[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Electrolysis of Methylmagnesium Iodide in *n*-Butyl Ether

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The electrolysis of the methyl Grignard reagents in ether solution has been studied[1] thoroughly for the three halides in ethyl ether using bright platinum electrodes. The products of the electrolyses in ethyl ether pointed definitely to the fact that the solvent played an important role. The ether appeared to be directly responsible for the ethylene, ethyl alcohol and isopropyl alcohol found, as a result of decomposition after the loss of a hydrogen to a free methyl radical to form methane. In order to bear this out and investigate further the mechanism involved, an electrolysis was carried out using *n*-butyl ether as the solvent.

It was also shown previously that the ratio between the methane and ethane formed depended on the current density independent of the concentration of the solution. This fact drew attention to the function of the surface of the electrode in the electrolysis. With this in view the effect of platinizing the anode where the gases evolved was determined by performing another electrolysis in ethyl ether.

Experimental

The apparatus and procedure were the same as that previously described. For the experiment with a platinized anode a platinized electrode of identical size and shape, dried by washing in anhydrous ether, was slipped over the anode.

On attempting the electrolysis of methylmagnesium iodide in butyl ether it was found necessary to introduce a new variable, that of temperature. At 40° polarization was so great that 110 volts would pass a sustained current of only 0.005 ampere. On raising the temperature to 90° polarization was still pronounced, a current of 0.2 ampere passing initially, dropping off to 0.05 ampere in one minute. The composition of the gases evolving at 90° was determined so as to enable an estimation of the effect of temperature to be made. The temperature was then raised to 143°, at which the solution refluxed gently. Polarization was almost completely absent and currents approaching 0.5 ampere could be maintained. A series of current densities was used at this temperature.

Methane and ethane predominated in the gases and small and erratic amounts of carbon dioxide were obtained just as in ethyl ether. Ethylene, formerly present, was absent; butane and butene-1 (the absence of butene-2 was not definitely proved) were new products, proved by a Podbielniak distillation of the 5 liters of gas collected during the run not used for Orsat analyses. The absence of ethyl ether vapor made the absorption analysis simple. The presence of the three saturated gases made it necessary to assume the amount of butane present before the simple combustion analysis could give the ratio of methane to ethane. The purely arbitrary assumption was made that butane was present to one-half the extent of the butene because this reduced the observed variations in the combustion values under apparently identical conditions to a minimum. The analyses are shown in Table I, where the arbitrary value for butane is given as well as the observed and corrected values for *n* in the formula C_nH_{2n+2}. The corrected value of *n*, representing the methane and ethane only, was used to calculate the fraction of methyls coupled, *Fc*, which is shown plotted as curve 1, Fig. 1.

The efficiency of the electrolysis was 43.3% based on the change in basic magnesium determined by titration. This is much lower than in ethyl ether. On the basis of the gas evolved using the corrected analysis for ethane and making use of the previously demonstrated[1] equivalency of methyls evolved to Grignard decomposed, the efficiency was 42%. The excellent agreement confirmed the assumptions made.

When the electrolysis was completed the solution was hydrolyzed in a nitrogen atmosphere and fractionally distilled through a 75-cm. vacuum jacketed spiral coil column; 2.6 cc. (0.043 equivalent per faraday) of butanol-1 was isolated (b. p. 116–116.5°, 3,5-dinitrobenzoate m. p. 63.5–64° and confirmed by a mixed melting point). A small amount of pentanol-2 was also found present, estimated at 0.2 cc. The presence of a secondary alcohol was first proved by the $ZnCl_2 \cdot HCl$ reagent; fractional crystallization of the dinitrobenzoate followed by means of mixed melting points with the known pentanol-2 deriva-

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(1) Evans and Field, THIS JOURNAL, 58, 720 (1936).

TABLE I

ELECTROLYSIS OF METHYLMAGNESIUM IODIDE IN BUTYL ETHER WITH BRIGHT ELECTRODES

Initial concn. 1.900 *N*; final concn. 1.056; average concn. 1.422. Over-all efficiency: 0.433 equiv. decomp./faraday; 0.343 mole gas/faraday; 0.42 methyl/faraday; 0.97 methyl/equiv.

Temp., °C.	Order taken	Amp./sq. dm.	CO_2	C_4H_8	C_4H_{10}	C_2H_6	CH_4	*n*, obsd.	*n*, corr.	100F_c
143	11	1.60	0.2	9.5	4.8	23.1	62.4	1.41	1.27	43
	7	1.60	.4	13.5	6.8	23.0	56.3	1.51	1.29	45
	10	1.20	.7	4.2	2.1	17.7	75.3	1.25	1.19	32
	9	1.20	2.1	6.7	3.4	19.3	68.5	1.32	1.22	46
	3	0.80	0.0	4.4	2.2	19.6	73.8	1.27	1.21	35
	8	.40	.0	2.7	1.4	15.4	70.5	1.20	1.16	28
	5	.12	.0	5.2	2.6	4.6	87.6	1.13	1.05	10
	4	.12	.0	4.5	2.3	5.6	87.6	1.13	1.06	11
	6	.04	.0	3.8	1.9	5.8	88.5	1.12	1.06	11
90	2	.20	.0	1.0	0.5	23.7	74.8	1.25	1.24	39
	1	.20	.0	0.9	0.4	22.7	76.0	1.24	1.23	37

TABLE II

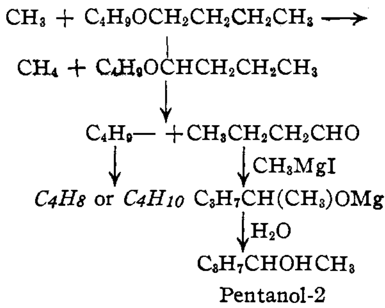
ELECTROLYSIS OF METHYLMAGNESIUM IODIDE IN ETHYL ETHER WITH PLATINIZED ANODE

Initial concn. 1.794 *N*; final concn. 0.892; average concn. 1.34. Over-all efficiency: 0.467 mole gas/faraday; 0.761 equiv. decomp./faraday; 0.772 methyl/faraday; 1.01 methyl/equiv. decomp.

Order taken	C. d. amp./sq. dm.	Gas constituents				100F_c
		Ethane	Methane	Ethylene	Carbon dioxide	
4	0.060	25.7	73.0	1.1	0.2	41
3	.12	29.6	68.9	1.3	.2	46
5	.24	40.4	58.2	1.1	.3	58
2	0.40	50.4	48.7	0.9	0.0	68
9	.60	58.6	40.6	0.6	.2	74
1	.80	63.0	35.5	1.3	.2	78
8	.80	63.6	35.7	0.5	.2	78
7	1.60	72.3	26.8	.6	.3	84
6	2.40	77.3	22.3	.7	.1	88

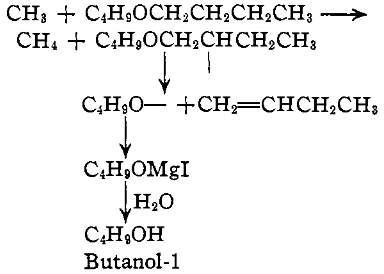
tive proved its presence. There was also found 5 cc. of high boiling liquid products.

Decomposition of the Ether.—The products obtained were in excellent agreement with the mechanism proposed for the electrolysis in ethyl ether. Applied to the α- and β-hydrogens in butyl ether we have



$$\begin{array}{l} CH_3 + C_4H_9OCH_2CH_2CH_2CH_3 \longrightarrow \\ CH_4 + C_4H_9O\overset{|}{C}HCH_2CH_2CH_3 \\ \qquad\qquad \downarrow \\ \quad C_4H_9\text{—} + CH_3CH_2CH_2CHO \\ \quad \downarrow \qquad\qquad \downarrow CH_3MgI \\ C_4H_8 \text{ or } C_4H_{10} \quad C_3H_7CH(CH_3)OMgI \\ \qquad\qquad\qquad \downarrow H_2O \\ \qquad\qquad\qquad C_3H_7CHOHCH_3 \\ \qquad\qquad\qquad \text{Pentanol-2} \end{array}$$

and



$$\begin{array}{l} CH_3 + C_4H_9OCH_2CH_2CH_2CH_3 \longrightarrow \\ CH_4 + C_4H_9OCH_2\underset{|}{C}HCH_2CH_3 \\ \qquad\qquad \downarrow \\ C_4H_9O\text{—} + CH_2{=}CHCH_2CH_3 \\ \quad \downarrow \\ C_4H_9OMgI \\ \quad \downarrow H_2O \\ C_4H_9OH \\ \text{Butanol-1} \end{array}$$

These two sets of reactions account for all the products identified and explain the absence of ethylene. There can be no question that the solvent furnishes the fourth hydrogen for the methane and that its subsequent decomposition is responsible for the secondary products formed.

The above mechanism applied to the other two kinds of hydrogen present in the ether molecule predicts products which were not found; this would seem to cast some doubt on the free radical mechanism and suggest another such as an ionic reaction. It is not necessary, however, to assume that these positions were not subject to attack, but merely that the intermediate radicals thus formed were stable enough to polymerize in some manner instead of breaking down, explaining the appreciable amount of high molecular weight liquid compounds obtained.

Fraction of Methyls Coupling.—The amount of coupling to form ethane was much lower in butyl ether than in ethyl ether, as is shown when curves I and II are compared with III and IV in Fig. 1. This indicates a greater rate of reaction of the butyl ether with the methyl radicals. Since this effect was obtained by changing both solvent and temperature, the individual effect of each remained to be determined. The two temperatures used showed that the coupling decreased as the temperature increased. An extrapolation down to the 40° used with ethyl ether by means of the Arrhenius equation gave a value for *Fc*, the fraction of methyls coupled, of 0.62; the observed value in ethyl ether at the same current density was 0.77. This may be interpreted to show that the loss of a hydrogen to a methyl radical takes place more readily in the case of butyl ether even at the same temperature. The slope of the line determined by the two points gave the low value of 1100 calories per mole for this reaction.

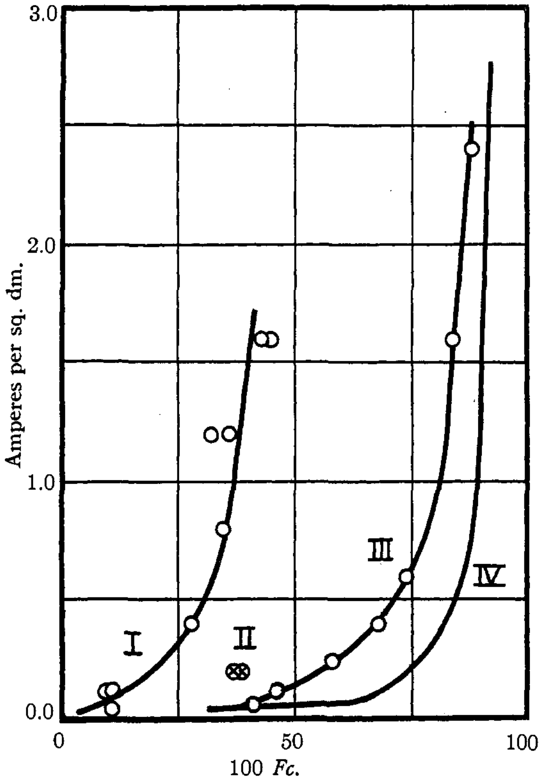


Fig. 1.—Effect of current density in electrolysis of methylmagnesium iodide: I, in butyl ether at 143°, bright electrodes; II, in butyl ether at 90°, bright electrodes; III, in ethyl ether, platinized anode; IV, in ethyl ether, bright electrodes.

Platinized Anode.—As was expected, the effect of platinizing the anode was a significant change in the methane–ethane ratio. The results are given in Table II. The perfect agreement between the first and eighth sample taken was good evidence that the platinized electrode was unchanged during the course of the electrolysis. One and one-half liters of gas was evolved before samples were taken in order to allow the electrode surface an opportunity to come to equilibrium.

The efficiency of electrolysis was entirely unaffected by platinizing the anode since an interpolation to the same concentration on our previously determined curve[1] also gives an efficiency of 76%. *Fc* showed the same dependence on current density as with bright electrodes, but is somewhat lower as may be seen in curves III and IV, Fig. 1. The platinizing seemed merely to cut down the apparent current density by exactly 5 in comparison with the bright electrode throughout the whole range studied. Evidently platinizing the anode served to increase its effective area by five so that the effective current density was decreased by that amount. Apparently the electrode merely provides an inert surface on which the reactions take place.

Summary

1. The theory that the solvent ether furnished the fourth hydrogen for the formation of the methane, with subsequent decomposition to give the secondary liquid and gaseous products found, was confirmed.

2. Butyl ether was more readily attacked by methyl radicals than was ethyl ether.

3. Increase in temperature favored the reaction with the solvent, increasing the proportion of methane.

4. The electrolysis efficiency was much less in butyl than in ethyl ether.

5. Platinizing the anode had no effect other than to increase the effective area by exactly five, with a resultant decrease in effective current density by that factor.

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