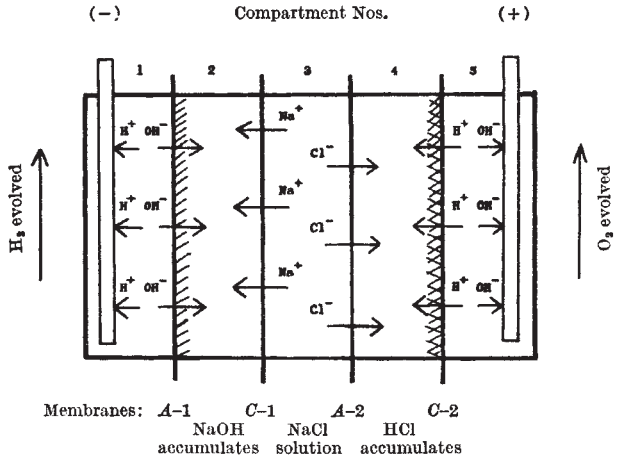

Fig. 1. Diagonal lines, zone of high *p*H; hatching, zone of low *p*H

accumulation of electric charge in these compartments. Since this manifestly does not occur, some mechanism must be found to account for the continued transport of charge across the cell.

The following mechanism was postulated:

(1) Na^+ ions from compartment 3 migrate across the cation-permeable membrane *C*–1 into compartment 2.

(2) Simultaneously, OH^- ions arising from the dissociation of water migrate from compartment 1 through the anion-permeable membrane *A*–1 and into compartment 2.

(3) The H^+ ions formed from the dissociation of water travel to the cathode and are discharged to give hydrogen gas.

(4) The net result is the accumulation of sodium hydroxide in compartment 2 and the evolution of hydrogen at the cathode.

A similar process involving the migration of H^+ ions from compartment 5 to compartment 4, through the cation-permeable membrane *C*–2, is accompanied by the discharge of OH^- ions at the anode and leads to the accumulation of hydrochloric acid in compartment 4 and the evolution of oxygen at the anode.

To test the proposed mechanism, a normal solution of sodium chloride containing a few drops of B.D.H. Universal Indicator was placed in compartment 3 and the other compartments were filled with distilled water mixed with indicator. Although the electrodialyser had been designed to operate with water flowing through the electrode compartments[1], in this particular experiment the outlets from the bottom of the electrode compartments were blocked off and the water in the compartments remained static. The current was switched on and adjusted to 40 m.amp (at 100 V) and the changes in colour of the indicator in each compartment were carefully observed (Table 1). Almost immediately, a zone of very high *p*H (about 11) was seen to advance from the surface of the anion-permeable membrane *A*–1 into compartment 2 but no coloured zone was seen in the solution at the surface of the membrane *C*–1 in this compartment. Shortly afterwards, a zone of very low *p*H (< 4) was seen to advance from the cation-permeable membrane *C*–2 into compartment 4.

The zone of high *p*H did not spread throughout the whole of compartment 2, but after 5 min had elapsed, the contents of the compartment were stirred and all the solution then reached a *p*H of about 11. A similar *p*H gradient was seen in compartment 4 and after mixing the solution attained a *p*H below 4. At no time was a *p*H gradient observed in the centre compartment. At the end of 10 min the current was switched off; the solutions were removed and their *p*H was measured with a *p*H-meter, and they were tested for chloride with acidified silver nitrate (Table 1).

Table 1

Time (min)	Compartment 1 (*p*H)	2 (*p*H)	3 (*p*H)	4 (*p*H)	5 (*p*H)
0	5	5	5	5	5
2	4	*p*H gradient	6	*p*H gradient	4
4	< 4	*p*H gradient	6	*p*H gradient	< 4
10	< 4	11	6	< 4	< 4
Final *p*H (by meter)	4·3	11·2	6·1	3·1	3·4
Test for Cl^-	—	Trace	+ + + +	+ +	—

Changes in *p*H and chloride concentration during the fractionation of NaCl by electrodialysis in a 5-compartment cell.

The results indicate that alkali and acid had accumulated in compartments 2 and 4 respectively and the *p*H changes at the surface of the membranes were as predicted for the proposed mechanism. The traces of chloride detected in compartment 2 may be expected since the 'Permaplex' cation-permeable membranes are not 100 per cent permselective for cations[3]; however, no chloride ion appeared to have penetrated the cation-membrane *C*–2. It was of interest that, on dismantling the apparatus, the membrane *A*–1, on the side facing compartment 2, was found to be stained a deep purple (*p*H 11 colour) with adsorbed indicator, and likewise the membrane *C*–2, on the side facing compartment 4, was stained a bright red (*p*H < 4 colour).

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Radiation-induced Oxidation of Perfluoropropylene

Recently it has been shown that the tetrafluoroethylene–oxygen reaction[1–3] occurs through a simple chain process leading to the formation of carbonyl fluoride, tetrafluoroethylene oxide and a polymeric peroxide. Previous work[4,5] on the oxidation of perfluoropropylene by H_2O_2 in basic medium or by molecular oxygen in the presence of catalysts has shown that the reaction products may vary widely according to the procedure adopted.

We have found that perfluoropropylene is completely oxidized by molecular oxygen when irradiated in the gas phase with γ-rays of a cobalt-60 source. The dose-rate was 0·35 Mr./h and the mixtures were irradiated for 25 h. The oxygen uptake by the olefine is about 1·2 on a molar basis and this also occurs when the reactants are in a 1 : 1 ratio. The reaction products are mainly gaseous at room temperature, and carbonyl fluoride and trifluoroacetylfluoride account for 80 per cent of the total pressure (50 per cent of the olefine consumed). These substances are in a 1 : 1 ratio.

Attempts to isolate the remaining products by distillation in a Podbielniak column have failed. Three fractions have been obtained but no pure compounds have been separated. The boiling points of these fractions are between −30° C and +60° C and the molecular weights range from 120 to 330. Full characterization has not been accomplished. From the mass balance it appears that the O/C ratio of these fractions is about 1 : 1. The infra-red spectra show a strong absorption band in the CO region for all fractions. The nuclear magnetic resonance spectra of the same fractions reveal chemical shifts at near-zero or negative p.p.m. with respect to trifluoroacetic acid and this is in agreement with the high content of oxygen. A liquid having a vapour pressure of less than 1 mm remains in the reaction flask. This liquid accounts for 10 per cent of C_3F_6 consumed. The analysis gives C 18·33, F 53·27, O 28·41 per cent.

From these preliminary results some features concerning the oxidation of perfluoropropylene seem of particular interest. It is tempting to correlate the 1 : 1 ratio of COF_2 and CF_3COF with the depolymerization mechanism as proposed for the oxidation of tetrafluoroethylene[3]. The infra-red spectrum of the fraction boiling at about −30° C suggests the presence of an epoxidic product together with perfluoropropionyl fluoride. However, the analysis of the liquid indicates a high O/C ratio which disagrees with the expected composition of the polyperoxide.

The large uptake of oxygen may be due to some secondary oxidation process, as, for example, for the attack of oxygen to CF_3 groups. Finally, it may be remarked that contrary to polymerization the oxidation of perfluoropropylene proceeds at a rate comparable with that of tetrafluoroethylene[6].

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Synthesis of Pentafluorophenylalanine

Our interest in fluorine-containing α-amino-acids[1–3] has led us to an investigation of the chemistry of β-pentafluorophenylalanine (I). We wish to report here the synthesis of this novel amino-acid by two different routes. (In a personal communication, Dr. P. L. Coe, University of Birmingham, England, has informed us that he has prepared compound I in impure form by means of the azlactone route. Preliminary tests with several micro-organisms indicated that the amino-acid was inactive.)

$C_6F_5CH_2CH(NH_3^+)CO_2^-$ (I) $C_6F_5CH_2C(NHCOCH_3)(CO_2C_2H_5)_2$ (II)

In the method of choice, pentafluorobenzyl bromide[4] reacts with sodiodiethylacetamidomalonate in dimethylformamide at 40° for 20 h to give a 44 per cent yield of the condensation product (II), m.p. 124°–126°. Compound II (3·0 g) was heated under reflux for 8 h with 20 per cent hydrochloric acid to furnish the hydrochloride of I. This salt readily loses hydrogen chloride on crystallization from 95 per cent ethanol to give 1·4 g (73 per cent) of the free amino-acid I, m.p. 251°–254° (uncorrected). Analysis: Calc. for $C_9H_6F_5NO_2$: C, 42·36; H, 2·37; N, 5·49 per cent. Found: C, 41·98; H, 2·63; N, 5·77 per cent. The amino-acid gives a strong positive ninhydrin test and its infra-red spectrum is consistent with the structure proposed. The weakly basic character of the amino group in I relative to the amino group in β-phenylalanine is reflected by the rapid loss of hydrogen chloride and by preliminary *p*Ka data. We attribute this effect in some measure to an interaction between an ortho fluorine atom and the NH_3^+ group across intramolecular space.

The second method involves the conversion of α-bromo-β-pentafluorophenylpropionic acid (III) (obtained from pentafluoroaniline and acrylic acid by means of the Meerwein arylation method[5]) to the α-azido compound[6] and subsequent hydrogenolysis, using 10 per cent palladium-on-charcoal, to give compound I. The reaction of III with ammonia leads to elimination, rather than to nucleophilic displacement.

$C_6F_5CH_2CH(Br)CO_2H$ (III)

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BIOCHEMISTRY

Micro-technique for Cell Electrophoresis

Several apparatuses have been described for measuring the electrical charge of small particles, such as cells[1–9]. Due to the relatively large volume of the chambers used, and the minimum cell concentration necessary for adequate measurements, the total number of cells required for each measurement is rather large. When working with small samples, one sometimes finds it impossible to meet these requirements, and micromethods have therefore been developed. Theoretically, three different approaches are possible: to decrease the total volume of the chamber, to build the apparatus from several parts and fill only one of them with the cell suspension, or to introduce the sample to the measuring-place of a previously-filled chamber. The first of these possibilities is made complicated because of contamination by the electrodes. The second has been used by Seaman and Heard[10], who built their apparatus from three parts. In their device only the microelectrophoresis tube is filled with the sample, while the electrode compartments remain 'cell-free'. This system handles samples of the order of 1 ml. or even less. The third possibility has recently been explored by Forrester *et al.*[11], who have been able to reduce the minimum suspension volume to 0·1–0·2 ml. (ref. 12). The small size and low cell numbers of the organ rudiments we have been investigating have forced us to use even smaller volumes. This led us to modify the apparatus described by Bangham *et al.*[9].

The modification is illustrated in Fig. 1. It is based entirely on the apparatus described by Bangham *et al.* and produced for our laboratory by Rank Bros., Bottisham, Cambs. Therefore, only alterations to this apparatus will be described here. To the original U-tubing (*G*) two additional horizontal 'Pyrex' tubes 2 mm in internal diameter are fitted (D_1–D_2), which are closed symmetrically with glass taps of vacuum quality (C_2, C_4). The diameter of the drilled holes of these taps is also 2 mm. In addition, two vertical tubes closed by similar glass taps (C_1, C_3) have been fitted to the lateral tubes in corresponding positions. The necks of the upper ends of the vertical tubes are 10 mm in diameter (B_1, B_2). The lateral tubes penetrate the glass walls of the waterbath through drilled holes 50 mm in diameter, and to facilitate manipulation the left lateral tap is left outside the waterbath. A pair of rubber collars seal the holes in the glass wall against leakage while allowing the tube to be easily placed into the bath and to be moved vertically when calibrating the apparatus[9]. A mirror (*M*) has been placed under the microscope at a 45° angle in order to follow the pipetting of the sample.