

Can Ionic Concentrations in Diethyl Ether be Determined by Emf Measurements?

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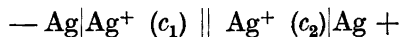
The present investigation was started in order to find methods for studying the equilibria in solutions of organomagnesium compounds RMgX (R =alkyl or aryl radical, X = halogen) in diethyl ether, so-called Grignard solutions. As is well known, such solutions have found extensive use in preparative organic chemistry.

It was shown by Kondyrew^{1,2} that Grignard solutions are conductors of electricity and thus contain ions; Kondyrew measured their conductivity at different concentrations. Evans and various co-workers (see *e. g.* Evans and Pearson³) have studied also the changes in concentrations and the electrode products during electrolysis and have tried to explain their results by assuming the solutions to contain ions such as RMg^+ , RMgX_2^- , and $\text{R}_2\text{MgX}_2^{2-}$.

Schlenk and Schlenk⁴ have tried to measure the equilibria $2 \text{RMgX} \rightleftharpoons \text{MgX}_2 + \text{MgR}_2$ by precipitating MgX_2 and RMgX with dioxane. However, certain sources of error in this method have been pointed out by Probert⁵ and by Noller and White⁶ (*cf.* Noller and Raney⁷).

It was (and is) our intention to study the Grignard solutions by the same methods that have proved so useful in investigating complex formation in aqueous solutions, namely by measuring the free concentration of individual ionic species by emf methods. However, as far as we know, nobody has ever before been able to measure ionic concentrations by emf methods in a solvent with such a low dielectric constant as diethyl ether, and we were quite aware that our task would be a difficult one.

In an *aqueous* solution, the concentration of an ionic species such as Ag^+ can be measured comparatively easily by means of concentration cells of the type



(|| = salt bridge for eliminating the liquid junction potential, E_d). The emf E of such a cell is given by Nernst's equation in its modern form

$$E (-E_d) = RTF^{-1} \ln \{Ag^+\}_2 \{Ag^+\}_1^{-1} = RTF^{-1} \ln \frac{f_2 c_2}{f_1 c_1}$$

If one works with dilute solutions, the activity factors f_1 and f_2 can be estimated with the aid of some approximative formula, and then, if c_2 is known, c_1 can be calculated from the measured emf. It is, of course, of no importance whether the potential difference between the two electrodes concerned is measured directly in a single cell or if they are both measured against the same reference electrode. — In an analogous way, the concentration of Cl^- can be determined by means of Ag, AgCl electrodes.

The higher the ionic strength of a solution, the less reliable are the approximate formulae for activity factors, especially if polyvalent ions are considered. For this reason it is in many cases advantageous to use a device first proposed by Bodländer (according to Grossmann⁸). To both the solutions to be compared a *neutral salt*, e. g. KNO_3 or $NaClO_4$, is added in such amounts as to make the ionic strengths of the solutions equal and rather large. In this way the influence of the liquid junction potential is made negligible, and, above all, the activity factors f_1 and f_2 are made equal so that we can use the simple form of Nernst's formula

$$E = RTF^{-1} \ln \frac{c_2}{c_1}$$

In *diethyl ether*, the dielectric constant is only 4.4 as compared with about 80 in water. For this reason the interionic forces are much stronger than in aqueous solutions, the ions aggregate in clusters, the activity factors decrease very rapidly with increasing concentration, and no approximate formulae for the activity factors of individual ionic species can be used in the range of concentration suitable for practical work (*cf.* McInnes⁹ and Kortüm¹⁰).

Thus it would certainly not be possible to calculate the ionic concentrations of e. g. Mg^{2+} and Br^- from the emfs that might be obtained using cells with pure Grignard solutions. However, we decided to try whether it would be possible to fix the activity factors by adding a high concentration of a suitable neutral salt. A salt that seemed promising is *lithium perchlorate*, since Willard and Smith¹¹ have shown that the solubility of anhydrous $LiClO_4$ is as high as 53.21 % by weight in diethyl ether at 25° C (whereas that of $LiClO_4(H_2O)_3$ is only 0.196 %).

The preparation of anhydrous LiClO_4 involved considerable difficulties which were overcome as described below. Preliminary experiments seemed to show that LiClO_4 in ether solution does not react with Mg metal or Mg amalgam; at least no Cl^- could be detected in the solution after prolonged contact. Solutions of $\text{C}_2\text{H}_5\text{MgBr}$ and LiClO_4 did not seem to react on mixing. Thus there seemed to be no difficulties arising from unwanted reactions.

MATERIALS

The *diethyl ether* used has been distilled over Na metal and is stored in contact with Na.

The *lithium perchlorate* is prepared in the 1 liter Pyrex bulb shown to the left in Fig. 1. First, solid lithium carbonate, *pro analysi* or purest available make, is neutralized with a slight excess of 70 % perchloric acid *pro analysi*. The bulb is then brought into a large cylindrical electric oven which is heated to 140°C . By applying a water pump to the tube at the extreme left of Fig. 1 (this tube is heated by an electric coil in order to prevent the condensation of water), a current of dry air filtered through cotton is passed through the LiClO_4 solution.

The temperature of the oven is slowly increased to 200°C and kept there till the volume of the liquid has decreased to one third of the original volume. Then the solution is allowed to cool to about 140°C , the left three-way stopcock in Fig. 1 is turned, and distilled water is pressed into the bulb until the volume is two-thirds of the original one. The current of air is again turned on, and the temperature of the oven is slowly increased to 300°C and kept there for about 12 hours (the addition of water is made in order to remove remaining traces of HClO_4).

After the temperature has attained 300°C , the right three-way stopcock in Fig. 1 is turned so that the air is dried. As is seen from the simplified Fig. 1, the air is first filtered through cotton for removing particles of dust, then passed through a washing bottle with 40 % NaOH, two washing bottles both containing 50 % H_3PO_4 saturated with KMnO_4 , a desiccating tower with NaOH pellets and one with P_2O_5 on glass wool, a U-tube with $\text{Mg}(\text{ClO}_4)_2$ and one with blue gel and cotton. This device for filtering the air, which is essential for obtaining a pure product, is principally the same as that described by Richards and Cox¹².

On cooling, the contents of the bulb solidifies; the solid can be assumed to consist of anhydrous LiClO_4 with a certain admixture of $\text{LiClO}_4(\text{H}_2\text{O})_3$. The anhydrous salt is extracted by reflux boiling with ether on a water bath for 12 hours.

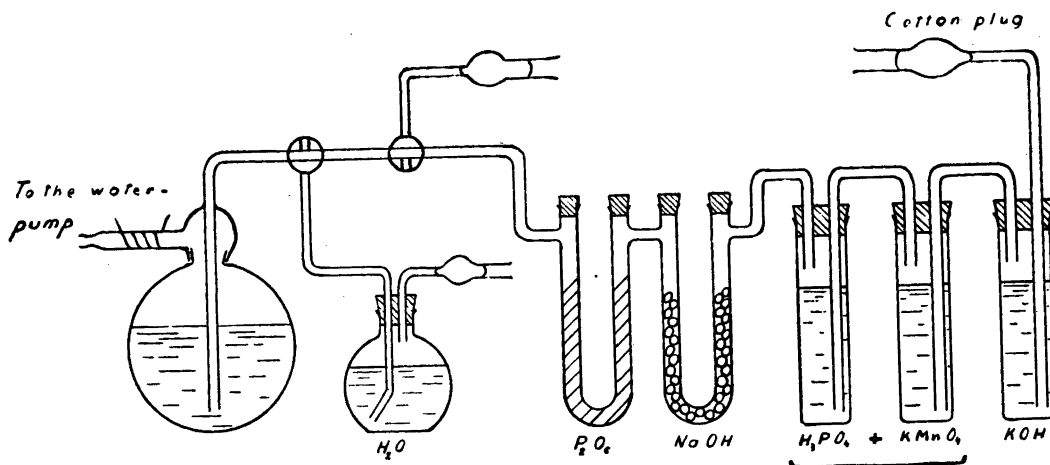


Fig. 1. Apparatus for preparing anhydrous LiClO_4 . The picture is very much simplified in comparison with the present large-scale apparatus. Instead of test tubes, washing bottles are used for KOH and $\text{H}_3\text{PO}_4 + \text{KMnO}_4$, and instead of U-tubes, desiccating towers are used for P_2O_5 and NaOH . The U-tubes with $\text{Mg}(\text{ClO}_4)_2$ and blue gel have been left out.

The ether solution, which contains about 35% LiClO_4 , is used as stock solution. In our first experiments, ether was usually driven off till crystals of LiClO_4 appeared. (The boiling point of the saturated solution was found to be about 72°C .) In this way solutions containing 50–52% LiClO_4 were obtained, which agrees well with 53.21% given as the solubility at 25°C by Willard and Smith¹¹.

Lithium bromide, Merck *pro analysi*, was dried at 200°C and extracted with ether in the same apparatus as LiClO_4 .

Magnesium perchlorate, Merck *pro analysi*, was dried just below the melting point of anhydrous $\text{Mg}(\text{ClO}_4)_2$ at 250°C , and extracted with ether in the same way as LiClO_4 . In this way solutions were obtained containing as much as 20–25% $\text{Mg}(\text{ClO}_4)_2$, whereas Willard and Smith¹¹ give the solubility at 25°C as 0.29%.

Magnesium was available in the form of rods (Merck *pro analysi*), ribbon (*pro analysi*), granules (for Grignard syntheses) and powder (*purum*).

The emfs were measured with a Radiometer valve potentiometer with an accuracy of about ± 0.1 mV.

Liquid *magnesium amalgam* (with about 0.3% Mg, *cf.* Hansen¹³) is prepared by bringing Mg powder and Hg into a glass tube, provided with stopcocks at both ends, evacuating, and keeping the tube in an oven at 110°C

for 12 hours. The liquid amalgam is filtered through glass wool, still in vacuum, in order to remove solid amalgam ($\text{Hg}_2\text{Mg}^{13}$) and traces of MgO . The use of stopcocks is possible thanks to Dow-Corning silicone stopcock grease, which maintains the vacuum at 110°C without making the stopcock immobile at room temperature. Otherwise the method is similar to that used by Sillén and Liljeqvist¹⁴ for preparing zinc amalgam.

We tried first to use the same method as used by Granér and Sillén¹⁵ for preparing bismuth amalgam, namely heating the metal-Hg mixture to 110°C under a cover of paraffin oil (alpha-chloronaphthalene was also tried). In this way also, pure magnesium amalgam was obtained, but between the amalgam and the oil there was a disagreeable black film, which may have consisted of MgO , Hg , and decomposition products of the paraffin oil. For this reason the vacuum method was preferred.

The *nitrogen* gas used was made free from oxygen by passing it over activated copper (Meyer and Ronge¹⁶), and dried by bubbling through a glass filter in conc. H_2SO_4 . For most purposes it was afterwards bubbled through diethyl ether or through a suitable solution of LiClO_4 in ether in order to give it a certain partial pressure of ether vapour.

APPARATUS

The cell is shown schematically in Fig. 2, for the case with Ag,AgBr electrodes; with amalgam electrodes the same glass vessels were used, with slight modifications. The counter electrode vessel (left) is connected to the titration vessel (right) by means of a salt bridge. As is seen from the figure, the five necks of the titration vessel (a 200 ml Pyrex bulb) are provided with an electrode, a burette, the end of the salt bridge, a stirrer with a Hg lock, and a thermometer.

In order to lessen the diffusion, which is much more prominent in ether solution than in water, the end of the salt bridge is drawn out to a bent tip. In the salt bridge there is also a stopcock with a Hg lock; this stopcock is kept open only for the short intervals of time when the emf is being measured.

The stopcocks are greased with silicone, which does not react with and dissolves only slightly in the solutions.

The cell is immersed in a paraffin oil thermostat at $25.0 \pm 0.1^\circ\text{C}$. The resistance of the cell is usually 0.5—1.0 $M\Omega$.

PROCEDURE

It is important that the solutions do not change their concentrations by evaporation or by taking up moisture from the air; in the latter case LiClO_4 (H_2O)₃ precipitates.

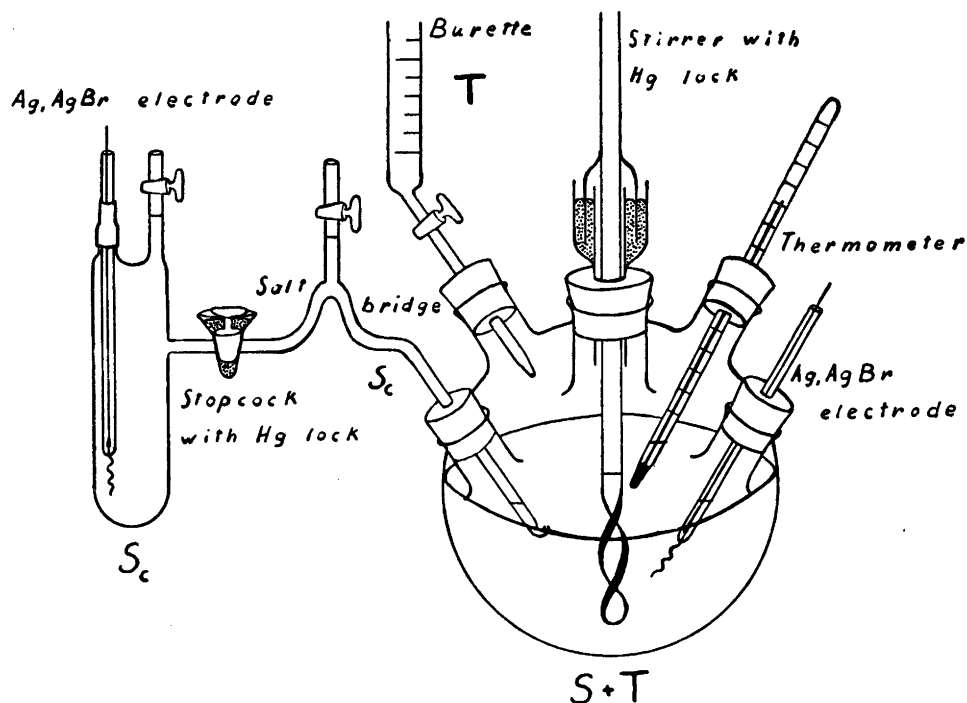


Fig. 2. Cell for emf measurements (schematic).

The solutions were always transferred from one vessel to another by pressure, using dry nitrogen gas, saturated with ether vapour. All air inlets of the different containers were provided with tubes with anhydrous $Mg(ClO_4)_2$.

Stock solutions were prepared of $LiClO_4$, $LiBr$, and $Mg(ClO_4)_2$ in ether. The stock solutions were placed into burettes, and calculated amounts of them were introduced into a measuring flask, which was filled to the mark with pure ether (a considerable volume contraction was observed).

About two hours before the beginning of a titration, the solutions were transferred to bubbling tubes (Sillén¹⁷, Fig. 2) where a slow current of nitrogen, saturated with ether vapour, was passed through them for about 90 minutes in order to remove traces of dissolved oxygen. The change of volume during this operation proved to be negligible.

The solution was then introduced into a burette and from this to the electrode vessels. All vessels and tubes in the path of the solution had previously been rinsed free from air with nitrogen gas.

The volume of the original solution, S, in the titration vessel was measured accurately; it was usually made to be 100.0 ml. The counter electrode vessel and the salt bridge were filled with another solution, S_c, and placed in position. A third solution, T, was added from the burette in Fig. 1 during the titration.

Of course the fire and explosion hazards were considered. Peroxide tests with benzidine on the ether solutions have hitherto given negative results, even after storing for a long time. If intentionally ignited the concentrated solution of LiClO₄ in ether burns rapidly with a beautiful red flame, but does not detonate. It was possible to make the solution detonate by applying a primer, but the detonation was rather a weak one.

ANALYSIS

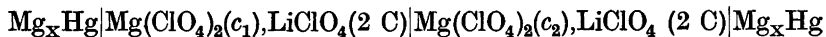
For determining *lithium perchlorate*, 10—15 ml water was added to a known volume, usually 3.00 ml, of the stock solution. The sample was evaporated to dryness, first on a water bath and then over a small flame. Water and excess of H₂SO₄ was added. The sample was again evaporated to dryness, ignited to dull red heat, and weighed as Li₂SO₄.

Lithium bromide was determined by Volhard titration, after adding excess of water to a known volume of ether solution. The ether was usually evaporated before titrating. — For control, the Br⁻ analysis was applied to the solutions S_c, S and T as well as to the stock solution.

Magnesium perchlorate was transformed to MgSO₄ by the method described for LiClO₄. The sulfate was ignited to 600° C and weighed.

EXPERIMENTS

The first cells studied were of the type



The stirrers were made to serve as electrodes also. A stirrer consisted of a long glass tube, the lower end of which was sealed and pierced by five Pt needles, which dipped into the pool of Mg amalgam on the bottom of the titration vessel. Electrical contact between the Mg amalgam and the potentiometer was obtained by filling the stirrer tube with mercury and dipping into it a copper wire connected with the potentiometer. Sometimes contact was also obtained by means of a capillary filled with mercury which was dipped into the amalgam. When the stirrer was rotated, the thin film of

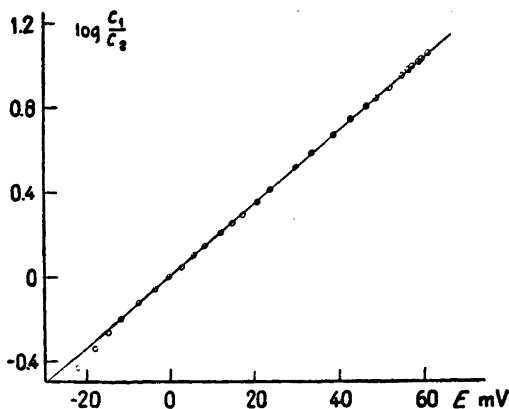


Fig. 3. Plot of E_{obs} against $\log (c_1/c_2)$ for cells $+ \text{Ag,AgBr}|\text{LiBr}(c_2)|\text{LiBr}(c_1)|\text{AgBr}, \text{Ag}-$. Values for three different titrations are given (Tab. 3): those of the first and third titration are given as circles, those of the second as dots. Straight line: calculated E according to Nernst's equation $E_{\text{calc}} = 59.16 \log (c_1/c_2)$.

oxide that tends to form on the amalgam surface was removed, and a clean surface was exposed.

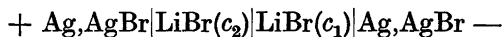
With cells of this type it proved difficult to obtain reproducible emfs, and in any case it was very inconvenient to have a stirrer in the counter electrode vessel. It was decided to try to find another type of electrode that would be more easily handled, to study the behaviour of this electrode, and then to study cells with a Mg or Mg amalgam electrode in the titration vessel and with the new electrode as counter electrode.

We prepared a cell $\text{Hg, Hg}_2\text{Cl}_2|\text{LiCl}$ in ether $|\text{AgCl, Ag}$, which proved after a few hours to give a steady emf. Thus we concluded that both the calomel and the Ag, AgCl electrode can be employed in ether solutions. Since we intended to work with bromides we decided to try the Ag, AgBr electrode.

A number of Ag, AgBr electrodes were prepared by the same method as that given for Ag, AgCl electrodes by Brown¹⁸. After washing, the water was removed by prolonged soaking, first in ethanol and then in ether.

These electrodes were immersed in ether solutions of LiBr and proved to acquire a steady potential very quickly. When inserted in the same solution they gave same potential within the limits of error.

The following cell was studied



where both solutions contained 2 C LiClO₄. The right solution, in the titration vessel, was obtained by adding v ml of T to (usually 100 ml of) S. The left solution, S_c, in the counter electrode vessel, had a constant concentration c_2 .

Table 1 and Fig. 3 give the measured emfs and those calculated by means of Nernst's formula

$$E_{\text{calc}} = RTF^{-1} \ln \frac{c_1}{c_2} = 59,16 \log \frac{c_1}{c_2} \text{ mV}$$

The agreement is seen to be rather good, even at the highest c_1 used, 25 mC. At the very lowest c_1 , about 1 mC, small deviations are observed, which may have been caused by diffusion from S_c.

DISCUSSION

The very high solubility of anhydrous LiClO₄ and Mg(ClO₄)₂ in ether is remarkable. One might imagine that the small cations Li⁺ and Mg²⁺ surround themselves with a cover of (C₂H₅)₂O dipoles, which should greatly lessen the electrostatic attraction between the ions. This view, however, cannot apply to the saturated solution of LiClO₄, where there is only 1.26 (C₂H₅)₂O for every Li⁺. In this case some sort of cluster or lattice formation seems probable, which is also indicated by the high viscosity. It is also remarkable that small quantities of water added to these solutions are immediately removed by the precipitation of LiClO₄(H₂O)₃.

The experiments seem to prove that Nernst's equation applies to an ionic species such as Br⁻, added in small amounts to a concentrated solution of LiClO₄ in ether. Thus the activity coefficient is not appreciably changed by small shifts in the Br⁻ concentration. This indicates that the external forces acting on a Br⁻ ion, which must be imagined as taking part in incessantly changing clusters of Li⁺, ClO₄⁻ and (C₂H₅)₂O, are determined chiefly by the large concentration of LiClO₄.

SUMMARY

In cells of the type—Ag, AgBr|LiBr(c_1) in ether|LiBr(c_2) in ether|AgBr, Ag +, the emf obeys Nernst's law: $E = RTF^{-1} \ln(c_1 c_2^{-1})$, if both solutions contain large and equal concentrations of LiClO₄. By adding LiClO₄ it will thus be possible to measure ionic concentrations in diethyl ether. This principle will be used in an investigation of so-called Grignard solutions.

The solubility of anhydrous Mg(ClO₄)₂ in ether is much greater than has hitherto been stated.

Table 1. Titrations with cells + Ag, AgBr/c₂ mC LiBr/c₁ mC LiBr/AgBr, Ag—.

a) S = 2 C LiClO ₄ (100.0 ml)				
T = 2 C LiClO ₄ , 25.4 ₂ mC LiBr (v ml)				
S _c = 2 C LiClO ₄ , 2.65 mC LiBr (= c ₂)				
v ml	c ₁ mC	log $\frac{c_1}{c_2}$	E _{calc} mV	E _{obs} mV
4.0	0.978	— 0.431	— 25.5	— 22.2
5.0	1.213	— 0.339	— 20.1	— 18.0
6.0	1.442	— 0.264	— 15.6	— 14.8
7.0	1.666	— 0.202	— 11.9	— 10.8
8.5	1.995	— 0.123	— 7.3	— 7.5
10.0	2.315	— 0.059	— 3.5	— 3.5
11.5	2.627	— 0.004	— 0.2	+ 0.2
13.0	2.93	+ 0.044	+ 2.6	3.0
15.0	3.32	0.098	5.8	5.9
17.0	3.70	0.145	8.6	8.4
20.0	4.24	0.204	12.1	12.3
22.5	4.68	0.247	14.6	15.1
25.0	5.09	0.284	16.8	17.5
30.0	5.86	0.345	20.4	21.0
35.0	6.60	0.396	23.5	24.0
b) S = 2 C LiClO ₄ , 2.65 mC LiBr (92.2 ml)				
T = 2 C LiClO ₄ , 98.7 mC LiBr (v ml)				
S _c = 2 C LiClO ₄ , 2.65 mC LiBr (= c ₂)				
v ml	c ₁ mC	log $\frac{c_1}{c_2}$	E _{calc} mV	E _{obs} mV
4.0	6.64	0.399	23.6	23.8
6.0	8.51	0.507	30.0	30.0
7.5	9.87	0.571	33.8	33.8
10.0	12.05	0.658	38.9	38.9
12.6	14.20	0.729	43.1	42.9
15.0	16.09	0.782	46.3	46.0
c) S = 2 C LiClO ₄ , 14.10 mC LiBr (100.0 ml)				
T = 2 C LiClO ₄ , 47.47 mC LiBr (v ml)				
S _c = 2 C LiClO ₄ , 2.30 mC LiBr (= c ₂)				
v ml	c ₁ mC	log $\frac{c_1}{c_2}$	E _{calc} mV	E _{obs} mV
4.0	15.39	0.825	48.8	49.0
10.0	17.14	0.872	51.6	52.1
15.0	18.45	0.904	53.5	53.5
20.0	19.66	0.932	55.1	55.0
25.0	20.76	0.956	56.5	56.5
30.0	21.81	0.977	57.8	57.4
35.0	22.75	0.995	58.9	59.0
40.0	23.63	1.012	59.9	59.6
49.0	25.07	1.037	61.4	61.2

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