Characterisation of Free-radical Intermediates in the Oxidation of Aromatic Compounds by Ruthenium Tetroxide

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Summary Free radicals participate in the reactions of ruthenium tetroxide with chlorophenols and arylfurans, as shown by the capture of solvent fragments during product formation and the e.s.r. spectra of the more stable intermediates.

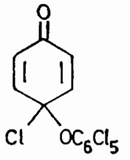
THERE is increasing interest in synthetic applications of ruthenium tetroxide but few studies of the mechanism of these oxidations have been made, and although evidence of free-radical participation has been sought[1] none has been obtained hitherto.

We noticed that exothermicity and an induction period characterise the reactions of RuO_4 with phenyl ethers[2] and many other aromatic compounds. These indications of radical participation were confirmed by a study of the oxidation of 2,6-dichlorophenol, where the intermediate is stabilised by the nature and position of the substituents. In aqueous solution 2,6-dichlorobenzoquinone was formed in 60% yield from sodium 2,6-dichlorophenoxide, but in acetone solution the only isolable product (20% yield) was 3,3',5,5'-tetrachloro-4,4'-dihydroxybiphenyl.[3] The change in the course of reaction is probably the result of clustering of the sodium salt in the less polar solvent,[4] which evidently favours a pairing of 2,6-dichlorophenoxyl radicals and coupling at the *para*-position.

The e.s.r. spectrum of the radical was obtained after the addition of the sodium dichlorophenoxide in acetone to RuO_4 (0·5 equiv.) in CCl_4 and rapid filtration from precipitated ruthenium dioxide. The *g* value of 2·00605 is as previously reported[5] and typical coupling constants were obtained. The e.s.r. spectrum of the 2,5-dichlorophenoxyl radical was produced similarly and the dimeric reaction product[6] (**1**) formed by the action of RuO_4 on sodium pentachlorophenoxide provides additional evidence of a single-electron process.

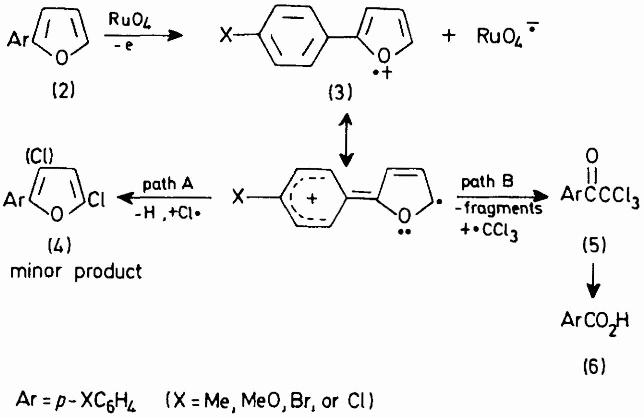
In view of the relationship with phenols and their ethers we also investigated the oxidation of furans and found that furan itself reacted very rapidly, but the stabilised 2-arylfurans afforded additional evidence of free-radical activity. π-Complexation was indicated by a broadening in the absorption maximum of the arylfuran [see Scheme, (**2**, X=Me), λ_{max} 287 nm] on addition of RuO_4 (0·5 equiv.)

and the n.m.r. spectrum (60 MHz) of the resulting purple intermediate showed peak broadening typical of a free radical. Furthermore the benzenoid proton signals were displaced downfield by *ca.* 50 Hz relative to the precuror and a broad e.s.r. signal was detected with g 2·0036. In view of these characteristics and its long life (2–3 days) this intermediate is probably the radical-cation (**3**, X = Me). It has been proposed[7] that the analagous thienyl radical-cation is formed during the oxidation of thiophen with dibenzoyl peroxide, which, like RuO_4, also depends for its effectiveness on the donation of a single electron to an electronegative acceptor. The reaction between dibenzoyl peroxide and 2,5-dimethylfuran has also been interpreted[8] in this way.



(1)

We have not attempted to characterise any intermediates in the oxidation of other arylfurans (**3**, X = MeO, Br, Cl) but the products of the reactions of these compounds are so similar to those formed from *p*-tolylfuran that a common mechanism is strongly indicated. Thus in all instances when reaction occurs in a two-phase system of CCl_4 (or $CHCl_3$) and aqueous hypochlorite the organic solvent participates by donating a chlorine atom (path A of Scheme) yielding the 2-chloro (40%) or 2,4-dichloro derivative (**4**) (5%) of the mesomeric furyl radical (**3** or the 2-chloro-radical). Alternatively (path B) the major product is a trichloromethyl ketone (**5**) (20% yield) obtained by fragmentation of the furan ring with capture of a trichloromethyl radical; on continued contact of the organic phase with the hypochlorite this substance undergoes the haloform reaction and the corresponding benzoate (**6**) (45% yield) accumulates in the aqueous layer.



Scheme. The progress of arylfuran oxidation by RuO_4 in hypochlorite–CCl_4 mixtures.

All the products (**4**), (**5**), and (**6**) have been characterised (for X = MeO, Me, Br, Cl) either by comparison with known compounds and/or by mass, n.m.r. and other spectral data. A proposed mechanism for the incorporation of the $\cdot CCl_3$ radical, based on the fragmentation of radical cations produced from furans in a mass spectrometer, will be published elsewhere. In the light of these findings a radical mechanism must be considered for other oxidations of organic compounds including aliphatic substrates.

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