[Contribution from the Chemical Laboratories of Northwestern University]

The Ionic Nature of the Grignard Reagent

By Ward V. Evans and Ralph Pearson[1]

Work has been done in this Laboratory for the past nine years on various phases of the electrolysis of organo-magnesium halides, in ethyl ether.[2] The products of electrolysis are magnesium metal at the cathode, various hydrocarbons at the anode and magnesium halide formed in solution. Since the magnesium halide was believed to form at the anode,[3] several equations were suggested to represent the electrode reactions[4]

(a) at the cathode: $Mg^{++} + 2e^- \longrightarrow Mg$
   at the anode: $R_2MgX_2^- - 2e^- \longrightarrow 2R\cdot + MgX_2$
(b) at the cathode: $2RMg^+ + 2e^- \longrightarrow Mg + R_2Mg$
   at the anode: $2RMgX_2^- - 2e^- \longrightarrow 2R\cdot + 2MgX_2$
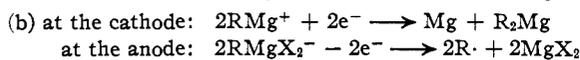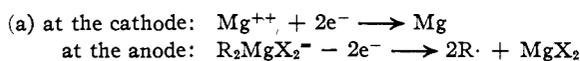
The symbol $R\cdot$ stands for an alkyl or aryl free radical that immediately underwent coupling, disproportionation or other reactions.

Because of the very great interest in the Grignard reagent in synthetic work and the need to understand its method of operation, it was thought desirable to do further work to prove or disprove the suggested electrode reactions and to investigate more fully the ionic equilibria involved in ether solutions of the Grignard reagent. This was done by means of transference studies, conductance data and chemical evidence. New light is also thrown upon the equilibrium

$$2RMgX \longrightarrow R_2Mg + MgX_2$$
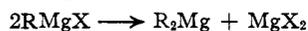
known to be present in solutions of the Grignard reagent.[5]

Transference Studies

Experimental.—An H-tube transference cell with large internal bore in order to reduce resistance was used. Three glass stopcocks were provided for draining out the anode, cathode and middle portions. Circular platinum electrodes mounted horizontally so that no potential drop existed along their length were used. Rubber stoppers freed from sulfur, one of which was fitted with a glass tube connected to two mercury traps to allow for expansion and contraction, supported the glass tubing holding the electrodes. The whole cell was immersed almost completely in a large jar and surrounded by a mixture of ice and water. Voltages used were from 90 to 180, current was

(1) Universal Oil Products Fellow.
(2) See This Journal, **63**, 2574 (1941), for complete references.
(3) (a) Gaddum and French, *ibid.*, **49**, 1295 (1927); (b) Lee, Ph.D. Thesis, Northwestern University, 1931.
(4) (a) Evans and Lee, This Journal, **56**, 654 (1934); (b) Evans and Field, *ibid.*, **58**, 720 (1936).
(5) Schlenk and Schlenk, *Ber.*, **54**, 1665 (1921).

from 0.03 to 0.04 ampere filtered through a no. 80 Radiotron tube. A copper coulometer in series was used to measure the total number of coulombs. Runs were from eight to twelve hours. Sampling before and after electrolysis was by means of 25-cc. washout pipets in a hood of nitrogen to prevent decomposition by air and moisture. The anode, cathode and middle portions were weighed to the closest 0.01 g., cooled in an ice-bath, samples withdrawn, and then reweighed to get weight of sample. In this way the loss of ether by evaporation was at a minimum. Each sample was hydrolyzed with excess standard nitric acid and then back-titrated using sodium hydroxide and methyl orange indicator. This gave the equivalents of R present. Then eosin and dextrin were added to the neutral or slightly basic sample and the total halogen was titrated with standard silver nitrate. The equivalents of magnesium were then equal to the sum of R and X, where R is the alkyl group and X the halogen. In many cases this was confirmed by determining the magnesium separately as the pyrophosphate.

Results.—The only Grignards tried were ethylmagnesium bromide, n-butylmagnesium bromide and phenylmagnesium bromide. The ethylmagnesium bromide was found to be unsuitable for transference study as the tabulated results of Table I show. There was a considerable transport

TABLE I

TRANSFERENCE STUDY OF ETHYLMAGNESIUM BROMIDE

$T = 0°$, v. $= 90$, $I = 0.03$, R $= 1.44$ molar, X $= 1.63$ molar, total current $= 17.4$ milli-faradays. Changes in each portion expressed in milliequivalents.

	Anode	Cathode	Middle
R	+36.0	−22.3	−32.1
X	+ 5.0	+ 1.3	− 5.6
Mg	+41.0	−21.0	−37.7

This is one run out of a dozen that were made. It is selected as representative of all of them.

of matter to the anode portion, indicating a large, mobile anion. Since the cathode portion did not gain by transport, it became more dilute and solute diffused from the middle portion into the cathode portion. Hence a true middle portion could not be obtained. This difficulty could have been avoided by using a vertical transference cell with the cathode on top and the anode on the bottom so that diffusion to the cathode would be prevented by gravity. However, instead of changing the cell, the Grignard reagent was changed, one being chosen that would possess a larger, heavier alkyl radical both to slow down the anion and to decrease its coördinating power by virtue of its

TABLE II

TRANSFERENCE STUDIES OF n-BUTYLMAGNESIUM BROMIDE

(a) $T = 0°$, v. $= 90, I = 0.03,$ R $= 1.57$ molar, X $= 1.78$ molar, total current $= 11.6$ milli-faradays.

	Anode	Cathode	Middle
R	+4.2	−15.5	−0.5
X	−0.3	+ 0.8	− .4
Mg	+3.9	−14.7	− .9

(b) $T = 0°$, v. $= 180, I = 0.035,$ R $= 1.89$ molar, X $= 2.69$ molar, total current $= 11.0$ milli-faradays.

	Anode	Cathode	Middle
R	+1.2	−14.3	+0.7
X	+8.0	− 8.2	+ .2
Mg	+9.2	−22.5	+ .9

(c) $T = 0°$, v. $= 180, I = 0.035,$ R $= 1.29$ molar, X $= 1.48$ molar, total current $= 12.6$ milli-faradays.

	Anode	Cathode	Middle
R	+4.6	−16.8	−0.4
X	−1.1	+ 1.6	− .3
Mg	+2.9	−15.2	− .7

These runs were taken as representative from about two dozen that were made.

bulk. n-Butylmagnesium bromide was selected and as the data of Table II show, fairly good results were obtained. The total loss of R agreed with the number of faradays passed through the cell to within one or two milliequivalents, excellent agreement considering the great reactivity of the RMgX compounds and the volatility of the solvent. Other workers have previously shown that for the aliphatic Grignards one equivalent of magnesium is plated out per faraday of electricity.[6] It was also known that the amount of gaseous hydrocarbons formed in the electrolysis of simple aliphatic Grignards corresponds closely to 100% current efficiency.[7] All calculations were made on a weight basis making due allowance for the weight of solution due to the solute.

Although the data of Table II are not suitable for quantitative calculations, a number of interesting observations can be made from them:

1. All of the losses occur in the cathode portion. The anode portion shows a gain in solute at all times even after losing an equivalent amount of R by electrolysis.

2. The relative amounts of R and X gained by the anode portion are not constant but depend upon the ratio of R to X in the original solution, that is, upon the concentration of MgX_2 present. When the MgX_2 concentration is low, R_2Mg or RMgX is transported to the anode so that the anode gains in R. When the MgX_2 concentration is high, MgX_2 is transported to the anode and the anode gains in X.

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

(7) Braithwaite, Ph.D. Thesis, Northwestern University, 1940.

3. The net migration of magnesium to the anode shows that it is present in the anion as well as in the cation.

4. The cathode losses show that MgX_2 is always gained since the loss of R is always greater than the loss of X. However, this gain is probably due to two factors, a real gain in MgX_2 as a product of electrolysis and an apparent gain in MgX_2 because of the loss of R_2Mg from the cathode portion by transference.

The behavior of phenylmagnesium bromide in a transference cell is unusual. After several hours of running all of the Grignard reagent settles out at the anode and the cathode, leaving a clear supernatant liquid that has no RMgX in it and only a little MgX_2. This appears to be an electrophoretic effect. The colloidal nature of the aromatic Grignards is further shown by the dark color of their ether solutions and their pronounced Tyndall effect. The aliphatic C_2H_5MgBr and n-C_4H_9-MgBr solutions were water white, optically clear liquids after settling and filtering through glass wool. The conclusion is that while the aliphatic Grignards form true solutions, the aromatic Grignards are in part colloidal. The difference may be due to the greater coördinating power of the benzene ring. Benzene, for example, forms complexes with aluminum chloride.[8] With ions for nuclei, large complexes could be formed in ether, so large as to be of colloidal dimensions. This colloidal nature does not affect the reactivity of the aromatic Grignards, which behave in general like the aliphatic Grignards in synthesis. Nor is the molecular weight as measured by boiling point rise any different from the aliphatics, both C_6H_5-MgBr and C_2H_5MgBr being approximately $(RMgX)_2$ in half molar solution.[9] Presumably because of the low ionic concentration only a small percentage of the Grignard molecules are involved in the colloidal complexes. In an electrolysis, however, as the ions were continuously discharged leaving the rest of the particle neutral and free to settle out, more ions would form and new complexes build up until the solution was exhausted of ArMgX.

Conductance Data

The conductances of several Grignards in ethyl ether have been reported.[10] The form of

(8) Gustavson. Chem. Zentr., **14**, 344 (1883).

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

(10) (a) Evans and Lee, THIS JOURNAL, **55**, 1474 (1933); (b) Konduirev and Ssusi, Ber., **62B**, 1856 (1929); (c) Konduirev, J. Gen. Chem. U. S. S. R., **4**, 203 (1934).
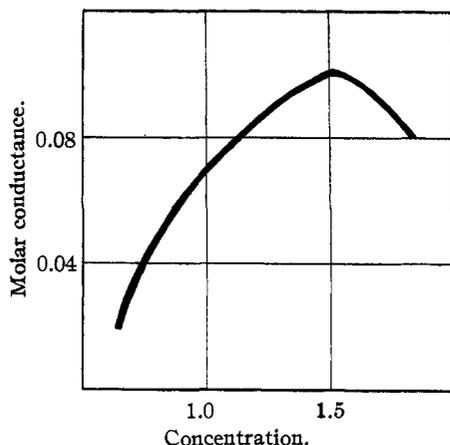
Fig. 1.—Molar conductance of ethylmagnesium iodide plotted against molar concentration.

Fig. 2.—Log molar conductance of ethylmagnesium iodide plotted against log molar concentration.

the conductance–concentration curves for ethyl magnesium iodide is shown in Fig. 1. The molar conductance increases rapidly with the concentration, a general phenomenon in solvents of low dielectric constant. A maximum is reached at about 1.5 molar concentration, then the molar conductance falls off rapidly. This decrease in conductance is not surprising since the solvent is no longer ether but is 30% MgX_2 and RMgX by weight. In addition to changes in the dielectric constant and nature of the medium, the viscosity has changed from that of a mobile liquid to a sirupy solution. The great decrease in conductance could be explained by the change in viscosity alone. If the log of the molar conductance is plotted against the log of the concentration up to 1.5 molar, a curve is obtained (Fig. 2) that is not a straight line but falls off as log c increases. The slope of the straightest portion of the curve varies from 0.75 to 1.5. The interpretation of this according to the Kraus–Fuoss theory of multiple ions[11] is that the over-all formula for the ionization involves not one molecule of RMgX but from three to five. Accordingly, the ions formed are not simple but complex. This is in accordance with the size of the ions as indicated by the transference studies of ethylmagnesium bromide, where several times as many equivalents of R and X are transported as faradays of electricity are used.

Measurement of the gross conductance of RMgX does not give any information as to the contribution to the total of the conductances of R_2Mg, MgX_2, and RMgX. Consequently the conductances of several organometallic com-

pounds in ether have been measured and compared with the conductance of ethylmagnesium bromide and magnesium bromide in ether. The results are included in Table III and for comparison the amounts of ionic character in the various bonds as calculated from the electronegativities of the elements according to the method of Pauling[12] are also presented. There is good agreement between the specific conductance and the amount of ionic character expected for each bond. The prediction of almost as much ionic character in the C-Mg bond as in the Mg-Br bond as predicted by Pauling's table of electronegativities is confirmed by the fair conductance of magnesium diethyl, prepared by the method of Noller.[13]

TABLE III

SPECIFIC CONDUCTANCE OF HALF MOLAR SOLUTIONS IN ETHYL ETHER AT 20°

		Bond	% Ionic character
$MgBr_2$	2.0×10^{-5}		
C_2H_5MgBr	1.6×10^{-5}	Mg-Br	47
$(C_2H_5)_2Mg$	1.0×10^{-5}	Mg-C	34
$(C_2H_5)_2Zn$	5×10^{-6}	Zn-C	24
$(C_2H_5)_2Hg$	0	Hg-C	10

A specific conductance of zinc diethyl in ether was reported as 10^{-4} by Rodebush.[14] The conductance of a half molar solution is somewhat less than this. The conductance of magnesium bromide at half molar concentration was extrapolated from lower concentrations since the limiting solubility of $MgBr_2$ in ether alone is only 0.15 molar.[10a] The presence of RMgX greatly increases the solubility of MgX_2 in ether as was

(11) Fuoss and Kraus, THIS JOURNAL, 55. 2387 (1933).

(12) Pauling. "Nature of the Chemical Bond," Cornell University Press. Ithaca. N. Y., 1940. p. 64.

(13) Noller, THIS JOURNAL, 53, 635 (1931).

(14) Rodebush and Peterson. ibid., 51. 638 (1929).

shown by Doering and Noller.[15] The actual concentration of MgX_2 in the Grignard solution may easily be half molar or above depending on the total concentration of RMgX. The total conductance of a Grignard is then due to the ionization of R_2Mg, MgX_2, and RMgX, with the R_2Mg contributing almost as much as the MgX_2. The conductance of RMgX alone cannot be measured since disproportionation to R_2Mg and MgX_2 always occurs. However, it seems reasonable to believe that the molar conductance of RMgX lies between those of R_2Mg and MgX_2 and that the ionic character of one bond does not greatly affect the ionic character of another bond in the same molecule.

Chemical Evidence

In the majority of its reactions the Grignard reagent behaves as an R^- anion and a MgX^+ cation. The anion with its unshared pair of electrons goes on an atom with an open sextet and the cation adds on to an atom with an unshared pair of electrons. The reaction with a ketone may be taken as illustrative

$$\begin{array}{c} R' \\ \diagdown \\ R' \diagup \end{array} C{=}O \rightleftharpoons \begin{array}{c} R' \\ \diagdown \\ R' \diagup \end{array} \overset{+}{C}{-}\overset{-}{O} \xrightarrow{\quad R^- + MgX^+ \quad}$$

$$\begin{array}{c} R' \\ \diagdown \\ R' \diagup \end{array} \underset{\underset{R}{|}}{C}{-}O{-}MgX$$
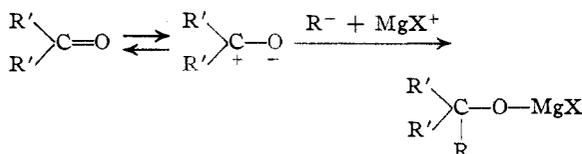
Instead of an atom with an open sextet, an ionizable hydrogen may furnish the necessary orbital for the unshared pair of the anion which in this sense acts as a base. The hydrogen ion may come from OH, NH, SH, or activated CH. The behavior of the Grignard reagent in enolization and condensation is due to this reaction. The reducing effect of Grignard reagents is particularly noticed in the case of highly branched R^- anions and branched chain carbonyl compounds.[16] Here, due to steric factors, a hydride ion, H^-, adds to the carbonyl group, giving a reduction product and an olefin. In other cases, as in the reaction with allyl bromide, the R^- behaves like any other anion, pushing out the Br^- by the usual displacement reaction. In all of these cases the reaction is carried to completion by the irreversibility of the formation of the carbon–carbon or carbon–hydrogen bond. Because of this only the R^- seems to react. Actually the X^- must be undergoing the same reactions but to a lesser degree because of

the lower basicity of the halide ion as compared with an alkide ion

$$\begin{array}{c} R' \\ \diagdown \\ R' \diagup \end{array} C{=}O + RMgX \rightleftharpoons \begin{array}{c} R' \\ \diagdown \\ R' \diagup \end{array} \underset{X}{C}{-}OMgR$$
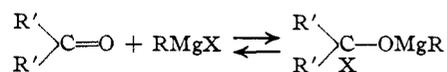
But in such cases the reaction is readily reversible because of the lability of the carbon halogen bond alpha to an oxygen atom. Similarly, if HX were formed from an ionizable hydrogen, it would react further to give RH. In cases where the carbon–halogen bond is not easily broken, stable halogenated products can be formed from the Grignard reagents or simply magnesium halide in ether. For example, ethylene oxide reacts with RMgX to give both RCH_2CH_2OH and XCH_2CH_2OH.[17]

The nature and extent of the reaction $2RMgX \rightarrow R_2Mg + MgX_2$ has been the subject of numerous papers.[18] It has been shown that the dioxane precipitation of the halogen compounds does not give true values for the position of equilibrium nor for the time necessary to reach equilibrium.[19] Some speculation can be made on the subject with the aid of a study on a related reaction, the exchange between anhydrous zinc chloride and ethylmagnesium bromide in ether. When equal volumes of molar solutions of these two substances were mixed, white fumes of zinc oxide were given off immediately and a precipitate of magnesium chloride and ethylmagnesium chloride was formed. The fuming is typical of organo-zinc compounds. The mixture was treated with dioxane at once to precipitate all the halogen and then centrifuged. The clear solution, free from halogen, was analyzed for zinc and magnesium. It was found that 95% of the ethyl radical present was zinc diethyl and less than 5% was magnesium diethyl. Allowing the solution to stand overnight before precipitating with dioxane did not change the per cent. conversion from RMgX to R_2Zn. The exchange was evidently instantaneous. Reasoning by analogy, if MgX_2 were added to a solution containing R_2Mg the exchange would be instantaneous and equilibrium reached in a very short time. Such rapid reaction in a solution of as low dielectric constant as ether cannot proceed by a purely ionic mechanism since the concentration of ions is

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

(16) Kharasch and Weinhouse, J. Org. Chem., 1, 209 (1936).

(17) (a) Blaise, Compt. rend., 134, 552 (1902); (b) Magrane and Cottle, THIS JOURNAL, 64, 484 (1942).

(18) (a) Noller, ibid., 53, 635 (1931); (b) Cope, 57, 2238 (1935); (c) Gilman and Brown, 52, 4480 (1930); (d) Noller and Raney, 62, 1749 (1940).

(19) Noller and White, ibid., 59, 1354 (1937).

probably too small. The most likely method is a collision leading to an association of these highly polar molecules and a dissociation with the groups interchanged.

$$R_2Mg + MgX_2 \longrightarrow \begin{array}{c} R\!-\!Mg\!-\!R \\ | \quad | \\ X\!-\!Mg\!-\!X \end{array}$$

$$\begin{array}{c} R\!-\!Mg\!-\!R \\ | \quad | \\ X\!-\!-\!Mg\!-\!X \end{array} \longrightarrow 2RMgX$$
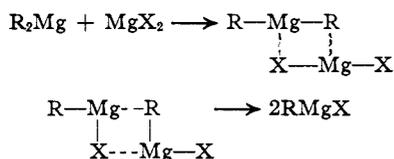
The ease with which the groups are lost by one atom and gained by another suggests strongly that primarily ionic linkages are involved and that the molecules can be considered to a first approximation as being simply ion pairs held together by coulombic forces. This is not strictly true, of course, since the physical properties, especially of R_2Mg, suggest a considerable amount of covalent character in the bonds. There is, unfortunately, no direct evidence as to the position of equilibrium above, but if the undissociated molecules are considered as ion pairs, it seems likely that only statistical factors will determine the relative numbers of R_2Mg, MgX_2 and $RMgX$ molecules. In such case the equilibrium constant $K = [R_2Mg][MgX_2]/[RMgX]^2$ should be unity. Actually the constants calculated by the dioxane method are of this order of magnitude for most Grignards. The dioxane constants cannot be regarded as more accurate than an order of magnitude since undoubtedly as the least soluble component, presumably MgX_2, is precipitated first the reaction is dragged to the direction that causes the formation of more MgX_2. The chloride always gives a greater percentage of R_2Mg than the bromide, and the bromide gives a greater percentage of R_2Mg than the iodide.[18b] This is the same order as increasing solubility of the magnesium halides. The iodide should give the most nearly correct results, though even here the values are doubtful because the concentration of R_2Mg changes with rate of addition of the dioxane and the time and intimacy of contact of the mother liquor with the precipitate.[19] That the yields of R_2Mg are increased by shaking the precipitate with the mother liquor indicates that R_2Mg is coprecipitated with the halogenated compounds to a considerable extent. Since the Grignard reagents are undoubtedly associated, such coprecipitation is not surprising and invalidates the quantitative value of the dioxane precipitation as a means of comparing various Grignard reagents.

Discussion

Taking into account the foregoing evidence, a fairly lucid picture of the ionization and electrode reactions of the aliphatic Grignard reagents in ethyl ether can now be given. The specific properties of the four types of molecules present must be first taken into account. The ether molecule is strictly an electron donor molecule by virtue of the unshared pairs on the oxygen atom. The R_2Mg, $RMgX$ and MgX_2 molecules are all acceptor molecules because of the two stable unfilled orbitals of the magnesium atom. The $RMgX$ and MgX_2 molecules are also donor molecules because of the unshared pairs of the halogen atoms, but the donor power of a halogen atom is much less than that of oxygen atoms. The following ionic ruptures undoubtedly all occur

$$RMgX \rightleftharpoons R^- + MgX^+ \text{ or } X^- + RMg^+$$
$$R_2Mg \rightleftharpoons R^- + RMg^+$$
$$MgX_2 \rightleftharpoons X^- + MgX^+$$
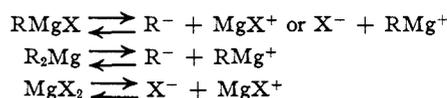
The presence of Mg^{++} is unlikely in view of the low dielectric constant of the medium. As is true in any solution, ionization only occurs because the energy of solvation is great enough to overcome the coulombic attraction. The positively charged cation must be strongly solvated by the ether molecules. Since the cation MgX^+ has at least three stable orbitals, more than one molecule of ether is coordinated with it. This is of importance in determining the mobility of the cation since it eliminates the possibility of its jumping from one ether molecule to the next and possessing a high mobility analogous to the proton in water solution.

The anion having an unshared pair of electrons is but weakly attracted to the ether molecules, or repelled, and is coordinated instead with an acceptor molecule containing a magnesium atom

$$\begin{bmatrix} R\!-\!Mg\!-\!X \\ | \\ R \end{bmatrix}^- \qquad \begin{bmatrix} R\!-\!Mg\!-\!X \\ | \\ X \end{bmatrix}^-$$

$$\begin{bmatrix} R\!-\!Mg\!-\!R \\ | \\ R \end{bmatrix}^- \qquad \begin{bmatrix} X\!-\!Mg\!-\!X \\ | \\ X \end{bmatrix}^-$$
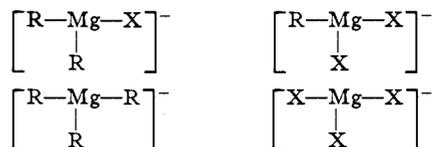
It is unlikely that the process stops at this point since the negative charge makes the anion a stronger base than the ether molecule. Consequently the ether molecules are displaced from other magnesium atoms and an anion involving several molecules of $RMgX$ or R_2Mg or MgX_2 may be built up. This is in accordance with the conductance data in that several molecules of Grignard are necessary for the ionization re-

action to occur. We have then a small, highly solvated cation which is not mobile because of its attraction for the solvent and a large anion which is mobile because it has little attraction for the electron donating solvent. This is in accordance with the transference data where, especially with ethylmagnesium bromide, there is a large transference of matter to the anode. Even with the butylmagnesium bromide there are more equivalents of R plus X transferred to the anode than faradays of electricity used. More R is transferred to the anode than X, probably because R_2Mg is a better electron acceptor than MgX_2 and coördinates with the anion more readily. If the MgX_2 concentration is high, however, more of it is carried to the anode in place of R_2Mg, since the concentration of the latter must be small and the difference in concentration balances the difference in acceptor power.

The cation upon reaching the electrode is discharged to give an $RMg\cdot$ or $MgX\cdot$ free radical which reacts in pairs to give magnesium plus MgX_2 or R_2Mg

$$2RMg^+ + 2e^- \longrightarrow Mg + R_2Mg$$
$$2MgX^+ + 2e^- \longrightarrow Mg + MgX_2$$
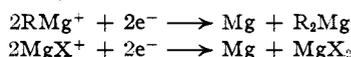
The anion upon reaching the electrode is discharged in such a way that the R or X group having the lowest discharge potential is liberated as a free atom or radical. In the case of the aliphatic Grignards, and the aromatic Grignards at low current density, the R group is most easily discharged[2]

$$R_2MgX^- \longrightarrow R\cdot + RMgX + e^-$$
$$\text{or} \quad R_3Mg^- \longrightarrow R\cdot + R_2Mg + e^-$$
$$\text{or} \quad RMgX_2^- \longrightarrow R\cdot + MgX_2 + e^-$$
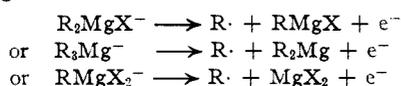
However, under certain circumstances the halide ion may be discharged

$$R_2MgX^- \longrightarrow X\cdot + R_2Mg + e^-$$
$$\text{or} \quad MgX_3^- \longrightarrow X\cdot + MgX_2 + e^-$$
$$\text{or} \quad RMgX_2^- \longrightarrow X\cdot + RMgX + e^-$$
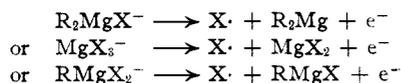
The following series of reactions would then occur

$$2X\cdot \longrightarrow X_2$$
$$X_2 + RMgX \longrightarrow RX + MgX_2$$
$$RX + Mg \longrightarrow RMgX$$
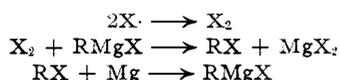
In the electrolysis of phenylmagnesium bromide, for example, it was shown that bromobenzene formed at the anode and, unless prevented from diffusion, would migrate to the cathode and react with the magnesium plated out there.[2] That the halogen molecule is an intermediate is shown by the electrolysis of phenethinylmagnesium iodide, $C_6H_5C\equiv C-MgI$. In this electrolysis the C_6H_5-

$C\equiv C^-$ ion is not discharged but the iodide ion is. Since iodine reacts only slowly with this particular Grignard, a mass of crystalline iodine collects upon the anode and can be readily identified.

The discharge of halogen instead of the alkyl or aryl radical is favored by several factors: high electronegativity of the radical, low electronegativity of the halogen, and high voltages. Aryl radicals are more electronegative than alkyl radicals and the electrolysis of aromatic Grignards gives current efficiencies, based upon the amount of hydrocarbons formed, that are very much lower than for the aliphatic Grignards.[2] Among the several halogens the order of increasing current efficiency is iodide, bromide, and chloride in accordance with increasing decomposition potentials for these ions.[20] High voltages favor the release of halogen and lower the current efficiency because a saturation current due to anions containing the alkyl or aryl group is reached. Anions such as MgX_3^- are then discharged because the source of more easily discharged ions is momentarily exhausted.

The necessity for having both electron donors and electron acceptors present to promote ionization in solutions of low dielectric constant is shown by several other organo-metallic compounds in solution. Zinc diethyl and magnesium diethyl etherate are non-conductors in benzene, while magnesium bromide etherate and ethylmagnesium bromide etherate in benzene conduct fairly well.[21] The explanation is in the low electron donating power of benzene compared to ether which leaves the zinc and magnesium diethyl with no means of solvating the cation. Magnesium bromide and ethylmagnesium bromide have the halogen atom to serve as electron donor and coördinate the cation. Zinc diethyl by itself is known to be a non-conductor, but in ether it conducts because the ether solvates the RZn^+ cation. Sodium ethyl conducts in zinc diethyl and Hein showed that the anion was $Zn(C_2H_5)_3^-$ with the zinc atom acting as the acceptor molecule.[22] There is no molecule present to solvate the sodium ion, but solvation other than that furnished by the negative end of the zinc–carbon dipole is not necessary for the sodium ion, which has a low coördinating power at all times. The organo-lithium compounds, C_2H_5Li, C_6H_5Li and $n\text{-}C_4H_9Li$ in ethyl ether solution have been tested in this

(20) Evans and Field, THIS JOURNAL, **58**, 2284 (1936).
(21) Unpublished work in this Laboratory.
(22) Hein, Z. Elektrochem., **28**, 469 (1922).

Laboratory and found to be non-conductors.[21] This non-conductance is due in part to a high amount of covalent character in the lithium–carbon bond as shown by the much lower conductance of lithium ethyl in zinc diethyl than the corresponding sodium and potassium compounds.[22] It is probably due more to the inability of the lithium atom to serve as an acceptor atom for the unshared pair of the alkide ion in comparison with the high coördinating power of the zinc and magnesium atoms.

Summary

Transference studies of *n*-butylmagnesium bromide and ethylmagnesium bromide in ether are reported.

The conductances of magnesium diethyl and zinc diethyl in ether have been measured.

The exchange reaction between zinc chloride and ethylmagnesium bromide in ether has been found to be instantaneous.

From a consideration of all available data a theory is proposed for the ionization of the aliphatic Grignard reagents and for the electrode reactions in their electrolysis.

Both the halogen and the alkyl group can ionize. The cation is coördinated with ether and is small and slow. The anion is coördinated with RMgX, MgX₂ and R₂Mg and is large and mobile.

The importance of having both molecules with electron donor properties and molecules with electron acceptor properties to promote ionization in solvents of low dielectric strength is brought out.

The Stability of β-Methylmaltoside toward Hot Alkali

BY THOMAS JOHN SCHOCH, E. JUSTIN WILSON, JR., AND C. S. HUDSON

In connection with studies on the decomposition of starch in alkaline medium, it was desirable to establish whether the 1,4-α-glucosidic linkage is susceptible to direct hydrolytic scission by hot aqueous alkali. Evans and Benoy[1] have shown that the action of hot alkali upon maltose results primarily in a rapid enediol splitting. If this reaction could be prevented by blocking the aldehyde group against enolization, as in β-methylmaltoside, then any acids developed during hot alkali digestion could be attributed to direct hydrolysis of the disaccharide linkage, and subsequent enolic splitting of the former glucosido portion of the maltoside molecule. β-Methylglucoside is known to be fully resistant to hot aqueous alkali.

β-Methylmaltoside and calcium maltobionate have been so tested, by dissolving 0.5 g. in 100 ml. of 0.1 N sodium hydroxide, heating at 100° for one, two and five hour periods, and then back-titrating the unconsumed alkali. Except for the use of longer heating periods, the technique is identical with that described by Schoch and Jensen[2] for alkali number evaluation of starches; in their method the time of heating is one hour.

Production of acidity is similarly expressed, as the number of milliliters of 0.1 N sodium hydroxide consumed per gram of carbohydrate. Each value in Table I represents the average of three to five determinations; blank runs (without carbohydrate) showed negligible loss of alkali. As an additional check on the results obtained, beta-methylcellobioside was tested in the same manner.

TABLE I

ALKALI CONSUMPTION AT 100°

Digestion time, hr.	β-Methyl-maltoside	β-Methyl-cellobioside	Calcium maltobionate	Calcium gluconate
1[a]	0.32 ± 0.04	0.10 ± 0.05	0.72 ± 0.06	0.76 ± 0.03
2	.24 ± .04	.13 ± .05	.99 ± .06	.93 ± .08
5	.16 ± .04	.08 ± .05	1.60 ± .09	1.78 ± .11

[a] Starches give alkali numbers of about 4 (waxy maize), 7 (potato) and 11 (corn).

Since the alkaline decomposition of 1 g. of anhydrous glucose consumes 85.2 ml. of 0.1 N sodium hydroxide,[2] it may be calculated that β-methylmaltoside hydrate and calcium maltobionate would consume 41.0 ml. and 40.7 ml., respectively, if the disaccharide bond were completely hydrolyzed. The very slight consumption by the two glycosides is barely detectable and is not progressive, which leads us to believe that it is caused by traces of impurities which recrys-

(1) Evans and Benoy. THIS JOURNAL. 52, 294 (1930).

(2) Schoch and Jensen, Ind. Eng. Chem., Anal. Ed., 12, 531 (1940).