxidation of the ether in this manner is usually a slow one, but it has been reported[8] that the oxidation may be catalyzed by the Grignard compound.

Thus the carbon dioxide and the ethyl alcohol are easily explained. The secondary alcohol would be the product of the reaction between the acetaldehyde and the Grignard compound. This seems to be a very complex mechanism, but it must be remembered that this is by no means the major course of the reaction but merely offers an explanation for the products that appear practically as traces. A Podbielniak distillation was run on the gas liberated from the isopropyl run to see if it would be possible to find any of the methane that this newer theory predicts. None was found. This does not prove the theory in error, because the amount of methane formed would be so small that it might easily be missed on a distillation. From the distillation, however, a considerable amount of hydrogen was obtained, proving without a doubt that it is a product of the electrolysis. The presence of the hydrogen is most likely explained on the basis of the disproportionation of the isopropyl radical. Table III
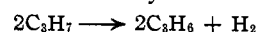
(7) Clover, This Journal, 44, 1107 (1922).
(8) Gilman and Wood, ibid., 48, 806 (1926).

indicates that the propylene is always in excess of the propane by a few per cent. This means that although most of the reaction was of the type

$$2C_3H_7 \longrightarrow C_3H_6 + C_3H_8$$
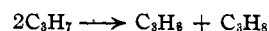
there was a small tendency toward

$$2C_3H_7 \longrightarrow 2C_3H_6 + H_2$$

All of the propylene formed by the latter reaction would be in excess of the amount necessary to balance the propane. Also the amount of hydrogen should correspond to one-half the difference of the propylene and the propane. On reference to the tables it is found that within experimental error this is the case.

Summary

1. The formation of the liquid products in the electrolysis of n-propyl- and isopropylmagnesium halides is explained.

2. As the length of the straight chain increases, the tendency of the free radical formed to couple increases.

3. If a branched chain compound is electrolyzed, the tendency for the free radical to couple is much less than that of the corresponding straight chain compound.

4. The current density has no effect on the composition of the gaseous products in the electrolysis of n-propyl- and isopropyl-magnesium bromides.

A Study of Organic Parachors. II. Temperature, and (III) Constitutive Variations of Parachors of a Series of Tertiary Alcohols[1]

By Katherine Owen, Osborne R. Quayle and Ellington M. Beavers[2]

It has been noted that irregularities between observed and calculated parachors are encountered when the normal, straight chain is departed from. In the case of the compounds containing branched chains the observed parachors are consistently lower than the calculated. With the establishment of this observation, Mumford and Phillips[3] in 1929 reëvaluated the parachor con-

stants to give better agreement with the observed parachors of compounds of high molecular weight. Among these reëvaluated constants were two new "strain constants": -3 units for a branched chain of the secondary type; -6 units for tertiary branching.

Each "strain constant" was evaluated as the mean of many observations on secondary and tertiary compounds, and there are many cases of large deviations from these values.

The present program of research was begun in an endeavor to examine the apparent irregularities in parachor values and to discover, where possible, any existing consistencies caused by con-