Homogeneous Catalytic Oxidation of Secondary Alcohols to Ketones by Molecular Oxygen under Mild Conditions

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Summary $PdCl_2$–NaOAc catalyses the homogeneous oxidation of secondary alcohols to ketones by O_2 at room temperature.

TRANSITION metal complexes have been shown to be effective as catalysts for the selective oxidation of organic substrates in combination with oxidizing agents such as hydroperoxides[1] or amine oxides.[2] While such procedures are of obvious utility, they do require the consumption of expensive organic oxidants. Clearly the ability to use molecular oxygen in a procedure which selectively oxidizes organic compounds under mild conditions would be of greater desirability, and the search for catalytic systems which will indeed perform such oxidations is broadly based. We now report our results involving one such O_2-based catalytic oxidation procedure: secondary alcohols can be oxidized to ketones, homogeneously, by O_2 under mild conditions and in high yield in the presence of $PdCl_2$–NaOAc. Whereas it has been previously reported[3] that $PdCl_2$ in the presence of a Cu^{II} salt will catalyse the oxidation of alcohols at elevated temperatures (70—120 °C) and under O_2 pressure (3 atm), we find that this transformation can be accomplished easily in the absence of a Cu^{II} salt† at or near ambient temperatures and at 1 atm O_2 pressure.

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† In fact, oxidation of the alcohol is retarded by the presence of Cu^{II} salts; Cu^{II} slowly precipitates as a blue-green material (probably a basic oxide).

Results for several substrate alcohols obtained under similar conditions are given in the Table.‡ In a typical procedure, a yellow–orange solution of $PdCl_2$ (0·170 mmol), NaOAc (8·5 mmol) and *trans*-3,3,5-trimethylcyclohexanol (17 mmol) was stirred in ethylene carbonate (18 ml) at 38 °C)§ in a flask attached to a gas burette filled with O_2 at 1 atm. The reaction was monitored by measuring the O_2 uptake and by quantitative v.p.c. analysis. In this way the stoicheiometry and yield of the reaction were determined as shown in the Table.

Table

$$R^1R^2CHOH + \tfrac{1}{2} O_2 \xrightarrow[38\,^{\circ}C]{PdCl_2\text{–}NaOAc} R^1R^2C{=}O + H_2O$$

Alcohol	% Yield (h)
Propan-2-ol	76(56); 92(100)
Octan-2-ol	76(36); 86(133)
Cyclohexanol	88(56)
trans-4-t-Butylcyclohexanol	83(49); 91(79)
cis-4-t-Butylcyclohexanol	76(54); 85(98)
trans-3,3,5-Trimethylcyclohexanol	94(34); 98(54)
cis-3,3,5-Trimethylcyclohexanol	85(49)
Cyclobutanol	62(36); 96(129)
Cyclopentanol	78(36); 98(100)
Cycloheptanol	76(36); 96(128)
Cyclo-octanol	68(34); 89(103)
p-Menth-8-en-3-ol[a]	0(72)
[Benzyl alcohol]	[89(51)]

[a] See ‡ footnote

The following variety of complexes was examined for potential activity under the conditions described above but these were found to be of no use for alcohol oxidation: Pd black, $(NH_3)_2PdCl_2$, $(PPh_3)_2PdCl_2$, $Pd(OAc)_2$, $PtCl_2$, $FeCl_3$, $RuCl_3$, and $RhCl_3$. The complex Na_2PdCl_4 is an inefficient catalyst; Na_2IrCl_6 or $IrCl_3$ yield only a stoicheiometric amount of ketone as does $PdCl_2$–NaOAc under argon. $PdCl_2$ in the absence of acetate also gives practically no ketone. Catalytic oxidations may be performed using $PdCl_2$–NaOAc in other solvents of low co-ordinating ability and moderate dielectric constant, such as sulpholan or acetone (at room temperature). Although H_2O is produced in an equimolar amount with alcohol consumed, it is not useful as a solvent; in fact, excess of water inhibits catalysis.

A possible mechanism for this catalytic cycle involves complexation of the alcohol to Pd^{II} and then deprotonation of co-ordinated ROH¶ to give a Pd^{II}-alkoxide. This is followed by a β-hydride transfer from C to Pd to yield the ketone and a Pd^{II}-hydride complex,[4] which is then oxidized by O_2 to give H_2O and an active Pd^{II} species.[5] The rate of oxidation of a given alcohol is not enhanced by increased O_2 pressure.** It is likely that, in this series of reactions, β-H transfer from C to Pd is rate determining. Also, it is interesting to note the parallel between this sequence and the catalytic oxidation of alcohols by $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ (with concomitant consumption of acid)[6] or stoicheiometrically by chromate complexes.[7–9] β-Hydride transfer from carbon to the metal atom is implicated in the Pd and Ru systems; it may be involved in chromate oxidations as well.[9]

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‡ Olefins or unhindered amines poison the catalyst by strong complexation.

§ M. p. 35—37 °C; admixing 30% acetone enables the reaction to be performed at room temperature.

¶ Acetate is not basic enough to deprotonate an uncomplexed aliphatic alcohol to any substantial degree; complexation of the alcohol with a Lewis acid such as Pd^{II} should enhance its acidity.

** We have observed up to 100 turnovers of catalyst. Under 1 atm of oxygen pressure, Pd metal eventually precipitates; under 3 atm of O_2 pressure, however, no precipitation of Pd metal occurs.

[1] K. B. Sharpless and R. C. Michaelson, *J. Amer. Chem. Soc.*, 1973, **95**, 6136, and refs. cited therein.

[2] K. B. Sharpless, K. Akashi, and K. Oshima, *Tetrahedron Letters*, 1976, 2503.

[3] W. G. Lloyd, *J. Org. Chem.*, 1967, **32**, 2816.

[4] This reaction is known for several group VIII metals including Pd^{II}: J. V. Kingston and G. R. Scollary, *Chem. Comm.*, 1969, 455; L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 4989.

[5] For example, see H. L. Roberts and W. R. Symes, *J. Chem. Soc.* (*A*), 1968, 1450.

[6] A. Dobson and S. D. Robinson, *J. Organometallic Chem.*, 1975, **87**, C52; *Inorg. Chem.*, 1977, **16**, 137.

[7] J.-C. Richer and C. Gilardear, *Canad. J. Chem.*, 1965, **43**, 538; J.-C. Richer and N. T. T. Hoa, *Canad. J. Chem.*, 1969, **47**, 2479.

[8] H. G. Kuivila and W. J. Becker, *J. Amer. Chem. Soc.*, 1952, **74**, 5329.

[9] A rate-determining step involving intramolecular transfer of hydride to an oxygen atom in chromate oxidation of alcohols has been proposed: H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.*, 1959, **81**, 2116 and refs. cited therein.