Oxo(phosphine)ruthenium(IV) Redox Chemistry: Substrate Oxidation Selectivity Based on Substrate Hydrophobicity

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The oxidation of primary alcohols by oxo(phosphine)ruthenium(IV) complexes is shown to display a unique hydrophobic selectivity, on the basis of the dependence of the oxidation rate constant on alcohol hydrophobicity, phosphine hydrophobicity, and solvent.

Recently, much attention has been given to the oxidation of organic substrates by oxoruthenium complexes, because of their potential usefulness as oxidation catalysts.[1—4] In addition, the influence of solvent effects on the kinetics of organic and inorganic reactions is a topic of current research.[5,6] We present here the results of a study on the oxidation of a series of primary alcohols in aqueous solution by *cis*-$[(bpy)_2(PPh_3)Ru^{IV}(O)]^{2+}$ (bpy = 2,2′-bipyridine). A linear correlation between rate of oxidation and alcohol hydrophobicity provides evidence for a novel selectivity of alcohol oxidation based primarily on alcohol hydrophobicity.

The reaction between *cis*-$[(bpy)_2(PPh_3)Ru^{IV}(O)]^{2+}$ and a primary alcohol proceeds according to equation (i). The kinetics of this reaction were determined spectrophotometrically at 430 nm, under pseudo-first-order conditions, where the target alcohol was in excess. For all reactions, the final spectrum, after the complete reaction, corresponded exactly to that of *cis*-$[(bpy)_2(PPh_3)Ru^{II}(OH_2)]^{2+}$; the intermediate spectra were isosbestic in nature, corresponding to a mixture of only the Ru^{IV} oxo and the Ru^{II} aqua species. The kinetics of all alcohol oxidations were strictly second order, first order in both substrate and oxidant.

The oxidation of propan-2-ol with *cis*-$[(bpy)_2(PPh_3)Ru^{IV}(O)]^{2+}$ proceeds with a primary isotope effect (k_H/k_D) of 9.9, and secondary isotope effects of 1.4 for each methyl group and 1.2 for the hydroxy group. These values suggest that the rate-determining step involves hydrogen atom or hydride transfer from the α-carbon atom of the primary alcohol to the oxo group of the ruthenium(IV) centre.[7—9] Thus, the target alcohol must approach close to the oxo ligand for oxidation to occur.

Values of second-order rate constants for the oxidation of a variety of saturated aliphatic primary alcohols are listed in Table 1. In order to quantify the hydrophobic character of the target alcohols, octan-1-ol/water partition coefficients (*P*) were used.[10—12] A plot of log *P* *versus* the second-order rate constants for primary alcohol oxidation shows a linear relationship: an increase in alcohol hydrophobicity results in an increase in second-order rate constant. The fact that the more hydrophobic alcohols exhibit faster oxidation suggests

Table 1. Second-order rate constants for the oxidation of alcohols by $[(bpy)_2(L)Ru^{IV}(O)^{2+}]$.

L	Substrate	Solvent	log P^a	10^3k/dm^3 mol^{-1} s^{-1}
PPh_3	Methanol	H_2O	−0.66	0.17^b
PPh_3	Ethanol	H_2O	−0.16	0.52
PPh_3	Propan-1-ol	H_2O	0.34	0.79
PPh_3	2-Methylpropan-1-ol	H_2O	0.61	0.88
PPh_3	Butan-1-ol	H_2O	0.84	1.1
PPh_3	3-Methylbutan-1-ol	H_2O	1.14	1.2
PPh_3	Pentan-1-ol	H_2O	1.34	1.5
PPh_3	Propan-1-ol	MeCN		3.0
PPh_3	Butan-1-ol	MeCN		2.7
PPh_3	Pentan-1-ol	MeCN		3.0
PPh_3	Allyl alcohol	H_2O		170
PEt_3	Allyl alcohol	H_2O		0.67

[a] For a discussion of Hansch Partition Coefficients (log P) see references 10—12. [b] Corrected for statistical differences, with normalization to primary alcohols containing two α-protons; see reference 13.

that, prior to alcohol oxidation, the target alcohol leaves the bulk aqueous phase and hydrophobically associates with the *cis*-phosphine ligand, thus increasing the concentration of the alcohol in the vicinity of the oxo site; this results in an enhancement of the rate of oxidation according to the hydrophobicity of the target alcohol.

$$[L_5Ru^{IV}{=}O]^{2+} + RCH_2OH \xrightarrow{k} [L_5Ru^{II}{-}OH_2]^{2+} + RCHO \quad \text{(i)}$$

In non-aqueous solvents, such as acetonitrile, there is little difference in rate of oxidation by *cis*-$[(bpy)_2(PPh_3)Ru^{IV}(O)]^{2+}$ for propan-1-ol, butan-1-ol, pentan-1-ol (see Table 1). Since the steric and electronic properties of the target alcohol that affect the rate of oxidation should be observed to a similar degree in both water and acetonitrile, the rate constant data concerning alcohol oxidation in acetonitrile suggest that the hydrophobicity of the target alcohol is primarily responsible for the observed rate enhancements in aqueous media.

In addition, the hydrophobicity of the phosphine ligand has a dramatic effect on the rate of alcohol oxidation. For example (Table 1), the rate of allyl alcohol oxidation by $[(bpy)_2(PPh_3)Ru^{IV}(O)]^{2+}$ is 250 times greater than the rate of oxidation by $[(bpy)_2(PEt_3)Ru^{IV}(O)]^{2+}$ in aqueous media; in methylene chloride, the rate of allyl alcohol oxidation by $[(bpy)_2(PPh_3)Ru^{IV}(O)]^{2+}$ is only 1.9 times greater than the rate of oxidation by $[(bpy)_2(PEt_3)Ru^{IV}(O)]^{2+}$. These observations are also consistent with a hydrophobic mechanism, where the increased hydrophobicity of triphenylphosphine relative to triethylphosphine is primarily responsible for the difference in rates in aqueous media.

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References

1 P. H. J. Carlsen, T. Katsuki, V. S. Martin, and K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936.
2 M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4106, 5070.
3 J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790.
4 M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1986, **108**, 510.
5 For an example of solvent effects on the rate of an organic reaction, see T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, 1982, **104**, 5741.
6 For an example of solvent effects on the rate of an inorganic reaction, see M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, A. W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C. D. Hubbard, and E.-E. A. Abu-Gharib, *J. Chem. Soc., Faraday Trans.*, 1986, 1471.
7 J. March, 'Advanced Organic Chemistry,' 3rd edn., Wiley, New York, 1985, pp. 198—199.
8 D. G. Lee, U. D. Spitzer, J. Cleland, and M. E. Olson, *Can. J. Chem.*, 1976, **54**, 2124.
9 A. M. Maione and A. Romeo, *Synthesis*, 1984, **11**, 955.
10 A. Leo, C. Hansch, and D. Elkins, *Chem. Rev.*, 1971, **71**, 525.
11 C. Tanford, 'The Hydrophobic Effect: Formation of Micelles and Biological Membranes,' Wiley Interscience, New York, 1980.
12 C. Hansch, J. E. Quinlan, and G. L. Lawrence, *J. Org. Chem.*, 1968, **33**, 347.
13 K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, New York, 1965, pp. 84—85.