chloride ceased water was added, the carbon tetrachloride layer removed and a saturated solution of salt added to the aqueous layer. About 25 g. of the sodium sulfonate was obtained. The loss in weight of the air-dried salt when heated in an oven at 120° indicated the presence of one molecule of water of hydration. The dry salt was analyzed for sodium.

Anal. Calcd. for $C_{12}H_7O_4S_2Na$: Na, 7.61. Found: Na, 7.66.

Refluxing the dry sodium salt with excess phosphorus oxychloride gave the sulfonyl chloride which separated from petroleum ether as a light yellow solid that melted at 127–128°.

Anal. Calcd. for $C_{12}H_7O_3S_2Cl$: Cl, 11.88. Found: Cl, 11.90.

Warming the sulfonyl chloride with concentrated ammonia for a few minutes gave the amide, obtained as colorless crystals from boiling water. This melted at 177–178°.

Anal. Calcd. for $C_{12}H_9O_3S_2N$: S, 22.96. Found: S, 22.78.

Phenoxthin-3,6-disulfonic Acid.—Sodium phenoxthin-3,6-disulfonate was obtained in exactly the same manner as the monosulfonate except for the use of 46.4 g. (0.4 mole) of chlorosulfonic acid. It is much more soluble in water than the monosulfonation product. Heating the air dried salt at 120° indicated two molecules of water of hydration. The analysis for sodium was made on the dry salt.

Anal. Calcd. for $C_{12}H_6O_7S_3Na_2$: Na, 11.48. Found: Na, 11.39, 11.52.

Addition of silver nitrate to a hot aqueous solution of the sodium salt gave an immediate precipitate of silver phenoxthin-3,6-disulfonate as glistening white crystals.

Anal. Calcd. for $C_{12}H_6O_7S_2Ag_2$: Ag, 37.59. Found: Ag, 37.57.

Refluxing the sodium salt with phosphorus oxychloride for two hours gave the disulfonyl chloride, which separated as light yellow crystals from benzene, m. p. 142–143°. The same compound was obtained from phenoxthin as follows. To 20 g. (0.1 mole of phenoxthin was added slowly 71 g. (0.61 mole) of chlorosulfonic acid. After one and one-half hours of standing at room temperature the mixture was poured on ice and the resulting greenish tar crystallized from benzene. The yield was 9 g. or 23% of the theoretical amount of the same product as was obtained above.

Anal. Calcd. for $C_{12}H_6O_5S_3Cl_2$: Cl, 17.86. Found: Cl, 17.90.

A 2-g. sample of the disulfonyl chloride was heated for thirty minutes with an equal weight of phosphorus pentachloride. The mixture was poured into water and the tarry insoluble material recrystallized from methanol. There was obtained a small amount of crystals, m. p. 134–135°, which when mixed with the original sulfonyl chloride depressed the m. p. to 107–110°. The 3,6-dichlorophenoxthin obtained by another method[7] melted at 135°.

Summary

1. The reaction of sulfur and aluminum chloride upon phenyl ether, *p*-bromophenyl phenyl ether and di-(*p*-bromophenyl) ether has been investigated. The reaction with phenyl ether gives a 74% yield of phenoxthin.

2. In bromination, sulfonation and Friedel–Crafts reactions the directive influence of the oxygen in phenoxthin is dominant over that of the sulfur, substitution invariably occurring para to the ether linkage.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 20, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Electrolysis of Methylmagnesium Halides in Ether Solutions

BY WARD V. EVANS AND EDMUND FIELD

Ether solutions of the Grignard reagent have been shown to possess properties characteristic of electrolytes in low dielectric media. Konduirev[1] has shown that the equivalent conductance of ethylmagnesium iodide goes through a maximum which varies with temperature. Definite and reproducible potentials have been obtained by Evans and Fosdick[2] between hydrogen electrodes and magnesium electrodes immersed in various Grignard solutions. The decomposition potentials of Grignard reagents have been shown by Evans and Lee[3] to be characteristic of the organic radical involved.

On electrolysis of ethylmagnesium bromide Evans and Lee[4] showed that magnesium migrates to both electrodes, with magnesium plating out on the cathode and magnesium bromide, ethane and ethylene forming at the anode. This was evidence for the existence of complex ions in the solution such as Mg^{++} $[Br_2MgEt_2]^=$ which must also participate in the equilibrium generally postulated for the Grignard reagent

$$2EtMgBr \rightleftharpoons MgEt_2 + MgBr_2 \text{ (Schlenk)}^5$$

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[1] Konduirev and Ssusi, *Ber.*, **62B**, 1856 (1929).

[2] Fosdick, Ph.D. Dissertation, Northwestern University, 1932.

[3] Evans and Lee, THIS JOURNAL, **57**, 489 (1935).

[4] Evans and Lee, *ibid.*, **56**, 654 (1934).

[5] Schlenk and Schlenk, *Ber.*, **62B**, 920 (1929).

or

$$Et_2Mg\cdot MgBr_2 \rightleftharpoons MgEt_2 + MgBr_2 \text{ (Noller)}^{6}$$

The anode reaction was considered to be

$$[Br_2MgEt_2]^- \longrightarrow 2e + MgBr_2 + 2Et$$

The two ethyl radicals disproportionate to form ethane and ethylene, or to a lesser extent couple to form butane thus explaining their experimental results exactly.

The methylmagnesium halides did not behave in such a simple fashion, apparently due to the fact that methyl radicals cannot undergo simple disproportionation. A more thorough study of these compounds was therefore undertaken in the hope of learning something of the behavior of free methyl radicals in ether solution as well as to gain further insight on the nature of the Grignard reagent.

Experimental

The apparatus is shown in Fig. 1. The electrodes were of bright platinum 5 cm. square and 2.2 cm. apart. Pyrex glass was used throughout and the ground-glass joint to the cell was mercury sealed and unlubricated. During electrolysis the solution was kept refluxing both for agitation and for constant temperature.

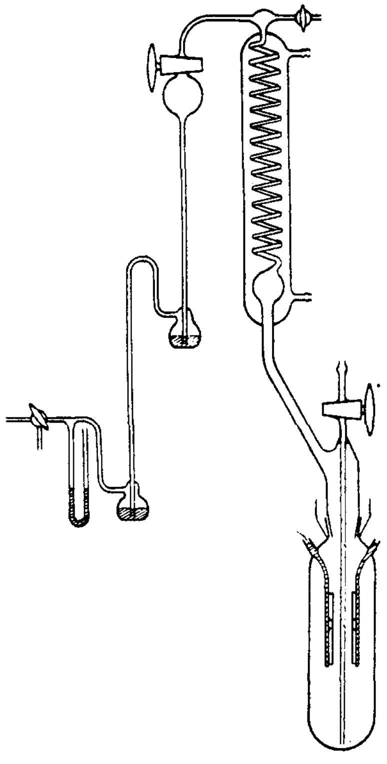

Fig. 1.—Electrolysis apparatus.

The methylmagnesium bromides and iodides were prepared according to standard procedure, and the chloride by the method of Schmalfuss.[7] The solutions were filtered through glass wool and transferred to the cell in an atmosphere of nitrogen. Analyses were made before and after electrolysis by Gilman's acid titration method.

In the electrolysis direct current up to 120 volts was used. An ammeter and a modified form of the Wright[8] coulometer (Fig. 2) were kept in series, giving a continuous and cumulative record of the current passed. This coulometer uses a carbon cathode from which mercury drips into the measuring tube below where the height of the column is a measure of the quantity of electricity passed. It is of simple construction and accurate within 1% for currents up to 0.5 ampere.

The gases evolved were collected in a large bottle over saturated salt solution until equilibrium was established at a given current density and then a small sample was taken for analysis. The analysis was accepted only when two successive samples checked. The two mercury traps in series effectively protected the cell from the water in the collecting bottle.

The gases were analyzed by the usual absorption procedure followed by slow combustion of the saturated hydrocarbons, with two useful modifications. After proving the absence of isobutylene with the Denigès[9] solution, the ether vapor could be removed very efficiently by the use of 63% sulfuric acid. Ethylene was absorbed by 95% sulfuric acid activated with nickel and silver as recommended by Tropsch.[10] A Podbielniak distillation confirmed the results obtained by the absorption method.

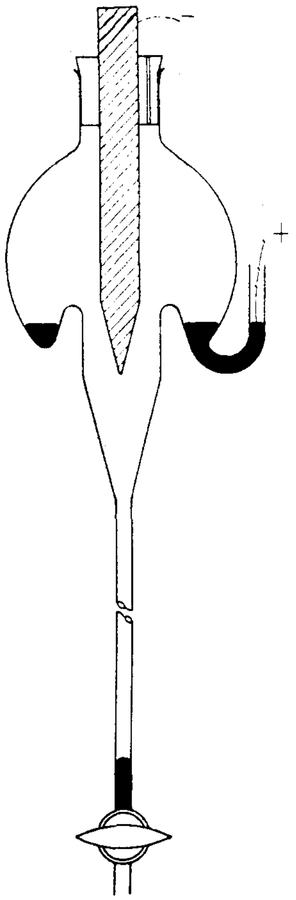

Fig. 2.—Modification of the Wright coulometer.

Gaseous Products.—Table I shows the complete results of a typical run using a single solution of methylmagnesium iodide sufficiently concentrated to allow a full range of current densities. The current densities were stepped up and down in random order during the run as indicated in column 1. The purpose of this was to be sure the changes observed were due to current density and

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[6] Noller, This Journal, 53, 635 (1931).

[7] Schmalfuss, *J. prakt. Chem.*, **108**, 88 (1924).

[8] Hatfield, *Z. Elektrochem.*, **15**, 728 (1909); Dole, "Theoretical Electrochemistry," McGraw-Hill Book Co. Inc., New York, 1935, p. 35.

[9] Denigès, *Compt. rend.*, **126**, 1043 (1898).

[10] Tropsch, *Ind. Eng. Chem., Anal. Ed.*, **6**, 404 (1934).

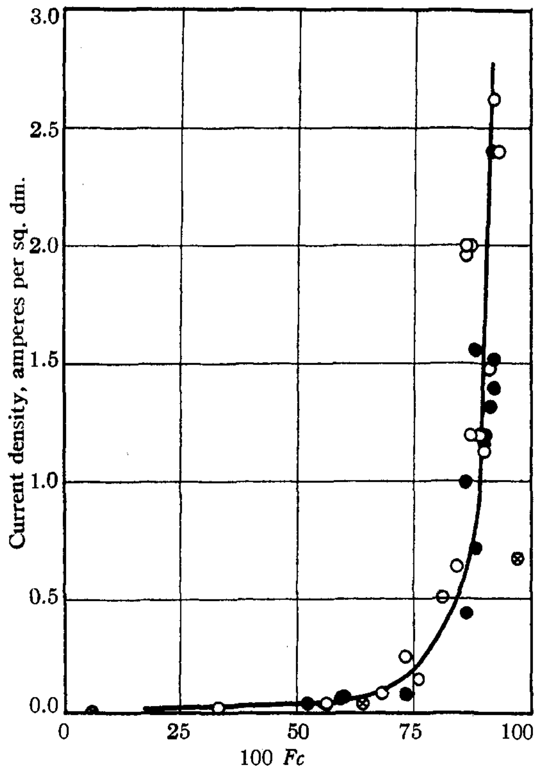
TABLE I

ELECTROLYSIS OF A METHYLMAGNESIUM IODIDE SOLUTION

Initial concn. 1.82 *N*, final concn. 1.38 *N*. Over-all efficiency: 0.419 mole/faraday, 0.718 equiv. decomposed/faraday, 0.933 methyls/equiv. decomposed.

Order taken	C. d. amp./sq. dm.	Gas constituents Ethane	Methane	Ethylene	Carbon dioxide	*Fc*	Moles gas per faraday
7	0.02	19.5	78.8	1.7	0.0	0.33	0.52
1	.04	38.1	59.8	1.2	.9	.56	(.42)
2	.08	51.2	47.4	0.5	.9	.68	.49
5	.245	57.2	41.5	.7	.6	.73	.46
4	.545	68.2	30.7	.5	.6	.82	.43
3	1.13	81.0	17.8	.3	.9	.90	.40
8	1.48	83.1	15.9	1.0	.0	.91	.37
6	2.62	84.2	14.9	0.3	.6	.92	.38

not the effects of electrolysis. In all, twenty different solutions were used, with concentrations of methylmagnesium iodide ranging from 0.41 to 4.0 *N*, bromide from 0.24 to 2.85 *N*, and chloride from 0.12 to 1.6 *N*. In general methane and ethane predominate, with the remaining 1 to 4% being made up of ethylene and carbon dioxide. No hydrogen or isobutylene, previously reported present,[4] were found.



○, Iodide; ●, bromide; ⊗, chloride.

Fig. 3.—Effect of current density on the fraction of methyls coupled for the three methylmagnesium halides in ether solution.

Since it is almost certain, as we shall show, that each methane molecule evolved corresponds to a single methyl radical while each ethane corresponds to two methyls, we are particularly interested in the fraction of methyls liberated which couple to form ethane. This fraction, which we have called *Fc* ($Fc = 2C_2H_6/(2C_2H_6 + CH_4)$) has been found to be independent of the concentration but definitely a function of the current density. Figure 3 shows all our experimental values of *Fc* plotted against the current density at which the sample of gas was evolved. The values for the bromides and iodides form a single curve unaffected by the concentration; the three points obtained for the chloride, as might be expected, indicate an appreciable difference from the others at higher current densities.

Ethylene varies between 0.5 and 3% in the various runs apparently at random. Carbon dioxide is absent in about half the runs and, as Table I shows, falls off on running. Both are probably intimately related to the solvent.

Efficiency of Electrolysis.—The work of several investigators indicates that the electrolysis of ethylmagnesium bromide is 100% efficient. Konduirev and Manoiev[11] found that magnesium, zinc and aluminum electrodes lose weight during electrolysis equivalent to the number of faradays passed; French and Drane[12] showed that if the electrode was not attacked an equivalent amount of the Grignard reagent was decomposed; Konduirev[13] found an equivalent amount of magnesium amalgamated with a mercury cathode; Evans and Lee[4] confirmed this for ethylmagnesium bromide using platinum electrodes. On the basis of the amount of gas evolved the latter workers indicate a rather lower efficiency: 96% for propylmagnesium bromide, 95% for ethylmagnesium chloride, 90% for ethylmagnesium bromide, 87% for ethylmagnesium iodide and much less but indefinite amounts for the methyl compounds.

A summary of efficiencies determined in the present work is given in Table II.

The number of equivalents of Grignard reagent decomposed was determined by titration of basic magnesium before and after electrolysis; dividing this by the number of faradays passed gives the efficiency, which ranges from 48 to 100% and is seen to fall off with increasing concentration. The efficiency may also be measured by the volume of gas liberated; converting the volume to the num-

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[11] Konduirev and Manoiev, *Ber.*, **58**, 469 (1925).

[12] French and Drane, THIS JOURNAL, **52**, 4924 (1930).

[13] Konduirev, *J. Russ. Phys.-Chem. Soc.*, **60**, 545 (1928).

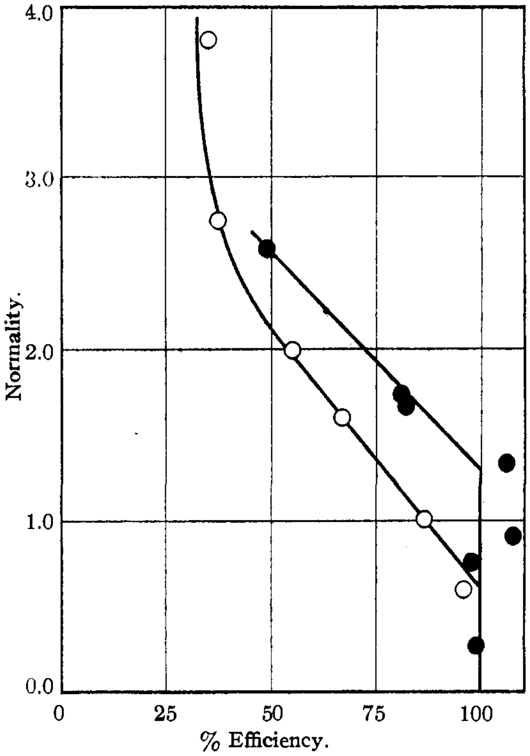
TABLE II

EFFICIENCY OF ELECTROLYSIS

Compound	Av. concn. N	Equiv. decomp. per faraday	Methyls liberated per faraday	Methyls per equiv. decomposed
CH_3MgI	0.51	1.00	0.96	0.96
CH_3MgI	1.01	0.88	.87	.99
CH_3MgI	1.60	.72	.67	.93
CH_3MgI	1.89	.54	.55	1.02
CH_3MgI	2.75	..	.37	..
CH_3MgI	3.80	..	.35	..
CH_3MgBr	0.27	.99	.99	1.00
CH_3MgBr	.76	..	.98	..
CH_3MgBr	.91	..	1.08	..
CH_3MgBr	1.34	..	1.06	..
CH_3MgBr	1.67	..	0.82	..
CH_3MgBr	1.74	..	.81	..
CH_3MgBr	2.58	.48	.49	1.02
CH_3MgCl	0.92	..	.98	..
CH_3MgCl	1.60	..	1.07	..

ber of moles of "methyls," we find within experimental error one methyl liberated per equivalent of methylmagnesium halide decomposed. This equivalency is a strong confirmation of the assumption that each methane represents one methyl and each ethane two methyls from the Grignard compound. Accepting this, we then have a more convenient measure of the electrolysis efficiency in the number of methyls liberated per faraday, which is shown plotted against concentration in Fig. 4. For both the bromide and the iodide the efficiency decreases linearly with increasing concentration, the slopes being roughly the same with the iodide the least efficient. It is also evident that 100% efficiency is only obtained for methylmagnesium iodide when below 0.7 N and the bromide below 1.5 N under the experimental conditions. The highest concentration of the chloride used, 1.6 N, was still 100% efficient, but it seems likely that at sufficiently high concentrations the efficiency in this case also will drop off. This series of chloride, bromide and iodide in order of decreasing efficiency was seen also in the results for the ethyl compounds by Evans and Lee[4] and may be generalized to hold for any alkyl group at the same concentration. Significant loss in efficiency seems to be restricted to the methyl compounds, however.

Liquid Products.—On completion of some of the longer runs the solution was carefully hydrolyzed and examined for liquid products. A small but definite amount of ethyl alcohol was always found, identified by the 3,5-dinitrobenzoate derivative; a trace of isopropyl alcohol was indicated by the vanillin color test.[14] A nonvolatile, ether-soluble, halogen-free, completely saturated substance was also found.



○, Iodide; ●, bromide.

Fig. 4.—Effect of concentration on efficiency of electrolysis.

Theoretical

It is convenient to consider the gaseous products obtained in the electrolysis of the compound RMgX as coming from the intermediate free radical R, since an adaptation of the free radical theory seems to explain qualitatively all the products found. The ethane is thus formed by the combination of two methyl radicals at the surface of the electrode.

The source of the extra hydrogen required to form methane from a methyl radical is an interesting point; that the hydrogen could not have come from another methyl is shown by the fact that for each equivalent of methyl compound decomposed an equivalent of methyl is liberated as a gas. The work of Paneth[15] on free methyls confirms this point, indicating that in an inert atmosphere of helium the reaction $CH_3 + CH_3 \longrightarrow C_2H_6$ is exclusive; whereas in a hydrogen atmosphere a second reaction takes place at the same time, CH_3 +

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[14] Brown, *Pharm. J.*, **133**, 560 (1934).

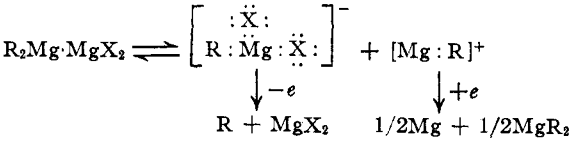
[15] Paneth, Hofeditz and Wunsch, *J. Chem. Soc.*, 372 (1935).

$H_2 \longrightarrow CH_4 + H$. Methane cannot therefore be formed by disproportionation of free methyls, but a methyl radical can take a hydrogen from a hydrogen molecule and from certain hydrogen-bearing compounds as well.

The source of the hydrogen in our work then can only be the solvent ether. Under quite analogous conditions Leermakers[16] found that free methyl radicals produced by photochemical decomposition of acetone initiate short chains in ethyl ether, showing that our statement is entirely reasonable. There are two kinds of hydrogen in the ether molecule; if we assume a single hydrogen to be removed and the resulting radical to be unstable and decompose in the presence of excess methylmagnesium halide, an application of the mechanism suggested by Rice[17] for the pyrolysis of ethers leads to the prediction of C_2H_6, C_2H_4 and $(CH_3)_2CHOMgX$, or CH_4, C_2H_4 and C_2H_5OMgX depending on which hydrogen is removed. A polymerization to a tar might also be predicted. We thus explain the formation of methane as well as ethylene and the ethyl and isopropyl alcohols which would result from the hydrolysis of the above magnesium compounds.

It follows that at very low current densities where the number of methyls liberated is few compared to the number of ether molecules at the electrode the formation of methane should predominate. As the current density increases the number of methyls liberated in unit area increases and coupling to ethane should be favored. This is experimentally true as Fig. 3 shows; since the limiting value at decreasing current densities seems to be pure methane, it follows that methyls are liberated singly and not in pairs.

A quantitative treatment of the variation with current density requires a more thorough understanding of the ions involved in the current transfer and of the influence of the electrode surface. The ions postulated by Evans and Lee,[4] Mg^{++} and $[R_2MgX_2]^{--}$, on the basis of transport experiments seem incorrect in the light of the work of Evans and Fosdick.[2] They found that concentration of ethylmagnesium bromide gave no potential using magnesium electrodes, apparently proving the absence of magnesium ions. Also, the above ions suggest that radicals would be liberated in pairs in contradiction to experimental evidence for the methyl compounds at least. In the light of these facts the following ionization may be postulated



$$\begin{array}{ccccc} R_2Mg\cdot MgX_2 & \rightleftharpoons & \left[\begin{array}{c} :\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}: \\ R:\overset{\cdot}{\underset{\cdot}{Mg}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}: \end{array}\right]^- & + & [Mg:R]^+ \\ & & \Big\downarrow -e & & \Big\downarrow +e \\ & & R + MgX_2 & & 1/2Mg + 1/2MgR_2 \end{array}$$

Work is now in progress to test this mode of ionization and the influence of a change in the nature of the electrode surface.

Carbon Dioxide.—The solvent ether must be responsible in some manner for the carbon dioxide sometimes evolved since there is no other source of oxygen. The length of time elapsed between the distillation of the ether and the electrolysis of the solution appeared to determine the quantity of carbon dioxide. This might be related to the autoxidation of the ether.

Efficiency.—The only effect of variation in concentration was in the efficiency of electrolysis. The simplest explanation of the low efficiency at higher concentrations would be the formation of CH_3X at the anode as a secondary reaction; this would then diffuse to the cathode to dissolve the magnesium and restore the original Grignard compound. This mechanism can be tested easily since in a transference experiment where diffusion is avoided the efficiency would be 100%. The increasing efficiency on changing from iodide to bromide to chloride is significant in this respect.

Summary

1. Methylmagnesium halides have been electrolyzed; the gaseous products are predominantly methane and ethane, the remaining 1 to 4% being ethylene and carbon dioxide which are definitely produced from the solvent ether.

2. The proportion of ethane increases rapidly with current density to a limiting value, unaffected by concentration. The bromides and iodides are similar in this respect.

3. The solvent ether provides the hydrogen for the formation of methane and undergoes decomposition.

4. The efficiency of the electrolysis is inversely proportional to the concentration above a limiting concentration. The chloride is the most efficient, bromide next and iodide least.

5. An ionic mechanism is suggested.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 26, 1936

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[16] Leermakers, THIS JOURNAL, **56**, 1899 (1934).

[17] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins, 1935.