With the solution method total polarizations of 26.0 cc. and 25.91 cc. were reported by Williams and by Smyth, respectively. These values appear to be too high, possibly due to the presence of moisture in the solution or to some solvent action. Using the value given by Smyth, P_E = 21.6 cc., and our value of 24.5 cc. for the total polarization, the atomic polarization for dioxane is 24.5 cc. − 21.6 cc. or 2.9 cc. This value for P_A is of an expected order of magnitude for a compound with a structure such as dioxane.

The apparatus used in this investigation has been described in the literature.[2]

The dioxane was dried for several days over metallic sodium and fractionally distilled. The fraction which boiled between 100.2 and 100.5° and which had a refractive index of 1.04208_D^{25} was employed.

(2) Schwingel and Williams, *Phys. Rev.*, **35**, 855 (1930), Greene and Williams, *ibid.*, **42**, 119 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Electrolysis of Ether Solutions of the Grignard Compound. Isolation, Identification and Quantitative Determination of Anodic Products

W. V. EVANS AND F. H. LEE

Little quantitative work has been done on the electrolytic products obtained at the anode during the electrolysis of the Grignard reagent. Jolibois[1] electrolyzed ethylmagnesium iodide expecting to isolate gaseous hydrocarbons but did not succeed. He assumed that methyl iodide instead of hydrocarbons was discharged.

Gaddum and French[2] aimed to reveal the mechanism of the reaction, but they used Grignard compounds which yield ether-soluble solid hydrocarbons. They were unable to tell where these hydrocarbons were formed, and their yield was poor. Rodebush and Peterson[3] thought the ethyl radical was liberated at the anode but they never isolated and identified it.

Along quite another line several workers have used different metals as anodes. Kondyrew and Manojew[4] found that a magnesium, zinc or aluminum anode will lose weight equivalent to the Faraday of electricity during electrolysis.

Recently French and Drane,[5] using aluminum, bismuth, gold, nickel, silver, tin, zinc, and cadmium as anodes, found that aluminum, zinc and cadmium were attacked while only aluminum exists in quantity in the solution. They comment that in cases where the anode was not attacked an equivalent amount of Grignard compound was decomposed. One well-known fact is that on electrolysis of the Grignard reagent using inert elec-

trodes, magnesium is deposited on the cathode. One faraday of electricity liberates one equivalent of magnesium. This fact was demonstrated by Kondyrew,[6] who amalgamated his magnesium with mercury. We have checked this result, plating out the magnesium on platinum and determined the faraday equivalent. The present work was undertaken to determine the composition of the gaseous hydrocarbons evolved at an inert anode.

Experimental

The apparatus is shown in Fig. 1. The platinum electrodes 20 sq. cm. in area and 3 cm. apart were placed in the upper part of the cell, thus leaving a large space underneath for the accumulation of spongy magnesium.

A stirrer with a mercury seal was set between the electrodes. The gaseous products of electrolysis were led through a reflux condenser, washing bottle, delivery tube, salt water bath and finally to a eudiometer. No gas was evolved in the beginning of the electrolysis so the cell was allowed to run until the solution was saturated with the products of electrolysis and the temperature became constant. After the evolution of gas became constant, a copper coulometer was put in the circuit and a sample of gas collected. The volume of gas collected in the eudiometer (after correction) was taken as the total volume of hydrocarbons. The Grignard solutions were made by the usual method, heated in contact with excess magnesium, and analyzed by Gilman's acid titration method. A solution of 45% sulfuric acid was found suitable for removing ether from these hydrocarbons. The gases were collected over a saturated salt water solution. The gas was subsequently analyzed, mainly according to the method devised at the United States Bureau of Mines[7]

(1) Jolibois, *Compt. rend.*, **155**, 353 (1912); **156**, 712 (1913).

(2) Gaddum and French, THIS JOURNAL, **49**, 1295 (1927).

(3) Rodebush and Peterson, *ibid.*, **51**, 638 (1929).

(4) Kondyrew and Manojew, *Ber.*, **58**, 469 (1925).

(5) French and Drane, THIS JOURNAL, **52**, 4924 (1930).

(6) Kondyrew, *J. Russ. Phys.-Chem. Soc.*, **60**, 545 (1928).

(7) Bulletin 197, U. S. Bureau of Mines.

as modified by C. D. Hurd.[8] The following constituents were determined in respective order: isobutylene, n-butylene, propylene, ethylene, oxygen, hydrogen and saturated hydrocarbons. Tables I and II give the results obtained.

TABLE I

Reagents	Concn., n	Amp.	Voltage	Gas constituents Ethane	Gas constituents Ethylene	Gas constituents Hydrogen	Moles of gas per faraday
C_2H_5MgI	1.32	0.4	110	51.8	47.4	0.8	0.863
C_2H_5MgI	1.53	.4	100	50.2	48.8	1.0	.877
C_2H_5MgI	2.23	.4	85	53.3	45.6	1.1	.902
C_2H_5MgBr	1.22	.4	110	48.1	50.8	1.1	.863
C_2H_5MgBr	1.50			50.7	48.6	1.0	.925
C_2H_5MgBr	3.53	.4		47.4	51.4	1.2	.907
C_2H_5MgCl	1.53	.4	100	50.5	48.2	1.3	.934
C_2H_5MgCl	2.36	.4	80–90	51.3	47.8	0.9	.968
				Propane	Propylene	Hydrogen	
C_3H_7MgBr	1.36	.2		50.1	49.0	0.9	.965
C_3H_7MgBr	1.34	.2		50.9	48.0	1.1	.960

Table I shows that the electrolytic products of ethyl and propylmagnesium halide are independent of the concentration. It also shows that ethane, ethylene and small amounts of hydrogen are obtained from ethylmagnesium halides and propane, propylene and small amounts of hydrogen from propylmagnesium halides.

It is also shown that the main reaction was disproportionation. Viewing Paneth's idea[9] that free alkyl radicals exist for a finite length of time,

lecular weight. The average number of carbon atoms in each molecule, revealed through slow

Fig. 1.—Electrolytic cell for collecting gas.

combustion experiments, came out about 2.15. It is assumed that a small amount of butane was

TABLE II

Reagents	Concn.	Amp.	Voltage	Saturated hydrocarbons Methane	Saturated hydrocarbons Ethane	Saturated hydrocarbons C_2H_6:CH_4	Unsaturated hydrocarbons Ethylene	Unsaturated hydrocarbons Isobutylene	Mole per faraday
CH_3MgBr	1.09 M	0.2	110	79.3		0:100	3.5	17.2	0.566
CH_3MgBr	1.43	.2	80–110	62.8	19.9	24:76	5.3	12.0	.547
CH_3MgBr	1.43	.2	80–110	64.4	23.8	27:73	3.7	8.1	.538
CH_3MgBr	1.45	.4	100–110	66.7	18.8	22:78	4.2	10.3	.573
CH_3MgBr	1.65	.2	24	40.0	51.0	56:44	3.6	5.4	.490
CH_3MgBr	1.65	.4	40–52	41.0	48.2	54:46	3.9	6.9	.499
CH_3MgBr	2.08	.4	80	24.9	67.0	73:27	2.5	5.6	.493
CH_3MgBr	2.08	.4	80	21.2	71.5	77:23	2.1	5.2	.477
CH_3MgBr	2.83	.4	45–48		100.0	100:0			.437
CH_3MgBr	2.83	.4	45–51		100.0	100:0			.439
CH_3MgI	2.10 M	.4	80–90	64.3	13.2	17:83	5.9	16.7	.358
CH_3MgI	4.11	.4	40	56.6	27.8	33:67	6.9	8.5	.463

we may suppose that the alkyl radical has been discharged and subsequently disproportionates according to the following equations:

$$2C_2H_5 = C_2H_4 + C_2H_6 \quad \text{primary reaction}$$
$$2C_2H_5 = 2C_2H_4 + H_2 \quad \text{secondary reaction}$$
$$2C_3H_7 = C_3H_6 + C_3H_8 \quad \text{primary reaction}$$
$$2C_3H_7 = 2C_3H_6 + H_2 \quad \text{secondary reaction}$$
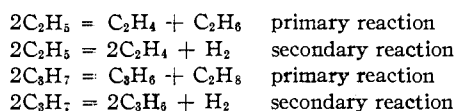
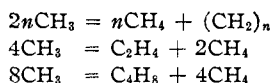The saturated hydrocarbons obtained from ethylmagnesium halide consist of, besides ethane, a small amount of hydrocarbons of a higher mo-

formed. In the case of propylmagnesium halide, if combination had taken place at all we should have hexane in solution. No hexane could be isolated. The number of carbon atoms in each molecule of saturated hydrocarbon in this case came out very close to 3.0, indicating that the gas was chiefly propane.

The above types of reactions can be correlated with reactions in quite different experiments. Schorigin[10] heated ethyl sodium and obtained ethane and ethylene. A similar type of reaction

(8) Hurd, THIS JOURNAL, 51, 3353 (1929).

(9) Paneth, Ber., 62, 1335 (1929); Nature, 125, 564 (1930).

(10) Schorigin. Ber., 43, 1931 (1910).

occurs when ethylmagnesium halide is heated with ethyl halide. Späth[11] worked with a large number of compounds and found the following types of reactions: $R + R = (R-H) + (R + H)$, $R + R = R \cdot R$. Which of these two reactions will take place depends upon the nature of the radicals. With ethyl and propyl the former reaction takes place.

Ethyl zinc consisting of zinc cation and ethyl anion should behave very similarly to the Grignard compound in electrolysis. Hein[12] and his co-workers electrolyzed ethyl sodium solutions of ethyl zinc and plated out zinc on the cathode and obtained ethane and ethylene with small amounts of methane, propane and butane as anodic products.

From Table II, we notice that the methyl radical undergoes a rather complicated rearrangement. Two types of reaction were taking place simultaneously. Which type predominates depends on the concentration. At lower concentration methane, ethylene, isobutylene and traces of butylene and propylene are produced. As the concentration increases the amount of methane and unsaturated hydrocarbons decreases while ethane increases. At about 3 molar concentration, the only product is ethane. For low concentration the reactions seem to be

$$2n\mathrm{CH_3} = n\mathrm{CH_4} + (\mathrm{CH_2})_n$$
$$4\mathrm{CH_3} = \mathrm{C_2H_4} + 2\mathrm{CH_4}$$
$$8\mathrm{CH_3} = \mathrm{C_4H_8} + 4\mathrm{CH_4}$$

where $(\mathrm{CH_2})_n$ represents ethylene, isobutylene, etc. At higher concentration the following reaction possibly takes place

$$2\mathrm{CH_3} = \mathrm{C_2H_6}$$
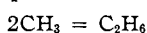
It is suggested that methyl is first obtained as a free radical. In concentrated solution, the free methyl radical may react with a methyl ion forming ethane and an electron which will be taken up by the anode.

$$\mathrm{CH_3^-} + \mathrm{CH_3} = \mathrm{C_2H_6} + e$$
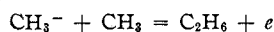
Späth[11] found that the methyl radical stands unique; the reaction between methyl iodide and methylmagnesium iodide gave 51.6% ethane.

The number of moles of gas evolved per faraday of electricity is given in the last column of Tables I and II. In the case of ethyl or propylmagnesium halide, according to the following type of reaction:

$$2\mathrm{C_2H_5} \longrightarrow \mathrm{C_2H_4} + \mathrm{C_2H_6} \qquad (1)$$
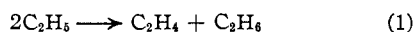
(11) Späth. Monatsh.. **34**, 1965 (1914).

(12) Hein, Z. anorg. Chem.. **141**, 161 (1925).

we should obtain 1 mole of gas per faraday. But two other reactions are taking place simultaneously

$$2\mathrm{C_2H_5} \longrightarrow 2\mathrm{C_2H_4} + \mathrm{H_2}, \text{ and} \qquad (2)$$
$$2\mathrm{C_2H_5} \longrightarrow \mathrm{C_4H_{10}} \qquad (3)$$
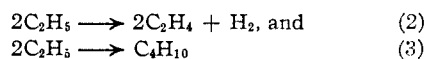
Reaction (2) gives more gas while reaction (3) gives less than reaction (1). However, these two reactions take place to only a very small extent. If reaction (1) was the main reaction, we should get one mole of gas per faraday. We obtained 0.97 to 0.86 mole of gas. The amount of gas varies with the kind of halide being electrolyzed. In general, a chloride gives the highest yield, bromide less, and iodide least.

When methylmagnesium halide is used, more gas is evolved at lower concentrations, because the reactions are of the types

$$4\mathrm{CH_3} \longrightarrow 2\mathrm{CH_4} + \mathrm{C_2H_4}$$
$$8\mathrm{CH_3} \longrightarrow 4\mathrm{CH_4} + \mathrm{C_4H_8}$$
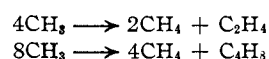
As the concentration is increased more ethane is produced. The reaction is $2\mathrm{CH_3} \longrightarrow \mathrm{C_2H_6}$ and a less amount of gas per faraday is evolved. If ethane were the only product of the electrolysis of methylmagnesium bromide we should obtain one-half a mole of gas per faraday. We find in the case when 100% ethane is produced, 0.44 mole of gas per faraday. As the percentage of ethane decreases, we have reactions where a faraday would give five-eighths and three-fourths moles. We should find the moles of gas increasing slightly and such is the case. The greatest yield of gas should be found where we have the largest percentage of isobutylene. Such is the case.

Electrolysis of Mixtures of Grignard Reagents.—An equimolecular mixture of ethylmagnesium and propylmagnesium bromide was prepared and electrolyzed. The following percentages were obtained

| Ethane	Propane	Ethylene	Propylene	Hydrogen
30.3	24.2	22.6	22.0	0.7

We notice from these results that both the ethyl and propyl radicals were discharged but slightly more of the ethyl radical. From an equimolecular mixture of ethylmagnesium bromide and phenylmagnesium bromide, 0.8 to 0.85 mole of gaseous hydrocarbons per faraday was obtained. This indicates that only the ethyl radical was electrolyzed.

Electrolysis Using an Active Anode.—When an aluminum anode was used, no gas was evolved even after running the electrolysis for four hours.

Examination showed the aluminum to be partially consumed. The reaction at the anode now becomes clear. When an inactive metal like platinum is used the alkyl radical is first discharged and then rearranges to form saturated and unsaturated hydrocarbons.

$$2C_2H_5^- - 2e \longrightarrow 2C_2H_5 \longrightarrow C_2H_6 + C_2H_4$$

When the anode is active the radical is not discharged but metal ions go into solution.

$$Al - 3e \longrightarrow Al^{+++}$$
$$Al^{+++} + 3C_2H_5^- \longrightarrow Al(C_2H_5)_3$$
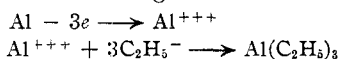
This theory is supported by the facts observed by Kondyrew and Manojew[4] and also by French and Drane.[5]
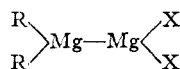
General Discussion

From some yet unpublished work in this Laboratory we have shown that if solutions of the Grignard reagent are electrolyzed for long periods with no stirring and the changes in concentration at the anode and cathode be determined considerable information as to the nature of the formula of the Grignard reagent can be determined. From these changes in concentration we discover that magnesium bromide accumulates in the anodic compartment. One mole of magnesium bromide is formed in the anodic section for each faraday of electricity. Also at the anode ethyl groups are discharged. At the cathode one equivalent of magnesium is discharged and approximately one equivalent migrates out for every equivalent discharged since the loss in this compartment is two equivalents. These facts seem to favor the formula $R_2Mg \cdot MgX_2$ for the Grignard reagent. Schlenk and Schlenk[13] have proposed the following equilibrium for the Grignard compound
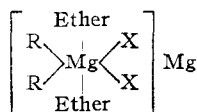
$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

Noller[14] proposes

$$R_2MgMgX_2 \rightleftharpoons R_2Mg + MgX_2$$
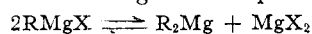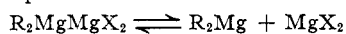
Jolibois' formula is

$$R{\scriptstyle\diagdown}{\atop{}} \!\!\!\! Mg{-}Mg{\atop{}}\!\!\!\! {\diagup X \atop \diagdown X}$$
$$R{\scriptstyle\diagup}$$

Terentjew's formula[15] is

$$\begin{bmatrix} & \text{Ether} & \\ R{\diagdown} & | & {\diagup}X \\ & Mg & \\ R{\diagup} & | & {\diagdown}X \\ & \text{Ether} & \end{bmatrix} Mg$$
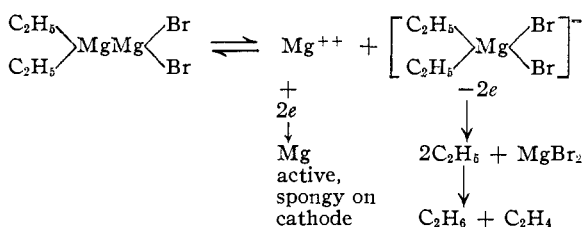
(13) Schlenk and Schlenk, *Ber.*, **62**, 920 (1929).
(14) Noller, THIS JOURNAL, **53**, 635 (1931).
(15) Terentjew, *Z. anorg. Chem.*, **156**, 73 (1926).

Terentjew's double formula is based on boiling point data. Meisenheimer and Schlichenmaier[16] spoke of associated instead of double molecules. Their data show methylmagnesium bromide at concentrations as dilute as 0.3 mole to consist of $1.9CH_3MgBr$ per molecule and in solution 0.07 molar $1.3CH_3MgBr$ per molecule. Thus we see that a double formula seems justified not only on the basis of boiling point data but from electrolysis and migration ratios as well, if we postulate that this compound is slightly ionized. The results can be briefly represented as follows:

$$\begin{array}{ccc} {C_2H_5}{\diagdown \atop }Mg Mg{\diagup Br \atop \diagdown Br} & \rightleftharpoons & Mg^{++} + \begin{bmatrix} {C_2H_5}{\diagdown \atop }Mg{\diagup Br \atop \diagdown Br} \end{bmatrix}^- \\ {C_2H_5}{\diagup \atop } & & {C_2H_5}{\diagup \atop } \\ + & & -2e \\ 2e & & \downarrow \\ \downarrow & & 2C_2H_5 + MgBr_2 \\ Mg & & \downarrow \\ \text{active,} & & \\ \text{spongy on} & & C_2H_6 + C_2H_4 \\ \text{cathode} & & \end{array}$$

The Mg^{++} migrates to the cathode and appears there as spongy magnesium. The negative radical loses two electrons and appears as $MgBr_2$ in a heavy oily layer and the two ethyl groups disproportionate

$$2C_2H_5 \rightleftharpoons C_2H_6 + C_2H_4 \qquad (3)$$

Summary

1. Ethylmagnesium halides have been electrolyzed and the anodic products are ethane, ethylene and traces of hydrogen.

2. Propylmagnesium halides give, on electrolysis, propane, propylene and traces of hydrogen.

3. Mixtures of ethyl and propylmagnesium halides give as products chiefly ethane, propane, ethylene and propylene.

4. When ethylmagnesium bromide and phenylmagnesium bromide are electrolyzed, only the ethyl group is discharged.

5. The electrolytic products of methylmagnesium halides vary with the concentration. At high concentration ethane is the chief product. At low concentration more methane and unsaturated hydrocarbons as ethylene and isobutylene are produced.

6. The mechanism for these reactions is suggested.

(16) Meisenheimer and Schlichenmaier, *Ber.*, **61**, 720 (1928).