Anodic Functionalization of 1*H*-Perfluoroalkanes. Observtion of ^{19}F C.I.D.N.P.

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Summary The anodic oxidation of 1*H*-perfluoroalkanes in HSO_3F–KSO_3F (0·5M) leads to perfluoroalkyl fluorosulphates, through an indirect process as confirmed by ^{19}F C.I.D.N.P.

THE $-CF_2H$ group of monohydrofluorocarbons is known to be rather inert chemically;[1] in particular radical oxidation needs drastic conditions.[2] However, the oxidation can be carried out under very mild conditions electrochemically.

The electrochemical reaction was carried out at 25 °C in an undivided cell, with platinum gauze electrodes, at constant current, using fluorosulphuric acid (FSO_3H) as solvent and its potassium salt (0·5M) as electrolyte. The results described here were obtained with n-$C_6F_{13}H$. The product is the pure perfluoroalkyl fluorosulphate [reaction (1)].

$$C_5F_{11}CF_2H \xrightarrow[HSO_2F\text{–}KSO_3F]{-2e} C_5F_{11}CF_2OSO_2F \qquad (1)$$

The fluorosulphate produced, characterized by its ^{19}F n.m.r. spectrum (Figure, b), was obtained in a coulombic

yield of 75% which was not appreciably improved by using a divided electrolysis cell. It was isolated from the electrolyte by decantation and purified by distillation under atmospheric pressure (b.p. 109 °C). Alkaline hydrolysis of the fluorosulphate does not produce the corresponding alcohol but instead the salt of a perfluorocarboxylic acid.[3] Primary perfluoro-alcohols are unstable,[4] eliminating HF to give a carboxylic acid derivative [reaction (2)].

$$C_5F_{11}CF_2OSO_2F \xrightarrow[-HSO_3F]{OH^-} [C_5F_{11}CF_2OH] \xrightarrow{-HF} C_5F_{11}C(=O)F \xrightarrow[-HF]{OH^-} C_5F_{11}CO_2^- \qquad (2)$$

The electrochemical reaction was followed by ^{19}F n.m.r. spectroscopy. Figure a shows the spectrum of an aliquot portion of the electrolyte after the passage of 0·2 Faraday per mol. It was recorded, at 30 °C, < 30 s after the current flow was stopped. The α-fluorine atoms of the product give rise to a large emission that disappears after 5 min. The observation of a C.I.D.N.P. effect under these conditions shows that the product is formed from a radical mechanism[5] in the bulk solution. However, the absence of dimeric products ($C_{12}F_{26}$) indicates that $C_6F_{13}\cdot$ radicals are not involved. Moreover, the fact that $C_6F_{13}H$ does not show anodic waves in a polarographic study on a rotating platinum disc electrode in HSO_3F–KSO_3F (0·5M), proves that an indirect electrochemical process is involved. This is confirmed by the formation of the same fluorosulphate when the 1*H*-perfluoroalkane is added after preliminary anodic oxidation of the solvent HSO_3F–KSO_3F. A C.I.D.N.P. effect is also observed under these conditions.

Since peroxydisulphuryl difluoride, $(FSO_3)_2$, has been prepared by anodic oxidation of HSO_3F,[6] we assume that the reaction occurs *via* this intermediate. This assumption is supported by the ability of this peroxide, prepared by an alternative procedure,[7] to cause substitution of isolated hydrogen by the fluorosulphate group in perfluorinated chains.[8] It is also corroborated by the work of Pletcher *et al.*[9] on the anodic fluorosulphonation of methane and ethane.

In order to explain these results, particularly the net nuclear polarization, we suggest the mechanism in the Scheme.

$$2FSO_3^- \longrightarrow (FSO_3)_2$$
$$(FSO_3)_2 \longrightarrow 2FSO_3\cdot$$
$$2FSO_3\cdot \xrightarrow{R_FCF_2H} HSO_3F + R_FCF_2\cdot + \cdot O_3SF \longrightarrow R_FCF_2OSO_2F$$

SCHEME

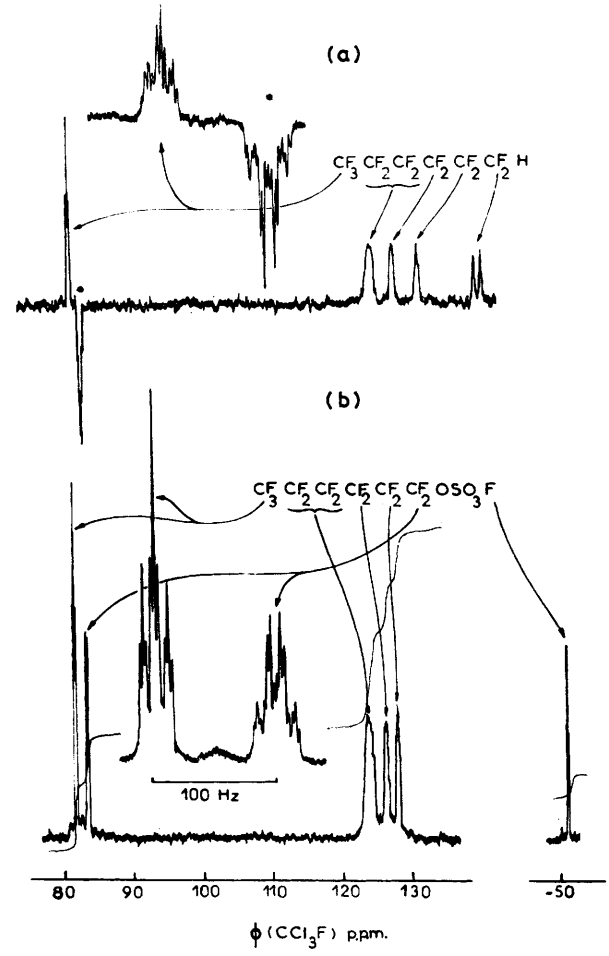

FIGURE. ^{19}F N.m.r. spectra (56·4 MHz) of: (a) electrolytic solution at the beginning of the anodic oxidation of 1*H*-perfluorohexane in HSO_3F–KSO_3F; (b) the perfluorohexyl fluorosulphate obtained.

In a similar electro-oxidation of $C_6F_{13}H$ in CF_3SO_3H–CF_3SO_3Na (0·5M) the corresponding trifluoromethanesulphonate is not obtained. In this case, the intermediate

$$2CF_3SO_3^- \xrightarrow{-2e} (CF_3SO_3)_2 \longrightarrow CF_3SO_3CF_3 + SO_3 \qquad (3)$$

peroxide decomposes before reacting with the substrate to produce trifluoromethyl trifluoromethanesulphonate [reaction (3)].[10] A C.I.D.N.P. effect is not observed during the formation of $CF_3SO_3CF_3$.

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