determined chemically or the solution must be fractionated into mixtures containing only four acids in significant quantities before applying the Duclaux method. If necessary, the acids may be freed partially from their salts and distilled, as suggested by Liebig[6] and Gillespie and Walters.[1]

To use the Duclaux method most successfully, the acids met with should be identified qualitatively before calculating the results. The tests suggested by Agulhon and rearrangement by Dyer seem the most practicable. These tests depend upon the relative solubility of the iron and copper salts of the fatty acids in various organic solvents.[7]

Summary

A new procedure has been outlined, illustrated by an example, for the estimation of four acids by the Duclaux method. In the new procedure one or more acids are determined quantitatively by chemical methods and the remainder determined by the Duclaux method.

(6) Liebig, *Ann.*, **71**, 355 (1849).

(7) *J. Biol. Chem.*, **28**, 445–473 (1917).

Received June 11, 1932
Published April 6, 1933

[Contribution from the Chemical Laboratory of Northwestern University]

The Conductivity of Grignard Reagents in Ether Solutions

By W. V. Evans and F. H. Lee

The conductivity of the Grignard reagent in ether solutions has been studied by numerous investigators. Kondyrew and Manojew[1] measured the conductivity of ethylmagnesium bromide at various temperatures. Kondyrew and Ssusi[2] studied the effect of dilution on the conductivity of ethylmagnesium iodide and postulated the formation of complex organic compounds at certain concentrations. Recently Dufford and his coworkers[3] investigated the effect of light on the conductivity of these solutions. In the present work we have extended this investigation to several other Grignard compounds.

Experimental

Preparation of Solutions.—Pure dry alkyl or aryl bromide was mixed with ether and added to dry magnesium turnings in slight excess of the amount necessary for the reaction $RX + Mg = RMgX$. After reaction the flask was heated for two hours on a water-bath. All precautions were taken against the entrance of air and moisture.

Measurement of Conductivity.—The conductivities of ethylmagnesium bromide, benzylmagnesium bromide, *n*-butylmagnesium bromide, phenylmagnesium bromide, and magnesium bromide have been measured at 20, 0 and $-10°$. The solubility of magnesium bromide in ether is so small that only the conductivity of dilute solutions of

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(1) Kondyrew and Manojew, *Ber.*, **58**, 464 (1925).

(2) Kondyrew and Ssusi, *ibid.*, **62**, 1856 (1929).

(3) Dufford, *Phys. Rev.*, **35**, 998 (1930); *J. Phys. Chem.*, **34**, 1544 (1930).

this salt could be obtained. Solutions half saturated at 22° were used in the conductivity measurements. From the specific conductivity of this solution of magnesium bromide a very rough approximation of the specific conductivity of a molar solution can be made. The results are given in Table I.

TABLE I

SPECIFIC CONDUCTIVITY OF *M* GRIGNARD REAGENTS

Temp., °C.	C_2H_5MgBr	$C_6H_5CH_2MgBr$	n-C_3H_7MgBr	C_6H_5MgBr	$MgBr_2$(0.0705M)
20	6.25×10^{-5}	5.55×10^{-5}	4.75×10^{-5}	4.40×10^{-5}	0.137×10^{-5}
	6.08×10^{-5}	6.08×10^{-5}	4.50×10^{-5}	5.00×10^{-5}	
	6.14×10^{-5}	6.00×10^{-5}	4.71×10^{-5}	4.83×10^{-5}	
	6.16×10^{-5}	5.88×10^{-5}	4.65×10^{-5}	4.74×10^{-5}	(1.93×10^{-5})[a]
0	8.95×10^{-5}	7.48×10^{-5}	8.03×10^{-5}	4.86×10^{-5}	0.180×10^{-5}
	10.53×10^{-5}	8.38×10^{-5}	7.70×10^{-5}	5.38×10^{-5}	
	10.23×10^{-5}	8.00×10^{-5}	8.00×10^{-5}	5.35×10^{-5}	
	9.90×10^{-5}	7.95×10^{-5}	7.91×10^{-5}	5.20×10^{-5}	(2.55×10^{-5})[a]
−10	13.95×10^{-5}	8.46×10^{-5}	11.00×10^{-5}	6.17×10^{-5}	0.296×10^{-5}
		8.09×10^{-5}	11.80×10^{-5}		
		8.28×10^{-5}	11.40×10^{-5}		(4.16×10^{-5})[a]

[a] Specific conductance of *M* $MgBr_2$ calculated.

Order of Conductivity.—It is observed from Table I that the order of the conductivities at any given temperature seems to be ethyl-, *n*-butyl-, benzyl- and phenyl- with magnesium bromide showing the least conductivity. The calculated specific conductivity of a molar solution of magnesium bromide is about one-third the conductivity of a molar solution of ethylmagnesium bromide. We also observe that in all cases between the limits of 20 and −10° the conductivity of ethylmagnesium bromide is of the order of twice the value for phenylmagnesium bromide. Benzyl- and *n*-butyl-, however, seem to have approximately the same conductivity. We would, therefore, reach the conclusion that ethylmagnesium bromide is the more highly ionized. In order to test this conductivity further, measurements were made on 2 *M* and 0.5 *M* solutions of ethylmagnesium bromide and phenylmagnesium bromide. The results are shown in Tables II and III.

Temperature Coefficient

Table I shows very definitely that all of these compounds have negative temperature coefficients between 20 and −10°. Ethylmagnesium bromide, for instance, has more than twice the conductivity at −10° that it has at 20°. Benzylmagnesium bromide and phenylmagnesium bromide also increase but the increase is not so striking. We also note from Tables II and III that the 0.5 *M* solutions of ethylmagnesium bromide and

TABLE II

SPECIFIC AND MOLAR CONDUCTIVITY OF ETHYLMAGNESIUM BROMIDE[a]

Temp., °C.	2 Molar		1 Molar		1/2 molar	
	L	μ	L	μ	L	μ
20	18.3×10^{-5}	9.2×10^{-2}	6.14×10^{-5}	6.14×10^{-2}	1.62×10^{-5}	3.24×10^{-2}
0	21.8×10^{-5}	10.9×10^{-2}	9.95×10^{-5}	9.95×10^{-2}	3.99×10^{-5}	7.98×10^{-2}
−10	24.4×10^{-5}	12.2×10^{-2}	13.80×10^{-5}	13.80×10^{-2}	5.65×10^{-5}	10.30×10^{-2}

TABLE III

SPECIFIC AND MOLAR CONDUCTIVITY OF PHENYLMAGNESIUM BROMIDE[a]

Temp., °C.	2 Molar		1 Molar		1/2 Molar	
	L	μ	L	μ	L	μ
20	10.07×10^{-5}	5.04×10^{-2}	4.83×10^{-5}	4.83×10^{-2}	1.21×10^{-5}	2.42×10^{-2}
0	8.24×10^{-5}	4.12×10^{-2}	5.35×10^{-5}	5.35×10^{-2}	1.94×10^{-5}	3.88×10^{-2}
−10	7.50×10^{-5}	3.75×10^{-2}	6.17×10^{-5}	6.17×10^{-2}	2.64×10^{-5}	5.28×10^{-2}

[a] We realize that these solutions do not contain the theoretical amount of Grignard compound since a considerable quantity of magnesium halide is always formed. However, we have discovered that the conductivity of this compound is slight compared to the conductivity of the complex compound in equilibrium with the simple Grignard reagent. Furthermore, we were determining the relative conduction of Grignard solutions as they exist.

phenylmagnesium bromide have negative temperature coefficients. The conductivity of 2 *M* ethylmagnesium bromide, however, does not increase so markedly with decreased temperature and 2 *M* phenylmagnesium bromide has less conductivity at −10° than at 20°, and hence at some concentration between 2 *M* and 1 *M* the temperature coefficient changes its sign. This same change in conductivity with temperature would no doubt take place with ethylmagnesium bromide. In fact, Kondyrew[1] found that 2.3 *N* ethylmagnesium bromide had a positive temperature coefficient and at 1.4 and 0.7 *N* the coefficient had a negative value.

Effect of Dilution on Molar Conductivity.—Our results show that the molar conductivity decreases with dilution between 2 *M* and 0.5 *M*. This is just the opposite of the effect we would expect if this weak electrolyte was obeying classical dilution laws. These results are not in accord with Kondyrew's results for ethylmagnesium bromide owing to the fact that he was working with more concentrated solutions in most cases. They do, however, check his results for ethylmagnesium iodide where he finds conduction to increase with concentration to 4 *N* and then decrease. Facts such as are tabulated here can be explained by postulating a complex structure to the Grignard reagent such that in dilute solutions the ionization decreases with dilution. We are at present investigating this phenomenon by determining the migration rates of the ions and identifying the products of electrolysis.

Summary

1. The conductivities of ethylmagnesium bromide, benzylmagnesium bromide, *n*-butylmagnesium bromide and magnesium bromide have been determined at 20, 0 and −10° and at various concentrations.

2. The conductivity of the ethylmagnesium bromide solution is the greatest. The order of conductivity is ethylmagnesium bromide, *n*-butylmagnesium bromide, benzylmagnesium bromide, phenylmagnesium bromide, and magnesium bromide.

3. The conductivity in all cases except 2 *M* phenylmagnesium bromide increases with decreased temperature.

4. Molar conductivity of ethylmagnesium bromide decreases with dilution.

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RECEIVED JULY 1, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relative Extractability of Vitamins B and G by Plain and Acidified Alcohol

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Introduction

By adding gallic or tannic acid to the alcohol used in extracting wheat germ, McCollum and Kruse[1] obtained a more potent extract of water-soluble B than by the use of plain alcohol. They interpreted their results to indicate that the solubility of the salt of the vitamin was greater than that of the vitamin itself, or that the molecular structure of these acids favored the formation of the salt.

Water-soluble B has since been shown to comprise at least two factors, the antineuritic vitamin B, and the more heat-stable vitamin G. Since reviews of the literature have so recently been published by Kruse and McCollum[2] and by Sherman and Smith,[3] a review of the solubility of the vitamins in alcohol is not included here. In general, both vitamins B and G are soluble in alcohol. Vitamin B appears to be soluble in ethyl alcohol of all concentrations, and vitamin G in the more aqueous solutions. However, Sherman and Sandels[4] have found it necessary to consider the physical and chemical nature of the source material as well as the solvent and the method of extraction in evaluating the evidence regarding the solubilities (extractabilities) of vitamins. This paper reports the relative extractabilities of the two vitamins by plain and acidified alcohols from the same source material and under the identical extraction procedures. The original source material and the extracts and residues resulting from the alcoholic extraction were assayed for each of the vitamins.

(1) McCollum and Kruse, *Am. J. Hyg.*, **6**, 197 (1926).

(2) Kruse and McCollum, *Physiol. Rev.*, **9**, 125 (1929).

(3) Sherman and Smith, "The Vitamins," Am. Chem. Soc. Monograph (1931).

(4) Sherman and Sandels, *Proc. Soc. Exptl. Biol. Med.*, **26**, 536 (1929); *J. Nutrition*, **3**, 395 (1931).