Homogeneous Catalytic Oxidation of Amines and Secondary Alcohols by Molecular Oxygen

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Summary Ruthenium trichloride catalyses the homogeneous oxidation of secondary alcohols to ketones, primary amines to nitriles, and 2-aminoalkanes to imines by O_2; this is the first example of a homogeneous catalytic oxidation of an amino-group.

Recent studies suggest that ruthenium complexes should be suitable as catalysts for the oxidation of amines and alcohols by molecular oxygen.[1–4] We have now discovered that hydrated $RuCl_3$ does indeed catalyse these oxidations at *ca.* 100 °C and oxygen pressures of 2—3 atm. This finding represents the first example of a homogeneous catalytic oxidation of amino-groups by molecular oxygen.

In a typical procedure,† the catalyst (0·1 mmol), solvent (toluene; *ca.* 4 ml), and substrate (*ca.* 10 mmol) were placed in a Fisher–Porter glass pressure reactor. The contents were frozen, evacuated, pressurized with O_2 (*ca.* 35 lb in^{-2}), and stirred in an oil bath at 100 °C. The reaction mixture was analysed by gas chromatography using internal standards. The product assignments were confirmed by gas chromatography–mass spectrometry and, in some cases, by i.r. and n.m.r. spectroscopy as well. Some of the results are summarized in the Table.

The oxidation of benzylamine results in the formation of benzonitrile and benzamide (product of nitrile hydrolysis) in 86% yield. No benzoic acid was detected.‡ Analogous products, though in lower yields, were observed in the oxidation of n-butylamine. The oxidation of 2-aminoalkanes affords ketones (products of imine hydrolysis), *N*-alkylimines (condensation products of the ketone and starting amine), and high boiling materials which were not characterized. Note that higher selectivity is found at <100 °C and conversions below 30% (compare examples 3 and 4 of Table) owing to the increased stability of the products.

For the oxidation of secondary alcohols $RuCl_3$ seems to be a selective catalyst, affording moderate yields of the corresponding ketones (Table). Formation of olefins can be substantially curbed by the addition of water (compare examples 6 and 7 of Table). Under similar conditions RuO_2, $RhCl_3$, $Rh_2(OAc)_4$, and IrO_2 proved to be only very poor catalysts while $CuCl_2$ and $Cu(OAc)_2$ yielded no ketone whatsoever.

In both the amine and alcohol oxidations, formation of metallic Ru from $RuCl_3$ is not apparent in contrast to $RhCl_3$-catalysed reactions where metal particles and metal mirrors are clearly visible. An excess of free radical inhibitor (*e.g.*, 2,6-di-t-butyl-4-methylphenol) does not affect the course of the oxidation and, in the absence of catalyst, little if any oxidation is observed.

Two reaction mechanisms may be considered. Ruthenium(III) amide complexes (formed from $RuCl_3$ and amine[5]) may undergo β-hydride elimination to ruthenium(III) hydride complexes and the imine.[4] Oxidation of this hydride by molecular oxygen to regenerate $RuCl_3$ and water is presumed to involve peroxides as intermediates.[6] A second path may involve a reaction of the ruthenium(III) hydride complex formed as above with a molecule of a ruthenium(III) amine complex to form two molecules of the ruthenium(II) amine complex. These species are known to be oxidized by molecular oxygen to ruthenium(II) imines.[2] The competition between the ruthenium(III) amine complex and molecular oxygen for the ruthenium(III) hydride will then determine which of these two reaction paths will predominate.

Table. Oxidation of amines and secondary alcohols by molecular oxygen[a]

Example	Substrate (mmol)	Time/h	Conversion %	Products (mmol; selectivity %)
1	Benzylamine (11·7)	24	100	Benzonitrile (6·2; 53) Benzamide (3·5; 30)
2	n-Butylamine (10·3)	7·5	92	Butyronitrile (2·2; 23) Butyramide (0·1; 1)
3	2-Aminohexane (12.3)	20	70	Hexan-2-one (2·2; 19) Imine[b] (0·7; 8)
4	2-Aminohexane (9·2)	26	14[c]	Hexan-2-one (0·5; 39) Imine[b] (0·4; 31)
5	Octan-2-ol (10·0)	100	63	Octan-2-one (4·4; 70)
6	Cyclohexanol (9·8)	95	92	Cyclohexanone (2·0; 21) Cyclohexene (5·6; 57)
7	Cyclohexanol (9·5) and water (21)	95	36	Cyclohexanone (2·6; 76) Cyclohexene (0·2; 6)

[a] Unless otherwise noted, see text for conditions. [b] Imine = 2-[methyl(pentyl)imino]hexane. [c] At 60 °C.

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† No attempt has been made to optimize the reaction conditions.

‡ The products were transferred *in vacuo*, sublimed, and then identified.

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