

ELECTROCHEMICAL FLUORINATION IN ANHYDROUS
ORGANIC SOLVENTS*

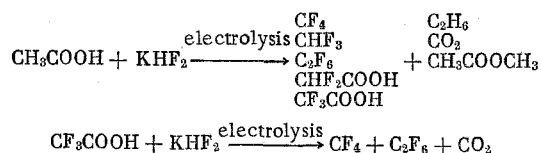
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Electrochemical fluorination (ECF) in anhydrous HF is one of the basic methods of introducing fluorine into an organic molecule. Despite the fact that there have been more than 100 published works in this field, ECF remains a practically uncontrollable process, which almost always proceeds exhaustively, is accompanied by destruction, and is characterized by low reproducibility of the results [1, 2]. The basic electrochemical principles of ECF and its mechanism have remained uninvestigated, which is due to the extreme difficulty in work in anhydrous HF and the absence of a reliable reference electrode for this medium.

The use of systems of electrolytes in ECF differing from solutions in anhydrous HF seemed extremely improbable, since the discharging potential of the F^- ion is very high, while all the investigated organic solvents are oxidized at far more positive potentials. However, the high adsorption activity of F^- ions at anodic potentials of 1.5 V, noted recently [3], can lead to a substantial increase in the overvoltage of the oxidation of the solvent. Moreover, a decrease in the solvation of the fluoride anion in the organic solvent (in comparison with anhydrous HF) lowers the potential necessary for the discharging of fluorine (E_0 of F^-/F_2 was calculated as 2.87 V for aqueous solutions and 2.43 V for methanol [4]). We investigated the possibility of the electrochemical oxidation of the fluoride anion in a number of anhydrous organic solvents: methanol, sulfolane, acetonitrile, pyridine, acetic and trifluoroacetic acids.

It was found that electrochemical fluorination in anhydrous organic solvents does take place, and in certain cases proceeds with high current yields. Thus, in acetic and trifluoroacetic acids, a mixture of fluorination products is formed without appreciable decomposition of the Ni anode



In the electrolysis of solutions of KF, CsF, and KHF_2 in acetonitrile and pyridine, ECF proceeds to a negligible degree on the Ni anode — CF_4 , C_2F_6 , and NF_3 are formed, while there is chiefly a decomposition of the anode or oxidation of the solvent. In the case of methanol, sulfolane, and aqueous acetic acid, no fluorination products were detected. In a study of the electrolysis of a solution of KHF_2 in acetic acid on Pt electrodes, only a Kolbe reaction and dissolution of the metal were observed [5, 6].

To study the factors producing such a substantial difference in the behavior of Ni and Pt, we investigated the i versus V curves of a number of metals (Ni, Pt, Ag, Au, Pb), subjected to anodic polarization in a solution of $\text{CH}_3\text{COOH} - \text{KF}$ (or KHF_2). The investigations were conducted in a Teflon cell, using a rotating microelectrode. A saturated aqueous calomel electrode was used as the reference electrode. An analysis of the polarization curves and the data of preliminary electrolysis indicated that passivation of anodes of Pb and Ag does not occur, and only their dissolution is observed (Fig. 1). The polarization curves of Pt

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and Au microanodes have one point of inflection at a potential of 1.85–1.95 V. Since this value is close to the potential of the beginning of the Kolbe reaction [1], and the main products of preparative electrolysis on Pt are C_2H_6 and CO_2 , we may consider that the point of inflection at 1.9 V is associated with the beginning of discharging of the acetate ion.

An entirely different dependence was observed for an anode of electrolytic nickel. A study of the polarization of the anode in a solution of $CH_3COOH - CH_3COONa$ revealed a direct proportionality of the current strength to the voltage in the region of anodic potentials 0–2 V (with respect to the saturated calomel electrode). In preparative electrolysis with a solution of anhydrous $CH_3COOH - CH_3COONa$, traces of C_2H_6 and CO_2 are formed, and 84% of the current is consumed for the dissolution of Ni. When KF is added to the solution, in contrast to Pt, a typical picture of passivation of the metal is observed, the rate of which depends on the concentration of F ions in solution (Fig. 2, curves 1–5). Evidently the passivation of pure Ni is associated with the discharging F^- anions and the formation of a film on the surface (or part of the surface), containing nickel fluorides. This film is extremely labile; when the electrode is kept in the solution without current (10–15 h), it dissolves, while during anodic polarization a Flade potential is observed on the i versus V curve. Prolonged passivation of the electrodes evidently leads to an increase in the thickness of the film up to a definite limit. In this case there is a gradual increase in the anodic potential, and at a current of $0.0125 A/cm^2$, the point of inflection on the i versus V curve is displaced from 2.4 V to the maximum value of 4.3–4.4 V (see Fig. 2) (measured by a compensation method on a stationary macroanode). Higher maximum values of the anodic potential correspond to high current densities.

To solve the problem of the nature of this natural point of inflection, we conducted preparative electrolysis at controlled potential (ECP) on the initial portion of the curve of increase in the current. An analysis of the gaseous products of ECP revealed CF_4 , traces of CHF_3 and C_2H_6 . Thus, the point of inflection on the polarization curve is associated with the process of electrochemical fluorination. The data obtained permit us to draw a number of conclusions on the mechanism of ECF in the system $CH_3COOH - KF$ on nickel.

1. The presence of a Flade potential on the i versus V curves of the Ni microanode, the increase in the potential during further passivation, and its decrease in the case of exposure of the anode to the electrolyte are evidence of the formation of a labile film on the surface of the anode, containing nickel fluorides as one of the components. The prolonged process of growth of the film to the maximum value is the cause of the "induction period," noted by many authors in ECF in anhydrous HF on new electrodes.

2. Electrochemical fluorination in the system $CH_3COOH - KF$ on Ni proceeds at an anode potential above 2.4 V and evidently includes adsorption of the organic molecule as one of the first steps. In the case of fluorination without adsorption, greater similarity to the action of elementary fluorine on CH_3COOH should have been observed. However, this reaction proceeds under rigorous conditions at 100° and leads to monofluoroacetic acid [7], the formation of which we did not note. In the electrolysis of a solution of $CH_3COOH - KHF_2$, only negligible amounts (current yield up to 1%) of di- and trifluoroacetic acids were obtained.

3. The absence of F_2O in the gaseous reaction products is evidence that the fluorination of the C–O bonds in the CH_3COOH molecule does not occur, and fluorocarbons are obtained by the replacement of the hydrogen atoms by fluorine in the hydrocarbon radical. The possibility of the formation of fluoroalkanes from the intermediately formed fluorinated acids according to a further Kolbe reaction is refuted by the substantial discrepancy of the composition of the gaseous reaction products in the ECF of the systems $CH_3COOH - KF$ and $CF_3COOH - KF$.

A scheme including initial oxidation of the adsorbed anion of the acid to an acetoxy radical, subsequent elimination of CO_2 , and the formation of a $CH_3^*(ads)$ radical seems most probable for the formation of the basic products of the electrode reaction: fluorocarbons in the case of acetic acid. Subsequently the $CH_3^*(ads)$ radical reacts along three pathways, forming: 1) methyl acetate (yield ~1%); 2) ethane as a result of dimerization; 3) fluorocarbons by replacement of hydrogen atoms by fluorine. The ratio of the two basic pathways of further conversions of the CH_3^* radical – dimerization and fluorination – depends on the electrode material. The largest yield of polyfluoroalkanes is observed on an electrolytic nickel anode (Table 1); in this case dimerization proceeds only to a slight degree. The formation only of polyfluoro-compounds is evidence that the hydrocarbon radical adsorbed on the anode should remain on the surface for a long time. This is evidently associated with the formation of complex compounds of the type of CH_3NiF_n , containing a carbon–nickel bond, on the anode. The fluorination of this complex at first proceeds with replacement of hydrogen atoms by fluorine. In the further attack of $F^*(ads)$, the C–Ni bond is broken, and the complex

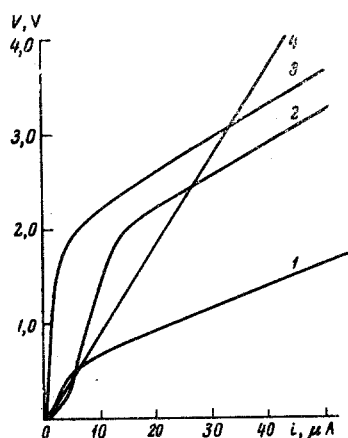


Fig. 1

Fig. 1. Anodic polarization curves in the system $\text{CH}_3\text{COOH} - \text{KF}$: 1) Ag; 2) Pt; 3) Au; 4) Pb.

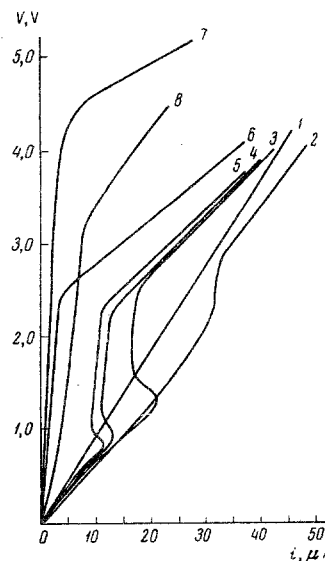
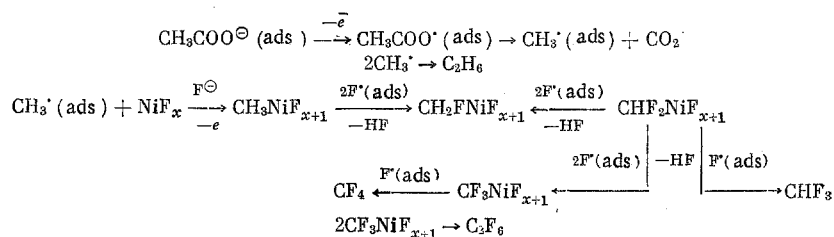


Fig. 2

Fig. 2. Polarization curves of the Ni anode: 1) 5% solution of $\text{CH}_3 \cdot \text{COONa}$ in CH_3COOH ; 2-5) solution of KF in glacial CH_3COOH : 0.32, 0.65, 0.98, and 1.63%, respectively; 6) saturated solution of KF in CH_3COOH , passivation for 1.0 h, current 0.0125 A/cm^2 ; 7) saturated solution of KF in CH_3COOH , passivation 8.0 h, current 0.0125 A/cm^2 ; 8) saturated solution of KF in CF_3COOH , current 0.0125 A/cm^2 .

breaks down, generating a polyfluoroalkane:



EXPERIMENTAL

Electrolysis of $\text{CH}_3\text{COOH} + \text{KHF}_2$. The electrolysis was conducted in a 100 ml steel electrolyzer with replaceable electrodes with an area of 47 cm^2 . A solution of 18.3 g KHF_2 in 100 ml glacial CH_3COOH (specific electric conductivity $2.92 \cdot 10^{-4} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$) was used as the electrolyte. The temperature of the electrolyte was maintained within the range $20-25^\circ$ at a current density of 0.0125 A/cm^2 and a voltage of 8-15 V. The gaseous reaction products were analyzed by the method of gas-liquid chromatography on Porapak-Q at 20, 60, and -50° , column length 3 m. The volume of the gaseous products was determined after the elimination of hydrogen, for which the gaseous mixture was slowly passed through a trap cooled with liquid N_2 , then the condensed gases were evaporated. To determine the content of gases in the mixture, calibration was preliminarily performed for CF_4 , C_2F_6 , CHF_3 , CO_2 , and C_2H_6 . The error of the chromatographic analysis was 2-5 mole %. The current yield of fluorinated products in the case of electrodes of electrolytic nickel was 60-70%. An analysis of the electrolyte, also performed on Porapak-Q at 200° , revealed $\text{CHF}_2 \cdot \text{COOH}$ and CF_3COOH with a current yield of $\sim 1\%$ and methylacetate with a yield of 0.5%. The results obtained are cited in Table 1.

Electrolysis of $\text{CF}_3\text{COOH} - \text{KHF}_2$. The electrolysis of a solution of 33 g KHF_2 in 100 ml anhydrous CF_3COOH was conducted in a steel electrolyzer on electrodes of electrolytic nickel at $20-25^\circ$, current density 0.0125 A/cm^2 , and voltage 12-18 V. After the passage of 0.342 A-h, the gaseous products were condensed in a trap cooled with liquid N_2 . After evaporation of the condensate we obtained 304 ml of the gas

TABLE 1. Electrolysis of a Solution of $\text{CH}_3\text{COOH} - \text{KHF}_2$

Anode	Cathode	Content in mixture, mole %				
		CF_4	CHF_3	C_2F_6	C_2H_6	CO_2
Nickel-NVK Nickel-NVK Nickel, electrolytic	Stainless steel	2	5	—	28	65
	Nickel-NVK	4	12	0,6	22	61
	Stainless steel	18	10	0,8	5	66
The same	Lead	34	7	1	1	57
"	Nickel electrolytic	44	7	2	2	45
Smooth platinum	Smooth platinum	4	4	—	35	55

TABLE 2. Value of the Discharge Potential of the Background E_b in the Case of Passivation with a Current of 0.0125 A/cm^2

Time of passivation, hours	E_b , V	Time of passivation, hours	E_b , V
1,0	2,40	6,5	4,3
3,0	2,92	7,0	4,36
6,0	3,32	8,0	4,36

a stream of argon. The test electrode was a metallic rod, pressed into a Teflon sleeve. The visible surface of the electrode was 0.07 cm^2 . A saturated aqueous calomel electrode, which was connected to the cell by an electrolytic bridge, representing a polyethylene tube 12 mm in diameter with a diaphragm of porous Teflon 3 mm thick, was used as the reference electrode. The bridge was filled with the test solution. Before the measurement, the electrode was covered, polished, then subjected to anodic passivation (1.7 mA for 75 min, 4.0 mA for 10 min, and 7.1 mA for 10 min). For nickel the electrode was kept in the solution for 12 h, then rinsed with acetone and polished. With such treatment of the nickel electrode, an acceptably reproducible value of the discharge potential of the background, equal to 2.40 ($\pm 50 \text{ mV}$), was obtained. The value obtained for the discharging of the background did not remain constant in numerous subsequent measurements and increased slowly.

Method B. The measurements were performed in a Teflon cell under argon by a compensation method on an R-307 high-resistance potentiometer and an M-195-3 zero galvanometer. The electrodes were made of two plates ($2 \times 2 \text{ cm}$) of spectrally pure nickel, pressed in polystyrene. To measure the potential, a polyethylene geber, filled with the test solution, was brought up to the anode. The reference electrode was connected to the geber with an electrolytic bridge with a Teflon stopcock, equipped with a diaphragm of porous Teflon. Before the measurement, the electrode was also purified, polished, and passivated with a current of 0.0125 A/cm^2 . The results obtained are cited in Table 2.

In the case of prolonged passivation at a current density of 0.038 A/cm^2 , the maximum value $E_b = 5.0 \text{ V}$ was obtained.

Electrolysis at Controlled Potential (ECP). ECP was conducted in the cell used in method B. The electrode was preliminarily treated by the same method, and then passivated for 3 h at a current density of 0.0125 A/cm^2 . After passivation, the cell was purged for 1 h with dry argon and evacuated to remove gaseous products. Then electrolysis was conducted at an anodic potential of $3.16 \pm 3.20 \text{ V}$ for 30 min with a current of 10 mA. Gas-liquid chromatographic analysis of the gaseous products revealed CF_4 , CHF_3 , and C_2H_6 .

CONCLUSIONS

1. The electrolysis of solutions of inorganic fluorides in anhydrous organic solvents was investigated. Electrochemical fluorination forming a mixture of fluorohydrocarbons takes place in acetic and trifluoroacetic acids.

2. On the basis of an analysis of the polarization measurements for a number of metals in the system $\text{CH}_3\text{COOH}-\text{KF}$, a scheme of the process of electrochemical fluorination of acetic acid was proposed.

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