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Review

ELECTROCHEMICAL SYNTHESIS OF ORGANOMETALLIC COMPOUNDS

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Contents

I. Introduction

The chemistry of organometallic compounds has been developing rap-

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* With the participation of I.N. Chernykh and A.P. Tomilov.

idly since the end of the 19th century and at present is an important part of organic synthesis.

Organic compounds of lithium, sodium, zinc, cadmium, mercury, titanium, arsenic, antimony, selenium, manganese, iron, phosphorus, magnesium are produced on an industrial scale. They are used as catalysts in stereospecific polymerization of olefins, as stabilizers of polymeric materials and lubricants, antiknock compounds and additives to motor and jet fuels, antiseptics, biocides and pigments [1].

Some cases are known where organometallic compounds are formed electrochemically as the result of anodic and cathodic processes. Although this interesting method of preparation of organometallic compounds began to attract the attention of scientists only fairly recently, certain advances have already been made in this field. A considerable body of experimental data has been collected, testifying to the large potential of the electrochemical method. An electrochemical synthesis of tetraethyllead has been carried out industrially [2].

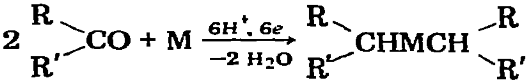
The aim of this review is to try to outline the range of applicability of electrochemical methods in the synthesis of hetero-organic compounds and to consider the possible mechanisms of the processes leading to formation of the carbon—element bond.

II. Cathodic processes

Organometallic compounds are formed at the cathode during electrolysis of carbonyl, unsaturated and halogen-containing compounds.

A. Electrolysis of carbonyl compounds

Electrolysis of acidic/aqueous solutions of ketones in some cases yields organometallic compounds. This reaction can be represented by equation 1.



$$2\,\begin{matrix}R\\R'\end{matrix}\!\!>\!CO + M \xrightarrow[-2\,H_2O]{6H^+,\,6e} \begin{matrix}R\\R'\end{matrix}\!\!>\!CHMCH\!<\!\!\begin{matrix}R\\R'\end{matrix} \qquad (1)$$

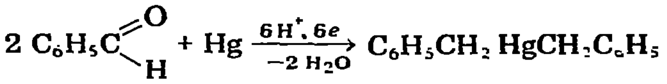
A reaction of this type was first carried out by Tafel and Schmitz in 1902 [3] and later was studied in detail [4-10]. On the basis of available evidence, it is mainly aliphatic and alicyclic ketones which form organometallic compounds by this procedure.

Among metals, mercury and lead react most readily. There also is some evidence that organometallic compounds are formed during electrolysis of ketones at cadmium [11] and germanium [12] cathodes. Extensive disintegration of a zinc cathode used during acetone reduction is also attributed to formation of an unstable organozinc compound [13].

Organometallic compounds are mostly obtained by electrolysis of unsymmetrical ketones in sulfuric acid solution. There is some evidence that increase of the solution temperature [4, 5, 8] and acid concentration [5, 8] favor formation of organometallic compounds, their yield passing through a maximum with increasing current density [14].

There is much less information available on the formation of organometallic compounds during electroreduction of aldehydes. An unidentified organolead compound was obtained during electrolysis of citral [15]. The reduction of propionic and butyric aldehydes at a tin cathode yielded substances containing carbon, hydrogen and tin, but their structure was not determined [16].

The only organometallic compound formed during electrolysis of aldehydes which has been identified as dibenzylmercury obtained from benzaldehyde [17].



$$2\,C_6H_5C{\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}}} + Hg \xrightarrow[-2\,H_2O]{6H^+,\,6e} C_6H_5CH_2HgCH_2C_6H_5 \qquad (2)$$

The attempts to carry out a similar reaction with vanillin, anisaldehyde, salicyclic and propionic aldehydes, piperonal, furfural, *p*-oxybenzaldehyde at lead, cadmium and mercury cathodes failed [17, 18].

The known examples of formation of organometallic compounds during electrolysis of carbonyl compounds are listed in Table 1.

B. Reduction of unsaturated compounds

During electrolysis of unsaturated compounds a carbon—metal bond is formed at the site where the double bond breaks, one of the carbon atoms undergoing protonation.

$$2\,RCH{=}CH_2 + M \xrightarrow{2\,H^+,\,2e} RCH_2CH_2MCH_2CH_2R \qquad (3)$$

This type of reaction was studied in greatest detail for the case of electroreduction of unsaturated nitriles [20-24] at a tin cathode. The electroreduction of acrylonitrile at a graphite cathode in the presence of finely-dispersed sulfur, selenium and tellurium yielded organic compounds of these elements [22-23]. A low current density and elevated temperature favor their formation. The coelectrolysis of white phosphorus and styrene at a lead cathode gave organophosphorus compounds [25].

The formation of organometallic compounds was observed also during reduction of methyl vinyl ketone at a mercury cathode [26]. Dimethylvinylcarbinol seems to follow the same reaction scheme [27]. The data on the formation of organometallic compounds from unsaturated substances are listed in Table 2.

C. Electrolysis of halogen-containing compounds

The electrolysis of halogen-containing compounds yielded symmetrical organometallic compounds (eqn. 4). This reaction was used first for preparation of tetraethyllead by electroreduction of ethyl iodide at a lead cathode in alkaline alcohol [28] or water solution [29]. Later the formation of organolead compounds during electrolysis of alkyl halides was found to depend strongly on the electrolyte solvent system [30]. Thus the current efficiency in tetraethyllead preparation can be raised to 98-100 % by substituting ethyl bromide for ethyl iodide and using as electrolytes solutions of onium salts

$$2\,RX + M \xrightarrow{2e} RMR + 2\,X^- \qquad (4)$$

(Continued on p. 6)

TABLE 1

ORGANOMETALLIC COMPOUNDS SYNTHESIZED BY ELECTROLYSIS OF CARBONYL COMPOUNDS

Cathode material	Electrolyte (solvent)	Starting substance	I (A/cm^2)	T (°C)	Compound obtained	Yield (%)	References
Mercury	40% H_2SO_4	Acetone	0.6		Diisopropylmercury		5
Mercury	H_2SO_4	Methyl ethyl ketone			Di-sec-butyl-mercury		4
Mercury	H_2SO_4	Menthone		80	Dimenthylmercury		9, 19
Mercury	HCl + CH_3COOH	Phenylacetone	0.135	18	Bis(phenylisopropyl)-mercury	25-30	8
Mercury	5% H_2SO_4	Cyclohexanone	0.328	15-66	Dicyclohexylmercury	25-30	8
Mercury	3% H_2SO_4	2-Methylcyclo-hexanone	0.197	55	Bis(methylcyclo-hexyl)mercury	25-30	8
Mercury	3% H_2SO_4	3-Methylcyclo-hexanone	0.197	55	Bis(3-methylcyclo-phexyl)mercury	25-30	8
Mercury	3% H_2SO_4	4-Methylcyclo-hexanone	0.197	55	Bis(4-methylcyclo-hexyl)mercury	25-30	8
Mercury	HCl + CH_3COOH	Cyclopentanone	0.197	20	Dicyclopentylmercury	25-30	8
Mercury	50% H_2SO_4	Benzaldehyde	0.197	25	Dibenzylmercury	6.5	17
Mercury	45% H_2SO_4	1-Acetylnaphthalene			Bis(1-naphthylethyl)-mercury	26	10
Lead	20% H_2SO_4	Acetone	0.05	20	Tetraisopropyllead		6
Lead	20% H_2SO_4	Methyl ethyl ketone	0.05	20	Tetra-sec-butyllead		7
Lead	20% H_2SO_4	Diethyl ketone	0.05	20	Tetra-sec-3-amyllead		7
Lead	20% H_2SO_4	Methyl isoamyl ketone			not identified		19
Lead	20% H_2SO_4	Citral			not identified		15
Cadmium	20% H_2SO_4	Acetone			not identified		11
Germanium	H_2SO_4	Acetone			not identified		12
Tin	3 *N* K_2HPO_4	Propionaldehyde			not identified		16
Tin	3 *N* K_2HPO_4	Butyraldehyde			not identified		16

TABLE 2

ORGANOMETALLIC COMPOUNDS SYNTHESIZED BY ELECTROLYSIS OF UNSATURATED COMPOUNDS

Cathode material	Electrolyte (solvent)	Starting substance	*I* (A/cm^2)	*T* (°C)	Compound obtained	Yield (%)	References
Graphite	1*N* Na_2SO_4	Acrylonitrile, selenium	0.016	45	Bis(β-cyanoethyl)selenide	23	21
Graphite	1*N* Na_2SO_4	Acrylonitrile, tellurium	0.016	50	Bis(β-cyanoethyl)telluride	3.4	21
Graphite	1*N* Na_2SO_4 (ethanol)	Acrylonitrile, sulfur	0.016	50	Bis(β-cyanoethyl)sulfide	15.1	20
Lead	CH_3COOK-CH_3COOH	Styrene, phosphorus	0.10	26	2-Phenylethylphosphine	18.6	25
					Tris(2-phenylethyl)-phosphine		
					Bis(2-phenylethyl)-phosphine		
					Tetrabis(2-phenylethyl)-diphosphine		
Tin	0.7*N* NaOH	Acrylonitrile	0.02	15	Tetrakis(β-cyanoethyl)tin	60	22
Tin	0.7*N* NaOH	Metacrylonitrile	0.02	15	Tetrakis(β-cyanopropyl)tin		23
Tin	0.7*N* NaOH	1-Cyano-1,3-butadiene	0.005	30	not identified		23
Tin	0.5*N* K_2HPO_4	Acrylonitrile	0.03	20	Hexakis(β-cyanoethyl)ditin	24	24
Mercury		Methyl vinyl ketone			$Hg(CH_2CH_2COCH_3)_2$		26
Mercury	10% NaOH	Dimethylvinyl-carbinol	0.0125	25	not identified		27

in propylene carbonate and acetonitrile [31-33]. In dimethylformamide the reaction occurs in good yield in the presence of sodium salts [34].

Galli [33] studied in detail the processes occurring during reduction of ethyl bromide at a lead cathode in propylene carbonate solution in the presence of tetraethylammonium bromide. Formation of tetraethyllead starts when cathodic polarization exceeds 500 mV, and when it approaches 1400 mV the current efficiency of the organolead product reaches 100 %, the current density being 0.001 A/cm^2.

The best current efficiency in tetramethyllead preparation (92%) was obtained during electrolysis of methyl bromide in a mixed solvent containing aprotic (acetonitrile) and hydroxyl (water, alcohol) components [35].

Organomercury compounds were obtained during electrochemical reduction of allyl bromide [36], benzyl iodide [37], benzyl bromide and substituted benzyl bromides [38], and 1-iodo-1-methyl-2,2-diphenylcyclopropane [39]. The electrolysis of pentafluoroiodobenzene at a mercury cathode yielded bis(pentafluorophenyl)mercury [40]. From the reduction products of *o*-bromoiodobenzene and *o*-diiodobenzene, *o*-phenylenemercury was obtained [41].

β-Iodopropionitrile proved to be very reactive. It was found [42] that electroreduction of this compound yields cyanoethyl derivatives of tin, mercury, lead and thallium. It is interesting to note that tetrakis(β-cyanoethyl)tin was the main organometallic product obtained at a tin cathode during electrolysis of β-iodopropionitrile, whereas the electrolysis of β-chloropropionitrile under the same conditions yielded hexakis(β-cyanoethyl)ditin. By electroreduction of alkyl halides in the presence of phosphorus at a graphite electrode, some organophosphorus compounds were prepared: primary, secondary and tertiary phosphines [44, 43] and phosphonium salts [44].

The organometallic compounds separated and identified during electrolysis of halogen-containing compounds are listed in Table 3.

D. Some other cases of formation of organometallic compounds during cathodic processes

Formation of organometallic compounds was observed during electrolysis of onium salts. Thus, in the presence of tetraethylammonium chloride, lead and tin cathodes undergo disintegration and the reaction products contain organometallic polymers of general formula [45]: $[(C_2H_5)Sn]_x$ and $[(C_2H_5)Pb]_y$.

Electrolytic reduction of diphenyliodonium hydroxide and its 4,4′-dimethyl and 4,4′-dimethoxy derivatives at a mercury cathode at a controlled potential of —1.6 V vs. SCE* yielded diphenylmercury, bis(*p*-tolyl)mercury and bis(4-methoxyphenyl)mercury according to reaction 5 [46].

$$2\ Ph_2I^+ + Hg \xrightarrow{2e} Ph_2Hg + 2\ PhI \qquad (5)$$

When speaking of cathodic processes, one should mention also a somewhat peculiar mode of formation of organometallic compounds consisting of electrolytic reduction of an organic substance to an anion, followed by further interaction of the latter with the metal cation present in electrolyte, rather than with the elemental metal of the cathode [47, 48].

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* SCE = standard calomel electrode.

TABLE 3

ORGANOMETALLIC COMPOUNDS SYNTHESIZED DURING ELECTROLYSIS OF HALOGEN-CONTAING COMPOUNDS

Cathode material	Electrolyte (solvent)	Starting substance	i (A/cm^2)	T (°C)	Synthesized compound	Yield (%)	References
Lead	10% NaOH	Ethyl iodide	0.01	50	Tetraethyllead		29
Lead	10% NaOH 2% $(CH_3COO)_2Pb$ ethanol	Ethyl iodide	0.01	50	Tetraethyllead		28
Lead	$(CH_3)_4NBr$	Ethyl bromide			Tetraethyllead	72	32, 51
Lead	$(C_2H_5)_4NClO_4$	Ethyl bromide	0.012		Tetraethyllead	100	33
Lead	$(C_2H_5)_4NBr$ acetonitrile 0.65% H_2O	Methyl bromide	0.06	45	Tetramethyllead	92	35
Lead	0.5N H_2SO_4	β-Iodopropionitrile	0.035	15	Tetrakis(β-cyanoethyl)lead	13	41
Lead	Acetonitrile	$(C_2H_5)_4NCl$	0.5	25	Polymeric $[(C_2H_5)_2Pb]_x$		42
Tin	Acetonitrile	$(C_2H_5)_4NCl$	0.5	25	Polymeric $[(C_2H_5)_2Sn]_x$		44
Tin	0.5N H_2SO_4	β-Chloropropionitrile	0.035	15	Hexakis(β-cyanoethyl)ditin	12	41
Thallium	0.5N H_2SO_4	β-Iodopropionitrile	0.035	10	Bis(β-cyanoethyl)thallium iodide		41
Mercury	1N LiBr methanol	Benzyl bromide		25	Dibenzylmercury	41	38
Mercury	1N LiBr + methanol	p-t-Butylbenzyl bromide		25	Bis(p-t-butylbenzyl)mercury	50	38
Mercury	1N LiBr + methanol	p-Methylbenzyl bromide		25	Bis(p-methylbenzyl)mercury	64	38
Mercury	1N LiBr + methanol	3,4-Dichlorobenzyl bromide			Bis(3,4-dichlorobenzyl)mercury	27	38
Mercury	0.5$N$$(C_2H_5)_4NBr$ + acetonitrile	1-Iodo-1-methyl-2,2-diphenylcyclopropane			Bis(1-methyl-2,2-diphenylcyclopropyl)mercury		39

Thus, 1,1-diphenylethylene in hexamethylphosphorotriamide containing lithium bromide at a platinum electrode yielded 1,1,4,4-tetraphenylbutanedilithium; tetraphenylethylene gave tetraphenylethanedilithium, and triphenylchloromethane gave triphenylmethyllithium. Sodium and calcium derivatives also were obtained.

$$(C_6H_5)_2C{=}CH_2 \xrightarrow{2Li,\ 2e} [(C_6H_5)_2\bar{C}CH_2CH_2\bar{C}(C_6H_5)_2]_2\ (Li^+)_2 \qquad (6)$$

$$(C_6H_5)_2C{=}C(C_6H_5)_2 \xrightarrow{2Li,\ 2e} [(C_6H_5)_2\bar{C}{-}\bar{C}(C_6H_5)]_2\ (Li^+)_2 \qquad (7)$$

$$(C_6H_5)_3CCl \xrightarrow{2Li, 2e} (C_6H_5)_3\bar{C}Li^+ + LiCl \qquad (8)$$

A novel synthesis of transition-metal complexes has been carried out by electrochemical reduction of a mixture of a readily obtainable transition metal compound and cyclooctatetraene (COT) [49]. Depending on the affinity

$$MX_n + COT \xrightarrow[-nX^-]{ne} M(COT) \qquad (9)$$

for electron, the criterion of which is the polarographic half-wave potential, two reaction mechanisms are possible: first step, reduction of metal-containing substance, followed by addition of ligand (as, for example, in electrolysis of zirconium tetrachloride and cyclooctatetraene) or first step, reduction of cyclooctatetraene to the anion, followed by interaction with the metal compound, such as, e.g., diacetylacetonate of iron. This method was used for synthesis of dicyclooctatetraenetitanium (45%) yield, dicyclooctatetraeneiron (35%), cyclooctatetraenenickel (85%) and corresponding compounds of cobalt and zirconium, the electrochemical method giving much better results just for these two last-mentioned complexes.

Electrolysis of acetylacetonates of cobalt and nickel, in the presence of 1,5-cyclooctadiene yielded π-cyclooctenyl-1,5-cyclooctadienecobalt [50] and di-1,5-cyclooctadienenickel [51]. If a cell without a diaphragm and with an electrochemically soluble anode is used, it is possible to obtain also such complexes from the anode metal. For instance, electrolysis of cyclooctatetraene with a nickel anode yielded cyclooctatetranenenickel.

Of the same reaction type also is the formation of complex manganese compounds during electrolysis of cyclopentadiene or its derivatives with manganese salts, or in their absence, with the use of soluble manganese anodes [52-54]. Table 4 lists the manganese complexes synthesized by this method.

E. On the mechanism of formation of the carbon—metal bond during cathodic processes

The occurrence of cathodic dissolution of metals seems to be paradoxical. Tafel, the first to observe the dissolution of cathodically polarized mercury during electrolysis of acetone and to obtain an organomercury product, called this phenomenon a "strange formation of alkylmercury" [4]. Some other processes are known which involve a decrease in the weight of the cathode, such as the electrolysis of aqueous solutions of alkali metal salts. In this case, the dissolution of the cathode material is explained by the interaction of metal with hydrogen at the moment of its evolution to form hydrides [55-58] or visible metal dispersion occurs due to the action of hydrogen and also as the result of a chemical decomposition by water of the electrochemically formed

TABLE 4

SYNTHESIS OF MANGANESE COMPLEXES (ANODE MANGANESE)

Cathode material	Starting substances	Solvent	*i* (A/cm^2)	*T* (°C)	Synthesized compound	Yield (%)	References
Manganese	Methylcyclopentadiene + $MnBr_2$	*N*-Methylpyrrolidone	0.1	165	Methylcyclopentadienylmanganese tricarbonyl.	good	52
Copper	Methylcyclopentadienyllithium + methylcyclopentadiene	Tetrahydrofuran/diethylene glycoldimethyl ether 1/4[a]	0.005-0.05	180	Methylcyclopentadienylmanganese tricarbonyl		53
Graphite	Ethylcyclopentadienylpotassium	Tetrahydrofuran[a]	0.1	100	Ethylcyclopentadienylmanganese tricarbonyl	good	53
Manganese	Indene + LiBr + $Mn(CH_3COO)_2$ + $Co_4(CO)_{12}$	Dicyclohexylamine[a]	0.1	200	Indenylmanganese tricarbonyl		52
Manganese	Phenylcyclopentadiene + MnI_2 + $Mn_2(CO)_{10}$	*N,N*-Dimethyl formamide[a]	0.1	150	Phenylcyclopentadienylmanganese tricarbonyl		52
Manganese	Fluorene + $MnCl_2$ + $Cr(CO)_6$	Hexamethylphosphorotriamide[a]	0.1	85	Fluorenylmanganese tricarbonyl	good	52
Copper	Methylcyclopentadienyl sodium + 0.8 *M* methyl-cyclopentadiene	Tetrahydrofuran/dimethyl formamide 1/4	0.005-0.05		Dicyclopentadienylmanganese	25	50
Copper	Methylcyclopentadienylsodium	Dimethyl ether of diethylene glycol	0.005-0.05		Dicyclopentadienylmanganese	good	50

[a] Experiments were carried out under pressure in carbon monoxide.

intermetallic compound of the cathode metal with the alkali metal [59, 60].

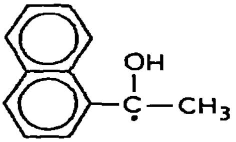
The process of cathodic formation of organometallic compounds differs from other electrochemical reactions in that it involves a chemical reaction of electrochemically generated particles with the electrode material. In this respect the process under consideration is similar to cathodic incorporation of alkali metals into electrodes [61].

Several hypotheses have been proposed to explain the formation of organometallic compounds during cathodic processes. According to one [62], the primary product of electrolysis is the anion derived from the organic reactant which draws out the metal cation from the crystal lattice of the cathode material. It also is possible that the initial step could be the formation of a hydride of the cathode element, which then reacts further with the organic compound [63]. Reutov [64], Waters [65] and Walling [66] suppose that organometallic substances are formed by interaction of radicals generated at the cathode with cathode element. Another hypothesis has been advanced, namely of the formation of an intermediate chemisorbed complex of the organic compound with metal [67]. Upon electron transfer, a covalent metal—carbon then is formed.

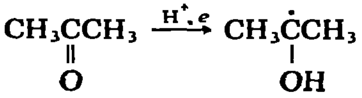
Below, on the basis of the experimental evidence available, we shall consider the applicability of the concepts of the mechanism of cathodic formation of the carbon—metal bond to the electroreduction of carbonyl, unsaturated and halogen-containing compounds.

1. On the mechanism of formation of organometallic products during the electrolysis of carbonyl compounds

In the case of formation of organomercury compounds from acetylnaphthalene [10] it is assumed that the first reaction step is the generation of the radical I which then attacks the electrode surface. The synthesis of a germanium compound with acetone is interpreted in the same way: first, the radical II is formed (eqn. 10) then it interacts with germanium. Since the electronegativity of germanium is less than that of carbon, the electrons of the outer germanium atoms can approach so closely the carbon of the radical that the bonds of the germanium atom to adjacent atoms are weakened and the new compound formed passes into solution [12]. This last-mentioned assumption agrees with Tafel's conclusions [4], who affirmed that the cathodically polarized metal participates in formation of organometallic substances as a free atom, rather than as a cation. This fact was proved experimentally. Thus, during electrolysis of methyl ethyl ketone at a mercury electrode, introduction of mercury salts into the solution did not affect the yield of di-sec-butylmercury.



(I)

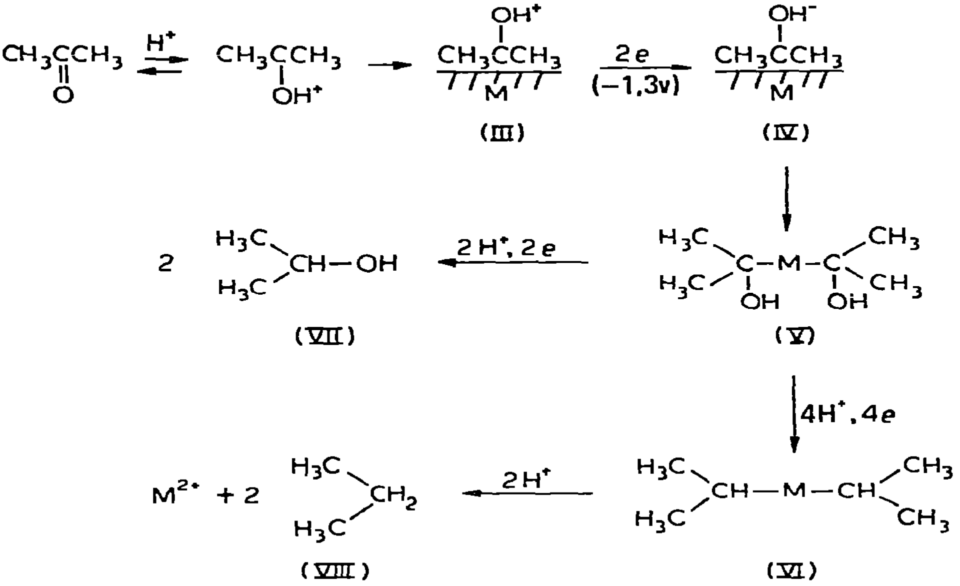


$$\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{CH_3CCH_3}}} \xrightarrow{H^+,\, e} \underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{CH_3\dot{C}CH_3}}} \qquad (10)$$

(II)

In a detailed survey [68] on the electroreduction of acetone, on the basis of an analysis of literature data, Scheme 1 is considered, which explains the formation of organometallic compounds in acid medium.

SCHEME 1



According to this scheme, the protonated form of acetone, preadsorbed on the cathode and adding two electrons, is reduced in sulfuric acid. On the basis of the experimental data, the authors consider the transfer of precisely two electrons to be the first reduction step. The acetone anion thus formed reacts with the metal to form an unstable organometallic compound V, which is either reduced to isopropyl alcohol or to a more stable organometallic compound VI. The fact that no organometallic compounds have been obtained from aromatic ketones, although intermediate free radicals have been proved to form during their electroreduction, possibly is a point in favor of the ionic mechanism.

2. *On the mechanism of formation of the carbon—metal bond during electrolysis of unsaturated compounds*

During electrolysis of acrylonitrile, cyanoethyl derivatives of tin, sulfur, selenium and tellurium have been obtained. It has been established that α,β-unsaturated nitriles are reduced at a dropping mercury electrode in one step with addition of two electrons [69]. On this basis, it can be assumed that the acrylonitrile anion formed after addition of two electrons and one proton, reacts with the cathode metal cation (eqn. 11).

$$Sn^{4+} + 4(CH_2CH_2CN)^- \rightarrow Sn(CH_2CH_2CN)_4 \qquad (11)$$

In ref. 20 and 21 concerned with the investigation of the electrolytic reaction of acrylonitrile with sulfur, selenium and tellurium, this process is con-

TABLE 5

EFFECT OF ACRYLONITRILE ON THE ELECTROREDUCTION OF TIN, SULFUR, SELENIUM AND TELLURIUM

Substance	Current efficiency (%)		Electrolysis conditions		
	Hydride[a]	Organometallic product	Temperature (°C)	Current density (A/cm²)	pH
Tin	traces	46.2	15	0.006	6-7
Sulfur	56.0	15.1	40	0.016	6-7
Selenium	83.4	23.0	46-50	0.016	7.5-8
Tellurium	4.0	13.4	46-50	0.016	6-7

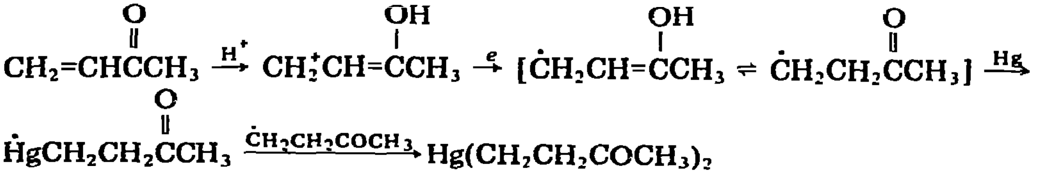
[a] Electrolyte 1*N* Na_2SO_4.[b] Electrolyte 1*N* Na_2SO_4 + acrylonitrile.

sidered to proceed by the hydride mechanism; sulfur is electrochemically reduced to hydrogen sulfide at a graphite electrode in neutral and alkaline media with the current efficiency 55-57% [20]. Hydrogen selenide has been obtained with a current efficiency of 93-97% [20]. Tellurium is also reduced to hydrogen telluride [70].

It is known that in alkaline solutions acrylonitrile interacts readily with hydrogen sulfide to form bis(β-cyanoethyl) sulfide [71]. Table 5 lists the results of the electroreduction of tin, sulfur, selenium and tellurium in the presence, or absence, of acrylonitrile [63]. It is clear from these data that in the case of sulfur and selenium, the formation of the cyanoethyl derivative can proceed via a hydride stage, whereas for tin and tellurium, where under the same conditions, the current consumption in hydride formation is much less than for formation of a cyanoethyl product, this mechanism is unlikely. This conclusion is supported by the fact that tin hydride can be obtained in appreciable amounts at a current density greater than 100 A/dm² [56], while the maximum yield of tetrakis(β-cyanoethyl)tin is obtained at a current density of 1-2 A/dm² [23].

The observations made during simultaneous electroreduction of phosphorus and styrene [25] show that organophosphorus compounds are not the product of interaction of initially formed phosphine with styrene since for phosphine and organophosphorus products of electrolysis the dependence of the current efficiency on temperature is of an opposite kind.

The formation of an organomercury substance during electroreduction of methyl vinyl ketone in acid medium is accounted for by the reaction with mercury of the radical obtained by addition of one electron to the protonated form of ketone [26] (eqn. 12).



$$CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{H^+} CH_2^+CH{=}\overset{\overset{OH}{|}}{C}CH_3 \xrightarrow{e} [\dot{C}H_2CH{=}\overset{\overset{OH}{|}}{C}CH_3 \rightleftharpoons \dot{C}H_2CH_2\overset{\overset{O}{\|}}{C}CH_3] \xrightarrow{Hg}$$

$$\dot{H}gCH_2CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{\dot{C}H_2CH_2COCH_3} Hg(CH_2CH_2COCH_3)_2 \qquad (12)$$

3. On the mechanism of formation of the carbon—metal bond during electrolysis of halogen-containing compounds

Reduction of alkyl halides with a mobile halogen atom, such as benzyl iodide and allyl bromide, to hydrocarbons at a mercury cathode involves formation of an intermediate organomercury compound. It has been established by polarographic investigations [72, 73] that benzyl iodide interacts chemically with mercury. The benzylmercury iodide thus obtained is further reduced to the radical $C_6H_5CH_2Hg$, which dimerizes with separation of mercury to dibenzylmercury, or is reduced in aqueous solution to the hydrocarbon. The same mechanism is suggested for formation of diallylmercury from allyl bromide.

In ref. 38 the formation of bis(1-methyl-2,2-diphenylcyclopropyl)mercury is interpreted in terms of the radical mechanism. The electroreduction process of 1-bromo-1-methyl-2,2-diphenylcyclopropane in acetonitrile occurs according to eqns. 13-16.

$$R{-}Br + e \rightarrow [R^{\cdot}{-}Br^{-}] \qquad (13)$$

$$[R^{\cdot}{-}Br^{-}] \rightarrow R^{\cdot} + Br^{-} \qquad (14)$$

$$R^{\cdot} + Hg_n^0 \rightarrow R{-}Hg_n^{\cdot} \qquad (15)$$

$$2\,R{-}Hg_n^{\cdot} \rightarrow R{-}Hg{-}R + Hg_{n-1}^0 \qquad (16)$$

In the first reaction step the electron is transferred to the σ-anti-bonding orbital of the C—Br bond to form the anion radical (eqn. 13), which on the mercury surface can dissociate to the radical $R^{\cdot}$ (eqn. 14). The radicals are adsorbed on the mercury surface (eqn. 15) and dimerized to the dialkylmercurial (eqn. 16). The competing reaction is a further reduction of the radicals to the hydrocarbon. However, this mechanism does not agree with the experimental data. Investigation of the time dependence of the current and initial substance concentration has shown that the current drop is not proportional to the consumption of the halogen compound in solution, whose concentration decreases much faster. Thus, in this case the reaction mechanism is more complicated than shown in eqn. 13-16.

The authors of ref. 39 during their investigations of the electroreduction of pentafluoroiodobenzene in dimethyl formamide, obtained bis(pentafluorophenyl)mercury quantitatively at a mercury cathode and at a copper cathode decafluorodiphenyl was produced. These data show conclusively that at the potential of the first polarographic wave at which electrolysis was carried out, a one-electron reduction takes place with formation of the anion-radical, which dissociates to radical and a halogen anion. Further, depending on the nature of the cathode metal, the radicals interact with the metal (mercury) or are dimerized (copper). The supposed primary formation of the anion-radical in aprotic medium is admissible, if we take into account the strong electron-attracting effect of the five fluorine atoms.

$$C_6F_5I + e \rightarrow [C_6F_5I^{\cdot-}] \qquad (17)$$

$$[C_6F_5I^{\cdot-}] \rightarrow C_6F_5^{\cdot} + I^{-} \qquad (18)$$

$$2\,C_6F_5^{\cdot} + Hg \rightarrow C_6F_5HgC_6F_5 \qquad (19)$$

The radical mechanism of formation of bis(pentafluorophenyl)mercury can be considered as proved.

The formation of bis(β-cyanoethyl)mercury is explained in a different manner [63, 69]. At a dropping mercury electrode β-iodopropionitrile is reduced in two one-electron steps. Investigation of the polarographic behavior of β-iodopropionitrile and β-cyanoethylmercuric iodide has shown that the latter compound is not an intermediate reaction product as might have been assumed by analogy with the benzyl iodide reaction. The phenomena observed during electroreduction of iodopropionitrile can be explained by assuming that an adsorption complex $\mathrm{I}\underset{\mathrm{Hg}}{\overline{\cdot\;\;\;\;\cdot}}\mathrm{CH_2CH_2CN}$ is formed on the electrode surface, but the nature of the bonding in this species has not been determined. The adsorption complex adds an electron, a covalent C—Hg bond being formed and iodine passing into the ionic state (eqn. 20).

$$\mathrm{I}\underset{\mathrm{Hg}}{\overline{\cdot\;\;\;\;\cdot}}\mathrm{CH_2CH_2CN} + e \rightarrow \mathrm{I}^- + \dot{\mathrm{H}}\mathrm{gCH_2CH_2CN} \qquad (20)$$

This is followed by dimerization to bis(β-cyanoethyl)mercury.

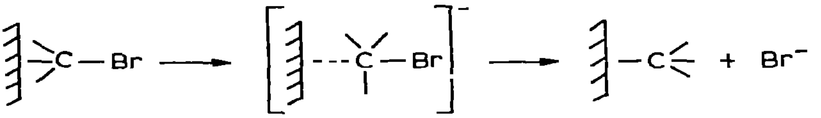
$$2\ \dot{\mathrm{H}}\mathrm{gCH_2CH_2CN} \rightarrow \mathrm{Hg(CH_2CH_2CN)_2} + \mathrm{Hg} \qquad (21)$$

Unlike the concepts described above, a conclusion is made in ref. 74 that the electron is transferred directly to the β-iodopropionitrile molecule, and the mercury-containing reduction products are formed as the result of subsequent reactions. This conclusion was based on the explanation of the complex dependence of the half-wave potential of β-iodopropiontrile on its volume concentration, proceeding from the concepts of the reduction on the electrode surface of the molecules whose adsorption is described by an *S*-shaped isotherm.

Unlike β-iodopropionitrile, alkyl halides form one two-electron polarographic wave at a mercury cathode. However, one-electron reduction is possible on other cathode materials.

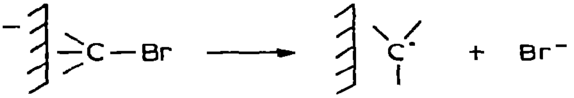
It was shown by Bagotskaya and Durmanov [75] that alkyl iodides are reduced at a dropping gallium electrode in water—alcohol medium with addition of one electron. With increasing RI concentration, the reduction becomes inhibited due to formation of a film on the electrode surface. Using the polarographic and the differential capacity curve methods, it was shown that this film does not result from adsorption of initial substances and is not a product of their chemical reaction with metal, but that it is formed by interaction of the electrochemically generated radical R with gallium, i.e. an organogallium compound. This conclusion is quite reasonable if we consider that gallium shows a greater affinity for organic radicals that does mercury.

The most comprehensive work concerned with the investigation of the formation of the carbon—metal bond during electroreduction of alkyl halides at a lead electrode was done by Ulery [76]. By polarography of alkyl halides (RX, where R = Me, Et, Pr, Bu and X = Br, I) at a stationary lead electrode in acetonitrile in the presence of $\mathrm{Et_4NBr}$, it has been found that under these conditions they are reduced via addition of one electron. Correlation of the half-wave potentials of alkyl bromides with the logarithms of the rate constants of the solvolysis reactions of the same alkyl bromides in water—alcohol medium has shown an almost linear relationship between $E_{1/2}$ and log (k_1). Hence it can be concluded that the electroduction rate of RBr and the solvolysis rate are determined by the same factors. This result corresponds to Elving's postulate about the nucleophilic substitution process, if it is assumed that the cathode acting as a nucleophilic agent, attracts the carbon atom bonded with halogen.



(22)

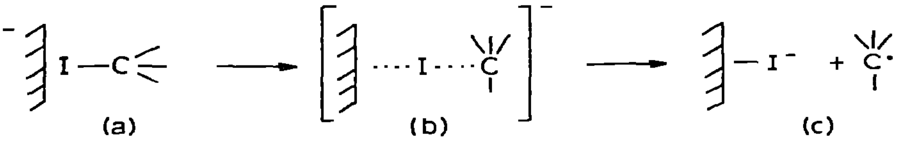
By analogy with the S_N2 reaction, the rupture of the C—Br bond to a measure is compensated by formation of a new C—M bond. However, a rupture of the bond without formation of a new bond is possible:



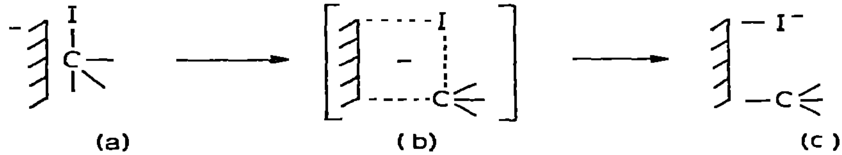
(22a)

The formation of C—M bond according to eqns. 22 and 22a should to a considerable extent depend on steric factors, the stability of R or on the presence of readily adsorbed substances. From the fact that electrosynthesis of tetramethyl- and tetraethyl-lead occurs with a high current efficiency, it is concluded that alkyl bromides are reduced on lead according to reaction 22.

On the basis of data on the electronegativity of elements, their chemisorption and the direction of polarization of the carbon—halogen bond, it is assumed that under the action of an electric field alkyl iodides become oriented with respect to the cathode in two modes, as shown in eqns. 23 and 24 i.e., iodine approaches the cathode closer than does bromine.



(23)



(24)

Molecular models show that the state 24a should be valid for CH_3I and C_2H_5I; with increasing carbon chain length, the orientation into position 23a begins to prevail.

High tetraalkyllead yields suggest that the alkyl group obtained as the result of the reduction is either incapable of diffusion into solution, or alkylation occurs at a greater rate than diffusion. In accordance with the foregoing, a mechanism of electrochemical synthesis of tetraalkyllead in electrolysis of alkyl halides is proposed (eqn. 25, $(Pb)_xPb$ is an alkylated surface element).

$$(Pb)_xPb \xrightarrow[-X^-]{RX,e} (Pb)_xPbR \xrightarrow[-X^-]{RX,e} (Pb)_xPbR_2 \xrightarrow[-X^-]{RX,e} (Pb)_xPbR_3 \xrightarrow[-X^-]{RX,e} \rightarrow (Pb)_x + PbR_4 \qquad (25)$$

The authors of ref. 34 investigated the reduction of alkyl halides at a lead electrode in dimethylformamide containing sodium salts by means of pulse polarography and by analysis of the current-time curves. In their opinion, the observed dependence of the limiting current on the alkyl halide concentration and the electrode potential, as well as the change of the current with time, can be explained only by a catalytic reaction in which the catalyst is present as a thin layer and the equilibrium with this layer is reached slowly. A surface substance, whose formation has been proved to be independent of potential, is supposed to be this catalyst.

It can be concluded from the foregoing that the reduction of alkyl halides at lead is a very complex process, whose mechanism and kinetics depend on the nature of solvent and electrolyte. This influence can be probably accounted for by the competing adsorption of solvent molecules and electrolyte ions.

In some cases, the process of organometallic compound formation at the cathode is accompanied by a preceding chemical reaction of organic substance with the cathode material. In this case, a monomolecular film of an organometallic halide is formed at the cathode surface, which sometimes can undergo electrochemical transformations to form a fully alkylated organometallic compound.

Thus, in the reduction of allyl iodide [77], benzyl iodide [37, 38] and benzyl bromide [38], intermediate formation of organomercuric halides appear to play an important role. The electrochemical behavior of some ethyl esters of α-iodine and α-bromine substituted aliphatic acids was investigated recently [79]. A kinetic wave was found, whose height, in the author's opinion [79], is limited by the rate of the preceding chemical reaction (eqn. 26).

$$\mathrm{RX + Hg \rightarrow RHgX} \tag{26}$$

The mercuric derivative formed is reduced at a high rate, which causes a kinetic wave to appear.

Investigating the electrochemical reduction of benzyl iodide and benzylmercuric iodide, Hush and Oldham [37] found that at sufficiently low concentrations both compounds are reduced with formation of two diffusion waves. The half-wave potentials both of the first and the second waves coincide. It was believed that the reduction of benzyl iodide is preceded by reaction 27, occurring only at "negatively polarized mercury", the reaction being catalyzed by the electrolysis products. For instance, the electrochemical step 27a is followed by the steps 27b-27d.

$$\mathrm{RX} + e \rightarrow \dot{\mathrm{R}} + \mathrm{X}^- \tag{27a}$$

$$\dot{\mathrm{R}} + \mathrm{Hg} \rightarrow \dot{\mathrm{R}}\mathrm{Hg} \tag{27b}$$

$$\dot{\mathrm{R}}\mathrm{Hg} + \mathrm{RX} \rightarrow \mathrm{RHgX} + \dot{\mathrm{R}} \tag{27c}$$

$$\mathrm{RHgX} + e \rightarrow \dot{\mathrm{R}}\mathrm{Hg} + \mathrm{X}^- \tag{27d}$$

The chronopotentiometric study of the electrochemical reduction at mercury of ethyl esters of bromoacetic (EBAA) and α-bromobutyric (EBBA) acids has shown [79] organomercury compounds to be formed as intermediate products. In particular, it has been found that during electrode polarization with high density direct current, an electrochemical process is observed to occur, which is associated with the reduction of some intermediate product of EBAA or EBBA reduction which accumulated on the electrode surface at the potentials of a rising polarization curve. The above authors have proved by special experiments that most likely it is the product of the one-electron reduction of symmetrical organomercury compounds which accumulates. Assuming the rate of the chemical reaction 26 to be small, they arrive at the following mechanism of formation of organomercury compounds:

$$\mathrm{RBr} + \dot{\mathrm{R}} + e \xrightarrow{\mathrm{Hg}} \mathrm{R_2Hg} + \mathrm{Br}^-$$

$$\mathrm{RBr} + \mathrm{RHg} + e \rightarrow \mathrm{R_2Hg} + \mathrm{Br}^-$$

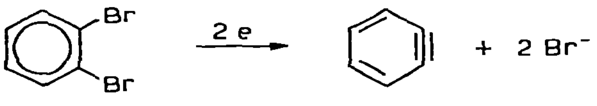
$$\mathrm{RHgBr} + \mathrm{RHg} + e \xrightarrow{-\mathrm{Hg}} \mathrm{R_2Hg} + \mathrm{Br}^-$$

Further transformation of organomercury compounds of type R_2Hg were studied in ref. 80, whose authors, having examined a number of compounds with R = C_2H_5, $C_6H_5C{\equiv}C$ and CH_2COOCH_3, came to the conclusion that compounds of the R_2Hg type accumulate at the electrode and are stable only at the potentials at which the corresponding radicals $\mathrm{RH\dot{g}}$ are electrochemically inactive. This means that there is always equilibrium at the electrode surface:

$$\mathrm{Hg} + \mathrm{R_2Hg} \rightleftharpoons 2\ \mathrm{RH\dot{g}}$$

The electrochemical transformation of pentafluorophenylmercuric bromide at a mercury electrode was observed by Ershler et al. [79]. By means of polarographic and chronopotentiometric methods, the authors found that C_6F_5HgBr gives two polarographic waves, one of which corresponds to formation of bis(pentafluorophenyl)mercury and the other to its further reduction products, $(C_6F_5)_2$ and Hg.

As regards the reaction mechanism, the preparation of *o*-phenylenemercury constitutes a special case [41]. During electrolysis at a mercury cathode 1,2-dibromobenzene undergoes dehalogenation to form dehydrobenzene (eqn. 28) which interacts chemically with mercury. During this process the primary electrochemical and the secondary chemical reactions become separated.



(28)

III. Anodic processes

So far only one type of anodic process leading to formation of organometallic compounds has been studied in sufficient detail, viz., the electrolysis of solutions, or melts of organic complex electrolytes.

Organometallic compounds of type RMR, or their solutions in polar solvents, possess an insignificant electrical conductivity [81,82] and therefore can not be subjected to electrolysis. However, mixtures of such compounds with salts of type MX, alkyl halides, RX, metal hydrides and, finally, with other organometallic compounds, sometimes give conducting solutions. This phenomenon is explained by formation of dissociating complexes.

This phenomenon was observed first by Hein [83] in 1924, who found that a mixture of diethylzinc with ethylsodium forms a solution whose electrical conductivity is as high as that of a 0.1 *N* potassium chloride solution. He explained this appearance of electrical conductivity by formation of the dissociating complex (eqn. 29).

$$NaZn(C_2H_5)_3 \rightleftarrows Na^+ + Zn(C_2H_5)_3^- \qquad (29)$$

At present a large number of complexes of similar composition have been studied, of greatest practical interest among them being those of magnesium, aluminum and boron.

Table 6 lists the data on the electrical conductivity of some of the better studied complexes.

To explain the abnormally high electrical conductivity of triethylaluminium derived melts it is assumed that owing to their high dipole moment, the molecules of the complex under the action of electric field form molecular chains directed along the lines of force, through which the charge transfer occurs [87].

The plot of the electrical conductivity of the melt versus the inverse temperature shows a distinct inflection, which is explained by the association of monomeric molecules existing at high temperature into the dimeric form (eqn. 30).

$$[(AlR_3)_2NaF]_2 \rightleftarrows 2\,(AlR_3)_2NaF \qquad (30)$$

A. Electrolysis of organomagnesium complexes (Grignard reagents)

When studying the electrolysis of solutions of Grignard reagents in ether, French and Drane [88] observed dissolution of aluminum, zinc and cadmium anodes and deposition of magnesium on the cathode. Evans [89] later suggested that dissolution of an aluminum anode in ethylmagnesium bromide yields triethylaluminum (eqn. 31).

$$6C_2H_5MgBr + 2Al \rightarrow 3Mg + 3MgBr_2 + 2Al(C_2H_5)_3 \qquad (31)$$

Only fairly recently has this reaction attracted attention as a method of preparation of organometallic compounds.

TABLE 6

ELECTRICAL CONDUCTIVITY OF SOME COMPLEXES USED FOR SYNTHESIS OF ORGANO-ELEMENT COMPOUNDS IN ANODIC PROCESSES

Complex	Solvent	Equivalent electrical conductivity (ohm^{-1}cm^2)	References
$NaF \cdot 2Al(C_2H_5)_3$	Melt	4×10^{-2}	84
$KF \cdot 2Al(C_2H_5)_3$	Melt	7×10^{-2}	84
$NaAl(C_2H_5)_4$	Melt	3.3×10^{-2}	84
$KAl(C_2H_5)_4$	Melt	8×10^{-2}	84
$NaB(C_2H_5)_4$	Water (saturated solution)	9×10^{-3}	85
	Water (10-15% solution)	5×10^{-2}	85
C_2H_5MgBr	Ether (1 *M* solution)	3.2×10^{-2}	86
C_2H_5MgI	Ether (1 *M* solution)	7×10^{-2}	86

The electrolysis of Grignard reagents can be used successfully for synthesis of organic compounds of lead, boron, phosphorus and other elements (Table 7). Owing to the hazards involved in working with diethyl ether, in preparation of Grignard reagents for electrolysis, higher ethers, such as dibutyl ether, are used as solvents.

Primary consideration has been given to the development of an economic method of preparation of tetraethyllead. Several versions of the method have been proposed [97, 100, 109, 110]. In patents [97, 100] it is suggested that polyethers of type $C_6H_5CH_2(OCH_2CH_2)_nOC_2H_5$ be used as solvents for the Grignard reagent. The solution obtained after electrolysis is diluted with water, the top layer is separated and tetraethyllead is extracted from it with another solvent, such as diethylene glycol or tetramethyl sulfone. Tetraethyllead is separated from the solution thus obtained. It is possible [110] to use tetrahydrofuran as solvent. In this case, for separation of tetraethyl lead after electrolysis the solution is steam distilled and the distillate in the counterflow column is treated with a water jet. Tetraethyllead, which is insoluble in water, separates out. Then the aqueous tetrahydrofuran solution is distilled to recover the solvent. The flow sheet for an industrial synthesis of tetraethyl- and tetramethyl-lead via Grignard reagent electrolysis, as practised in the U.S.A., is shown in Fig. 1 [105].

B. Organoaluminum complexes

Owing to the fact the Ziegler has developed a practical method of preparation of triethylaluminum [91, 111], the interest in the use of this compound for synthesis of other alkylmetals has grown considerably.

As has been pointed out above, the melts of complexes of type $MX \cdot AlR_3$ or $MR \cdot AlR_3$ (where M is a univalent metal, X is shown is halogen or hydrogen) posses sufficient electrical conductivity. In 1956 Ziegler carried out an electrochemical synthesis of tetraethyllead using the complex $NaF \cdot 2\,Al(C_2H_5)_3$ as electrolyte [11]. During electrolysis of this complex, aluminum metal is deposited on the cathode and tetraethyllead is formed at the lead anode undergoing dissolution.

An electrolyte of this composition has been used for synthesis of alkyl derivatives of tin, zinc, antimony, indium, magnesium [113-116], silicon and germanium [117] (Table 8). It is interesting to note that an attempt to synthesize organogermanium compounds at the anode from a germanium single crystal has failed [118].

In spite of the first successful attempts to use organoaluminum complexes of the type described, their practical application has met with considerable difficulties. Thus, aluminum was formed on the cathode as a loose deposit which hardly could be separated from the electrolyte. Also, aluminum suspended in the solution partly reacted with alkylmetal. In order to eliminate this undesirable reaction, it was necessary to separate the anodic and cathodic compartments which has its own drawbacks.

If electrolysis is carried out for a sufficiently long time, the ratio of NaF and $Al(C_2H_5)_3$ approaches unity and together with aluminum, metallic sodium is deposited on the cathode. In order to precipitate aluminum as easily separable dendrites, it was suggested to use high current densities, but this did not lead to a continuous process either.

TABLE 7

ELECTROLYSIS OF GRIGNARD REAGENTS

Anode	Cathode	Electrolyte	Solvent	I (A/cm^2)	T (°C)	Compound obtained	Yield (%)	References
Aluminum	Platinum	C_2H_5MgI	Diethyl ether			$Al(C_2H_5)_3$		86
Aluminum	Aluminum	$C_6H_{13}MgBr$	Hexyl ether of diethylene-glycol		35	$Al(C_6H_{13})_3$	134.2	90
Aluminum	Aluminum	C_6H_5MgBr	Hexyl ether of diethylene glycol			Phenylaluminum		90
Boron	Platinum	RMgCl	Diethyl ether			BR_3		91
Boron	Platinum	C_6H_5MgCl	Diethyl ether			$B(C_6H_5)_3$		91
Boron	Platinum	$C_6H_{13}MgCl$	Diethyl ether			$B(C_6H_{13})_3$		91
Zinc	Zinc	$C_6H_{13}MgBr$	Hexyl ether of diethylene glycol			$(C_6H_{13})_2Zn$		90
Lead	Lead	RMgCl + RCl (R = CH_3 or C_2H_5)	Ethers of ethylene glycols RO-$(C_2H_4O)_n$R + benzene + tetrahydrofuran	0.02-0 07	35	PbR_4 (R = CH_3 or C_2H_5)	150-170	93-98
Lead	Lead	RMgCl (R = CH_3 or C_2H_5)	Tetrahydrofuran + hexamethyl-phosphortriamide	0.01	27	PbR_4 (R = CH_3 or C_2H_5)	150	99
Lead	Lead	RMgCl (R = CH_3 or C_2H_5)	Tetrahydrofuran + tetrahydrofurfuryl ether	0.02	48	PbR_4 (R = CH_3 or C_2H_5)		100
Lead	Steel	C_2H_5MgBr	Diethyl ether	0.002	25	$Pb(C_2H_5)_4$		101,102
Lead	Steel	C_2H_5MgCl + C_2H_5Cl	Diethyl ether of diethylene glycol	0.001-0.003	40-60	$Pb(C_2H_5)_4$	74-85	103,104
Lead	Steel	CH_3MgCl + C_2H_5Cl	Hexyl ether of diethylene glycol			Mixture of PbR_4, (R = CH_3, C_2H_5)		106
Lead	Steel	CH_3MgCl + t-C_4H_9MgCl	Hexyl ether of diethylene glycol			Mixture of PbR_4, (R = CH_3, t-C_4H_9)		106
Lead	Lead	CH_2=CHMgCl	Tetrahydrofuran or tetrahydropyran			$Pb(CH=CH_2)_4$		107
Lead	Lead	CH_3CH=CHMgCl	4-Methoxytetrahydrofuran			$Pb(CH=CHCH_3)_4$		107
Lead	Lead	CH_2=CHMgCl + CH_3Cl	Dibutylcarbitol + tetrahydrofuran + benzene			Mixture of PbR_4 (R = CH_3, CH=CH_2)		99
Silicon	Nickel	C_2H_5MgBr	Diethyl ether	0.15-0.25		$Si(C_2H_5)_4$	8-85	108

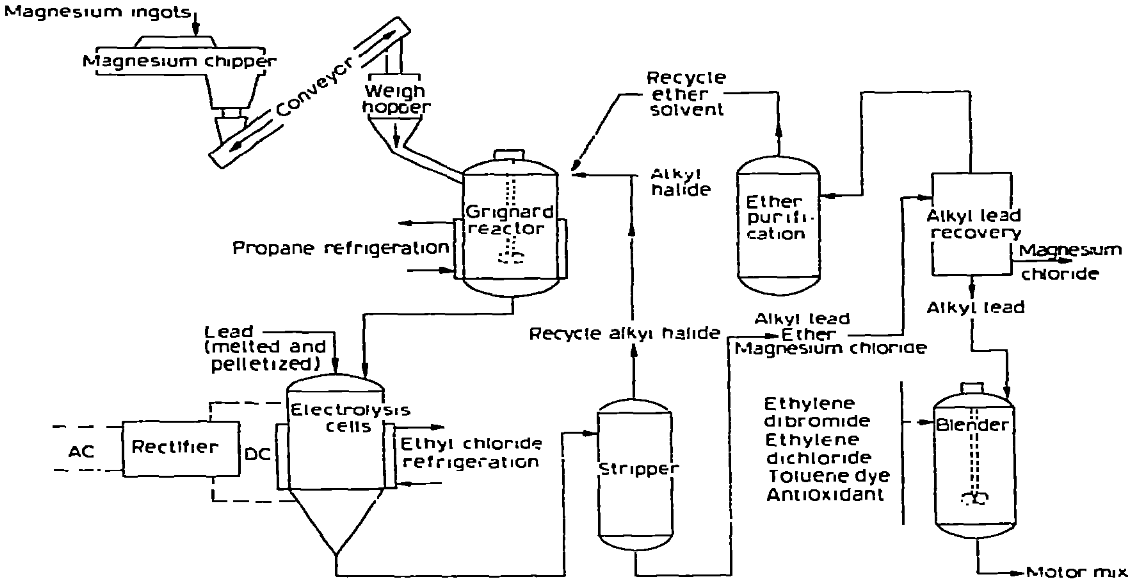


Fig. 1. Flow sheet for Nalco Chemical Co., electrolytic tetraethyl- and tetramethyl-lead process (from D. Seyferth and R.B. King (Eds.), Annual Survey of Organometallic Chemistry, Vol. 1, Elsevier, Amsterdam, 1965, p. 149).

Later, in 1959 Ziegler showed that if the complex of the type $NaAl(C_2H_5)_4$ is used as electrolyte, during its electrolysis with an aluminum anode, metallic sodium is deposited at the cathode and triethylaluminum at the anode [127].

$$3\,NaAl(C_2H_5)_4 + Al \rightarrow 4\,Al(C_2H_5)_3 + 3\,Na \qquad (32)$$

In this case the problem of electrolyte regeneration is easily solved, because if a part of the triethylaluminum formed is returned to the cycle, by its reaction with sodium, ethylene and hydrogen, it is possible to prepare the initial complex again [123].

$$3\,Na + 3\,H_2 + 3\,C_2H_4 + 3\,Al(C_2H_5)_3 \rightarrow 3\,NaAl(C_2H_5)_4 \qquad (33)$$

In addition to its easy regeneration, the complex of the type $NaAl(C_2H_5)_4$ has another advantage, viz. sodium at the cathode can be obtained as an amalgam, or in liquid form and can be readily removed from the electrolyzer.

Ziegler's investigations initiated intensive search for a continuous process of electrochemical synthesis of alkylmetals, primarily of tetraethyllead. A detailed consideration of various processes for the preparation of tetraethyllead is beyond the scope of this review, and we shall discuss only a few of them. However, in order to obtain a general idea of the investigations carried out, in Table 9 are listed the electrolytes recommended for preparation of tetraethyllead, and in Table 10 the electrolytes recommended for synthesis of other alkyl compounds of lead.

In his initial efforts [84] Ziegler proposed to carry out the electrolysis using a solid cathode under vacuum. In this case the tetraethyllead formed is distilled off, which eliminates the possibility of its contact with sodium. In

(Continued on p. 26)

TABLE 8

ORGANOMETALLIC COMPOUNDS SYNTHESIZED BY ELECTROLYSIS OF TRIALKYLALUMINUM COMPLEXES

Anode	Cathode	Electrolyte	I (A/cm^2)	T (°C)	Compound obtained	Yield (%)	References
Aluminum	Copper	$NaAl(C_2H_5)_4$	0.04	140	$Al(C_2H_5)_3$	99	119
Aluminum	Copper	$NaAl(C_3H_7)_4$	0.04	100	$Al(C_3H_7)_3$	94	119
Aluminum	Copper	$NaAl(C_4H_9)_4$	0.04		$Al(C_4H_9)_3$		119
Magnesium	Copper	$NaAl(C_2H_5)_4$	0.04	100	$Mg(C_2H_5)_2$	95	119
Magnesium	Copper	$NaF \cdot 2Al(C_2H_5)_3$			$Mg(C_2H_5)_2$		115
Magnesium	Steel	$NaAl(CH_3)_4 + NaAl(C_2H_5)_4$	0.25	100	$Mg(C_2H_5)_2$	95	120
Magnesium	Steel	$KAl(CH_3)_4 + Al(i\text{-}C_3H_7)_4 (1/8)$	0.25	100	$Mg(i\text{-}C_3H_7)_2$		120
Magnesium	Steel	$LiAl(CH_3)_4 + NaAl(C_4H_9)_4 (1/3)$	0.25	100	$Mg(C_4H_9)_2$		120
Magnesium	Steel	$RbAl(CH_3)_4 + NaAl(CH_3)_4 (1/5)$	0.25	140	$Mg(CH_3)_2$		120
Zinc	Copper	$NaAl(CH_3)_4 + NaAl(C_2H_5)_4$	0.35	105	$Zn(C_2H_5)_2$	80	121
Zinc	Copper	$NaAl(CH_3)_4 + CsAl(C_2H_5)_4 (1/2)$	0.35	80	$Zn(C_2H_5)_2$		121
Zinc	Copper	$NaF \cdot 2\ Al(C_2H_5)_3$			$Zn(C_2H_5)_2$		115
Zinc	Copper	3320 g $NaAl(C_2H_5)_4$ + 740 g KCl		100	$Zn(C_2H_5)_2$		115
Zinc	Copper	$Na[Al(C_2H_5)_3(OC_2H_5)]$	0.04	100	$Zn(C_2H_5)_2$	100	122
Zinc	Copper	$Na[Al(C_2H_5)_3(OC_4H_9)]$	0.04	100	$Zn(C_2H_5)_2$		123
Zinc	Copper	$NaF \cdot 2Al(C_3H_7)_3$			$Zn(C_3H_7)_2$		114
Zinc	Copper	$RbAl(CH_3)_4 + NaAl(CH_3)_4 (5/1)$	0.35	100	$Zn(CH_3)_2$		121
Zinc	Copper	$KAl(CH_3)_4 + KAl(C_3H_7)_4 (1/8)$	0.35	180	$Zn(C_3H_7)_2$		121
Zinc	Copper	$LiAl(CH_3)_4 + NaAl(C_{10}H_{21})_4 (3/10)$	0.35	40	$Zn(C_{10}H_{21})_2$		121
Zinc	Copper	$NaAl(CH_3)_4 + NaAl(C_6H_5)_4 (1/10)$	0.35	190	$Zn(C_6H_5)_2$		121
Zinc	Copper	$NaAl(C_4H_9) + Na[Al(C_2H_5)_3(OC_{10}H_{21})]$	0.04		$Zn(C_4H_9)_2$	82	122

Zinc	Copper	$KAl(C_3H_7)_4 + NaAl(C_3H_7)_4$	0.04		$Zn(C_3H_7)_2$	88	122, 124
Zinc	Copper	$NaAl(C_5H_{11})_4 + Na[Al(C_5H_{11})_3(OC_6H_5)]$		100	$Zn(C_5H_{11})_2$	90	123
Tin	Mercury	$NaAl(CH_3)_4 + NaAl(C_2H_5)_4$	0.25	100	$Sn(C_2H_5)_4$	80	122, 124
Tin	Mercury	$KAl(CH_3)_4 + NaAl(C_2H_5)_4$	1.0	100	$Sn(C_2H_5)_4$		125
Tin	Mercury	$NaAl(CH_3)_4 + CsAl(C_2H_5)_4$ (2/1)	0.25	120	$Sn(C_2H_5)_4$		125
Tin	Mercury	$NaAl(CH_3)_4 + KAl(C_2H_5)_4 + LiAl(C_2H_5)_4$	0.25		$Sn(C_2H_5)_4$		125
Tin	Mercury	$NaAl(C_2H_5)_3(OC_4H_9)$	0.04	100	$Sn(C_2H_5)_4$	85	123
Tin	Copper	3320 g $NaAl(C_2H_5)_4$ + 740 g KCl			$Sn(C_2H_5)_4$		110, 115
Tin	Copper	$NaF \cdot 2Al(C_2H_5)_3$			$Sn(C_2H_5)_4$		114, 115
Tin	Copper	$RbAl(CH_3)_4 + NaAl(CH_3)_4$ (5/1)	0.25	100	$Sn(CH_3)_4$		125
Tin	Copper	$KAl(CH_3)_4 + KAl(i\text{-}C_3H_7)_4$ (1/8)	0.25	160	$Sn(i\text{-}C_3H_7)_4$		125
Tin	Copper	$LiAl(CH_3)_4 + NaAl(C_8H_{17})_4$ (3/10)	0.25	40	$Sn(C_8H_{17})_4$		125
Tin	Copper	$NaAl(CH_3)_4 + NaAl(C_6H_5)_4$ (1/1)	0.25	180	$Sn(C_6H_5)_4$		125
Antimony	Copper	$NaF \cdot 2Al(C_2H_5)_3$		70-100	$Sb(C_2H_5)_3$	80-90	115
Antimony	Copper	3320 g $NaAl(C_2H_5)_4$ + 740 g KCl		100	$Sb(C_2H_5)_3$		122
Antimony	Copper	$Na[Al(C_2H_5)_3(OC_4H_9)]$	0.04	100	$Sb(C_2H_5)_3$	96	123
Antimony	Copper	$NaAl(C_3H_7)_4 + Na[Al(C_3H_7)_3(OC_6H_{11})]$		100	$Sb(C_3H_7)_3$	89	122, 124
Antimony	Mercury	$KAl(C_2H_5)_4$	0.465	110	$Sb(C_2H_5)_3$	100	126
Mercury	Mercury	$NaF \cdot 2Al(C_2H_5)_3$			$Hg(C_2H_5)_2$	100	84
Mercury	Mercury	$KAl(C_2H_5)_4$	0.35	110	$Hg(C_2H_5)_2$		126
Mercury	Copper	3320 g $NaAl(C_2H_5)_4$ + 740 g KCl		100	$Hg(C_2H_5)_2$		122
Mercury	Copper	$Na[Al(C_2H_5)_4(OC_4H_9)]$	0.04	100	$Hg(C_2H_5)_2$	82	123
Cadmium	Copper	3320 g $NaAl(C_2H_5)_4$ + 740 g KCl		100	$Cd(C_2H_5)_2$		122
Cadmium	Copper	$NaAl(C_2H_5)_4(OC_4H_9)$	0.04	100	$Cd(C_2H_5)_2$	81	123
Bismuth	Copper	3320 g Na $Al(C_2H_5)_4$ + 740 KCl			$Bi(C_2H_5)_3$		122
Bismuth	Copper	$Na[Al(C_2H_5)_4(OC_4H_9)]$	0.04	100	$Bi(C_2H_5)_3$	95	123
Indium	Copper	$NaF \cdot 2Al(C_2H_5)_3$			$In(C_2H_5)_3$		114, 115

TABLE 9

SYNTHESIS OF TETRAETHYLLEAD BY ELECTROLYSIS OF ALUMINUM COMPLEXES (ANODE LEAD)

Cathode	Electrolyte	i (A/cm^2)	T (°C)	Yield (%)	References
Platinum	$Al(C_2H_5)_3$ in diethyl ether	0.7	25	99	126
Mercury	$KAl(C_2H_5)_4$	0.465	110	100	126, 129
Mercury	$NaAl(C_2H_5)_4$	0.8		92	84, 119
Steel	$NaAl(C_2H_5)_2(CH_3)_2$				124, 130
Steel	$NaAl(CH_3)_4 + NaAl(C_2H_5)_4 + CaAl(C_2H_5)_5$	0.125	100		131
Steel, copper	$NaAl(CH_3)_4 + NaAl(C_2H_5)_4$	0.25	100	77	131
Copper	$MAl(C_2H_5)_4 + MAl(CH_3)_4$(M = 25% K, 75% Na)	0.5	100	96	131, 132
Copper	$NaAl(CH_3)_4 + CsAl(C_2H_5)_4$ (2/1)	0.25	80		132
Copper	$NaAl(CH_3)_4 + KAl(C_2H_5)_4 + LiAl(C_2H_5)_4$.	0.25	100		132
Copper	$NaF \cdot 2Al(C_2H_5)_3$	0.022	28-45	87	114, 133
Copper	3320 g $NaAl(C_2H_5)_4$ + 740 g KCl		100		122
Copper	$Na[Al(C_2H_5)_3(OC_{10}H_{21})]$	0.04	100		122
Copper	$M[Al(C_2H_5)_3(OC_4H_9)]$ (M = K or Na)	0.04	100	93	122, 134
Copper	5 *M* $NaAl(C_2H_5)_4$ + 5 *M* $NaAl(C_2H_5)_3(OC_4H_9)$	0.053	100	95	122, 134
Copper	$Na[Al(C_2H_5)_3(i\text{-}C_6H_{11}O)]$				134
Copper	$NaAl(OC_2H_5)_4$	0.3			134
Copper	$NaAl(C_2H_5)_4 + Al(C_2H_5)_2(OC_4H_9) + Na[Al(C_2H_5)_3(OC_4H_9)]$		100		135
Platinum	$NaF \cdot Al(C_2H_5)_3$	0.25	80		128
Iron/copper	29.7 kg $NaAl(C_2H_5)_4$ + 27.7 kg $NaF \cdot Al(C_2H_5)_3$ + 12.1 kg $NaF \cdot 2Al(C_2H_5)_3$	0.08	70	98	136
Mercury	$NaF \cdot 2Al(C_2H_5)_3 + NaAl(C_2H_5)_4$	0.25-0.5	112-117	100	84
Mercury	$LiAl(C_2H_5)_3(OC_6H_5)$	0.005	105		137
Mercury	$NaAl(C_2H_5)_3(OC_2H_5)$				137
Mercury	1.7 *M* $KAl(C_2H_5)_4$ + 0.5 *M* $KF \cdot Al(C_2H_5)_3$	0.185	85	98.5	138

TABLE 10

TETRAALKYLLEAD COMPOUNDS SYNTHESIZED BY ELECTROLYSIS OF ALUMINUM COMPLEXES (ANODE LEAD)

Cathode	Electrolyte	i (A/cm^2)	T (°C)	Compound obtained	Yield (%)	References
Mercury	200 g $NaAl(CH_3)_4$ + 400 g THF	0.14	90	$Pb(CH_3)_4$	90	139, 140
Mercury	200 g $NaAl(CH_3)_4$ + 500 g of diglyme.	0.3	100	$Pb(CH_3)_4$	96	140
Mercury	$Na[Al(CH_3)_3(OC_4H_9)]$	0.14	90	$Pb(CH_3)_4$	94	140
Mercury	$Na[Al(CH_3)_3(OC_2H_5)]$	0.05	105	$Pb(CH_3)_4$		137
Copper	$RbAl(CH_3)_4 + NaAl(CH_3)_4$ (5/1)	0.25	100	$Pb(CH_3)_4$		131, 132
Copper	$NaAl(C_2H_5)_4 + NaAl(C_3H_7)_4$			$Pb(C_3H_7)_4$	95	122
Copper	$KAl(CH_3)_4 + KAl(i\text{-}C_3H_7)_4$ (1/8)	0.25	180	$Pb(i\text{-}C_3H_7)_4$		131, 132
Copper	$NaF \cdot 2Al(i\text{-}C_3H_7)_3$	0.022	50	$Pb(i\text{-}C_3H_7)_4$		133
Copper	$Na[Al(C_3H_7)_3(OC_9H_{11})] + NaAl(C_3H_7)_4$	0.04	100	$Pb(C_3H_7)_4$	90	122, 134
Copper	$NaAl(C_2H_5)_4 + NaAl(C_4H_9)_4$			$Pb(C_4H_9)_4$		123
Copper	$NaAl(C_4H_9)_4 + Na[Al(C_4H_9)_3(OC_{10}H_{21})]$	0.04	100	$Pb(C_4H_9)_4$	80	122, 134
Copper	$NaAl(C_3H_7)_4 + Na[Al(C_3H_7)_3(OC_6H_5)]$	0.04	100	$Pb(C_3H_7)_4$	80	123
Copper	$K[Al(C_4H_9)_3(OC_4H_9)]$	0.002	90	$Pb(C_4H_9)_4$		137
Steel	$NaAl(i\text{-}C_4H_9)_4 + KAl(i\text{-}C_4H_9)_4$	0.2		$Pb(i\text{-}C_4H_9)_4$		131
Copper	$NaF \cdot 2Al(C_6H_5)_3$			$Pb(C_6H_5)_4$		133
Copper	$NaAl(CH_3)_4 + NaAl(C_6H_5)_4$ (1/10)	0.25	220	$Pb(C_6H_5)_4$		133
Copper	$LiAl(CH_3)_4 + NaAl(C_{10}H_{21})_4$ (3/10)	0.25	40	$Pb(C_{10}H_{21})_4$		132
Steel	$NaB(C_6H_5)_4 + NaAl(C_2H_5)_4$ (2/3)		110	$Pb(C_6H_5)_4 + Pb(C_2H_5)_4$		131
Steel	10% biphenyl + $NaAl(C_6H_5CH_2)_4 + KAl(C_6H_5CH_2)_4$			$Pb(C_6H_5CH_2)_4$		131
Steel	$NaAl(\beta\text{-}C_6H_5C_2H_4)_4 + KAl(\beta\text{-}C_6H_5C_2H_4)_4$			$Pb(C_6H_5C_2H_4)_4$		131
Steel	$NaAl(C_6H_{11})_4 + KAl(C_6H_{11})_4$	0.25	100	$Pb(C_6H_{11})_4$		131

vacuum sodium is deposited as a film which wets well the surface and is readily removed from the electrolyzer. However, in addition to tetraethyllead, a small amount of gaseous products always was formed at the anode, so that a powerful pump was needed to maintain vacuum. For this reason the so-called "vacuum method" did not come into wide use.

The "three cycles" method proved to be much more successful. In this process mercury is used as the cathode. During electrolysis sodium forms an amalgam, which does not interact with alkylmetal compounds and this eliminates the necessity of using a diaphragm. Metallic sodium can be separated from the amalgam by repeated electrolysis [141, 142].

A potassium cation electrolyte has a better electrical conductivity, but the separation of metallic potassium from the amalgam is difficult. This led to development of a method for regeneration of potassium-containing electrolytes based on the reaction of potassium amalgam with $NaAlR_4$ [84, 143]. The use of this exchange reaction gave reactions 34-37 for the preparation of tetraethyllead with complete electrolyte regeneration.

$$KAl(C_2H_5)_4 + Pb \xrightarrow{\text{electrolysis}} Pb(C_2H_5)_4 + 4\ Al(C_2H_5)_3 + 4\ K(Hg)_x \qquad (34)$$

$$Al(C_2H_5)_3 + Na(Hg)_x + C_2H_4 \rightarrow NaAl(C_2H_5)_4 \qquad (35)$$

$$NaAl(C_2H_5)_4 + K(Hg)_x \rightarrow KAl(C_2H_5)_4 + Na(Hg)_x \qquad (36)$$

$$KOH + Na(Hg)_x \rightarrow NaOH + K(Hg)_x \qquad (37)$$

Several methods of separation of the resulting alkylmetal compound from the electrolyte have been proposed. If the differences in the boiling points are large enough, vacuum distillation can be used [144]. Sometimes prior separation of the alkylmetal compound by addition of sodium—aluminum alkoxide [145] or sodium hydride [146, 147] is recommended. In both cases the bottom layer enriched in the alkylmetal compound is separated from which it is easy to isolate a pure compound. In some cases it is recommended to use additives which with the particular alkylmetal compound form complexes insoluble in the electrolyte. In particular, tributylamine [148], sodium azide [149] and potassium cyanide [150] are used for this purpose.

In spite of the fact that by electrolysis of aluminum complexes it is possible to synthesize a large number of different alkylmetal compounds, the use of these electrolytes presents significant difficulties due to their high reactivity. It is sufficient to note that triethylaluminum is inflammable in air, which makes special precautions necessary.

C. Organoboron complexes

The organoboron complexes of the type $MR{\cdot}BR_3$ and $MBR_4{\cdot}MAlR_4$ are of interest in that they are safe to work with. Numerous alkylmetal compounds can be prepared by their electrolysis (Table 11). The dimethyl ether of diethylene glycol is recommended as solvent. To increase the electrical conductivity, a small amount of water is added to the solution [152]. The electrolysis of tetraalkylboron complexes in an aqueous solution with a soluble anode has also been described [85]. This method has been used to prepare alkyl derivatives of mercury, bismuth and lead. The anodes from tin and antimony undergo passivation and the yield of corresponding organometallic compounds is not high.

D. Other anodic processes

Electrolyses of some other complex compounds have been reported. It is difficult as yet to assess their practical value, but they are undoubtedly of theoretical interest.

For instance, electrolysis of the system $NaGe(C_6H_5)_3$ in liquid ammonia [155] has yielded hexaphenyldigermane and triphenylgermane. These products were believed to be formed as the result of two independent reactions (eqns. 38, 39). The dimerization product content varies from 10 to 35%, depending

$$2Ge(C_6H_5)_3^- \xrightarrow{-2e} [Ge(C_6H_5)_3]_2 \tag{38}$$

$$6Ge(C_6H_5)_3^- + 2NH_3 \xrightarrow{-6e} 6\,Ge(C_6H_5)_3H + N_2 \tag{39}$$

on the anode material. The anode material also affects the secondary chemical reactions leading to nitrogen evolution.

A new process of preparation of organotin compounds has been developed [156, 157], which is based on the electrolysis of alkyl halides in butyl acrylate or in another ester with bromine or tin bromide additions. Tin acts as anode, magnesium as cathode. Of great importance is the presence in solution of free bromine. The authors of the above references note that a magnesium cathode undergoes destruction in the course of electrolysis. Apparently, during electrolysis, bromine, magnesium of the cathode and butyl bromide react to form intermediate complexes, which at a soluble tin anode lead to organotin compounds. Under optimum conditions, the current efficiency of dibutyltin is about 60%.

Anodic dissolution of ferrosilicon in absolute ethanol acidified by concentrated sulfuric acid has yielded a mixture of alkyl silicates, in which the molar ratio of silicon to the ethoxy group is 2.4/1.9 [158]. Electrolysis of a chlorobenzene—xylene mixture containing as a conducting addition aluminum trichloride has yielded tetraphenylsilane (70%), whereas by anodic dissolution of ferrosilicon, tetraphenoxysilane has been prepared from phenol containing dissolved lithium chloride [108].

Some organoaluminum compounds have been synthesized by anodic dissolution of aluminum in nonaqueous media. Thus, electrolysis of aluminum triiodide solution in methyl iodide with the use of an aluminum anode has yielded methylaluminum iodide [159]. If dichloromethane is used instead of methyl iodide, the main electrolysis product is bis(dichloroaluminum)methane [160]. The electrode occurring in this case can be represented by the equations 40 and 41:

$$\text{at the cathode: } CH_2Cl_2 \rightarrow ClCH_2CH_2Cl \tag{40}$$

$$\begin{aligned} &\text{at the anode: } Cl^- - e + Al \rightarrow AlCl \\ &\qquad AlCl + CH_2Cl_2 \rightarrow Cl_2AlCH_2Cl \xrightarrow{AlCl} Cl_2AlCH_2AlCl_2 \end{aligned} \tag{41}$$

In conclusion, it should be mentioned that electrolysis has been reported to have been used for preparation of dicyclopentadienyliron [161]. The method is based on the electrolysis of cyclopentadienylthallium in dimethylformamide solution with an iron anode. The process occurring in this case is expressed by equation 42.

$$Fe + 2TlCp \rightarrow FeCp_2 + 2Tl^+ + 2e \tag{42}$$

(Continued on p. 30)

TABLE 11

ELECTROLYSIS OF BORON COMPLEXES

Anode	Cathode	Complex compound	Solvent	I (A/cm^2)	T (°C)	Compound obtained	Yield (%)	References
Lead	Copper	$B(C_2H_5)_3 + KCN$		0.05	65	$Pb(C_2H_5)_4$		151
Lead	Copper	0.754 parts $B(C_2H_5)_3$ + 0.354 parts 1-hexynylsodium	12 parts of toluene		20	$Pb(C_2H_5)_4$	high	151
Lead	Copper	$NaB(C_2H_5)_4$	Diethyl ether of diethylene glycol		25	$Pb(C_2H_5)_4$	100	151
Lead	Copper	$NaB(C_2H_5) \cdot R_3$ ($R = C_4H_9, C_6H_5, C_{18}H_{37}$)	Tetrahydrofuran or diethyl ether of diethylene glycol		60-100	$Pb(C_2H_5)_4$	high	152
Lead	Copper	$NaB(C_2H_5)_4 + KB(C_2H_5)_4$	Diethyl ether of diethylene glycol		100	$Pb(C_2H_5)_4$	high	151, 152
Lead	Copper	$NaB(C_2H_5)_4$ + 1% KI	Methyl ethyl ether of diethylene glycol		30	$Pb(C_2H_5)_4$	high	151, 152
Lead	Copper	$NaB(C_2H_5)F_3$	Tetrahydrofuran		50	$Pb(C_2H_5)_4$	high	151, 152
Lead	Copper	$LiB(C_2H_5)_4$	Diethyl ether			$Pb(C_2H_5)_4$	high	151, 152
Lead	Copper	$(C_2H_5)_4N \cdot B(C_2H_5)_4$	Triethylamine			$Pb(C_2H_5)_4$	100	151, 152
Lead	Copper	$NaNH_2 \cdot B(C_2H_5)_3$	Pyridine	0.01	70	$Pb(C_2H_5)_4$	high	151, 152
Lead	Copper	0.75M $B(C_{18}H_{37})_3$ + 1 M $Na(C_2H_5) \cdot BH_2$-$(C_{18}H_{37})$.			110	$Pb(C_2H_5)_4$	high	151, 152

Lead	Copper	0.354 parts $B(C_2H_5)_3$ + 0.1 parts $TiCl_4$ + 1.86 parts $NaB(C_2H_5)_4$	40 parts of dimethyl-ether of diethylene glycol		20	$Pb(C_2H_5)_4$	high	151, 152
Lead	Mercury	$NaB(C_2H_5)_4$	water	0.03-0.1	20	$Pb(C_2H_5)_4$	91	85
Lead	Copper	1 part $NaB(C_2H_5)_4$ + 3 parts $NaF \cdot 2Al(C_2H_5)_3$				$Pb(C_2H_5)_4$	high	153
Lead	Copper	$NaB(C_2H_5)_4$ + $NaAl(CH_3)_2(C_2H_5)_2$			110	$Pb(C_2H_5)_4$	high	153
Lead	Copper	$KB(C_2H_5)_4$ + $K[Al(C_2H_5)_3(OC_2H_5)]$			110	$Pb(C_2H_5)_4$	high	153
Lead	Copper	10% $NaB(C_6H_5CH_2)_4$ + 40% $NaAl(C_6H_5CH_2)_4$ + 50% $KAl(C_6H_5CH_2)_4$		0.04		$Pb(C_6H_5CH_2)_4$	high	153
Lead	Copper	1 part $KB(C_6H_{11})_3$	20 parts of benzene		75	$Pb(C_6H_{11})_4$	high	151, 152
Lead	Copper	0.5*M* $B(C_6H_{11})_3$ + 1*M* $KB(C_6H_{11})_4$	Cyclohexane			$Pb(C_6H_{11})_4$	high	151, 152
Lead	Copper	$NaB(C_6H_5)_4$	Dioxane		70	Phenyllead	high	151, 152
Lead	Copper	$NaB(C_8H_{17})_4$	Dimethyl ether of diethylene glycol		20	$Pb(C_8H_{17})_4$	high	154
Lead	Mercury	200 g of $MB(CH_3)_4$ (M = Na, K)	100 g of tetrahydro-furan		90	$Pb(CH_3)_4$	94	85
Lead	Mercury	$NaB(CH_3)_4$	Water	0.035	20	$Pb(CH_3)_4$	78	85
Mercury	Mercury	$NaB(C_2H_5)_4$	Water	0.13	20	$Hg(C_2H_5)_2$	81	85
Bismuth	Mercury	$NaB(C_2H_5)_4$	Water	0.035	20	$Bi(C_2H_5)_3$	98	85

The dicyclopentadienyliron yield was 91.2%. Nickelocene, dicyclopentadienylnickel, was prepared by a similar method.

E. On the mechanism of the anodic process leading to the formation of the metal—carbon bond

Practically all workers who have studied the anodic dissolution of metals during elecetrolysis of organometallic complexes are of the opinion that the formation of the carbon—metal bond is due to the action of organic radicals formed during electrolysis on the electrode material. For instance, during the electrolysis of the complex of NaC_2H_5 and $Zn(C_2H_5)_2$ the $Zn(C_2H_5)_3^-$ ions are discharged at the anode (eqn. 43).

$$Zn(C_2H_5)_3^- \xrightarrow{-e} Zn(C_2H_5)_2 + \dot{C}_2H_5 \qquad (43)$$

From the complex $Al(C_2H_5)_3$—KF it is $AlF(C_2H_5)_3^-$ anions which are discharged (eqn. 44).

$$AlF(C_2H_5)_3^- \xrightarrow{-e} AlF(C_2H_5)_2 + \dot{C}_2H_5 \qquad (44)$$

These radicals ($\dot{C}_2H_5$) react with the anode material, e.g., with lead (eqn. 45).

$$4\,\dot{C}_2H_5 + Pb \rightarrow Pb(C_2H_5)_4 \qquad (45)$$

The work of Evans on the electrolysis of Grignard reagents solutions in ethers [162], on the whole, supports the radical nature of the anodic process. Thus, he established that the electrolysis of Grignard reagents with an insoluble, anode yields products whose formation can be due to disproportionation, dimerization of the initially formed radicals and their interaction with the solvent. Investigating the dependence of the current strength on the applied potential, Evans found that at a certain potential, which he called "the potential of decomposition", the current increases sharply. The dependence of "the potential of decomposition" of organomagnesium compounds on the nature of an organic radical (Table 12) is consistent with the concept that the particle participating in the electrode process contains an organic radical.

However, not all phenomena can be explained in terms of radical theory. Thus, there is no doubt now that the formation of hydrocarbons during electrolysis of carboxylic acids, the Kolbe synthesis, occurs by the radical mechanism [163]. In spite of this, not a single case has been mentioned of alkylmetal compounds being formed during electrolysis of carboxylic acids at anodes from different materials.

TABLE 12

"DECOMPOSITION VOLTAGE" OF GRIGNARD REAGENTS

R in the compound RMgBr	Decomposition voltage (V)	R in the compound RMgBr	Decomposition voltage (V)
C_6H_5	2.17	$(CH_3)_2CH$	1.07
CH_3	1.94	$(CH_3)_3C$	0.07
C_3H_7	1.42	$CH_2{=}CHCH_2$	0.86
C_4H_9	1.32		

Fairly recently it was found that the composition of anodic gases formed during electrolysis of organic complexes is almost independent of the current density, but depends significantly on the anode material. Thus, during electrolysis of the solution of the complex $NaF—2Al(C_2H_5)_3$ in $Al(C_2H_5)_2H$, hydrogen, C_2H_6, C_4H_{10} and C_2H_4 evolution occurs as the result of anodic processes [164]. At a copper anode the hydrogen content in anodic gas reached 93.5%. The greatest ethane yield (68.7%) was observed at a palladium anode and the dimerization of radicals with formation of butane occurred most effectively (with the yield of 39.5%) at an iron anode. Also, during electrolysis of $NaGe(C_6H_5)_3$ in liquid ammonia, the composition of the electrolysis products depended considerably on the anode material [155].

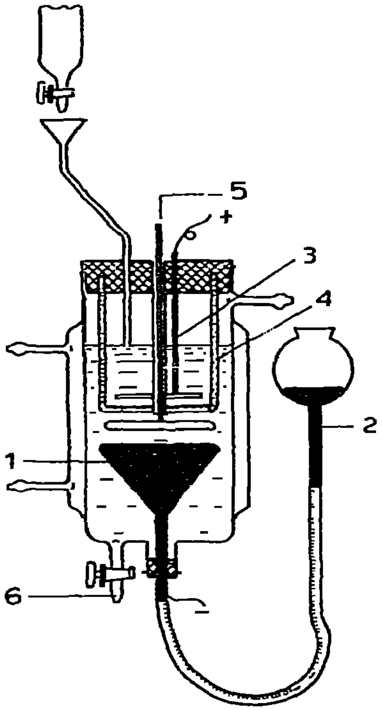
These facts show that the radicals arising at the anode do not exist as kinetically independent particles, but are somehow associated with electrode material.

IV. Electrolyzers for preparation of organometallic compounds by the electrochemical method

The preparation of organometallic compounds by electrochemical methods is specific in that the electrode is dissolved in the course of reaction. Therefore, with usual laboratory equipment used for electrosynthesis, only relatively short experiments can be carried out. This equipment is inapplicable for more or less large scale preparation and we shall not dwell on it here. We shall consider only the electrolyzers applicable for continuous processes.

The problem of continuous preparation of organometallic compounds is most readily solved if liquid electrodes are used. Figure 2 shows an electrolyzer used for continuous preparation of diisopropylmercury. The electrolyzer is fitted with a mercury cathode (3). The diisopropylmercury formed accumulates at the bottom of the electrolyzer and is removed through an overflow pipe (6). The mercury level (1) is maintained constant by moving receiver 2.

A continuous process with a solid electrode presents much greater difficulties. It is quite clear that a periodic change of electrodes is out of the question when working with a relatively powerful electrolyzer. Much attention has been given to the development of a convenient electrolyzer for preparation of tetraethyllead. Of great interest is the application of a granulated anode [109, 115, 165]. In a patent [165] an original electrolyzer for electrolysis of the Grignard reagent is described (Fig. 3). The body of the electrolyzer is a metal cylinder 1 connected to the anodic busbar and fitted with a lid 2 and a conical bottom 3. Lead granules are charged inside the body; they are then in contact with it and act as soluble anode. In the lower part of the body there is a screen holding the granules. On the electrolyzer lid, by means of pins passing through insulating sleeves are fitted the cathodes 5. The cathodes are in the shape of flat boxes covered on the outside by a membrane preventing the cathode from making electrical contact with the lead granules. The Grignard reagent solution enters through the lower connecting pipe 6, passes through the layer of granulated lead, where the electrochemical reaction occurs, and is removed through the upper connecting pipe 7 for separation of organolead compounds. Fresh portions of lead granules are introduced as they are used up also through 7.



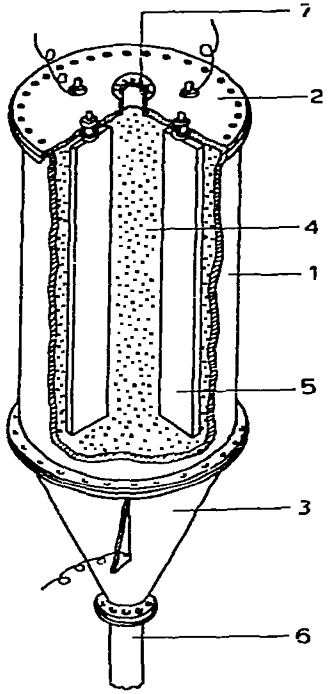


Fig. 2. Electrolyzer used for continuous preparation of diisopropylmercury.

Fig. 3. Electrolyzer used for electrolysis of Grignard reagents.

V. Conclusion

On the basis of the work covered in this review, it can be concluded that both anodic and cathodic processes can be used for synthesis of organometallic compounds.

The mechanism of these processes is not yet quite clear and apparently cannot be covered by one scheme. The mechanisms of the formation of the metal—carbon bond so far proposed have been confirmed only in some particular cases.

The majority of the electrochemical syntheses studied are intended for use with alkyl halides as starting materials. For preparation of organometallic compounds from alkyl halides, anodic processes are preferable (through the Grignard reagent), where the highest yields of the products have been achieved. The anodic method of preparation of tetraethyllead is already used on an industrial scale.

However, in anodic processes it is necessary to exchange one metal in an organometallic compound by another and the first stage of this method is the preparation by chemical means of a more readily obtainable compound such as the Grignard reagent or triethylaluminum.

The electrochemical preparation of organometallic compounds from unsaturated substances and from ketones can be carried out only at the cathode. The cathodic processes have an advantage over the anodic processes in that they make it possible to carry out a more direct synthesis, starting from a metal and an organic substance. The cathodic processes have not yet been used for large scale synthesis, but they are more promising in this respect since they yield organometallic compounds without intermediate stages.

Note added in proof

In the years 1972-1974 some works were published on the electrosynthesis of organometallic compounds:

On the anodic synthesis of tetraethyllead: U.S. Pat., 3655536 (1972).
On the cathodic synthesis of gallium, indium and thallium compounds: I.N. Chernykh and A.P. Tomilov, Elektrokhimiya, 9 (1973) 1025; 10 (1974) 971.
On mercuric compounds: O.R. Brown and K. Taylor, J. Electroanal. Chem., 50 (1974) 211; U.S. Pat., 3649483 (1972).
On tin compounds: H. Ulery, J. Electrochem. Soc., 119 (1972) 1474; M. Fleischmann, G. Mengoli and D. Pletcher, Electrochim. Acta, 18 (1973) 231; O.R. Brown, E.R. Gonzalez and A.B. Wright, Electrochim. Acta, 18 (1973) 369; 18 (1973) 555.
On lead compounds: M. Fleischmann, D. Pletcher, C. Vance, J. Electroanal. Chem., 29 (1971) 325.
On bismuth compounds: I.N. Chernykh and A.P. Tomilov, Elektrokhimiya, 10 (1974) 1424.
On synthesis of the transition metal complexes: H. Lehmkuhl, W. Leuchte and W. Eisenbach, Ann. Chem., (1973) 692. U.S. Pat., 3668086 (1972).

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