

Oxidation of Alcohols by Hydrogen Peroxide Using a new Catalyst

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ABSTRACT. A mixture of hydrogen peroxide and lead (II) nitrate in the acidic medium has been found to be a new oxidising reagent for various alcohols. Products of oxidation by this reagent have been identified.

Hydrogen peroxide is used as a common oxidising agent for inorganic as well as organic compounds. But the oxidation of organic compounds by hydrogen peroxide at ordinary temperatures is generally slow in the absence of a catalyst. However, in the well known Fenton's reagent, Fe(II) ion catalyses the oxidation of a variety of organic compounds by hydrogen peroxide (Fenton 1894, Merz and Waters 1949). The derivatives of various metals, e.g. Cr, Os, Rh, Ru, Se, Ta, Ti, U, V, W and Zr have been also used as catalyst (Allan 1964, Beg and Ahmad 1975) for the oxidation of unsaturated compounds by hydrogen peroxide.

We have already reported that Pb (II) ion also acts as a suitable catalyst for the deamination reaction by hydrogen peroxide (Ashraf *et al.* 1981). In order to extend the scope of this new catalyst, oxidation of various alcohols have been carried out by hydrogen peroxide using this catalyst, and are reported in this paper. In these oxidations, which were carried out in the acidic medium, lead (II) nitrate has been used as the catalyst and hydrogen peroxide as an oxidising agent. It may be pointed out that lead (II) nitrate or hydrogen peroxide when used alone, do not oxidise these compounds in the present conditions.

Experimental

A typical reaction mixture consisted of :

20 ml of 0.5 M organic substrate in water, 10 ml of 5.0 M hydrogen peroxide (prepared from 30% solution), 10 ml of 1.0 M perchloric acid (prepared from 60-62% solution), 10 ml of 0.1 M lead (II) nitrate aqueous solution and 50 ml of water.

Oxidation was achieved after heating at 70°C during 6 hr. The products obtained from different compounds along with the mode of their confirmation are summarised in Table 1.

The formation of formic acid in the relevant reaction mixture was tested by its reduction with a known procedure. The formaldehyde thus obtained was confirmed by chromotropic acid, which gave a violet pink colour (Eegriwe 1937). Its formation was further substantiated by reaction with mercuric chloride solution. The mercurous chloride produced was treated with ammonia, which yielded greyish-black colour (Hopton 1953). The organic reaction products were identified via

Table 1. Alcohols oxidised and products identified.

Alcohols oxidised	Products identified	Test or derivatives	% Yield of 2,4-DNP
Methanol	Formaldehyde	2,4-DNP	43
Ethanol	Acetaldehyde	2,4-DNP	54
<i>n</i> -Propanol	<i>n</i> -Propionaldehyde	2,4-DNP	59
<i>iso</i> -Propanol	Acetone	2,4-DNP, Indigo	63
<i>n</i> -Butanol	<i>n</i> -Butyraldehyde	2,4-DNP	58
<i>iso</i> -Butanol	<i>iso</i> -Butyraldehyde	2,4-DNP	70
<i>n</i> -Pentanol	<i>n</i> -Butyraldehyde	2,4-DNP	56
	Formic acid	Chromotropic acid test	—
<i>n</i> -Hexanol	<i>n</i> -Valeraldehyde	2,4-DNP	45
	Formic acid	Chromotropic acid test	—
3-Methyl-butan-2-ol	<i>iso</i> -Propylmethyl ketone	2,4-DNP	54
Butane-2,3-diol	Butane-2,3-dione	2,4-DNP*	61
Pinacol	Acetone	2,4-DNP, Indigo	53
Ethanediol	Hydroxyacetaldehyde (acyloin)	2,4-DNP	60
Cyclohexanol	Cyclohexanone	2,4-DNP	42

2,4-DNP = 2,4-Dinitrophenylhydrazine.

* mono- and di-.

comparison of the infrared spectra of the 2,4-dinitrophenylhydrazones with those of standard samples, obtained from known compounds. Their mixed melting points did not show any depression.

The carbonyl compounds were collected along with aqueous distillate from the reaction mixtures. The yield obtained in Table 1 are based on the amount of 2,4-dinitrophenylhydrazones obtained from the aqueous distillate of various carbonyl compounds. Majority of organic products were also confirmed by TLC of the aqueous distillate of the reaction mixtures.

Results

It is quite obvious, from Table 1, that monohydroxy alcohols upto *n*-butanol and even *iso*-butanol (a branched-chain primary alcohol) are oxidised to the corresponding aldehydes. However, *n*-pentanol and *n*-hexanol do not follow this pattern, and aldehydes having one carbon less than the expected aldehydes are obtained in these cases. Thus, when the chain length increases, the reagent tends to be destructive. From secondary alcohols, the corresponding ketones are obtained. The primary diol, ethanediol, yields the acyloin, when the tertiary diol, pinacol, is cleaved to acetone.

In analogy with the Fenton's reagent, the reaction with this new reagent appears to involve a free radical mechanism similar to our recently published work (Ashraf *et al.* 1980) since it polymerised acrylonitrile. However, the kinetics of oxidation of various organic compounds by this new system are currently underway, which may give a better understanding of the mechanism of the reaction and the reaction conditions. The future investigations also aim at more exhaustive treatment of the reaction including effect of pH, oxidation in the presence of other oxidisable groups, etc. This will enrich the range of experimental facts about the reaction and presumably help in tracing the mechanism of this reaction.

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