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Catalysis: Autoxidation in the Presence of Active Cobalt Oxide

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Summary An active oxide of cobalt is an effective autoxidation catalyst towards organic substrates.

HETEROGENEOUS oxidations of benzyl alcohol and related compounds occur with active oxides of manganese[1] and nickel[2] prepared by ozonisation. We have now found that a black oxide of cobalt prepared in a similar manner is a good autoxidation catalyst.

There are numerous examples[3–5] of cobalt salts acting as homogeneous oxidation catalysts. A recent patent[6] describes the oxidation of n-butanol to butyric acid with a mixture of sodium hypochlorite, sodium hydroxide, and cobalt(II) chloride. The patent describes the substitution of a cobalt oxide, prepared by the reaction of cobalt(II) chloride and sodium hypochlorite, for cobalt(II) chloride in the procedure, presumably, leading to a heterogeneous reaction. The black cobalt oxide, prepared by ozonisation, when used with oxygen and an aprotic solvent behaves as manganese dioxide and nickel peroxide in the oxidation of benzylic alcohols, active methylene groups, aniline, and benzylamine. All substrates gave the expected products except 2-phenylethanol from which benzaldehyde was obtained. This last reaction involved carbon to carbon bond cleavage which may have proceeded *via* abstraction

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TABLE 1

Reactant	Ratio catalyst : substrate	Time (h)	Product	Yield (%)
Benzyl alcohol	7 : 1	0·5	Benzaldehyde	81[a]
			Benzoic acid	3
Cinnamyl alcohol	2 : 1	0·5	Cinnamaldehyde	94[a]
2-Phenylethanol	10 : 1	6·0	Benzaldehyde	68[a]
Diphenylmethanol	7 : 1	0·5	Benzophenone	91[a]
Fluorene	1 : 1	1·5	Fluorenone	99
Diphenylmethane	6 : 1	6·0	Benzophenone	99[a]
4-Methylcyclohexanol	10 : 1	6·0	4-Methylcyclohexanone	10[b]
Aniline	7 : 1	6·0	Azobenzene	62
Benzylamine	7 : 1	0·5	Benzonitrile	85

[a] Determined as 2,4-dinitrophenylhydrazone. [b] Determined by g.l.c.

of a benzylic hydrogen or a terminal hydrogen atom followed by rearrangement in a similar manner to that postulated for the oxidation of carboxylic acids with cobalt(III) perchlorate.[7]

All reactions reported in Table 1 were conducted in dry benzene at 80° and oxygen was passed through at a rate of approximately 45 cm³/min. The concentration of substrate in all cases was about 200 mg in 30 cm³ of dry benzene.

Benzyl alcohol was studied at various catalyst : substrate ratios with and without added oxygen. It is seen in Table 2 that yields were significantly lower when oxygen was not added, and no improvement was observed with increased catalyst ratio.

The cobalt oxide was prepared by addition of 7N-sodium hydroxide (200 cm³) dropwise during 4 h to a stirred solution of cobalt(II) sulphate heptahydrate (281 g) in water (1·2 l) while an ozone–oxygen mixture was passed through the solution for 20 h at room temperature. The black oxide was washed well with water and dried over anhydrous calcium chloride at reduced pressure.

TABLE 2

Oxidation of benzyl alcohol

Ratio catalyst : substrate	Yield (%)[a] Atmosphere	Oxygen added
1 : 1	9	34
3 : 1	14	50
5 : 1	12	76
7 : 1	12	85

[a] Determined by g.l.c.

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