

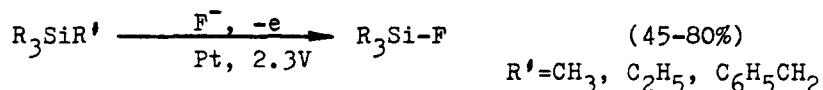
ANODE CHEMISTRY OF ORGANOSILANES. OXIDATIVE REPLACEMENT
OF ALKYL GROUP BY FLUORIDE ION.

I.Y.Alyev; I.N.Rozhkov, I.L.Knunyants
Institute of Organoelement Compounds, USSR Academy of Sciences
Moscow, USSR

(Received in UK 6 May 1976; accepted for publication 7 June 1976)

Anode oxidation of aromatic compounds on Pt in the presence of fluoride ion results in C-F bond formation in substrate molecules. The mechanism excludes the radical fluorination, since the anode potentials used are lower than that of anode discharge of fluoride (2.55V vs Ag/AgNO₃ 0.1 mol)^{1,2}.

We present now the results of anodic oxidation of some tetraalkyl- and tri-alkylarylsilanes using Pt-electrodes under the condition of constant potential 2.3V (versus Ag/AgNO₃ 0.1 mol). The supporting electrolyte was 1.0 mol tetraethylammonium trihydrogentetrafluoride (TEAF) in CH₃CN. The anodic oxidation of organosilanes at these conditions has led to the fluorosilanes as a result of the replacement of alkyl-group attached to Si by fluoride ion.

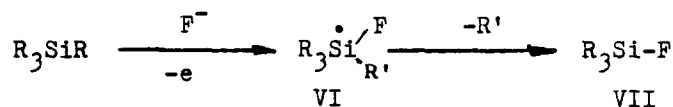


The typical procedure of anodic oxidation consisted in the electrolysis of the solution of 2 mMol of organosilane in CH₃CN in presence of TEAF. All the electrolyses were carried at the controlled potential using the membrane in the cell described earlier², until 1.2F/mol was passed. Then the solution was extracted with C₅H₁₂, distilled and products were identified by GLC and ¹⁹F NMR technique. The obtained results listed in Table show the replacement of alkyl group is rather selective. Thus a methyl group only was replaced in the oxidation of I and II. Analogically benzyl group only was replaced in the electrolyses of III and IV. The oxidation of V led to the replacement of ethyl group mainly. It should be noticed that the oxidation of I in non nucleophilic medium (Et₄NClO₄ in CH₃CN) was found to proceed at anodic potential equal to 2.6V. The presence of fluoride was found to decrease the oxidation potential to 2.3V. No radical fluorination process is possible at this potential due to the reasons discussed above.

Table. Anodic oxidation of organosilanes.

Reactant		Products (yield %)
$C_6H_5Si(CH_3)_3$	(I)	$C_6H_5Si(CH_3)_2F$ (80), CH_4 , C_2H_6
$p-F-C_6H_4-Si(CH_3)_3$	(II)	$p-F-C_6H_4-Si(CH_3)_2F$ (80), CH_4 , C_2H_6
$(CH_3)_3SiCH_2C_6H_5$	(III)	$(CH_3)_3SiF$ (50), C_6H_5CHO
$(C_2H_5)_3SiCH_2C_6H_5$	(IV)	$(C_2H_5)_3SiF$ (70), C_6H_5CHO
$CH_3Si(C_2H_5)_3$	(V)	$CH_3Si(C_2H_5)_2F$ (45), C_2H_5F , $CH_2=CH_2$ $FSi(C_2H_5)_3$ (5), CH_4 , C_2H_6

All these results may be satisfactorily interpreted mechanistically as the one-electron anodic oxidation of organosilanes assisted by fluoride ion. After electron transfer and formation of Si-F bond the intermediate pentacoordinate Si-radical (VI) eliminates rapidly the most stable alkyl radical giving fluoro-silane (VII).



The further fate of the eliminated alkyl radical is rather significant. This intermediate may undergo either radical reactions (coupling, hydrogen abstraction), or oxidize on the anode provided its oxidation potential $E_{1/2}$ is not higher than that of the anode. Indeed $E_{1/2}$ of methyl radical is $2.98V^3$ and accordingly the electrolyses of I and II at the potential $2.3V$ produced C_2H_6 (the coupling reaction) and CH_4 (the hydrogen abstraction). The oxidation potential of ethyl and benzyl radicals are lower than $2.3V$. Accordingly the anodic oxidation of III, IV and V produced the products arising from $C_2H_5^+$ and $C_6H_5CH_2^+$ cationic species (C_2H_5F , C_2H_4 and C_6H_5CHO).

It should be noted that organosilanes with Si-H bond may be fluorinated as above with the selective cleavage of Si-H bond. However, this reaction can't be treated as only electrochemical process, because we have found that uncharged Pt is able to catalyze the protodesilylation reaction of R_3SiH in acetonitrile solution of TEAF yielding R_3SiF .

REFERENCES

- ¹C.J.Lundmann, E.McCarron, R.E.O'Malley, J.Electrochem.Soc., 119, 874 (1972)
- ²I.N.Rozhkov, I.Y.Alyev, Tetrahedron, 31, 977 (1975) and references cited there
- ³L.Eberson, Acta Chim.Scand., 17, 2004 (1963)