Translated from *Uspekhi Khimii*, **44**, 2088 - 2119 (1975) U.D.C. 541.138 : 541.64

Anodic Dimerisation, Addition and Substitution Reactions of Organic Compounds

L.A.Mirkind

The review deals with certain general characteristics of the behaviour of organic substances at high positive potentials, which determine the mechanism and kinetics of anodic dimerisation (condensation), addition, and substitution reactions. A systematic account is given of the most significant results of studies in recent years on organic electrosynthesis based on the above classes of reactions.
The bibliography includes 303 references.

CONTENTS

I.	Introduction	999
II.	Certain characteristics of anodic processes at high positive potentials	1000
III.	Characteristics of the adsorption of neutral organic substances on oxidised platinum	1002
IV.	Anodic dimerisation reactions	1005
V.	Anodic addition reactions	1009
VI.	Substitution reactions	1010

I. INTRODUCTION

There has been a considerable growth in recent years of research on anodic dimerisation (condensation), addition, and substitution reactions dealing with the study of the kinetics and mechanism of anodic processes and with the development on the basis of the above classes of reactions of effective methods for the electrochemical synthesis of various monofunctional and polyfunctional compounds which are valuable intermediates in many branches of polymer chemistry and organic synthesis. Since a systematic account has been given of the data accumulated in 1970–1971 in a number of special reviews dealing with the problem as a whole [1-3] or with individual classes of reactions [4-8], we shall confine ourselves to the consideration of the results in later publications, concentrating attention on general characteristics and also on certain problems concerning which there is still controversy in the literature.

The enhanced interest in the study of reactions of the above classes has been aroused primarily by the fact that the electrochemical methods for carrying them out have many advantages over chemical methods [9,10].

1. The anodes used for the oxidation (platinum, graphite, lead dioxide, etc.) are inert, in contrast to chemical oxidising agents which give rise to undesirable side reactions. There is also no need for the subsequent separation of the oxidant reduction products.

2. The possibility of a smooth variation of the potential within wide limits makes it possible to achieve selective reactions in the presence of several oxidisable groups or of degrees of oxidation and also to carry out oxidations in the same apparatus under conditions ranging from very mild to very severe.

3. It is easy to control the changes in the nature and rate of formation of the intermediate species by regulating the potential and anodic current density and by modifying the electrical double layer, which makes it possible to generate under mild conditions high local concentrations of such species in the vicinity of the electrode and this frequently facilitates a selective or specific course of the reaction.

4. Since the electron transfer is determined by the changes in the anodic potential, the temperature can be in many instances freely selected, which is also an important preparative advantage†.

The above characteristics are responsible for the specific features of the reaction pathways and the products formed in anodic reactions and in many cases make it possible to achieve processes which either have no chemical analogues or lead to the same products in a simpler way. As an example one may quote the reactions of organic-inorganic synthesis in the electrolysis of mixtures of organic (acetic, propionic) and inorganic (sulphuric, perchloric, nitric) acids [11-14]. At low temperatures (−20°C) and high potentials ($\varphi \geqslant 3.0$ V) peroxy-compounds having the general formula $RCOOOR_1$ are formed at a platinum anode in concentrated acid solutions:

$$RCOO^- + R_1O^- \xrightarrow{-2e} RCOOOR_1;$$
$$R=CH_3,\ C_2H_5;\ R_1=SO_3H,\ ClO_3,\ NO_2\ .$$

The chemical procedures for the preparation of such substances are fairly complex.

There are also no chemical analogues of addition reactions such as the carboxydimerisation of conjugated dienes resulting in the formation of higher unsaturated dicarboxylic acids [15]:

$$2\,(HOOC)_2 + 2\,C_nH_{2n-2} \xrightarrow{-2e,-2H^+,-2CO_2} HOOC\,(C_nH_{2n-2})_2\,COOH;$$

the synthesis of dicarbonyl compounds in the oxidation of sodium dimethylmalonate and sodium acetylacetonate in the presence of styrene or ethyl vinyl ether [10,16] ($k = 1$ or 2):

$$2\,(RCO_k)_2CH^- + \rangle\!=\!\langle^{Y} \xrightarrow{-2e} (RCO_k)_2CH\left(\begin{array}{c}|\\-\!-\!-\\|\end{array}{}^{Y}\right)_k CH\,(CO_kR)_2;$$

and the anodic aroyloxylation of 1,3-dienes [17,18]:

$$2\ XArCOO^- + C_nH_{2n-2} \xrightarrow{-2e} XArCOOC_nH_{2n-2}OOCArX;$$
$$X=C_nH_{2n+1},\ C_nH_{2n+1}OOC,\ OH\ .$$

† Reactions involving unstable radicals, for example RCOO·, the occurrence of which is promoted by low temperatures, constitute an exception [14].

The unusual features of the reaction pathways in anodic processes of the above classes are determined in many respects also by the fact that at least the individual stages of these processes are electrocatalytic, since they occur at an interface and depend significantly on the state of the electrode surface.

II. CERTAIN CHARACTERISTICS OF ANODIC PROCESSES AT HIGH POSITIVE POTENTIALS

The majority of anodic dimerisation, addition, and substitution reactions require comparatively high positive potentials (1.5–3.5 V) and, in order to understand their mechanism, it is necessary to take into account many common features of electrode processes under these conditions.

At high anodic potentials the oxidation of the substrate is in most cases accompanied by the oxidation of the solvent usually employed (water, lower aliphatic alcohols, acetone, etc.). Under these conditions, there is a change in the state of the electrode surface and in the composition and bonding energies of the adsorbed components of the electrolyte and the oxidation intermediates, which is inevitably reflected in the direction or relative rates of secondary chemical reactions.

The water in the electrolyte, which is almost always present as an impurity even in dried organic solvents, leads to the liberation of oxygen, accompanying the oxidation of the organic substance. On platinum metals (which are most frequently used), certain oxides are formed, which alter sharply the adsorption and catalytic properties of the surface and lead to a decrease of the effective potential in the zone corresponding to the formation of the transition state of the species undergoing oxidation.

It is therefore reasonable that, in the study of the mechanisms of such reactions, it is necessary to take into account in the first place the influence of heterogeneous factors on the rate and direction of electrode processes. It is also necessary to discover whether chemical reactions preceding electron transfer (including those accompanied by the adsorption of the neutral substrate or oxidation intermediates) occur and also the requirements for the orientation of the molecule on the electrode surface and the preferred orientation. It is essential to determine the nature of the oxidant (the electrode itself, oxygen, or the intermediates in the oxidation of water and OH^- ions), the species being oxidised, and the intermediates formed initially (radicals, radical-ions, or ions), and the sequence of stages in their reactions.

In certain cases it is possible to determine the nature of the primary product formed on the electrode by direct measurements. For example, the formation of phenylacetoxy-radicals in the oxidation of phenylacetic acids in acetonitrile has been demonstrated[19,20] by ESR; the influence of the solvent on the hyperfine structure of the spectrum indicates the stabilisation of the radicals by solvation effects. The formation of adsorbed phenoxy-radicals in the oxidation of sterically hindered phenols (SHP) on a graphite electrode over a wide pH range has been demonstrated by ESR.[21] This finding shows that, in both alkaline and in acid and neutral solutions, the primary step in the electrochemical oxidation of SHP is a one-electron transition. Analysis of the ESR spectra in the oxidation of substituted phenols on platinum and of stable phenoxy-radicals on graphite leads to a similar conclusion[23].

However, the above problems have not been fully elucidated for any reaction of the classes under consideration, largely because of experimental difficulties associated with the study of electrode processes and potentials in excess of the reversible oxygen potential (φ_0). In most cases the methods used as low potentials for the unoxidised metal are insufficiently effective under these conditions and the adsorption and kinetic characteristics discovered for dilute aqueous solutions of simple organic substances at $\varphi < \varphi_0$[22] cannot be reliably extrapolated to this region[2,3,24,25]. When non-aqueous solvents are used, addition complications arise.

Nevertheless vigorous studies in recent years of new methodological approaches to the investigation of electrode processes under these conditions and the combined application of various electrochemical[26-41], optical-spectroscopic[42-48], radiochemical[49-56], mass-spectrometric[57], electron diffraction[58-60], and conductimetric[61] methods together with methods based on the identification of the products of potentiostatic electrolysis[2,3,62-64] have already made possible certain qualitative or semiquantitative generalisations. This applies in the first place to problems concerning the state of the electrode surface (mainly the platinum electrode) over a wide range of potentials and its influence on the direction and rate of electrochemical reactions. However, most of the studies have dealt with inorganic systems. Among these mention should be made in the first place of the series of investigations by Veselovskii, Kasatkin, Yakovleva, and coworkers on the synthesis of oxidants at high positive potentials[63,64] and also by Tyurin and coworkers on the oxygen evolution reaction on platinum metals[26-29,65-68]. Among reactions involving organic substances, only the electrochemical oxidation of carboxylates has been studied in this way[69].

Numerous experimental data confirming the thesis of the decisive influence of the compositions and properties of surface compounds of the electrode with the components of the solution and the intermediates in the electrochemical oxidation on the direction and rate of electrode reactions at $\varphi > \varphi_0$ have now accumulated. Unfortunately in most of the studies devoted to preparative organic electrochemical synthesis at high anodic potentials this factor has so far been ignored and the conclusions concerning the mechanism are reached mainly on the basis of a comparison of the composition of the products of the electrolysis and the corresponding chemical reactions. The necessity to take into account the characteristics of the surface phenomena, in particular the adsorption processes at the electrode/solution boundary, has been acknowledge in only a few studies carried out in recent years[70-78].

The $i-\varphi$ curves and the variation of the double layer capacitance, the adsorption pseudocapacitance, and the polarisation resistance with the potential, measured in solutions of different compositions at platinum metals, gold, and graphite, exhibit sharp breaks, maxima, and minima. As an illustration, Fig. 1 presents $\lg i-\varphi$ curves for a solution of monomethyl glutarate in methanol using gold (curve *1*), iridium (curve *2*), rhodium (curve *3*), platinum (curve *4*), pyrographite (curve *5*), and vitreous carbon (curve *6*)[77] electrodes, while Fig. 2 illustrates the variation of the double layer capacitance with potential at smooth platinum in 1 *N* H_2SO_4 solutions with added $n\text{-}C_5H_{11}COOH$ obtained by an a.c. bridge method[28].

In many cases the reaction is inhibited by the electrolyte component which begins to be oxidised vigorously at a value of φ more positive than that corresponding to the potential jump or current (capacitance) drop. Fig. 3 presents plots of polarograms, in terms of semilogarith-

mic coordinates, recorded at a rotating platinum anode in alkaline solutions of pelargonic acid[78]. Evidently, with increase of the concentration of the carboxylate anion, the oxidation of which with formation of hexadecane takes place mainly at potentials corresponding to section V, there is a decrease of both the potential and the maximum current of the discharge of the OH^- ion—the dominant oxidation process along the lower sections.

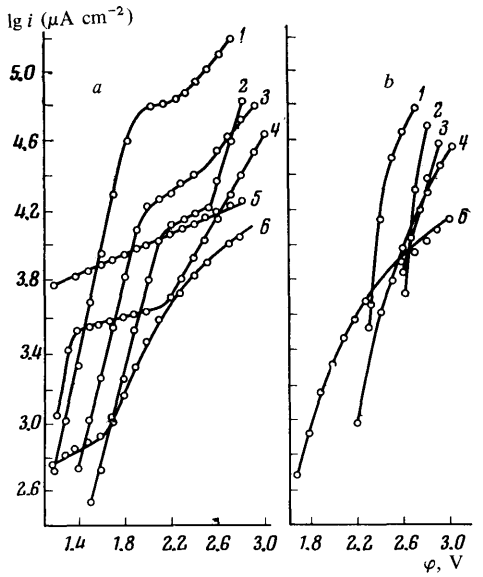


Figure 1. Anodic polarisation curves (*a*) and partial polarisation curves (*b*) for the oxidation of monomethyl glutarate in a methanol solution of 0.3 M $CH_3OOC(CH_2)_3$. .$COONa$ + 1 M $CH_3OOC(CH_2)_3COOH$ on electrodes made of different materials.

The adsorption of stable final or intermediate products[79,80] and the electrolyte anions[81,82], the change in the rate-determining stage[83-86], and the formation of surface oxides[26-29,38,64,88] have been considered in the literature as the probable causes of the inhibition of electrochemical oxidation and of the change in the properties of the interface in various systems. In many instances the relation between the surface coverage, the composition and properties of the chemisorbed products of the dissociation of water (OH^-), and the kinetic properties of the oxidation reactions were characterised quantitatively[28,29,38,67,88,90].

A wide variety of surface oxygen compounds of platinum metals and gold are known to exist[91-95]. The number of studies dealing with the nature and stoichiometry of surface oxides, their relative stabilities, the conditions governing their formation and interconversions, and their involvement in oxygen evolution reactions and in oxidation of organic substances greatly increased in recent years. The greatest number of studies have dealt with platinum[24-32,36,38,40,43,48,96-102], much less attention being devoted in this respect to graphite[39,101,104,106], gold[33,37,42,43], palladium[33,52,107], iridium[102,103], ruthenium[102], and rhodium[102,108-110].

Potentiodynamic measurements in solutions of inorganic acids and alkalies[26,27,56,83,85,111,112] have shown that the overall degree of coverage of the surface of smooth platinum by chemisorbed oxygen increases monotonically up to potentials φ_r‡ ≃ 2.1 V and reaches a limiting value (2.3–2.7 monolayers), which no longer changes as the potential is increased further (Fig. 4).[56]§

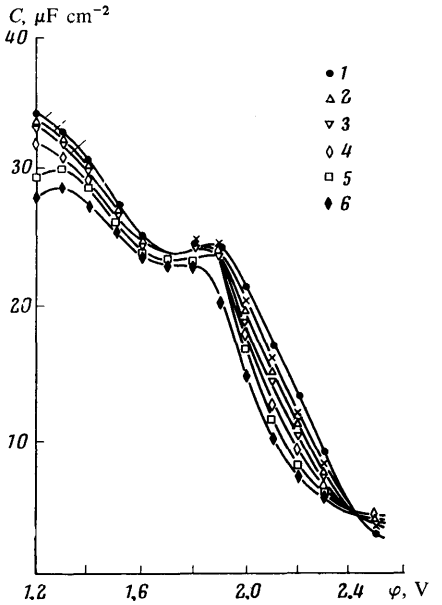


Figure 2. Variation of the double layer capacitance with potential on smooth platinum in 1 *N* H_2SO_4 with added $n\text{-}C_5H_{11}COOH$ at different molar concentrations: 1) 0; 2) 3×10^{-5}; 3) 10^{-4}; 4) 3×10^{-4}; 5) 10^{-3}; 6) 3×10^{-3}.

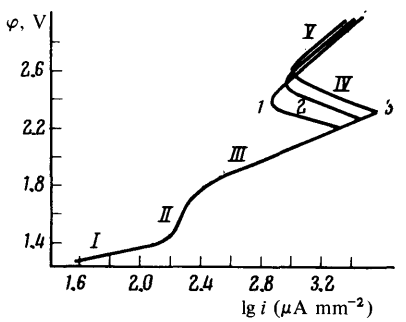


Figure 3. Anodic polarograms obtained on platinum in 0.5 *N* $NaOH + xN$ $CH_3(CH_2)_7COONa$ solutions for different *x*: 1) 1; 2) 0.5; 3) 0.1; the rate of application of potential was 10 mV s^{-1}.

‡ φ_r is the potential relative to the hydrogen electrode in the same solution.

§ Q_O and Q_H are the amounts of electricity consumed in the reduction of oxygen and the "deposition" of hydrogen respectively.

At $\varphi_r = 1.4-1.6$ V monolayer coverage by the oxide is attained, the oxide being reduced at $\varphi_r \simeq 0.6$ V (the so called first form of the oxide); at higher potentials the second form of the oxide is formed, being reduced at hydrogen adsorption potentials ($\varphi_r \simeq 0.2$ V). Multilayer bulk-phase deposits are formed in the range $\varphi_r = 2.1$ to 2.3 V,[26,27,59,113-115], mainly in dilute solutions at an elevated temperature, evidently only after the saturation of the surface by chemisorbed oxide layers and at a small number of active centres on the metal[27]. For both platinum and gold electrodes, a significant change in the properties of the surface oxide with time has been noted, in consequence of the increase of bonding energy or the incorporation of oxygen atoms in the crystal lattice of the subsurface layers of the metal.

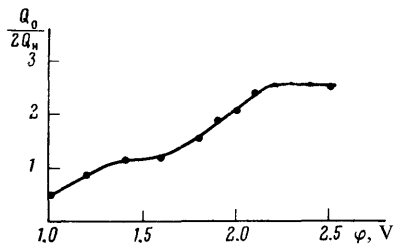


Figure 4. Variation of the degree of surface coverage of smooth platinum by chemisorbed oxygen with potential.

The oxides on platinum belonging to the second form are chemically inert with respect to many organic (and inorganic) substances; an increase of the degree of surface coverage by an oxide of the second form θ_{OII} in the range 1.6–2.3 V results in the inhibition of the electrochemical oxidation of the majority of the compounds investigated, which is reflected in a decrease of the current or an increase of the Tafel slope. The influence of the surface coverage of the platinum electrode by chemisorbed oxygen on the inhibition of the electrochemical oxidation of organic substances has been characterised quantitatively in some investigations[24-29,62,90].

The adsorption of oxygen on platinum at high positive potentials has a competitive mechanism: depending on the concentration and nature of the substance, the fraction of the surface atoms O_{ads} [or other intermediates in the oxygen evolution reaction (OEV)] displaced by the specifically adsorbed inorganic anions, neutral atoms (for example Cl°), or organic compounds changes[24-29,34,35,38,46,65-68,88].

The behaviour of organic substances has been so far inadequately investigated along these lines. In contrast to the range of low potentials, it is much more difficult to determine the structure of the adsorbed species on an oxidised electrode and the nature of their interaction with the surface (associative or dissociative); there are very few data concerning the surface phenomena on electrodes in non-aqueous solvents. The quantitative study of the adsorption of neutral molecules of high potentials involves significant methodological difficulties. These processes are in fact of great importance for the classes reactions under consideration, since it has been shown in recent years[1-3] that the adsorption of a neutral substrate predetermines the efficiency and mode of addition and substitution processes involving short-lived radicals and radical-ions generated on the electrode surface as a result of charge transfer.

III. CHARACTERISTICS OF THE ADSORPTION OF NEUTRAL ORGANIC SUBSTANCES ON OXIDISED PLATINUM

The possibility of the chemisorption of organic molecules on platinum at potentials exceeding significantly that of the reversible oxygen electrode (up to $\varphi_r = 3.0$ V) has been established[116,117] for conjugated dienes and then for other systems[24,25,35,55,118,129]. In recent years this phenomenon has been investigated vigorously by Tyurin and coworkers, who demonstrated the general nature of the adsorption characteristics at high potentials discovered previously[26-29,67,68,133]. It is useful to consider this problem in greater detail, since the existence of this effect is, on the one hand, of fundamental importance for the understanding of the mechanisms of the majority of reactions of the classes being considered and, on the other hand, in many studies it has hitherto been either denied or simply ignored in the discussion of the possible reaction pathways. In the majority of investigations the impossibility of appreciable adsorption of neutral molecules in the range of potentials corresponding to vigorous evolution of oxygen and coverage of the surface by oxides is postulated *a priori*.

On the basis of earlier data[116-119], Kuhn and Sunderland[120] recently investigated the possibility of the adsorption of certain olefins by analysing their oxidation products in aqueous solutions and concluded that the nature of the substances formed (their amount is extremely small owing to the negligible solubility of the olefin) may be interpreted from the standpoint of homogeneous reactions. Therefore, according to the authors[120] the effects observed previously[116-119] may be identified as a result of physical adsorption. It must be emphasised that a one-sided study of the nature of the oxidation products only is hardly a fruitful procedure for obtaining evidence for adsorption and even less so for the determination of its energy characteristics or steric effects. This must be mentioned because such an approach has been widely used recently—for example in studies of anodic substitution reactions with participation of indane[73-76] and stilbene[70] and of the postanodic condensation of carboxylates[71,72], in which unusual directing effects of the substituents and relative amounts of isomeric products were observed. Without casting doubt on the possibility of the adsorption of the substrate in the reactions considered, one must emphasise that such results can be associated also with other features of electrochemical oxidation reactions, for example with a structure which is not characteristic of chemical analogues or with a high local concentration of intermediate species[121,123].

In order to investigate the adsorption of organic substances at high positive potentials, indirect electrochemical methods were mainly used previously, namely coulometric adsorption displacement methods, methods involving a diminution of the capacitance or pseudocapacitance, and the method based on the inhibition of oxidation reactions[2,3]. However, it has been emphasised[2,24,56] that they all suffer from significant limitations and probably yield reliable information only when several are combined. In certaininstances there is a quantitative

correspondence between all the criteria of surface coverage by an organic adsorbate, characteristic of each of these methods, as has been observed, for example, in the adsorption of pentyl alcohol and valeric acid on platinum (Fig. 5).[28] However, all the methods enumerated are based on a number of assumptions. As shown for the adsorption of ethylene[124], aliphatic alcohols[125], and dienes in methanol solutions of oxalic acid[15], cycloalkanes[25,35], and chloride ions[126], they do not always permit an unambiguous interpretation of experimental data, leading to results such as negative adsorption, negative slopes of kinetic isotherms, etc. When the potentiodynamic rapid cathodic pulse method, which has been widely used for adsorption measurements at $\varphi > \varphi_0$, is applied, the conditions governing the correct determination of θ by the integration of $i-\varphi$ curves are not always ensured (and may not hold) since no account is taken of the possible change in the stoichiometry of the displacement[127] and of the influence of the adsorbate on the maximum surface coverage by electrochemically active species and on the kinetics of their reduction under pulsed conditions. The separation of the effects due to the blocking of the active centres of the metal and the inhibition of the reduction of the chemisorbed oxygen is usually difficult[68].

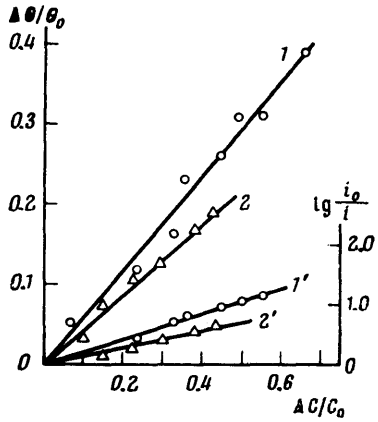


Figure 5. Variation of the inhibition coefficients for the oxygen evolution reaction $\lg(i_0/i)$ (lines *1'* and *2'*) and for the displacement of oxides $\Delta Q/Q_0$ (lines *1* and *2*) with the depression of the capacitance $\Delta C/C_0$ for 1 *N* H_2SO_4 + n-$C_5H_{11}OH$ (lines *1* and *1'*) and 1 *N* H_2SO_4 + n-$C_5H_{11}COOH$ (lines *2* and *2'*) at $\varphi = 2.2$ V; the circles on the straight lines correspond to different concentrations of additives.

It is therefore useful to compare the results obtained by electrochemical methods with data derived from direct adsorption measurements. The fruitfulness of this approach has been emphasised[124]. The study of the adsorption of a number of organic substances has been undertaken[55,56,128-133]: aromatic hydrocarbons[35,55,56], alcohols[128,129], carboxylic acids[53,54,129], and thiourea[130,133] on smooth platinum in 1 *N* H_2SO_4 solutions up to $\varphi_r \simeq 2.5$ V using a combination of electrochemical methods and the ratioactive tracer method. Direct adsorption measurements with the aid of compounds labelled by radioactive isotopes fully confirmed both the very fact of an appreciable adsorption of organic molecules at high positive potentials and the principal quantitative characteristics found previously. Fig. 6[56] illustrates the variation of the surface coverage θ and the degree of adsorption Γ with potential obtained by the potentiodynamic method (lower curves) and with the aid of labelled compounds (upper curves) for benzene and naphthalene. The nature of the curves is basically similar; the differences between them are associated with the fact that the values of θ actually characterise the degree of displacement of chemisorbed oxygen and those of Γ characterise the overall surface excess of the organic substances both within the oxide and on the oxide. Comparison of the measurements by electrochemical and isotopic methods permits conclusions to be made about the stoichiometry of the displacement, the relative distribution of the adsorbed substances in the surface layers, and many other features.

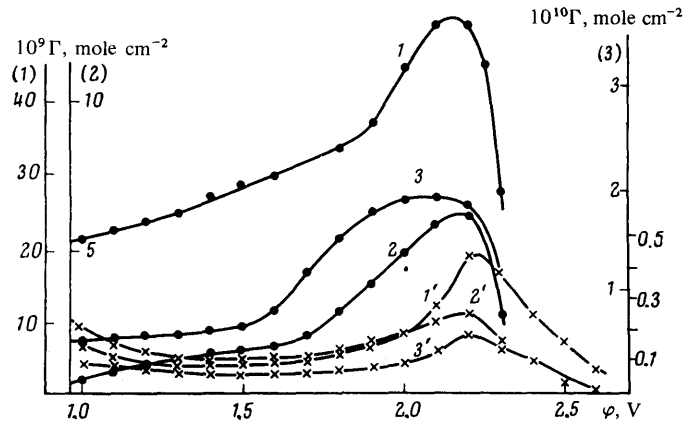


Figure 6. Variation of the degree of adsorption Γ (curves *1–3*) and of the degree of surface coverage θ (curves *1'–3'*) of platinum with potential: 1) and 1') 0.089 M benzene; 2) and 2') 2×10^{-4} M naphthalene; 3) and 3') 0.01 M benzene.

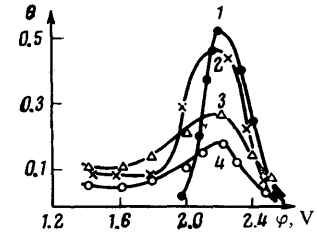


Figure 7. Variation of the degree of surface coverage of platinum by different substances with potential: 1) 5×10^{-4} M cyclohexane; 2) 5×10^{-4} M cyclohexene; 3) 10^{-4} M naphthalene; 4) 10^{-3} M benzene.

Figs. 7 and 8 illustrate the $\theta-\varphi$ and $\Gamma-\varphi$ relations obtained by the potentiodynamic method for hydrocarbons (butadiene, cyclohexene, and cyclohexane)[35] and by the radioactive tracer method for C_{1-6} aliphatic alcohols[128].

The data presented confirm the general nature of the effect of the adsorption of organic substances at $\varphi > \varphi_0$ and show that, apart from the familiar maximum in the double layer region, the $\Gamma-\varphi$ curves have yet another maximum at potentials of 2.1–2.3 V, where the limiting coverage of the platinum anode by chemisorbed oxygen is reached. A similar phenomenon has been observed for oxidised rhodium [108]. The presence of a number of adsorption maxima for smooth platinum has also been confirmed by other data [132–136], according to which there exists yet another region of enhanced adsorption activity of platinum at high positive potentials.

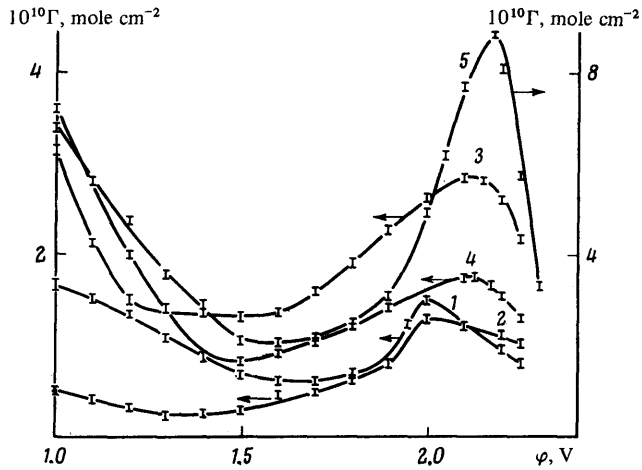


Figure 8. Variation of the degree of adsorption Γ of different substances on platinum with potential: 1) 0.15 M CH_3OH; 2) 0.0532 M C_2H_5OH; 3) 0.1 M i-C_3H_7OH; 4) 0.090 M t-C_4H_9OH; 5) 0.048 M n-$C_6H_{11}OH$.

Analysis of the experimental data accumulated in recent years permits certain generalisations of the characteristics of the adsorption of organic substances on oxidised platinum.

1. The adsorption of organic compounds (at least of the major proportion of the adsorbate) is as a rule irreversible and is accompanied by the displacement of chemisorbed oxygen. The introduction of molecules into the oxide layer stabilises them on the surface. There is a broad overall spectrum of energy states, including weakly bound species [128].

2. In the series of compounds of the same type and having similar molecular weights, those with multiple bonds exhibit a greater adsorbability.

3. In contrast to unoxidised smooth and platinised platinum, on which far-reaching degradation of molecules takes place, the adsorption of organic compounds on the oxidised metal may be manifested as an associative process [2,3,62,137].

4. In contrast to the range of low potentials, for which a logarithmic adsorption isotherm with similar values of the inhomogeneity factor f (Damaskin et al. [22]) is typical, at $\varphi > \varphi_0$ the variation of surface coverage with concentration c is not of a single type. In some cases it is described satisfactorily by the Temkin equation with f depending on the potential and the nature of the substance [62,131]:

$$\theta = \frac{1}{f}\ln(Bc);\ B = \text{const.},$$

while in others (for example, for alcohols [128,135] or acids [129]) the agreement with the Freundlich equation is better (Fig. 9):

$$\theta = Bc^n;\ n < 1.$$

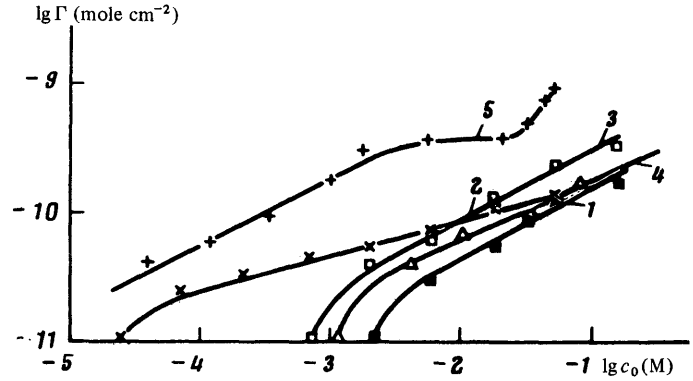


Figure 9. Variation of the degree of adsorption of different substances on platinum at the maximum potentials with the concentration of alcohols in terms of logarithmic coordinates: 1) CH_3OH; 2) C_2H_5OH; 3) i-C_3H_7OH; 4) t-C_4H_9OH; 5) n-$C_6H_{11}OH$.

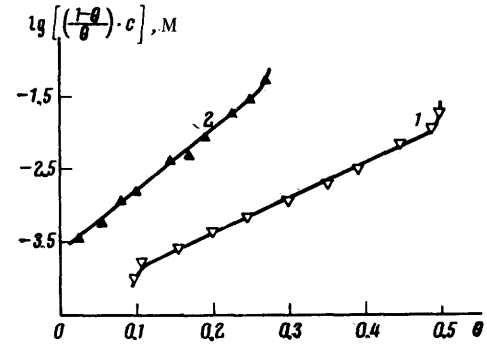


Figure 10. Variation of the degree of surface coverage of platinum with the concentration of buta-1,3-diene at different potentials (V): 1) 2.1; 2) 2.8.

The adsorption of dienes from sulphuric acid solutions obeys the Frumkin equation (Fig. 10): [134]

$$Bc = \frac{\theta}{1-\theta}\exp(f_1\theta);\ f_1 = \text{const}.$$

5. The adsorption kinetics are described by power equations of the Banham–Barth (Kwan) type [128]:

$$\theta = k\cdot\tau^n;\ \tau - \text{time},\ k = \text{const.};$$

or the Zel'dovich–Roginskii type [35,130]:

$$\theta = A + \frac{1}{\alpha f}\ln\tau;\ \alpha \leqslant 1;\ A = \text{const.}$$

6. The formation of multilayer coatings at concentrations differing by not more than an order of magnitude from saturation has been observed for certain substances [55,56]. Fig. 11 [56] presents curves relating Γ and θ to c for benzene and naphthalene; the ascending branches of the curves correspond to the appearance of multilayer deposits. Weber and Loučka also concluded recently that multilayer adsorption is possible (for sulphur on smooth platinum) [138].

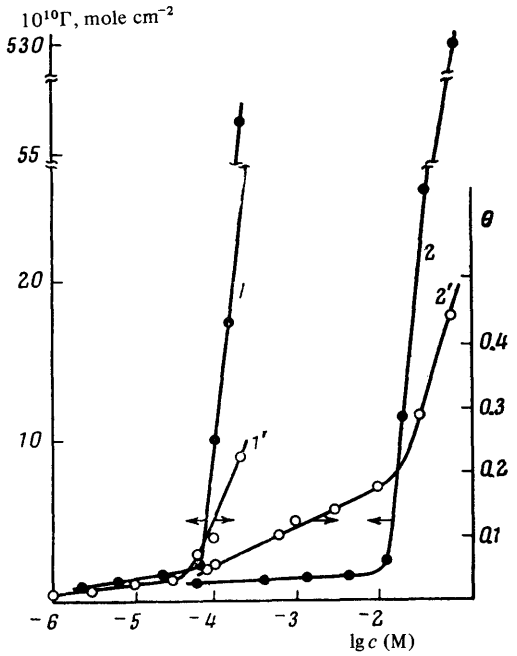


Figure 11. Variation of the degree of adsorption Γ (curves *1* and *2*) and of the degree of surface coverage θ (curves *1′* and *2′*) by different substances with concentration: 1) and 1′) naphthalene; 2) and 2′) benzene.

7. The substance adsorbed on energetically inhomogeneous surfaces of platinum metals and graphite can not only block the active centres but can also have a significant influence on the kinetics of the oxidation and the energy of adsorption on the unoccupied sections. In conformity with the model of the "surface electron gas" [139,140], one can predict both an inhibiting and a promoting influence of the initially adsorbed substance on the rate of discharge and also a change in the metal–adsorbate bond strength on the free sections of the surface.

The sign of the effect will be determined by the nature of the adsorbate and of the oxidation process. Indeed Gileadi and coworkers [141–143] observed the selective inhibition of oxidation reactions by certain compounds, particularly by phenols. The inhibition of the electrochemical oxidation of benzaldehyde and acetophenone (compounds which are readily oxidised by atmospheric oxygen but are resistant to anodic oxidation), reported by Solomin and Kryuchkova [144], probably belongs to phenomena of this type. The authors [144] begin with the following process mechanism (postulating the intermediate formation of benzoyl hydroperoxide, the decomposition of which results in the appearance in solution of a process inhibitor—phenol):

$$C_6H_5CHO \rightarrow C_6H_5COOOH \rightarrow C_6H_5OH + CO_2.$$

Kazarinov and Dolidze observed an appreciable increase in bonding strength and a decrease of the rate of oxidation of methanol adsorbed on platinum together with hexyl alcohol [145].

Effects with a different sign, namely selective promotion of the oxidation of oxalic acid at low coverages of the platinum anode by dienes in alcoholic solutions [15,146] and the stimulating effect of the adsorbate on coverage by oxygen [24,35], have been observed. Similar phenomena were recently noted in the adsorption of submonolayer amounts of noble metals [147] as well as arsenic, sulphur [148,149], mercury, and acetonitrile [150] on platinum. It was shown that, depending on θ and the nature of the substance being oxidised, the reaction is either accelerated or inhibited.

Since the thermodynamic method developed by Frumkin [151–152] and experimentally validated [22] for degassed platinum metals is inapplicable to the analysis of irreversible adsorption processes on oxidised metals, in certain investigations attempts were made to interpret the nature and characteristics of adsorption at high values of φ on the basis of other concepts.

In the first studies carried out in this field [116–119] it was assumed that the high bonding energy between the adsorbate and the metal, which stabilises the latter with respect to oxidation by the oxygen evolved, is due to the presence in the adsorbate molecule of valence-unsaturated groups, the interaction of π electrons of which with the positively charged surface of the anode leads to the formation of stable chemisorbed compounds (of the type of π complexes). The interpretation of the nature of the adsorption effects at high potentials was developed further in studies by Tyurin and coworkers [66,67]. In particular, the authors postulate that the second form of the surface oxide formed on the platinum electrode above 1.5 V is a coordination compound of the metal and the intermediate products of the oxygen evolution reaction and other components of the electrolyte: ions and neutral molecules. All the species enumerated behave as ligands, which compete with one another in the half-sphere of the complex in which the electron-accepting species is Pt^{4+}. Within the framework of this mechanism, the increase of the degree of adsorption in the range 1.5–2.2 V is caused by the increase of the degree of surface coverage $\theta_{O_{II}}$ and its decrease at higher potentials is associated with the increase of the rate of oxidation of the adsorbate. However, it has been noted [3] that both treatments suffer from a number of disadvantages. The complex-adsorption model was improved further in recent investigations [153].

We shall consider next the characteristics of each of the reaction classes discussed taking into account the above considerations.

IV. ANODIC DIMERISATION REACTIONS

The most important of the anodic dimerisation processes is the Kolbe electrochemical condensation of carboxylic acids and its modification—the condensation of dicarboxylic

acid monoesters (the Brown–Walker reaction):

$$2\,RCOO^- - 2e \rightarrow RR + CO_2 .$$

These reactions are of preparative interest for the synthesis of many valuable bifunctional compounds and in many cases there are favourable prospects for their industrial application. This involves the synthesis of sebacic acid diesters by the electrolysis of monoalkyl adipates [154] and also the synthesis of suberic acid by the condensation of monomethyl glutarate [77,159]. A number of reviews have been devoted to the synthetic and kinetic aspects of Kolbe type reactions [3,4,69,154,156,157]. Here we shall note the principal process conditions and also certain trends in the recent research in this field.

The yield of the dimeric product is determined by a number of experimental and structural factors. The dimer is formed mainly at high potentials ($\varphi > 2.1$ V), using smooth platinum, iridium, and graphite anodes in an aqueous medium. The use of non-aqueous solvents promotes condensation; in organic media (alcohols, acetonitrile, dimethylformamide, etc.) the choice of the anodic material is less limited—anodes made of gold, palladium, lead dioxide, and certain other materials are suitable in addition to platinum metals. An increase of temperature and the addition of extraneous electrolytes lead to a decrease of the yield of the dimer. The influence of structural factors is discussed below. The investigation of the influence of a series of experimental conditions on the kinetics of the electrochemical oxidation of monomethyl glutarate on platinum in methanol has been reported [77,155]. In particular, it has been shown that the nature of the anode material does not have a decisive influence on the electrochemical oxidation process. The observed fractional order of the reaction of the monoester shows, according to the authors, that the rate-determining stage is the discharge of the monoester anions (on a uniformly inhomogeneous surface).

A similar conclusion concerning the nature of the rate-limiting stage was reached also in studies on the electrochemical oxidation of propionate in an aqueous medium [160] and of acetate in anhydrous acetic acid [158]. Very low reaction orders $n \ll 1$ were also observed in the oxidation of alkylboronic acids, the electrochemical oxidation reactions of which have much in common with the Kolbe reaction [161]. The influence of the nature of the monoester on the oxidation kinetics in methanol solutions on platinum has been discussed [155]. The principal kinetic features are identical with those observed earlier for monomethyl adipate and acetate [116,117,119], which permits the fully justified conclusion that there is a profound analogy between the kinetics of electrode processes in the Brown–Walker and Kolbe reactions in aqueous and alcoholic solutions of many monocarboxylic acids and dicarboxylic acid monoesters. With increase of the length of the hydrocarbon chain, the adsorbability of the carboxylate anion increases also, as has been observed in aqueous solutions [119]; as a result, the maximum solvent oxidation current falls and there is a linear relation between the logarithm of current density and the number of methylene groups in the molecule. The necessity for the adsorption of the carboxylates on the anode prior to their discharge also follows from the results of a study of a Kolbe cross-reaction (mixed reaction) [71].

The problem of the use of carbon electrodes in the oxidation of carboxylates in various solvents (water, methanol, ethanol, and dimethylformamide) has been thoroughly investigated [162]. Experiments have been performed on the electrolysis of oenanthic acid solutions and pure oenanthic acid, solutions of phenylacetic and phenoxyacetic acids, and also methyl and ethyl succinates on soft and hard graphite, vitreous carbon, and baked carbon electrodes. The Kolbe reaction proceeds in protic solvents on vitreous and baked carbon, while side reactions mainly occur on soft graphite (alkyl oenanthates are the main products in oenanthic acid solutions). Considerable differences were observed when pyrolytic graphite anodes with the surface parallel and at right angles to the plane of the lattice unit cells were used; in the former case the yield of products was appreciably lower. The above experiments appear to confirm the necessity to take into account the role of the adsorption stages also in anodic reactions on graphite materials.

This view is supported by the results of studies of other oxidation reactions on carbon anodes [163]. The authors postulate that, in accordance with Balandin's multiplet theory, the efficiency of the electrochemical oxidation is determined by the structural and energy correspondence between the substrate molecule and the electrode surface.

Despite the fact that Kolbe type anodic condensation reactions have already been studied for a long time and particularly vigorously in the last five–eight years, many problems involving their mechanism have still not been unambiguously solved and have been the subject of a lively discussion in papers by Conway, Eberson, Fioshin, and many other workers [1–3,69,154,156]. Since the kinetic aspects of the reaction based on an analysis of the literature up to 1967 have been summarised in an extensive review [69], we shall not consider here these problems in detail. We shall only note that analysis of numerous experimental data obtained in recent years using a number of electrochemical, radiochemical, and optical methods for the indentification of products of potentiostatic electrolysis and also the interpretation of these results in original studies lead (with rare exceptions [165,166]) to the following mechanisms of the processes corresponding to different sections of the polarisation curve (Fig. 3) in carboxylate solutions on platinum: section I—evolution of oxygen on a surface partly coated by the first form of the oxide and by adsorbed carboxylate ions; section II—ditto on a surface coated by a monolayer of the first form of the oxide and onset of the formation of the second form. Along section III, the discharge of anions begins, with formation of acyloxy- and alkyl-radicals adsorbed on platinum and displacing oxygen (mainly the second form). The high adsorption energy prevents their surface mobility and recombination. The transition region IV corresponds to the reorganisation of the surface oxide with the coadsorbed radicals, resembling the surface "two-dimensional crystallisation", which has been observed in solutions of inorganic acids [168]. Section V corresponds to the discharge of carboxylate ions on this modified surface with formation of condensation products via an electrochemical desorption mechanism.

Other views on the mechanisms of anodic processes in the oxidation of carboxylic acids have been developed in a study by Fioshin and Vasil'ev [82], where it was assumed that the discharge of carboxylate anions begins only at potentials corresponding to section V, i.e. when $\varphi \geqslant \varphi_{cr}$¶, while the inhibition of the oxidation in the transition region is caused by the specific features of the adsorption of these anions. This view, which has been supported by other workers [77,155], has been criticised in a review by Vijh and Conway [69].

¶ φ_{cr} is the initial potential on section V.

The results published in a number of communications[78,167,169,170] can serve as an additional argument in support of the above scheme, postulating the discharge of $RCOO^-$ under the conditions corresponding to the lower sections of the $i-\varphi$ curves. At potentials corresponding to section III the formation of alcohols and of a small amount of dimers was observed in the oxidation of pelargonic acid at a platinum anode in an alkaline medium[78,167], while in the electrolysis of ω-chloroacids in the presence of 1,3-dienes the formation of additive dimers was also noted[170]. The study of the electrochemical oxidation of propionate in an aqueous medium by the pulse and voltage-current methods also indicates the adsorption of the carboxylate up to φ_{cr}.[172] According to the authors, the rate-limiting stage is in the oxidation of $C_2H_5COO^-$; the adsorbed propionyloxy-radical formed decomposes into CO_2 and $C_2H_5^{\cdot}$, the latter reacting with $C_2H_5COO^{\cdot}$ to form ethylene and propionic acid. According to Takeda et al.[160] the charge transfer in the rate-limiting stage in glacial acetic acid on platinum, palladium, gold, lead dioxide, and graphite electrodes takes place via a layer of adsorbed $CH_3^{\cdot}$ or $CH_3COO^{\cdot}$ radicals.

Among the unsolved problems concerning the mechanism of the Kolbe reaction, that of the so called "anomalous" carboxylates occupies an important place. They include aromatic, substituted, and unsaturated carboxylic acids with multiple bonds and substituents X (X = halogen, OH, NH_2, Ph, or RCH=CH) in the α- and β-positions with respect to the carboxy-group. These compounds either do not undergo the dimerisation reaction at all or a dimer is formed in an insignificant yield,which appreciably limits the preparative scope of the Kolbe electrochemical synthesis. For example, in the anodic oxidation of acids of the adamantane series in an alcoholic medium[171] the main electrolysis product is the corresponding alkoxy-derivatives and not the dimers.

On the other hand, when the carboxy-group is linked to the bridgehead carbon atom via a methylene group, then electrochemical oxidation leads to ring expansion. The latter reaction can serve as a new method for the preparation of cyclic compounds with large rings.

The formation of a methoxy-derivative together with the dimer was observed by Coleman and Eberson[173] in the anodic oxidation of caesium 9-methylanthracene-10-acetate in a mixture of methanol and tetrahydrofuran. In a reaction involving the anodic decarboxylation of sodium epoxy-β-phenyl propionate at a platinum anode Japanese investigators[160] failed to detect the corresponding dimer; the main reaction products were benzaldehyde, acetophenone, benzyl acetate, and methyl benzoate. The desired product of the Kolbe electrochemical synthesis was not found (or was obtained in a negligible yield) also in the electrolysis of 2,2-dichloro-3-phenylcyclopropanecarboxylic acid on platinum in hydroxylated solvents[174], in the oxidation of cyclohexene-3-carboxylic acid and norborn-5-ene-2-carboxylic acid in acetonitrile[175], of 2-methoxy-1-cyclopentene-1-carboxylic acids in methanol[169], and of α-chloro- and α-fluoro-acids (valeric, caproic, and isobutyric)[176].

It has been shown[177,178] that, under the usual conditions of the Kolbe reaction, the electrolysis of aqueous solutions of perfluoro-acids also does not yield the dimeric product. In the electrochemical oxidation of trifluoroacetate at an oxidised platinum anode in the presence of added water, Na_2HPO_4, and H_2SO_4 in the electrolyte Knunyants and coworkers[179] obtained CF_3OOCF_3 and CF_3OCF_3 instead of hexafluoroethane. The results of Korchinskii and Andreev[180] confirm the fact that dicarboxylic acids also do not give rise to the corresponding dimers. In the oxidation of maleic and fumaric acids in the potential range corresponding to the upper section of the polarisation curve they observed the formation of acetylene. In a study[185] of the products of the preparative electrolysis of tri-t-butylcyclobutenedicarboxylic acid it was shown that, depending on the composition of the solution, various substances are obtained (2,3,5-tri-t-butylfuran, etc.), but the Kolbe dimer was not identified.

According to the majority of the investigators of these reactions (Eberson, Woolford, Fleischmann, etc.[1-3]), the anomalous behaviour of substituted carboxylates is associated with a lower ionisation potential of the radicals formed and their subsequent oxidation to the corresponding carbonium ions which then react with the nucleophilic components of the solution Z^- [reaction (1b)]:

$$RCOO^- \xrightarrow{-e,-CO_2} R^{\cdot} \begin{cases} \longrightarrow RR & (1a) \\ \xrightarrow{-e} R^+ \xrightarrow{Z^-} RZ\,. & (1b) \end{cases}$$

This view is shared also by the authors of the communication[171] concerning the adamantane acids. The results of the preparative electrolysis of phenylacetic acids[181] and also the study of the "pseudo-Kolbe reaction" mentioned above[173] lead to the same conclusion; in the latter case the authors concluded on the basis of voltage–current measurements that the electron is removed from the aromatic ring and not from the carboxy-group.

The occurrence of the substitution reaction with formation of the products RZ is favoured by the following conditions: low current densities, the use of graphite materials for the anode and of water as the solvent, pH > 10, and the addition of extraneous anions (HCO_3^-, HSO_4^-, $H_3PO_4^-$, Hal^-) and cations (Fe^{2+}, Mn^{2+}, Pb^{2+}, etc.). RZ can be formed either via a carbonium ion [reaction (1b)] or via the homolytic addition of R$^{\cdot}$ and Z$^{\cdot}$. It is usually difficult to differentiate the two reaction pathways. The so called "method of detecting radicals by an acceptor" is extremely effective in many cases for this purpose; its characteristics and examples of its practical application have been described[3,62].

Berenblit, Sokolov, and coworkers, who made a thorough study of the main products and by-products of the direct anodic condensation and cross-condensation of β-perfluoromethoxypropionic acid and certain monoesters of perfluorodicarboxylic acids in non-aqueous media, also concluded that the nature of the by-products cannot be accounted for solely by the homolytic interaction of the intermediate perfluoroalkyl radicals and requires the assumption of their simultaneous oxidation to the corresponding perfluorocarbonium ions[182,183].

On the basis of the mechanism described above for anodic processes in the oxidation of carboxylates, the ratio of the rates of reactions (1a) and (1b) will presumably depend, other conditions being equal, on the strength of the bond between the surface and the adsorbed RCOO$^{\cdot}$ (R$^{\cdot}$) radicals. In view of these considerations, a study was undertaken[17,18,184] of the electrochemical oxidation of carboxylates which are known not to from dimers (monoesters of $\alpha\beta$-unsaturated aliphatic dicarboxylic, aromatic, and alicyclic acids) in the presence of small amounts of vigorously adsorbed additives (for example unsaturated hydrocarbons, conjugated dienes, etc.). Indeed, under these conditions the heterogeneous-catalytic influence of such compounds on the dimerisation process was observed and the Kolbe reaction was achieved with an acceptable yield. In particular, in the oxidation of monomethyl maleate the product is the dimethyl ester of muconic

acid—the starting material for the synthesis of high-quality polymeric materials; the chemical methods developed for the synthesis of muconic acid are still insufficiently effective. Dimeric products were obtained also for other classes of anomalous carboxylates. There is a close relation between the adsorbability of the catalytic additive and its influence on the mode of the process—there is a direct correlation between the adsorption criteria and the yield of the dimer.

A similar effect is apparently encountered also in the case of perfluorocarboxylic acids, which are oxidised with formation of Kolbe products only in non-aqueous media, particularly those containing acetonitrile. The modification of the surface layer occurring in the adsorption of acetonitrile molecules in carboxylate solutions [186] probably leads to a weakening of the metal–adsorbate bond and to a change in the relative rates of reactions (1a) and (1b) in favour of the former, which increases. These considerations are supported by results [177,182,187], which confirm the influence of the solvent on the effectiveness of the dimerisation, including "cross dimerisation". In the latter case 1,1,1-trideuterotrifluoroethane and 1,1,1-trideuteropentafluoropropane were synthesised [187] in the electrolysis of mixtures of deuterated acetate with trifluoroacetic and pentafluoropropionic acids respectively by regulating the composition of the solution.

Anodic dimerisation reactions of the non-condensation type occur in the electrochemical oxidation of certain aromatic hydrocarbons, amines, phenols, and olefins. According to the ideas developed previously [188], the reactions can proceed via two mechanisms: ECC_N [reaction (2a)] and ECC_B [reaction (2b)], where the subscripts N and B denote respectively nucleophilic and electrophilic reaction stages:

$$2\,RH \xrightarrow{-2e} 2\,RH^{+\cdot} \rightarrow {}^{+}HRRH^{+} \begin{cases} \xrightarrow[X_N]{2Z^-} ZHRRHZ & (2a) \\ \xrightarrow{-2H^+} RR\,. & (2b) \end{cases}$$

(E) (C) (C_B)

Either dehydropolymers [reaction (2b)] or (in the presence of a suitable nucleophilic agent Z^-) disubstituted dimers [reaction (2a)] are formed under these conditions. The first pathway reduces in fact to an addition reaction, permits a different interpretation of the mechanism (via a homolytic addition stage), and will be discussed in the next Section. Some examples of reactions of this kind were described previously [189–191], but only the studies in recent years have shown that dimerisation of this type can serve as an effective method for preparative synthesis. In many instances nearly quantitative yields of the desired products were obtained.

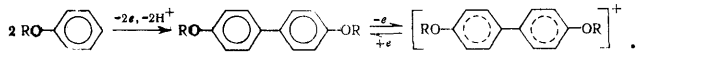
The electrolysis of benzene leads to a mixture of oligomers [192,193] with a yield reaching $A = 90\%$ in a solution containing $AlCl_3$ and HCl; [193] the electrochemical oxidation of 1,2,4-trimethoxybenzene and tetraphenylethylene resulted in the formation of 2,4,5,2′,4′,5′-hexamethoxybiphenyl ($A = 85\%$) [191] and 8,10-diphenylphenanthrene ($A = 100\%$) [194] respectively. The anodic dimerisation of many substituted anilines and phenols and also the mixed dimerisation of certain compounds have been achieved similarly.

The most important examples of these reactions have been compiled [1]. In recent years a series of studies on these lines was undertaken by Nyberg [195–197], who put forward an interesting concept to account for the mechanisms of the direct and mixed dimerisation of aromatic hydrocarbons. According to this concept, the higher the spin density or the positive charge density in the radical-cation formed, the greater the ease of its formation. It is thus possible to explain the preferential formation of biphenyls compared with diphenylmethanes and also the dependence of the yield of products on the concentration of the initial hydrocarbons in the anodic oxidation of polymethylbenzenes in non-nucleophilic media (CH_3NO_2 and CH_2Cl_2). [196] If the spin density (and the positive charge density) is higher in the ring of the radical-cation, biphenyls are mainly formed. On the other hand, if the spin density is higher in the substituent, then the benzylmethyl radical-cation with the charge located in the methyl group is formed preferentially; this radical-cation loses a proton and is converted into a benzyl radical, which is rapidly oxidised to a benzyl cation. The latter reacts with the initial hydrocarbon, giving rise to a diphenylmethane derivative:

$$ArCH_3 \xrightarrow{-e} ArCH_3^{+\cdot} \xrightarrow{-H^+} ArCH_2^{\cdot} \xrightarrow{-e} ArCH_2^{+} \xrightarrow{ArCH_3,\,-H^+} ArCH_2ArCH_3\,.$$

This view makes it possible to explain, for example, the formation of 1-mesitylnaphthalene in the absence of bimesityl in the mixed anodic dimerisation of naphthalene and mesitylene on platinum [196]. According to the above considerations, the more readily formed naphthyl radical-cation either dimerises in accordance with Eqn. (2b) to binaphthyl or interacts with mesitylene to form a mixed dimer; the absence of bimesityl confirms the fact that the corresponding mesityl radical-cation is not formed under these conditions.

The anodic dimerisation of a number of aryl esters derived from anisole, *o*-bromoanisole, and *o*-methylanisole has been achieved in high yields [198,199] by using trifluoroacetic acid or its mixtures with methylene chloride as solvents. Under these conditions, the dimeric radical-cation is stabilised and can be detected by the voltage–current procedure. According to the authors [198], the reaction proceeds as follows:



The dimerisation takes place only in the *p*-position and if the latter is blocked the radical-cation cannot be detected.

An interesting example of an effective combination of anodic and cathodic dimerisation in the same electrolyser has been described [200]. By electrolysing a solution of diethyl malonate and methyl acrylate in acetonitrile in the presence of potassium iodide under conditions favouring anodic dimerisation (high dilution, low current densities), the authors obtained high yields of the ester $(C_2H_5OOC)_2$–CH–HC$(COOC_2H_5)_2$ on the anode and dimethyl adipate on the cathode. The use of $LiClO_4$ instead of KI almost completely suppresses the formation of tetraethoxycarbonylethane but does not effect the yield of dimethyl adipate. The dimerisation of acetoacetic ester also does not occur in the presence of ClO_4^-—the product is 2-ethoxycarbonyl-4-methoxycarbonyl-1-methylfuran.

In other cases the anodic dimerisation of anionic dicarbonyl compounds such as sodium dialkylmalonate and sodium acetylacetonate was achieved successfully with satisfactory yields [201–203]. A large number of examples of the anodic dimerisation of the anions of polar organic compounds have been described:

$$2\,R^{-\delta}\text{—}X^{+\delta} \xrightarrow{-2e;\,-nX^+} 2R^{\cdot} \rightarrow RR,$$

in particular phenols, oximes, aliphatic nitrocompounds, organometallic compounds, alkynes (see Eberson and

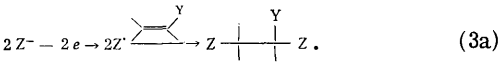
Schäfer[1], Table 12), and also enolic ethers[204]. In certain cases a mixed dimerisation can be achieved with a high degree of efficiency[205].

V. ANODIC ADDITION REACTIONS

This class of reactions, which has been vigorously investigated in the last decade, probably involves the greatest concentration of the advantages of electrochemical methods formulated above. Processes of this type are in many cases distinguished by a high efficiency, selectivity, and ease of the synthesis of relatively high-molecular-weight compounds from simple monomers.

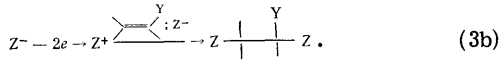
According to modern ideas, it is possible to achieve three versions of the anodic addition of a nucleophilic agent to the double bonds of the acceptor.

(a) Via a radical generated on the anode:



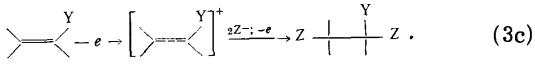
(3a)

(b) Via the electrophilic agent formed initially:



(3b)

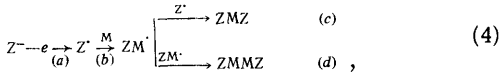
(c) Via the radical-cation formation stage:



(3c)

These reaction pathways can be by no means always distinguished; the criteria proposed are as a rule insufficiently reliable[1-3].

The radical pathway is assumed by the majority of investigators for the electrochemical additive dimerisation of olefins initiated by the electrochemical oxidation of carboxylic acids, alcohols, water, and nitric acid[206-238]:



(4)

where M is the olefin molecule and Z = RCOO, $H_2C_2O_4$,[15, 206,211-216,223,224,227] RO,[217-221] halogen[226], (CH_3CO_n). $.CH_{n=1,2}$,[10,230-232] $O_2NC_nH_{2n-2}$,[234,235] N_3,[237] etc.[197,236] Among unsaturated compounds, mainly conjugated dienes[15,52,206-227], styrene[229,234-236], and ethyl vinyl ether[230,234,235] as well as other activated olefins, are involved in this reaction. The dimerisation reactions of Z as well as the homolytic abstraction of hydrogen from the electrolyte components ($Z^{\cdot} + RH \rightarrow HZ + R^{\cdot}$) take place simultaneously with reaction (4). When $Z^- = AlkCOO^-$, stage (4a) is followed by the spontaneous decarboxylation stage, but, when $Z^- = ArCOO^-$, this does not occur, because of the much greater stability of the aroyloxy-radicals compared with acyloxy-radicals. Certain substituted boronic acids behave similarly to aliphatic carboxylates[232].

The interpretation of the mechanism of the anodic additive dimerisation in accordance with Scheme (4) has not been altogether generally accepted. For variants of the reaction in which $Z^- = AlkO^-$, $ArCOO^-$, and certain other species, heterolytic pathways are assumed in a number of investigations, postulating a preliminary oxidation of the substrate on the anode followed by the interaction of the resulting carbonium ions by Z^-. A number of reports are devoted to the mechanism of reactions of this type[1-3].

The accumulated experimental data for this field were recently analysed and the possible reaction pathways were discussed in relation to the additive dimerisation initiated by the oxidation of carboxylates[3] and alcohols[7]. The study of the influence of various factors on the mode and efficiency of additive dimerisation has shown that, regardless of the nature of Z^- ($HC_2O_4^-$, $C_nH_{2n-2}COO^-$, $AlkOOCArCOO^-$, ω-ClC_nH_{2n-2}. $.COO^-$, and $AlkO^-$[62,206-215]), the fundamental kinetic characteristics are similar. This apparently indicates a common mechanism for such processes. The homolytic mechanism of the addition reaction is unambiguously indicated by the nature of the products obtained in certain variants of the additive dimerisation, for example that initiated by alkyl radicals formed in the electrochemical oxidation of carboxylates[206-209,223,224]. In some investigations experiments on potentiostatic electrolysis showed that the additive dimers are formed at potentials lower than those required for the oxidation of substrate molecules[170].

Analysis of the results of studies of the additive dimerisation reactions has shown that the necessary condition for their occurrence is the adsorption of acceptor molecules on the electrodes.

High yields of adducts were obtained using as acceptors compounds for which an appreciable adsorption activity has either been found or postulated (on the grounds of structural considerations) at the high positive potentials required for the formation of $RCOO^{\cdot}_{ads}$. This is also indicated by the following considerations. Whereas the formation of $R^{\cdot}$ in the bulk of the solution[165,166] is in principle possible for unsubstituted straight-chain carboxylates (this is particularly likely for phenylacetic acids[19]), such a reaction is probably ruled out in the oxidation of "anomalous" carboxylic acids, which are not dimerised. The products formed indicate the oxidation of $R^{\cdot}$ to the corresponding carbonium ion. Such radicals can therefore be formed only in the adsorbed state and the formation of additive dimers in these instances constitutes convincing evidence for the involvement of the substrate also in the adsorbed form. In the studies quoted previously[17,18,184,225] the above phenomenon was confirmed for non-dimerising carboxylates of various classes in the presence of an adsorbable acceptor (adsorption has been demonstrated by independent methods[35,55,56,116,134]). As a result of the reaction, appreciable amounts of polymeric products were obtained only under special conditions (at extremely low current densities); chain termination at stages where $m \leq 2$ (m is degree of polymerisation) also indicates a heterogeneous process. The transfer of $R^{\cdot}$ to the bulk of the solution (which usually contains high acceptor concentrations) would inevitably lead to the appearance of at least oligomers in consequence of the "cage effect".

It follows from the foregoing considerations that similar reactions involving suitable acceptors, for example 1,3-dienes, can serve as an effective method for the detection of the intermediates formed during electrolysis.

Elementary kinetic analysis of the reaction mechanisms involving adsorbed acceptor molecules on the electrode demonstrates a satisfactory agreement between the variations of the yields of individual adducts with a number of process parameters[238]. It follows from Eqns.(4a), (4b), (4c), and (4d) that the relative rates of formation of the reaction products must be extremely sensitive to changes in the effective concentrations of $R^{\cdot}$, which is determined, other conditions being equal, by the anodic current density, and to the degree of surface coverage by the olefin. Indeed, it has been frequently shown that, by altering the anodic current density, the nature of the electrode

material, and the acceptor concentration, it is possible to vary within wide limits the ratios of the products formed and to carry out the process under conditions favouring the synthesis of each separately [208-221]. This factor converts the reaction into a unique method of synthesising many valuable polyfunctional compounds.

The mechanism of addition via an anodically generated electrophilic agent is apparently assumed only for oxidative halogenation at double bonds and also for the electrochemical analogue of the Ritter reaction, achieved by Foita et al. for cyclohexene [239] and then by Weinberg and Hoffmann [240] for other compounds on chlorination in acetonitrile. In the former case chlorination of cyclohexene yielded 2-acetamido-1-chlorocyclohexane, while in the latter electrochemical halogenation of 1-phenylbut-2-ene and cyclopentene also led to 2-acetamido-1-halogeno-adducts. The introduction of acetamido-groups likewise takes place in the electrochemical oxidation of α-substituted and aromatic carboxylic acids [241,242], adamantane, 1-halogenoadamantanes and esters [243,244] in nitriles. According to the ideas of Eberson and Nyberg [241], the electrochemical introduction of acetamido-groups into carboxylates proceeds via the intermediate formation, as a result of two-electron oxidation of a carbonium ion, which reacts further with acetonitrile in the following way:

$$R_3CCOO^- \xrightarrow{-2e,-CO_2} R_3C^+ \xrightarrow{CH_3CN} R_3CN{=}\overset{+}{C}CH_3 \xrightarrow{H_2O,-H^+} R_3CNHCOCH_3 \quad (5a)$$

Similar views on the reaction mechanism have been expressed by other workers [243,244]. However, Japanese investigators, who studied the oxidation of benzoic acid in acetonitrile and propionitrile [242], suggest that the addition products (*N*-acetylanthranilic and *N*-propionylanthranilic acids) are formed via the oxidation of the benzoate ion to the benzoyloxy-radical, which is deprotonated and reacts further with the nitrile.

A number of studies on the anodic chlorination of ethylene [245], vinyl chloride, and butadiene [246] in an aqueous medium and in aliphatic alcohols have been published in recent years. In the case of ethylene dichloroethane was obtained under optimal conditions in an aqueous medium in yields up to 80%, while in the oxidation of olefins in a hydrochloric acid solution in methanol mixed chloro-methoxy-adducts were formed together with chloro-derivatives. Comparison of the electrochemical and chemical chlorination of ethylene (the influence of the nature of the anode, of admixtures in HCl, and other factors) demonstrated definite differences between the mechanisms of the two processes and led the authors [245] to the conclusion that adsorption processes play a significant role in the electrochemical reaction.

The third variant of the anodic addition reaction presupposes a two-electron transition in stages, initiated by the oxidation of the substrate molecule itself (an olefin or an aromatic compound). The addition products are formed in accordance with an EC_BEC_B mechanism:

$$\underset{(E)}{M} \xrightarrow{-e} \underset{(C_B)}{M^+} \xrightarrow{Z^-} \underset{(E)}{ZM^\cdot} \xrightarrow{-e} \underset{(C_B)}{ZM^+} \xrightarrow{Z^-} ZMZ \quad . \quad (5b)$$

This pathway has been postulated by some investigators for the alkoxylation and acetoxylation of furan derivatives, quinones, and substituted pyridines [7]. The anodic depolarisation effect, observed in many instances when the substrate is introduced into the electrolyte, has been frequently used as a criterion of the occurrence of the process via this mechanism. Critical comments have often been made concerning this approach [2,3,62].

VI. SUBSTITUTION REACTIONS

The study of anodic substitution reactions has also attracted much attention in recent years, since processes of this type give rise to a wide variety of synthetic possibilities. Studies in this field have been reviewed [1,247,248]. Here we shall deal only with certain general considerations concerning reactions of this kind.

Processes in which a group X (usually a hydrogen atom) in the substrate molecule RX is replaced on electrochemical oxidation by a substituent Z (Z = OR, OCOR, halogen, CN, etc.) belong to this class. The reactions can be divided into three groups in accordance with their mechanism [1].

(a) Homolytic substitution of hydrogen by a radical generated on the electrode:

$$Z^- \xrightarrow{-e} Z^\cdot \xrightarrow{RX,-XZ} R^\cdot \xrightarrow{Z^\cdot} RZ \quad . \quad (6a)$$

(b) Substitution of the condensation type in the electrolysis of carboxylates:

$$RCOO^- + Z^- \xrightarrow{-2e,-CO_2} RZ \quad . \quad (6b)$$

(c) Nucleophilic substitution via a radical-cation:

$$RX \xrightarrow{-e} RX^+ \xrightarrow{Z^-} RXZ^\cdot \xrightarrow{-e,-X} RZ \quad . \quad (6c)$$

As for anodic addition reactions, it is frequently difficult to distinguish the substitution processes involving different mechanisms.

The most striking examples of the first type are apparently those involving electrochemical halogenation. Among these, anodic fluorination is of the greatest practical importance. It constitutes a convenient method for the synthesis of perfluoro-compounds and has a number of advantages over the analogous chemical reactions, obviating the necessity for working with elemental fluorine [5,6,249-252].

The radical mechanism of the electrochemical fluorination proposed by Simons [250] is not, however, generally accepted at present. This reaction exhibits a high electrocatalytic specificity and proceeds in liquid hydrogen fluoride, mainly on nickel anodes. In an early study by Gramstad and Haszeldine [251] it was suggested that the active principle in this reaction is higher nickel fluorides. Subsequently a similar view was developed in another investigation [252]; the authors believe that many kinetic features of the reaction (for example the induction period) agree well with the hypothesis of the intermediate formation of complexes by the organic substance and nickel fluorides, such as $(RH_2)_2NiF_6$ and $(RH)_3NiF_6$.

The influence of the preliminary treatment of the electrodes on the electrochemical fluorination process has been established [253]. In particular, the induction period is shortened for nickel anodes coated chemically by NiF_2. The authors base their treatment on the mechanism of the anodic fluorination of organic compounds involving the initial formation of their complexes with nickel fluoride followed by electrochemical oxidation at the C–H bond with formation of radicals, which recombine with F$^\cdot$. In a study of the fluorination of aliphatic amines by Japanese workers [256], a mechanism was proposed for the electrode processes involving the discharge of F^-, the homolytic substitution of H by F, and oxidative cleavage of the C–C and C–N bonds followed by polymerisation.

On the basis of the results of the anodic fluorination of fluorobenzenes on platinum in acetonitrile[255], Knunyants and coworkers concluded that in this case the first stage of the process is one-electron oxidation of the substrate followed by the interaction of the radical-cation with a fluoride anion; the second stage is accompanied by the simultaneous transfer of a second electron with abstraction of a proton.

Thus the mechanism of the anodic fluorination is still controversial. Various hydrocarbons, including halogenohydrocarbons, carboxylic acids, ethers, amines, nitriles, and other classes of organic compounds have been used as the substrates in this reaction. Apart from the investigations the results of which are discussed in earlier reviews[1,5,6,247], mention should also be made of a number of recently published communications dealing with the fluorination of carbon monoxide, phosgene, substituted benzene and pyridine[259,260], methane, propane, ethylene[254], fluorobenzene and trifluoromethylbenzene[255], amines[256,257], tetrahydrofuran[261], ethylene chlorohydrin[262], dithiols and cyclic sulphides[263], *NN*-dialkylanilines and *NN*-dimethyltoluidines[264], ethylene glycol ethers[265], chloroethers[266], and other compounds[258].

In all cases a complex mixture of fluoro- and perfluoroderivatives, including degradation products and polymers (their amount is particularly large in the fluorination of alcohols and amines), is usually formed. The highest selectivity has apparently been achieved in a study[265] of the fluorination of triphenylmethane; under the conditions discovered in that investigation, fluorotriphenylmethane is formed in 80% yield.

Under the conditions of electrochemical fluorination, carboxylic acids do not undergo anodic condensation, but give rise to a mixture of substitution products with different fluorine contents in the molecule of the initial acid; the yields of the fluoro-derivatives increase with the molecular weight of the homologues. It has been shown[267,268] that the presence of alkoxy-groups in the carboxylic acid greatly facilitates the fluorination reaction compared with the unsubstituted analogues. The yields of perfluoromethoxyacyl fluorides are significantly higher than in the fluorination of the corresponding acids (14–41%); with increase of the chain length of the alkoxy-group, its stability in the electrochemical fluorination processes falls appreciably. The organic solvents usually employed in anodic reactions are not inert under the fluorination conditions, in particular acetonitrile gives rise to monofluoroacetonitrile and to succinodinitrile.

The homolytic mechanism has been adopted in most investigations for other halogenation reactions. However, these problems have been studied in much less detail than fluorination because they can be achieved without significant difficulties by the usual chemical methods. Several communications dealing with the behaviour of various electrodes (platinum, iridium, and ruthenium) in chloride solutions and also with the electrochemical chlorination of simple aliphatic hydrocarbons on graphite, platinum, and iridium anodes were published recently[269-271]. It has been shown[269] by the potentiodynamic method that the adsorption of Cl^- on platinum begins at hydrogen desorption potentials; it is postulated that Cl˙ atoms are adsorbed on a $Cl\bar{a}ds$ layer. Cl^- ions are not adsorbed on iridium anodes at Cl_2 and O_2 evolution potentials. Experiments on the electrochemical chlorination of methane, ethane, and ethyiene in the dark and under illumination led Kuhn and coworkers[270] to the conclusion that the substituion process has no specific heterogeneous features and is the result of a photochemically or thermally initiated reaction of the organic substance with molecular chlorine. This mechanism makes it possible to explain the observed higher rate of reaction compared with the value calculated on the basis of diffusion kinetics. According to the authors, the depolarising influence of the test gases is caused by the decrease of the concentration of Cl_2 evolved at the anode.

On the other hand, the results of the anodic chlorination of ethane on a graphite electrode, where a mixture of dichloroethane (75%) and ethyl chloride (20%) is formed, differ significantly from those obtained in chemical chlorination with molecular chlorine, which apparently indicates a heterogeneous mechanism of the reaction under these conditions[272]. Mastrogostino et al.[273], who carried out the electrochemical chlorination of aromatic hydrocarbons (benzene, toluene, and xylene) in anhydrous acetic acid at chlorine oxidation potentials, concluded that in this case the chlorinating agent is Cl_2^- and not Cl˙.

The radical substitution pathway has been adopted for the alkoxylation and acetoxylation of organosilicon compounds[274,275] and substituted amides[276]. However, Eberson and Nyberg[277] assume for this reaction the pathway corresponding to the third case, which is discussed in detail below. Substitution reactions accompanying the electrolysis of carboxylates have already been mentioned in the appropriate Section. Conditions favouring this reaction and hindering dimerisation are low current densities, high temperatures, water as the solvent, the addition of extraneous inorganic anions and cations, pH > 10, and graphite and non-platinum metal anodes. The preferential formation of substituted products is observed in the electrochemical oxidation of "anomalous" carboxylates (Section IV). Alcohols are formed in an alkaline medium (the Hofer–Moest reaction; $Z = OH^-$).

It is extremely difficult to decide unambiguously whether there is substitution via a carbonium ion R^+ or whether mixed radical recombination of R˙ with Z˙ takes place. In many instances the products RZ formed in electrolysis (ethers, esters, and alcohols) have a structure typical for heterolytic substitution involving a carbonium ion[278]. Sometimes the nature of the substances formed in the electrolysis can be more readily accounted for by postulating the formation of an intermediate alkoxonium ion $RCOO^+$, which then either combines with Z^- or undergoes solvolysis[279-281].

The substitution reactions occurring in the electrolysis of carboxylates have been used successfully to synthesise alcohols, acetamides, nitro- and alkoxy-derivatives, and many other classes of organic compounds[1,248]. The necessity for the preliminary substrate oxidation stage has been assumed by the majority of the investigators of the substitution reactions of aromatic compounds. This conclusion is frequently justified by the depolarising influence of the substrate on the anode under galvanostatic conditions, although, as stated previously[2,3], such arguments are not always sufficiently convincing. This also applies to the interpretation of certain results of potentiostatic electrolysis. For example, the acetoxylation of aromatic substances at $\varphi < \varphi_{cr}$, which has been regarded[282-284] as an important confirmation of mechanism (6c), can be readily interpreted also as a result of homolytic interaction with a substrate molecule of the radical AcO adsorbed on the electrode below φ_{cr}.

A detailed comparison of the composition of the anodic substitution products of many aromatic compounds with the results of the analogous chemical reactions has shown, however, that in many instances pathway (6c) is preferable to the homolytic mechanism. In particular an $EC_N\bar{E}C_B$ mechanism has been adopted for the introduction of

acyloxy-, cyano-, and bromo-groups into the benzene ring or at the α-carbon atom in alkylamines:

$$\underset{(E)}{HArR} \xrightarrow{-e} \underset{(C_N)}{\overset{+}{HAr}R} \xrightarrow{Z^-} \underset{(E)}{ZHArR} \xrightarrow{-e} \underset{(C_B)}{\overset{+}{ZHAr}R} \xrightarrow{-H^+} ZArR . \qquad (7a)$$

The substitution in the side chain is best explained by an EC_BEC_N mechanism [285-288]:

$$\underset{(E)}{ArCH_2R} \xrightarrow{-e} \underset{(C_B)}{\overset{+}{ArCH_2}R} \xrightarrow{-H^+} \underset{(E)}{ArCHR} \xrightarrow{-e} \underset{(C_N)}{\overset{+}{ArCH}R} \xrightarrow{Z^-} ArCHZR . \qquad (7b)$$

The anodic substitution reactions constitute in many cases convenient and effective methods for the synthesis of a wide variety of compounds and are frequently a useful alternative to purely chemical methods. In addition to earlier studies in this field, discussed previously [1-3,248], mention should also be made of certain investigations in recent years. In particular, Japanese workers [289] achieved the electrolytic benzoyloxylation of a number of *NN*-dimethylamides in the oxidation of benzoic acid in organic solvents and demonstrated a significant influence of the nature of the solvent and of the supporting electrolyte on the yield of products. The maximum yields were achieved in acetonitrile in the presence of $(Et_4N)ClO_4$. An appreciable role of solution composition has also been noted for reactions involving the introduction of hydroxy- and acetamido-groups [290] and also in the methoxylation of alkylbenzenes [291] and in the acetoxylation of propene [301]. In a study [292] of the anodic introduction of bromo- and cyano-groups into *p*-dimethoxybenzene and 9-phenylanthracene in acetonitrile by the volt-amperometric method and the method based on a rotating electrode with a ring it was possible, according to the authors, to refine the mechanism of the anodic substitution of aromatic compounds. It was concluded that the interaction with the nucleophilic agent proceeds at the stage involving the formation of an aromatic radical-cation and not after the formation of a carbonium ion. In another report the results of the introduction of cyano-groups into substituted diphenylamines are considered [293]. The reaction with *o*- and *m*-derivatives takes place only at the *p*-position and the yield is high (44–61%). It is suggested that the oxidation is accompanied by the formation of a radical-cation, which then interacts with CN^-. Comparison of the results obtained for the introduction of cyano- and acetoxy-groups into a number of aromatic hydrocarbons and their derivatives (biphenyl, toluene, chlorobenzene, anisole, naphthalene, and mesitylene) has shown that substitution by CN groups takes place almost exclusively in the *p*-position, in contrast to the acetyl group, which the authors explained by the more marked nucleophilic properties of the cyano-group [302]. Eberson and coworkers support a heterolytic mechanism for this reaction [302,303].

The formation of products of anodic substitution (Z^- = CH_3O^- or AcO^-) in the allyl position was established in a study of the oxidation of olefins in acetic acid, methanol, acetonitrile, and in an acetonitrile–water mixture at a carbon electrode [294]. To account for the results, the authors base their treatment on an ECEC mechanism. Nyberg and coworkers [295] succeeded in achieving the acetoxylation of a number of methylbenzenes in the side chain with a high yield and selectivity. The results were interpreted from the standpoint of the above concept of positive charge and spin densities. In another study [296] aromatic hydrocarbons (mesitylene, naphthalene, and butylbenzene) were oxidised anodically in the presence of NO_3^-. It was established that in this case three types of substitution processes take place: hydroxylation, nitration, and nitrohydroxylation, the ratios of the products of these reactions depending on the concentration of the substrate, the potential, and the nature of the anode. Other variants of the anodic substitution reactions were also investigated: the introduction of the pyridyl group into substituted anthracenes [297] and hydroxylation of phenols [298-300]. It has been shown [274,275] that the electrochemical pathway is also extremely effective for the synthesis of methoxy- and acetoxy-derivatives of a number of organosilicon compounds.

In most of the earlier studies in this field the results were treated from the standpoint of homogeneous chemistry. However, many data obtained recently conflict with this approach.

Thus in a study of the electrolytic acetoxylation of indane by Eberson and coworkers [73,74] it was not possible to detect indene —the elimination product from the 1-indanyl cation, the formation of which was to be expected when an ECEC mechanism was postulated for reactions of this type. The nature of the products indicates further oxidation of indene, which is formed in the adsorbed state according to the authors. In another study [76], dealing with the anodic acetoxylation of 2-t-butylindan on platinum and PbO oxides, the authors obtained an anomalous ratio of the *cis*- and *trans*-isomers, compared with homogeneous reactions, and suggested that the adsorption partly controls the stereochemistry of this reaction. From the authors point of view, the influence of the addition of extraneous aromatic compounds (naphthalene and pentamethylbenzene) on the relative amounts of the *o*- and *p*-substituted derivatives obtained in the anodic acetoxylation of anisole is consistent with the conclusion that the substrate is adsorbed on the anode [75]. The effect is observed even at a very low concentration of the additive, tending to a limit with its increase. Certain compounds (biphenyl and t-butylbenzene) do not affect the relative amounts of the isomers, which is explained by their weak adsorbability under these conditions.

Regardless of the reliability of this type of procedure for the estimation of the degrees of adsorption of the electrolyte components on electrodes, the above results confirm the fruitfulness of the combined approach to the study of chemical reactions and surface phenomena for a more correct understanding of the mechanisms of reactions of the classes considered.

REFERENCES

1. L. Eberson and H. Schäfer, Fortschr. chem. Forsch., 21, 1 (1971).
2. L. A. Mirkind and Yu. M. Tyurin, Symposium, "Elektrosintez i Mekhanizm Organicheskikh Reaktsii" (Electrochemical Synthesis and Mechanisms of Organic Reactions), Izd. Nauka, Moscow, 1973, p. 181.
3. M. Ya. Fioshin and L. A. Mirkind, Symposium, "Itogi Nauki i Tekhniki. Elektrokhimiya" (Advances in Science and Engineering. Electrochemistry), Izd. VINITI, Moscow, 1973, Vol. 8, p. 273.
4. H. G. Gilde, Methodes "Free-radical Chemistry", New York, 1972, Vol. 3, p. 1.
5. G. Zuliani and G. Pizzolotto, Nuovo chim., 47, 45 (1971).
6. S. Nagase, J. Japan. Chem., 24, 516 (1970).
7. M. Ya. Fioshin, L. A. Mirkind, and M. Zh. Zhurinov, Uspekhi Khim., 42, 677 (1973) [Russ. Chem. Rev., No. 4 (1973)].
8. A. Swelin, A. I. A. Khodair, and F. El-Sheikh, Int. J. J. Sulfur Chem., B6, 195 (1971).

9. M. Ya. Fioshin and L. A. Mirkind, Symposium, "Itogi Nauki, Elektrokhimiya, 1966" (Advances in Science. Electrochemistry, 1966), Izd. VINITI, Moscow, 1968, p. 114.
10. H. Schäfer and A. Al. Azrak, Chem. Ber., 105, 2398 (1972).
11. A. A. Yakovleva, E. I. Tovpinets, and V. I. Veselovskii, Elektrokhimiya, 7, 735 (1972).
12. G. F. Potapov, A. A. Rakov, and V. I. Veselovskii, Elektrokhimiya, 9, 1054 (1973).
13. A. A. Yakovleva, R. K. Bairamov, and V. I. Veselovskii, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Izd. Zinatne, Riga, 1973, p. 41.
14. E. I. Tovpinets, Ya. D. Skuratnik, A. A. Yakovleva, and V. I. Veselovskii, Elektrokhimiya, 8, 301 (1972).
15. A. T. Kornienko, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 5, 1003 (1966); 6, 1592 (1970).
16. H. Schäfer and R. Pistorius, Angew. Chem., 84, 893 (1972).
17. L. A. Aniskova, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 9, 425 (1973).
18. L. A. Aniskova, A. G. Dubinin, L. A. Mirkind, and M. Ya. Fioshin, Zhur. Org. Khim., 9, 425 (1973).
19. N. B. Kondrikov, V. V. Orlov, V. I. Ermakov, and M. Ya. Fioshin, Elektrokhimiya, 8, 945 (1972).
20. N. B. Kondrikov, V. V. Orlov, V. I. Ermakov, and M. Ya. Fioshin, Zhur. Fiz. Khim., 47, 657 (1973) [Russ. J. Phys. Chem., No. 3 (1973)].
21. Yu. V. Vodzinskii, A. A. Vasil'eva, I. A. Korshunov, and G. A. Abakumov, Elektrokhimiya, 7, 24 (1971).
22. B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorbtsiya Organicheskikh Soedinenii na Elektrodakh" (The Adsorption of Organic Compounds on Electrodes), Izd. Nauka, Moscow, 1968.
23. E. P. Platonova and V. D. Pokhodenko, Elektrokhimiya, 10, 278, 789 (1974).
24. L. A. Mirkind, M. Ya. Fioshin, and A. G. Dubinin, Symposium, "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Izd. Tartu. Gos. Univ., Tartu, 1972, p. 179.
25. L. A. Mirkind, M. Ya. Fioshin, and A. G. Dubinin, Elektrokhimiya, 8, 794 (1972).
26. Yu. M. Tyurin and G. F. Volodin, Elektrokhimiya, 5, 1203 (1969); 6, 1186 (1970).
27. Yu. M. Tyurin, G. N. Afon'shin, G. F. Volodin, and V. E. Goncharuk, Elektrokhimiya, 6, 1854 (1970).
28. V. I. Naumov and Yu. M. Tyurin, Elektrokhimiya, 8, 1220 (1972).
29. V. I. Naumov and Yu. M. Tyurin, Elektrokhimiya, 9, 1011 (1973).
30. A. A. Yakovleva and A. N. Grimberg, Elektrokhimiya, 6, 1478 (1970).
31. A. A. Yakovleva and V. I. Veselovskii, Elektrokhimiya, 6, 967 (1970); 7, 683 (1971).
32. T. Biegler, D. A. J. Rand, and R. Woods, J. Electroanalyt. Chem., 30, 269 (1971).
33. D. A. J. Rand and R. Woods, J. Electroanalyt. Chem., 31, 29 (1971).
34. M. A. Khrizolitova, L. A. Mirkind, Yu. B. Vasil'ev, M. Ya. Fioshin, and V. S. Bagotskii, Elektrokhimiya, 8, 1004 (1972).
35. L. A. Mirkind, M. Ya. Fioshin, and A. G. Dubinin, Elektrokhimiya, 9, 257 (1973).
36. L. A. Khanova, E. V. Kasatkin, and V. I. Veselovskii, Elektrokhimiya, 8, 451 (1972).
37. M. D. Gol'dshtein, Ts. I. Zalkind, and V. I. Veselovskii, Elektrokhimiya, 8, 606 (1972); 9, 699, 1396 (1973); 10, 1533 (1974).
38. D. V. Kokoulina, Yu. K. Drasovitskaya, and L. I. Krishtalik, Elektrokhimiya, 7, 1154, 1318 (1971).
39. Ngo Dai V'et [Ngo Dai Viet?], D. A. Kokoulina, and L. I. Krishtalik, Elektrokhimiya, 8, 221, 384 (1972).
40. K. J. Vetter and J. W. Schultze, J. Electroanalyt. Chem., 34, 131, 141 (1972).
41. K. J. Vetter and J. W. Schultze, Ber. Bunsenges. Phys. Chem., 75, 470 (1971).
42. Yu. Ya. Vinnikov, V. A. Shepelin, and V. I. Veselovskii, Elektrokhimiya, 8, 1229, 1384 (1972); 10, 650 (1974).
43. Yu. Ya. Vinnikov, V. A. Shepelin, and V. I. Veselovskii, Elektrokhimiya, 9, 552, 649 (1973).
44. F. Chao, M. Costa, and A. Tadjeddine, Bull. Soc. chim. France, 7, 2465 (1971).
45. F. Gorn and K. J. Vetter, Z. Phys. chem. (Frankfurt), 77, 317 (1972).
46. R. Parsons and W. H. M. Visscher, J. Electroanalyt. Chem., 36, 329 (1972).
47. M. A. Barret and R. Parsons, J. Electroanalyt. Chem., 42, 1–4 (1973).
48. D. Laser and M. Ariel, J. Electroanalyt. Chem., 35, 405 (1972).
49. G. Horanyi, J. Solt, and F. Nagy, J. Electroanalyt. Chem., 31, 87 (1971).
50. V. E. Kazarinov, Elektrokhimiya, 8, 393 (1972).
51. J. W. Schultze, Electrochim. Acta, 17, 451 (1972).
52. J. F. Llopis, G. M. Gamboa, and L. Victori, Electrochim. Acta, 17, 2225 (1972).
53. E. I. Tovpinets, Ya. B. Skuratnik, A. A. Yakovleva, and V. I. Veselovskii, Elektrokhimiya, 8, 301 (1972).
54. A. A. Yakovleva, S. N. Kaidalova, Ya. B. Skuratnik, and V. I. Veselovskii, Elektrokhimiya, 8, 1799 (1972).
55. V. E. Kazarinov, L. A. Mirkind, A. G. Dubinin, and M. Ya. Fioshin, Dokl. Akad. Nauk SSSR, 208, 1130 (1973).
56. L. A. Mirkind, V. E. Kazarinov, A. G. Dubinin, and M. Ya. Fioshin, Elektrokhimiya, 9, 1067, 1069 (1973).
57. L. A. Khanova, E. V. Kasatkin, and V. I. Veselovskii, Elektrokhimiya, 9, 562 (1973); 10, 800, 1098 (1974).
58. S. Shibata and M. P. Sumino, Electrochim. Acta, 16, 1089 (1971).
59. S. Shibata, Electrochim. Acta, 17, 393 (1972).
60. K. S. Kim, N. Winograd, and R. E. Davis, J. Amer. Chem. Soc., 93, 6296 (1971).
61. N. Katsumi and S. Takehide, J. Electroanal. Chem., 42, 7–10 (1973).
62. L. A. Mirkind and M. Ya. Fioshin, "Kataliticheskie Reaktsii v Zhidkoi Faze" (Catalytic Liquid-phase Reactions), Izd. Nauka, Kazakh. SSR, Alma-Ata, 1972, pp. 121, 226.
63. V. I. Veselovskii, A. A. Rakov, and A. A. Yakovleva, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 17, 621 (1971).
64. V. I. Veselovskii, A. A. Rakov, E. V. Kasatkin, and A. A. Yakovleva, Symposium, "Adsorbtsiya i Dvoinoi Sloi v Elektrokhimii" (Adsorption and the Double Layer in Electrochemistry), Izd. Nauka, Moscow, 1972, p. 132.
65. G. F. Volodin and Yu. M. Tyurin, Elektrokhimiya, 7, 233 (1971).

66. G.N.Afon'shin, G.F.Volodin, and Yu.M.Tyurin, Elektrokhimiya, 7, 1338 (1971).
67. Yu.M.Tyurin, G.F.Volodin, and V.F.Paducheva, Elektrokhimiya, 7, 1872 (1971).
68. Yu.M.Tyurin, G.F.Volodin, L.A.Smirnova, and Yu.V.Battalova, Elektrokhimiya, 9, 532 (1973).
69. A.K.Vijh and B.E.Conway, Chem.Rev., 67, 623 (1967).
70. V.D.Parker and L.Eberson, Chem.Comm., 340 (1969).
71. L.Eberson and G.Ridde-Petterson, Acta Chem. Scand., 87, 1159 (1973).
72. G.E.Hawkes, I.H.P.Utley, and G.B.Yates, Chem.Comm., 305 (1973).
73. E.Bernhardson, L.Eberson, K.Nyberg, and B.Rietz, Acta Chem.Scand., 25, 1224 (1971).
74. L.Eberson and H.Sternerup, Acta Chem.Scand., 26, 1431 (1972).
75. L.Eberson and R.G.Wilkinson, Acta Chem.Scand., 26, 1671 (1972).
76. L.Dirlam, L.Eberson, and H.Sternerup, Chem. Ing.-Tech., 14, 178 (1972).
77. G.A.Tarkhanov, E.P.Koveman, G.N.Freidlin, and Yu.B.Vasil'ev, Elektrokhimiya, 10, 625 (1974).
78. A.G.Kornienko, L.A.Mirkind, M.Ya.Fioshin, and A.A.Korobanov, Symposium, "Kataliticheskie Reaktsii v Zhidkoi Faze" (Catalytic Liquid-phase Reactions), Alma-Ata, 1974, Vol.2, p.482.
79. A.I.Shlygin and G.A.Bogdanovskii, Zhur.Fiz. Khim., 31, 2428 (1957); 34, 57 (1960) [Russ.J. Phys.Chem., No.1 (1960)].
80. L.A.Mirkind, B.R.Livshits, A.G.Kornienko, and M.Ya.Fioshin, Zhur.Obshch.Khim., 40, 1909 (1970).
81. Yung-Tsao Tsu, Symposium, "Osnovnye Voprosy Sovremennoi Teoreticheskoi Elektrokhimii" (Fundamental Problems of Modern Theoretical Electrochemistry) (Translated into Russian), Izd. Mir, Moscow, 1965, p.335.
82. M.Ya.Fioshin and Yu.B.Vasil'ev, Dokl.Akad. Nauk SSSR, 134, 879 (1960).
83. M.F.Fleischmann, J.R.Mansfield, and W.F.K.Wynne-Jones, J.Electroanalyt.Chem., 10, 511, 522 (1965).
84. M.F.Fleischmann and F.Goodridge, Discuss. Faraday Soc., 45, 254 (1968).
85. B.E.Conway and A.K.Vijh, J.Phys.Chem., 71, 3637 (1967).
86. B.E.Conway and A.K.Vijh, Z.Analyt.Chem., 224, 149, 160 (1967).
87. Yu.M.Tyurin and G.N.Afon'shin, Elektrokhimiya, 5, 1198 (1968).
88. V.S.Bagotskii, Yu.B.Vasil'ev, O.A.Khazova, and S.S.Beskorovainaya, Symposium, "Toplivnye Elementy" (Fuel Cells), Izd.Nauka, Moscow, 1968, p.198.
89. G.Horanyi, G.Vertes, and P.König, Magyar Kem. folyóirat., 77, 508 (1971).
90. A.G.Kornienko, L.A.Mirkind, and M.Ya.Fioshin, Elektrokhimiya, 3, 1370 (1967).
91. S.Gilman, "Electroanalytical Chemistry" (Edited by A.J.Bard), London, 1967, Vol.2, p.111.
92. J.P.Hoare, "Advances of Electrochemistry and Electrochemical Engineering", 6, Interscience, New York, 1968, p.201.
93. J.P.Hoare, "The Electrochemistry of Oxygen", Interscience, New York, 1968.
94. M.A.Genshaw, "Electrosorption", Plenum Press, New York, 1967, p.73.
95. A.Damjanovič, "Modern Aspects of Electrochemistry", Butterworths, London, 1969, Vol.5, p.369.
96. H.Angerstein-Kozlowska, B.E.Conway, and W.B.A.S.Sharp, J.Electroanalyt.Chem., 43, 9 (1973).
97. B.V.Tilak, B.E.Conway, and H.Angerstein-Kozlowska, J.Electroanalyt.Chem., 48, 1 (1973).
98. M.R.Tarasevich, B.A.Bogdanovskaya, and V.S.Vilinskaya, Elektrokhimiya, 8, 89 (1972).
99. V.I.Luk'yanycheva, A.V.Yuzhanina, and V.S.Bagotskii, Elektrokhimiya, 10, 475 (1974).
100. J.P.Hoare, Electrochim.Acta, 17, 1907 (1972).
101. L.Dunsch and R.Naumann, Z.Chem., 14, 31 (1974).
102. A.T.Kuhn and P.M.Wright, J.Electroanalyt.Chem., 41, 329 (1973).
103. B.D.Kurnikov and Yu.B.Vasil'ev, Elektrokhimiya, 9, 1203, 1845 (1973); 10, 77 (1974).
104. A.Dodson and V.J.Jennings, Nature, Phys.Sci., 240, 15 (1972).
105. R.E.Panzer and P.E.Elving, J.Electrochem.Soc., 119, 864 (1972).
106. K.F.Blurton, Electrochim.Acta, 18, 869 (1973).
107. V.N.Flerov, Yu.V.Battalova, and Yu.M.Tyurin, Elektrokhimiya, 10, 502 (1974).
108. V.I.Naumov and Yu.M.Tyurin, Elektrokhimiya, 9, 426 (1973).
109. Yu.M.Tyurin, V.I.Naumov, V.N.Flerov, and Yu.V.Battalova, Elektrokhimiya, 10, 1119 (1974).
110. T.Okamura, J.Electrochem.Soc.Japan, 42, 257 (1974); Ref.Zhur.Khim., No.2, 1252 (1975).
111. T.Bigler and R.Woods, J.Electroanalyt.Chem., 20, 73 (1969).
112. J.S.Mayell and S.N.Langer, J.Electrochem.Soc., 111, 438 (1964).
113. S.D.James, J.Electrochem.Soc., 116, 1681 (1969).
114. J.Balej and O.Špalek, Coll.Czech.Chem.Comm., 37, 499 (1972).
115. W.Visscher and M.Blulevens, Electrochim.Acta, 19, 387 (1974).
116. L.A.Mirkind and M.Ya.Fioshin, Dokl.Akad.Nauk SSSR, 154, 1163 (1964).
117. L.A.Mirkind, M.Ya.Fioshin, and V.I.Romanov, Zhur.Fiz.Khim., 38, 2233, 2840 (1964) [Russ.J. Phys.Chem., No.9, No.12 (1964)].
118. A.G.Kornienko, L.A.Mirkind, and M.Ya.Fioshin, Elektrokhimiya, 4, 69 (1968).
119. L.A.Mirkind, M.Ya.Fioshin, and D.Constantinescu, Elektrokhimiya, 2, 193, 1095 (1966).
120. A.T.Kuhn and J.G.Sunderland, Electrochim. Acta, 18, 119 (1973).
121. L.Eberson, K.Nyberg, M.Finkelstein, R.C.Peterson, S.D.Ross, and J.I.Uebel, J.Org. Chem., 32, 16 (1967).
122. S.D.Ross, M.Finkelstein, R.C.Petersen, and J.J.Uebel, J.Org.Chem, 34, 1018 (1969).
123. K.Koyama, T.Ebara, T.Tani, and S.Tsutsumi, Canad.J.Chem., 47, 2484 (1969).
124. E.Gileadi, L.Duic, and J.O'M.Bockris, Electrochim.Acta, 13, 1915 (1968).
125. J.Sobkovski, Roczniki Chem., 45, 1711 (1971).
126. P.Sidheswaran, Electrochim.Acta, 18, 125 (1973).
127. H.P.Dhar, B.E.Conway, and K.M.Joshi, Electrochim.Acta, 18, 789 (1973).
128. L.A.Mirkind, V.E.Kazarinov, A.G.Dubinin, and M.Ya.Fioshin, Elektrokhimiya, 10, 1307 (1974).
129. L.A.Mirkind, V.E.Kazarinov, A.G.Dubinin, and M.Ya.Fioshin, Symposium, "Kataliticheskie Reaktsii v Zhidkoi Faze" (Catalytic Liquid-phase Reactions), Alma-Ata, 1974, Vol.2, p.352.

130. V. E. Kazarinov and V. N. Andreev, Elektrokhimiya, 10, 1561 (1974).
131. L. A. Mirkind and M. Ya. Fioshin, Symposium, "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Izd. Tartu. Gos. Univ., Tartu, 1972, Vol. 3, p. 174.
132. L. A. Mirkind, M. Ya. Fioshin, and K. G. Bogoslovskii, Elektrokhimiya, 9, 286 (1973).
133. Yu. M. Tyurin, G. V. Volodin, V. I. Naumov, and L. A. Smirnova, Symposium, "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Izd. Tartu. Gos. Univ., Tartu, 1972, Vol. 3, p. 258.
134. L. A. Mirkind, A. G. Dubinin, M. Ya. Fioshin, and K. G. Bogoslovskii, Elektrokhimiya, 10, 1037 (1974).
135. L. A. Mirkind and E. S. Bobina, Symposium, "Kataliticheskie Reaktsii v Zhidkoi Faze" (Catalytic Liquid-phase Reactions), Alma-Ata, 1974, Vol. 2, p. 478.
136. V. A. Gromyko, T. B. Tsygankova, V. B. Gaidadymov, Yu. B. Vasil'ev, and V. S. Bagotskii, Elektrokhimiya, 9, 1685 (1973); 10, 57 (1974).
137. V. I. Naumov and Yu. M. Tyurin, Elektrokhimiya, 10, 413 (1974).
138. J. Weber and T. Loučka, "Power Sources, 1970", preprint No. 26, p. 11; quoted after Ref. 149.
139. M. I. Temkin, "Voprosy Khimicheskoi Kinetiki, Kataliza i Reaktsionnoi Sposobnosti" (Problems of Chemical Kinetics, Catalysis, and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1955, p. 484.
140. L. I. Krishtalik, Symposium, "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Izd. Tartu. Gos. Univ., Tartu, 1970, Vol. 2, p. 210.
141. T. Bajerano, C. Forgacs, and E. Gileadi, J. Electroanalyt. Chem., 27, 69 (1970).
142. E. Zeigerson and E. Gileadi, J. Electroanalyt. Chem., 28, 421 (1970).
143. T. Bajerano and E. Gileadi, J. Electroanalyt. Chem., 38, 137 (1972).
144. A. V. Solomin and E. I. Kryuchkova, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Izd. Zinatne, Riga, 1973, p. 39.
145. V. E. Kazarinov and S. V. Dolidze, Elektrokhimiya, 9, 1183 (1973).
146. M. A. Khrizolitova, L. A. Mirkind, Yu. B. Vasil'ev, M. Ya. Fioshin, and V. S. Bagotskii, Elektrokhimiya, 8, 548 (1972).
147. H. Binder, A. Kühling, and G. Sandstede, Angew. Chem., 83, 928 (1971).
148. P. Stonehart and G. Kohlmair, Electrochim. Acta, 17, 369 (1972).
149. T. Loučka, J. Electroanalyt. Chem., 36, 355, 369 (1972).
150. H. Angerstein-Kozlowska, B. Mac-Dougall, and B. E. Conway, J. Electrochem. Soc., 120, 756 (1973).
151. A. N. Frumkin, Dokl. Akad. Nauk SSSR, 154, 1432 (1964).
152. A. N. Frumkin, Elektrokhimiya, 1, 394 (1965).
153. V. I. Naumov, V. E. Kazarinov, and Yu. M. Tyurin, Elektrokhimiya, 9, 1412 (1973).
154. M. Ya. Fioshin, Symposium, "Itogi Nauki. Elektrokhimiya, 1965" (Advances in Sciences. Electrochemistry, 1965), Izd. VINITI, Moscow, 1967, pp. 152, 169.
155. G. A. Tarkhanov, E. P. Kovsman, G. N. Freidlin, and Yu. B. Vasil'ev, Elektrokhimiya, 10, 952 (1974).
156. L. Eberson, Electrochim. Acta, 12, 1473 (1967).
157. B. C. L. Weedon, Adv. Org. Chem., 1, 1 (1960).
158. J. Sekine and T. Sekine, Repts. Sci. Univ. Tokyo, 283 (1970), repr. J. Electrochem. Soc. Japan, 38, 283 (1970); quoted after Ref. 160.
159. E. P. Kovsman, S. S. Gluzman, G. A. Tarkhanov, N. I. Faingol'd, G. N. Freidlin, and T. F. Samoshina, Elektrokhimiya, 10, 543 (1974).
160. A. Takeda, T. Moriwake, S. Toru, and T. Takaki, Bull. Chem. Soc. Japan, 45, 3718 (1972).
161. A. A. Humffray and L. F. G. Williams, Electrochim. Acta, 17, 401, 409, 1157 (1972).
162. M. P. Brennan and R. Brettle, J. Chem. Soc., Perkin Trans., 1, 257 (1973).
163. Yu. V. Vodzinskii, N. P. Skvortsov, and I. A. Korshunov, Elektrokhimiya, 9, 469 (1973).
164. N. P. Skvortsov, Yu. V. Vodzinskii, Yu. M. Tyurin, and I. A. Korshunov, Elektrokhimiya, 9, 821 (1973).
165. W. Smith, Electrochim. Acta, 16, 653 (1971).
166. L. Eberson, Acta Chem. Scand., 17, 2004 (1963).
167. A. G. Kornienko, L. A. Mirkind, M. Ya. Fioshin, and A. A. Korobanov, Elektrokhimiya, 10, 350 (1974).
168. A. N. Frumkin and V. V. Sobol', Dokl. Akad. Nauk SSSR, 141, 917 (1961).
169. S. Torii, H. Tanaka, T. Fukuoka, and E. Hirai, Bull. Chem. Soc. Japan, 46, 2534 (1973).
170. L. A. Mirkind, M. A. Khrizolitova, and L. V. Aniskova, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Kazan, 1970, p. 81.
171. F. N. Stepanov, A. G. Yurchenko, S. S. Isaeva, and M. I. Novikova, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Izd. Zinatne, Riga, 1973, p. 29.
172. A. Kunugi, S. Iseku, J. Izumi, T. Tanimoto, and S. Nagaura, J. Chem. Soc. Japan, 92, 768 (1971).
173. J. P. Coleman and L. Eberson, Chem. Comm., 1300 (1971).
174. A. Takeda, S. Wada, and Y. Murakami, Bull. Chem. Soc. Japan, 44, 2729 (1971).
175. A. Laurent, E. Laurent, and M. Thomalla, Compt. rend. C, 274, 1537 (1972).
176. C. A. Parkash and R. G. Woolford, Canad. J. Chem., 49, 2681 (1971).
177. A. I. Levin, O. A. Chechina, and S. V. Sokolov, Zhur. Obshch. Khim., 25, 1778 (1965); 39, 440 (1969).
178. O. A. Chechina and A. I. Levin, Elektrokhimiya, 10, 1170 (1974).
179. N. B. Kaz'mina, L. S. German, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 199, 825 (1971).
180. G. A. Korchinskii and G. V. Andreev, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Izd. Zinatne, Riga, 1973, p. 32.
181. N. B. Kondrikov, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Izd. Zinatne, Riga, 1973, p. 27.
182. V. V. Berenblit, E. S. Panitkova, V. P. Sass, S. V. Sokolov, and Yu. K. Starobin, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of

Organic Compounds), Izd. Zinatne, Riga, 1973, p. 31.
183. V. V. Berenblit, E. S. Panitkova, D. S. Bondarev, V. P. Sass, and S. V. Sokolov, Zhur. Prikl. Khim., 47, 2427 (1974).
184. L. A. Mirkind, M. Ya. Fioshin, and L. V. Aniskova, Dokl. Akad. Nauk SSSR, 219, 1127 (1974).
185. G. Maier and T. Boblet, Tetrahedron Letters, 4485 (1972).
186. G. A. Korchinskii and G. V. Andreev, Ukrain. Khim. Zhur., 37, 1234 (1971).
187. R. N. Renauld and D. L. Sullivan, Canad. J. Chem., 50, 3034 (1972).
188. R. N. Adams, "Electrochemistry at Solid Electrodes", New York, Dekker, 1969.
189. F. Fichter and M. Rinderspacher, Helv. Chim. Acta, 10, 40 (1927).
190. F. Fichter and S. Herzbein, Helv. Chim. Acta, 11, 1269 (1928).
191. G. Erdtmann, Proc. Roys. Soc., A143, 191 (1934).
192. T. Osa, A. Yildiz, and T. Kuwana, J. Amer. Chem. Soc., 91, 3994 (1969).
193. N. E. Wisdom, Meeting of the Electrochemical Society, Extended Abstracts, New York, 1969, p. 338.
194. W. E. Ohnesorge and J. D. Stuart, Meeting of the Electrochemical Society, Extended Abstracts, New York, 1969, p. 338.
195. K. Nyberg, Acta Chem. Scand., 24, 1669 (1970); 25, 534, 2499, 2983 (1971).
196. K. Nyberg, Acta Chem. Scand., 25, 3770 (1971).
197. K. Nyberg, Acta Chem. Scand., 27, 503 (1973).
198. K. Bechgard, O. Hammerich, N. S. Moe, A. Ronlán, U. Svanholm, and V. D. Parker, Tetrahedron Letters, 2271 (1972).
199. A. Rohlán, K. Bechgard, and V. D. Parker, Acta Chem. Scand., 27, 2375 (1973).
200. H. G. Thomas and E. Lux, Tetrahedron Letters, 965 (1972).
201. K. Brettle and J. G. Parkin, J. Chem. Soc. (C), 1352 (1967).
202. T. Okubo and S. Tsutsumi, Bull. Chem. Soc. Japan, 37, 1794 (1964).
203. C. M. Wright and D. R. Levering, Tetrahedron, 19, 3 (1963).
204. D. Koch, H. Schäfer, and E. Steckhan, Chem. Ber., 107, 3640 (1974).
205. R. F. Heck and W. Yokoyama, Meeting of the Electrochemical Society, Extended Abstracts, New York, 1969, p. 361.
206. R. V. Lindsey and M. L. Peterson, J. Amer. Chem. Soc., 81, 2073 (1959).
207. W. B. Smith and H. G. Gilde, J. Amer. Chem. Soc., 81, 5325 (1959); 83, 1355 (1961).
208. M. Ya. Fioshin, A. I. Kamneva, L. A. Mirkind, and L. A. Salmin', Dokl. Akad. Nauk SSSR, 138, 173 (1961).
209. M. Ya. Fioshin, A. I. Kamneva, L. A. Mirkind, L. A. Salmin', and A. G. Kornienko, Neftekhimiya, 2, 557 (1962).
210. M. Ya. Fioshin, A. I. Kamneva, L. A. Mirkind, L. A. Salmin', and A. G. Kornienko, Khim. Prom., 804 (1966).
211. M. Ya. Fioshin, L. A. Mirkind, and A. G. Kornienko, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 19, 600 (1964).
212. M. A. Khrizolitova, L. A. Mirkind, and M. Ya. Fioshin, Dokl. Akad. Nauk SSSR, 182, 617 (1968).
213. M. A. Khrizolitova, L. A. Mirkind, and M. Ya. Fioshin, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 15, 230 (1970).
214. M. A. Khrizolitova, L. A. Mirkind, and M. Ya. Fioshin, Zhur. Org. Khim., 4, 1705 (1968); 6, 219 (1970).
215. M. A. Khrizolitova, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 5, 1018 (1969).
216. M. Ya. Fioshin, M. A. Khrizolitova, L. A. Mirkind, and A. G. Kornienko, USSR P. 215 959 (1968); Buyl. Izobret., No. 14, 24 (1968).
217. M. Zh. Zhurinov, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 4, 885 (1968); 5, 1257 (1969).
218. M. Zh. Zhurinov, L. A. Mirkind, and M. Ya. Fioshin, Izv. Akad. Nauk Kazakh. SSR, No. 2, 57 (1970).
219. M. Zh. Zhurinov, M. Ya. Fioshin, and L. A. Mirkind, USSR P. 263 592 (1969); Byul. Izobret., No. 8, 21 (1970).
220. M. Zh. Zhurinov, M. Ya. Fioshin, and L. A. Mirkind, USSR P. 3 080 000 (1971); Byul. Izobret., No. 21, 76 (1971).
221. M. Zh. Zhurinov, L. A. Mirkind, and M. Ya. Fioshin, Symposium, "Khimiya i Khimicheskaya Tekhnologiya" (Chemistry and Chemical Engineering), Izd. Kazakh. Gos. Univ., Alma-Ata, 1972, Vol. 2, pp. 170, 174.
222. A. K. Erimbetov, M. Ya. Fioshin, and M. Zh. Zhurinov, Elektrokhimiya, 10, 1293 (1974).
223. A. G. Kornienko, A. V. Uvarov, L. A. Mirkind, and M. Ya. Fioshin, Elektrokhimiya, 4, 1140 (1968).
224. M. Ya. Fioshin, L. A. Salmin', L. A. Mirkind, and A. G. Kornienko, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 10, 594 (1965).
225. L. V. Aniskova, L. A. Mirkind, and M. Ya. Fioshin, USSR P. 3 76354 (1972); Byul. Izobret., No. 17, 71 (1973).
226. M. A. Khrizolitova, A. G. Kornienko, M. Ya. Fioshin, and L. A. Mirkind, USSR P. 376 348 (1970); Byul. Izobret., No. 17, 70 (1973).
227. F. Bruno and J.-E. Dubois, Bull. Soc. chim. France, 2280 (1973).
228. M. Katz, O. Saygin, and H. Wendt, Electrochim. Acta, 19, 193 (1974).
229. H. Sternerup, Acta Chem. Scand., B, 28, 579 (1974).
230. H. Schäfer and A. Al. Azrak, Angew. Chem., 80, 485 (1968).
231. E. Steckhan and H. Schäfer, Angew. Chem., 86, 480 (1974).
232. H. Schäfer and E. Steckhan, Chem. Ing.-Tech., 44, 186 (1972).
233. M. Chkir and D. Lelandais, Chem. Comm., 1369 (1971).
234. H. Schäfer, Chem. Ing.-Tech., 41, 179 (1969).
235. H. Schäfer, Chem. Ing.-Tech., 42, 164 (1970).
236. H. Schäfer and H. Küntzel, Tetrahedron Letters, 3333 (1970).
237. H. Schäfer, Angew. Chem., 82, 134 (1970).
238. L. A. Mirkind, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Engineering, 1964.
239. G. Foita, M. Fleischmann, and D. Pletscher, J. Electroanal. Chem., 25, 455 (1970).
240. N. L. Weinberg and A. K. Hoffmann, "21st CITCE Meeting, Prague, 1970, Extended Abstracts", p. 467.
241. L. Eberson and K. Nyberg, Acta Chem. Scand., 18, 1567 (1964).
242. Y. Matsuda, K. Kimura, and C. Ywakura, Bull. Chem. Soc. Japan, 46, 430 (1973).
243. V. R. Koch and L. L. Miller, Tetrahedron Letters, 1430 (1973).

244. L.L. Miller and V. Ramanhandran, J. Org. Chem., 39, 369 (1974).
245. G.A. Tedoradze, V.A. Paprotskaya, and A.P. Tomilov, Elektrokhimiya, 10, 1103, 1292, 1612 (1974).
246. A.P. Tomilov, Yu.D. Smirnov, and Yu.I. Rozin, Zhur. Obshch. Khim., 44, 2028 (1974).
247. A.P. Tomilov, Uspekhi Khim., 30, 1462 (1961) [Russ. Chem. Rev., No. 12 (1961)].
248. L. Eberson and K. Nyberg, Accounts Chem. Res., 6, 106 (1973).
249. M. Schmeiser and P. Sartori, Chem. Ing.-Tech., 36, 9 (1964).
250. J. Simons, J. Electrochem. Soc., 95, 47 (1949).
251. T. Gramstad and R. Haszeldine, J. Chem. Soc., 1, 173 (1956).
252. J. Burdon and J.C. Tatlow, Symposium, "Uspekhi Khimii Ftora" (Advances in Fluorine Chemistry) (Translated into Russian), Inostr. Lit., Moscow, 1964, p. 472.
253. Ya.N. Voĭtovich and V.Ya. Kazakova, Zhur. Prikl. Khim., 44, 2452 (1971).
254. G. Zuliani and G. Pizzolotto, Nuovo cim., 48, 47 (1972).
255. I.L. Knunyants, I.N. Rozhkov, and A.V. Bukhtiarov, Izv. Akad. Nauk SSSR, Ser. Khim., 1369 (1971); 1130 (1972).
256. N. Watanabe, M. Haruta, and B. Chang, Bull. Chem. Soc. Japan, 45, 1273 (1972).
257. B. Chang, H. Yanase, K. Nakanishi, and N. Watanabe, Electrochim. Acta, 16, 1179 (1971).
258. H.M. Fox, F.N. Ruelen, and W.V. Childs, J. Electrochem. Soc., 118, 1246 (1971).
259. S. Nagase, T. Abe, H. Baba, and K. Kodira, Repts. Govt. Ind. Res. Inst. Nagoya, 20, 99 (1971); quoted after Ref. 266.
260. J. Inoue, S. Nagase, K. Kodaira, H. Baba, and T. Abe, Repts. Govt. Ind. Res. Inst. Nagoya, 22, 424 (1973); quoted after Ref. 266.
261. V.V. Berenblit, V.I. Grachev, and I.M. Dolgopol'skii, Zhur. Obshch. Khim., 45, 2256 (1972).
262. N.M. Arakelyan and E.A. Aikazyan, Arm. Khim. Zhur., 26, 419 (1973).
263. T. Abe, S. Nagase, and H. Baba, Bull. Chem. Soc. Japan, 46, 3845 (1973).
264. V.S. Plashkin, L.N. Pushkina, Yu.P. Dolnakov, and S.V. Sokolov, Zhur. Org. Khim., 9, 2525 (1973).
265. I.N. Rozhkov and I.L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1223 (1970).
266. K. Okazaki, S. Nagase, H. Baba, and K. Kodaira, J. Fluorine Chem., 4, 387 (1974).
267. V.V. Berenblit, V.A. Byzov, I.M. Dolgopol'skii, and Yu.P. Doknakov, Zhur. Prikl. Khim., 47, 2433 (1974).
268. V.V. Berenblit, B.A. Byzov, V.I. Grachev, I.M. Dolgopol'skii, and Yu.P. Dolnakov, Zhur. Prikl. Khim., 48, 709 (1975).
269. A.T. Kuhn and P.M. Wright, J. Electrochem. Soc., 41, 329 (1973).
270. F. Acquah, A.T. Kuhn, and C.J. Mortimer, J. Appl. Chem. Biotechnol., 22, 1195 (1972).
271. W.B. Mather and E.R. Kerr, US P. 3 692 646 (1972); Chem. Abs., 77, 171 996 (1972).
272. G.A. Tedoradze, V.A. Paprotskaya, N.B. Vladimirov, and Yu.V. Yuzbekov, Elektrokhimiya, 11, 502 (1975).
273. M. Mastrogostino, G. Casalbare, and S. Valcher, J. Electroanalyt. Chem., 55, 117 (1974).
274. N.P. Kharitonov, B.P. Nechaev, and G.T. Fedorova, Zhur. Obshch. Khim., 39, 824 (1969).
275. G.T. Fedorova, N.P. Kharitonov, and B.P. Nechaev, Symposium, "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Developments in the Electrochemistry of Organic Compounds), Izd. Zinatne, Riga, 1973, p. 43.
276. S.D. Ross, M. Finkelstein, and R.C. Petersen, J. Amer. Chem. Soc., 88, 4657 (1966).
277. L. Eberson and K. Nyberg, J. Amer. Chem. Soc., 88, 1686 (1966).
278. G.G. Traynham and I.S. Dehn, J. Amer. Chem. Soc., 89, 2139 (1967).
279. T. Shono, I. Nishiguchi, S. Yamane, and R. Oda, Tetrahedron Letters, 1965 (1969).
280. R.G. Gassman and F.V. Zalar, J. Amer. Chem. Soc., 88, 2252 (1966).
281. P.S. Skell and P.H. Reichenbacher, J. Amer. Chem. Soc., 90, 2309, 3436 (1968).
282. L. Eberson and K. Nyberg, Acta Chem. Scand., 18, 1568 (1964).
283. M. Leung, I. Herz, and H.W. Salzberg, J. Org. Chem., 30, 310 (1965).
284. H.W. Salzberg and M. Leung, J. Org. Chem., 30, 2873 (1965).
285. L. Eberson, J. Amer. Chem. Soc., 89, 4669 (1967).
286. V.D. Parker and B. Burgert, Tetrahedron Letters, 1721 (1969).
287. V.D. Parker and R.N. Adams, Tetrahedron Letters, 1721 (1969).
288. L. Eberson and B. Olofsson, Acta Chem. Scand., 23, 2355 (1969).
289. A. Seiji, H. Nobuko, N. Yukio, and T. Kenjiro, J. Chem. Soc. Japan, Chem. Ind. Sect., 302 (1973).
290. E.A. Mayada and L.L. Miller, Tetrahedron, 28, 3375 (1972).
291. A.V. Solomin and E.I. Kryuchkova, Izv. Akad. Nauk Kazakh. SSR, Ser. Khim., No. 6, 62 (1971).
292. K. Sasaki and H. Ohishi, Electrochim. Acta, 17, 2391 (1972).
293. K. Yoshida and R. Fueno, J. Org. Chem., 37, 4145 (1972).
294. T. Shono and A. Ikeda, J. Amer. Chem. Soc., 94, 7892 (1972).
295. C. Magnusson, B. Olofsson, and K. Nyberg, Chem. Scripta, 1, 57 (1971).
296. K. Nyberg, Acta Chem. Scand., 25, 3246 (1971).
297. H.N. Blount, J. Electroanal. Chem., 42, 271 (1973).
298. L. Papouchado, G. Petrie, and R.N. Adams, J. Electroanal. Chem., 38, 389 (1972).
299. A. Ronlan and V.D. Parker, J. Chem. Soc. (C), 3214 (1971).
300. A. Nilsson, A. Ronlan, and V.D. Parker, J. Chem. Soc., Perkin Trans., 2337 (1973).
301. L. Formaro, G. Fiori, and M. Colombi, J. Electroanal. Chem., 44, 255 (1973).
302. L. Eberson and S. Nilsson, Discuss. Faraday Soc., 45, 242 (1968).
303. L. Eberson and B. Helgel, Chem. Scripta, 5, 47 (1974).

State Research and Design
Institute for the Paint and
Varnish Industry