Mechanism of the Grignard Addition Reaction. XI.

Electrode Kinetics and Chemical Reactivity of Grignard Reagents

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Electrolysis of alkylmagnesium bromides using platinum electrodes lead to Tafel plots of slope 0.13 for allyl-, benzyl-, and t-butylmagnesium bromide, but 0.32 for methylmagnesium bromide. Two different mechanisms for the discharge process are therefore indicated. Ethyl-, butyl-, and isopropylmagnesium bromide behave like methyl at low current densities, but change over toward the t-butyl slope at high current densities. Values of the anodic polarisation at high current densities are correlated to the reactivity of the reagent toward benzophenone.

By electrolysis of alkylmagnesium bromides in ether solution using platinum electrodes a polarization is observed which varies with the nature of the alkyl group. These "decomposition potentials" were measured by Evans et al. in 1935.[1] Since magnesium is produced at the cathode and hydrocarbons attributable to the free radical form at the anode, the difference in decomposition potentials was assumed by Evans to reflect a characteristic difference in the anodic discharge potential of each alkyl anion.

In the study of the reactivity of the Grignard reagent toward benzophenone an initial transfer of a single electron from Grignard reagent to ketone has been assumed to be rate determining[2,3] and since this SET process might be related to the electrode process it was found of interest to try to correlate the chemical reactivity of the Grignard reagents with the electrochemical reactivity.

No experimental details were given by Evans concerning electrodes or current densities and serious objections may be raised against the oversimplified interpretation. More recently Psarras and Dessy[4] made an investigation of the polarographic behaviour of Grignard reagents, but failed to determine characteristic anodic potentials. Martinot made an electrokinetic investigation of several Grignard reagents[5] and found decreasing electrochemical reactivity in the order t-butyl > i-butyl > ethyl > butyl. Martinot found identical Tafel slopes of 0.20 for the four reagents in the anodic process, while the cathodic process for the four reagents had a Tafel slope of -0.008.

During the present work a simple procedure was used which usually gave reproducible values for the polarisation of the anode and allowed the determination of Tafel slopes as well as relative values of the electrochemical reactivity for several alkylmagnesium bromides.

A cell with two platinum electrodes was charged with ca. 0.8 M alkylmagnesium bromide in ether. A potential was set up by means of a constant current generator. The equilibrium value of the potential was measured exactly by means of a digital voltmeter for values of the current density I_D varying from 10^{-5} to 10^{-1} A/cm². For each reading of the potential E, a correction was made by increasing the current to two times the original value and noting the following increase in electrode potential E_{inc}. The apparent back electromotoric force was then taken as:

$$bEMF = E - E_{inc} \qquad (1)$$

The values of bEMF were plotted against the logarithm of the current density; Fig. 1.

The potential between the electrodes is considered the sum of ohmic resistance potentials, concentration potentials, and overvoltage for both electrode processes. It was assumed that
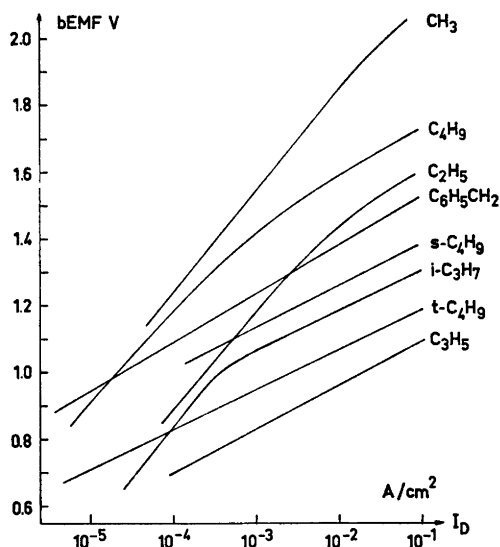
Fig. 1. Back electromotoric force (see text) *versus* log current density during electrolysis of alkylmagnesium bromides between platinum electrodes in diethyl ether at 20 °C.

the current densities applied were so small that the concentration polarisation was proportional to I_D just like the ohmic potential drop. Variations in the calculated values of bEMF was therefore considered representative for variations in overvoltage, and since for reasons which will be explained later the cathodic potential could be considered almost constant, the variations were ascribed specifically to anodic overvoltage.

Overvoltage usually follows the Tafel equation

$$\eta = a + b \log I_D \qquad (2)$$

From the Tafel plots obtained with the various Grignard reagents it seems that the values of the slope b in eqn. (2) may vary between two extremes. A low value, *ca.* 0.13, is observed with allyl, benzyl, and *t*-butylmagnesium bromide, while a high value, *ca.* 0.32, is obtained for methylmagnesium bromide. With reagents like isopropyl-, ethyl-, butylmagnesium bromide, *etc.* a change in slope is observed from the high value, 0.32, at low current densities to the low value 0.13, at high current densities. A simple interpretation would be the operation of two mechanisms for discharge of alkylmagnesium species at the anode: (1) reaction at plati-

num, and (2) reaction at "radical saturated" platinum. The simple discharge of alkylmagnesium species at the platinum surface to form alkyl radical and magnesium ion would be in operation at low current densities or with extremely shortlived radicals like methyl. A more complex discharge mechanism would apply if a sufficient concentration of surface bound radicals are present on the anode. The electron transfer may in this case occur with a lower activation than necessary with pure platinum, as if the surface bound radicals served as a catalyst for the electron transfer. With reagents forming stable radicals like allyl, benzyl, and *t*-butyl, the saturation is obtained even with the lowest current densities and with methyl it is not obtained even with the highest, but with isopropyl and ethyl saturation may be obtained of the current density is high enough.

For identical values of b the value of a in (2) would represent a measure of the electrochemical reactivity of the reagent. Since at the highest I_D values the slopes of the plots tended toward a common value (0.13), bEMF for the various Grignard reagents are given in Table 1 for a current density of 0.06 A/cm². The Tafel slope problems of course make the values for especially methyl and ethyl rather dubious.

It has been implicated in the interpretation that the overvoltage may be ascribed to the anode process. This conclusion seemed permissible from experiments in which a Mg/MgBr₂ reference electrode was included in the system. At low current densities the potential between the reference electrode and the cathode was near zero and at increasing I_D the potential increased linearly with I_D indicating that overvoltage is of much less importance at the magnesium cathode than at the anode. In the work of Martinot the cathodic overvoltage for six alkylmagnesium bromides varied ± 5 mV for 0.6 M solutions, and the Tafel slope for the cathodic processes was smaller than 0.01.

In order to see if the electrode process is related to the rate determining step in the reaction of Grignard reagents with benzophenone, pseudo first order rate constants were obtained by means of the thermographic method [6] for the reaction of 0.02 M Grignard reagent with 0.25 M benzophenone in ether as shown in Table 1.

Table 1. Pseudo first order constants, k_{obs}, in s^{-1} for the reaction of 0.02 M alkylmagnesium bromide with 0.25 M benzophenone in diethyl ether at 20 °C. Excess bromide relative to the base titration is given as % Br$^-$. Anodic overvoltage $\eta_{0.06}$ (see text) is given in Volts, molarity of electrolysed solution given as [RMgBr].

R	% Br$^-$	k_{obs}	$\eta_{0.06}$	[RMgBr]
CH$_3$	0.8	0.3	1.98	1.00
C$_2$H$_5$	2.8	5.0	1.57	0.87
i-C$_3$H$_7$	13.0	133	1.28	0.99
C$_4$H$_9$	4.4	2.6	1.70	1.09
i-C$_4$H$_9$	9.6	0.90	1.60	0.98
s-C$_4$H$_9$	19.5	64	1.36	1.00
t-C$_4$H$_9$	30.0	400	1.16	0.69
C$_3$H$_5$	19.7	16 000	1.07	0.68
C$_6$H$_5$CH$_2$	15.0	21	1.50	1.02
c-C$_5$H$_{10}$	9.9	214	1.35	0.98

The logarithm of the rate constants was plotted against the anodic overvoltage for $I_D = 0.06$ A/cm^2 relative to the magnesium cathode; see Fig. 2. An approximate linear correlation is obtained for methyl-, ethyl-, isopropyl-, t-butyl, and benzylmagnesium bromide, which might indicate that the SET mechanism which was suggested for t-butylmagnesium bromide [3] may be a relevant model for many simply alkylmagnesium bromides. This would not mean that free radicals are actual intermediates, but
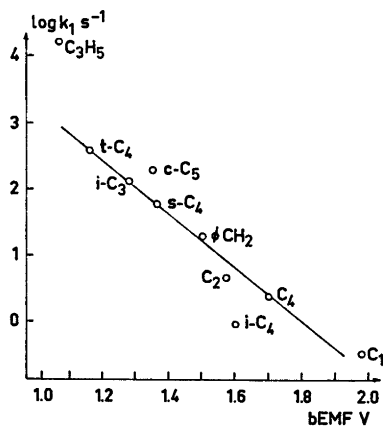

Fig. 2. Pseudo first order rate constants for the reaction at 20 °C of alkylmagnesium bromide (0.02 M) in diethyl ether with 0.25 M benzophenone. C$_1$, C$_2$, C$_3$, C$_4$, *etc.* means methyl-, ethyl-, propyl-, butylmagnesium bromide, *etc.*

only that the alkyl assumes a significant amount of radical character in the transition state. The stability of the radical type transition state may be increased by pairing between benzophenone ketyl radical and the alkyl radical.

The reactivity of some Grignard reagents is not very well correlated with the discharge potential. It seems that β-branching as in isobutyl represents more steric hindrance for the chemical reaction than for the electrode process. For allyl- and cyclopentylmagnesium bromide the reaction is faster than would be predicted from the discharge potentials. The mechanism of reaction for these reagents may be different or it may be a hybrid between the stepwise SET mechanism and appropriate polar or concerted mechanisms.

A certain amount of radical character or at least electron deficiency at the α-carbon in the transition state is always indicated in reactions in which the ethyl reagent is more reactive that the methyl reagent which applies to most of the reactions of Grignard reagents which have been investigated kinetically. A correlation of rate data for the metalation of 1-hexyne with Grignard reagents with Evans decomposition potentials was attempted by Dessy in 1955.[7] If this correlation is established it would suggest the operation of a SET mechanism even in this type of reaction.*

EXPERIMENTAL

The Grignard reagents were prepared from sublimed magnesium ("Specpure", Johnson, Matthiey & Co.) as reported.[8] The electrolysis cell consisted of a 10×75 mm Pyrex test tube. The electrodes were smooth platinum wires (0.6 mm) which were placed 6 mm apart in a rubber stopper with 65 mm extending into the tube. The electrodes were cleaned before each experiment by washing with dilute acid and with acetone. They were then heated in a bunsen burner. The cell was assembled and copper leads were connected to a Fluke 382 A current calibrator and to a Takeda-Riken digital volt-

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Note added in proof. A recent report [9] demonstrates a linear correlation of log rate for reaction of RMgBr with di-t-butyl peroxide in ether with Evans decomposition potentials. The correlation is improved if $\eta_{0.06}$ is used. Reaction of Grignard reagents are shown to have a rate determining SET step. The reactivity of benzophenone is 3.3×10^5 times greater than the reactivity of di-t-butyl peroxide toward the same Grignard reagent.

meter. The cell was evacuated to 0.1 mmHg through a hypodermic needle and 3 ml of the Grignard reagent were injected through the rubber stopper. The tube was placed in water at 20 °C and the current calibrator was adjusted to 1.000 mA. After 10 min the potential between the electrodes was read with two decimals and the current was increased to 2.000 mA. The new value of the potential was read exactly and from the measurements obtained the back electromotoric force was calculated according to eqn. (1). The procedure described was repeated every 10 min until a constant value for the bEMF was obtained, which usually occurred within 30 min. With methyl- and ethylmagnesium bromide up to $1-2$ h were required to obtain a constant value. After the measurement at 1.000 mA the bEMF was measured according to the same principle at 0.4, 0.2, 0.1, 0.04, 0.02, 0.01, 0.004, 0.002, 0.001, 0.0004, 0.0002, and 0.0001 mA. The results are shown as plots of bEMF *versus* log I_D in Fig. 1.

For measurements using an external reference electrode two cells were connected through a Pyrex G 4 fritte. The reference electrode was a piece of sublimed magnesium connected to a platinum wire and suspended in a saturated solution of magnesium bromide in diethyl ether (2.5 M). During measurements using isopropyl- and allylmagnesium bromide the reference electrode was only $35-40$ mV anodic to the cathode of the electrolysis cell at low current densities. Based on this observation and on the observation of Martinot [5] the magnesium-coated platinum cathode was considered useful as an intrinsic reference for comparison of anodic potentials.

The values of the back electromotoric force at a current density of 60 mA/cm² was taken as representative for the anodic discharge potential of the specific Grignard reagent relative to the $Mg/MgBr_2$ reference and are tabulated in Table 1.

The kinetic measurements were performed using a thermographic method.[6] The standard concentrations were 0.02 M Grignard reagent and 0.25 M benzophenone. The liquid speed in the reaction tube was usually 3 000 mm/s, but for measurement of allylmagnesium bromide the speed was 13 800 mm/s in a glass capillary of 0.24 mm inside diameter. The high speed allowed temperature measurement *ca.* 0.15 ms after mixing. From the time/temperature readings pseudo first order plots were prepared according to the expression

$$\ln\left[(T_\infty - T_0)/(T_\infty - T_r)\right] = kt$$

The plots were linear usually for more than 50 % of the reaction and values of k_1 were obtained from this linear part of the plot.

The logarithm of the rate constants were plotted *versus* the anodic discharge potentials of the respective reagents as shown in Fig. 2.

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