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ANODIC SUBSTITUTION REACTIONS

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1. INTRODUCTION

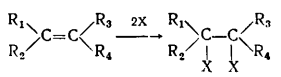
Among the processes occurring at the anode during the electrolysis of electrolyte solutions in the presence of organic compounds a group of processes can be distinguished which can be represented by the general equation,

$$RH \rightarrow RX,$$

where X = F, Cl, Br, I, OH, CNS, CNSe, ONO_2, $O.CH_3$, SO_3H, N:N.Hal, etc.

These processes are usually described collectively as "anodic substitution". Depending on the nature of the substituting agent, anodic substitution can bring about fluorination, chlorination, bromination, iodination, hydroxylation, thiocyanation, selenocyanation, preparation of nitric esters, nitration, methoxylation, sulphonation, and diazotisation.

Addition to multiple bonds in organic compounds can also take place at the anode



By analogy with "anodic substitution" such reactions could be termed "anodic addition" reactions. Since "anodic addition" reactions are comparatively few, and do not differ fundamentally from anodic substitution reactions, we will consider them together under the general term "anodic substitution".

2. MECHANISM OF "ANODIC SUBSTITUTION"

Anodic substitution processes can be divided into two main groups.

(i) Radical Processes

In radical processes the primary step at the electrode is the discharge of anions present in the solution, with the formation of free radicals

$$2X^- \xrightarrow{-2e} 2X;$$

which react with the organic substance

$$R{-}H + 2X \cdot \longrightarrow R{-}X + HX...$$

Such a mechanism has been proposed by Knunyants and Sokol'skii[1] for all cases of electrochemical fluorination. Some workers, however, think this process more complicated. Thus Gramstad and Haszeldine[2] suggested that the formation of organic fluorine compounds involves reaction between the organic compound and higher fluorides of nickel formed on the anode.

In order to explain the formation of organic fluorine compounds during the electrolysis of a solution of an olefine in acetic acid containing potassium hydrogen difluoride, Schmidt[3] postulates the discharge at the anode of a complex of the organic compound with hydrogen fluoride, whereby the coordinate link in the complex is converted into a covalent bond.

Youtz[4] suggested a radical mechanism for electrochemical chlorination on the basis of measurements of anode potential during the chlorination of several organic compounds (malonic acid, phenol, and toluene).

This group includes, in addition to the above mentioned fluorination and chlorination, the reactions of bromination, thiocyanation, hydroxylation, preparation of nitric esters, iodination in part, and probably alkoxylation.

The mechanism of electrochemical alkoxylation is apparently that the bromine radicals formed at the anode react with the alcohol present as solvent, *e.g.* with methyl alcohol to form methoxyl radicals

$$Br \cdot + CH_3OH \longrightarrow HBr + CH_3O \cdot,$$

which can effect the methoxylation of furan and its derivatives according to the equations considered below (see section on alkoxylation).

(ii) Chemical "Anodic Substitution" Reactions

The occurrence of such reactions is due to the accumulation in the layer adjacent to the anode, as a result of the anodic process, of products which can react with the organic compound. They include nitration, nitrosation, sulphonation, diazotisation, some cases of iodination, and also the addition of HOCl.

The addition of HOCl to ethylene during electrolysis in the presence of chlorides, for example, is due to the chlorine evolved at the anode dissolving to form hypochlorous acid, which reacts with the ethylene

$$Cl_2 + OH^- \longrightarrow Cl^- + HClO,$$

$$HClO + CH_2{=}CH_2 \longrightarrow CH_2OH{\cdot}CH_2Cl$$

The formation of iodoform apparently takes place in an analogous manner, since alcohol is not a depolariser with respect to the platinum anode at which iodine is deposited.

In nitration and sulphonation the action of the electric current is essentially to produce concentrated solutions of nitric and sulphuric acids around the anode as a result of ionic migration.

3. ANODIC SUBSTITION REACTIONS: CONDITIONS

(*a*) Choice of Electrolyte and of Solvent

The solution in which anodic substitution is to be effected must be sufficiently conducting, and its electrolysis should involve the discharge at the anode of the anions required for the substitution. The choice of solvent is dictated by this requirement.

The only anodic process possible in the electrolysis of aqueous alkaline solutions is the discharge of hydroxyl ions, so that these solutions are most suitable for anodic hydroxylation.

Bromide, iodide, and thiocyanate anions are discharged with high efficiency from aqueous solutions of their salts, and therefore bromination, iodination, and thiocyanation are carried out in aqueous solutions, concentrated ammonium thiocyanate solutions being recommended for the last-named process.

The discharge of chloride ions requires a more positive potential than that of bromide, iodide, and thiocyanate ions. The chlorine evolved at the anode during the electrolysis of aqueous chloride solutions always contains some oxygen, since the discharge of hydroxyl ions accompanies that of chloride ions. If the substance is comparatively readily oxidised, some oxidation cannot be avoided during electrochemical chlorination in aqueous solutions. In such cases it is necessary to use non-aqueous solutions. The chlorination of benzene, for example, has been carried out in ether saturated with hydrogen chloride[5], in acetic acid saturated with lithium chloride[6], in a mixture of acetic and concentrated hydrochloric acids[7], and in methyl alcohol saturated with hydrogen chloride[8,9].

The discharge of fluoride ions requires a considerably more positive potential than that of hydroxyl ions, so that aqueous solutions are unsuitable for electrochemical fluorination. The chemical reactivity of elementary fluorine makes the choice of solvent extremely difficult. The only solvent which gives satisfactory results is apparently liquid hydrogen fluoride[10]. The electrical conductivity of pure hydrogen fluoride is slight[11], but it is a good solvent for most organic compounds (alcohols, ethers, carboxylic acids, nitriles, ketones, amines, etc.), forming electrically conducting solutions, which indicates that dissociation occurs on dissolution. Solutions in hydrogen fluoride differ fundamentally in the nature of their dissociation from aqueous solutions, for it is not the solute but the solvent, *i.e.* the hydrogen fluoride, which undergoes dissociation[12]. When alcohol and ether, for example, are dissolved in hydrogen fluoride, the dissociation which takes place can be represented by the following equations:

$$C_2H_5OH + HF \rightleftarrows C_2H_5OH_2^+ + F^-$$

$$C_2H_5OC_2H_5 + HF \rightleftarrows (C_2H_5)_2OH^+ + F^-,$$

i.e. the only anions present in the solution are fluoride ions, and electrochemical processes other than the discharge of fluoride ions are impossible.

A number of organic compounds, hydrocarbons for example, are almost insoluble in hydrogen fluoride and do not form electrically conducting solutions in it. It has been suggested that electrochemical fluorination of such compounds can be effected by adding to the hydrogen fluoride a small quantity of a substance which will make the mixture electrically conducting, *e.g.* water, mercurous cyanide, ammonia, methyl alcohol, acetic acid, pyridine, 2-fluoropyridine, or alkali-metal fluorides[10].

There are indications that electrochemical fluorination is possible by the electrolysis of an organic substance in anhydrous acetic acid saturated with potassium hydrogen difluoride[3,13], but this solvent is probably applicable only in rare instances.

Methoxylation and ethoxylation are carried out respectively in absolute methyl and ethyl alcohol in which a little ammonium bromide has been dissolved[14-17].

(*b*) Anode Material

The main requirement of an anode material for electrochemical substitution is that it shall be chemically inert. The choice of materials unaffected by anodic processes is very restricted.

Nickel is generally employed for electrochemical fluorination in liquid hydrogen fluoride[10], and a platinum anode is recommended for fluorinations in potassium hydrogen difluoride–acetic acid solution[3,13].

As already noted in sub-section (*a*), electrochemical chlorination in aqueous solutions may be accompanied by the discharge of hydroxyl ions, and a material of high oxygen overpotential must be used as anode to minimise possible oxidation processes. This requirement is best met by smooth platinum, the use of which is advisable for almost all electrochemical chlorination[5-9,18-30].

An attempt to use graphite or magnetite anodes in the chlorination of benzene did not give satisfactory results[7]. Chlorination of toluene at a graphite anode is accompanied by oxidising processes, leading to the formation of *o*- and *p*-chlorobenzoic acids[31].

It has been reported that benzene and ethylene can be satisfactorily chlorinated at a graphite anode impregnated with cyanuric acid[32], or by using anode rods made by compressing a mixture of 50 parts of graphite + 40 parts of sodium chloride + 10 parts of potassium iodide. The activity of such electrodes is apparently due to the formation of iodine chloride, which acts as a chlorine carrier. The use of anodes having this composition has a qualitative effect on the course of the chlorination. When, for example, toluene is chlorinated at a platinum anode, a mixture of *o*- and *p*-chlorotoluenes is formed[33], but on the pressed graphite anodes, 2,4-dichlorotoluene is also formed[34].

Platinum anodes are usually employed for bromination, iodination, methoxylation, and the preparation of nitric esters[14-16,35-46], although graphite anodes appear to be equally suitable for the first three processes[17,47,48], and thiocyanation is even more successful on graphite than on platinum[49-55].

Since anodic substitution is usually carried out in a bath without a diaphragm, the choice of cathode material is also fairly critical. Electrodes made of copper, nickel, iron, or other metal of low hydrogen overpotential are apparently

the most suitable, since they are least likely to cause undesirable reduction processes.

(*c*) Current Density

In most cases current density has no effect on the mechanism of the discharge of anions until its limiting value is reached. However, products in which the hydrogen atoms have been completely substituted are more likely to be obtained at high current densities.

By employing a high concentration of organic acid and a low current density, for example, it is possible to obtain incompletely fluorinated propionic and butyric acids[56], whereas at current densities of ~400 A m^{-2} the hydrogen atoms are completely replaced by fluorine[57]. Increasing the current density favours the formation of polychloro--derivatives from benzene and its homologues[7]. Iodination of 8-hydroxyquinoline at 0.001 A cm^{-2} yields mainly a monoiodo derivative, whereas at 0.01 A cm^{-2} the chief product is diiodoquinolinol[44].

Increasing the current density has a favourable effect on the bromination of indigo[38] and on the formation of nitric esters from ethylene[45]. It may happen that at high current densities the rate of formation of inorganic radicals at the anode becomes greater than the rate at which they react with the organic compound, making additional processes possible. In the case of halogenation, for example, the free halogens may be evolved at the anode. This process is particularly dangerous with electrochemical fluorination, since the evolution of elementary fluorine at the anode leads to degradation of the organic substances. Thus electrochemical fluorination of succinic anhydride, for example, yields a mixture of the fluorides of perfluoropropionic and perfluorosuccinic acids, the yield of the latter increasing from 9.6% to 23.4% when the current density is decreased from 0.03 to 0.01 A cm^{-2}: *i.e.* increase in current density substantially accelerates decarboxylation processes[58].

The use of excessive current densities is undesirable also with other types of anodic substitution. Under these conditions an appreciable diminution in the yield has been observed in the bromination of indigo[38] and also, for example, in the preparation of iodoform[42].

It is clear from the above that each case should have an optimum current density, at which the process is carried out most efficiently. These optimum values usually lie within the range 100–1000 A m^{-2}.

Fluorination is normally carried out at ~200 A m^{-2}.[1,10,11,59] The optimum current densities (in A m^{-2}) for various processes are — preparation of chloral[32] 300, preparation of chloroform from alcohol[60] 400–800, and from acetone[29] 150, chlorination of higher ketones[61] 640–1250, chlorination of ethylene[30,62] 700–1500, chlorination of benzenesulphonic acid[63] 330, bromination of succinimide[40] 465, preparation of iodoform from acetone[43] 130, and thiocyanation[49–53] 200–300.

(*d*) Concentration of Organic Substance

Increasing the concentration of the organic substance has in most cases a favourable effect on the substitution process. In the bromination of acetone, for example, a high concentration of acetone in the solution favours the formation of bromoform[35], and increasing the concentration of alcohol undergoing iodination favours the formation of iodoform[41].

Many organic substances, however, have poor solubility in aqueous solutions, and therefore numerous attempts have been made to increase the concentration of the organic compound by using various solvents.

The use of solvents cannot be accepted as desirable, since they usually take part to some extent in the anodic process, and contaminate the reaction products. Instead of using solvents, it is sometimes better to stir vigorously the solution undergoing electrolysis[64], or to introduce the organic substance directly through a porous anode[32,65–68], since this practically eliminates any possible concentration effects and ensures the maximum possible concentration of the organic compound during the process. On the other hand, a large excess of the organic compound favours the formation of incompletely substituted derivatives: thus electrolysis of solutions of carboxylic acids containing comparatively low concentrations of hydrogen fluoride (1–5 moles of HF per mole of acid) results in partial replacement of the hydrogen atoms by fluorine, propionic acid giving a 10% yield of β-fluoropropionyl fluoride, and butyric acid a 20–30% yield of a mixture of α-, β-, and γ-fluorobutyric acids[56].

Another example of the effect of concentration of the organic substance on the substitution process is provided by the electrochemical fluorination of dimethyl sulphate. The main fluorination product of the electrolysis of a 5–10% solution of dimethyl sulphate in hydrogen fluoride is bistrifluoromethyl sulphate[69], but with a small concentration of hydrogen fluoride in the dimethyl sulphate (molecular ratio 1 : 5.5), the main product under the same conditions of electrolysis is fluoromethyl methyl sulphate[70].

(*e*) Solution pH

The optimum pH value is different for each individual substitution. Halogens, for example, react vigorously with alkalis, and therefore chlorination, bromination, and iodination are carried out in acid or neutral media. The main product of the chlorination of alcohol in acid medium is chloral[67,71], whereas in neutral or faintly alkaline medium chloroform is produced almost exclusively[18,20]. A neutral medium is necessary for the preparation of iodoform from alcohol[41] and of chloroform and bromoform from acetone[20,35] as well as in the bromination of succinimide[40] and the iodination of 8-hydroxyquinoline[44]. Other processes, such as the chlorination of ketones while preserving the carbonyl group[22,23,61], the chlorination of aniline[29,72,73], the bromination of indigo[38,72,73], etc , are carried out successfully in acid media.

Strongly alkaline media are more suitable for hydroxylation processes. An electrolyte of 25% caustic soda solution is recommended for the hydroxylation of ethylene[74].

We must consider here in more detail processes which require the medium to be kept neutral. Since the pH of the solution is continually changing during electrolysis, great attention has been paid to methods for buffering the medium in continuous-flow processes. Several ways of solving this problem have been suggested — (1) use of solutions of alkaline-earth salts (*e.g.* calcium chloride, barium chloride, etc.) as electrolyte[20,60,67,77], (2) employment of an addi-

tional (neutralising) cathode[20,43], (3) addition of hydrochloric acid to the solution[18], and (4) employment of a mercury–iron cathode[18,19].

A detailed consideration of the merits and defects of all these methods is beyond the scope of the present paper. The most reliable method is probably the continuous controlled acidification of the solution during electrolysis.

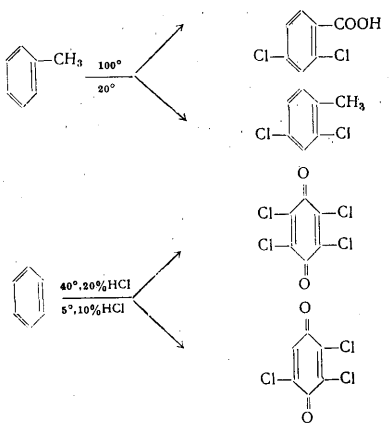
(*f*) Temperature

Temperature has a very important effect on the substitution process, but published information is inadequate for a complete explanation of the observed phenomena.

The role of temperature in electrochemical fluorination has been discussed in some detail[1]. As the temperature of fluorination is raised, the percentage of the most highly volatile products increases (see ref. 78) and the extent of degradation of the hydrocarbon skeleton decreases[79].

In a number of cases of chlorination, bromination, and iodination, a slight increase in temperature (to 40°–60°) has a favourable effect on the substitution.

At still higher temperatures the yield of substitution products begins to fall owing to side-reactions. In electrochemical chlorination, for example, a rise in temperature usually results in more extensive oxidation, and also favours the formation of the more highly chlorinated products. This has been observed in the chlorination of benzene[28], toluene[31], benzenesulphonic acid[63], and aniline[75].



In other cases, for example in the chlorination of ketones[61], the bromination of succinimide[40], the iodination of 8-hydroxyquinoline[44], thiocyanation[51], and methoxylation[14], the use of low temperatures is recommended.

4. ANODIC SUBSTITUTION REACTIONS: APPARATUS

The apparatus for carrying out anodic substitution reactions in liquids is extremely simple, since in most cases other than nitration and diazotisation there is no need to separate the anodic and cathodic compartments by a porous diaphragm.

On a small scale the electrolytic cell can be a glass tube sealed at one end, in which are placed cylindrical electrodes. The required temperature is maintained by immersing the cell in a water-bath.

The reaction products in a number of cases of electrochemical chlorination, bromination, and fluorination are insoluble in the solution undergoing electrolysis, and separate as a heavy oil, which simplifies the treatment of the products. A laboratory type of cell suitable for carrying out such reactions has been designed by Izgaryshev and Polikarpov[36].

In order to obtain substitution products on a larger scale, it is advisable to use a cell fitted with a stack of electrodes of alternate polarity. The cell is provided with a jacket, a stirrer, and a reflux condenser in order to maintain the required temperature and avoid concentration effects and loss of the organic compound. An electrolytic cell of this type, intended for electrochemical fluorination, has been described in detail in Simons' monograph[59,80].

Electrochemical fluorination often results in the formation of gaseous products, which escape through the condenser and can be separated by intense cooling of the issuing gases.

The design of apparatus for carrying out the anodic substitution of gaseous substances presents great difficulty. One type of cell, intended for the addition of HOCl to ethylene and used in Stender's experiments[30], is shown in Fig. 1. The ethylene reaches the anode surface through a porous glass plate. This design of cell is extremely wasteful in ethylene, however, and cannot be accepted as satisfactory.

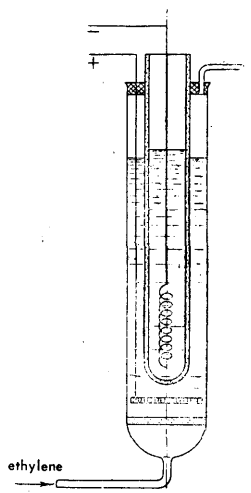


Fig. 1. Laboratory electrolytic cell for preparation of ethylene chlorohydrin.

McElroy's ingenious design of industrial cell for this process[81] is illustrated in Fig. 2. The gas is forced under pressure into the electrolytic cell, where it bubbles continuously through the solution. As reaction proceeds, the pressure drops and more ethylene is admitted.

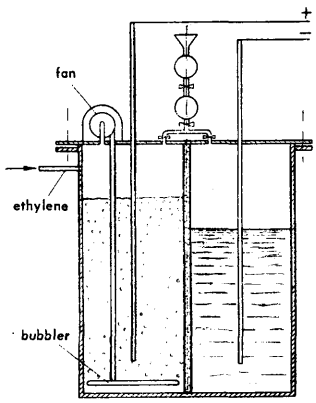


Fig. 2. Electrolytic cell for the industrial production of ethylene chlorohydrin.

Diazotisation and nitration should be carried out in a bath fitted with a diaphragm, since the products formed in these reactions are readily reduced at the cathode. The type of apparatus required for these reactions does not need to be specially described.

5. RANGE OF APPLICATION OF ANODIC SUBSTITUTION REACTIONS

In order to obtain a clear idea of the applicability of "anodic substitution" reactions in organic chemistry, the reactions which can be carried out electrochemically are summarised below.

A. Fluorination

(*a*) Fluorination of hydrocarbons and their chloro-derivatives. The electrochemical fluorination of saturated hydrocarbons is represented by the equation

$$C_nH_{2n+2}+2(2n+2)F\cdot \longrightarrow C_nF_{2n+2}+(2n+2)HF,$$

completely fluorinated compounds being formed. The current efficiency of formation of fluorocarbons is 10–30%.

Completely fluorinated analogues of octane, iso-octane, toluene, dodecane, and tetradecane have been prepared by the electrochemical method [82].

The electrochemical fluorination of hydrocarbons usually results in the complete replacement of all the hydrogen atoms by fluorine. Partly fluorinated compounds are formed in the electrochemical fluorination of halogenated hydrocarbons. The electrochemical fluorination of chloroform or methylene chloride [78,83], for example, yields a complex mixture containing CF_4, CHF_3, CH_2F_2, $CHClF_2$, CCl_2F_2, CH_2ClF, $CHCl_2F$, $CClF_3$, and CCl_3F. The proportions of the various species depend to a considerable extent on the experimental conditions.

Electrolysis of an HF–NaF mixture in the presence of $CHCl:CCl_2$ with vigorous stirring yielded the compound $CHFCl.CFCl_2$. [84] Similar products have been obtained by the electrochemical fluorination of brominated and iodinated hydrocarbons [85].

It is possible to add fluorine to the double bond of unsaturated compounds by electrolysis of a solution of potassium hydrogen difluoride in anhydrous acetic acid. In this electrolyte the efficiency of fluorination of vinyl chloride is a few per cent, but addition of fluorine to 1,1-diphenylethylene

$$(C_6H_5)_2C=CH_2+2F\cdot \longrightarrow (C_6H_5)_2CF\cdot CH_2F,$$

takes place with a current efficiency of ~70%. [3,13]

(*b*) Fluorination of carboxylic acids and their derivatives. Electrolysis of a mixture of acetic acid and hydrogen fluoride [86] or of potassium acetate in HF.KF yields a gaseous mixture containing fluoroform, carbon tetrafluoride, oxygen difluoride, difluoromethane, and methyl fluoride [86,87].

Electrolysis of higher carboxylic acids in hydrogen fluoride solutions leads to the formation of fluorides of completely fluorinated acids containing the same number of carbon atoms as the original acid

$$C_nH_{2n+1}C\overset{O}{\underset{OH}{<}}+(4n+6)F\cdot \longrightarrow C_nF_{2n+1}\cdot C\overset{O}{\underset{F}{<}}+(2n+2)HF+F_2O.$$

This reaction has been recommended for the preparation of fluorides of perfluorinated propionic [57,88], β-methoxy- and β-ethoxy-propionic [89,90], sebacic [91,92], benzoic, and phenylacetic acids [57,88].

Fluorides of fluorinated carboxylic acids can also be obtained by the electrochemical fluorination of anhydrides and chlorides of the corresponding carboxylic acids. The fluorination of acid anhydrides yields numerous fluorides of fluorinated carboxylic acids containing 2–13 carbon atoms in the chain [93,94].

The preparation of trifluoroacetyl fluoride by the electrolysis of acetic anhydride in hydrogen fluoride has been described in detail. The maximum yield of trifluoroacetic acid is achieved [95] by electrolysing a mixture of 40.5 g of acetic anhydride + 25.5 g of acetone + 80.0 g of anhydrous HF at 0.028 A cm^{-2}.

Anhydrides of dibasic acids yield fluorides of monobasic as well as dibasic acids. Thus the electrochemical fluorination of succinic anhydride followed by hydrolysis produced a mixture of perfluoropropionic and perfluorosuccinic acids. Electrolysis of an 8% solution of adipic anhydride yielded perfluorovaleric acid with a very small amount of perfluoroadipic acid [58].

Trifluoroacetyl fluoride has been produced on an industrial scale [59].

(*c*) Fluorination of ethers. Perfluorinated analogues of ethers have been obtained by electrolysis of solutions of the latter in hydrogen fluoride, *e.g.*

$$CH_3\cdot O\cdot CH_3+12F \longrightarrow CF_3\cdot O\cdot CF_3+6HF.$$

Completely fluorinated ethers containing 2–12 carbon atoms in the molecule have been prepared in this way [96,97].

Cyclic oxides of general formula $\overline{CH_2.[CH_2]_n.O}$, where $n = 2-4$, and their chloro-derivatives of the type $\overline{CHCl.[CH_2]_2.O}$, behave in a similar manner to ethers [98].

The fluorination of dioxan takes place in a rather unexpected manner, the ring opening at a C–C bond with formation of the diether $CF_3.O.CF_2.CF_2.O.CF_3$. [96]

(*d*) Fluorination of amines. Tertiary aliphatic and aromatic amines can be converted into perfluorinated derivatives electrochemically, *e.g.*

$$(CH_3)_3N+18F\cdot \longrightarrow (CF_3)_3N+9HF.$$

The fluorination of cyclohexylamine and of numerous other amines takes place in an analogous manner [10,99-101]. The benzene nucleus in aromatic amines is fluorinated to a perfluorocyclohexane nucleus during electrolysis.

The fluorination of several more complicated amines does not differ fundamentally [23,102-107].

(*e*) Fluorination of nitriles. The electrochemical fluorination of nitriles can be represented by the equation [12]

$$C_nH_{2n+1}CN+2(2n+1)F\cdot \longrightarrow C_nF_{2n+1}CN+(2n+1)HF.$$

However, no concrete data have been published on the electrochemical fluorination of compounds of this type, apart from an indication [10] that electrolysis of a solution of acetonitrile in anhydrous hydrogen fluoride yields a minute amount of the compound $CF_3.CF_2.NF_2$.

(*f*) Fluorination of sulphur-containing compounds. Electrochemical fluorination of compounds containing $\rightarrow$C.SH or $\rightarrow$C.S.C$\leftarrow$ groups can give the corresponding perfluorinated compounds, usually with considerable amounts of sulphur hexafluoride and numerous products of destructive fluorination. Table 1 lists the products obtained in the electrochemical fluorination of various representatives of this class.

The electrochemical fluorination of dibutyl sulphoxide can be represented as [110]

$$(C_4H_9)_2SO \rightarrow \begin{cases} (C_4H_9)_2SF_4 \\ C_4F_9SF_5 \end{cases}$$

Dimethyl sulphate on electrochemical fluorination forms bistrifluoromethyl or methyl monofluoromethyl sulphate depending on the conditions of electrolysis [69,70]. Methanesulphonyl fluoride yields a complex mixture of products [113]. Methanesulphonyl chloride is readily fluorinated electrochemically, with an almost quantitative yield of the perfluorinated derivative [114]:

$$CH_2SO_2Cl+6F\cdot \longrightarrow CF_3SO_2F+HCl+2HF.$$

The fluorination of ethanesulphonyl chloride, where the yield of perfluorinated derivative reaches 87%, [115] and of several other sulpho-derivatives takes place analogously. In particular, a method has been patented for obtaining the following fluorides of perfluorinated sulphonic acids:

$$n\text{-}C_5F_{11}SO_2F;\quad n\text{-}C_{16}F_{33}SO_2F;\quad n\text{-}C_{18}F_{37}SO_2F;\quad \text{cyclo-}C_6F_{11}SO_2F,$$

which are recommended as starting materials for the preparation of surface-active additives for chromium-plating baths [116,117].

Organic selenium compounds do not form fluorine-containing derivatives under the same conditions [108].

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In all the above cases of electrochemical fluorination, a perfluorinated derivative of the original organic substance is formed, in varying yield. However, this is always accompanied by destructive fluorination. In the electrochemical fluorination of hydrocarbons, for example, the formation of fluorocarbons having a smaller number of carbon atoms than the original hydrocarbon is observed [82,118].

Destructive fluorination is still more marked in the case of compounds containing oxygen or nitrogen. Both monobasic and dibasic carboxylic acids are partly decarboxylated [58,87].

The electrochemical fluorination of acetone [86] yields a mixture of almost equal volumes of fluoroform and carbon tetrafluoride; alcohols split off the hydroxyl group, forming a complex mixture of fluorocarbons with larger and smaller numbers of carbon atoms than in the original alcohol: methyl alcohol yields CF_4, C_3F_8, and C_2F_6; phenol forms a mixture of fluorocarbons having five and six carbon atoms [82,119].

In the electrochemical fluorination of a solution of guanidine in anhydrous hydrogen fluoride, the only products formed at the anode are nitrogen, nitrogen trifluoride, and carbon tetrafluoride in the molecular proportions 1 : 6 : 2.22, the nitrogen trifluoride being formed [120] with a current efficiency of 47%.

The methyl ester of *NN*-dimethylglycine gives the following mixture of products [102]

$$(CH_3)_2N.CH_2.C(=O)OCH_3 \rightarrow \begin{cases} (CF_3)_2N.CF_2.COOH \\ (CF_3)_2N.CF_2.COF \\ (CF_3)_3N \\ (CF_3)_2N.CFO.CF_2.N(CF_3).CF_2 \\ CF_3.N.CF_2.CF_2.C.CF_2. \end{cases}$$

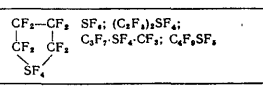
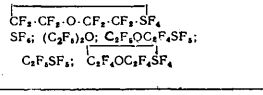
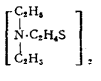
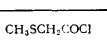
In the electrolysis of a solution of mercurous cyanide in hydrogen fluoride, destructive fluorination of the cyano-group results in the formation of nitrogen trifluoride and carbon tetrafluoride [10]. Fluorination of acetonitrile yields [10], in addition to its fluorinated analogue, considerable quantities of CF_4 and C_2H_5F. Pyridine on electrochemical fluorination forms nitrogen trifluoride and perfluoropentane as well as decafluoropyridine [105], while the main products of the fluorination of quinoline [10] are nitrogen trifluoride and the fluorocarbon C_9F_{18}. Destructive breakdown in the fluorination of sulphur-containing compounds has already been mentioned (see Table 1).

Owing to destructive fluorination, the formation of fluorine-containing compounds having the same carbon skeleton as the original substance does not usually exceed 20–30%.

B. Chlorination

(*a*) Chlorination of hydrocarbons. There are no data on the electrochemical chlorination of individual saturated aliphatic hydrocarbons.

TABLE 1.

Starting material: name	Starting material: formula	Fluorination products obtained	Ref.
Carbon disulphide	CS_2	SF_6; CF_3SF_5; $CF_2(SF_5)_2$; $CF_2(SF_5)_2$	108
Dimethyl sulphide	$(CH_3)_2S$	SF_6; CF_4; CF_3SF_5; $(CF_3)_2SF_4$	108
Dimethyl disulphide	$(CH_3S)_2$	SF_6; CF_3SF_5; $CF_3{\cdot}SF_4{\cdot}CH_2F$	109
Diethyl sulphide	$(C_2H_5)_2S$	C_2F_6; $C_2F{\cdot}SF_5$; $(C_2F_5)_2SF_4$	110
Dipropyl sulphide	$(n\text{-}C_3H_7)_2S$	SF_6; $C_3F_7SF_5$; $(C_3F_7)_2SF_4$	110
Dibutyl sulphide	$(n\text{-}C_4H_9)_2S$	SF_6; $C_4F_9SF_5$; $(C_4F_9)_2SF_4$	110
Dibutyl disulphide	$(n\text{-}C_4H_9S)_2$	SF_6; $C_4F_9SF_5$; $(C_4F_9)_2SF_4$	110
Di-t-butyl disulphide	$(t\text{-}C_4H_9S)_2$	products could not be separated	110
Tetrahydrothiophen			110
Oxathiane			110 109
Bis-(2-diethyl-aminoethyl) disulphide		SF_6; $(C_2F_5)_2NCF_2CF_2SF_5$	110
1,3,5-Trithiane	$(CH_2S)_3$	SF_6; CF_3; SF_5; $SF_4{\cdot}SF_2{\cdot}SF_5$; $(CF_2SF_4)_3$	109
1,2-Bismethyl-thioethane		CF_2SF_5; $C_2F_5{\cdot}SF_4{\cdot}CF_3$; $(C_2F_5SF_4)_2$; $(C_2F_5)_2SF_4$; $CF_3{\cdot}SF_4{\cdot}CF_2{\cdot}CF_2{\cdot}SF_5$; SF_4	109
Methylthioacetyl chloride	CH_3SCH_2COCl	SF_6; $SF_5{\cdot}SF_5$; $(CF_3)_2SF_4$; SF_5CF_4COF; $SF_4{\cdot}CF_2{\cdot}CF_3$; $CF_3SF_4CF_2COF$ $CF_3SF_4CF_2CF_3$	111
Mercaptoacetic (thioglycollic) acid	$HSCH_2COOH$	SF_6; CHF_3; CO_2F_2; COF_2; C_2F_6; CF_3SF_5; CF_3COF; CF_4; $SF_5{\cdot}CF_2COOH$; CF_3CO_2F; $SF_5{\cdot}CF_2CO_2H$; SF_5CF_2COF	112

The only case of the electrochemical chlorination of an unsaturated compound which has yet been investigated is the chlorination of ethylene[30]. In aqueous solution, partial or complete hydroxylation is also possible, leading ultimately to the formation of three products:

$$CH_2{=}CH_2 \rightarrow \begin{cases} CH_2Cl{-}CH_2Cl \\ CH_2OH{-}CH_2Cl \\ CH_2OH{-}CH_2OH \end{cases}$$

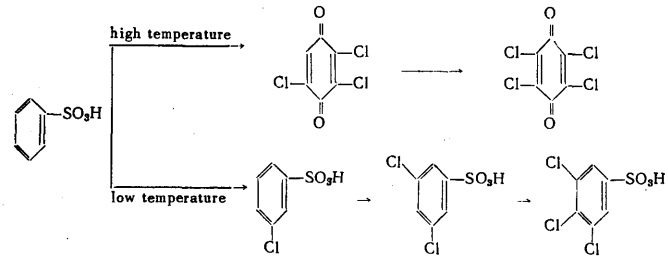
The aim of nearly all the research on this reaction has been to find optimum conditions for obtaining ethylene chlorohydrin[30,62,81,121-125] which is widely used as a solvent and in various organic syntheses. With a current density of 1400 A m^{-2} at a platinum anode at 25°, the yield of ethylene chlorohydrin[30] reaches 89.0% at a current efficiency of 85.5%.

A solid mixture of products containing up to 50% of chlorine has been obtained[126] by the electrochemical chlorination, with a platinum anode, of an emulsion of molten paraffins in concentrated hydrochloric acid at 90°.

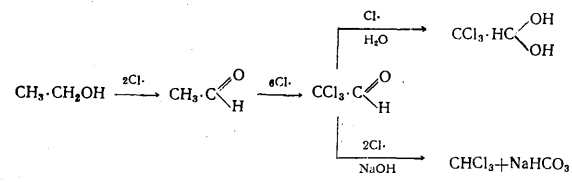
The electrochemical chlorination of aromatic hydrocarbons has been studied in considerably greater detail. Benzene is readily acted on by chlorine evolved at the anode, with the formation of a number of chlorinated products[5-9,27,32,127]. A certain amount of hydroxylation of the benzene nucleus occurs with the chlorination.

The chlorination of toluene is analogous to that of benzene, the nucleus being chlorinated first[7,31,34,35]. 1-Chloronaphthalene has been obtained electrochemically from naphthalene[9]. The possibility of chlorinating phenanthrene, anthracene, and biphenyl has also been reported[128].

Benzenesulphonic acid forms tri- and tetra-chloro-*p*-benzoquinone, together with the mono-, di-, and tri-chlorinated sulphonic acids[63]



(*b*) Chlorination of alcohols. When an attempt is made to chlorinate methyl alcohol electrochemically, formaldehyde is formed. The process of electrochemical chlorination has been studied in greatest detail with ethyl alcohol. The general course of the process can be represented by the scheme



In acid medium the main reaction product is chloral, but in alkaline medium it is chloroform. Since the latter is widely used as a solvent, a great amount of work has been done on the development of an industrial method for producing chloroform[18,19,128,129]. Under the optimum conditions of electrolysis, both the yield and the current efficiency[20,41,60] can reach 90%.

The maximum yield of chloral achieved[61-67,130] is 51.3%. Electrolytic chlorination of isopropyl alcohol produces a small amount of chlorine-containing compounds, the composition of which has not been investigated[20].

(*c*) Chlorination of aldehydes. As already indicated at (*b*), acetaldehyde is an intermediate product in the production of chloral and chloroform from ethyl alcohol. No special investigation has been made of the electrochemical chlorination of aldehydes.

(*d*) Chlorination of ketones. The electrochemical chlorination of acetone in acid medium yields monochloroacetone[21,23] with a current efficiency of up to 80%.

$$CH_3{-}CO{-}CH_3 \xrightarrow{Cl\cdot} CH_3{-}CO{-}CH_2Cl + HCl$$

The chlorination of cyclohexanone and of several aromatic ketones — acetophenone, propiophenone, and benzophenone — also results in the formation of monochloro--derivatives[61]. The current efficiency of formation of chlorination products is 70–90%.

The chlorination of acetone in alkaline solutions takes place according to the following equation

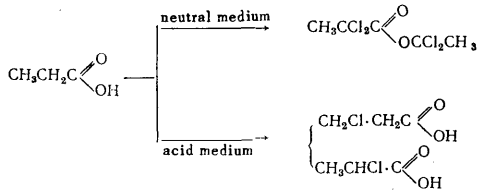
$$CH_3—CO—CH_3+4NaOH+6Cl^- \longrightarrow CHCl_3+CH_3COONa+3NaCl+3H_2O,$$

with the formation of chloroform and an acetate.

This reaction has been much studied[20,43,131-133] since the formation of chloroform from acetone requires a smaller expenditure of electrical energy than its preparation from ethyl alcohol. Under optimum conditions the yield of chloroform can reach 79%, and the current efficiency 60%.

Chloroform and acetic acid have been obtained by the electrochemical chlorination of ethyl methyl ketone in alkaline medium[20].

(*e*) Chlorination of carboxylic acids. Acetic acid is difficult to chlorinate electrochemically[134], and it is therefore a suitable solvent for electrochemical chlorinations in non-aqueous solutions[6,7]. The higher acids form chlorinated compounds. The electrochemical chlorination of propionic acid yields dichloroethyl $\alpha\alpha$-dichloropropionate, β-chloropropionic acid, and traces of α-chloropropionic acid[25].

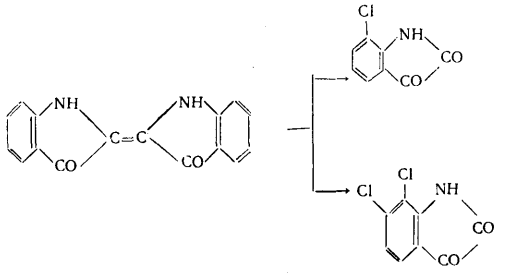


Butyric acid forms a mixture of β-chlorobutyric and $\beta\beta$-dichlorobutyric acids, isopropyl β-chlorobutyrate, isopropyl dichlorobutyrate, and a little chloroform[25].

Pentyl chloride, 1,2-dichloropentane, and chloroform have been obtained from hexanoic acid[135].

(*f*) Chlorination of amines. Data are lacking on the electrochemical chlorination of aliphatic amines. Aniline on electrolysis in hydrochloric-acid solution is oxidised to a considerable extent, with the formation of Aniline Black and small amounts of chloroquinone, chloroaniline and tetrachloroquinone[29,72]. This last compound is formed in considerable amounts when solutions in concentrated hydrochloric acid are used[73].

(*g*) Chlorination of other compounds. The chlorination of indigo at a platinum anode in hydrochloric--acid solution yields mono- and di-chloroisatin[27]:



A product of formula $C_{21}H_{27}O_7N_2Cl_7$ has been prepared from brucine[136], but its nature could not be established.

Electrochemical chlorination of hydrogen cyanide in dilute hydrochloric acid yields cyanogen chloride; when concentrated hydrochloric acid is used, a crystalline compound having the composition $[HCNCl_2]_3.3HCl$ is formed[137].

Interesting work has been done on the electrochemical chlorination of sulphite liquor[138], a waste product from the manufacture of viscose rayon. Electrolysis of a mixture of sulphite waste liquor, caustic potash, and potassium chloride has yielded, for example, $CH_2Cl.CHO$, $CHCl_2.CHO$, and several other compounds which can serve as raw material for the manufacture of a number of organic compounds.

Electrochemical chlorination has been suggested as a method for delignifying straw and wood[139,140].

C. Bromination

(*a*) Bromination of hydrocarbons. Monobromobenzene is obtained with a current efficiency of up to 23% by the bromination of benzene[141]

$$C_6H_6+2Br^- \longrightarrow C_6H_5Br+HBr.$$

The electrolysis of the complex $AlBr_3.3C_6H_6$ between platinum electrodes has also been investigated[142].

When toluene is brominated electrochemically in the dark, bromination of the nucleus takes place, whereas under illumination benzyl bromide is the only product[47].

(*b*) Bromination of alcohols. Attempts to obtain bromoform by electrolysing a solution of an alkali--metal bromide together with alcohol did not give positive results[41,143]. Carbon dioxide and a minute amount of bromoform were isolated as products of the electrolysis. The maintenance of a strictly neutral medium is apparently of immense importance in this process, since there are indications that bromoform can be obtained when calcium bromide is employed as electrolyte[77].

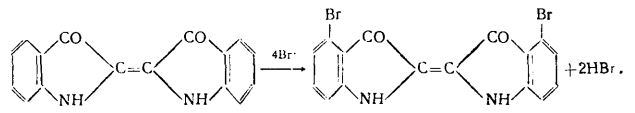
(*c*) Bromination of ketones. The only example of the electrochemical bromination of ketones described in the literature is that of acetone.

In acid medium, monobromoacetone is obtained in good yield[22]:

$$CH_3COCH_3+2Br^- \longrightarrow CH_3COCH_2Br+HBr.$$

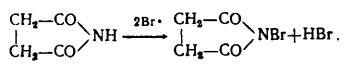
In alkaline medium, bromoform is produced in almost quantitative yield. This reaction is analogous to the preparation of chloroform from acetone[35,60,129,144].

(*d*) Bromination of other compounds. The principal reaction product in the electrochemical bromination of indigo is 5,5'-dibromoindigo[38,74,75], apart from small amounts of 2,4,6-tribromoaniline, 5-bromoisatin, and probably tribromophenol and formic acid



Attempts to introduce electrochemically four bromine atoms with the aim of obtaining the valuable dye 5,5',7,7'-

-tetrabromoindigo proved unsuccessful. Bromination of succinimide gave a 54% yield of *N*-bromosuccinimide[40]



It has been reported that eosin can be obtained by the electrochemical bromination of fluorescein[145].

Pentabromoacetone is obtained by the electrolysis of a sulphuric-acid solution of citric acid and potassium bromide[146]. Since the bromination is quantitative, this reaction has been suggested for the estimation of traces of citric acid.

D. Iodination

Iodine radicals formed at the anode react with organic compounds only rarely: examples of electrochemical iodination are therefore very limited.

(*a*) Iodination of hydrocarbons. Benzene[141] does not interact with iodine radicals formed at the anode.

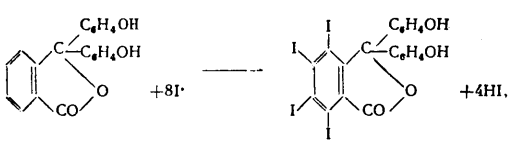
(*b*) Iodination of alcohols. The only case of the iodination of alcohols which has been investigated is the preparation of iodoform from ethyl alcohol, where iodination takes place[41,129,147-149] with a yield of 90–98%.

The electrochemical method of preparing iodoform from alcohol has been successfully employed[150,151] to synthesise iodoform containing the heavy isotope iodine-131.

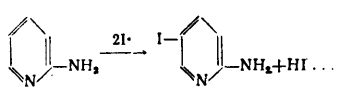
(*c*) Iodination of ketones. The preparation of iodoform from acetone has been investigated in detail, a 95% yield being achieved[42,43,152]. The reaction is completely analogous to the preparation of chloroform from acetone.

(*d*) Iodination of carboxylic acids. It has been reported[153] that propyl iodide is formed by the electrolysis of a mixture of potassium propionate and potassium iodide, and that potassium succinate and potassium iodide give β-iodopropionic acid. However, these results require verification.

(*e*) Iodination of other compounds. The iodination of phenolphthalein yields tetraiodophenolphthalein[29]:

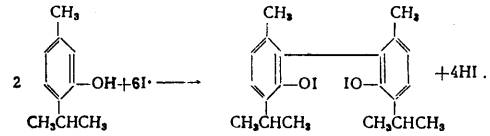


and 2-aminopyridine gives 2-amino-5-iodopyridine[154]



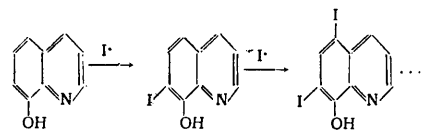
More complicated processes take place in the iodination of phenol and naphthol derivatives in alkaline solutions.

Thymol, for example, forms bisthymol diiodide[155-157]:



The following compounds are similarly iodinated with the formation of dimeric products — 2-naphthol, resorcinol, salicylic acid, *p*-isobutylphenol, *p*-isobutyl-*m*-cresol, *p*-isobutyl-*o*-cresol, methyl-*o*-cresol, ethyl-*o*-cresol, propyl-*o*-cresol, isopentyl-*o*-cresol, propyl-*m*-cresol, and isopentyl-*m*-cresol[154].

8-Hydroxyquinoline forms mono- and di-iodo derivatives[44]

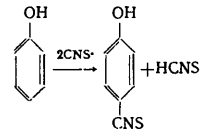


For the monoiodo derivative, the yield and the current efficiency are 68% and 34% respectively, whereas for 8-hydroxy-5,7-diiodoquinoline they are 82.4% and 32.4%.

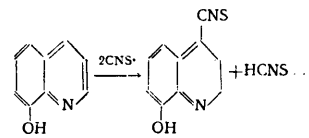
E. Thiocyanation and Selenocyanation

Until recently, thiocyanogen derivatives of aromatic compounds only had been obtained by the electrochemical method.

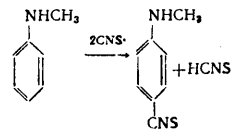
Thiocyanation of phenol gives a 67% yield of *p*-thiocyanatophenol[51]:



Thiocyanation of various phenol derivatives takes place similarly. Among these compounds are resorcinol (yield of thiocyanogen compound not indicated)[49], *o*-cresol[51] (72%), guaiacol[50] (20%), thymol[51] (76%), carvacrol[51] (50%), and diethylphenol[51] (82%). With all these compounds the thiocyanato-group enters the *para* position with respect to the hydroxyl group. An exception is provided by *m*-cresol, thiocyanation of which yields 2-hydroxy-5-thiocyanatotoluene. Thiocyanation of 8-hydroxyquinoline gives 8-hydroxy-4-thiocyanatoquinoline[51]:

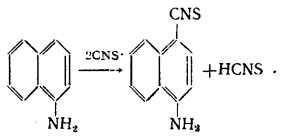


The thiocyanation of aromatic amines is completely analogous to that of phenols. With methylaniline, for example, a 41% yield of *p*-thiocyanato-*N*-methylaniline is obtained[52]



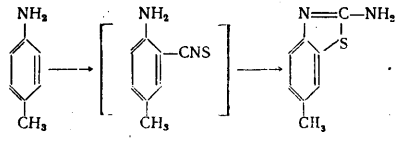
Thiocyanation of the following substances takes place in a similar manner — *o*-toluidine[49,51] (yield 44%), *N*-ethyl-*m*-toluidine[52] (60%), ethylaniline[51] (60%), propylaniline[52] (44%), butylaniline[52] (47%) dimethylaniline[50] (85%), diethylaniline[50] (68%), ethylbenzylaniline[52] (84%), anthranilic acid[52] (54%), and methylanthranilic acid[52] (63%). In all these examples the thiocyanato-group enters the *para*-position to the amino-group. Exceptions are *m*-toluidine, thiocyanation of which gives a 62% yield of 3-amino-5-thiocyanatotoluene[51], and *NN*-dimethyl-*p*-toluidine, from which a 21% yield of *NN*-dimethylamino-4-methyl-2-thiocyanatobenzene was obtained[50].

1-Naphthylamine gives 1-amino-4-thiocyanatonaphthalene[49]:



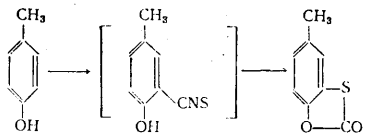
When the thiocyanato-group enters the *ortho* position to the active functional group in the molecule, a thiazole rearrangement takes place with amines, and a thiocarbonate rearrangement with hydroxy compounds.

For example, 2-amino-6-methylbenzothiazole is prepared from *p*-toluidine[53]:



Thiocyanation of the following amines takes place according to this scheme — phenetidine (yield 60%), anisidine (57%), *p*-ethylaniline (90%), and methyl *p*-aminobenzoate[53].

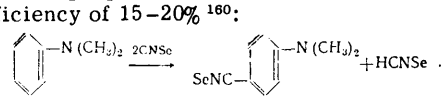
In the thiocyanation of *p*-cresol, the product rearranges to a methylphenylene thiocarbonate[51]



Since the rearrangement does not usually go to completion during electrolysis, it is advisable to boil the resulting solution under reflux for $1\frac{1}{2}$–2 h.

An interesting application of electrochemical thiocyanation proposed in a German patent[158,159] is the electrolysis of an aqueous solution of lignosulphonic acid and a thiocyanate, sodium chloride being added to the solution to diminish the formation of polythiocyanogen. The water-insoluble thiocyanato derivative of the acid is precipitated during the electrolysis, and can be used as a starting material for the manufacture of plastics and as an insecticide.

Electrochemical selenocyanation can be carried out by analogy with thiocyanation. *NN*-Dimethyl-*p*-selenocyanatoaniline has been prepared from dimethylaniline with a current efficiency of 15–20%[160]:

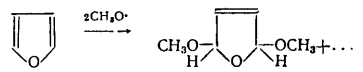


Selenocyanation of diethylaniline, methylaniline, and ethylaniline can be carried out similarly[160] with current efficiencies of 10–25%.

F. Alkoxylation

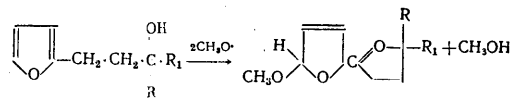
Alkoxylation is effected by electrolysing a solution of the organic substance in absolute alcohol containing an inorganic salt (*e.g.* ammonium bromide).

Methoxylation of furan[15] gave dihydrodimethoxyfuran with a current efficiency of 86%:



It has been possible in the same way to methoxylate furfuryl alcohol, furfuryl acetate, furfuraldehyde dimethylacetal[14], and other furan derivatives[161–163] to the corresponding dimethoxy derivatives.

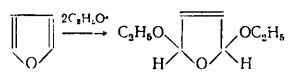
Electrochemical methoxylation has been applied to the synthesis of spiro compounds of the 1,6-dioxaspiro[4,4]-nonane group by the alkoxylation of furylalkanols, the reaction being represented by the general equation:



In this process, alkoxylation is accompanied by cyclisation, probably also initiated by the action of methoxy radicals[17].

The applicability of this reaction has been demonstrated with derivatives in which R = H, CH_3, $(CH_3)_2CH.CH_2$, C_2H_5, and R_1 = H, H, H, and CH_3 respectively. The yield of spiro compounds is 53–76%.

Ethoxylation of furan[16] can be carried out in a similar manner to methoxylation, the electrolyte being ammonium bromide in ethyl alcohol. Diethoxydihydrofuran is obtained with a current efficiency of ~74%:



G. Preparation of Nitric Esters

Electrolysis of nitrates in the presence of ethylene[45,46,164] gives a mixture of nitric esters according to the equation:

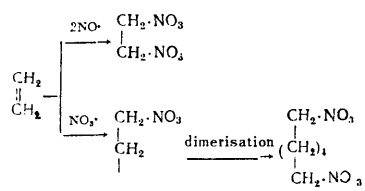


Table 2 lists the compounds which are formed by the electrolysis of solutions of organic acids in the presence of nitrates[153,165–173]. In most cases the olefines produced when aqueous solutions of the acids are electrolysed undergo reactions apparently similar to the formation of nitric esters from ethylene.

A process has been patented for the electrochemical preparation of cellulose nitrate[174–176] and is claimed to be completely safe.

TABLE 2. Products obtained in the electrolysis of solutions of carboxylic acids in the presence of nitrates.

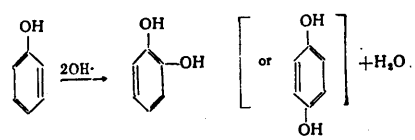
Initial acid		Products	Ref.
name	formula		
Propionic	CH_3CH_2COOH	$C_2H_5NO_2$; $C_2H_5ONO_2$; $O_2NO(CH_2)_2ONO_2$; $CH_3(CH_2)_2ONO_2$; $O_2NO(CH_2)_4ONO_2$	153, 165
Butyric	$CH_3(CH_2)_2COOH$	$CH_3(CH_2)_3NO_2$; $(CH_3)_2CHONO_2$; $(CH_3)_2CCH_2CH_2ONO_2$; $CH_3(CH_2)_2CH(CH_3)ONO_2$; $(CH_3)_2CHCH_2ONO_2$; $CH_3-CH(ONO_2)-CH_2ONO_2$	166
Valeric	$CH_3(CH_2)_3COOH$	$CH_3(CH_2)_3ONO_2$; $CH_3-CH(ONO_2)-CH(ONO_2)-CH_3$	167
Isovaleric	$(CH_3)_2CHCH_2COOH$	$(CH_3)_2CHCH_2ONO_2$; $CH_2(ONO_2)-CH_2-CH_2ONO_2$; $CH_3-CH(ONO_2)-CH(ONO_2)-CH_3$	168
Hexanoic	$CH_3(CH_2)_4COOH$	$CH_3(CH_2)_4ONO_2$; $CH_3(CH_2)_3CH(O_2NO)-CH_2ONO_2$	169
α-Methylbutyric	$CH_3CH(C_2H_5)COOH$	$CH_3-CH(O_2NO)-CH_2ONO_2$	170
β-Methylvaleric	$CH_3CH(C_2H_5)CH_2COOH$	$CH_3CH(C_2H_5)-CH_2ONO_2$	171
Heptanoic	$CH_3(CH_2)_5COOH$	$CH_3(CH_2)_5ONO_2$; $C_{12}H_{24}ONO_2$	171
Laevulinic	$CH_3CO(CH_2)_2COOH$	$H_3C-(CH_2)_2-CH_2ONO_2$; $H_2C(ONO_2)-CH_2-CH(ONO_2)-CH_2ONO_2$; $CH_2(ONO_2)-CH(O_2NO)-CH(ONO_2)-CH_2ONO_2$; $H_3C-CH(ONO_2)-CH_2ONO_2$	172
β-Isopentyloxypropionic	iso-$C_5H_{11}O(CH_2)_2COOH$	iso-$C_5H_{11}O-CH_2-CH(ONO_2)-O(CH_2)_2-CH(CH_3)_2$	172
Malonic	$HOOCCH_2COOH$	$(CH_2ONO_2)_2$; $(CH_2{\cdot}CH_2ONO_2)_2$	173
Adipic	$HOOC(CH_2)_4COOH$	$H_2C(ONO_2)-CH_2-CH(ONO_2)-CH_2ONO_2$; $H_2C(ONO_2)-CH(ONO_2)-CH(ONO_2)-CH_2ONO_2$; $H_2C(ONO_2)-CH_2-CH(ONO_2)-CH_2ONO_2$; $H_2C(ONO_2)-CH(ONO_2)-CH(ONO_2)-CH_2ONO_2$	171

H. Hydroxylation

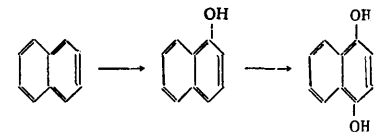
When ethylene is passed under pressure through an apparatus in which 25% caustic soda is being electrolysed, ethylene glycol is obtained[76]

$$CH_2=CH_2+2OH\cdot \longrightarrow HO-CH_2-CH_2-OH.$$

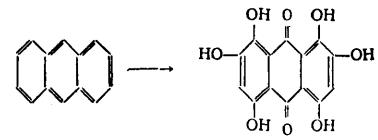
Anodic oxidation of phenol yields quinol and catechol[177,178]



Electrochemical oxidation of naphthalene leads to the formation of 1-naphthol and naphthalene-1,4-diol[179]:



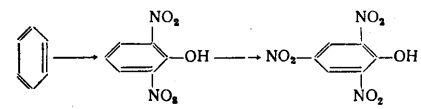
Oxidation of anthracene at the anode gave hexahydroxyanthraquinone[180]



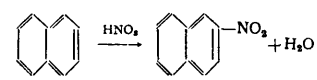
I. Nitration

Electrochemical nitration has been investigated only in the case of aromatic compounds.

Electrolysis of an emulsion of benzene in aqueous nitric acid at 70° has given dinitrophenol and picric acid[181]:



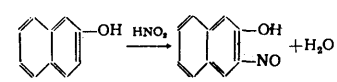
Under analogous conditions toluene and xylene give the same products as those obtained by chemical nitration[182,183], nitrobenzene yields *m*-dinitrobenzene[184], and nitration of naphthalene results in a 90% yield of mononitronaphthalene[185-187]:



J. Nitrosation

By analogy with nitration, several naphthalene derivatives have been nitrosated by electrolysis in an aqueous solution of sodium nitrite.

2-Naphthol gives a 53.8% yield of nitroso-2-naphthol[188]



and 1-naphthol and 1-hydroxynaphthalene-4-sulphonic acid are also nitrosated[189]. An attempted electrochemical nitrosation of ethers of phenol did not give positive results[190].

K. Sulphonation

Information on electrochemical sulphonation is extremely limited. Puls' reported electrochemical sulphonation of toluene[191] has been refuted by Fichter[192].

The only electrochemical sulphonation reactions which have been reliably demonstrated so far are the formation of methylsulphuric [193] and ethylsulphuric [143] acids:

$$ROH + H_2SO_4 \longrightarrow ROSO_3H + H_2O,$$
where R = CH_3; C_2H_5.

induced by the high concentration of sulphuric acid around the anode. The main requirements of these reactions are a high anodic current density and the absence of stirring.

L. Diazotisation and Coupling

In order to effect diazotisation and coupling electrochemically, an equimolecular mixture of the amine, the coupling component (preferably in the form of a soluble salt), and sodium nitrite is subjected to electrolysis.

A large number of different types of dyes have been prepared in this way, *e.g.* Orange II, [194-196] Congo Red [194,196,197], Chrysamine G, [194,196] Bismarck Brown [196], and several others which are produced in bulk.

Azo dyes obtained electrochemically differ slightly in colour from samples prepared by chemical means.

An attempt has been made to apply electrochemical diazotisation to aliphatic compounds. The chief product of the diazotisation of glutamic acid is said to be an isodiazoate [198].

An interesting application of electrochemical diazotisation and coupling has been described in a series of American patents [199-201]. A method is disclosed of forming a dye directly in the pores of the fibrous material to be coloured. The material is impregnated with a solution containing the amine to be diazotised, sodium nitrite, and the coupling component. Metal printing moulds are pressed against the impregnated material, and an electric current is passed. Dye is formed at the points of contact with the anode, accurately reproducing the design of the mould. Later patents [202,203] propose certain modifications to this process: the porous material to be coloured is impregnated with a solution containing an already diazotised compound in the form of a diazonium salt, a coupling component, an inorganic salt to make the solution electrically conducting, and a compound which retards azo coupling, *e.g.* tartaric acid. When a current is passed, dye formation takes place at points of contact with the cathode, since the pH increases at these sites. The proposed method of dyeing, which is applicable to textiles, paper, and other fibrous materials based on cellulose, is of considerable interest.

Since dye is formed directly in the pores of the material to be coloured, this method of coloration approaches vat dyeing in fastness.

6. COMPARISON OF CHEMICAL AND ELECTROCHEMICAL SUBSTITUTION PROCESSES

It can be concluded, from the products obtained, that there is no fundamental difference between chemical and electrochemical substitution processes: the two methods generally lead to the same products. However, the electrochemical method possesses certain special features, which sometimes make it preferable for substitution reactions. In cases of halogenation, for example, the electrochemical method avoids the need to use the free halogen, and allows the halogen to be used up quantitatively, whereas in chemical halogenation one-half of the halogen is wasted in forming a hydrogen halide.

Elimination of the use of free halogen is especially desirable in fluorination processes, owing to the corrosive nature of elementary fluorine. Furthermore, the high cost of compounds of fluorine, bromine, and iodine, makes the more complete utilisation of the halogens particularly attractive.

Electrochemical thiocyanation, methoxylation, nitration, and hydroxylation are evidently of considerable practical interest; the first two processes have been said [15,50,51] to give more satisfactory results than do chemical methods.

Finally, the electrochemical deposition of azo dyes directly in the pores of the substrate also merits careful study. The method of anodic substitution may prove useful in the synthesis of derivatives of labile compounds, which undergo changes at elevated temperatures or under the influence of very active reagents.

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