A New Epoxidation Catalyst: the Reactivity and X-Ray Crystal Structure of $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ (bipy = 2,2′-bipyridine)

Alan J. Bailey, William P. Griffith,* Andrew J. P. White and David J. Williams*

Inorganic and Chemical Crystallographic Research Laboratories, Department of Chemistry, Imperial College of Science, Technology and Medicine, London UK SW7 2AY

The crystal structure of $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ **1** is reported: with $NaIO_4$ or $NBu^n{}_4IO_4$ as cooxidant it is an efficient catalyst for alkene epoxidations under mild conditions; it also oxidises primary alcohols to aldehydes and secondary alcohols to ketones.

Currently there is much interest in both the homogeneous transition metal-catalysed epoxidation of alkenes[1] and in the use of oxoruthenium complexes as catalysts for organic oxidations.[2] Few ruthenium epoxidation catalysts have been identified, the most effective to date being the $RuCl_3$–bipy–IO_4^- (bipy = 2,2′-bipyridine) reagent of Balavoine and coworkers[3] but for which nothing is known as to the nature of the catalytic species involved. During investigation of this latter system and variations thereof we have synthesised $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$ **1**, which proves to be an even more effective epoxidation catalyst. Furthermore it is the first example of a complex containing the coordinated $[IO_3(OH)_3]^{2-}$ ligand. It is also a rare example of a complex in which both the metal *and* ligand centres have oxidative functions[4,5] and the first example in which alkenes are epoxidised in such a fashion.

Orange-yellow crystals of **1** were obtained by the addition of ruthenium tetraoxide (in aqueous sodium periodate) to an acetone–water (1 : 1) solution of 2,2′-bipyridine.† The X-ray crystal structure,‡ Fig. 1, which contains two crystallographically independent molecules, shows that in both molecules the ruthenium and iodine centres have distorted octahedral geometries with angles at the ruthenium and iodine ions in the ranges 78–104 and 167–178° and 81–96 and 170–176° respectively. The deviations from ideal octahedral geometries are caused by the bite of the bipyridine and periodate ligands. The ruthenium(VI) dioxo 'ruthenyl' units have the expected *trans* configuration [Ru–O(oxo) 1.727 Å]§ but with a noticeable distortion from linearity [O(1)–Ru–O(2) 167.5°]; we have noted similar bending in the ruthenyl unit in $[Ru_2O_6(py)_4]$.[6] There is also a small deformation in the O(axial)–I–O(axial) units [O(5)–I–O(6) 174.1°].

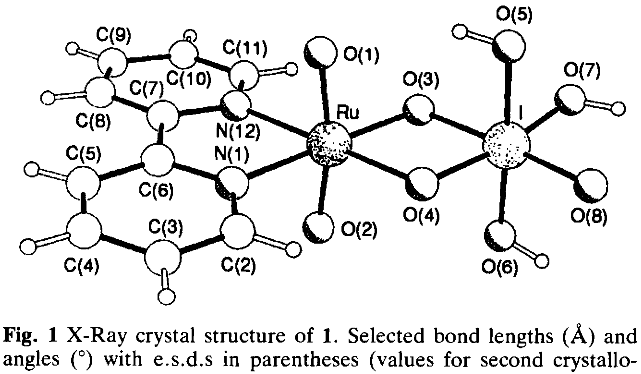

Fig. 1 X-Ray crystal structure of **1**. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses (values for second crystallographically independent molecule in square brackets): Ru–O(1) 1.722(5) [1.732(4)], Ru–O(2) 1.730(5) [1.725(4)], Ru–N(1) 2.095(5) [2.096(5)], Ru–N(12) 2.125(5) [2.116(5)], Ru–O(3) 2.002(4) [1.993(4)], Ru–O(4) 1.974(4) [1.965(4)], I–O(3) 1.920(4) [1.915(4)], I–O(4) 1.913(4) [1.913(4)], I–O(5) 1.896(6) [1.931(5)], I–O(6) 1.903(6) [1.895(5)], I–O(7) 1.897(5) [1.887(5)], I–O(8) 1.801(4) [1.791(4)], O(1)–Ru–O(2) 167.3(2) [167.6(2)], N(1)–Ru–O(3) 177.9(2) [177.0(2)], O(4)–Ru–N(12) 178.1(2) [177.7(2)], N(1)–Ru–N(12) 77.7(2) [77.5(2)], O(3)–Ru–O(4) 77.6(2) [78.1(2)], N(1)–Ru–O(4) 100.4(2) [100.3(2)], O(3)–Ru–N(12) 104.3(2) [104.2(2)], Ru–O(3)–I 100.0(2) [99.8(2)], Ru–O(4)–I 101.3(2) [100.8(2)], O(5)–I–O(6) 176.4(2) [171.7(2)], O(3)–I–O(8) 175.9(2) [174.3(2)], O(4)–I–O(7) 170.0(2) [171.0(2)], O(3)–I–O(4) 81.1(2) [81.3(2)], O(7)–I–O(8) 94.8(2) [95.5(2)], O(3)–I–O(7) 89.2(2) [89.7(2)], O(4)–I–O(8) 95.0(2) [93.5(2)].

The single oxo group on the iodine(VII) centres occupies an equatorial position [I–O(8) 1.796 Å] with the axial positions filled by two of the three hydroxyl groups [I–O 1.90 Å]. The two Ru–O–I linkages are asymmetric, with both the bridging oxygen atoms displaced towards the iodine atoms [Ru–μO 1.99, I–μO 1.92 Å, Ru–μO–I 101°].

The RuO_2I rings are planar to within 0.02 Å, and the transannular Ru···I and O···O distances are 3.00 and 2.49 Å respectively. Indeed, with the exception of the axial substituents on the ruthenium and iodine atoms, the remainder of the molecule is coplanar to within 0.15 Å.

Complex **1** in a biphasic water–dichloromethane mixture is an efficient stereospecific epoxidation catalyst, using $NaIO_4$ as cooxidant under mild conditions. Typically 0.02 mmol of **1**, 5.00 mmol of substrate and 7.50 mmol of $NaIO_4$ were stirred in water (20 cm^3) and dichloromethane (25 cm^3) at 2 °C for 15 hours, the mixture brought to pH 12 and the aqueous layer extracted with dichloromethane (3 × 25 cm^3). All products were characterised by GC and their purity checked by ^1H NMR spectroscopy; 1,2-epoxycyclooctane was isolated as a solid (83% yield). Such oxidations are also successful on a larger scale: thus 5.5 g of cyclooctene was converted to 5.4 g of the epoxide, a yield of 87%, using 0.05 g of catalyst with the above procedure. The results are summarised in Table 1.

Stoichiometrically the reagent functions as a six-electron oxidant (thus 1.0 mole of catalyst oxidises 3.0 moles of *trans*-stilbene) and after the addition of alkali, IO_3^- can be identified in the residue together with a ruthenium(II) bipyridine complex, suggesting that the iodine(VII) and ruthenium(VI) centres function as two- and four-electron oxidants respectively. The oxidations are stereospecific (thus

Table 1 Oxidations of alkenes by $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot1.5H_2O$

Substrate	Product	Yield (%) (Turnover)
Cyclopentene	1,2-Epoxycyclopentane	48 (120)
Cyclooctene	1,2-Epoxycyclooctane	83 (208)
Cyclododecene	1,2-Epoxycyclododecane	56 (140)
Styrene	Styrene oxide	25 (63)
trans-Stilbene	*trans*-Stilbene oxide	99 (249)
cis-Stilbene	*cis*-Stilbene oxide	75 (189)
Norbornene	2,3-Epoxynorbornane	19 (48)
Dec-1-ene	1,2-Epoxydecane	45 (113)
2,3-Dimethylbut-1-ene	2,3-Dimethyl-1,2-epoxybutane	59 (148)
2,3-Dimethylbut-2-ene	2,3-Dimethyl-2,3-epoxybutane	64 (161)

Table 2 Oxidations of alcohols by $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$

		Yield (%) (Turnover)	
Substrate	Product	Method A[a]	B[a]
4-Methoxybenzyl alcohol	4-Methoxybenzyl aldehyde	71 (48)	90 (61)
Benzyl alcohol	Benzaldehyde	67 (45)	72 (49)
Cinnamyl alcohol	Cinnamaldehyde	57 (39)	83 (56)
Cyclohexanol	Cyclohexanone	45 (31)	47 (32)
Geraniol	Citral	45 (31)	33 (23)
(±)-Menthol	(±)-Menthone	40 (28)	42 (29)

[a] Method A, NMO as co-oxidant; Method B, $NBu^n{}_4IO_4$ as cooxidant.

cis- and *trans*-stilbene give the respective epoxides) and the ^1H NMR of the epoxy products, in all cases, show no evidence of contamination by side products. Attempts to use monophasic organic systems with $NBu^n{}_4IO_4$ as cooxidant, have so far proved unsuccessful with only low yields of epoxide being obtained, but the use of substituted bipyridines is being investigated.

The complex also catalytically oxidises primary alcohols to aldehydes and secondary alcohols to ketones with *N*-methylmorpholine-*N*-oxide (NMO), or $NBu^n{}_4IO_4$ as co-oxidant, stirred at room temperature for 4 h. The yields and turnovers are less than for some of the other oxoruthenates which we have developed for alcohol oxidations.[2]

The infrared and Raman spectra of **1** show, in addition to bands arising from the $[IO_3(OH)_3]^{2-}$ moiety, bands at 817 (IR) and 797 cm^{-1} (Raman), assigned to the asymmetric and symmetric vibrations of the RuO_2 unit, ν_{as} (RuO_2) and ν_s (RuO_2) respectively, similar to those found in *trans*-$Na_6[RuO_2\{IO_5(OH)\}_2]\cdot 8H_2O$.[7]

We thank the SERC for the diffractometer and Shell Research Limited for a CASE award to one of us (A. J. B.), Dr Paul D. Savage for helpful discussions, Johnson Matthey Plc for the loan of ruthenium and the ULIRS for the Raman spectrometer.

Received, 12th May 1994; Com. 4/02827I

Footnotes

† Satisfactory elemental analyses were obtained.

‡ *Crystal data*: $C_{10}H_{11}IN_2O_2Ru\cdot 1.5H_2O$, M = 542.2, triclinic, space group $P\bar{1}$, a = 9.504(3), b = 11.028(3), c = 15.103(6) Å, α = 84.14(2), β = 88.70(2), γ = 75.46(2)°, V = 1524 Å^3, Z = 4, D_c = 2.36 g cm^{-3}, μ(Mo-Kα) = 31 cm^{-1}, $F(000)$ = 1044. An orange–yellow plate of dimensions 0.33 × 0.33 × 0.06 mm was used. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically using absorption corrected data to give R = 0.033, R_w = 0.035 for 4481 independent observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leqslant 50°]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Because there are two crystallographically independent molecules in the asymmetric unit, throughout the text mean values are cited.

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