

**Polarographic Reduction of
1,1'-Dimethyl-4,4'-oxybispyridinediium
Bis(fluorosulfonate)**

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Diquaternary Salt of 4,4'-Oxybispyridine,
Polarography

The diquaternary salt of 4,4'-oxybispyridine, 1,1'-dimethyl-4,4'-oxybispyridinediium bis(fluorosulfonate), is reduced polarographically by a one electron transfer not involving hydrogen to an unstable radical cation at a potential (E_0) of -0.80 V in the pH range 5.1–10.4.

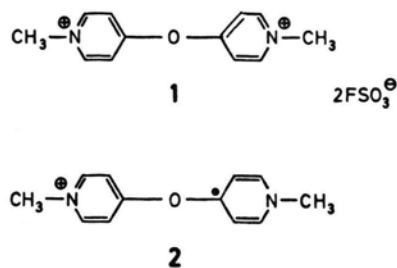
We have been interested in the past few years in the behaviour of diquaternary salts of oxybispyridines on polarographic reduction in aqueous solution in connection with our study of the relationship between chemical constitution and biological activity in bipyridinium herbicides [1, 2]. So far diquaternary salts of 2,2'-oxybispyridine [3] and 3,3'-oxybispyridine [4] have been studied. We now report the results of an extension of the investigation to a diquaternary salt of 4,4'-oxybispyridine.

4,4'-Oxybispyridine [5] was converted to the diquaternary salt, 1,1'-dimethyl-4,4'-oxybispyridinediium bis(fluorosulfonate) (**1**), by reaction with methyl fluorosulfonate in benzene. The salt **1** is stable in aqueous solution up to about pH 11.0 but above that pH value it rapidly decomposes.

The salt **1** was examined by polarography in the pH range 5.1–10.4. In this range it gave a typical symmetrical reduction wave, which corresponded approximately to the uptake of one electron, with half-wave reduction potential (E_0) of -0.80 V independent of pH and concentration. This is attributed to the formation of the radical cation of which **2** is one canonical form. This behaviour is analogous to that of many bipyridinium diquaternary salts [1] and to the reduction of diquaternary salts of 2,2'-oxybispyridine [3] and 3,3'-oxybispyridine [4]. The polarography of the salt **1** showed no evidence for the presence of a second reduction wave at lower potential. On NMR evidence it was clear that the salt **1** was slowly reduced in aqueous solution by zinc dust to products as yet unidentified presumably by way of the unstable radical cation **2**.

As expected in view of its very low reduction potential compared with the bipyridinium herbicides [1] diquat and paraquat which are reduced to

stable radical cations at a potential (E_0) of -0.35 V and -0.45 V respectively, the salt **1** was inactive as a post-emergent herbicide at 8 kg/hectare.



Experimental

Microanalyses were performed by the Australian Microanalytical Service. NMR spectra (60 M Hz) were determined for 10% w/v solutions using sodium 3-trimethylsilylpropane-1-sulfonate as the internal standard. The polarography experiments were carried out as described previously [6] except that the solutions contained 0.1% gelatine to suppress wave maxima.

1,1'-Dimethyl-4,4'-oxybispyridinediium Bis(fluorosulfonate)

4,4'-Oxybispyridine (0.2 g) was dissolved in dry benzene (4 ml). Methyl fluorosulfonate (0.2 ml) was then added dropwise. A white precipitate developed immediately. The reaction mixture was refluxed for 30 min and more methyl fluorosulfonate (0.2 ml) was added. Heating was continued for a further 30 min. The white solid was collected and recrystallised from methanol/water (9:1) to give the product, m.p. 140° (dec.) (Yield 20%).

$\text{C}_{12}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_7\text{S}_2 \cdot \text{H}_2\text{O}$

Calcd C 34.4 H 3.85 N 6.7,
Found C 34.6 H 3.9 N 6.8.

UV-spectrum (H_2O , pH 5.1): λ_{max} 255 (log ϵ 4.31) [nm].

NMR spectrum (D_2O): $\delta = 4.48$ (s, 6H, 1-Me, 1'-Me), 7.90–8.03 (d, 4H, 3,3', 5,5'), 8.95–9.08 (d, 4H, 2,2', 6,6') [ppm].

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