

## Anodic Functionalization of 1*H*-Perfluoroalkanes. Observtion of <sup>19</sup>F C.I.D.N.P.

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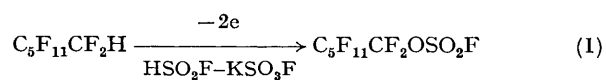
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*Summary* The anodic oxidation of 1*H*-perfluoroalkanes in HSO<sub>3</sub>F-KSO<sub>3</sub>F (0.5M) leads to perfluoroalkyl fluorosulphates, through an indirect process as confirmed by <sup>19</sup>F C.I.D.N.P.

constant current, using fluorosulphuric acid (FSO<sub>3</sub>H) as solvent and its potassium salt (0.5M) as electrolyte. The results described here were obtained with n-C<sub>6</sub>F<sub>13</sub>H. The product is the pure perfluoroalkyl fluorosulphate [reaction (1)].

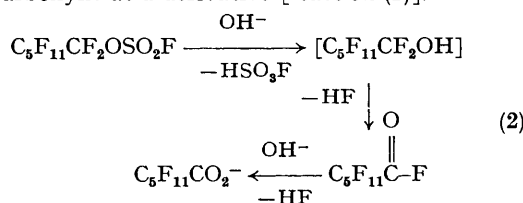
THE -CF<sub>2</sub>H group of monohydrofluorocarbons is known to be rather inert chemically;<sup>1</sup> in particular radical oxidation needs drastic conditions.<sup>2</sup> However, the oxidation can be carried out under very mild conditions electrochemically.

The electrochemical reaction was carried out at 25 °C in an undivided cell, with platinum gauze electrodes, at



The fluorosulphate produced, characterized by its <sup>19</sup>F n.m.r. spectrum (Figure, b), was obtained in a coulombic

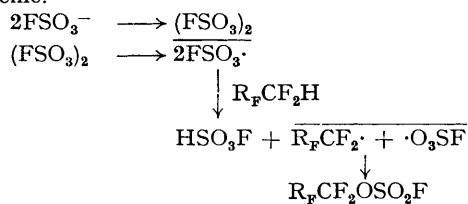
yield of 75% which was not appreciably improved by using a divided electrolysis cell. It was isolated from the electrolyte by decantation and purified by distillation under atmospheric pressure (b.p. 109 °C). Alkaline hydrolysis of the fluorosulphate does not produce the corresponding alcohol but instead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



The electrochemical reaction was followed by <sup>19</sup>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<sup>5</sup> in the bulk solution. However, the absence of dimeric products (C<sub>12</sub>F<sub>26</sub>) indicates that C<sub>6</sub>F<sub>13</sub>· radicals are not involved. Moreover, the fact that C<sub>6</sub>F<sub>13</sub>H does not show anodic waves in a polarographic study on a rotating platinum disc electrode in HSO<sub>3</sub>F-KSO<sub>3</sub>F (0.5M), proves that an indirect electrochemical process is involved. This is confirmed by the formation of the same fluorosulphate when the 1H-perfluoroalkane is added after preliminary anodic oxidation of the solvent HSO<sub>3</sub>F-KSO<sub>3</sub>F. A C.I.D.N.P. effect is also observed under these conditions.

Since peroxydisulphuryl difluoride, (FSO<sub>3</sub>)<sub>2</sub>, has been prepared by anodic oxidation of HSO<sub>3</sub>F,<sup>6</sup> we assume that the reaction occurs *via* this intermediate. This assumption is supported by the ability of this peroxide, prepared by an alternative procedure,<sup>7</sup> to cause substitution of isolated hydrogen by the fluorosulphate group in perfluorinated chains.<sup>8</sup> It is also corroborated by the work of Pletcher *et al.*<sup>9</sup> 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.



SCHEME

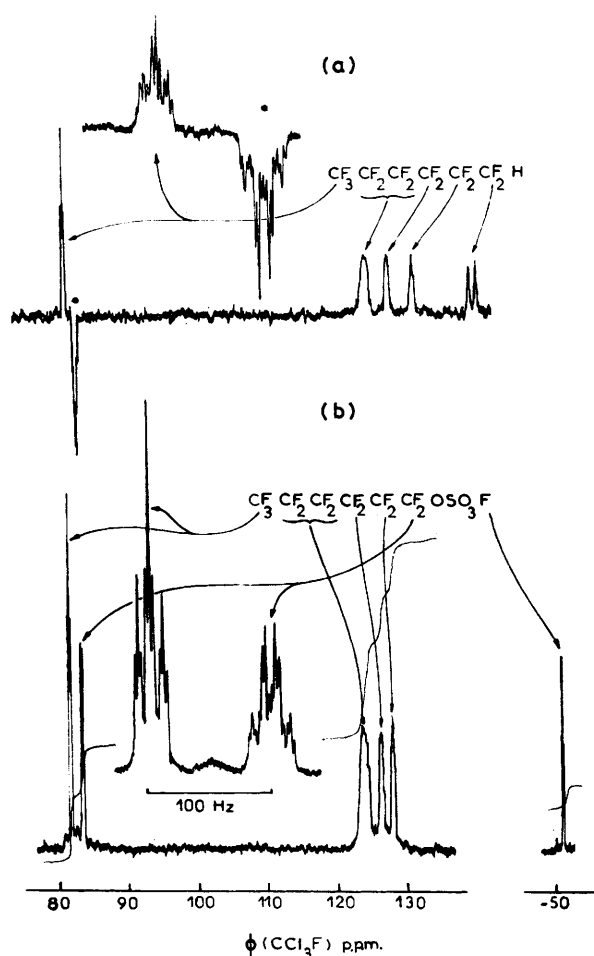
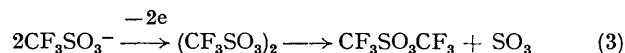


FIGURE. <sup>19</sup>F N.M.R. spectra (56.4 MHz) of: (a) electrolytic solution at the beginning of the anodic oxidation of 1H-perfluorohexane in HSO<sub>3</sub>F-KSO<sub>3</sub>F; (b) the perfluorohexyl fluorosulphate obtained.

In a similar electro-oxidation of C<sub>6</sub>F<sub>13</sub>H in CF<sub>3</sub>SO<sub>3</sub>H-CF<sub>3</sub>SO<sub>3</sub>Na (0.5M) the corresponding trifluoromethanesulphonate is not obtained. In this case, the intermediate



peroxide decomposes before reacting with the substrate to produce trifluoromethyl trifluoromethanesulphonate [reaction (3)].<sup>10</sup> A C.I.D.N.P. effect is not observed during the formation of CF<sub>3</sub>SO<sub>3</sub>CF<sub>3</sub>.

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