



Scheme 2.

(FHH) in perdeuterioacetic acid, using sodium acetate(perdeuterioacetate) or tetrabutylammonium tetrafluoroborate as supporting electrolyte. The mechanism predicts that the substrate should undergo hydrogen–deuterium exchange at the position of proton loss from the radical cation $\text{FHH}^{\cdot+}$, *i.e.*, the benzylic 9-position.

RESULTS AND DISCUSSION

Oxidation of fluorene in 1 M sodium acetate–acetic acid. Cyclic voltammetry at a platinum bead electrode gave an irreversible wave with a peak potential of +1.70 V *vs.* s.c.e.. Comparison of the peak height with that of ferrocene suggested that the process was a two-electron oxidation. However, caution should be exercised when comparing such dissimilar electrode processes. Further electro-analytical investigation in this medium was not attempted and preparative scale electrolyses with subsequent product determination were used in this study.

FDD was oxidized at both constant potential (+1.7 V *vs.* s.c.e.) and constant current (5 mA cm^{-2}). Table 1 gives some typical examples of the product distribution. Concentrations from 7 to 200 mM

were employed. The product distribution appears to be independent of concentration, current density and whether constant current or controlled potential conditions were used. The mixture was worked-up and analyzed by GLC/MS and ^1H NMR spectroscopy. Note that when the internal standard was added directly to the crude electrolyte, GLC analysis gave yields identical to those determined by addition of the standard to the ethereal extract of the electrolyte. Thus, it is ascertained that none of the products listed in Table 1 are lost in the work-up procedure.

It was thought possible that dimeric products could be formed from either the relatively stable fluorenyl radicals or the cation radicals. Dimerization of fluorenyl radicals has been reported,³ albeit in non-nucleophilic media. However, the medium used here is too nucleophilic to allow formation of 9,9'-bifluorenyl or other dimeric products. Oxidation of fluorene to fluorenone was also considered a possibility and small amounts of fluorenone were indeed found in the product mixture. The major products detected were nuclear and, to a lesser extent, side-chain acetates, the identities of which were confirmed by ^1H NMR, comparison of their retention times with authentic samples and GLC/MS (the latter of which distinguishes between nuclear and side-chain acetates when the substrate is FDD but not FHH). The exact identity of the isomer(s) "1,3,4-acetoxyfluorene" is not known. The ratio of nuclear to side-chain acetoxylation is high, as previously reported.¹

We also note, as before,¹ that the total current yield of identified products is low, around 20 %,

Table 1. Typical product distributions from the anodic oxidation of fluorene^a (FHH or FDD).

Substrate (conc./mM)	Electrolyte	Charge passed/F mol^{-1}	Recovered fluorene/%	Yield/% ^h				Material not accounted for/%
				F=O	9-OAc	2-OAc	1,3,4-OAc	
FDD (200) ^b	$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$	2.0	69 ^f	≈0.1	0.2	16	1.9	12.8
FDD (94) ^c	$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$	2.0	64 ^g	0.6	0.2	17	2.0	16.2
FHH (8.2) ^c	$\text{CD}_3\text{COOD}/\text{CD}_3\text{COONa}$	1.0	73 ^g	6.0	0.5	5.9	0.6	14.0
FHH (7.0) ^{c,e}	$\text{CD}_3\text{COOD}/\text{CD}_3\text{COONa}$	1.0	73 ^g	6.8	1.6	3.4	—	15.2
FDD (38) ^d	$\text{CH}_3\text{COOD}/\text{Bu}_4\text{NBF}_4$	2.0	77 ^g	—	—	—	—	23
FHH (36) ^d	$\text{CD}_3\text{COOD}/\text{Bu}_4\text{NBF}_4$	2.0	67 ^f	4.8	0.9	2.9	—	24.4

^a Undivided cell, Pt electrodes (1 cm^2 each). ^b Constant current electrolysis (c.c.e.) at 5 mA cm^{-2} . ^c C.p.e. at 1.7 V *vs.* s.c.e. ^d C.c.e. at 0.5 mA cm^{-2} . ^e Divided cell. ^f Yield determined by analysis of the ethereal extract of the electrolyte. ^g Yield determined by analysis of the crude electrolyte. ^h F=O is fluorenone, 9-OAc is 9-acetoxyfluorene, *etc.* Yields are based on the amount of starting fluorene.

which now at least partly can be ascribed to the fact that *ca.* 15 % of the starting material cannot be accounted for in the analysis. Isotope analysis of the recovered fluorene (GLC/MS and ^1H NMR) showed that no H–D exchange had occurred, even in experiments in which charges up to 8 F mol^{-1} has been passed through the electrolyte. Thus the cyclic mechanism proposed earlier¹ (Scheme 2) is refuted. This mechanism in principle can only account for low current yields (*i.e.* inefficient oxidation) but of course not for missing material. Oxidation of FDD in a divided cell gave results virtually identical to those discussed above where an undivided cell was used. Thus the possibility of some cathodic mechanism being responsible for the lost material is excluded.

Nondeuterated fluorene, FHH, was also oxidized in $1\text{ M NaOOCd}_3\text{–CD}_3\text{COOD}$ (Table 1). Product analysis again confirmed that no H–D exchange had occurred and the yields of the products were similar to those from the oxidation of FDD in nondeuterated medium. Due to the weaker C–H bond at the side-chain position, it was expected that higher yields of fluorenone and 9-acetoxyfluorene would be found and this is in fact observed (see Table 1).

Oxidation of fluorene in 0.1 M Bu₄NBF₄-acetic acid. FDD was oxidized at both constant current (current densities from 0.3 to 10 mA cm^{-2}) and controlled potential (initially $+1.6\text{ V}$, then $+1.8\text{ V vs. s.c.e.}$) until 2 F mol^{-1} had been passed. In every case the anode became coated with a black film. In the controlled potential experiments this resulted in a rapid initial decrease in current and continual switching of the potentials of the counter and working electrodes only partly alleviated this problem. Removal and cleaning of the anode temporarily restored the current to its original value. Concentrations of FDD ranging from 20 to 170 mM were used. In every case GLC/MS and ^1H NMR examination of the electrolysis product showed that the isotopic composition of the fluorene was unchanged, no FDH or FHH being present. The ^1H NMR analysis gave a "clean" spectrum of FDD with no other signals present. No acetates, fluorenone, bifluorenyl or bifluorenylidene could be detected by GLC. However, only about 75 % of the substrate, FDD, was recovered at the end of the electrolysis. Control experiments in the absence of FDD showed that the blackening and associated anode passivation only occurred when FDD was present. We believe that this film

may be either the results of polymerization of a fluorene radical species (FDD $^{\cdot+}$ or FD $^{\cdot}$) or of attack of such a species on the substrate and/or supporting electrolyte and that the formation of the film probably accounts for the missing material.

Oxidation of FHH at constant current in $0.1\text{ M Bu}_4\text{NBF}_4\text{–CD}_3\text{COOD}$ gave similar results (*i.e.*, no H–D exchange). However, fluorenone, 9-acetoxyfluorene and 2-acetoxyfluorene were formed in low yields (Table 1). That neither fluorenone nor 9-acetoxyfluorene were detected when FDD was oxidized can presumably be attributed to the stronger C–D bond at the 9-position.

Further evidence of electrode passivation was supplied by cyclic voltammetry of fluorene ($4.5 \times 10^{-3}\text{ M}$) in $0.1\text{ M Bu}_4\text{NBF}_4\text{–acetic acid}$ at a platinum bead electrode. An irreversible peak with a peak potential of $+1.61\text{ V vs. s.c.e.}$ was observed. Repetitive cycling of the electrode potential resulted in a markedly greater than normal drop in peak current, shifting of the peak to less anodic potentials and a crossing-over of the anodic and cathodic branches at $+2.0\text{ V vs. s.c.e.}$. Furthermore, subsequent stirring of the solution and resweeping did not fully restore the peak current to the original value. Removal and cleaning of the electrode did however accomplish this. No such effects were observed in sodium acetate–acetic acid solutions. The peak height was virtually the same as that for the same concentration of fluorene in $1\text{ M NaOAc–acetic acid}$.

From the above-mentioned results we conclude that the cyclic mechanism proposed earlier¹ (Scheme 2) to account for the low current yields of acetates is incorrect. One can support this conclusion by an estimate of the energy of activation for hydrogen abstraction by FH $^{\cdot}$ on a C–H bond of acetic acid. Using the benzyl radical as a model for FH $^{\cdot}$ (necessitated by the lack of data for the FH $^{\cdot}$ system) the bond energy–bond order (BEBO)⁴ and equibonding⁵ method both give $E_a = ca. 20\text{ kcal mol}^{-1}$ for attack on H–CH₂COOH.⁶ To compare, the much more reactive methyl radical has an experimental E_a of $10.2\text{ kcal mol}^{-1}$ for the same process,⁷ and it is known that anodically generated methyl radical just barely can effect hydrogen abstraction from H–CH₂COOH.⁸

In $\text{Bu}_4\text{NBF}_4\text{-acetic acid}$ media electrode passivation occurs and the oxidation is inhibited. It is probable that the film formation accounts for part or all of the lost fluorene in this medium. In $\text{NaOAc-acetic solutions}$ nuclear acetoxylation is favoured

with platinum electrodes (1 cm²) at room temperature. At the end of the electrolysis the electrolyte was slowly pipetted into a separating funnel containing saturated sodium bicarbonate solution and diethyl ether. The aqueous phase was extracted with two more portions of ether and the combined ethereal extracts were then washed with saturated sodium bicarbonate solution and water (twice). Drying (anhydrous sodium sulfate) and concentration gave a solution suitable for analysis by GLC (2 m × 0.3 mm 5% neopentylglycol succinate on Chromosorb W at 210 °C with pentamethylbenzyl acetate as an internal standard). Isotopic analyses were carried out by GLC/MS. Subsequently the solvent was removed and the residue examined by both ¹H NMR and MS. The yields of fluorene and the acetoxyfluorenes, as determined by ¹H NMR were in agreement with those found by GLC. Note that the GLC/MS method was capable of distinguishing between nuclear and side-chain acetates when the substrate was the dideuterio form, FDD. The identities of all peaks observed on analysis by GLC were confirmed by GLC/MS and comparison of their retention times with authentic samples. The absence (less than 0.1%) of bifluorenyl and bifluorenylidene was confirmed by GLC (3% OV1 on Chromosorb W at 270 °C). The efficiency of the extraction procedure was determined by extraction of three samples of fluorene in 0.1 M Bu₄NBF₄ – acetic acid. GLC analysis gave an average “yield” of 102%. In addition analysis of various electrolysis products before and after extraction gave virtually identical results.

A few experiments were carried out in a divided cell with a platinum foil anode (1 cm²) and a working compartment containing 15 cm³ of solution. The work-up and analysis procedure was identical to that described above. Analysis of the catholyte showed that virtually no diffusion of the substrate into the cathode compartment had occurred.

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