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THE ELECTROMOTIVE FORCE DEVELOPED IN CELLS CONTAINING NONAQUEOUS LIQUIDS.

[PRELIMINARY PAPER.]

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In connection with the study of the ionizing character of many complex addition compounds, the possibility suggested itself that organo-metallic compounds, like the etherates of magnesium alkyl halides, or the so-called Grignard reagent, might lower the electrical resistance of nonaqueous solvents, such as dry ether or dry benzene. This was found to be the case. The electrical resistance of dry ether, a dry ethereal solution of ethyl bromide, and a dry ether-benzene solution of ethyl bromide, were compared with the resistance of the same solvents and solutions, when they contained varying amounts of etherates of magnesium ethyl bromide compounds. The table below shows the lowering effect of the magnesium compound. The resistance of a 0.02 *M* aqueous solution of potassium chloride is also given for the sake of comparison.

	Resistance in ohms.
Ether.....	Above 1×10^7
Benzene.....	Above 1×10^7
Ether containing ethyl bromide.....	Above 1×10^7
Ether, benzene and ethyl bromide.....	Above 1×10^7
Ether containing 1.2 g. Mg as Grignard reagent per 100 cc....	7.1×10^3
Ether containing 0.6 g. Mg as Grignard reagent per 100 cc....	2.4×10^4
Ether containing 0.3 g. Mg as Grignard reagent per 100 cc....	1.0×10^6
Conc. of Mg as Grignard reagent above 0.3 g. per 100 cc....	9.0×10^2
Ether-benzene soln. 0.3 g. Mg as Grignard reagent per 100 cc...	1.3×10^6
0.02 <i>M</i> aqueous potassium chloride solution.....	$1.26 + 10^2$

The resistances were determined in an ordinary conductivity apparatus. The ether was washed free from alcohol and dried over sodium. The benzene was freed from thiophene and recrystallized. The ethyl bromide was carefully redistilled.

It is well known that it is impossible to determine by ordinary methods the electromotive force of ordinary aqueous cells in which the resistance between the electrodes is too high, and very often it is necessary to add some electrolyte to lower this resistance, before an accurate measurement can be made. In order to see whether any similar effect occurred when a cell as made up similarly to an ordinary zinc-platinum cell with a dilute aqueous solution of an acid between the electrodes, magnesium was used in place of the zinc, and a dry ethereal solution of ethyl bromide, containing a small amount of previously prepared Grignard reagent, instead of the aqueous acid solution. Upon connecting the two electrodes to a potentiom-

eter, an electromotive force ranging from 0.5 to 1.5 volt was obtained, depending upon the concentration of the solution, and the size and distance apart of the electrodes. If no Grignard reagent was added at the start, no difference of potential was noticeable at the beginning, but gradually developed as the organo-metallic compound was being formed in the cell.

Similar experiments were conducted where other metals like zinc, aluminium, etc., were used in place of the magnesium electrode. Instead of adding the Grignard reagent at the start, in these cases a minute amount of iodine was added in order to form a soluble etherate of the metal and thus lower the resistance between the two electrodes more quickly. Each of these metals behaved in a similar way to that of the magnesium. It, therefore, appears as if the phenomenon is a general one. If this should turn out to be the case, its conceivable significance will be important in connection with our present theories concerning the solution of metals. It is known that when magnesium dissolves in an ethereal solution of an alkyl halide, the alkyl halide adds to the magnesium and forms the organo-metallic compound $(Et_2O)_x.MgRX$, or Grignard reagent. Since this process, in the light of the above results, appears to be analogous to the solution of a metal in an aqueous acid solution, in that similar electrical effect, same salt of the metal (the organo-metallic compound, $MgRX$, reacting with more alkyl halide, RX , forming the salt, MgX_2), and hydrocarbon in place of hydrogen, are obtained, the question arises whether acids do not first add to the metal also, forming a compound similar to the Grignard reagent. Since compounds of this type are very sensitive to hydrolysis, their existence would not be evident in an aqueous solution. Some preliminary experiments have been tried in this laboratory, where an ethereal solution of hydrogen chloride has been allowed to react with a metal, but up to the present no satisfactory results have been obtained.

If, as indicated, the solution of a metal by alkyl halides is similar to that of the ordinary solution of a metal by aqueous solutions of acids, many reactions in organic chemistry will be brought into line with those of inorganic chemistry. Thus the formation of the Grignard reagent, the reduction of halogen derivatives of hydrocarbons by means of the zinc-copper couple, the Wurtz and Fittig reactions, etc., might all belong to the same type of reaction as the solution of a metal by an aqueous solution of an acid. It is hoped that, by further work in this field, this apparent similarity can either be confirmed or accounted for in some other way. It is also hoped that more exact measurements of the difference of potential can be made, and the work extended in other directions.