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ELECTROCHEMICAL OXIDATION OF PENTAFLUOROPHENOL IN HYDROGEN FLUORIDE AND SUPERACID MEDIA

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SUMMARY

The electrochemical behaviour of pentafluorophenol was examined by means of Classic and Cyclic Voltammetry at a platinum electrode in strongly basic (KF) and strongly acidic (SbF<sub>5</sub>) media in HF as solvent. It was shown that the first electrochemical step is the formation of a radical which is chemically stable in strongly acidic media probably because of the protonation of pentafluorophenol. The products formed by controlled potential electrolysis were analysed by GCMS. The main products of electrolysis are perfluorocyclohexadienone and dimers of the radical pentafluorophenol. The yield of the various products was evaluated as a function of the acidic level.

INTRODUCTION

Electrofluorination processes in HF, derived from the methods of SIMONS [1] do not permit selective oxidation of aromatic compounds. Many products are generally obtained, which are usually perfluorinated derivatives

In a recent study [2], we have shown that a partial chemical oxidation of fluorinated aromatic derivatives is possible in superacidic media if the experiments are performed at a controlled potential at a fixed acidity level (media buffered with KF, BF<sub>3</sub>, TaF<sub>5</sub> or SbF<sub>5</sub> (see under 'experimen-

tal'). Under such conditions the first step results in the formation of a radical stable in strongly acidic ( $\text{HF} - \text{SbF}_5$ ) media .

The selectivity of oxidation of aromatic derivatives is also dependent on the number and the nature of the substituents on the aromatic ring ; selective oxidations have been performed in other non-aqueous media, for example in acetonitrile [3 - 5]. In the present study we describe the electrochemical behaviour of pentafluorophenol and the nature of the oxidation products obtained at different acidity levels in HF. The results are compared with those obtained in other non-aqueous media.

The presence of five fluorine atoms on the ring limits the possibility of evolution of the oxidation products and thus permits a better comprehension of the electrochemical or chemical steps in the oxidation of aromatic derivatives in superacidic media.

## RESULTS AND DISCUSSION

Classic and cyclic voltammetry show that the oxidation scheme of pentafluorophenol and the nature of electrolysis products depend on the acidity level in HF. A passivation of the electrode, probably due to the formation of polymers, is always observed at a potential independent of the acidity level ( $E > 2$  Volts). Characteristics of Voltammograms are reported in Tables I and II and typical curves are shown in Figure 1.

### Strongly basic medium (pH > 11)

The voltammetric oxidation of pentafluorophenol ( $\phi \text{OH}$ ) in solutions of KF in HF presents two very close oxidation waves. Although the systems are not reversible, the half wave potential of the first wave varies with fluoride ion concentration according to the following equation :

$$(E_{1/2})_1 = 0.612 + 0.058 \text{ pF}$$

or

$$(E_{1/2})_1 = 1.406 - 0.058 \text{ pH}$$

The slope of the straight line (0.058) is very close to that observed with a reversible system (0.054 at 0 °C).

We have verified that the wave height ( $I_1$ ) is pH-independent and that the limiting current is diffusion-controlled.

The half wave potential corresponding to the second oxidation step is pH independent and the current  $I_2$  is also diffusion-controlled.

TABLE I Characteristics of voltammograms of 3 mM pentafluorophenol in HF at a rotating platinum electrode (600 rpm) : half wave potentials ( $E_{1/2}$ ) and limiting diffusion currents ( $I$ )

medium	pH HF	1st wave		2nd wave		3rd wave	
		$E_{1/2}$ (V)	$I$ ( $\mu$ A)	$E_{1/2}$ (V)	$I$ ( $\mu$ A)	$E_{1/2}$ (V)	$I$ ( $\mu$ A)
KF(M)	1	13.7	0.612	101	0.855	98	7 (a)
	0.42	12,3	0.630	100	0.855	96	8 (a)
	0.19	13	0.653	98	0.857	89	13 (a)
SbF <sub>6</sub> <sup>-</sup> 0.15M +SbF <sub>5</sub>	0.12	0.92	0.920	85	1.85(a)		
	0.32	0.49	0.949	79	-		
	0.67	0.17	0.968	69	-		
	1.1	0	0.992	65	-		

(a) passivation of the platinum electrode

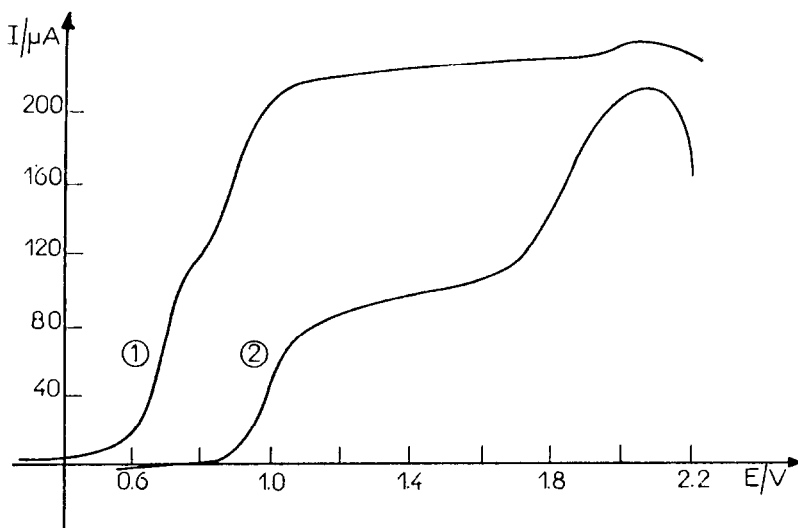


Figure 1 : Oxidation of pentafluorophenol (3mM) at a rotating platinum electrode (600 rpm) in (1) KF 0.1 M and (2) SbF<sub>5</sub> 0.1 M + SbF<sub>6</sub><sup>-</sup> 0.2 M.

The wave height diminishes with pH and a third oxidation step (wave height  $I_3$ ) appears at an ill-defined potential, the electrode being passived.

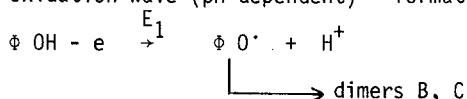
The total current  $I_2 + I_3$  is quite constant, equal to the diffusion current  $I_1$  of the first wave.

A controlled potential coulometry necessitates more than one but less than two faraday per mole, the number of electron diminishing when the initial concentration of pentafluorophenol increases. This is typical of a chemical reaction following the electrochemical oxidation of the initial compound [6].

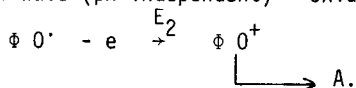
Analysis of the electrolysis products confirms this result: only one part of the pentafluorophenol is directly oxidized in a two electron process to give the hexafluorocyclohexadienone expected the oxidation of p. fluorophenol with similar techniques in acetonitrile containing tetraethylammonium fluoride gives a similar dienone [7].

According to these experimental results, the following reaction scheme can be proposed in basic media.

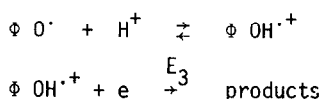
(1) First oxidation wave (pH-dependent) - formation of a radical :



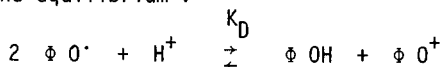
(2) Second wave (pH-independent) - oxidation of the radical :



(3) Third wave - oxidation of the radical after protonation :



when pH increases ( $[\text{F}^-]$  decreases), the first wave shifts towards the second and when  $\text{pH} < 10$ , there is a disproportionation of the radical  $\Phi \text{ O}^\cdot$  according to the equilibrium :



the value of the disproportionation constant  $K_D$  can be estimated from the variations of  $(E_{1/2})_1$  and from the value of  $(E_{1/2})_2$  :

$$K_D \neq 10^{9.5} \text{ mol}^{-1}$$

Strongly acidic media (pH < 3).

In  $\text{SbF}_5$  medium,  $\phi$  OH is oxidized in two steps, the first one ( $E'_{1/2}$ )<sub>1</sub> being quasi-reversible. The variation of  $I_c/I_a$  ( $I_c$  = reduction current,  $I_a$  = oxidation current) observed by cyclic voltammetry indicates that a chemical reaction precedes the exchange of electron (Table II)

TABLE II : Characteristics of cyclic voltamograms of pentafluorophenol in various media

media	$v$ (mv.sec <sup>-1</sup> )	$I_a$ ( $\mu\text{A}$ )	$I_c$ ( $\mu\text{A}$ )	$I_c/I_a$	$E$ (mv)
KF (0.2 M) $\phi$ OH (3 mM)	12.5	27.5			
	25	36			
	50	44.5			
	62.5	48.5	(a)	(a)	(a)
	89	54			
	125	63.5			
	166	67			
$\text{SbF}_6^-$ (0.15 M) + $\text{SbF}_5$ (0.2 M) $\phi$ OH (3-1 mM)	17.5	18	17.5	0.95	84
	35	25.5	25	0.97	96
	70	31	31	1.00	112
	87	34	34	1.00	124
	116	37	38	1.02	140
	175	43.5	42.5	0.98	172
	233	47	45	0.96	208
$\text{SbF}_6^-$ (0.1 M) + $\text{SbF}_5$ (0.5 M) $\phi$ OH (5 mM)	30	23.5	24	1.02	108
	45	28.5	30.5	1.07	120
	90	33.5	37.5	1.12	140
	112	35.5	41.5	1.17	164
	150	40.5	46.5	1.15	188
	225	45.5	52.5	1.15	252
	300	50	56	1.13	316

(a) The electrode process (EC) appears totally irreversible in this range of scan rates.

The half wave potential of the first wave  $(E'_{1/2})_1$  depends on the  $\text{SbF}_5$  concentration according to the following experimental relation :

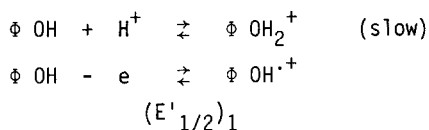
$$(E'_{1/2})_1 = 0.987 - 0.072 \text{ pH.}$$

The decrease in the wave height observed with increasing  $\text{SbF}_5$  concentration, indicates that the first oxidation step is preceded by a slow protonation of  $\phi \text{ OH}$ .

Controlled potential electrolysis at  $E = 1.3 \text{ V}$  confirms the exchange of one Faraday per mole, but the radical formed is stable (the solution is yellow) only below  $\text{pH } 0.7$  ( $\text{SbF}_5 < 0.2 \text{ M}$ ). When  $\text{pH}$  increases, the radical is not stable and disappears. This is the case when  $\text{SbF}_5$  is neutralized by  $\text{KF}$ .

Then, the first oxidation step is the formation of a radical in strongly acidic media (as in strongly basic media). Such radical compounds can be invoked in fluorination processes. An intermediate radical cation in fluorination by  $\text{XeF}_2$  or  $\text{CoF}_3$  has been suggested [8, 9].

The stabilization of the radical which was previously observed [2, 10, 11] may be due to the protonation of the phenolic group and the following oxidation scheme can be proposed :



the second step, corresponding to the oxidation of the radical is ill-defined. It leads to polymeric products and passivation of the electrode.

Thus, the radical formed by oxidation of  $\phi \text{ OH}$  is chemically stable in basic media, disproportionates in less basic media and then is stable again in strongly acidic media owing to the protonation, and to the corresponding very low fluoride ion activity.

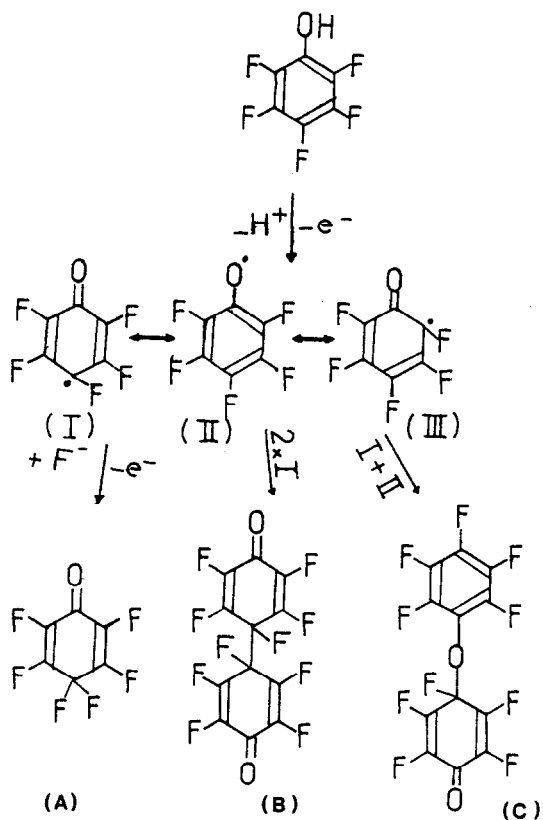
The products analysed after controlled potential coulometry are reported in Scheme 1 and the yields indicated in Table III. Only products (A) and (C) are extracted from reaction media.

Product (C) is formed by dimerization of the electrochemically generated radical, the acidity level stabilizing the form II (see scheme 1). This compound together with polymers was also formed by oxidation of pentafluorophenol by  $\text{PbO}_2$  [12].

The formation of (A) in this medium can be explained only if there is a chemical oxidation after the electrolysis during the separation process. Electrolysis at 1.3 Volt necessitates only one electron per mole and pentafluorophenol is completely oxidized to a radical and not to hexafluorocyclo-

TABLE III : Analysis of electrolysis products in basic (KF) and acidic ( $\text{SbF}_5$ ) media in HF

Products	% basic media (KF 0.2 M)	% acidic media $\text{SbF}_5/\text{SbF}_6^-$ (0.2 M)
A	56	44
B	20	~ 0
C	24	56



Scheme 1 : Electrochemical oxidation of pentafluorophenol in anhydrous hydrogen fluoride

hexadienone (A) (which necessitates two electrons per mole). The radical can be oxidized by  $\text{SbF}_5$  during the separation process. Such an oxidation in  $\text{SbF}_5$  media has already been suggested to perfluorocyclohexa 1.4 diene by SHTEINGART et al [ 13, 14 ], giving a low yield of product (A).

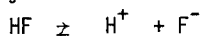
## EXPERIMENTAL

The line used for handling of HF and superacid mixtures has been described in a previous paper [ 15 ].

Electrochemical study : The reference electrode was made from Ag/Ag(I) system (Ag electrode in saturated AgF + KF (1 M) ; potential  $E = + 0.230$  Volt versus Cu/CuF<sub>2</sub> KF (0.2 M) system [ 16 ]. Working electrode is a bright platinum electrode  $S = 3.14 \text{ mm}^2$ .

### Acidity in HF

Owing to the autoprotolysis equilibrium of liquid HF, pure solvent is slightly dissociated according to the equilibrium :



with

$$K_i = |\text{H}^+| |\text{F}^-|$$

so, pH in HF may be expressed either by means of fluoride ion concentration,  $\text{pF} = - \log |\text{F}^-|$ , or by  $\text{H}^+$  concentration as in any protolytic solvent.

pF and pH are linked by the autoprotolysis constant and the acidity range of HF is limited by the value of pH corresponding to a 1 M strongly acidic solute, ( $\text{SbF}_5$ , for example) towards acidic media ( $\text{pH} = 0$ ), and to a 1 M strong base (alkaline fluoride, for example) towards basic media ( $\text{pH} = \text{p}K_i$ ).

According to these definitions, we have indicated all the pH values with reference to pure HF as solvent.

We have recently shown [ 17 ] that electrochemical indicators of the quinonic type (tetrachloro and tetrafluoroparabenzoquinone) retain their properties as pH indicators at this very high acidity level, and we have determined the autoprotolysis constant :

$$\text{p}K_i / \text{mol}^2 \text{ l}^{-2} = 13.7$$

The electrochemical indicators also permit the evaluation of the pH of various buffers in HF ( $\text{BF}_3/\text{BF}_4^-$ ,  $\text{TaF}_5/\text{TaF}_6^-$ ,  $\text{AsF}_5/\text{AsF}_6^-$ ,  $\text{TaF}_5/\text{TaF}_6^-$ , etc.). In the present study, pH is fixed by the concentration of  $\text{SbF}_5$  ( $0 < \text{pH} < 3$ ) or of KF ( $11 < \text{pH} < 13.7$ ).



TABLE IV : Characteristics of the mass spectrum of the products formed by electrolysis of pentafluorophenol

Pentafluoro phenol		A		B		C	
m/e	%	m/e	%	m/e	%	m/e	%
69	76	69	32	69	46	69	62
75	25	74	12	93	<u>100</u>	93	31
86	21	86	10	105	18	105	37
87	26	93	68	117	72	117	32
93	70	105	38	124	20	124	12
98	9	112	11	136	12	136	27
105	49	117	24	143	45	155	99
117	<u>100</u>	124	<u>100</u>	148	14	167	16
124	24	136	5	155	95	183	<u>100</u>
136	95	155	54	167	69	241	5
148	9	174	30	183	38	347	5
155	39	183	17	195	39	366	3
165	6	202	37	241	57		
				280	11		
				272	16		
				288	9		
				291	10		
				319	5		
				347	18		
				366	72		

The pH values in HF have been compared with pH values of aqueous solutions by means of R (H) acidity functions. The corresponding values are R (H) = - 26 (1 M SbF<sub>5</sub>) and R (H) = - 12.3 (1 M KF).

Product analysis : Separation of the electrolysis products was achieved in the following way : HF was removed by vacuum aspiration. The residue was dissolved in methylene chloride then the solution was treated with an excess of KF to remove traces of HF, filtered and concentrated. Analysis of reaction products was performed by gas chromatography coupled with mass spectrometry (chromatograph GIRDEL, detector flame ionization, Mass Spectrometer RIBER (France)).

Column chromosorb WAW 80-100, 1/8 inch, 1 = 2.50 m. The solvent is separated at 70 °C and the products are eluted with Nitrogen temperature programming (9°/mn), retention time of reaction products are:

(A) 1 mn at 70 °C, (B) 12.5 mn at 174 °C, and (C) 14 mn at 184 °C.

The characteristics of the mass spectrum are reported in Table IV. Products present in a concentration lower than 5 % are not reported except for molecular peaks.

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