

THE OXIDATION OF ETHYLALUMINIUM AND ETHYLMAGNESIUM COMPOUNDS AT A LEAD ANODE IN TETRAHYDROFURAN

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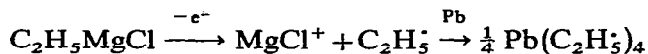
SUMMARY

The oxidation of the ethylmagnesium and ethylaluminium compounds has been shown to give *i/E* curves with well-formed waves and conveniently long limiting current plateaux. These limiting currents are, however, inconveniently low for preparative scale electrolyses due to slow chemical steps during the formation of alkyllead compounds.

These anodic processes have been shown to be very dependent on the state of the electrode surface. In tetrahydrofuran complete poisoning of the electrode eventually occurs and this may explain the preference for other ethers in the industrial scale process.

INTRODUCTION

A large number of papers and patents have considered preparative and technical aspects of the synthesis of alkylmetals formed by the electrolytic oxidation of organoaluminium¹⁻¹⁷ and organomagnesium¹⁸⁻²⁷ compounds in low temperature melts or ether solvents at an anode made from a metal which is capable of reaction with the alkyl radicals formed in the electron transfer step. A typical example of these syntheses is the oxidation of a Grignard reagent at a lead anode and, indeed, this



reaction carried out in a mixture of high-boiling ethers is the basis of a large scale industrial process for the preparation of tetraethyllead and tetramethyllead.

In view of the success of these processes, however, it is surprising to find that there have been no reports of detailed studies of these electrode reactions. In this paper, the results of a study of the oxidation of sodium tetraethylaluminate, diethylmagnesium and ethylmagnesium bromide at a lead anode in tetrahydrofuran are presented.

EXPERIMENTAL

The electrochemical experiments were carried out in a three compartment cell using a Chemical Electronics valve potentiostat and pulse generator (R.B.1); the

i/E curves were recorded on a Bryans series 26000 XY recorder or a Telequipment oscilloscope. The reference electrode, against which all potentials in this paper are quoted, was a silver wire dipping into a solution of $10^{-2} M$ silver perchlorate in the solvent/electrolyte mixture and it was separated from the working electrode by a Luggin capillary and a tap. The working electrode was constructed by melting lead in the end of a glass tube and allowing it to solidify; after polishing, a satisfactory glass-lead seal was obtained. The secondary electrode was a platinum sheet separated from the working electrode by a No. 2 glass sinter.

The tetrahydrofuran was obtained from B.D.H. Ltd. and purified by the method described by Mann²⁸. Tetrabutylammonium perchlorate was prepared by neutralising the hydroxide with aqueous perchloric acid; the crystals were recrystallised from water and dried at 80° in a vacuum oven. The sodium tetraethylaluminate²⁹, diethylmagnesium³⁰, ethylmagnesium bromide³¹ and the magnesium bromide solutions³⁰ in tetrahydrofuran were prepared by literature methods and all solutions were handled in a dry box with a nitrogen atmosphere. Before use all solutions were analysed for their aluminium or magnesium contents; the aluminium was determined gravimetrically³² and the magnesium alkyls were analysed by an acidimetric titration after hydrolysis^{31,33}.

RESULTS AND DISCUSSION

Sodium tetraethylaluminate

Steady state current-potential (i/E) curves were run at a lead electrode for a series of concentrations of sodium tetraethylaluminate in tetrahydrofuran containing $0.25 M$ tetrabutylammonium perchlorate. For each concentration a single, well formed oxidation wave was obtained; the process gave a half wave potential of $-1.25 V$ and a limiting current plateau which extended from $-1.1 V$ to $-0.70 V$ where dissolution of the lead electrode occurs in the base electrolyte solution. The i/E curves were replotted in the form of $\log i/E$ graphs and these showed linear portions with a Tafel slope of $(120 mV)^{-1}$. This Tafel slope is consistent with the rate of the electrode process in this potential region being controlled by the kinetics of the transfer of a single electron and a symmetry factor, $\alpha = \frac{1}{2}$.

The current for the oxidation process shows a first-order dependence on the

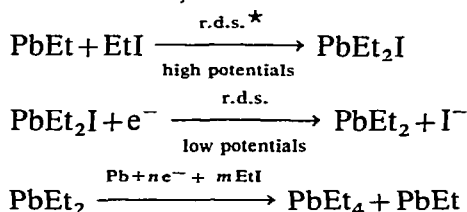
TABLE I

ELECTROCHEMICAL DATA FOR ETHYLMAGNESIUM AND ETHYLALUMINIUM COMPOUNDS AT A LEAD ELECTRODE IN $0.25 M Bu_4NClO_4/THF$

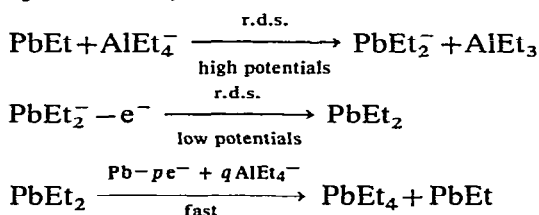
Potentials versus $Ag/10^{-2} M Ag^+$ reference electrode. The half peak potentials were taken from cyclic voltammograms run at $0.3 V/s$.

Alkyl	$E_{p/2}$ (volts)	Tafel slope (mV^{-1})	Limiting current for $5 \times 10^{-2} M$ substrate (mA/cm^2)
NaAlEt ₄	-1.25	120	3.5
AlEt ₃	> -0.6		
MgEt ₂	-1.72	60	1.0
EtMgBr	-1.73	120	1.8

concentration of the sodium tetraethylaluminate. The currents on the plateau of the oxidation wave are, however, lower by over an order of magnitude than those expected for an electrode process whose rate is controlled by diffusion of the electroactive species to the electrode surface. Therefore, the current must be determined by the rate of a chemical reaction, probably preceding the electron transfer, which itself is first-order with respect to the concentration of the sodium tetraethylaluminate. From an investigation of the cathodic reduction of ethyl halides at a lead electrode³⁴, it was concluded that the formation of tetraethyllead follows a complex reaction sequence involving a rate determining chemical process between a surface, ethylated lead intermediate and a solution free molecule of ethyl halide followed by a series of reactions which leads to the tetraethyllead and the quantitative regeneration of the surface intermediate, *i.e.*:



A similar mechanism seems appropriate in the case of the anodic oxidation of sodium tetraethylaluminate, *i.e.*:



The cyclic voltammetry of this system generally confirms the conclusions drawn from the steady state data. At all potential sweep rates the curves show a single, irreversible process. This process produces only a weak peak whose height is independent of the potential sweep rate. Therefore it is clear that the rate of the electrode reaction is determined neither by diffusion of a species in solution nor saturation of the surface by an intermediate but by a chemical process such as that outlined above.

Electrochemical data for the ethylaluminium and ethylmagnesium compounds at a lead electrode in tetrahydrofuran are summarised in Table 1.

Diethylmagnesium and ethylmagnesium bromide

Steady state *i/E* curves were run for both the ethylmagnesium compounds. The curve for diethylmagnesium shows a single oxidation process, $E_{\frac{1}{2}} = -1.72$ V, followed by a plateau which extends to the potential where dissolution of the lead electrode occurs; logarithmic analysis of the rising portion of the *i/E* curve gives a Tafel slope of $(60 \text{ mV})^{-1}$. The *i/E* curve for the Grignard reagent shows an oxidation wave with $E_{\frac{1}{2}} = -1.73$ V but in this case the current plateau only extends to -1.2 V where further electrode activity occurs. This latter process leads to deactivation of

* r.d.s. = rate determining step.

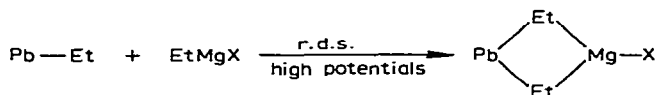
the electrode and a consequent decrease in the current; in fact the passive layer formed inhibits the anodic dissolution of the lead at more positive potentials. A logarithmic analysis of the wave at -1.73 V gives a Tafel slope of $(120 \text{ mV})^{-1}$. The limiting currents for the oxidation of both ethylmagnesium compounds are again very low and indicate that a chemical process of low rate is determining the current in these potential regions.

The interpretation of the curve for the Grignard reagent is complicated by the possible dissociation of the Grignard reagent in the Schlenck equilibrium:

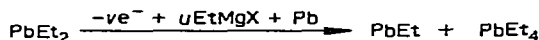
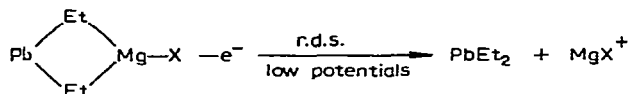


and three oxidation waves might have been expected. It is clear, however, that the waves at -1.72 V and -1.73 V for the two ethylmagnesium compounds cannot be due to the same species because of the markedly different Tafel slopes. Furthermore similar oxidation potentials would be expected for the two species since infrared studies in tetrahydrofuran have shown the carbon-magnesium bonds to be of similar strength³⁵. The results in this study would indicate that the Schlenck equilibrium lies to the left under the experimental conditions.

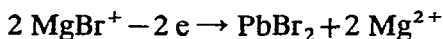
The formation of a lead-carbon bond during the electrode process may be inferred from the fact that the oxidation of ethylmagnesium compounds occur much less readily on an inert electrode. Indeed, at a platinum anode the half wave potentials are over 1.5 V more positive. The chemical reactions which determine the current in the plateau region of the i/E curves are probably of the type



followed by



where $X = \text{Et}$ or Br . The difference in Tafel slope is somewhat surprising but it may be explained if the electron transfer is reversible when $X = \text{Et}$ but slow when $X = \text{Br}$. The further electrode activity in the case of the Grignard reagent which occurs at -1.2 V is due to the formation of a layer of insoluble lead bromide on the electrode surface by the reaction



as may be shown by running an i/E curve on a solution of magnesium bromide in the electrolyte/solvent mixture. This layer of lead bromide then acts as a barrier to electron transfer and inhibits the anodic corrosion of the lead electrode.

Cyclic voltammograms run between -2.3 V and 1.3 V for solutions of the ethylmagnesium compound confirm the above results. Single waves are obtained for the oxidation of both species and the waveheights are independent of the poten-

tial sweep rate. Therefore it is clear that the current in the plateau regions is controlled by the rate of a chemical process. Furthermore there are no peaks on the sweep towards cathodic potentials showing the absence of stable, reducible intermediates.

Unusual behaviour is observed when a freshly cleaned and polished lead electrode is used for the cyclic voltammetry. On the first sweep towards anodic potentials, the wave for the oxidation of ethylmagnesium bromide occurs at -1.53 V while on subsequent cycles the half wave potential shifts in a cathodic direction (see Table 2).

TABLE 2

THE OXIDATION OF GRIGNARD REAGENT IN THF/0.25 M Bu_4NClO_4

Variation of $E_{p/2}$ and i_p with the number of potential cycles from a freshly cleaned lead electrode.

Sweep	$E_{p/2}$ (volts)	i_p (mA/cm ²)
1st	-1.52	4.8
2nd	-1.63	2.2
3rd	-1.69	1.5
4th	-1.71	1.4
nth	-1.72	1.4

The peak current shows a decrease during this procedure (also see Table 2). These observations indicate that the lead surface undergoes an irreversible change during the potential cycle. This change produces a surface which is more active for the oxidation process and which therefore allows the oxidation to occur at a less anodic potential. Unfortunately there is a parallel poisoning process which leads to the decrease in limiting current and accounts for the failure of preparative scale electrolyses in these systems. The importance of the state of the electrode surface is again emphasised if the potential range for the cyclic voltammograms of ethylmagnesium bromide is extended to include the potential where the lead bromide is formed. Although this process is quasi reversible the cyclic voltammetry on subsequent sweeps shows multiple peaks for the oxidation of the Grignard reagent indicating that a further non-uniformity of the electrode surface has been caused. Changes in the activity of lead electrodes with cycling were also noted during the reduction of alkyl halides in dimethylformamide³⁴.

The oxidation potentials of the ethylmagnesium and ethylaluminium compounds further show the magnesium-carbon bond to be much weaker than corresponding aluminium-carbon bonds. Indeed triethylaluminium does not oxidise within the potential range accessible on a lead electrode.

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