Cation–Radicals: Oxidation of Methoxide Ion with 1,1′-Dimethyl-4,4′-bipyridylium Dichloride (Paraquat Dichloride)

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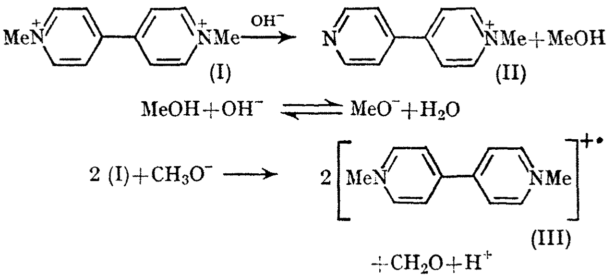
PYRIDINIUM AND BIPYRIDYLIUM ions readily undergo one-electron reduction to give stable free-radicals and cation radicals respectively.[1] The one-electron reduction[2] of 1,1′-dimethyl-4,4′-bipyridylium dichloride (paraquat dichloride) is of great interest because of the correlation between ease of reduction and herbicidal activity, in a range of bipyridylium salts.[3] Since the oxygen-sensitive cation–radical (III) produced by one-electron reduction of paraquat (I) has an intense blue colour paraquat salts have been used as oxidation–reduction indicators.[4] Treatment of 4,4′-bipyridylium salts with strong base also gives a blue colour and because of our interest in cation-radical chemistry[7] we have studied these reactions in some detail.

Under conditions of high-vacuum the reaction between sodium hydroxide and paraquat dichloride in water is highly reproducible With a 10-fold excess of alkali, the final yield† of cation-radical (based on paraquat) increased with temperature from 28% at 30° to a limiting maximum of 66% at *ca* 85° An identical limiting yield of cation-radical was observed when sodium hydroxide was replaced by sodium cyanide although the reaction times were longer. Other bases may also be used but at room temperature significant reaction does not occur below pH10.

After destruction of the cation radical by acidification and admission of air to the system, the reaction products were identified as paraquat dichloride and 1-methyl-4-(4-pyridyl)-pyridinium chloride (II) by paper chromatography. Formaldehyde and small amounts of formic acid were also identified by g.l.c. analysis. Paraquat (66%) was recovered directly and formaldehyde was further characterised by precipitation as the dimedone derivative, although the yield varied because of conversion into formate.

The following reaction sequence is suggested to explain these observations:



In this mechanism, the methanol required for reduction, is provided by initial dequaternisation of paraquat. Maximum yield of the cation-radical (III) would be 66% as observed experimentally. Presumably the less than theoretical yields observed at low temperatures represent inefficient dequaternisation.

The suggested mechanism was substantiated by addition of methanol to aqueous systems or by working in methanol solvent. In pure methanol at room temperature with excess alkali, the yield of (III) [based on (I)] was quantitative and with paraquat in excess, yields of (III) (based on OH^-) were never less than 90%.

Other alcohols with α-hydrogen atoms will also reduce paraquat in basic media and further evidence for the mechanism was provided by the observation that solutions of potassium t-butoxide in t-butyl alcohol do not reduce paraquat to the cation-radical. However on addition of

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† Typical reaction conditions were [paraquat dichloride] = 10^{-1}—10^{-3} M, [NaOH] = 5×10^{-1}—10^{-2} M. Reaction times for maximum yield varied from *ca.* 4 hr. at room temperature to a few minutes at 85°. The yield of cation radical was estimated from measurement of absorbance at 600 nm. (ϵ 1·2 × 10^4 l.mole^{-1} cm.$^{-1}$).

primary or secondary alcohols, reduction occurs immediately.

The oxidation of methoxide ion by the paraquat ion is essentially instantaneous in methanol or aqueous methanol when $[\mathrm{MeO}^-] \geqslant 0{\cdot}1$ M, and is in marked contrast to the more usual ring-substitution which occurs when pyridinium ions interact with bases.[8]

By analogy with the related de-diazoniation reactions,[9,10] it is probable that the actual electron transfer involves the following reactions:

$$\mathrm{(I)} + \mathrm{CH_3O^-} \rightarrow \mathrm{(III)} + {\cdot}\mathrm{CH_2{-}O^-} + \mathrm{H^+}$$

$$\mathrm{(I)} + {\cdot}\mathrm{CH_2{-}O^-} \rightarrow \mathrm{(III)} + \mathrm{CH_2O}$$

The base-induced reduction of 1,1′-dibenzyl-4,4′-bipyridylium dichloride (IV) is reported to involve initial removal of the benzylic proton followed by a complex series of reactions leading to the cation-radical, benzaldehyde, and 4,4′-bipyridyl.[6] Whilst it is possible that base-induced reduction of (IV) follows a reaction path different from that of (I), the correspondence between reaction products and the simplicity of the alkoxide-ion reduction argue strongly for the suggested electron-transfer process.

Apart from the de-nitrogenation reactions,[10] and the long-established reduction of nitrobenzene to azoxybenzene by refluxing alkaline methanol, the reducing potential of methoxide ion has been little used.‡ The efficiency and rate of the bipyridylium salt reductions suggests that there might be wider utilisation of methoxide ion as a reductant, and conceivably the alkoxide ion–pyridinium ion reaction may be relevant to the mechanism of NAD$^+$ reduction in biological systems.

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‡ For the reaction:

$$\mathrm{CH_2O}\ aq. + \mathrm{2H_2O}\ l. + 2e \rightleftharpoons \mathrm{CH_3OH}\ aq. + \mathrm{2OH^-}\ aq.$$

SEP (E^0) = $-0{\cdot}52$ v at 25° (An "introduction to Fuel Cells," ed. K. R. Williams, Elsevier, Amsterdam, 1966, p. 119).

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