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Rapid Oxidation of Chondroitin Sulphates and other Glycols by Periodic Acid in Organic Solvents

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Oxidation of chondroitin sulphates, hyaluronate etc. by periodate in aqueous solution is slow but specific (Scott, 1968). Presumably periodate must interact with hydroxyl groups of the substrate, no matter what the detailed mechanism, and one would therefore expect that hydroxyl groups in the solvent would compete with oxidizable glycols for periodate, thus diminishing oxidation rates. Since hydroxylic solvents would also be expected to associate with hydroxyl groups of the substrate, this should also impede periodate-glycol interaction. On these arguments, water should be a particularly unfavourable solvent in which to use periodate as a glycol-splitting reagent. Using pinacol, a 'hindered' glycol that is slowly oxidized in water, we have investigated solvents in which the 'hydroxyl group concentration' is lowered or zero. Wherever possible, solvents were spectroscopic, A.R. or redistilled, as indicated. Consumption of periodate was followed at 222 nm.

Rates of oxidation were very greatly increased (several thousandfold) in dioxan (spectroscopic). Inclusion of as little as 10% (v/v) of water in the dioxan drastically lowered the oxidation rate. Propan-2-ol (A.R.) and 2-methylpropan-2-ol, with 'hindered' hydroxyl groups, were effective solvents, allowing several hundredfold increases in rate as compared with water. Trifluoroethanol (spectroscopic) and methoxyethanol (redistilled), in which electron-attracting groups are adjacent to the hydroxyl group, also permit rapid oxidation, in general agreement with the concept that hydroxyl groups with increased electron availability at the oxygen atom interact better with periodate (Buist, Bunton & Miles, 1957). The results suggest that an unhindered, highly basic, oxygen atom in the solvent molecule is associated with a low rate of oxidation by periodate, presumably because of possible hydrogen-bonding to the glycol, and strong periodate-oxygen atom interaction. Thus in both *NN*-dimethylformamide and dimethyl sulphoxide oxidation is slow, whereas in sulfolane (a poor hydrogen acceptor) (Parker, 1962) oxidation is quite rapid.

Whereas many hours' oxidation in aqueous solution are needed to produce sufficient aldehyde groups in chondroitin sulphate and other polyuronides (Scott, 1968), a strong Schiff reaction is given by oxidizing them on glass-fibre paper within 1 min in dioxan. Keratan sulphate and commercial heparin do not react, as would be expected from the formulae, and can thus be easily distinguished. It is possible that the very rapid oxidation observed in organic solvents may avoid the side reactions, e.g. overoxidation, and degradation that are a consequence of lengthy reaction times in aqueous solvents.

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