Tetrabutylammonium Permanganate: an Efficient Oxidant for Organic Substrates

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Summary Tetrabutylammonium permanganate is an easily prepared crystalline stable compound soluble in organic solvents; its use for oxidations of organic substrates in pyridine under mild conditions is described.

POTASSIUM PERMANGANATE in aqueous solution is a commonly used oxidant in preparative organic chemistry.[1] Organic substrates are often poorly soluble in the reaction medium. The major disadvantage accompanying its use, however, is that permanganate is thermodynamically unstable with respect to water [reaction (1)]. The rate of this reaction is usually slow but it is catalysed by acids,

$$4MnO_4^- + 2H_2O \longrightarrow 4MnO_2 + 3O_2 + 4OH^- \qquad (1)$$

bases, and manganese dioxide. Since manganese dioxide is a product of permanganate oxidations of organic substrates the catalytic decomposition of the permanganate by the above pathway generally occurs. Potassium permanganate is therefore usually taken in large excess of the theoretical stoicheiometry required for the oxidation of the substrate, and yields are often low, probably owing to over-oxidation of the product.[1] The use of phase-transfer catalysts such as long-chain alkyl quaternary ammonium salts for potassium permanganate oxidations of organic substrates in water–benzene mixtures has been reported;[2] it still suffers from the same disadvantage. Dilute solutions of potassium permanganate (0·06 M) in benzene in the presence of an equimolar amount of dicyclohexyl-18-crown-6 are moderately stable ($t_{\frac{1}{2}}$ *ca.* 48 h at 25 °C).[3] Preparative oxidations of organic substrates in benzene using, for reasons of economy, a catalytic amount of the crown ether require the inconvenient technique of ball-milling the potassium permanganate with the solution. Yields, however, are excellent, and the oxidations, since water is absent, obey the stoicheiometry for the same oxidations in neutral aqueous solution.

We therefore sought a solution to the above disadvantages and have developed the use of tetrabutylammonium permanganate in pyridine† for this purpose. The reagent is easily and cheaply prepared in high yield by adding a slight excess of a concentrated aqueous solution of tetrabutylammonium bromide to a stirred aqueous solution of potassium permanganate. The crystalline precipitate is separated by filtration, washed with water, and dried *in vacuo*. This material may be stored for prolonged periods without decomposition, and the permanganate concentration may be easily determined, if desired, by redox titrimetry in acetone against standard aqueous acidic Fe^{II} solution. Analytically pure material may be obtained as glistening purple plates, m.p. 120—121 °C (decomp.) (block preheated to 115 °C), by crystallisation from dichloromethane–benzene. The ^1H n.m.r. spectrum is unexceptional, and the i.r. spectrum, like that of potassium permanganate,[4] exhibits a strong band at 900 cm^{-1}. The visible spectrum in pyridine, λ_{max} 474·5 (ϵ 720), 491 (1150), 509 (1800), 527·5 (2460), 549 (2430), and 572·5 (1380) nm, is very similar to that of aqueous potassium permanganate.[4] The salt is sparingly soluble in benzene, but easily soluble in polar solvents such as acetone, chloroform, and dichloromethane. It, however, slowly oxidises these solvents. It is very soluble in pyridine in which it is much more stable, and solutions as strong as 1·4 M may be obtained. The permanganate concentration of a 0·1 M solution in pyridine, determined spectrophotometrically, did not change during 30 h.

The yields obtained for the oxidation of a number of substrates by the dropwise addition of tetrabutylammonium permanganate in pyridine, as fast as it was consumed, to a stirred pyridine solution of the substrate at room temperature under dry nitrogen, are given in the Table. Work-up was conventional and involved pouring the reaction mixture into cold dilute hydrochloric acid containing sodium hydrogen sulphite. The stoicheiometry of these reactions appears to be the same as the theoretical stoicheiometry for the same reactions in water.

TABLE. Oxidations with tetrabutylammonium permanganate in pyridine at room temperature

Substrate	Product	Yield (%)	Permanganate: substrate ratio
m-Nitrobenzaldehyde	Acid	95	0·67 : 1
p-Chlorobenzaldehyde	Acid	99	0·67 : 1
4-Acetoxy-2-methoxy-benzaldehyde	Acid	85	0·67 : 1
Piperonal	Acid	99	0·67 : 1
p-Anisaldehyde	Acid	94	0·67 : 1
Benzyl alcohol	Acid	98	1·33 : 1
Benzhydrol	Benzophenone	97	0·67 : 1
cis-Stilbene	Acid	98	2·67 : 1
p-Nitrotoluene[a]	Acid	96	2·00 : 1

[a] At 65 °C (bath).

Tetrabutylammonium permanganate is therefore a valuable addition to the reagents available to the synthetic organic chemist.

We thank the Australian Research Grants Committee for financial support.

(*Received*, 12*th December* 1977; *Com.* 1255.)

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† Pyridine was stirred for 24 h with cerium(IV) sulphate and potassium carbonate, filtered, fractionated, and refractionated from potassium hydroxide on to 4 Å molecular sieves.

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