Hydroxylation of Methane by a Sterically Hindered Ruthenium Complex

Alan S. Goldstein and Russell S. Drago*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-2046, USA

The sterically crowded *cis*-[Ru(dmp)$_2$S$_2$](PF$_6$)$_2$ (dmp = 2,9 dimethyl-1,10-phenanthroline, S = Me$_3$CN or H_2O) is capable of hydroxylating methane under mild reaction conditions utilizing H_2O_2 as the primary oxidant; oxidation of this complex with H_2O_2 is studied spectrophotometrically by UV–VIS and NMR spectroscopy implicating ruthenium(VI) as the active oxidant.

The metal-catalysed hydroxylation of alkanes has been an important objective to further the understanding of the chemistry occurring in the iron-containing enzymes cytochromes P-450[1–3] and methane monooxygenase.[4,5] The active species in both enzymes is thought to be a high valent metal–oxo species. The conversion of methane to methanol, a storable fuel, makes this oxidation reaction a highly desirable goal.[6] These objectives have led to research directed towards the oxidation of hydrocarbons by metal–oxo complexes.[7] Many polypyridyl ruthenium–oxo systems have been investigated,[8–14] most are not catalytic,[9–11] and few[13,15] have been demonstrated to be capable of oxidizing alkanes. The oxidation of saturated hydrocarbons utilizing t-butyl hydroperoxide has been reported to be catalysed by several *cis*-[Ru^{II}(L)$_2$(OH$_2$)$_2$]$^{2+}$ complexes[15] (L = substituted 2,2′ bipyridine or 1,10 phenanthroline).

The complex, *cis*-[Ru(dmp)$_2$S$_2$](PF$_6$)$_2$ (S = MeCN **1** or H_2O **2**),[16] is shown in this work to be capable of hydroxylating methane with comparable selectivities, utilizing H_2O_2 as the primary oxidant. In a typical reaction, 10^{-5} moles of catalyst are dissolved in 20 ml of solvent and 30% aqueous H_2O_2 (10^{-2} mol) is added. This solution is then pressurized to 4 atm of methane and heated to 75 °C, with stirring. Samples were analysed by GC and GCMS. Under these reaction conditions methane is oxidized to a mixture of methanol and formaldehyde in a ratio of 4 : 1. Trace amounts of CO_2 and coupling products, such as dimethylether, are also observed. The reaction proceeds with a 1.7 conversion (125 turnovers per

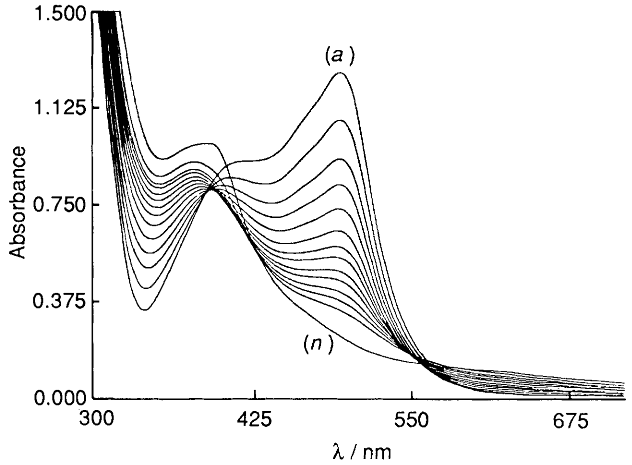

Fig. 1 UV–VIS Spectra of [Ru(dmp)$_2$(H$_2$O)$_2$](PF$_6$)$_2$ with the addition of hydrogen peroxide: (*a*) 0; (*b*) 0.5; (*c*) 1.0; (*d*) 1.5; (*e*) 2.0; (*f*) 2.5; (*g*) 3.0; (*h*) 3.5; (*i*) 4.0; (*j*) 4.5; (*k*) 5.0; (*l*) 5.5; (*m*) 6.0; (*n*) 7.0 equiv.

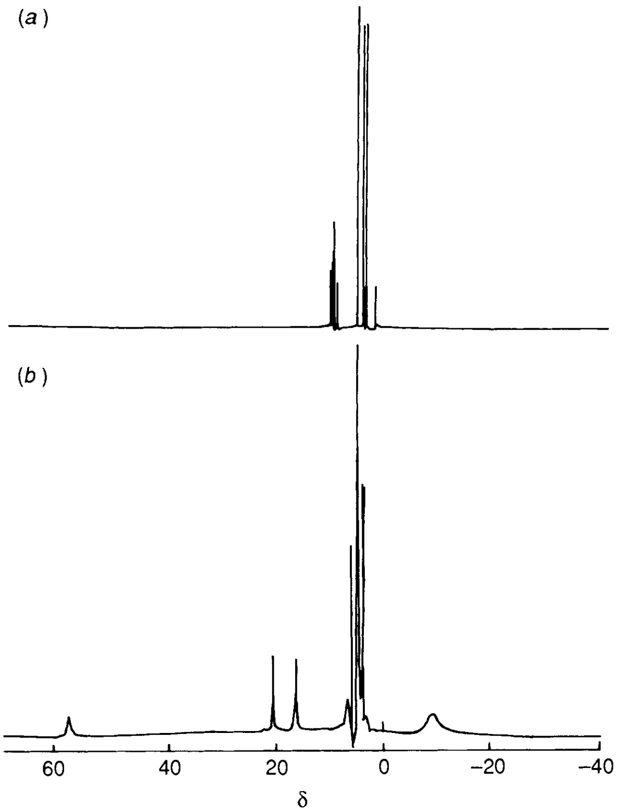

Fig. 2 ^{1}H NMR of $[Ru(dmp)_2(OH_2)_2](PF_6)_2$; (*a*) before addition of H_2O_2; (*b*) after addition of 3 equiv. of hydrogen peroxide

day) and a 1.9% conversion (140 turnovers per day) in water and acetonitrile respectively. Control reactions without CH_4 did not yield C_1 oxidation products. Utilizing OCl^- with **2**, gives rise to similar results as the H_2O_2–H_2O system, although a slightly lower conversion was observed (1.2%) with trace amounts of chloroform and dichloromethane. ^{1}H NMR and UV–VIS spectroscopy showed that decomposition of the catalyst had taken place after completion of the reaction (30 h).

Under the same conditions used in the methane reactions, ethane is oxidized to a mixture of ethanol and acetaldehyde, and propane to propan-1-ol, propanal and propan-2-ol. Small amounts of coupling products are also observed. Adamantane was also found to be oxidized to adamantan-1-ol. After 18 h adamantan-2-ol and adamantan-2-one were observed.

A 5 h induction period is observed in the oxidation of methane. A longer induction period is also observed in aerobic epoxidation reactions using this sterically crowded complex.[14] The nature of these induction periods are currently under study.

The addition of AIBN [a free radical initiator, azo-bis(isobutyronitrile)] to the methane oxidation in acetonitrile resulted in a 3% conversion with >1% of the products observed being coupling products (methyl ethyl ether and ethane). Addition of AIBN, in the absence of catalyst did not result in oxidation. In the presence of the free radical inhibitor, benzoquinone, oxidation was not observed. When the reaction was carried out in the presence of CCl_4, the formation of chloroform and dichloromethane was observed. These experiments suggest that radicals are involved in this oxidation.

The addition of H_2O_2 to the ruthenium(II) precursor complex was monitored by UV–VIS. As illustrated in Fig. 1, the addition of H_2O_2 to **2** leads to spectral changes and the appearance of three isosbestic points. At low concentration of added oxidant to **2**, an isosbestic point appears at 395 nm with a decrease in the absorption at 490 nm and an increase in the absorption at 365 nm. This isosbestic point has been assigned to the oxidation of the ruthenium(II) to ruthenium(III). From 3.5 to 4.5 equiv. of H_2O_2 a second isosbestic point is observed at 425 nm corresponding to the oxidation of the ruthenium(III) to ruthenium(IV). These spectral changes are similar to those observed by Meyer[14,18] for the formation of Ru^{IV} species by oxidation with Ce^{IV}. The 425 nm isosbestic point disappears upon further addition of H_2O_2 [curve (*n*)] and this is attributed to the formation of Ru^{VI}. These same results are observed using OCl^- as an oxidant.

As illustrated in Fig. 2, the ^{1}H NMR of **2** covers a δ-range of 10. When 3 equiv. of H_2O_2 are added to **2**, a spectrum with chemical shifts ranging from +60 to −20 results. These isotropic shifts are characteristic of a paramagnetic species. Groves and coworkers have observed similar shift due to $[Ru^{IV}O]^{2+}$[19] and $[Fe^{IV}O]^{2+}$[20] porphyrin complexes. We propose that the species shown in Fig. 2*b* is a ruthenium(IV) complex or a mixture of ruthenium(III) and (IV). An additional 4 equiv. of H_2O_2 results in a spectrum characteristic of a diamagnetic species in which the phenanthroline resonances are slightly shifted downfield compared to the resonances in **2**. This species is tentatively assigned as the *cis*-$[Ru^{VI}(dmp)_2(O)_2]^{2+}$. A similar ^{1}H NMR spectrum is observed in samples taken from the reaction mixture during the induction period.

The experiments reported here suggest that a ruthenium–oxo species is capable of hydroxylating alkanes. Attempts to isolate the active species are underway.

The authors would like to thank the National Science Foundation, grant 86 18766, as well as the US Army CRDEC for their financial support.

Received, 4th September 1990; Com. 0/04025H

References

1 F. P. Guengerich and T. L. MacDonald, *Acc. Chem. Res.*, 1984, **17**, 9.
2 J. T. Groves and T. E. Nemo, in *Coordination Chemistry of Metalloenzymes*, ed. R. S. Drago, Reidel, Dordrecht, 1982, 329.
3 G. H. Loew, J. Collins, B. Luke, A. Walch and A. Pudzianowski, *Enzyme*, 1978, **36**, 54.
4 H. Dalton, B. T. Golding and B. W. Water, *J. Chem. Soc., Chem. Commun.*, 1981, 482.
5 A. M. Khenkin, and A. E. Shilov, *New J. Chem.*, 1989, **13**, 659.
6 H. Dalton and D. J. Leak, *Mechanistic Studies on the Mode of Action of Methane Monooxygenase*, in *Gas Enzymology*, ed. H. Degan, Reidel, Dordrecht, 1985, 169.
7 R. H. Holm, *Chem. Rev.*, 1987, 1401.
8 P. H. J. Carlen, T. Katsuki, V. S. Martin and K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936.
9 M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4106, 5070.
10 J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790.
11 C.-M. Che, W.-T. Tang, W.-T. Wong and T.-F. Lai, *J. Am. Chem. Soc.*, 1989, **111**, 9048.
12 M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1986, **108**, 510.
13 T.-C. Lau, C.-M. Che, W.-O. Lee and C.-K. Poon, *J. Chem. Soc., Chem. Commun.*, 1988, 1406.
14 C. L. Bailey and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, 1987, 179.
15 T. Leung, B. R. James and D. Dolphin, *Inorg. Chim. Acta*, 1983, **79**, 25, 180.
16 J. P. Collins and J. P. Sauvage, *Inorg. Chem.*, 1986, **25**, 135.
17 B. A. Moyer and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 436.
18 J. C. Dobson, W. K. Seok and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 1514.
19 K.-H. Ahn and J. T. Groves, *Inorg. Chem.*, 1987, **26**, 3833.
20 J. T. Groves, R. Quinn, T. J. McMurry, M. Nakamura, G. Lang and B. Boso, *J. Am. Chem. Soc.*, 1985, **107**, 354.