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THE ANODIC FLUOROSULPHONATION OF SOME SATURATED ORGANIC COMPOUNDS

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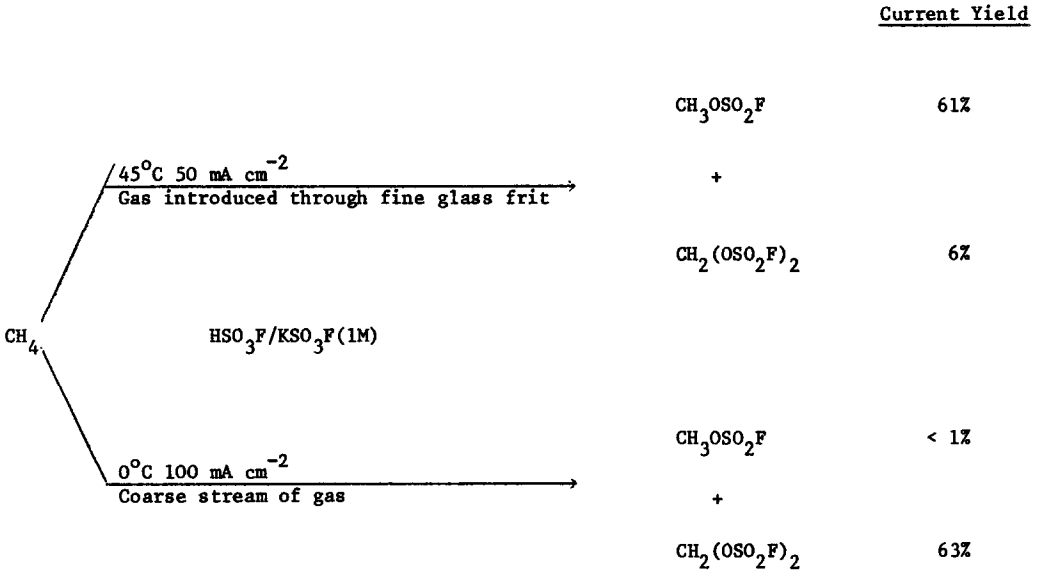
Although peroxydisulphuryldifluoride was first prepared a number of years ago[1], its potential as a reagent in synthesis has not previously been realised and, indeed, the only reactions which have been reported are those in the vapour phase with perfluoroolefins[2]. In this paper we describe some reactions between peroxydisulphuryldifluoride and some saturated organic molecules, namely methane, acetic acid, propionic acid and acetone, in anhydrous fluorosulphonic acid; the products are fluorosulphonate esters, species which are likely to be useful intermediates in synthesis. None of the organic compounds used in this work show anodic peaks for their direct oxidation when cyclic voltammetry was carried out on their solutions in fluorosulphonic acid containing potassium fluorosulphonate (1.0M). [Compare higher alkanes[3] and perfluoroaromatic compounds[4]].

The oxidation of fluorosulphonate ions in fluorosulphonic acid occurs at a potential just below +2.0V versus a Pd/H_2 reference electrode. The initial product is the fluorosulphonate radical which dimerises to give peroxydisulphuryldifluoride. A cyclic voltammogram on this system shows a reverse peak at +0.3V which is associated with the reduction of the dimer and the height of this peak may conveniently be used to follow the reactions of peroxydisulphuryl-difluoride with added substrates.

Peroxydisulphuryldifluoride is a liquid [b.p. 68°C] which may be isolated by conducting a controlled current electrolysis on a solution of potassium fluorosulphonate (1.0M) in anhydrous fluorosulphonic acid between two platinum electrodes in a cell under vacuum and collecting the product in a cold trap[5]. In practice, however, peroxydisulphuryldifluoride is such a vigorous reagent that it was found difficult to control its reactions with organic substrates when they were attempted by simply mixing solutions of the two reactants and it was found to be safer and more convenient to carry out reactions in situ in a simple electro-chemical cell as the peroxydisulphuryldifluoride is generated at the anode. Hence preparative electrolyses were carried out at a constant current in a cell where the platinum anode and

cathode were separated by a glass frit. Where possible the solutions contained the substrate in high concentration (1M) and the reactions were followed directly by N.M.R. spectroscopy on the anolyte; yields were determined by comparison with standard samples.

Methane is virtually insoluble in fluorosulphonic acid - potassium fluorosulphonate (1.0M), but when it was bubbled at atmospheric pressure over the anode operating at constant current either methyl fluorosulphonate or methylene difluorosulphonate could be formed selectively.



The methyl fluorosulphonate was monitored using the N.M.R. singlet[6] [δ(ext.TMS)FSO_3H: 4.1] and methylene difluorosulphonate using the characteristic triplet [δ:5.9, t, J_{HF} = 1.5 Hz]. Methyl fluorosulphonate is sufficiently volatile to be distilled from the cell while the other product may be isolated by quenching the anolyte with ice-water and rapidly extracting into methylene chloride.

Acetic acid also reacted with peroxydisulphuryldifluoride and the only product obtained was methylene difluorosulphonate. Methyl fluorosulphonate could not, however, be ruled out as an intermediate since a competition experiment showed that methyl fluorosulphonate is selectively oxidised in the presence of a ten fold excess of acetic acid. The oxidation of

acetic acid was carried out in several ways; the results are shown in table 1.

TABLE 1

Method	% Yield $CH_2(FSO_3)_2$	
	Chemical[a]	Current[b]
1. Divided cell	75	27
2. Undivided cell	65	20
3. Prior generation of $(FSO_3)_2$ in divided cell	70	38

a; based on acetic acid consumed

b; based on 4F/mole $CH_2(FSO_3)_2$

Propionic acid showed a different reaction route. At the end of the electrolysis, the anolyte was examined by N.M.R. spectroscopy. In addition to unreacted propionic acid, there was the spectrum expected for propionic acid-3-fluorosulphonate [δ;3.3,t,2H, J=6Hz and 4.7,t,2H J=6Hz]. Direct controlled potential oxidation of 3-bromopropionic acid in fluorosulphonic acid liberated bromine and gave a solution with the same N.M.R. spectrum. On standing for 24 hours both solutions showed the spectrum of acrylic acid. Attempts to isolate the fluorosulphonate substituted acid have so far failed.

$$CH_3CH_2COOH \xrightarrow[HSO_3F/KSO_3F]{0^\circ C,\ 100\ mA\ cm^{-2}} CH_2(OSO_2F) - CH_2COOH \xrightarrow{\text{on standing}} CH_2 = CHCOOH$$

chemical yield 50%
current yield 26%

An attempt to introduce a fluorosulphonate group into acetone was unsuccessful and

the reaction resulted in cleavage of a carbon-carbon bond.

		% Yield	
		Chemical	Current
CH_3COCH_3 $\xrightarrow{0^\circ,\ 100\ mA\ cm^{-2}}$	CH_3OSO_2F	35	26
	+ $CH_2(OSO_2F)_2$	13	19
	+ $CH_3CO{\cdot}OSO_2F$	74	55

The mechanism of these reactions probably involves initial hydrogen abstraction by fluorosulphonate radicals. The mechanism and scope of the reactions are being investigated further.

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