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Radical-cation Mechanism of the Anodic Fluorination of Organic Compounds

I.N.Rozhkov

The current state of the problem of the electrochemical fluorination of organic compounds is surveyed, and the mechanism of the substitution of hydrogen by fluorine during anodic oxidation in anhydrous hydrogen fluoride and in aprotic organic solvents is discussed. Formation of a carbon-fluorine bond during oxidation at platinum in the latter solvents is shown to be due to reaction of an organic radical-cation with a fluoride anion present in the electrolyte. Arguments are given in support of a mechanism of electrochemical fluorination in hydrogen fluoride not involving oxidation of the fluoride anion. A list of 160 references is included.

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I. INTRODUCTION

Electrochemical fluorination in anhydrous hydrogen fluoride is an important industrial method for obtaining perfluorinated organic compounds. This interesting process, devised by Simons more than twenty-five years ago[1,2], consists in the electrolysis at nickel electrodes of solution of organic compounds in anhydrous hydrogen fluoride. It is used to obtain completely fluorinated alkanes, carboxylic acids and their derivatives, ethers, tertiary amines, alkanesulphonyl fluorides, and other groups of organic compounds. The electrochemical production of organofluorine compounds possesses several advantages over other methods of fluorination. Firstly, it is a most economic and a comparatively safe process. Another attractive feature of the Simons method is that it yields perfluorinated products retaining the functional group of the original compound.

Although electrochemical fluorination is at first glance a simple and convenient method of preparation, it possesses many substantial disadvantages. This process usually results only in exhaustive fluorination of the organic molecule, and incompletely fluorinated products cannot be obtained. Electrochemical fluorination is accompanied by less degradation of the initial carbon framework of the molecule than in other methods, but this is still considerable. The yield of products retaining the original structure does not normally exceed 30%.

Since 1950 numerous attempts have been made to improve and modernise the Simons process. However, although more than 250 publications have appeared, the mechanism and the principal laws of electrochemical fluorination have remained until recently almost uninvestigated, owing to the extreme difficulty of working in anhydrous hydrogen fluoride[3-7]. In Dresdner's apt phrase[8] electrochemical fluorination is "...an art in many respects. The conditions of operation... ...are based on highly empirical considerations"

However, results have recently been obtained in Knunyants' laboratory that have drawn slightly aside the "curtain of secrecy" hiding the mechanism of this complicated reaction. The present Review will examine facts in support of a mechanism of anodic fluorination involving initial oxidation of the organic compounds.

II. FUNDAMENTAL IDEAS ON THE MECHANISM OF ELECTROCHEMICAL FLUORINATION IN ANHYDROUS HYDROGEN FLUORIDE

Several hypothetical mechanisms—(1) radical, (2) fluorination by higher fluorides of nickel, and (3) fluorination by complex nickel fluorides—have been suggested for electrochemical fluorination in hydrogen fluoride. The present Section is mainly confined to experimental results inconsistent with these hypothetical mechanisms, suggesting that anodic fluorination is quite different in character.

1. Radical Mechanism

According to this mechanism, suggested by Simons as early as 1950,[1] the first step is oxidation of a fluoride anion at the anode to the radical. The formation of perfluorinated organic compounds results from subsequent homolytic substitution of hydrogen atoms:

$$F^- \xrightarrow[Ni]{-e} F^\cdot \xrightarrow[-HF]{RH} R^\cdot \xrightarrow{F^\cdot} R{-}F \ .$$

Nagase[5] assumes that electrochemical fluorination is "an anodic reaction very definitely of free-radical type". Chang and Watanabe[9] consider that the molecular fluorine evolved is adsorbed on the nickel anode covered with a film of the difluoride. Fluorination takes place directly in hydrogen-fluoride solution at or below 20°C. The reason why only perfluorinated compounds are formed is that slightly fluorinated products are soluble in hydrogen fluoride, and therefore continue to be involved in the process. Completely fluorinated organic compounds, however, lose their basicity and become almost insoluble.

This is why only perfluorinated compounds are removed from the electrolyte, either as gaseous products or as heavy liquids separating out at the bottom of the cell.

The radical mechanism represented the first attempt—which proved to be greatly oversimplified—at explaining the results. A striking feature is the marked difference between the products obtained by electrochemical fluorination and those resulting from the action of elementary fluorine on organic compounds. It is incomprehensible, for example, why attempts to fluorinate molecular chlorine to the pentafluoride ClF_5 by the action of fluorine dissolved in hydrogen fluoride have been unsuccessful, whereas anodic fluorination gives a high yield of this product[10,11]. Such a radical mechanism leaves completely obscure also problems associated with the effect of the electrode material on the process: (i) nickel has proved the only suitable material for the anode[12]; (ii) even the brand of nickel and its crystalline structure influence the relative proportions of products of the fluorination of tertiary amines[13,14]; (iii) when new nickel electrodes are used, a peculiar, fairly long induction period is observed, during which perfluorinated products are not formed on passage of a current[4,13,14]; and (iv) fluorination is affected also by the material of the cathode, the use of soft iron instead of nickel lowering the yield of perfluorinated amines by two-thirds[15].

2. Fluorination by Higher Fluorides of Nickel

The fluorinating agents in this hypothetical mechanism are higher fluorides of nickel—NiF_3 and NiF_4—whose formation follows initial formation of nickel difluoride when nickel electrodes undergo anodic polarisation in hydrogen fluoride[16-19]. This is the reason for the induction period. An organic molecule present in solution then reacts with the modified surface of the anode. Such heterophase fluorination results in the appearance of perfluorinated compounds:

$$\begin{gathered} Ni - 2e + 2F^- \rightarrow NiF_2 \\ NiF_2 - n\,e + n\,F^- \rightarrow NiF_{n+2} \quad (n = 1,\ 2) \\ RH + NiF_{n+2} \rightarrow R{-}F + HF + NiF_2 \ . \end{gathered}$$

The formation of nickel difluoride in absolute hydrogen fluoride leads to very high ohmic polarisation[19]. Addition to the solvent of water (up to 2%) produces a marked decrease in the resistance of the cell, since the anodic coating becomes semiconducting. Water was regarded as necessary for stabilising species—NiOF and $NiOF_2$—containing the nickel atom in a higher state of oxidation. This concept was even used as basis for a tentative estimate[9] of the content of higher fluorides in the coating: their formation accounts for 0.1–1% of the current.

Nor does a mechanism of heterophase anodic fluorination of organic compounds by higher fluorides of nickel provide an acceptable explanation of many facts. Firstly, fluorination should be promoted by the introduction of additives such as cobalt into the nickel, since higher fluorides of cobalt are known[20] to be good fluorinating agents. However, such additions produce a marked deterioration in the electrochemical process, with increase in degradation and decrease in yield[21]. Furthermore, qualitative differences exist between the products of electrolysis and of fluorination by higher metal fluorides[3-5]. In particular, the electrochemical process is distinguished by preservation of the functional group of the initial compound, whereas fluorination by cobalt(III) fluoride involves detachment of functional groups from the organic molecule.

3. Fluorination by Complex Nickel Fluorides

In this mechanism, first suggested in 1960 by Burdon and Tatlow[4], highly conducting complexes of the organic compound with nickel fluorides—$(RH)_3NiF_6$ and $(RH)_2NiF_6$—are formed at the nickel electrode during electrolysis in hydrogen fluoride. Direct fluorination, i.e. replacement of hydrogen atoms in the organic molecule by fluorine atoms, occurs on decomposition of these complexes. Indirect evidence for this scheme was discovered later: (i) coloured anions—$[Ni^{3+}F_6]^{3-}$ and $[Ni^{4+}F_6]^{2-}$—were detected[22] in the anode layer during electrolysis of a solution of potassium fluoride in hydrogen fluoride; and (ii) potassium hexafluoronickelate, in anhydrous hydrogen fluoride at 0°C, reacts with xenon to form its difluoride[23].

Voitovich and Kazakov[24] regard this scheme as dubious, since the fluorinating effect of complex fluorides should be similar to the action of cobalt(III) fluoride. Electrochemical processes should not yield perfluorinated products with a retained functional group. In their opinion the primary act of the electrochemical process must be formation of nickel difluoride, which, in the presence of fluoride ions and e.g. a protonated tertiary amine, is oxidised electrochemically to a complex of type (I), sparingly soluble in hydrogen fluoride:

$$\begin{gathered} R_3N + HF \rightarrow R_3NH^+ + F^- \\ n\,(R_3NH)^+ + NiF_2 + 2F^- \rightarrow (R_3NH)_n\,NiF_{n+4} + 2e \ . \\ \text{(I)} \end{gathered}$$

The compound R_3N, having entered the complex, is then oxidised electrochemically at carbon–hydrogen bonds to form radicals, able to recombine with fluorine radicals appearing at the anode from the discharge of fluoride anions:

$$\begin{gathered} \rangle C{-}H \rightarrow \rangle C^{\cdot} + H^+ + e \\ F^- \rightarrow F^{\cdot} + e \\ F^{\cdot} + \rangle C^{\cdot} \rightarrow \rangle C{-}F \ . \end{gathered}$$

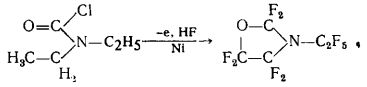
The completely (or almost completely) fluorinated amine loses its basicity, with the result that the complex breaks down:

$$\begin{gathered} [(R_F)_3\,NH]_n\,NiF_{n+4} \rightarrow n\,(R_F)_3N + n\,HF + NiF_4 \\ NiF_4 \rightarrow NiF_2 + 2F^{\cdot} \ . \end{gathered}$$

The main direction of electrochemical fluorination—substitution of hydrogen in the organic molecule by fluorine—is attributed to adsorption of the organic compound on the anode during formation of the complex, with a resultant weakening of carbon–hydrogen bonds. As a consequence, these bonds are preferentially attacked by the fluorine radical, while the carbon–carbon bonds are considerably less affected. In the case of substances that possess no basicity, fluorination takes place on the surface of complex inorganic fluorides such as K_2NiF_6. On such a surface electrochemical oxidation of carbon–carbon bonds predominates, which leads to considerable degradation of the initial molecule.

In spite of the great attractiveness of this mechanism, however, it cannot explain several facts. Firstly, if a complex is formed, why a large excess of the organic compound should favour the formation of incompletely fluorinated products is obscure[25,26]. Secondly, if anodic fluorination is a radical process, the introduction of acceptor substituents into the initial organic molecule should hinder radical fluorination and yield only partly fluorinated compounds; yet perfluorinated products

exclusively were isolated from the electrochemical fluorination of sulphones[27,28] and nitroalkanes[29] in hydrogen fluoride. Thirdly, it is incomprehensible with such a reaction scheme why fragmentation of the organic molecule increases when the current density is lowered[8,30]. Finally, it is difficult to explain the cyclisations[31,32] and isomerisations[33,34] typical of electrochemical fluorination at nickel in hydrogen fluoride:

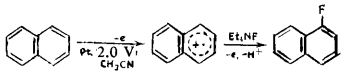


Replacement of hydrogen by fluorine atoms in the anodic fluorination of *N*-alkylpiperidines is accompanied by a peculiar isomerisation of the carbon skeleton. Fluorination of the isopropyl, isobutyl, and isopentyl derivatives gives mixtures of perfluoroalkylpiperidines having branched and unbranched alkyl chains. The content of the straight-chain isomer increases with chain length, to reach 75–90% with the isopentyl compound. Formation of perfluorinated products having an iso-structure is not observed on the fluorination of amines containing n-alkyl substituents[34].

III. *ECE* MECHANISM OF ANODIC FLUORINATION IN APROTIC SOLVENTS

A characteristic feature of the above hypothetical mechanisms of electrochemical fluorination in hydrogen fluoride is a homolytic reaction involving the fluorine radical. It was supposed[7] that "the only anions present in solution are fluoride ions, which excludes the possible occurrence of processes other than discharge of the fluoride anion". The radical type of fluorination can obviously take place at an anode potential adequate for oxidation of the fluoride ion, i.e. above 2.85 V.[35–39].

Many classes of organic compounds, however, are oxidised at considerably lower anodic potentials[40]. This difference in oxidation potentials has revealed a possible new route for the introduction of fluorine into an organic molecule in an electrochemical process. In 1970 Knunyants et al.[41–43] found that anodic oxidation can be used to generate at a platinum anode an organic cation that will then react with a fluoride anion in solution to form a carbon–fluorine bond. This process is applicable to the anodic fluorination of many classes of organic compounds having oxidation potentials below 2.85 V: e.g.



This mthod for the anodic fluorination of organic compounds opened up wide possibilities for studying the mechanism, since it enabled anhydrous hydrogen fluoride and nickel to be dispensed with as solvent and as the only suitable material for the anode. Anodic substitution of hydrogen by fluorine in an organic molecule occurred smoothly on platinum in solutions of fluorides in aprotic solvents. For example, 9,10-diphenylanthracene is oxidised on platinum at 1.45 V† in acetonitrile to form a radical-cation. This product is quite stable in a non-nucleophilic medium, and the reversibility of electron transfer could be demonstrated by cyclic voltammetry with a triangular pulse[44–46]. An oscillopolarogram obtained during anodic polarisation exhibits a peak representing the oxidation of diphenylanthracene to a radical-cation (Fig. 1*a*, curve BA_1M), which on reverse cathodic scanning acquires an electron and is reduced to the original compound (curve MC_1D). Anodic and cathodic peaks A_1 and C_1 have the same height[44].

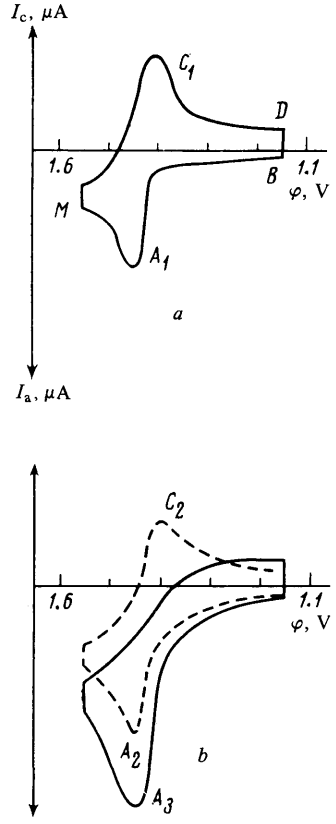


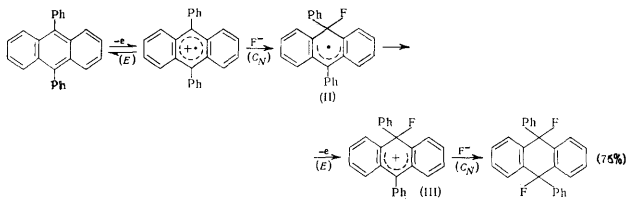
Figure 1. Cyclic voltammetry of 9,10-diphenylanthracene: *a*) non-nucleophilic medium (CH_3CN, $(C_2H_5)_4NClO_4$); *b*) as (*a*) in presence of the fluoride anion—$(C_2H_5)_4NF$.

Extremely significant changes are observed when tetraethylammonium fluoride is added to this solution[47–49] (Fig. 1*b*): the anodic peak A_3 expands at the same potential and now corresponds to a two-electron oxidation; and the transfer of electrons to the anode becomes irreversible, with no cathodic peak present on reverse scanning. Reaction of the radical-cation with the fluoride anion has a large rate constant, but lowering the temperature to −30°C and increasing a hundredfold the rate of scanning nevertheless enables a cathodic peak C_2 to be registered.

The picture obtained agrees excellently with the theory of the so called *ECE* mechanism (where *C* and *E* denote chemical and electrochemical stages respectively)[50–53]. It had been shown with 9,10-diphenylanthracene as example[54–56] that the addition of pyridine converted the

† Potentials in this Review are given relative to the normal hydrogen electrode.

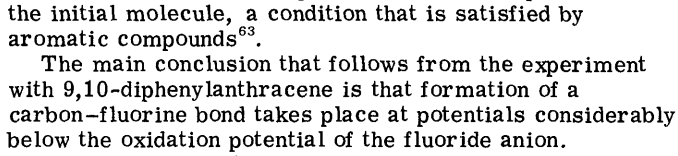
original one-electron mechanism of oxidation into a two-electron mechanism. Similarly in the oxidation of 9-phenylanthracene[57] the anodic peak in the oscillopolarogram increased greatly in the presence of water. The preparative electrolysis of 9,10-diphenylanthracene in the presence of the fluoride ion (tetraethylammonium fluoride in acetonitrile at 1.45 V) gives a 75% yield of 9,10-difluorodihydro-9,10-diphenylanthracene[58]. The same results are obtained when diphenylanthracene is electrolysed at 1.90 V [59] (corresponding to the formation potential of the bication[46]) in a solution of $(CH_3)_4NH_2F_3$ in acetonitrile. Thus in this case an EC_NEC_N mechanism operates (where C_N denotes a stage of nucleophilic chemical reaction)[56,60-62]:



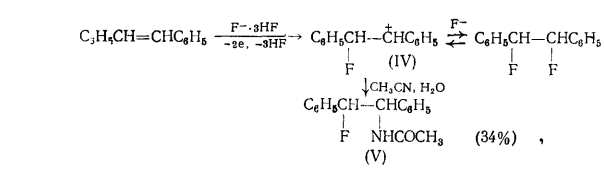
A condition for such a mechanism is that the potential for oxidation of the intermediate radical (II) to the cation (III) should be lower than or equal to the oxidation potential of the initial molecule, a condition that is satisfied by aromatic compounds[63].

The main conclusion that follows from the experiment with 9,10-diphenylanthracene is that formation of a carbon–fluorine bond takes place at potentials considerably below the oxidation potential of the fluoride anion.

An EC_NEC_N mechanism probably operates also in the anodic oxidation of alkenes[64,65]. In the presence of the fluoride anion their oxidation at platinum leads in several cases to addition of two fluorine atoms at the double bond:



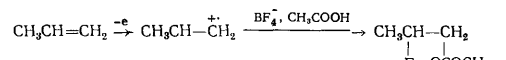
With stilbene use as electrolyte of a solution of tetraethylammonium fluoride–3-(hydrogen fluoride) in acetonitrile results in fluoroacetamidation, which is explained by the great mobility of the benzyl fluorine atom in acid medium:



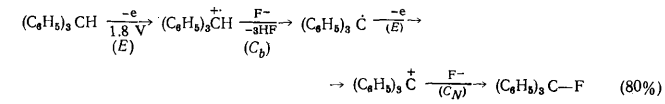
Addition of a fluoride anion to the cation (IV) in acid medium is reversible, so that (IV) undergoes an irreversible Ritter reaction with acetonitrile. Further substitution of the fluorine atom in (V) by an acetamido-group does not occur owing to its insolubility in acetonitrile. Schmidt[67,68] had earlier reported the addition of two fluorine atoms in the anodic oxidation of stilbene and cyclohexene in an acetonitrile solution of silver fluoride. However, these results could not be reproduced[66], since such solutions are non-conducting.

Acetamidation takes place in the anodic oxidation not only of alkenes but also of alkanes and alkylbenzenes[69]. To avoid this reaction other solvents, in particular dichloromethane, are usually employed in the electrolysis[70,71].

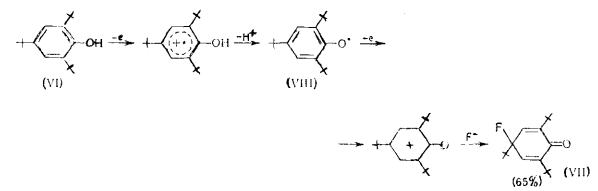
It has recently been found that the tetrafluoroborate anion may also be a source of the fluoride anion in the anodic fluorination of alkenes. Thus fluorinated acetates are formed in the anodic oxidation of alkenes in acetic acid with ammonium tetrafluoroborate as supporting electrolyte[72]:



Substitution of hydrogen by fluorine (also at potentials considerably below the oxidation potential of the fluoride anion) is also possible in the anodic oxidation of organic compounds at platinum in the presence of the fluoride anion in acetonitrile. This process has been observed with aromatic compounds (below) even in cases[73,75] in which the intermediate radical-cation of the organic molecule is capable of rapid elimination of a proton under the influence of a base. For example, the oxidation of triphenylmethane, obviously by an EC_bEC_N mechanism, gives a high yield of triphenylmethyl fluoride[73]:



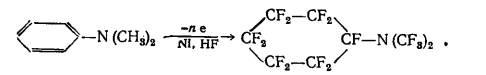
Such rapid elimination of a proton (stage C_b) is extremely characteristic of radical-cations not only of alkylbenzenes but also of phenols[40,74]. The oxidation of tri-t-butylphenol (VI) by the above mechanism yields the "quinofluoride" (VII).[75] The corresponding formation of a chlorocyclohexadienone had previously been observed in the oxidation of (VI) in the presence of the chloride anion[76,77]. The light blue stable radical (VIII) was recorded[78] in the anodic oxidation:



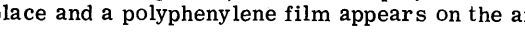
A distinguishing feature of the anodic oxidation of aromatic compounds in the presence of the fluoride anion is the partial replacement of hydrogen by fluorine while the aromatic structure is preserved, which involves an EC_NEC_b mechanism of fluorination. In the oxidation of benzene at platinum in acetonitrile, for example, fluorobenzene is obtained in 40% yield[79]:



Yet the Simons method of fluorinating aromatic compounds (at nickel in anhydrous hydrogen fluoride) usually occurs exhaustively to give derivatives of perfluorocyclohexane[5-7] and in some cases resinous products[2,80,81]:

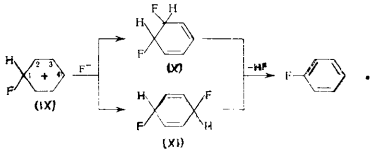


Oxidation by cyclic voltammetry at platinum[82] shows that at 2.63 V benzene forms a radical-cation, which rapidly eliminates a proton, after which polymerisation takes place and a polyphenylene film appears on the anode:



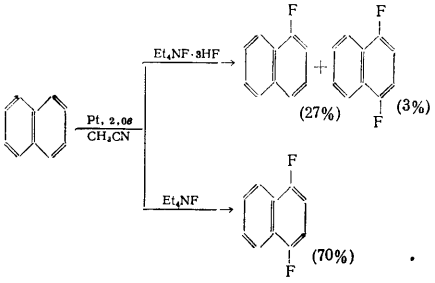
In the presence of the fluoride anion the radical-cation is stabilised by nucleophilic attack. The above EC_NEC_b scheme of formation of fluorobenzene may be rather more

complicated: the arenonium ion (IX) may add a second fluoride anion; this nucleophilic attack on (IX) should follow at the 2- and 4-carbon atoms with formation of the difluorocyclohexadienes (X) and (XI):

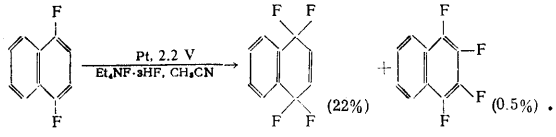


Calculations by the INDO method[83] using a TOREAMOR programme[84,85] show that the greatest positive charge is concentrated on these carbon atoms in the cation (IX): values for $C_{(1)}$–$C_{(4)}$ are respectively +0.254, +0.140, −0.012, and +0.275.

The anodic fluorination of naphthalene on platinum yields 1-fluoronaphthalene and 1,4-difluoronaphthalene depending on the conditions[41,42]:



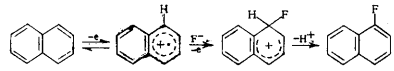
Prolonged electrolysis results in further fluorination to 1,1,4,4-tetrafluorodihydronaphthalene and traces of 1,2,3,4-tetrafluoronaphthalene:



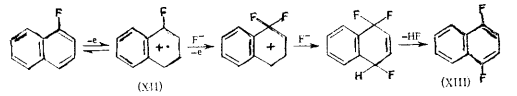
A striking feature is the sharp orientation of the substitution of hydrogen by fluorine: initially only 1-fluoronaphthalene is formed, after which 1,4-difluoronaphthalene appears. Yet anodic cyanation[86] and acetoxylation[87–89] yield mixtures of the 1- and 2-substituted naphthalenes. It must be emphasised that, in the anodic fluorination of naphthalene, a carbon–fluorine bond can be formed only by reaction with a fluoride anion. Radical fluorination by F· is excluded, for the anodic potential is only 2.0 V. Cyanation and acetoxylation, however, may be radical processes, since the oxidation potentials are 0.73 and 1.83 V for the cyanide[86] and acetate[90] ions respectively. Occurrence of a radical process in anodic acetoxylation is confirmed by the formation of methylnaphthalenes[88], which indicates that the acetate anion is oxidised to a radical, subsequently decarboxylated with formation of a methyl radical.

In the anodic fluorination of naphthalene (when homolytic substitution is exluded) it may be supposed that the orientation of nucleophilic attack by the fluoride anion will be determined by the distribution of positive charge in the radical-cation[42]. Inspection of Table 1 shows that, when anodic fluorination occurs on platinum, replacement of hydrogen by fluorine takes place at the carbon atom bearing the highest total positive charge in the radical-cation.

Thus the initial nucleophilic attack



is governed by the distribution of positive charge density. The positive charges at positions 1 and 4 in the radical-cation of 1-fluoronaphthalene are respectively 0.392 and 0.120. Nucleophilic attack is therefore extremely probable at position 1, with subsequent stabilisation of the cation by addition of a second fluoride anion and detachment of hydrogen fluoride:



This direction of attack on the radical-cation (XII) is confirmed indirectly by the formation of tetrafluorodihydronaphthalene on the anodic fluorination of (XIII).

Table 1. Distribution of charge in the radical-cation.



X	Y	Total charge on atom 1	2	3	4	5	6	7	8	9	10	Calcn.	Ref.
H	H	0.181	0.069	0.069	0.181	—	—	—	—	—	—	MOX	42
H	H	0.104	0.048	0.048	0.104	0.010	—	—	—	—	0.010	CNDO	91
F	H	0.392	0.004	0.080	0.120	0.032	0.101	0.066	0.067	0.117	−0.037	INDO	48
F	H	0.338	0.001	0.053	0.104	0.027	0.079	0.044	0.049	0.091	−0.020	CNDO	91
F	H	0.242	0.049	0.054	0.163	—	0.122	0.042	0.056	0.112	—	MOX	42
F	F	0.380	0.017	0.017	0.380	−0.016	0.099	0.066	0.066	0.099	−0.016	INDO	48
F	F	0.331	0.006	0.006	0.331	−0.006	0.049	0.047	0.047	0.049	−0.006	CNDO	91

All the above *ECE* schemes of anodic fluorination on platinum consist in the successive transfer of two electrons separated by an intermediate chemical stage (reaction with a nucleophile or elimination of a proton). In some cases anodic fluorination may involve the transfer of only one electron to the anode. An example is the anodic oxidation of tetra-alkylsilanes, which in the presence of fluoride ions leads to replacement of an alkyl group by fluorine[92]:

$$R_4Si \xrightarrow[F^-]{-e} R_4SiF^{\cdot} \xrightarrow{-R^{\cdot}} R_3Si{-}F \quad (50{-}80\%) .$$

In concluding this Section we must examine a recent paper by Eberson[93], who concludes, on the basis of certain experimental results[94–96] and a theoretical survey, that the interaction of an aromatic radical-cation with a halide anion X^- involves merely the transfer of an electron. In his opinion nucleophilic attack by halide anions is forbidden by the Dewar–Zimmerman rules[97]. Assuming that attack by a nucleophile takes place along the normal to the plane of the ring passing through the middle of a carbon–carbon bond, Eberson distinguishes between suprafacial and antarafacial attack (in which the nucleophile orbital interacting with the π-system of the ring is respectively symmetric and antisymmetric—(*a*) and (*b*) in Fig. 2). The transition state of the seven-membered ring corresponds respectively to Hückel and anti-Hückel systems. With eight electrons (systems having an odd number of electrons are treated as containing a fictitious

extra electron) the second transition state is aromatic and corresponds to an allowed process, whereas the first is antiaromatic and hence forbidden by the Dewar–Zimmerman rules. A vulnerable point in Eberson's argument is[58] the choice of nucleophile orbital interacting with the radical-cation. He considers only the p_Z orbital of halogens. Nevertheless, estimates of the overlap integrals for fluoride and chloride ions indicate close similarity of interaction of the p_Z and p_X orbitals of the halogen with the p_Z orbitals of carbon atoms[58]. Thus, although suprafacial interaction (Fig. 2*a*) is indeed prohibited by the Dewar–Zimmerman rules, nucleophilic attack on aromatic radical-cations by halide anions may result from the antarafacial interaction, disregarded by Eberson, of a lone pair of the halide ions located in a p_X orbital (Fig. 2*b*).

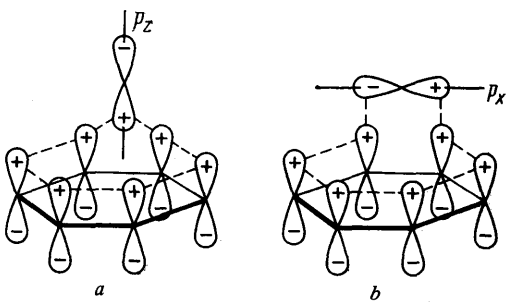
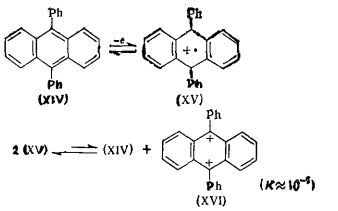


Figure 2. Arrangement of orbitals of transition state in nucleophilic attack on the radical-cation of an aromatic compound: *a*) suprafacial attack; *b*) antarafacial attack.

Nucleophilic attack by halide anions on aromatic radical-cations is supported by several experimental facts. (1) Millington[98] showed that high yields of 1-bromonaphthalene are formed by the anodic oxidation of naphthalene in the presence of bromide ions. (2) The radical-cation of diphenylanthracene reacts with the chloride anion to form chlorinated products of undetermined structure[99]. (3) In the presence of the chloride ion the chemical oxidation of anisole and naphthalene[100,101] by sodium peroxodisulphate to the radical-cations yields the corresponding monochlorinated aromatic compounds. (4) Nucleophilic attack on aromatic radical-cations by the fluoride anion probably occurs under the influence of xenon difluoride in hydrogen fluoride[102,103]. (5) Burdon[91] gives several forcible arguments for nucleophilic attack by the fluoride ion on aromatic radical-cations during fluorination with cobalt(III) fluoride. (6) In many cases the anodic oxidation of aromatic compounds in the presence of fluoride anions yields compounds containing fluorine.

Nucleophilic reaction between the fluoride ion and a radical-cation is convincingly confirmed by the kinetics of the cyclic voltammetry of diphenylanthracene (XIV) in the presence of the fluoride anion[58]:



$$(XVI) + F^- \rightarrow \text{Products}\ .$$

Other possible reaction paths are rejected. Thus disproportionation of the radical-cation[104–106] is unreal, since extraordinarily high rate constants must then be assumed for reaction of the fluoride ion with the bication (XVI). Furthermore, the kinetics of the reaction of (XV) with pyridine shows a first order with respect to diphenylanthracene, which excludes disproportionation of (XV).[107,108] The high oxidation potential of the fluoride ion excludes another possible path, which would have "avoided" nucleophilic attack by the ion on the radical-cation (XV)

$$(XIV) \rightleftharpoons (XV)$$

$$(XV) + F^- \not\rightarrow (XIV) + F^{\cdot}$$

$$(XIV) + F^{\cdot} \longrightarrow \text{Products}\ .$$

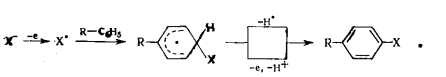
IV. ORIENTATION OF NUCLEOPHILIC ATTACK IN RADICAL-CATIONS OF AROMATIC COMPOUNDS

Results obtained during recent years showed convincingly that the electrochemical oxidation of aromatic compounds in non-nucleophilic media usually involves the transfer of a single electron to the anode with formation of a radical-cation[109]. In a nucleophilic medium the oxidation becomes a two-electron process: an *ECE* mechanism of anodic substitution operates (acetoxylation, cyanation, methoxylation)[110,111]. The exceptional character of anodic fluorination by an *ECE* mechanism lies in the impossibility of a parallel homolytic process (the anodic potential is insufficient for formation of the fluorine radical). Acetoxylation, cyanation, and methoxylation, however, occur at anode potentials sufficient for oxidation of the corresponding anions to radicals.

The formation of substitution products in an anodic process can be regarded as the result of reactions occurring by the following mechanisms.

(*a*) *ECE* Mechanism. It is assumed in this case that the orientation of nucleophilic attack and hence the relative proportions of isomers are determined by the distribution of positive charge density in the radical-cation of the aromatic compound[40,42,47,94,112].

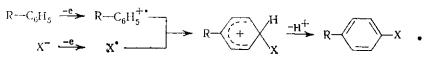
(*b*) Radical mechanism. An analogy with homolytic aromatic substitution should be observed:



The same products will result from initial oxidation of the aromatic substrate followed by a redox reaction of the radical-cation with the anion X^-:

$$R{-}H \overset{-e}{\rightleftharpoons} R{-}H^{+\cdot} \xrightarrow{X^-} R{-}H + X^{\cdot}\ .$$

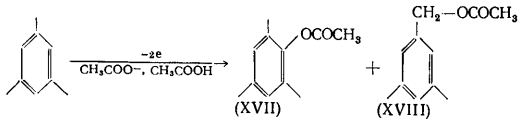
(*c*) Parallel oxidation. The aromatic molecule is oxidised to the radical-cation and the anion X^- is oxidised simultaneously. The orientation of substitution would then be determined by the distribution of density of the lone electron in the radical-cation:



It is evident that processes by all three mechanisms (*a*)–(*c*) involve the transfer of two electrons to the anode. Thus microcoulometry is uninformative in these cases. Several authors adduce the results of polarisation measurements, which register the anodic depolarisation effect on addition of an aromatic compound, as the main argument in support of an *ECE* mechanism for cyanation or acetoxylation. The weakness of such arguments has recently been pointed out by Mirkind[111].

In the Reviewer's opinion anodic acetoxylation and cyanation can take place by *ECE* and radical mechanisms simultaneously, the relative importance of the latter depending on the conditions[23]. The distribution of reaction products is greatly affected by the state of the anode surface and by adsorption. Very significant results have been obtained for the effect of adsorption in the acetoxylation of anisole on platinum[113]: whereas in the absence of any additive the ratio of the *o*- and *p*-methoxyphenyl acetates formed is 2.2, the addition of small quantities of napthhalene to the electrolyte produces a sharp decrease in the proportion of the *ortho*-isomer, and the ratio falls to unity. Acetoxylation probably occurs mainly by a radical mechanism in the absence of additives: the ratio of the products agrees well with the orientation of attack in the homolytic substitution of hydrogen in anisole. Addition of naphthalene, which is strongly adsorbed on platinum, blocks the anode surface, which hinders oxidation of the acetate anion. Only strong electron donors such as anisole can compete with naphthalene for a place on the surface of the platinum anode. In this case anisole is oxidised to the radical-cation, its acetoxylation takes place mainly by an *ECE* mechanism, and the *ortho/para* ratio agrees well with the results of anodic fluorination.

The influence of the anode material on the relative proportions of products of the acetoxylation of mesitylene



(XVII) (XVIII)

is also extremely significant[114]. The ratio of products of acetoxylation in the ring and in the side-chain (XVII)/(XVIII) has the values 4.4 and 23 on platinum and on graphite respectively. Adsorption of the acetate on platinum is large, and it undergoes oxidation with subsequent radical reaction in the side-chain. On graphite, however, the adsorption of acetate is small[7], so that the main process is the adsorption of mesitylene, its oxidation to the radical-cation, and subsequent reaction with the acetate ion. In this case acetoxylation occurs almost exclusively in the ring. The composition of the electrolyte also influences the ratio of the products of the acetoxylation of mesitylene[115].

We shall now consider the orientation of the substitution of hydrogen by fluorine in the anodic fluorination of aromatic compounds.

1. Donor Substituents

The special feature of the anodic fluorination of aromatic compounds by the *ECEC* mechanism—the impossibility of parallel homolytic reactions—is clearly revealed by a comparison with other anodic aromatic substitutions. Table 2 summarises data on the effect of substituents on the orientation of anodic substitution in aromatic compounds. It includes results for certain homolytic reactions and "oxidative" substitutions in the aromatic ring, to which is attributed a mechanism with intermediate formation of radical-cations and subsequent nucleophilic attack. Analysis of all these results leads to the following conclusions.

Table 2. Proportions of products in the substitutions $R.C_6H_5 \rightarrow R.C_6H_4.X + X.C_6H_5$.

No.	R	Anodic reaction: φ, V	Anodic reaction: anion	Anodic reaction: solvent*	Chemical reaction	X	Isomers, %: XC_6H_5	Isomers, %: *o*-	Isomers, %: *m*-	Isomers, %: *p*-	Ref.
1	CH_3	2.63	F·3HF	A		F	—	43	—	57	47, 116
2	»	—	CH_3COO	Y		CH_3COO	—	48	11	41	117
3	»	2.13	»	Y		»	—	43	11	46	89
4	»	—	CN	M		CN	—	40	8	52	118
5	»	—	CN	A		CN	—	32	2	65	86
6	»				$Na_2S_2O_8$+LiCl+$CuCl_2$	Cl	—	58	4	38	100, 101
7	»				$(R'OCO_2)_2$+$CuCl_2$	$R'OCO_2$	—	57	15	28	119
8	»				F_2, CF_3COOH	F	—	67	15	18	120
9	»				$(CH_3COO)_2$	CH_3	—	57	26	17	121
10	C_2H_5	2.13	CH_3COO	Y		CH_3COO	—	44	10	46	89
11	»		»	Y		»	—	48	12	40	88
12	*t*-C_2H_7	2.30	F·3HF	A		F	2	48	—	50	122, 123
13	»	2.13	CH_3COO	Y		CH_3COO	—	44	17	39	89
14	*t*-C_4H_9	2.20	F·3HF	A		F	17	17	—	66	122, 123
15	*t*-C_4H_9		CH_3COO	Y		CH_3COO	—	27	25	48	88
16	»	2.13	»	Y		»	—	35	22	43	89
17	»				$(C_6H_5COO)_2$	C_6H_5	—	24	49	27	121
18	OCH_3	1.85	F·3HF	A		F	2	43	—	55	47, 116
19	»	—	CH_3COO	Y		CH_3COO	—	70	2	28	117
20	»	1.73	»	Y		»	—	86	—	14	87
21	»	»	»	Y		»	—	67	4	29	89
22	»	2.03	»	Y		»	—	68	—	32	113
23**	»	»	»	Y		»	—	50	—	50	113
24	»	—	CN	A		CN	—	53	—	47	118
25	»	—	CN	A		CN	—	51	—	49	86
26	»	1.98	NO_2	A		NO_2	—	***	—	***	124
27	»				XeF_2, HF	F	—	52	5	42	125
28	»				$Ag_2S_2O_8$+CH_3COOH	CH_3COO	—	68	1	31	126
29	»				$(CH_3COO)_2$	CH_3	—	74	15	11	121
30	OC_2H_5	1.85	F·3HF	A		F	—	40	—	60	47, 116
31	F	2.63	F·3HF	A		F	—	—	—	99	127
32	»	2.19	CH_3COO	Y		CH_3COO	—	34	8	58	89
33	»				$(R'OCO_2)_2$+$CuCl_2$	$R'OCO_2$	—	33	22	45	119
34	»				XeF_2, HF	F	—	30	—	70	102
35	F				$(CH_3COO)_2$	CH_3	—	57	37	6	121
36	Cl	2.63	F·3HF	A		F	16	25	—	61	123, 127
37	»	2.19	CH_3COO	Y		CH_3COO	—	37	6	58	89
38	»		CN	A		CN	—	50	—	50	118
39	»				$Co(OCOCH_3)_3$	CH_3COO	10	30	—	60	128
40	»				$(R'OCO_2)_2$+$CuCl_2$	$R'OCO_2$	—	54	13	33	119
41	»				$Na_2S_2O_8$+LiCl+$CuCl_2$	Cl	—	40	5	55	101
42	»				$(CH_3COO)_2$	CH_3	—	62	28	10	121
43	Br	2.63	F·3HF	A		F	18	21	—	61	127
44	»	2.23	CH_3COO	Y		CH_3COO	—	30	4	66	89
45	»				$(CH_3COO)_2$	CH_3	—	62	28	10	121

*Solvents: A = acetonitrile; M = methanol; Y = acetic acid.

**Electrolysis in the presence of naphthalene.

***Isomers detected in the electrolysis products.

1. In no case of the anodic fluorination of an aromatic compound containing a donor substituent has the formation of a *m*-fluoro-isomer been recorded (Table 2, No. 1, 12, 14, 18, 30, 31, 36, and 43). In contrast, anodic acetoxylation and cyanation lead in most cases to a considerable

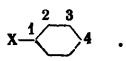
quantity of the *meta*-isomer among the reaction products (No. 2–4, 10, 11, 13, 15, 17, 21, 32, 37, and 44). "Oxidative" substitutions also yield the *meta*-isomer (No. 6, 7, 27, 33, 40, and 41). The *meta*-isomer is formed in all cases of homolytic substitution (No. 8, 9, 17, 29, 35, 42, and 45).

2. The anodic fluorination of aromatic compounds containing donor substituents (t-butyl, methoxyl, ethoxyl, chlorine, bromine) usually yields mainly the *para*-isomer, whose ratio to the *ortho*-isomer lies in the range 2–3. With methyl and isopropyl substituents the ratio is unity. Nevertheless, the *ortho*-isomer usually predominates in other anodic substitutions and in "oxidative" substitutions (Table 2, No. 2, 6, 7, 11, 13, 19–21, 24, 27, and 28). This isomer predominates also in homolytic substitutions (No. 8, 9, 17, 29, 35, 42, and 45).

3. A distinguishing feature of anodic fluorination is *ipso*-attack, leading to the replacement of isopropyl, t-butyl, and methoxyl groups, as well as chlorine and bromine atoms (Table 2, No. 12, 14, 18, 36, and 43).

4. Fluorobenzene exhibits a marked difference in orientation of substitution, with exclusive formation of the *para*-isomer.

Table 3. Distribution of total charge density in the radical-cation



X	Calcn.*	Total charge on atom				Ref.
		1	2	3	4	
CH_3	1	0.206	0.060	0.052	0.188	122, 123
»	2	0.130	0.073	0.076	0.064	103
$C(CH_3)_3$	1	0.178	0.051	0.048	0.168	122, 123
$O-CH_3$	1	0.185	0.037	0.045	0.095	»
$O-CF_3$	1	0.299	0.032	0.057	0.145	»
$S-CH_3$	1	0.074	0.046	0.048	0.063	»
$S-CF_3$	1	0.081	0.050	0.049	0.074	»
F	1	0.430	0.018	0.069	0.170	»
	2	0.276	0.131	0.103	0.093	103
	3	0.380	0.015	0.045	0.158	91
Cl	1	0.110	0.053	0.055	0.072	122, 123

* Methods of calculation: 1) INDO;[122,123] 2) MWH;[103] 3) CNDO/2.[91]

We shall now compare the data in Table 2 with calculated positive charge densities (Tables 3 and 4) and spin densities (Table 5) for the radical-cations of aromatic compounds. This leads to the following detailed conclusions on the mechanism of anodic fluorination and the orientation of nucleophilic attack in such radical-cations.

(1) Nucleophilic attack by a fluoride anion is governed by the density distribution of positive charge in the radical-cation. Only the π-component of the charge does not determine the position of attack. In the radical-cations of anisole and chlorobenzene, for example, the π-component of the charge at position 1 is respectively 0.047 and −0.135. Yet the corresponding total charges at this position are +0.185 and +0.110. Attack at position 1 occurs both in anisole and in chlorobenzene, since the product was fluorobenzene, resulting from replacement of the methoxy-group and the chlorine atom.

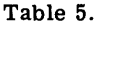
(2) The density distribution of the unpaired electron usually correlates well with the positive charge distribution in the radical-cation (the atom bearing the highest positive charge possesses also the greatest spin density). Nevertheless, the density distribution of the unpaired electron has no effect on the orientation of attack in anodic fluorination. For example, the distribution of spin density cannot explain the *ipso*-attack and simultaneous absence of the *meta*-isomer in the case of anisole.

Table 4. Distribution of density of π-component of charge in the radical-cation

X	Calcn.*	π-Component of charge on atom			
		1	2	3	4
CH_3	1	0.301	0.076	0.067	0.263
»	2	0.308	0.083	0.055	0.266
$C(CH_3)_3$	1	0.286	0.074	0.057	0.243
$O-CH_3$	1	−0.047	0.049	0.026	0.124
$O-CF_3$	1	0.117	0.067	0.050	0.210
$S-CH_3$	1	−0.109	0.017	0.018	0.071
$S-CF_3$	1	−0.108	0.031	0.020	0.090
F	1	0.233	0.065	0.070	0.257
»	2	0.341	0.081	0.068	0.299
Cl	1	−0.135	0.031	0.019	0.088
»	2	0.323	0.084	0.071	0.306
Br	2	0.304	0.084	0.067	0.294

* Methods of calculation: 1) INDO; 2) MOX.

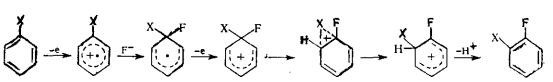
Table 5. Distribution of spin density in the radical-cation



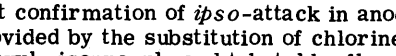
X	Calcn.*	Total spin density on atom			
		1	2	3	4
CH_3	1	−0.340	−0.115	+0.029	−0.410
»	2*a*	0.308	0.093	0.070	0.310
»	3	0.339	0.081	0.033	0.355
$O-CH_3$	1	+0.077	−0.166	+0.103	−0.205
»	2*b*	0.258	0.122	0.048	0.282
$O-CF_3$	1	−0.129	−0.166	+0.087	−0.331
$S-CH_3$	1	+0.064	−0.044	+0.030	−0.048
$S-CF_3$	1	+0.031	−0.064	+0.044	−0.077
F	1	−0.263	−0.138	+0.054	−0.401
»	4	−0.282	−0.114	+0.011	−0.355
Cl	1	+0.047	−0.045	+0.030	−0.051

* Methods of calculation: 1) INDO; 2*a*) MOX;[130] 2*b*) MOX;[129] 3) ASMO–SI;[130] 4) CNDO/2.[91]

(3) Nucleophilic attack by the fluoride anion takes place at positions 1 and 4 according to the highest positive charge in radical-cations of aromatic compounds containing donor substituents. The *ortho*-isomer is probably formed as a result of *ipso*-attack followed by oxidation and isomerisation of the arenonium ion[131]:

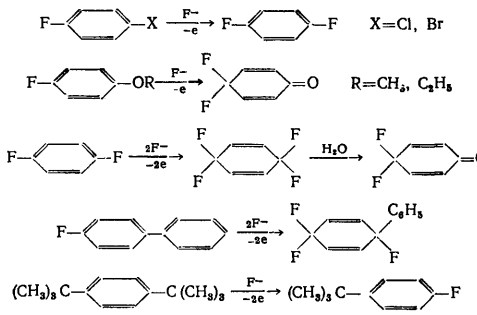


Direct confirmation of *ipso*-attack in anodic fluorination is provided by the substitution of chlorine, bromine, methoxyl, isopropyl, and t-butyl by fluorine to give fluorobenzene:



X=Cl, Br, OCH_3, i-C_3H_7, t-C_4H_9 .

Furthermore, *ipso*-attack is clearly evident also in the anodic fluorination of *para*-disubstituted benzene derivatives[86,127,132]:



(4) Absence of direct *ortho*-attack is assumed because the positive charges at the *ortho*- and *meta*- positions are very similar in the radical-cations of toluene and t-butylbenzene, and in those of anisole and chlorobenzene the *meta*-charge even exceeds the charge in the *ortho*-position. Nevertheless, a considerable quantity of the *ortho*-isomer is formed in all these cases, whereas the *meta*-isomer has not been detected. Fluorobenzene provides an especially clear example, being the only case in which the *ortho*-isomer is not formed, although the general pattern of positive charge distribution in the radical-cation is qualitatively the same as with other donor substituents. This fact is readily explained in terms of *ipso*-attack (migration of fluorine is impossible in the corresponding arenonium ion):

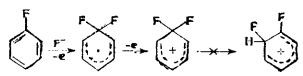
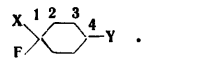


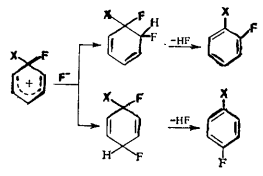
Table 6. Distribution of charge density in the cation



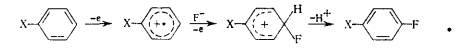
X	Y	Calcn.*	Charge density on atom			
			1	2	3	4
H	F	1	0.251	0.150	—0.072	0.508
H	F	2	0.186	0.135	—0.075	0.421
F	H	1	0.493	0.112	—0.026	0.300
F	H	2	0.399	0.120	—0.032	0.230
F	F	1	0.490	0.122	—0.057	0.527
F	F	2	0.399	0.118	—0.073	0.450
Cl	H	1	0.288	0.127	—0.012	0.244
CH_3	H	1	0.267	0.140	—0.026	0.248
F	*t*-C_4H_9	1	0.498	0.090	—0.021	0.267
F	O—CH_3	1	0.495	0.100	—0.045	0.414
F	C_6H_5	1	0.500	0.085	—0.009	0.252
F	*p*-C_6H_4F	1	0.481	0.091	—0.013	0.241

*Methods of calculation: 1) INDO; 2) CNDO/2.[91]

(5) *ipso*-Attack by the fluoride anion may result also in formation of the *para*-isomer:



A similar process may, perhaps, supplement the above *ECE* mechanism:



(6) The arenonium ion formed after *ipso*-attack can be stabilised only at *ortho*- and *para*-positions, as follows from the calculated positive charge distributions in these cations (Table 6).

(7) In conclusion it must again be emphasised that aromatic compounds containing donor substituents undergo anodic oxidation in the presence of the fluoride anion at potentials considerably lower than 2.87 V. Under these conditions oxidation of the fluoride anion to the radical is impossible, so that homolytic processes are excluded. For this reason we can speak of "pure" cases of the orientation of nucleophilic attack on aromatic radical-cations during anodic fluorination. The differences between orientation on anodic fluorination and on acetoxylation, cyanation, and methoxylation can evidently be regarded as contributions by the homolytic process in acetoxylation and cyanation.

2. Acceptor Substituents

Anodic processes involving aromatic compounds containing acceptor substituents (C_6H_5–A) have been very little studied: one paper was published in 1971, on the anodic fluorination of trifluoromethylbenzene[136], and in 1975 three communications appeared on anodic trifluoroacetoxylation[133–135]. The scarcity of publications in this field is due to the very high anodic potential (2.5–3.5 V) required for the oxidation of compounds of type C_6H_5–A. At such high potentials oxidation of the substrate is accompanied by many secondary processes—oxidation of the solvent, other components of the electrolyte, and, of course, the traces of water always present as impurity even in carefully dried aprotic solvents.

Introduction into an aromatic ring of an acceptor instead of a donor substituent leads to substantial changes in the proportions of products of anodic fluorination at platinum in acetonitrile. Knunyants et al. have shown that, when compounds containing such substituents as acetyl, methoxycarbonyl, fluoroformyl, cyano, and trichloromethyl are fluorinated[122], all three possible fluorinated isomers are formed in the relative proportions *ortho* > *meta* > *para* (Table 7). Unexpectedly, the pattern of distribution of fluorinated isomers from acetophenone, methyl benzoate, and benzonitrile was remarkably similar to the distribution obtained on the trifluoroacetoxylation of these compounds[134]. Exceptions were trifluoromethylbenzene (anodic fluorination yields exclusively the *meta*-isomer) and nitrobenzene (equal quantities of *ortho*- and *meta*-isomers formed).

Certain conclusions arise from an analysis of results for the anodic fluorination of aromatic compounds containing acceptor substituents and their comparison with the calculated distributions of positive charge and spin density in the radical-cations.

1. The orientation of substituents is not determined by the density distribution of positive charge in the radical-cation (Tables 8 and 9). In some cases (trifluoromethyl, nitro) the orientation of the substitution of hydrogen by fluorine is even opposite to the charge distribution. Yet the orientation of trifluoroacetoxylation correlates well[134] with the distribution of charge in the radical-cations of

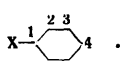
methyl benzoate, acetophenone, benzonitrile, trifluoromethylbenzene, and nitrobenzene. It was mentioned[134] that the calculations were made by the INDO method, but no specific results were given.

Table 7. Proportions of products in the substitutions $R.C_6H_5 \rightarrow R.C_6H_4.X$.

No.	R	Anodic reaction: φ, V	anion	solvent*	Chemical reaction	X	Isomers, %: o-	m-	p-	Ref.
1	$COOCH_3$	2.98	F·3HF	A		F	46	34	20	122
2	»	2.83	»	A		F	46	42	12	122
3	»	2.8	CF_3COO	T		CF_3COO	51	34	15	134
4	»	2.83	BF_4	M		»	69	—	31	135
5	»				$(C_6H_5COO)_2$	C_6H_5	58	17	25	121
6	COF	3.23	F·3HF	A		F	33	33	33	122
7	$CO—CH_3$	2.98	»	A		F	51	29	20	122
8	»	2.88	»	A		F	58	27	15	122
9	»	2.8	CF_3COO	T		CF_3COO	54	32	14	134
10	»	2.93	BF_4	M		»	100	—	—	135
11	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	50	33	17	119
12	CN	3.23	F·3HF	A		F	56	29	15	122
13	»	2.8	CF_3COO	T		CF_3COO	45	30	25	134
14	»				$(C_6H_5COO)_2$	C_6H_5	60	10	30	121
15	CCl_3	3.13	F·3HF	A		F	37	37	25	122
16	CF_3	3.4	»	A		F	—	100	—	136
17	»	2.8	CF_3COO	T		CF_3COO	35	47	18	134
18	»	3.5	»	T		»	72	—	28	133
19	»				$(R'OCO_2)_2+CuCl_2$	$R'OCO_2$	47	51	2	119
20	»				F_2+CF_3COOH	F	25	61	14	120
21	»				XeF_2+HF	F	32	54	14	103
22	»				$(C_6H_5COO)_2$	C_6H_5	29	41	30	121
23	NO_2	3.73	F·3HF	A		F	50	50	—	122
24	»	4.53	CF_3COO	T		CF_3COO	37	47	16	133
25	»	2.8	»	T		»	22	59	19	134
26	»				XeF_2+HF	F	19	51	12	103
27	»				F_2+CF_3COOH	F	20	65	15	120
28	»				$(C_6H_5COO)_2$	C_6H_5	62	10	28	121

*Solvents: A = CH_3CN; M = CH_2Cl_2 + CF_3COOH; T = CF_3COOH.

Table 8. Distribution of total charge density in the radical-cation



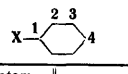
X	Calcn.*	Total charge on atom: 1	2	3	4
$COCH_3$	1	−0.025	0.083	0.025	0.098
$COOCH_3$	1	0.033	0.076	0.034	0.094
COF	1	−0.049	0.096	0.027	0.106
CF_3	1	0.013	0.103	0.076	0.065
»	2	0.02	0.08	0.05	0.04
»	3	0.106	0.082	0.085	0.070
CN	1	0.138	0.068	0.055	0.098
NO_2	1	0.071	0.038	0.060	0.075
»	3	0.192	0.096	0.080	0.088

*Methods of calculation: 1) INDO;[122] 2) CNDO/2;[91] 3) MWH.[103]

2. The density of the unpaired electron is distributed very characteristically in aromatic radical-cations containing acceptor substituents (Table 10). The orbitals of the ring carbon atom have a very small spin density, with almost the whole density of the unpaired electron concentrated on substituent atoms. Furthermore, the difference in spin density between *o*-, *m*-, and *p*-carbon atoms is negligible, e.g. 0.001 and 0.009 in the radical-cations of acetophenone and nitrobenzene respectively. Such differences are quite unable to determine the orientation in substitutions.

Thus the rules of orientation in the substitution of hydrogen by fluorine in the anodic fluorination of aromatic compounds containing acceptor substituents are no longer unambiguously consistent with an *ECE* scheme (as occurs with donor substituents). It must be emphasised that the anodic fluorination of compounds of type C_6H_5–A has been conducted at potentials above 2.87 V, i.e. under conditions such that oxidation of the fluoride anion and hence radical fluorination are possible. However, a purely homolytic mechanism for these reactions would be an oversimplification. Indeed, the type of adsorption and the behaviour of organic compounds on platinum at such high potentials are completely uninvestigated. Yet the formation of surface oxides or higher fluorides produces a marked change in the adsorption and catalytic properties of the anode surface. The high energy of adsorption in these regions may prevent surface mobility of the oxidisable species, in particular of aromatic radical-cations.

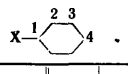
Table 9. Distribution of π-component of charge in the radical-cation*



X	π-Component of charge on atom: 1	2	3	4	X	π-Component of charge on atom: 1	2	3	4
$COCH_3$	−0.114	0.073	0.009	0.119	CN	−0.012	−0.014	0.014	0.025
$COOCH_3$	−0.111	0.062	0.014	0.105	CF_3	−0.150	0.023	0.011	0.057
COF	−0.146	0.076	0.063	0.131	NO_2	−0.138	0.028	0.033	0.078

*Calculation by INDO method[122].

Table 10. Distribution of spin density in the radical-cation*.



X	Spin density on atom: 1	2	3	4	X	Spin density on atom: 1	2	3	4
$COCH_3$	−0.067	0.008	−0.009	0.008	CF_3	−0.145	−0.065	−0.082	0.010
$COOCH_3$	−0.119	0.005	−0.012	0.004	CF_3**	0.141	0.072	0.076	0.002
COF	−0.078	0.005	−0.008	0.008	NO_2	−0.025	−0.010	0.003	−0.001

*Calculated by INDO method[122].
**Calculated by CNDO/2 method[91].

Therefore, as Mirkind has recently remarked[111], investigation of the mechanism of such reactions must first take into account the influence of heterogeneous factors on the rate and the direction of the electrode processes.

V. RADICAL-CATION PATH OF ELECTROCHEMICAL FLUORINATION IN HYDROGEN FLUORIDE

Right up to potentials of 2.8 V the oxidation of an aromatic compound at platinum in an aprotic medium involves the transfer of a single electron to the anode with formation of a radical-cation. It is therefore reasonable to suppose that the half-wave oxidation potential will be correlated with the energy of the highest occupied orbital and with the ionisation potential. Such a

relation has been detected, and several workers have shown a linear correlation at platinum in acetonitrile with ionisation potentials[129,137-140] and with energies of highest occupied orbitals calculated by self-consistent field methods[141]. The linear dependence can be understood from a detailed examination of the energetic factors[139] governing the half-wave potential for the reaction Red → Ox + e:

$$E_{1/2} = \alpha IP + \Delta E_{\text{solvn.}} - \beta EA - \frac{T \cdot \Delta S^0}{F} - \frac{RT}{F} \ln \frac{f_0 D_R}{f_R D_0} + C,$$

where IP is the ionisation potential, α a coefficient representing the effect of adsorption on the electrode in the presence of the solvent, ΔE_{solvn} the difference in energy of solvation between Red and Ox, β a coefficient representing the effect of the adsorbed substance and the solvent on transfer of the electron, f an activity coefficient, F Faraday's constant, D the diffusion coefficient, EA the electron affinity of the metal (anode), and C a constant depending on the reference electrode.

When the same metal (platinum), solvent (acetonitrile), and supporting electrolyte are used, many terms in this equation will obviously be the same. When compounds of similar structure are oxidised, furthermore, the differences in ΔS^0 and activity coefficients may be expected to be small in comparison with the changes in ionisation potentials. The observed linear correlations can be represented by the equations

$$E_{1/2} = 0.678IP - 3.72^{138};$$
$$E_{1/2} = 0.827IP - 4.87^{139};$$
$$E_{p/2} = 0.75IP - 4.55^{142} \ (E_p - \text{peak potential}).$$

A correlation between ionisation potentials and oxidation half-wave potentials (at platinum in acetonitrile) has been observed not only with aromatic compounds but also with alkenes and alkanes[143].

However, this clear picture changes on passing to systems in other solvents (Table 11). Thus alkanes undergo anodic oxidation in acetonitrile at potentials above 3.9 V.[143] But on the addition of a strong acid, trifluoroacetic, the oxidation potential of these compounds drops sharply (by about 0.5 V), and corresponding oxidation peaks can be recorded by cyclic voltammetry[144]. Further considerable fall in oxidation potentials is observed in a strongly acid medium—fluorosulphuric acid—in the absence of acetonitrile[145]. An analogous pattern is evident with anhydrous hydrogen fluoride[147], in which the half-wave potentials are more than 1.0 V lower. It must be stressed that reversible processes, similar to those in acetonitrile, are observed in the oxidation of aromatic compounds at platinum both in fluorosulphuric and in hydrofluoric acids. Thus long-lived radical-cations are formed by the oxidation of perfluorinated aromatic compounds in fluorosulphuric acid[146]; the oxidation of perylene in hydrogen fluoride involves formation of a radical-cation at +0.12 V and irreversible transfer of a second electron with formation of a bication at +0.69 V.[147] Irreversible transfer of two electrons to the anode has been recorded in the oxidation of alkanes. Thus replacement of acetonitrile by fluorosulphuric or hydrofluoric acid results merely in a sharp quantitative fall in the oxidation potentials of organic compounds on platinum: the qualitative character of the oxidation processes themselves remains unchanged, since the same products are formed and the same dependence of half-wave potential on ionisation potential is maintained.

Quite different changes in electrochemical processes are evident on passing from organic solvents to water. For example, the rate of oxidation on platinum falls with increase in chain-length of the hydrocarbon and decrease in its ionisation potential[148]: i.e. an antiparallel dependence is observed. The reason is the completely different character of the process: considerable degradative chemisorption of the organic molecule occurs, accompanied by dehydrogenation and cracking[137,149,150].

Table 11. Oxidation potentials of organic compounds on platinum*.

Compound	$E_{1/2}$, V [138,148] CH_3CN	$E_{p/2}$, V [145,146] HSO_3F	$E_{1/2}$, V [147] HF	Compound	$E_{1/2}$, V [138,148] CH_3CN	$E_{p/2}$, V [144] CH_3CN+CF_3COOH	$E_{p/2}$, V [145,146] HSO_3F
Naphthalene	1.77		0.65	Cyclohexene	2.58		
Mesitylene	2.03		0.91	But-2-ene	2.79		
p-Xylene	2.09		0.96	Pent-1-ene	3.27		
Toluene	2.21		1.17	But-1-ene	3.31		
Benzene	2.53		1.32	Propene	3.27		
Chlorobenzene	2.60		1.34	Ethylene	3.43		
Trifluorobenzene		1.07		Octane	>3.9	3.33	2.17
Pentafluorobenzene		1.13		Heptane	»	3.33	2.26
Hexafluorobenzene		1.32		Hexane	»	3.37	2.39
Perfluorobenzene		0.55		Pentane	»	3.41	2.54

* Potentials given relative to the normal hydrogen electrode.

Thus the anodic oxidation of aromatic compounds at platinum in hydrofluoric and chlorosulphuric acids and in aprotic organic solvents (acetonitrile) involves the transfer of one electron to the anode with formation of a radical-cation. In the absence of a nucleophile[82] the phenyl radical-cation rapidly eliminates a proton with subsequent recombination of radicals to give biphenyl or polyphenylenes:

$$C_6H_6 \xrightarrow{-e} C_6H_6^{+\cdot} \xrightarrow{-H^+} C_6H_5^{\cdot}.$$

Nyberg considers[151-154] that the mechanism of the formation of biphenyls consists in direct recombination of radical-cations with subsequent elimination of two protons[151]. In a later investigation of cross dimerisation he concluded[115] that the formation of dimeric products was the result of electrophilic attack on the radical-cation of the unoxidised aromatic molecule diffusing towards the electrode.

The anodic oxidation of benzene at platinum in hydrogen fluoride is very similar[158] to these processes: an electrically conducting polyphenylene film is formed, resembling soft graphite in its behaviour towards X-rays. The voltage in the cell does not exceed 1.1 V:

$$C_6H_6 \xrightarrow[HF]{Pt;\,1.1\ V} (C_6H_{6-x})_n.$$

Polymer films of the same type have been obtained from naphthalene and toluene at low voltages[158]. The probable explanation of these results is that smooth platinum in hydrogen fluoride is an example of a "purified" electrode. Indeed, adsorption of the fluoride anion is probably the lowest for any anion at potentials up to 1.5 V.[155] Adsorption of fluoride ions on platinum begins only at higher potentials, which is explained by their entry into the oxide film[156]. Thus platinum at 1.0 V in hydrogen fluoride contains no adsorbed species, and under these conditions benzene and its homologues undergo the above "mild" oxidation. Comparison with oxidation results in acetonitrile[82,137-139] suggests that, in the limiting stage of the oxidation of aromatic compounds, charge is transferred to

platinum through a layer of adsorbed acetonitrile molecules, which requires a considerable consumption of energy. A significant gain in energy ΔE_{solvn}, leading to a decrease in half-wave potential, is obtained also from the strong solvation of radical-cations in hydrogen fluoride.

Similar results have been obtained also at a nickel anode[158]. When benzene and toluene are oxidised at voltages up to 1.5 V in hydrogen fluoride, electrically conducting graphitic electrode coatings are formed, having the same elementary composition and structure as on a platinum anode. The yield of such "graphite" is quantitative. Polymerisation in attempts at the electrochemical fluorination of toluene had earlier been noted by Simons[2]. Similarly, an attempt at the electrochemical fluorination of anisole on nickel in hydrogen fluoride failed because of a rapid fall in conductivity and the separation of a black polymer[80]. Products of the polymerisation of benzene in this solvent were obtained also by Kokhanov[81].

Thus the products obtained at low potentials in hydrogen fluoride suggest that similar anodic processes occur on platinum and on nickel. As the anodic potential rises, however, considerable differences in behaviour appear between these anodes, owing to the different character of the adsorption of organic compounds on them. Electrolysis of a solution of hydrogen fluoride in trifluoroacetic acid at platinum, for example, yields mainly the Kolbe reaction product, hexafluoroethane, with a 2% yield of tetrafluoromethane[157] ($CF_4 : C_2F_6 = 2 : 100$), whereas at a nickel anode the latter is the main product (5 : 3). The probable reason for such a change in product composition is a difference in the energy of bonding of the adsorbed radical (XIX) with the anode surface, for on platinum this bonding is weak, the radical is mobile in the surface, and dimerisation occurs readily, whereas on nickel (more precisely on its difluoride) the adsorbed radical is firmly retained, dimerisation is difficult, and therefore oxidation to the cation (XX) is followed by the formation of carbon tetrafluoride:

$$CF_3COOH \xrightarrow[-H^+,\,-CO_2]{-e} \underset{(XIX)}{CF_3^{\cdot}} \begin{cases} \xrightarrow{Pt} CF_3{-}CF_3 \\ \xrightarrow[-e]{Ni} \underset{(XX)}{CF_3^+} \xrightarrow{F^-} CF_4 \end{cases}$$

Still more significant differences are observed in the chemisorption of the methyl radical. Electrolysis of an acetic-acid solution of potassium fluoride at platinum yields ethane, as would be expected. At nickel the main product is tetrafluoromethane (44%) accompanied by fluoroform (7%), while the yield of the dimer of the methyl radical (ethane) is only 2%. In the Reviewer's opinion the formation of fluorinated products does not involve oxidation of the fluoride anion but consists in intermediate generation of organic radical-cations at the anode followed by "ionic fluorination". The organic radical-cation eliminates a proton with formation of a radical, which is rapidly oxidised to the cation and stabilised by addition of a fluoride anion. Thus the anodic fluorination of alkanes on nickel (just as on platinum) can be represented by an EC_bEC_N scheme:

$$CH_3COO^- \rightarrow CH_3COO^-\,(ads) \xrightarrow{-e} CH_3COO^{\cdot}\,(ads) \xrightarrow{-CO_2} CH_3^{\cdot}\,(ads) \xrightarrow{-e}$$
$$\rightarrow CH_3^+\,(ads) \xrightarrow{F^-} CH_3F\,(ads) \xrightarrow[(E)]{-e} CH_3F^{+\cdot}\,(ads) \xrightarrow[C_b]{-H^+}$$
$$\rightarrow CH_2F^{\cdot}\,(ads) \xrightarrow[(E)]{-e} CH_2F^+\,(ads) \xrightarrow[(C_N)]{F^-}$$
$$\rightarrow CH_2F_2\,(ads) \xrightarrow[-H^+]{-2e} CHF_2^+\,(ads) \xrightarrow{F^-} CHF_3\,(ads) \xrightarrow[-H^+]{-2e} CF_3^+\,(ads) \xrightarrow{F^-} CF_4 .$$

The energy of adsorption of alkanes on nickel (difluoride) is very large, and they are firmly retained on the anode. As fluorination proceeds, the bonding of alkanes to the surface becomes weaker, and polyfluoroalkanes can now be described from the anode. This difference in adsorption energy between alkanes and perfluoroalkanes is the reason for the predominant formation of only completely fluorinated compounds.

The present scheme has recently been confirmed[158] by a modified method of pulse polarography. Fluorination can be interrupted at any stage, depending on the duration of the anodic current pulse, with predominant formation of either methyl fluoride, difluoromethane, or fluoroform. This is explained by the possibility of desorption of incompletely fluorinated compounds when anodic polarisation of the electrode is switched off.

Pivalic acid behaves similarly to acetic acid. On oxidation at nickel in the presence of the fluoride anion the main product is perfluorobutane, with very little rupture of carbon–carbon bonds:

$$(CH_3)_3CCOOH \xrightarrow[-CO_2]{-e,\,-H^+} (CH_3)_3C^{\cdot}\,(ads) \xrightarrow[-e,\,HF]{F^-,Ni} \underset{10}{C_4F_{10}} + \underset{1}{C_3F_8} + \underset{2}{C_2F_6} + \underset{1}{CF_4} .$$

Thus the fluorination of acetic and pivalic acids exemplifies the close analogy between these reactions and Simons electrochemical fluorination. Significantly, this analogy extends even to such "details" as the effect of the purity of the nickel anode and the material of the cathode on the yield of perfluorinated products[157,158].

It is noteworthy that the formation of fluorinated products in the electrolysis of an acetic-acid solution of potassium fluoride at a nickel electrode is observed at a potential of 2.6 V, which corresponds to the only inflexion on the polarisation curve. This inflexion is undoubtedly due to oxidation of the acetate ion[157]. It has recently been shown[159] by a galvanostatic pulse method that on nickel the oxidation of acetic acid in anhydrous hydrogen fluoride precedes the start of oxidation of the fluoride anion. Other workers have found[160] that 2-chloroethanol is oxidised at a rotating nickel disc electrode in hydrofluoric acid also before the fluoride ion is oxidised.

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Thus the above account can be summarised by a general scheme of anodic fluorination of organic compounds in which the first step is adsorption of the organic molecule on the electrode and its oxidation to the corresponding radical-cation, whose subsequent fate is governed both by the structure of the initial organic compound and by the character of its adsorption on the electrode. When oxidised on platinum, the radical-cations of aromatic compounds and alkenes react directly with the fluoride anion present in the electrolyte; those of saturated compounds usually eliminate a proton. The organic radicals formed in both cases are rapidly oxidised on the anode to the corresponding cations, whose stabilisation is effected by elimination of a proton or addition of a fluoride anion. During oxidation on nickel the organic compounds and their radical-cations are firmly adsorbed on the electrode surface. Only polyfluorinated organic molecules can be desorbed from the surface of the nickel anode, which is the probable reason for the predominant formation of perfluorinated products.

The anodic fluorination of organic compounds does not usually involve oxidation of the fluoride anion to the radical (with subsequent homolytic reaction): carbon–fluorine bond formation results from ionic fluorination.

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Institute of Organoelementary Compounds,
USSR Academy of Sciences,
Moscow