

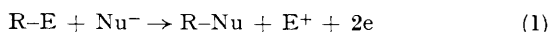
A Novel Anodic Substitution Reaction: Oxidative Displacement of Fluorine by an Acetoxy Group

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Summary Anodic oxidation of 2- and 4-fluoroanisole in a potassium acetate-acetic acid solution produces 2- and 4-acetoxyanisole, respectively, *via* a non-conventional reaction path.

ANODIC substitution reactions are commonly represented by equation (1)



where Nu^- is the nucleophile, and E^+ the electrophile, generally a proton or an alkoxonium ion.¹ Almost all examples of this reaction are classified as *ECEC* reactions (*E*: electron transfer step, *C*: chemical step).¹

We now report a novel anodic substitution reaction, unusual from the mechanistic point of view. When 4-fluoroanisole (**1**) was oxidized at a controlled anode potential (1.5 V *vs.* S.C.E.) at a Pt anode in an undivided cell in 0.5M KOAc-HOAc the major product was 4-acetoxyanisole (**2**)† and only traces of the expected substitution products (2- and/or 3-acetoxy-4-fluoroanisole) were observed. No reaction took place in the absence of current. A high current yield of (**2**) was obtained at low conversion (70–80%

based on a one-electron process when <0.5 F mol⁻¹ of substrate had passed). The yield gradually decreased on prolonged electrolysis (40% after a passage of 1 F mol⁻¹), probably owing to further oxidation of (**2**).‡ Coulometry at constant potential gave an *n* value of 1. On single sweep voltammetry an *n* value of 2 was calculated.§ Anodic oxidation of (**1**) in the absence of acetate ion ($\text{Bu}_4\text{NBF}_4\text{-HOAc}$) produced neither (**2**) nor any other aryl acetates.² 2-Fluoroanisole behaved similarly on anodic oxidation in 0.5M KOAc-HOAc yielding 2-acetoxyanisole. On the other hand anodic oxidation of 3-fluoroanisole, 4-bromoanisole, and 4-chloroanisole, respectively, in the same medium yielded normal substitution products (displacement of hydrogen by an acetoxy group) and only traces of acetoxyanisoles were detected.

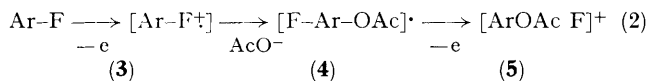
Our observation that a 2- or 4-fluorosubstituent in anisole changes the usual product pattern in anodic acetoxylation is not consistent with the common *ECEC* reaction sequence in anodic substitution, since this would require a loss of F^+ from (**5**) in equation (2); that is extremely unlikely from an energetic point of view. A reaction mechanism must take into account the fact that 4-bromo- and 4-chloro-anisole yield normal substitution products.

† All products were satisfactorily identified by comparison with authentic samples or by spectroscopic methods.

‡ The voltammetric peak potential of (**2**) is *ca.* 0.1 V lower than that of (**1**).

§ This value was determined in MeCN-HOAc (4:1) containing 0.17M NaOAc and 0.07M LiClO₄.

A reaction path involving a loss of fluorine radicals from either (3) or (4) [reactions (2)—(4)]



Ar = 2- or 4-anisyl



(yielding HF by hydrogen abstraction from a surrounding molecule or ion) might be energetically feasible, since the heat of formation of HF in a homolytic reaction is considerably higher than that of either HCl or HBr. However, several observations contradict such a radical pathway. A loss of a fluorine radical from (3) would yield an anisyl

¶ It has been shown that acetoxy radicals are not intermediates in the formation of acetoxyaromatic compounds during the electrolysis of a mixture of acetate ion and an aromatic compound in acetic acid.

¹ For a review, see: L. Ebersson and K. Nyberg, *Adv. Phys. Org. Chem.*, 1976, **12**, 1.

² L. Ebersson, *J. Amer. Chem. Soc.*, 1976, **99**, 4669; Traces of biaryl derivatives were detected. The major products are probably oligomers and polymers, *cf.* ref. 2.

³ For a review, see: L. Ebersson and K. Nyberg, *Accounts Chem. Res.*, 1973, **6**, 106.

⁴ J. Emsley, *J. Chem. Soc. (A)*, 1971, 2511.

cation that should yield (2) independently of acetate ions. The result obtained from the oxidation of (1) in the absence of acetate ions is inconsistent with that. A loss of a fluorine radical from (4) would yield (2). However, the voltammetric *n* value of 2 is not consistent with such a reaction path. We have not been able to detect any products resulting from radical reactions.^{3¶}

We are left with the assumption that at some intermediary stage in the formation of (2) a fluoride ion is lost as shown in equations (3) and (4). This idea seems attractive since the fluoride ion (as in KF) is strongly solvated in acetic acid.⁴ The different *n* values obtained by coulometry and voltammetry give an indication that an intermediate (formed after two *E* steps), *e.g.* (6), is oxidizing the starting material.

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