Tetrahedron Letters, Vol.32, No.9, pp 1153-1156, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Alkyl Hydroperoxide Oxidation of Alkanes and Alkenes with a Highly Active Mn Catalyst.

Joseph E. Sarneski*,† Demetrius Michos,¶ H. Holden Thorp,• Mary Didiuk,† Thomas Poon,† Jennifer Blewitt†, Gary W. Brudvig¶ and Robert H. Crabtree.¶
Chemistry Department, Yale University, 225 Prospect St., New Haven, CT, 06511,(¶)
Chemistry Department, Fairfield University, Fairfield CT, 06430, (†), and Chemistry
Department, N. Carolina State University, Raleigh, NC, 27695, (•).

Abstract The system ROOH/[$Mn_3O_4(dipy)_4(OH_2)_2](ClO_4)_4$ hydroxylates alkanes and converts ArCR=CH_2 to ArCR=O with extremely high activity and good conversions and yields.

Selective, partial alkane oxidation is a particularly challenging problem in organic chemistry.[1] Catalysis by metal complexes is a promising approach,[2] but an important goal is to try to avoid the usual free radical chemistry and its attendant 3°>2°>1° C-H bond selectivity pattern. While O_2 is useful for industrial applications, reagents such as t-BuOOH are more convenient for lab scale oxidations. Degradation of the catalyst is usually a severe problem in alkane conversion, and so we use the relatively oxidation-resistant ligand 2,2'-dipyridyl (= dipy). Fish et al.,[3] have previously studied some dipyridyl-substituted manganese cluster complexes for t-BuOOH oxidation of CH_4, C_2H_6, and C_6H_{12}.

Our own new cluster [$Mn_3O_4(dipy)_4(OH_2)_2](ClO_4)_4$ (1)[4] is particularly active for the oxidation of alkanes, alkenes, and alkylated arenes with alkyl hydroperoxides in CH_3CN. Unoptimized rates of up to 700 turnovers/h are seen for alkanes even at 0°. In addition, Only 2 mol of ROOH are required per mole of substrate, which implies that little of the oxidizing power is lost to O_2 formation, a side-reaction that is common in other systems (e.g., Fish[3] used a 150:1 ROOH/substrate ratio).

Not only are the rates exceptionally fast but the selectivity pattern is apparently nonradical in character (Table 1). For the alkane oxidations, the 3°/2° C-H bond selectivity is unusually low, a feature reminiscent of Gif iron chemistry.[2a] Alkanes give both alcohols and ketones at short times, but ketone formation is favored after 8 h. The ketone/alcohol ratio in the case of cyclohexane and t-BuOOH rises from 1.11 after 15 min to 2.19 after 6 hr. because alcohol is converted to ketone by the system. Primary alcohols give aldehyde as the major product, while alkylaromatics are rapidly oxidized at the benzylic position.

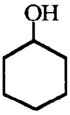
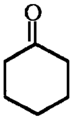
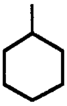
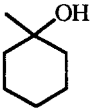
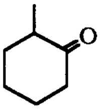
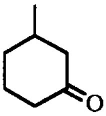
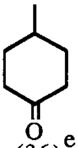
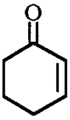
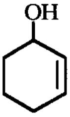
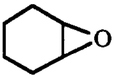
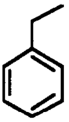
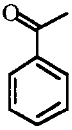
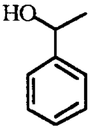
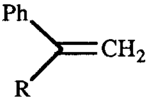
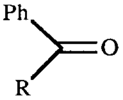
Methylcyclohexane gives an initial 3°/2° selectivity on a per bond basis of 1.6 at low conversion, rising to 2.1 in the presence of excess oxidant. These values are unlike those seen in radical reactions. The atypical alkane, adamantane (AdH), behaves very differently with an initial 3°/2° selectivity of 7, within the range found[1] for radical reactions. This suggests that caution must be used in determining 3°/2° selectivity in oxidation chemistry only with AdH, as is sometimes seen. Methylcyclohexane more closely resembles typical organic substrates and is therefore probably more appropriate for selectivity studies.

In further tests for free radical intermediates, we found that bicyclohexyl is not formed from cyclohexane and cyclohexyl chloride was not formed when CCl_4 is added to the reaction mixture. Free C_6H_{11} radicals normally dimerize rapidly to give bicyclohexyl and abstract Cl from CCl_4 to give cyclohexyl chloride.[1] The intermediacy of caged radical pairs cannot be excluded, however.

Aliphatic alkenes such as cyclohexene undergo allylic oxidation. Aromatic alkenes are converted to the corresponding keto-compounds in a reaction that resembles ozonolysis. In no case is more than a trace of epoxide observed, and so the catalyst does not act as an oxo transfer agent toward alkenes.

$PhCMe_2OOH$ can replace t-BuOOH as oxidant, but this leads to substantial changes in the rates and selectivity (Table). This suggests that the R group of the peroxide may be present in the species that oxidizes the substrate.

Table 1 Some Results of the Alkane Oxidations

Substrate	Oxidant	Rate[a]	Products[b]			
						
	t-BuOOH, 3 h.	240	(179)	(400)		
	PhCMe$_2$OOH, 3 h.	700	(593)	(793)		
						
	t-BuOOH, 30 min.	380	(30)	(31)[c]	(71)[d]	(36)[e]
	t-BuOOH, 3 h.	-	(81)	(103)	(213)	(77)
						
	t-BuOOH, 6 h.	-	(645)	(77)	(0)	
	PhMe$_2$COOH, 6 h.	1630	(1380)	(346)	(tr.)	
						
	PhMe$_2$COOH, 8 h.	-	(1700)	(200)		
						
	t-BuOOH, 8 h.	900	(2000, R = Ph 4000, R = Me)			
PhCH=CHPh			PhCHO			
	t-BuOOH, 8 h.	-	(180, from trans 110, cis)			

[a] initial rate (in turnovers/h calculated as moles product per mole catalyst)

[b] in turnovers (t.o.) [c] 6, 12 and 28 t.o. of 2-, 3- and 4-ol also formed. Conditions: 1, 0.002 mmol; 0°C; oxidant, 16 mmol, substrate 8 mmol; in CH$_3$CN, 10 mL. 4000 turnovers corresponds to complete conversion of the substrate.

The ROOH could displace H_2O ligand in **1** to form an Mn-OOR system. The mechanism is not yet clear, but we have extensive data on the redox properties of **1**, including its tendency to abstract H atoms by proton-coupled electron transfer.[4a] We find that neither the dinuclear cluster **2**[4] nor Mn^{2+}/dipy are as effective catalysts as **1** and so **1** is not simply reverting to **2** or Mn^{2+} under the reaction conditions.

Acknowledgment. We thank the DOE and the USDA for support.

References.

1. a) C.L. Hill, (ed.), "Activation and Functionalization of Alkanes", Wiley, 1989. b) R.H. Crabtree, Chem. Rev., 1985, 85, 245.

2. a) G. Balavoine, D.H.R. Barton, J. Boivin, P. Lecoupanec, P. Lelandais, New J. Chem., 1989, 13, 177 and refs. cited. b) D. Mansuy, ref. 1a, p. 195; D. Mansuy, J.F. Bartoli, J.C. Chottard and M. Lange, Angew. Chem., Int. Ed., 1980, 19, 909. c) A.M. Khenkin and A.E. Shilov, New J. Chem., 1989, 13, 659. d) N. Herron, New J. Chem., 1989, 13, 761. e) M. Faraj and C.L. Hill, Chem. Comm., 1987, 1487. f) J.T. Groves and T.E. Nemo, J. Amer. Chem. Soc., 1983, 105, 6243. g) N. Kitajima, H. Fukui and Y. Moro-Oka, Chem. Comm., 188, 485. h) H. Sugimoto and D.T. Sawyer, J. Amer. Chem. Soc., 1984, 106, 4283.

3. R.H. Fish, R.H. Fong, J.B. Vincent and G. Christou, Chem. Comm., 1988, 1504.

4. a) J.E. Sarneski, H.H. Thorp, G.W. Brudvig, R.H. Crabtree and G.K. Schulte, J. Amer. Chem. Soc., 1990, 112, 7255. b) The catalyst is made from Cooper and Calvin's[4c] dinuclear cluster $[(bipy)_2Mn(O)_2Mn(bipy)_2](ClO_4)_3$ (**2**) by adding c. HNO_3 to a stirred slurry of **2** (3.2 g) in 250 mL of water until the pH is 1.75. $NaClO_4$ (1.3 g, anhyd.) in H_2O (10 mL) is added to the brown solution and the mixture filtered (frit). Black air-stable crystals of **1** (77%) form over 3 d. when the solution evaporates in air; no recryst. is necessary. c) S. Cooper and M. Calvin, J. Amer. Chem. Soc., 1977, 99, 6623.

(Received in USA 22 October 1990)