95. D. E. Warren, Plastics Chicago, 78, No. 1, 39, 71 (1947).
96. A. D. F. Toy, Chem. Eng. News, 25, 2030 (1947).
97. A. D. F. Toy, Mod. Plastics, 24, No. 12, 226 (1947).
98. G. Kamai and V. A. Kukhtin, Trudy Kazan. Khim. Tekh. Inst., im. S. M. Kirova, No. 16, 29 (1952).
99. G. Kamai and V. A. Kukhtin, Dokl. Akad. Nauk SSSR, 89, 309 (1953).
100. A. D. F. Toy and R. S. Cooper, J. Amer. Chem. Soc., 76, 2191 (1954).
101. G. Kamai and V. A. Kukhtin, Zhur. Obshch. Khim., 24, 1855 (1954).
102. P. D. Bartlett and R. Altschul, J. Amer. Chem. Soc., 67, 816 (1945).
103. A. D. F. Toy, J. Amer. Chem. Soc., 70, 186 (1948).
104. A. D. F. Toy and L. V. Brown, Ind. Eng. Chem., 40, 2276 (1948).
105. E. C. Shokal and L. N. Whitehill, B. P. 645 222; Chem. Abs., 45, 4267 (1951).
106. J. Kennedy, E. C. Lane, and B. K. Robinson, J. Appl. Chem., 8, 459 (1958).
107. D. Harman and A. R. Stiles, U. S. P. 2 601 520; Chem. Abs., 46, 8417 (1952).
108. J. Kennedy, Chem. and Ind., 378 (1956).
109. R. W. Upson, U. S. P. 2 557 805; Chem. Abs., 45, 8298 (1951); J. Amer. Chem. Soc., 75, 1763 (1953).
110. E. L. Gefter and M. I. Kabachnik, Dokl. Akad. Nauk SSSR, 114, 541 (1957).
111. G. S. Kolesnikov and E. F. Rodionova, Vysokomol. Soed., 1, 641 (1959).
112. G. S. Kolesnikov and E. F. Rodionova, Vysokomol. Soed., 1, 367 (1959).
113. A. D. Petrov and S. I. Sadykh-zade, Dokl. Akad. Nauk SSSR, 85, 1297 (1952).
114. L. L. Shchukovskaya, A. D. Petrov, and Yu. P. Egorov, Zhur. Obshch. Khim., 26, 3383 (1956).
115. S. I. Sadykh-zade, I. A. Avgushevich, and A. D. Petrov, Dokl. Akad. Nauk SSSR, 112, 662 (1957).
116. S. I. Sadykh-zade and A. D. Petrov, Zhur. Obshch. Khim., 28, 1542 (1958).
117. A. D. Petrov and S. I. Sadykh-zade, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 513 (1958).
118. J. Speier, I. Webster, and G. Barnes, J. Amer. Chem. Soc., 79, 974 (1957).
119. M. F. Shostakovskii, E. I. Gracheva, and L. A. Kayutenko, Dokl. Akad. Nauk SSSR, 132, 153 (1960).
120. A. D. Petrov and S. I. Sadykh-zade, Dokl. Akad. Nauk SSSR, 129, 584 (1959).
121. V. V. Korshak, A. D. Petrov, N. G. Matveeva, V. F. Mirnov, G. I. Nikitin, and S. I. Sadykh-zade, Zhur. Obshch. Khim., 26, 1209 (1956).

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# FREE RADICAL REACTIONS IN THE ELECTROLYSIS OF ORGANIC COMPOUNDS

A. P. Tomilov and M. Ya. Fioshin

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## 1. INTRODUCTION

Electrolytic processes in aqueous and non-aqueous electrolytes often lead to the formation of free radicals. Free radical reactions during electrolysis do not appear to have attracted the attention they deserve, and very few published papers deal specifically with electrochemical methods of preparation of free radicals and with the characterisation of free radicals thus produced. Yet studies of the properties and behaviour of electrochemically generated free radicals offer great theoretical and practical possibilities.

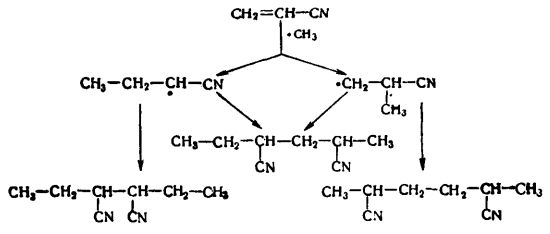
The present article discusses the electrochemical reactions of organic compounds in which free radicals are involved.

## 2. METHODS OF DETECTING FREE RADICALS IN THE ELECTROLYSIS OF ORGANIC COMPOUNDS

The formation of free radicals during electrolysis of organic compounds can be demonstrated by a number of methods.

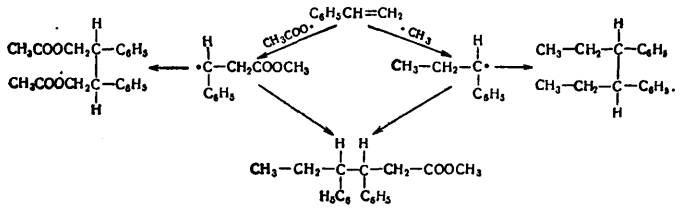
One can, for example, make a study of the products which appear when organic compounds are electrolysed in the presence of free radical acceptors, *i.e.*, of unsaturated compounds, which readily combine with free radicals. Styrene, acrylonitrile, butadiene, isoprene, and other similar compounds will readily accept free radicals.

The nature of the free radicals formed during electrolysis can often be inferred from the products obtained when organic compounds are electrolysed in the presence of such acceptors. The method was applied with success to the free radical reactions occurring during the Kolbe synthesis. Thus, electrolysis of a solution of potassium acetate in anhydrous acetic acid containing acrylonitrile gives a number of products [1] whose formation can be described by the following scheme if it is assumed that the anodic process generates methyl radicals which then react with molecules of acrylonitrile:



The electrolysis of sodium acetate solutions in acetic acid containing styrene [1,2], isoprene, or butadiene [3] yields

addition products of acetate radicals as well as of methyl radicals, thus:



An interesting reaction is observed when salts of dicarboxylic acid mono-esters are electrolysed in the presence of butadiene. For example, a salt of monoethyl maleate gives[3,4] substituted vinyl radicals at the anode:

$$2C_2H_5OOCH{=}CHCOO^- \xrightarrow{-2e} 2C_2H_5OOCCH{=}\dot{C}H{+}2CO_2,$$

which then react with butadiene:

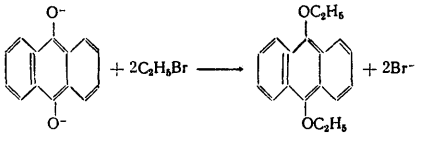
$$2C_2H_5OOCCH{=}\dot{C}H + CH_2{=}CHCH{=}CH_2 \rightarrow$$
$$\rightarrow C_2H_5OOCCH{=}CHCH_2CH{=}CHCH_2CH{=}CHCOOC_2H_5.$$

The resulting unsaturated compound gives sebacic acid upon saponification and hydrogenation. Electrolysis of the salt of monomethyl adipate in the presence of butadiene gives similar results[5].

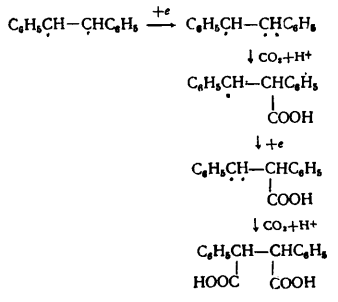
Certain other addition reactions between organic free radicals and organic compounds, which also can be used to detect the formation of free radicals during electrolysis, will be considered in Section 4d, "Interactions with the Solvent".

The free radicals formed during electrolysis are sometimes stable enough to cause observable changes in the colour and in the chemical properties of the solution. The following are a few examples:

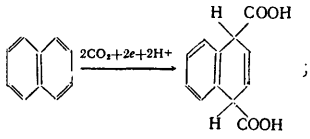
1. A solution of anthraquinone in acetonitrile develops new chemical properties during electrolysis. It reacts vigorously with ethyl bromide forming 9,10-diethoxyanthracene[6], probably *via* the electrolytically generated double anion:



2. The radical anions formed when a solution of stilbene in dimethylformamide is electrolysed can react with carbon dioxide, giving diphenylsuccinic acid[7]:



Addition of carbon dioxide to an organic radical with formation of a dicarboxylic acid has also been observed[8] with certain other hydrocarbons. Thus, naphthalene gives 1,4-dihydronaphthalene-1,4-dicarboxylic acid:

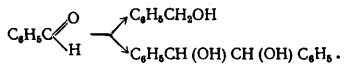


and phenanthrene gives 9,10-dihydrophenanthrene-9,10-dicarboxylic acid, whilst diphenylfumaric acid is obtained from diphenylacetylene.

3. The formation of free radicals during electrolytic reduction of naphthalene at a mercury cathode is also confirmed by the appearance of a green colour in the vicinity of the cathode. The same coloration is also observed during the reaction between naphthalene and metallic sodium[9], and is clearly due to free radicals.

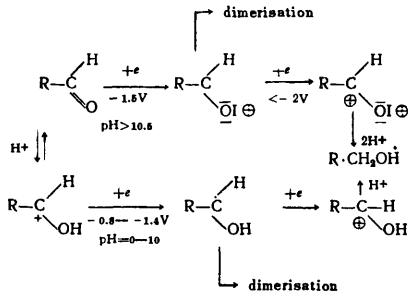
The chemical methods mentioned above can only detect free radicals which are sufficiently stable (and therefore long-lived) to diffuse into the solution. Physicochemical methods, above all polarographic analysis, are free from this limitation. By studying "current *vs.* potential" curves it is often possible to show that addition of electrons to an organic molecule at a dropping mercury cathode proceeds by a stepwise mechanism, which implies that the intermediate reduction product is a radical or a radical-ion. Polarographic data have proved very valuable for interpreting the mechanism of the electrolytic reduction of organic substances[10-12], and have shown that many electrochemical reactions proceed *via* free radical intermediates.

We shall consider, as an example, the electrolytic reduction of benzaldehyde[11,13], which can give two different products, benzyl alcohol or hydrobenzoin:



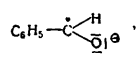
In an acid medium benzaldehyde gives two distinct one-electron waves, which merge into a single two-electron wave at pH 7. Further increase in pH gradually lowers the combined wave to one-half of its initial height, and a new wave appears whose height accounts for the decrease in height of the combined wave.

The following reaction mechanism[13] explains the behaviour of benzaldehyde during reduction:



In acid solution, a protonated molecule of aldehyde is reduced to the radical $C_6H_5\dot{C}HOH$, which then dimerises to hydrobenzoin. Further reduction of the radical (to benzyl

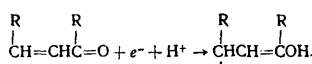
alcohol) is possible at sufficiently negative potentials (> -1.3 V). In strongly alkaline media the reduction follows a somewhat different path. An electron adds on to an unprotonated aldehyde molecule, giving the radical



which then dimerises. Further reduction of this radical occurs at potentials below -2 V, and appears to set in before protonation.

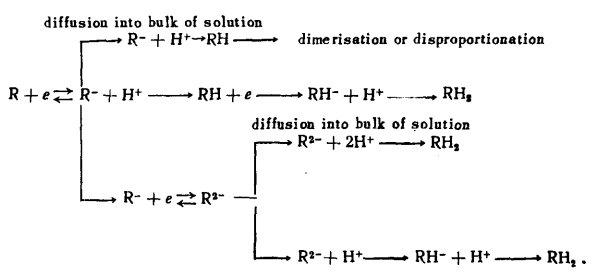
The above mechanism, originally put forward in connection with the electrolytic reduction of benzaldehyde, appears to be generally applicable to the reduction of other aromatic aldehydes and ketones [14-16], although some details of the electrode processes involved are still controversial.

The formation of free radicals has also been demonstrated during the electrolytic reduction of $\alpha,\beta$-unsaturated aliphatic ketones, and the following mechanism has been suggested [12]:



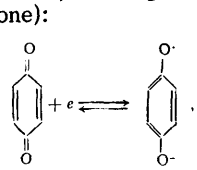
The structure of the resulting radical, however, has not yet been fully characterised.

Hoijtink *et al.*[17] made a careful polarographic study of the electrolytic reduction mechanism of many unsaturated hydrocarbons, and concluded that polycyclic aromatic hydrocarbons — and also aliphatic hydrocarbons containing conjugated double bonds, $(CH=CH)_n$ — are reduced through the intermediate stage of a radical anion, formed by addition of an electron:

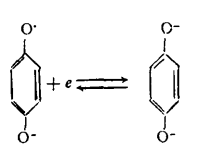



Polarographic studies [18] have also shown that free radicals are formed during the reduction of tropylium ions.

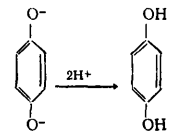
Some polarographic results [6] on the reduction of quinones are of considerable interest, because they confirm the above mechanism involving radical anions. The quinones investigated include the duroquinone of $\alpha$-hydroxyphenazine [19], of *N*-methyl-$\alpha$-hydroxyphenazine [20], and others [21,22]. Addition of one electron occurs, leading to the formation of radical ion (semiquinone):



which then adds on a second electron giving a di-anion:

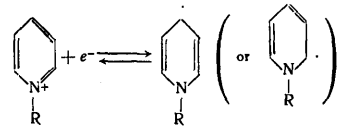


The di-anion captures protons from the solvent forming hydroquinone:




The reduction of anthraquinone, 2-methyl-1,4-naphthoquinone, and duroquinone proceeds according to this scheme.

The reduction of quaternary pyridinium ions has been shown, polarographically, to yield free radicals by a reversible one-electron step [23,24]:




*N*-ethylpyridinium salts with electron-acceptor substituents show a similar behaviour [25].

Holleck concluded, from a polarographic study of the reduction of aromatic nitro-compounds, that one-electron reactions can occur in alkaline media independently of hydrogen-ion concentration, giving rise to a radical anion [13,26]:

$$RNO_2 + e^- \rightarrow (RNO_2)^- .$$

Alternating-current, oscillographic voltammetry with a hanging-drop cathode [27-30] has given valuable indications of the formation of free radicals during electrolysis. Thus, the presence of free ketyl radicals during the reduction of benzophenone has been convincingly demonstrated by this polarographic technique [30]. Benzophenone and its reduction products are oxidised, at a mercury anode, at potentials more positive than -0.28 V. Using a.c. voltammetry, a well-defined peak is observed in the anodic branch at a potential of -1.34 V: this corresponds to the reversible oxidation of the ketyl radicals formed at the electrode during the cathodic polarisation.

Another successful technique for investigating the formation of free radicals during electrolysis is the method of paramagnetic resonance.

The method was first applied to solutions prepared by controlled-potential electrolysis and stabilised at liquid-nitrogen temperature. A qualitative proof was given of the formation of free radicals in the electrolysis of hydrocarbons and quinones, but no indication of the structure of the radicals was obtained because the EPR spectrum of frozen radicals has no hyperfine structure [31].

Some recent attempts have been made to place the electrolytic cell directly in the resonant cavity, thus enabling the structure and concentration of short-lived radicals to be studied. This improved technique has made it possible to demonstrate the presence of $ClO_4^{\cdot}$ radicals on the electrode in the electrolysis of 0.1 M solutions of lithium perchlorate in acetonitrile [32], and to prove that radical ions with single negative charges are formed during electrolytic oxidation of nitrobenzene [33], dinitrobenzene [34], phenothiazine [35], *p*-phenylenediamine [37], and various aliphatic nitro-compounds [36]. In these experiments the hyperfine structure of the EPR spectra was preserved, and the structure of the free radicals formed during electrolysis could be inferred from the results. Thus, it was shown that the

radical anion $(\dot{C}_6H_5NO_2)^-$ is present in the controlled-potential electrolytic reduction of nitrobenzene at a mercury cathode. Radicals of this type, it should be noted, had already been postulated by Holleck on the basis of his polarographic work [13,26].

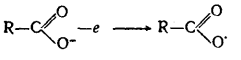
The structure $(NH_2C_6H_4NH_2)^+$, assigned by EPR to the positive radical ion formed during the controlled-potential oxidation of *p*-phenylenediamine at a mercury cathode [37], is also in full agreement with the conclusions of polarographic investigations of this compound [38-40].

## 3. CLASSIFICATION OF ELECTROCHEMICAL REACTIONS LEADING TO THE FORMATION OF FREE RADICALS

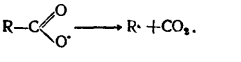
It has been shown, by the methods discussed in the previous section, that both anodic and cathodic electrochemical reactions can give rise to organic free radicals.

### a. Anodic Reactions

Discharge of organic anions. The most typical reactions of this class take place when carboxylic acids or organometallic compounds are electrolysed. The salts of organic acids dissociate in aqueous solutions, to which they impart a high electrical conductivity. The same anions are formed also when these salts are dissolved in other solvents of high dielectric constant, such as methanol, organic acids, dimethylformamide, acetonitrile, etc. Electrolysis of these solutions, under suitable conditions, results in discharge of the anions at the anode with the formation of free radicals [41]:



The free radicals formed by the electrode reaction are unstable, and usually undergo further decomposition according to the equation:



The subsequent fate of these radicals is discussed below (see Section 4).

Solutions of mono- and dithio-acids [42-45], and also ether solutions of organomagnesium compounds [46] have a fair electrical conductivity due to their dissociation:

$$RMgX \rightleftarrows R^- + MgX^+.$$

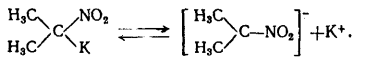
Only one anodic process is possible when such a solution is electrolysed: discharge of the anion and formation of the free radical R·.

Some other organometallic compounds (*e.g.* diethylzinc [47]), and certain organic compounds containing alkali metals, show a similar behaviour when their solutions are electrolysed. Thus, sodiomalonic ester dissociates in alcoholic solution according to the equation [48]:

$$NaHC(COOR)_2 \rightleftarrows Na^+ + HC(COOR)_2^-$$

and the anions can be discharged at the anode, giving the corresponding free radicals. This electrolysis scheme (dissociation followed by formation of free radicals) is also applicable to solutions of alkoxides [49] and mercaptides [50].

Some nitro-compounds form electrically conducting salts. For example, the dissociation of the potassium salt of nitroisopropane can be depicted as [51]:



Lastly, we should note that the salts of the oximido-derivatives of malonic acid can be electrolysed. Dissociation in this case proceeds [52] according to:

$$NaON{=}C(COOR)_2 \rightleftarrows Na^+ + ON{=}C(COOR)_2^-.$$

Oxidation of neutral organic molecules. The electrochemical oxidation of alcohols in sulphuric acid solution [53,54] is a reaction of this type. An alcohol molecule loses an electron at the electrode surface:

$$CH_3OH \xrightarrow{-e} [CH_3OH]^+ ,$$

and the resulting cation rapidly attacks water:

$$[CH_3OH]^+ + H_2O \longrightarrow CH_3O\cdot + H_3O^+ .$$

The methoxy radical now loses a second electron at the anode:

$$CH_3O\cdot \xrightarrow{-e} [CH_3O]^+ ,$$

and the $(CH_3O)^+$ ion gives up a proton to the solvent and is converted into formaldehyde:

$$[CH_3O]^+ + H_2O \longrightarrow HCHO + H_3O^+.$$

The electrochemical oxidations of aniline [55-57], *p*-phenylenediamine [37,39,40], and also of phenylthiourea [58], appear to follow a similar course.

Reaction of an organic compound with an inorganic free-radical primary anodic product. An organic free radical may be formed by a chemical reaction involving an inorganic free radical:

$$RH + X\cdot \longrightarrow R\cdot + HX,$$

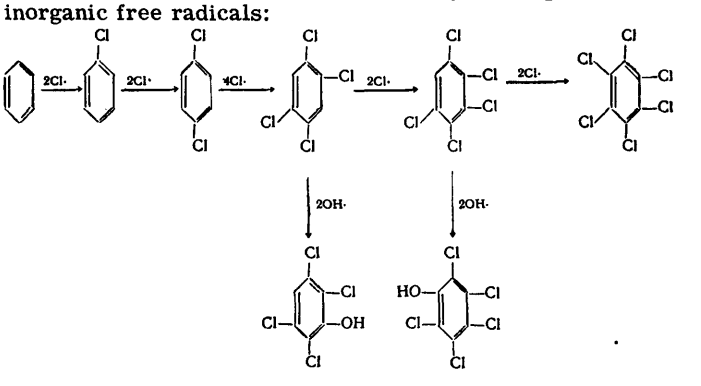
where X· is an inorganic free radical, formed as a primary product in an electrode reaction.

If the activity of the inorganic free radicals at the electrode surface is high enough, rapid combination with the R· radicals will take place:

$$R\cdot + X\cdot \longrightarrow RX .$$

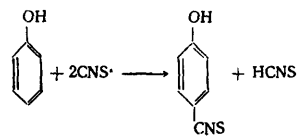
This sequence of events is usually termed "anodic substitution", and occurs in many electrochemical fluorinations, chlorinations, brominations, iodinations, hydroxylations, alkoxylations, thiocyanations, etc. [59]

The electrochemical chlorination of benzene, involving [60] the following scheme, is a good example of a reaction between an organic compound and electrolytically generated inorganic free radicals:

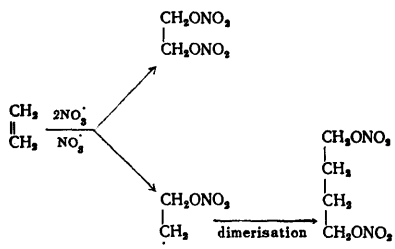


In addition to chlorination, hydroxylation occurs to some extent. A plausible explanation is an attack on the organic compound by anodically generated hydroxyl radicals.

Another typical reaction of this type takes place[61-65] between aromatic compounds and anodically generated thiocyanogen radicals. Thus, 4-thiocyanophenol can be obtained from phenol:



Ethylene reacts with the nitrate radicals formed in the electrolysis of aqueous solutions of nitrates[66]:



An interesting reaction has been reported[67] in the electrolysis of a solution of perchlorate in acetonitrile: the $ClO_4^{\cdot}$ radicals, formed at the anode, react with the acetonitrile, giving an organic free radical:

$$CH_3CN + ClO_4^{\cdot} \longrightarrow \dot{C}H_2CN + HClO_4.$$

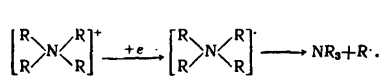
b. Cathodic Reactions

The following processes can give rise to free radicals at a cathode.

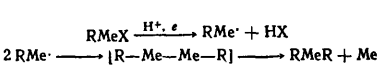
Discharge of organic cations. For example, tropyl radicals are formed[18] by discharge of tropylium ions:

$$C_7H_7^+ \xrightarrow{+e} C_7H_7^{\cdot}.$$

Free radicals also appear when quaternary ammonium cations are discharged[68]:



Fission of a halogen atom from an organic molecule. Many dehalogenation reactions[69-75], and symmetrisations of organometallic compounds, can be classified here. The symmetrisation process is described by the following general equations:



Addition of a proton and an electron to the double bond of an organic compound. Reactions of this type are fairly common. They can be visualised as



The cathodic reduction of hydrocarbons containing conjugated double bonds[7-9,82-84], and of many of their derivatives, and also the reduction of carbonyl compounds[14-16,85-88], involve this type of reaction.

4. FREE RADICAL REACTIONS

It is well established that free radicals can undergo the following reactions in solution[89,90].

1. Dimerisation. For example, ethane is formed from two methyl radicals:

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6.$$

2. Disproportionation, such as the formation of ethane and ethylene from ethyl radicals:

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4.$$

3. Addition to unsaturated compounds present in solution, or reaction with the electrode metal.

4. Solvent interaction. For example, the primary phenyl radicals, formed in the electrolysis of a solution of phenylmagnesium bromide in dry ether react with the ether almost quantitatively.

Some of the most typical examples of these four reaction types will now be discussed.

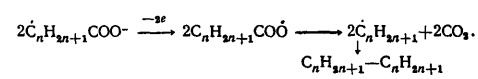
a. Dimerisation Reactions

Dimerisation is by far the commonest reaction of electrolytically generated free radicals.

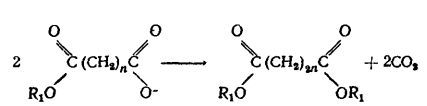
Anodic dimerisation. Nearly all cases of anodic dimerisation involve free radicals produced by the discharge of organic anions.

Aliphatic hydrocarbon radicals which appear when the salts of carboxylic acids or organometallic compounds are electrolysed invariably show some tendency to dimerise.

The dimerisation of hydrocarbon radicals formed during electrolysis of carboxylates is generally known as Kolbe's electrosynthesis, and is usually represented as:

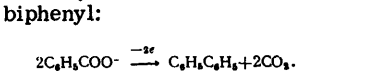


Practically all aliphatic acids with a normal carbon chain, and many of their derivatives such as the mono-esters of dicarboxylic acids, undergo the Kolbe reaction[91,92]:



A recent review[41] deals exhaustively with the dimerisation of radicals formed in the electrolysis of carboxylic acids and their derivatives.

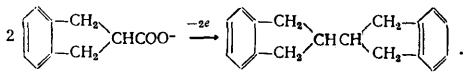
It was long believed that aromatic acids do not give dimeric products at the anode. Fichter[93] showed, however, that electrolysis of a solution of benzoic acid in pyridine yields biphenyl:



If, instead of benzoic acid, a solution of phenylacetic acid in pyridine is electrolysed, the yield of dibenzyl by the reaction

$$2C_6H_5CH_2COO^- \xrightarrow{-2e} C_6H_5CH_2CH_2C_6H_5+2CO_2,$$

is 50% of theoretical. This is due to the relatively high stability of the benzyl radical $C_6H_5\dot{C}H_2$, which favours dimerisation. Similar results are obtained when β-phenylpropionic acid is electrolysed. Electrolysis of a solution of indane-2-carboxylic acid in methanol gives a low yield of 2,2′-bi-indanyl at the anode[94]:



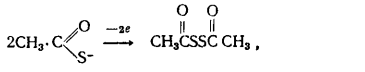
Dimerisation of hydrocarbon radicals has been observed in the electrolysis of n-butyl-, isobutyl-, and n-hexylmagnesium bromides[95].

The free radicals formed from anodically discharged xanthate anions undergo interesting dimerisation reactions at the anode. Thus, potassium methylxanthate reacts to give dimethylxanthogen[44]:

$$2CH_3OCSS^- \xrightarrow{-2e} CH_3OCSSSSCOCH_3 .$$

Other xanthogenates show an analogous behaviour.

Thioacetic acid gives diacetyl disulphide on electrolysis[42]:

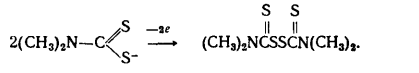


whilst sodium ethyl-, methyl-, and phenyl-mercaptides undergo a similar reaction[42]:

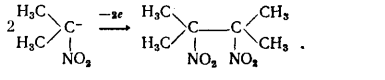
$$2C_2H_5S^- \xrightarrow{-2e} C_2H_5SSC_2H_5,$$

giving the disulphide.

Electrolysis of dimethyldithiocarbamate produces some tetramethylthiuram disulphide[96]:



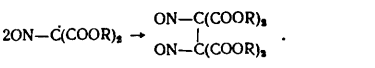
Zelinskii and Shilov[51] obtained some interesting results by electrolysing a concentrated aqueous solution of the potassium salt of nitroisopropane, $K[(CH_3)_2CNO_2]$, and showed that a dimeric product is formed at the anode:



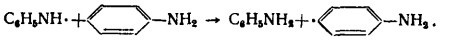
The radicals formed in solution during electrolysis of sodiomalonic ester dimerise to give tetracarboxylic acid derivatives:

$$2H\dot{C}(COOR)_2 \rightarrow (ROOC)_2CH-CH(COOR)_2.$$

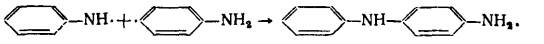
Oximido-derivatives of malonic acid undergo a similar reaction[52]:



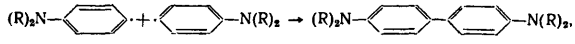
Dimerisation processes are observed during electrolytic oxidation of several amines, *e.g.* aniline[55–57]. Thus, electrolysis of an aqueous solution of aniline hydrochloride or sulphate with a platinum anode affords *p*-aminodiphenylamine. It seems probable that $C_6H_5NH\cdot$ radicals are formed initially at the anode, and that these subsequently react with the benzene ring, abstracting a hydrogen atom from the *para*-position:



The free radicals formed by this process can now react with the primary radicals:

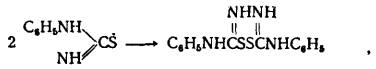


The reactions of dimethyl- and diethyl-aniline are particularly interesting[97,98]. They produce *N,N,N′,N′*-tetraalkylbenzidines, suggesting direct combination of two radicals:



where R = $CH_3$ or $C_2H_5$.

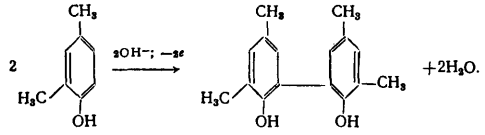
Some curious phenomena have been observed[58] in the electrochemical oxidation of hydrochloric acid solutions of phenylthiourea. It would seem that the primary process is the formation of the free radical $C_6H_5NH-\underset{\underset{S}{\|}}{C}-NH\cdot$, and that the anodic reaction follows the scheme suggested by Khomutov[56]. This is followed by a redistribution of electrons within the molecule, the unpaired electron being transferred to the sulphur atom with formation of the free radical $\overset{C_6H_5NH}{NH} \geqslant C-S^{\cdot}$. This radical can now dimerise



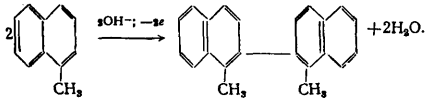
forming phenylformamidine disulphide. Electrolysis of thiourea, symmetrical diethylthiourea, and allylthiourea gives analogous results[58].

Lastly, we can distinguish a class of dimerisation processes in which the organic radicals are apparently formed by reaction with inorganic radicals, produced at the anode as the primary product. Reactions of this type usually involve the hydroxyl radical, as shown in the following list of examples.

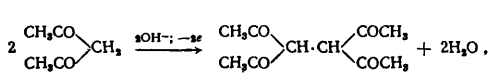
Oxidation of 2,4-dimethylphenol gave a derivative of biphenyl[99]:



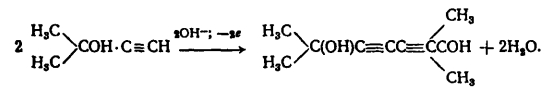
1-Methylnaphthalene undergoes a similar reaction at the anode[100]:



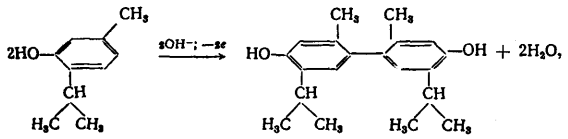
Also interesting are the dimerisation of acetylacetone[48]:



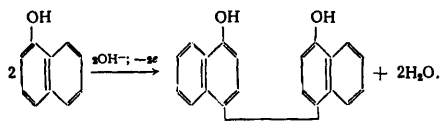
and of dimethylethynylcarbinol [101]:



Other reactions of this type include the synthesis of dithymol by oxidation of thymol at a lead dioxide anode [102]:



and the synthesis of 1, 1′-dinaphthol by the oxidation of 1-naphthol under similar conditions [103]:



Dimers of the same type are formed, by anodic dehydrogenation, in the electrolysis of several other organic compounds, *e.g.* *m*-cresyl methyl ether [104], *p*-cresyl methyl ether [104], veratrole [105], guaiacol [48], and a monoether of resorcinol [105].

An interesting anodic dimerisation is observed [67] during electrolysis of a solution of potassium perchlorate in acetonitrile, the perchlorate radical (formed as a primary product) reacting with the organic solvent. The resulting organic radicals dimerise to form succinonitrile:

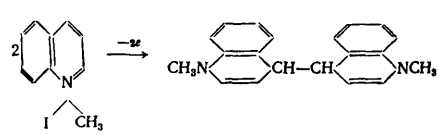
$$2\dot{C}H_2CN \rightarrow CNCH_2CH_2CN.$$

Cathodic dimerisation. Some instances of the formation of dimers from cathodically generated radicals will now be discussed.

The tropyl radical, which appears at the cathode when tropylium ions are discharged, dimerises to bitropyl [18]:

$$2C_7H_7^{\cdot} \longrightarrow C_7H_7C_7H_7.$$

Dimerisation processes sometimes occur in the electrolysis of quaternary ammonium ions. Thus, electrolysis of methylquinolinium iodide gives a low yield of the dimer [106]:



and a similar reaction takes place in the electrolysis of ethylquinolinium iodide.

Like these typical dimerisations of organic cations, dimerisation processes involving cathodic dehalogenation *via* a free radical intermediate have not been studied systematically. The following are a few examples of this type of reaction.

1. Electrolytic dehalogenation of ethyl iodide produces butane [69]:

$$2CH_3CH_2I \xrightarrow{+2e,\ 2H^+} CH_3CH_2CH_2CH_3 + 2HI.$$

2. Dehalogenation of 1, 1, 1-trichloro-2, 2-diphenylethane and of some of its derivatives containing substituents in the benzene ring affords a good yield of acetylene derivatives [70–75]:

$$2(Ar)_2CHCCl_3 \xrightarrow{+4e,\ 4H^+} (Ar)_2CHC{\equiv}CCH(Ar)_2 + 6HCl.$$

3. Symmetrisation of organometallic compounds can also be regarded as a dimerisation process. The reaction has been studied with organic compounds of mercury [76,77], tin [78], lead [79,80], and arsenic [81].

The cathodic reduction of multiple bonds has been the object of more detailed studies. Following the suggestion of Knunyants [107], reduction of an organic compound accompanied by simultaneous dimerisation is usually called hydrodimerisation.

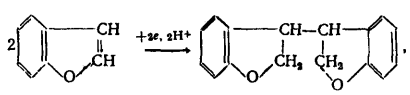
Hydrodimerisation processes can be carried out by purely chemical means (using various reducing agents) or by cathodic reduction. The following classes of compounds undergo hydrodimerisation: unsaturated and aromatic hydrocarbons, ketones, aldehydes, and compounds containing conjugated double bonds, such as 1, 2-unsaturated aldehydes, ketones, carboxylic acids, and nitriles. These unsaturated compounds frequently yield unsymmetrical derivatives as well as symmetrical hydrodimers.

We shall now discuss the hydrodimerisation of different classes of organic compounds.

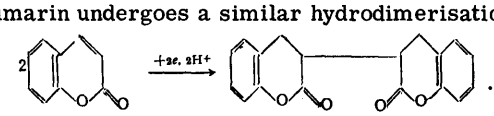
1. Hydrodimerisation at a C–H bond. Unsaturated aliphatic hydrocarbons can be converted into their hydrodimers by chemical hydrogenation [107], but little is known about their hydrodimerisation by electrolytic reduction.

The preparation of the hydrodimers of acyclic aliphatic hydrocarbons by electrolysis has not yet been accomplished, probably because isolated double bonds are relatively inactive and not easily reduced at a cathode. When conjugation is present, however, double bonds become much more reactive, and hydrodimerisation by electrolytic reduction is possible with heterocyclic and aromatic compounds, and with 1, 2-unsaturated aldehydes, acids, ketones, and nitriles.

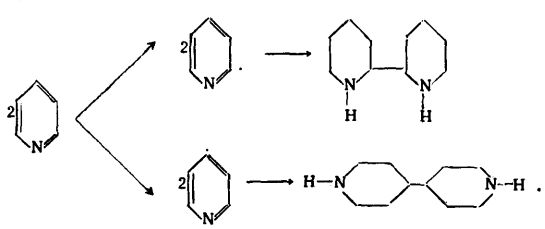
For example, coumarone forms a hydrodimer when reduced electrolytically at a mercury cathode [108]:



and coumarin undergoes a similar hydrodimerisation [109]:† 



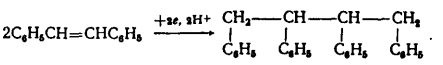
From pyridine, 2, 2′- and 4, 4′-bipiperidyl can be isolated [110,111]:



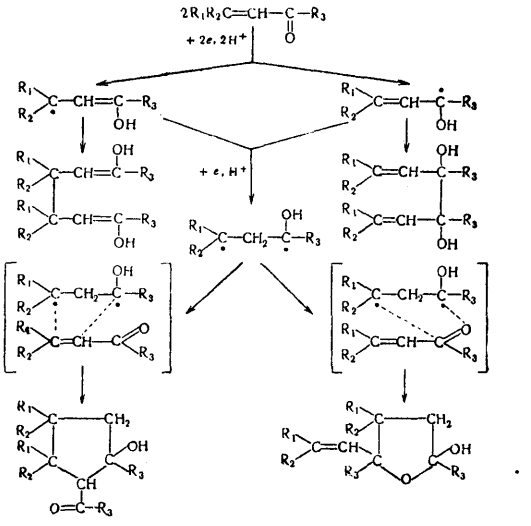
The formation of dimeric and trimeric reduction products has been observed in the electrolytic reduction of quinoline [112,113], quinaldine [114–116], and lepidine [117–120].

† But see R. Patzak and L. Neugebauer, Monatsh., 82, 662 (1951) (Ed. of Translation).

Dimeric products have been reported also from the reduction of 1, 2-diphenylethylene (stilbene) at a mercury cathode [7]:

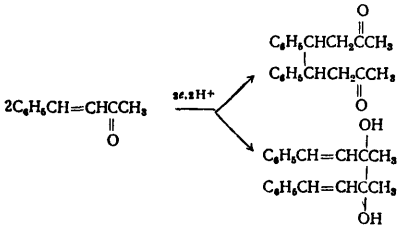


The formation of dimers by electrolytic reduction of crotonaldehyde, acrolein, and mesityl oxide has been explained [121-127] by the following scheme:

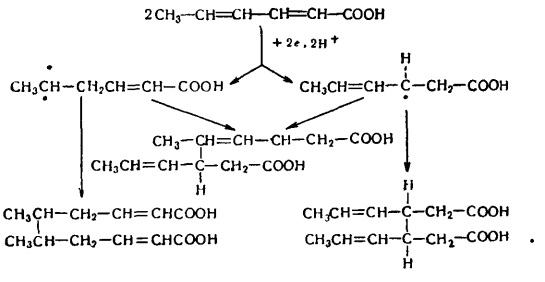


In this reaction cyclic derivatives of cyclopentane and furan are formed as well as linear dimers.

Methyl styryl ketone can give two hydrodimers by electrolytic reduction [128]:

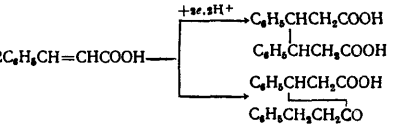


Three different dimers have been isolated from the cathodic hydrodimerisation of sorbic acid [129]:

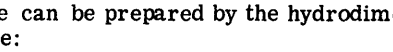


The reduction of vinylacrylic acid follows exactly the same path [130, 131].

Electrolytic reduction of cinnamic acid gave the isomeric $\beta,\gamma$-diphenyladipic acids and other similar products, among which a keto-acid was isolated and identified [132-134]:



Adiponitrile can be prepared by the hydrodimerisation of acrylonitrile:



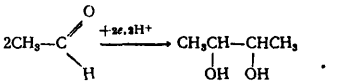
Some $\alpha,\beta$-unsaturated nitriles, such as

$C_6H_5CH=CHCN$,
$CH_3CH=CHCN$,
$(CH_3)_2C=CHCN$, etc.,

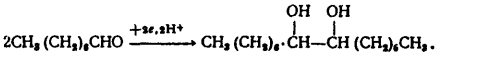
undergo an analogous dimerisation, induced by the development of a free valency at the $\beta$-carbon atom [135].

2. Hydrodimerisation at a >C=O bond. The hydrodimerisation of aldehydes has been demonstrated in a number of interesting systems.

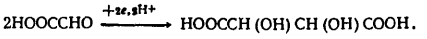
Electrolytic reduction of acetaldehyde in an alkaline medium produces 2, 3-butylene glycol [136]:



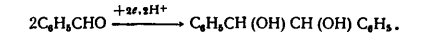
Octanal gives rise to hexadecan-7, 8-diol at a mercury cathode [137]:



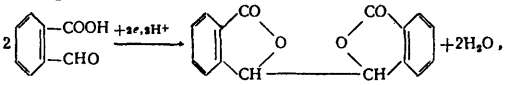
Tartaric acid has been prepared in good yield from glyoxylic acid [138, 139]:



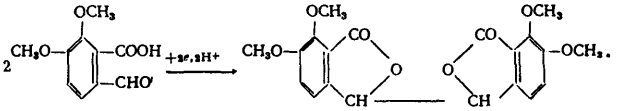
Benzaldehyde and many of its ring-substituted derivatives are reduced to hydrobenzoins [140, 141]:



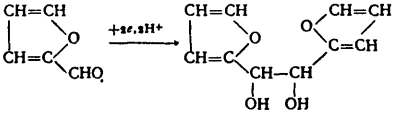
Derivatives of benzaldehyde with a carboxylic group in the *ortho*-position undergo a distinctive type of electrolytic reduction. Thus, two isomeric biphthalidyls [142] are formed from salicylic acid [*sic.* *o*-formylbenzoic acid (Ed. of Translation)]:



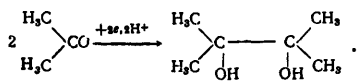
whilst electrolytic reduction of opianic acid follows a similar path, with formation of isomeric bimeconinyls [114]:



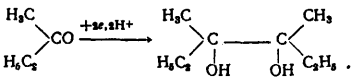
Furfural gives a high yield of hydrofuroin [143]:



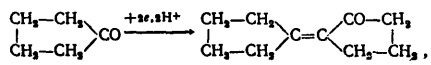
Ketones, like aldehydes, can undergo cathodic hydrodimerisation. Pinacone (tetramethylglycol) is obtained in good yield from acetone [144-165]:



1, 2-Diethyl-1, 2-dimethylglycol can be prepared by electrolytic reduction of ethyl methyl ketone [145]:

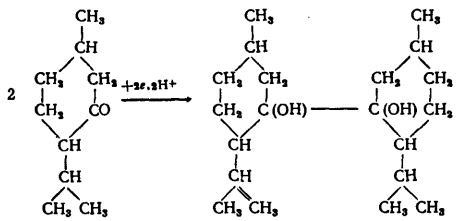


The reduction of cyclopentanone follows a rather unusual path, giving the dimer cyclopentylidenecyclopentanone [2]:

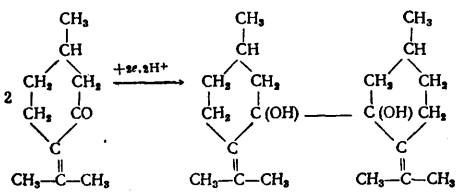


and also some more complex products with up to four molecules of cyclopentanone [166].

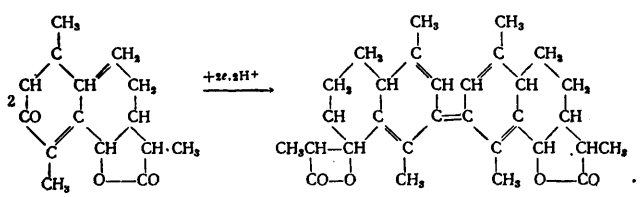
L-Menthone is converted into the corresponding pinacone [167,168]:



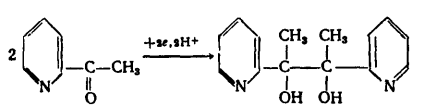
and pulegone undergoes a similar reduction [165]:



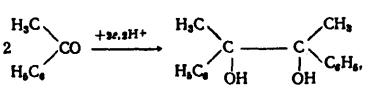
A hydrodimer of santonin has been prepared by electrolytic reduction [169,170]:



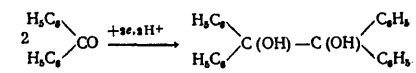
Hydrodimerisation can also be carried out with heterocyclic ketones. This has been demonstrated [171] in the case of acetylpyridine:



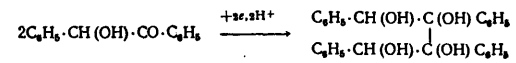
Aromatic ketones, however, have a much higher tendency to form dimeric products. Acetophenone, for example, can be reduced to diphenyldimethylglycol almost quantitatively [140,172]:



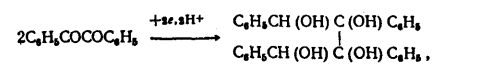
and benzophenone readily gives benzopinacone [145,169,172,178]:



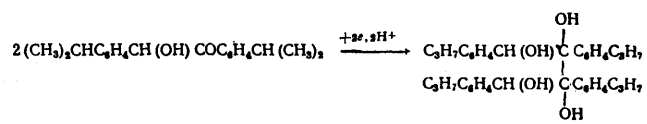
Some derivatives of benzophenone (hydroxybenzophenone, phenyl tolyl ketone, and 2, 4-dimethylbenzophenone) show the same behaviour under conditions of cathodic reductions [145,178]. Benzoin forms 1, 2, 3, 4-tetraphenylerythritol [140]:



The same product was obtained by electrolytic reduction of benzil [140]:



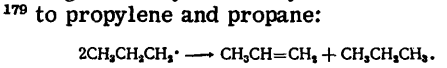
and an analogous hydrodimer was isolated from the acyloin of cumene [141]:



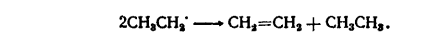
b. Disproportionation Reactions

Disproportionation reactions are one of the less frequently observed types of free radical reaction in the electrolysis of organic compounds.

Salts of saturated aliphatic acids give unsaturated hydrocarbons by disproportionation. Thus, the propyl radicals formed during electrolysis of butyric acid can disproportionate [179] to propylene and propane:



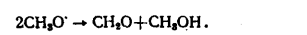
Ethyl radicals from propionic acid form ethylene and ethane [180]:



A similar explanation probably applies to the formation of unsaturated hydrocarbons by the electrolysis of isobutyric [181], valeric [182], and various other acids [183].

The hydrocarbon radicals formed during electrolysis of aliphatic organomagnesium compounds also show a tendency to disproportionate [184]. Propane and propylene are produced by disproportionation during the electrolysis of n-propylmagnesium, and t-butylmagnesium bromide yields isobutane and isobutylene [95].

The methoxy-radicals resulting from the discharge of methoxyl ions in the electrolysis of methanolic solutions of sodium methoxide disproportionate to formaldehyde and methanol [49]:



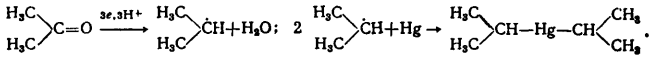
c. Reactions with the Electrode Metal

When organic substances are electrolysed, the electrode is sometimes attacked with formation of organometallic compounds. Reactions of this type appear to be confined almost exclusively to systems in which an aldehyde or ketone is electrolytically reduced at a lead or mercury

cathode. For example, diisopropylmercury has been prepared by electrolysis of acetone with a mercury cathode[185], and diisobutylmercury and dimenthylmercury have been obtained by a similar reaction from ethyl methyl ketone[186] and menthol[187] respectively. At a lead cathode, acetone forms a mixture of diisopropyl- and tetraisopropyl-lead; ethyl methyl ketone forms tetrabutyllead, and diethyl ketone forms tetrapentyllead[188,189].

Organomercury compounds have been isolated and identified when the following ketones are reduced in a sulphuric acid medium: phenylacetone, cyclohexanone, cyclopentanone, 2-, 3-, and 4-methylcyclohexanones[190]. Organolead compounds have been isolated from the electrolysis of various aldehydes[167,191], but not characterised. Electrolysis of aqueous alkaline solutions of acrylonitrile, with a tin cathode, has yielded tetra-(2-cyano-ethyl)-stannane[192].

Processes of this type may be explained by assuming that the primary electrode process forms active free radicals which spontaneously react with the cathode material to form organometallic compounds. For example, the formation of di-isopropylmercury by reduction of acetone at a mercury cathode can be represented by the reaction series:



Similar equations can be written for the other reactions listed above.

We should stress, perhaps, that the formation of organometallic compounds has been observed only with substances capable of giving hydrodimers on electrolytic reduction. This is further proof that the two processes are similar in that as they stem from the reactivity of the resulting free radicals.

Organometallic compounds have also been reported[193] among the products of the electrolytic reduction of alkyl halides at a lead cathode. The first stage of this reaction is obviously the formation of a free radical, by reduction of the alkyl halide, which then reacts with the cathode material.

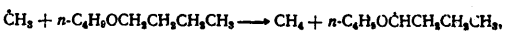
Organometallic compounds have also been detected in some anodic processes. When solutions of organometallic compounds are electrolysed, the anode material is sometimes attacked by the free radicals formed at the anode, resulting in metal exchange as the overall reaction. For example, if diethylzinc (containing ethylsodium) is electrolysed with a lead anode some tetraethyllead is formed[194]. A recently patented[195-198] method of preparation of tetraethyllead involves electrolysis of a triethylaluminium complex salt solution with a lead anode; metallic aluminium is deposited on the cathode.

Similarly, many alkyls of the alkali and alkaline earth metals, of gallium, indium, thallium, silicon, germanium, tin, and lead have been prepared[199] by the electrolysis of a mixture of diethylzinc and triethylaluminium containing lithium and sodium chloride (or fluoride). The preparation of organolead compounds by electrolysis of a solution of a Grignard reagent, using a lead anode, has been described[200,201].

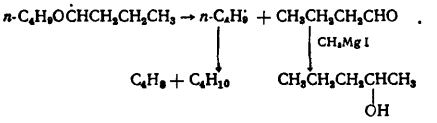
The formation of alkoxides during electrolysis of alcoholic solutions can also be mentioned here. When a solution of sodium methoxide in methanol is electrolysed with a magnesium or copper anode, magnesium or copper methoxide is formed[202]. Clearly, the anode material is attacked by the methoxy-radicals produced at the anode.

d. Interactions with the Solvent

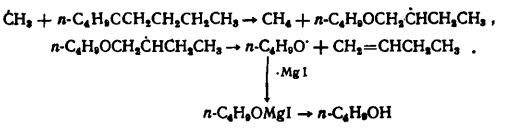
Free radicals can sometimes react with the solvent. The most detailed studies of reactions of this type have been concerned with the electrolysis of organomagnesium compounds. Thus, the methyl radicals formed anodically by the discharge of complex ions during electrolysis of methylmagnesium iodide in di-n-butyl ether undergo the following series of reactions[203-205]:



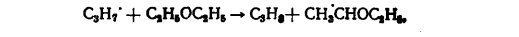
in which a hydrogen atom is abstracted from an $\alpha$-carbon atom of the ether by a methyl radical, the resulting radical undergoing further transformations:



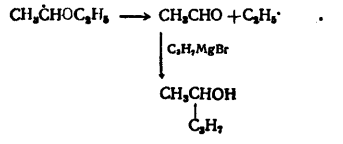
If the methyl radical abstracts a hydrogen atom from the $\beta$-position, the reaction follows a different path:



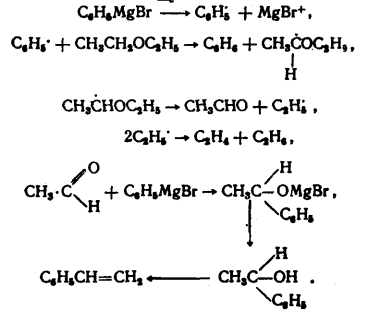
The propyl radical formed during electrolysis of propylmagnesium bromide in diethyl ether reacts as follows:



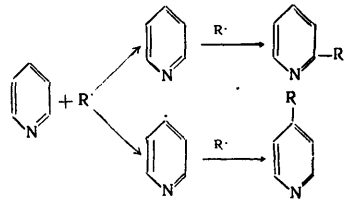
forming propane and a new free radical by solvent interaction. The new radical undergoes further decomposition, of which the final products are pentan-2-ol and an ethyl radical:



Further examples are provided by the reactions of phenyl and benzoyl radicals. Electrolysis of phenylmagnesium bromide in dry diethyl ether produces mainly benzene, styrene, ethane, ethylene, and other products[206], and only traces of biphenyl. The reaction scheme is probably as follows:

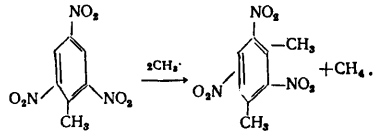


The free alkyl radicals formed in the electrolysis of pyridine solutions of salts of carboxylic acids also attack the solvent:



Reactions of this type have been observed during electrolysis of propionates and butyrates [2] and of benzoates [93].

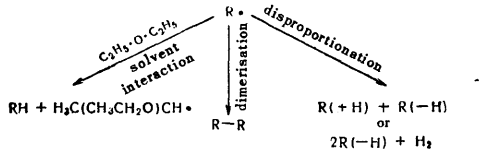
The methyl radicals formed by electrolysis of sodium acetate can react with trinitrotoluene [207]:



The phenyl radical is so reactive that it can remove hydrogen from water and from organic solvents. As a consequence, aromatic acids do not undergo the Kolbe synthesis [208].

This review of the reactivity of the free radicals formed during electrolysis of organic compounds indicates that a great variety of low-molecular-weight products can be expected, and that the path taken by the reaction is controlled by various factors, such as the nature of the radical and of the solvent, the electrode material, and the current density. Unfortunately, the data so far available do not allow us to establish firm relationships between all these factors. Of the few published papers which have dealt with the subject, those discussing the electrolysis of organomagnesium compounds have arrived at the most interesting general conclusions.

The free radicals formed in the electrolysis of organomagnesium compounds behave like typical alkyl radicals: they can react with the solvent, dimerise, or disproportionate. The three possibilities are summarised in the following reaction scheme, which applies to the free radicals formed at the anode when a diethyl ether solution of an organometallic compound is electrolysed:




In practice which reaction predominates is determined largely by the nature of the radical itself.

Some general conclusions concerning the behaviour of alkyl radicals can be made from a study of the relative amounts of the three types of product obtained when different organomagnesium compounds are electrolysed. These are summarised below.

Methyl radicals are the most reactive, and tend to react preferentially with the solvent. The ethyl radicals obtained from the electrolysis of organomagnesium compounds are somewhat less reactive, and undergo a characteristic, nearly quantitative disproportionation. Propyl radicals, on the other hand, tend to dimerise, and undergo solvent interactions and disproportionation only to a minor extent [184].

n-Butyl, isobutyl, and n-hexyl radicals dimerise almost quantitatively [209]. Thus, the stability (and tendency to dimerise) of alkyl radicals is seen to increase with chain length, while disproportionation and reaction with the solvent become progressively less favoured.

We have seen that the phenyl radical is very reactive, and tends to attack the solvent rapidly. The benzyl radical $C_6H_5CH_2^{\cdot}$, on the other hand, is relatively stable and readily gives dimerisation products. The inertness of the benzyl radical stems (quoting Semenov) from the fact that "when a new bond is formed in a reaction of the type:

$$C_6H_5\dot{C}H_2+RH\rightarrow C_6H_5CH_3+R^{\cdot},$$

the electron from the benzyl radical has to be extracted, loosely speaking, from the conjugated system of the benzene ring which in this case behaves very much like a 'negative' substituent. This effect decreases the bond energy and correspondingly increases the activation energy" [210].

The remaining type of free radical process observed in the electrolysis of organic compounds (initiation of polymerisation processes) will be considered in the following section.

### e. Initiation of Polymerisation Processes

We have already stated that electrolytically generated free radicals can interact with unsaturated compounds present in solution to give various addition products. Under certain conditions this can lead to chain polymerisation, with formation of macromolecular products.

Processes of this type have only recently been discovered, and their study has been confined to relatively few systems. Nevertheless, it is already well established that macromolecular products can be formed by electrolysis of the appropriate monomers at current densities of the order of $10^{-4}-10^{-3}$ A $cm^{-2}$. At higher current densities the process stops at the dimer or trimer stage. The use of non-aqueous solvents and a high monomer concentration favours polymerisation.

We shall now discuss some electrode reactions which have led to the formation of macromolecular products.

The radicals formed at the anode in the electrolysis of potassium propionate or acetate (dissolved, respectively, in anhydrous propionic or acetic acid) can initiate the polymerisation of styrene [1]. A similar effect is shown by the radicals formed in the electrolysis of a solution of potassium iodide in anhydrous pyridine [211].

Polymerisation of acrylonitrile can be initiated by cathodically generated radicals when an aqueous solution of a ferric salt and hydrogen peroxide is electrolysed [212], and also in aqueous hydrochloric acid electrolysed with a cathode of high hydrogen overpotential [213].

Acrylonitrile in aqueous solution is not polymerised by sodium amalgam, but in dry dimethylformamide polymeric products of molecular weight between 4100 and 5430 are formed [214].

Methyl methacrylate polymerises fairly readily at a cathode [214,215], giving a polymer of molecular weight proportional to the hydrogen overpotential of the cathode.

Although the number of publications dealing with the electrochemical initiation of polymerisation is quite considerable [216], most of these fail to comment on the mechan-

ism of the relevant electrode processes. The first serious study of cathodic processes in the electrochemically initiated polymerisation of methyl methacrylate was published by Fedorova *et al.*[217], who used polarography as well as isolation of the products formed at a large-area cathode. They initiated the polymerisation of methyl methacrylate by reducing oxygen at a dropping mercury electrode, and showed that the effect of oxygen on the reaction under study is twofold, both inhibition and initiation of the polymerisation process being attributable to the oxygen present in solution. The initiation reaction seems to involve the $HO_2^{\cdot}$ radicals formed at the cathode by the reduction of oxygen:

$$O_2 + e + H^+ \rightarrow HO_2^{\cdot}.$$

No initiation was observed in carefully deoxygenated solutions.

The polymerisation products were also allowed to accumulate for extended periods, so that their molecular weight could be ascertained. These experiments were carried out at constant cathode potential and constant concentration of methyl methacrylate. The molecular weight, deduced from viscosity measurements on benzene solutions of the polymer, was found to be $2.5-3 \times 10^6$. The authors believe that the polymerisation of methyl methacrylate under their experimental conditions proves that free radical intermediates are present in the electrolytic reduction of oxygen.

The F· radical, which appears at the anode when anhydrous hydrogen fluoride is electrolysed, can initiate the polymerisation of chlorotrifluoroethylene[214]. Similarly, tetrafluoroethylene polymerises under the influence of the radicals generated by the electrolysis of trifluoroacetic acid[219].

## 5. BEHAVIOUR OF FREE RADICALS FORMED DURING ELECTROLYSIS

Free radicals formed by electrolysis can differ in their behaviour and properties from the same free radicals prepared by other methods.

This phenomenon must be due to some specific feature of electrochemical reactions, such as the fact that the reaction occurs exclusively at the electrode surface. It follows that high concentrations of free radicals can be expected to arise at the surface of the electrode and in a thin layer of solution immediately adjacent to it: this favours reaction of the resulting free radicals with each other and with the electrode material rather than with the organic molecules in the bulk of the solution. The high concentration of electrolytically formed free radicals in a limited volume of the solution and their short lifetime (due to dimerisation) account for the electrochemical initiation of polymerisation only being possible under a narrow range of conditions.

The peculiarities of electrolytic free radicals can be studied by subjecting differently prepared free radicals to various reactions and comparing their behaviour. Some examples are given below.

A detailed free radical mechanism has been proposed for the processes occurring when potassium propionate solutions in anhydrous propionic acid are electrolysed[220], and for the decomposition of propionyl peroxide.

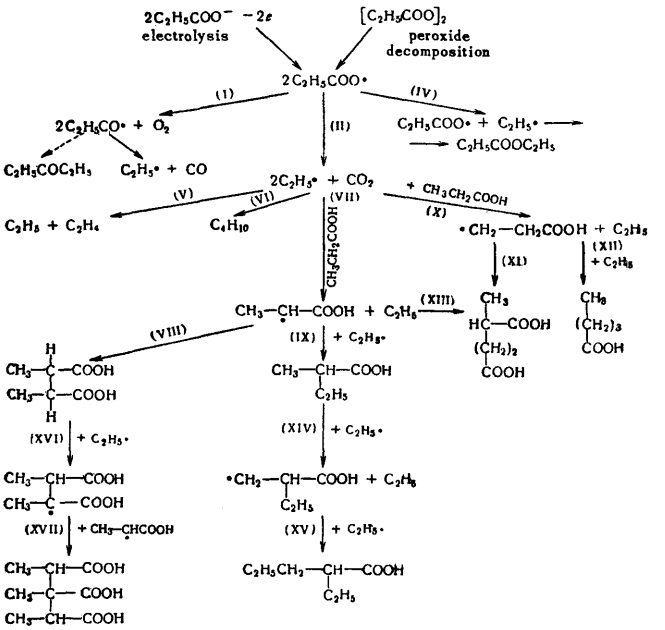
When propionic acid is electrolysed with a platinum anode, propionate ions are discharged and free radicals are formed:

$$2C_2H_5COO^- \xrightarrow{-2e} 2C_2H_5COO^{\cdot}.$$

The decomposition of propionyl peroxide produces the same free radicals:

$$[C_2H_5COO]_2 \rightarrow 2C_2H_5COO^{\cdot}.$$

The $C_2H_5COO\cdot$ radicals, whether chemically or electrochemically prepared, react further to give the same products but in different proportions (see below).

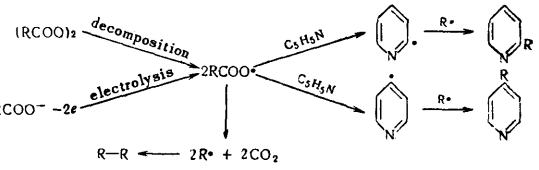



Reactions (I) and (IV), giving diethyl ketone and ethyl propionate respectively, need no comment.

The disproportionation reaction (V) produces ethane and ethylene, whilst the dimerisation reaction (VI) yields butane. All the other products stem from reactions between ethyl radicals and propionic acid in which a hydrogen atom is removed from the $\alpha$- or from the $\beta$-carbon atom of the acid, reactions (VII) and (X) respectively. New free radicals are thus produced, and these react together (XIII), forming methylglutaric acid, or with more ethyl radicals, forming ethylmethylacetic (IX) and butyric acid (XII). The dimerisation reaction (VIII) produces dimethylsuccinic acid which, like ethylmethylacetic acid, undergoes further reaction with ethyl radicals (XIV) and (XVI). The final products are tribasic acids, resulting from the reaction (XVII) between dimethylsuccinic acid and the free radical of reaction (VII). All the other products are also formed by free radical reactions. Thus the mechanism put forward by these authors[220] satisfactorily explains the formation of all the products.

The yield of butane, by reaction (VI), is 15.8% by electrolysis and only 6.9% when the peroxide is decomposed. This is further confirmation that electrolysis favours dimerisation as a result of the high concentration of $C_2H_5^{\cdot}$ radicals at the electrode surface. For the same reason, the yield of ethylene is higher (5.6%) in the electrolytic than in the decomposition reaction (3.0%): disproportionation is more effective under electrolysis conditions.

An even more striking illustration of the abnormal behaviour of electrolytically generated free radicals is provided by comparative studies of the electrolysis of pyridine solutions of acetic, propionic, and butyric acid and of the decomposition, in pyridine, of the corresponding peroxides[221]. The reactions can be summarised as follows:




Electrolysis gives mainly hydrocarbons (by the dimerisation of alkyl radicals), with traces of alkylpyridines. Decomposition of the peroxides, on the other hand, produces alkylpyridines in yields of 84–87%.

To quote one final example of the unusual behaviour of electrolytic free radicals, Lindsey and Peterson[3] have made a study of the electrolysis of alcoholic solutions of potassium acetate and 1,3-butadiene, acidifed with acetic acid. Among the electrolysis products some dimers were detected which must have arisen from the following reactions:

$$2CH_3COO^- \xrightarrow{-2e} 2CH_3COO^{\cdot},$$

$$2CH_3COO^{\cdot} \rightarrow 2\dot{C}H_3 + 2CO_2.$$

Even in the absence of butadiene the methyl radicals produced by electrolysis can recombine to give ethane:

$$2\dot{C}H_3 \longrightarrow C_2H_6.$$

Some of the methyl radicals, however, reacted with the butadiene, giving products of two types:

$$2\dot{C}H_3 + 2CH_2{=}CHCH{=}CH_2 \rightarrow 2CH_3CH_2\dot{C}H{=}CHCH_2^{\cdot} \rightarrow$$

$$\rightarrow CH_3CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH_3 \text{ (deca-3,7-diene)},$$

$$2\dot{C}H_3 + CH_2{=}CHCH{=}CH_2 \rightarrow CH_3CH_2CH{=}CHCH_2CH_3 \text{ (hex-3-ene)}.$$

Analysis of the products showed that in this reaction only some 30 to 50% of the methyl radicals react with butadiene, the remainder recombining to give ethane.

Goffman and Jenner, on the other hand, had shown[222] that the dimerisation of butadiene in the presence of hydroxyl free radicals generated by Fenton's reagent produces exclusively $C_{10}$-dienes: neither ethane nor hex-3-ene were detected among the products. Lindsey and Peterson[3] explain this difference by pointing to the large excess of free radicals (as compared with butadiene) which may exist at the electrode surface, thus greatly increasing the probability of radical–radical reactions.


1. S.Goldschmidt and E. Stockl, Chem.Ber., 85, 630 (1952).
2. S.Goldschmidt, Angew.Chem., 69, 132 (1957).
3. R.Lindsey and M.Peterson, J.Amer.Chem.Soc., 81, 2073 (1959).
4. R.Lindsey and M.Peterson, U.S.P. 2680713 (1954).
5. M.Ya.Fioshin, A.I.Kamneva, L.A.Mirkind, and L.A. Salmin', Dokl.Akad.Nauk SSSR, 138, 173 (1961).
6. S.Wawzonek, J.Electrochem.Soc., 103, 546 (1956).
7. S.Wawzonek, E.Blaha, R.Berey, and M.Runner, J.Electrochem.Soc., 102, 235 (1955).
8. S.Wawzonek and D.Wearring, J.Amer.Chem.Soc., 86, 2067 (1959).
9. D.Paul, A.Lipkin, and S.Weissman, J.Amer.Chem.Soc., 78, 116 (1956).
10. T.A.Kryukova, S.I.Sinyakova, and T.V.Aref'eva, "Polyarograficheskii Analiz" (Polarographic Analysis), Goskhimizdat, Moscow, 1959, pp.412–504.
11. M.von Stackelberg, in "Methoden der organischen Chemie" (J.Houben and T.Weyl), Vol.III/2, Georg Thieme Verlag, Stuttgart, 1955, pp.299–348.
12. H.W.Nürnberg, Angew.Chem., 72, 433 (1960).
13. B.Kastenig and L.Holleck, Z.Elektrochem., 63, 166 (1959).
14. I.A.Korshunov, A.S.Kirillova, and Z.B.Kuznetsova, Zhur. Fiz.Khim., 24, 551 (1950).
15. M.Ashworth, Coll.Czech.Chem.Comm., 13, 299 (1948).
16. P.Elving and J.Leone, J.Amer.Chem.Soc., 80, 1021 (1958).
17. G.Hoijtink and J.von Schooten, Rec.Trav.chim., 71, 1089 (1952).
18. S.I.Zhdanov and A.N.Frumkin, Dokl.Akad.Nauk SSSR, 122, 412 (1958).
19. L.Michaelis, M.Schubert, R.Reber, J.Kuck, and S.Granick, J.Amer.Chem.Soc., 60, 1678 (1938).
20. L.Michaelis, "Oxidations–Reductions–Potentiale" (Translated into Russian), Moscow–Leningrad, 1936, p.130.
21. L.Michaelis, Chem.Rev., 16, 243 (1935).
22. L.Michaelis and M.Schubert, Chem.Rev., 22, 437 (1938).
23. S.G.Mairanovskii, Dokl.Akad.Nauk SSSR, 110, 593 (1956).
24. S.G.Mairanovskii, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Electrochemical Congress), Izd. Akad.Nauk SSSR, Moscow, 1958, p.223.
25. W.Schwarz, E.Kosower, and I.Shain, J.Amer.Chem.Soc., 83, 3164 (1961).
26. L.Holleck and H.Exner, Z.Elektrochem., 56, 416 (1952).
27. W.Kemula and Z.Kublik, Analyt.Chim.Acta, 18, 104 (1958).
28. W.Kemula and Z.Kublik, Nature, 182, 793 (1958).
29. P.Valenta, Coll.Czech.Chem.Comm., 25, 853 (1960).
30. W.Kemula, Z.Grabowski, and M.Kalinowski, Naturwiss., 47, 515 (1960).
31. D.Austen, P.Given, D.Ingram, and M.Plover, Nature, 182, 1784 (1958).
32. W.Reinmuth, C.Reilley, and L.Rogers, Analyt.Chem., 31, 1450 (1959).
33. A.Maki and D.Geske, J.Chem.Phys., 30, 1356 (1959).
34. D.Geske and A.Maki, J.Amer.Chem.Soc., 82, 2671 (1960).
35. A.Maki and D.Geske, J.Chem.Phys., 33, 825 (1960).
36. J.Billon, G.Cauguis, and J.Combrisson, Bull.Soc.chim. France, 2062 (1960).
37. M.Melchior and D.Geske, J.Chem.Phys., 34, 471 (1961).
38. L.Piette, P.Ludwig, and R.Adams, J.Amer.Chem.Soc., 83, 3909 (1961).
39. L.Michaelis, M.Schubert, and S.Granic, J.Amer.Chem. Soc., 61, 1981 (1931).
40. R.Parker and R.Adams, Analyt.Chem., 28, 828 (1956).
41. G.E.Svadkovskaya and S.A.Voitkevich, Uspekhi Khim., 29, 364 (1960) [Russ.Chem.Rev., 161 (1960)].
42. N.Bunge, Ber., 3, 297 (1870).
43. C.Schall, Z.Elektrochem., 2, 475 (1896).
44. C.Schall, Z.Elektrochem., 3, 83 (1896).
45. C.Schall, Z.Elektrochem., 5, 226 (1898).
46. W.Evans and R.Pearson, J.Amer.Chem.Soc., 64, 2865 (1942).
47. F.Hein, Z.Elektrochem., 28, 469 (1922).
48. H.Mulliken, Amer.Chem.J., 15, 323 (1893).
49. G.Glacomello, Gazzetta., 65, 546 (1935).
50. N.Bunge, Ber., 3, 911 (1870).

51. N.D. Zelinskii and N.A. Shilov, Zhur. Russ. Fiz.-Khim. Obshch., 26, 608 (1894).
52. C. Ulpiani and G. Rodano, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., (5), 14, 601 (1905).
53. A.N. Shlygin and G.A. Bogdanovskii, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Electrochemical Congress), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 159.
54. G.A. Bogdanovskii, Thesis, Moscow State University, 1958.
55. T. Iasui, Bull. Chem. Soc. Japan., 10, 306 (1935).
56. N.E. Khomutov, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Electrochemical Congress), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 292.
57. N.E. Khomutov and S.V. Gorbachev, "Trudy III Soveshchaniya po Elektrokhimii" (Proceedings of the Third Electrochemical Congress), Moscow, 1953, p. 584.
58. F. Fichter and F. Braun, Ber., 47, 1528 (1914).
59. A.P. Tomilov, Uspekhi Khim., 30, 1462 (1961) [Russ. Chem. Rev., 639 (1961)].
60. F. Fichter and S. Glantzgtein, Ber., 49, 2473 (1916).
61. French P. 70 829 (1930); Chem. Zentr., II, 1940 (1931).
62. F. Fichter and P. Schonmann, Helv. Chim. Acta, 19, 1411 (1936).
63. E.M. Cherkasova, S.I. Sklyarenko, and N.N. Mel'nikov, Zhur. Obshch. Khim., 9, 1813 (1939).
64. N.N. Mel'nikov, S.I. Sklyarenko, and E.M. Cherkasova, Zhur. Obshch. Khim., 10, 1373 (1940).
65. N.N. Mel'nikov, Zhur. Obshch. Khim., 16, 1025 (1946).
66. V. Ohman, Z. Elektrochem., 42, 862 (1939).
67. H. Schmidt and J. Noack, Z. anorg. Chem., 296, 264 (1958).
68. M. Finkelstein, R. Petersen, and S. Ross, J. Amer. Chem. Soc., 81, 2361 (1959).
69. R. Plump and L. Hammet, Trans. Electrochem. Soc., 73, 523 (1938).
70. K. Brand and D. Krucke-Amelung, Ber., 72, 1029 (1939).
71. K. Brand, Z. Elektrochem., 16, 669 (1910).
72. K. Brand, Ber., 54, 2017 (1921).
73. K. Brand, O. Horn, and W. Bausch, J. prakt. Chem., [2], 127, 240 (1930).
74. K. Brand, Ber., 46, 2939 (1913).
75. K. Brand and M. Matsui, Ber., 46, 2945 (1913).
76. C. Kraus, J. Amer. Chem. Soc., 35, 1732 (1913).
77. N.N. Mel'nikov and M.S. Rokitskaya, Zhur. Obshch. Khim., 7 (69), 2596 (1937).
78. L. Riccoboni, Atti Ist. Veneto Sci. Lett., 96, 183 (1935).
79. C. Hochwalt and G. Calingaert, J. Amer. Chem. Soc., 45, 1821 (1923).
80. F. Hein, A. Klein, and E. Nebe, Ber., 71, 2381 (1938).
81. W. Dehn, Amer. Chem. J., 40, 97 (1908).
82. S. Wawzonek, Analyt. Chem., No. 5, 170 (1960).
83. G. Hoijtink and J. von Schooten, Rec. Trav. chim., 72, 691 (1953).
84. G. Hoijtink, J. von Schooten, E. Boer, and W. Allersberg, Rec. Trav. chim., 73, 355 (1954).
85. E. Müller, Z. Elektrochem., 33, 255 (1927).
86. G. Semerano, Gazzetta, 62, 959 (1932).
87. H. Wilson and K. Wilson, Trans. Electrochem. Soc., 80, 151 (1941).
88. P. Hennig and G. Kimball, J. Chem. Phys., 12, 415 (1944).
89. C. Walling, "Free Radicals in Solution", Wiley, New York, 1957, p. 23.
90. T.I. Temnikova, "Kurs Teoreticheskikh Osnov Organicheskoi Khimii" (The Theoretical Foundations of Organic Chemistry), Goskhimizdat, Leningrad, 1959.
91. A. Brown and J. Walker, Annalen, 261, 125 (1891).
92. S. Glasstone, "An Introduction to Electrochemistry" (Translated into Russian), Inostr. Lit., 1951.
93. F. Fichter and H. Stenzl, Helv. Chim. Acta, 22, 970 (1939).
94. F. Fichter and H. Stenzl, Helv. Chim. Acta, 22, 425 (1939).
95. W. Evans and D. Breitwaite, J. Amer. Chem. Soc., 62, 534 (1940).
96. V.V. Zolotarev, Russ. P. 53766 (1938); Chem. Abs., 35, 1413 (1941).
97. W. Löb, Z. Elektrochem., 7, 603 (1901).
98. F. Fichter and E. Rothenberger, Helv. Chim. Acta, 5, 169 (1922).
99. J. Meyer, Helv. Chim. Acta, 8, 74 (1925).
100. J. Herszbein, Helv. Chim. Acta, 11, 1264 (1928).
101. A.I. Lebedeva, Dokl. Akad. Nauk SSSR, 42, 71 (1944).
102. F. Fichter and M. Rinderspracher, Helv. Chim. Acta, 10, 104 (1927).
103. K. Ono, J. Chem. Soc. Japan, 42, 559 (1921).
104. F. Fichter and H. Ris, Helv. Chim. Acta, 7, 808 (1924).
105. F. Ficher and E. Brunner, Bull. Soc. chim. France (4), 19, 281 (1916).
106. B. Emmert, Ber., 42, 1999 (1909).
107. I.L. Knunyants and N.P. Gambar'yan, Uspekhi Khim., 23, 786 (1954).
108. A.G. Pozdeeva and A.G. Volkov, Zhur. Prikl. Khim., 25, 1058 (1952).
109. R. Patzak and L. Neugebauer, Monatsh., 83, 776 (1952).
110. B. Emmert, Ber., 46, 1716 (1913).
111. N.S. Drozdov, Zhur. Obshch. Khim., 3, 351 (1933).
112. F. Ahrens, Z. Elektrochem., 2, 577 (1896).
113. V.V. Levchenko, Zhur. Obshch. Khim., 18, 1245 (1948).
114. V.M. Rodionov, V.V. Belov, and V.V. Levchenko, Zhur. Obshch. Khim., 5, 1817 (1935).
115. V.V. Levchenko, Zhur. Obshch. Khim., 17, 1656 (1947).
116. V.V. Levchenko, Zhur. Obshch. Khim., 18, 1245 (1948).
117. J. Stock, J. Chem. Soc., 586 (1949).
118. J. Stock, J. Chem. Soc., 763 (1949).
119. V.V. Levchenko and A.A. Zats, Zhur. Obshch. Khim., 22, 1253 (1952).
120. V.V. Levchenko and A.A. Zats, Zhur. Obshch. Khim., 22, 2072 (1952).
121. H. Low, J. Chem. Soc., 101, 1544 (1912).
122. J. Wiemann and Ch. Clachet, Compt. rend., 226, 923 (1948).
123. R. Pasternak, Helv. Chim. Acta, 31, 735 (1948).
124. J. Wiemann and P. Maitte, Bull. Soc. chim. France, 430 (1952).
125. J. Wiemann and M. Jon, Bull. Soc. chim. France, 285 (1955).
126. J. Wiemann and M. Jon, Bull. Soc. chim. France, 1125 (1958).
127. N. Thooi and J. Wiemann, Compt. rend., 247, 212 (1958).
128. G. Shima, Mem. Coll. Sci., Kyoto Univ., 12A, 327 (1929).
129. C. Wilson and K. Wilson, Trans. Electrochem. Soc., 80, 136 (1941).
130. C. Wilson, Trans. Electrochem. Soc., 75, 353 (1939).
131. E. Isaacs and C. Wilson, J. Chem. Soc., 810 (1936).
132. C. Wilson, Trans. Electrochem. Soc., 92, 369 (1947).
133. C. Wilson and K. Wilson, Trans. Electrochem. Soc., 84, 153 (1943).
134. S. Ono and M. Uchara, J. Chem. Soc. Japan, 78, 929 (1957).
135. I.L. Knunyants and N.S. Vyazankin, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Electrochemical Congress), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 226.
136. German P. 274 201 (1912); Friedl., 11, 793.
137. German P. 277 392 (1913); Friedl., 12, 563.
138. German P. 292 865 (1912); Friedl., 12, 905.
139. H. Kauffmann, Z. Elektrochem., 2, 365 (1895); 4, 461 (1898).
140. M. Allen, J. Org. Chem., 15, 435 (1950); J. Amer. Chem. Soc., 72, 3797 (1950).
141. H. Lowy, J. Chem. Soc., 89, 1512 (1906).
142. V.M. Rodionov and V.V. Levchenko, Zhur. Obshch. Khim., 6, 1563 (1936).
143. W. Albert and A. Lowy, Trans. Electrochem. Soc., 75, 87 (1939).

144. German P. 113719 (1899); Friedl., 6, 22.
145. K. Brand and K. Elbs, Z. Elektrochem., 8, 783 (1902).
146. J. Tafel and S. Schmitz, Z. Elektrochem., 8, 288 (1902).
147. German P. 172644 (1903); Friedl., 8, 113.
148. J. Tafel and W. Schepass, Z. Elektrochem., 17, 974 (1911).
149. German P. 252759 (1912); Friedl., 11, 538.
150. German P. 303303 (1917); Friedl., 13, 69.
151. German P. 306304 (1917); Friedl., 13, 67.
152. German P. 306523 (1917); Friedl., 13, 68.
153. German P. 310023 (1918); Friedl., 13, 70.
154. German P. 324920 (1918); Friedl., 13, 72.
155. German P. 324919 (1918); Friedl., 13, 69.
156. S. Calvert, India Rubber and Tire Rev., 26, 52 (1926).
157. N. Kameyama and K. Takahashi, J. Soc. Chem. Ind., Japan, 36, 174 (1933).
158. H. Wilson and K. Wilson, Trans. Electrochem. Soc., 80, 151 (1941).
159. J. Henry, P. Drumm, and W. O'Connor, Proc. Roy. Irish Acad., 50B, 219 (1945).
160. U.S.P. 2408036 (1946); Chem. Abs., 41, 345a (1947).
161. U.S.P. 2408101 (1946); Chem. Abs., 41, 346a (1947).
162. U.S.P. 2422468 (1947); Chem. Abs., 41, 5805g (1947).
163. O. Slotterbeck, Trans. Electrochem. Soc., 93, 377 (1947).
164. Jap. P. 7310 (1954); Chem. Abs., 50, 3931B (1956).
165. Jap. P. 1830 (1954); Chem. Abs., 49, 82 (1955).
166. M. Godchot and F. Taboury, Bull. Soc. chim. France (5), 13, 12 (1913).
167. H. Law, J. Chem. Soc., 101, 1016, 1544 (1912).
168. M. Matsui and S. Shimizu, Mem. Coll. Sci., Kyoto Univ., 4, 245 (1920).
169. E. Pannain, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat. (5), 17, 499 (1908).
170. E. Pannain, Gazzetta, 39, 515 (1909).
171. M. Allen and H. Cohen, J. Electrochem. Soc., 106, 451 (1959); J. Chem. Soc., 757 (1961).
172. E. Müller, Z. Elektrochem., 16, 236 (1910).
173. K. Elbs, Z. Elektrochem., 7, 644 (1901).
174. W. Cohen, Rec. Trav. chim., 38, 83 (1919).
175. S. Swann, Trans. Electrochem. Soc., 63, 239 (1933).
176. S. Swann, Trans. Electrochem. Soc., 64, 312 (1933).
177. S. Swann, S. Briggs, V. Neklutin, and A. Jedome, Trans. Electrochem. Soc., 80, 26 (1941).
178. G. Shima, Mem. Coll. Sci., Kyoto Univ., (A), 13, 315 (1930).
179. H. Hofer and M. Moest, Annalen, 323, 290 (1902).
180. J. Petersen, Z. phys. Chem., 33, 99 (1900).
181. N. Bunge, Zhur. Russ. Fiz.-Khim. Obshch., 21, 552 (1889)
182. J. Petersen, Z. phys. Chem., 33, 306 (1900).
183. F. Fichter, "Organische Elektrochemie", Dresden, 1942.
184. O. A. Reutov, "Teoreticheskie Problemy Organicheskoi Khimii" (Theoretical Problems in Organic Chemistry), Izd. Moskov. Univ., 1956.
185. C. J. Haggerty, Trans. Amer. Electrochem. Soc., 56, 421 (1929).
186. J. Tafel, Ber., 36, 3626 (1906).
187. C. Schall and W. Kirst, Z. Elektrochem., 29, 537 (1923).
188. J. Tafel, Ber., 44, 323 (1911).
189. G. Renger, Ber., 44, 337 (1911).
190. T. Arai, Bull. Chem. Soc. Japan, 32, 184 (1959).
191. W. Schepps, Ber., 46, 2564 (1913).
192. A. P. Tomilov and L. V. Kaabak, Zhur. Prikl. Khim., 32, 2600 (1959).
193. U.S.P. 1539297 (1925); Chem. Zentr., II, 761 (1925).
194. F. Hein, Z. anorg. Chem., 141, 161 (1926).
195. K. Ziegler and H. Lehmkul, Angew. Chem., 67, 424 (1955).
196. B. P. 842090 (1960); Chem. Abs., 55, 5199e (1961).
197. B. P. 814609 (1959); Chem. Abs., 53, 17733c (1959).
198. B. P. 848364 (1960); Chem. Abs., 55, 5199i (1961).
199. B. Roetheke and J. Simpson, B. P. 797093 (1958); Chem. Abs., 53, 930B (1959).
200. U.S.P. 3007858 (1959); Chem. Abs., 56, 4526i (1962).
201. B. P. 839172 (1960); Chem. Abs., 54, 24036i (1960).
202. B. Szilard, Z. Elektrochem., 12, 393 (1906).
203. W. Evans and F. Lee, J. Amer. Chem. Soc., 56, 654 (1934).
204. W. Evans, J. Amer. Chem. Soc., 58, 720, 2284 (1936).
205. W. Evans and D. Braithwaite, J. Amer. Chem. Soc., 61, 898 (1939).
206. W. Evans, R. Pearson, and D. Braithwaite, J. Amer. Chem. Soc., 63, 2574 (1941).
207. L. Fieser, R. Clapp, and W. Daudt, J. Amer. Chem. Soc., 64, 2052 (1942).
208. W. A. Waters, "The Chemistry of Free Radicals" (Translated into Russian), Inostr. Lit., Moscow, 1948.
209. M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", New York, 1954, pp. 109–115.
210. N. N. Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems in Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958.
211. W. McEwen, J. Jang, and J. Kleinberg, J. Amer. Chem. Soc., 79, 5833 (1957).
212. C. Wilson, Record. Chem. Progr., 10, 25 (1949).
213. W. Kern and H. Quast, Makromol. Chem., 10, 202 (1953).
214. G. Parravano, J. Amer. Chem. Soc., 73, 628 (1951).
215. E. Dinnen, T. Schwann, and C. Wilson, Trans. Electrochem. Soc., 96, 226 (1949).
216. M. Ya. Fioshin and A. P. Tomilov, Plasticheskie Massy, No. 10, 2 (1960).
217. A. I. Fedorova, I. V. Shelepin, and N. B. Moiseev, Dokl. Akad. Nauk SSSR, 138, 165 (1961).
218. D. Goerrig, H. Jonas, and W. Moschel, German P. 935867 (1955); Chem. Abs., 53, 3949h (1959).
219. D. Goerrig and H. Jonas, German P. 937919 (1956); Chem. Abs., 53, 3950a (1959).
220. S. Goldschmidt, W. Leicher, and H. Maas, Annalen, 577, 153 (1952).
221. S. Goldschmidt and M. Minsinger, Chem. Ber., 87, 956 (1954).
222. D. Goffman and E. Jenner, J. Amer. Chem. Soc., 80, 2872 (1958).

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## METAL COMPLEXES OF HYDROXY-ACIDS

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