Oxidation of C_2, C_3 and Higher Alkanes by a Ruthenium–Oxo System

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Barium ruthenate, $BaRuO_3(OH)_2$, when dissolved in TFA–CH_2Cl_2 containing a few equivalents of 2,2′-bipyridine, generates a highly reactive ruthenium–oxo system that is capable of oxidizing ethane and propane at room temperature with good yields.

The design of highly reactive metal–oxo species capable of oxidizing unactivated C–H bonds continues to be a challenge to chemists.[1] Although quite a number of metal–oxo systems are capable of oxidizing cycloalkanes, few systems are efficient in oxidizing linear alkanes, especially the lower molecular mass homologues, under mild conditions,[2,3] We have previously shown that barium ruthenate(VI), $BaRuO_3(OH)_2$, when dissolved in AcOH–CH_2Cl_2, readily oxidizes alkanes at room temperature.[4] The active species generated in solution is most probably a *trans*-dioxoruthenium(VI) species containing acetate ligands. Substituting acetic acid with stronger acids such as TFA should generate a more reactive species since trifluoroacetate is a weaker σ-donor than acetate, and this would make the resulting ruthenium–oxo complex more strongly oxidizing. Moreover, more extensive protonation of the oxo ligands by the stronger TFA would be expected to occur, and this should also enhance the oxidizing power of the complex. Here we report that barium ruthenate, when dissolved in TFA–CH_2Cl_2 containing a few equivalents of α-diimine ligands, generates a highly oxidizing ruthenium–oxo system that is capable of oxidizing ethane and propane at room temperature with good yields.

Upon addition of TFA to a suspension of $BaRuO_3(OH)_2$ in CH_2Cl_2 containing cyclohexane, the brick-red solid rapidly dissolves to give a dark green solution. Analysis of the mixture after a few minutes by GC and GC–MS indicates the presence of cyclohexanol, cyclohexanone and cyclohexyl trifluoroacetate, with a total yield of 44%. Yields are based on the amount of $BaRuO_3(OH)_2$ used, assuming it acts as a two-electron oxidant (see below). In the absence of TFA, the barium ruthenate remained undissolved and no products could be detected. The only moderate yields obtained may be due to some disproportionation of ruthenate(VI) to ruthenium tetroxide and ruthenium(IV), which is known to occur in strong acid media.[5] In an attempt to stabilize the ruthenium(VI)–oxo species against disproportionation, and hence to increase the yield, various ligands were added to the mixture. We found that yields were substantially increased with the addition of pyridine and α-diimine ligands (Table 1). In particular, yields as high as 96% can be obtained with the introduction of just a few equivalents of 2,2′-bipyridine (bpy), although the rate of reaction is somewhat slower.

Table 2 shows the results of oxidation of various alkanes and aromatic hydrocarbons by barium ruthenate in TFA–bpy–CH_2Cl_2. The system is capable of oxidizing ethane and propane at room temperature with good yields. Oxidation of propane occurs exclusively at the *sec* C–H bond to produce propan-2-one while oxidation of ethane gives ethanoic acid. So far, we have not been able to detect any products when methane was used as the substrate. The system is also able to oxidize benzene to 1,4-benzoquinone. In the case of toluene and ethylbenzene, oxidation occurs both at the side chain and at the aromatic ring.

Table 1 Effect of pyridine and α-dimine ligands on the oxidation of cyclohexane (CyH) by barium ruthenate in TFA–CH_2Cl_2[a]

	% Yield of products				
Ligand[b]	CyOH	Cy=O	CyO_2CCF_3	Total	*t*/min[c]
none	13	29	2	44	2
py	4	71	1	76	20
bpy	31	64	1	96	13
phen	24	59	1	84	13

[a] *Reagents and conditions*: 22 °C, barium ruthenate (0.156 mmol), cyclohexane (1 ml), CH_2Cl_2 (4.5 ml), TFA (0.5 ml), ligand (1.28 mmol py, 0.64 mmol bpy and phen). [b] Abbreviations: py = pyridine; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline. [c] Time when there is no significant change in amount of products.

Attempts to isolate the active intermediate have not been successful due to the instability of the species. However, a greenish-yellow solid can be obtained upon adding 6 mol dm^{-3} HCl to a solution of $BaRu(O)_3(OH)_2$ in TFA–bpy–CH_2Cl_2. IR and elemental analyses are consistent with the complex $[Ru^{VI}(bpy)O_2Cl_2]$.[6] Thus it is reasonable to assume that the active intermediate is also a dioxoruthenium(VI) species with the formula $[Ru^{VI}(bpy)O_2(CF_3CO_2)_2]$ [eqns. (1) and (2)].

$$Ba[Ru(O)_3(OH)_2] + 4\ CF_3CO_2H + bpy \rightarrow [Ru(O)_2(bpy)(CF_3CO_2)_2] + 4\ H_2O + Ba(CF_3CO_2)_2 \quad (1)$$

$$[Ru(O)_2(bpy)(CF_3CO_2)_2] + 2\ HCl \rightarrow [Ru(O)_2(bpy)Cl_2] + 2\ CF_3CO_2H \quad (2)$$

Table 2 Oxidation of organic substrates by barium ruthenate in TFA–bpy–CH_2Cl_2[a]

Substrate (amount)	*t*/min[b]	Product (yield %)[c]
Cyclohexane (1 ml)	13	Cyclohexanol (31) Cyclohexanone (64) Cyclohexyl trifluoroacetate (1)
n-Hexane (1 ml)	15	Hexan-2-ol (10) Hexan-3-ol (6) Hexan-2-one (31) Hexan-3-one (20)
Adamantane[d] (200 mg)	2	Adamantan-1-ol (97) Adamantan-2-ol + Adamantanone (3)
2-Methylbutane (1 ml)	2	2-methylbutan-2-ol (70) 3-methylbutan-2-ol (trace) 3-methylbutanone (11) 2-methylbutanal (4.5)
Propane[d] (3 atm)	30	Propan-2-one (65)
Ethane[e] (5 atm)	240	Ethanoic acid (40)
Benzene[d] (1 ml)	5	1,4-Benzoquinone (20)
Methylbenzene[d] (1 ml)	5	Benzaldehyde (10) Benzyl alcohol (2) Methyl-1,4-benzoquinone (20) Benzyl trifluoroacetate (trace)
Ethylbenzene[d] (1 ml)	2	Acetophenone (10), 1-Phenylethanol (43) (1-Phenylethyl) trifluoroacetate (4) Ethyl-1,4-benzoquinone (9)

[a] *Reagents and conditions*: 20 °C, barium ruthenate (50 mg, 0.156 mmol), 2,2′-bipyridine (100 mg, 0.64 mmol), (0.5 ml), CH_2Cl_2 (4.5 ml), unless otherwise stated. [b] Time where there is no significant change in amount of product. [c] Based on amount of barium ruthenate used, assuming the system acts as a two-electron oxidant. [d] 5.5 ml CH_2Cl_2 used. [e] 3 ml TFA and 3 ml CH_2Cl_2 used.

Oxidation of PPh_3 by this system produces 2 mol equivalents of PPh_3=O, consistent with the dioxoruthenium(VI) formulation for the active species. On the other hand, even after reaction with cyclohexane, this system is still capable of producing one mol equivalent of PPh_3=O, indicating that the system acts as a two-electron oxidant in the reaction with alkanes.

As expected, the reactivity order for C–H bonds is $3° > 2° > 1°$. In the oxidation of adamantane, the ratio $2°:3° = 1:60$; in the case of 2-methylbutane, the ratio $1°:2°:3° = 1:11:280$. The kinetic isotope effects (KIE) for the oxidation of cyclohexane are (k_H/k_D) 4.0 and 7.7 for the formation of cyclohexanol and cyclohexanone, respectively. These results are consistent with a H-atom abstraction mechanism which is generally accepted for alkane hydroxylation by metal–oxo species [eqns. (3) and (4)].[2,4]

$$\mathrm{Ru^{VI}(O)_2 + H{-}R \rightarrow [O{=}Ru{-}OH, R\cdot] \rightarrow O{=}Ru^{IV} + ROH} \qquad (3)$$

$$\mathrm{Ru^{VI}(O)_2 + ROH \rightarrow O{=}Ru^{IV} + R{=}O\ (ketone)} \qquad (4)$$

The oxidation can also be made catalytic by using various terminal oxidants (Table 3). Excellent yields were obtained with PHIO, while reasonable yields were obtained with periodate, peracids and alkyl hydroperoxides. Detailed studies of these catalytic oxidations are in progress.

Table 3 Catalytic oxidation of cyclohexane (CyH) by barium ruthenate in TFA–bpy–CH_2Cl_2[a]

Terminal oxidant	t/h	Products (Turnover no.)[b] CyOH	Cy=O	CyO_2CCF_3	Yield %[c]
PhIO	1.5	37	9	3	100
$Bu_4^nNIO_4$	2	7.8	12	1.3	60
MCPBA	9	16	0.8	11	49
TBHP	2	15.4	0.5	3	34
H_2O_2	1.5	8.6	0.4	0.7	14

[a] Typical procedure: barium ruthenate (0.0072 mmol) was dissolved in CH_2Cl_2 (6 ml) containing TFA (0.5 ml), cyclohexane (1 ml) and 2,2′-bipyridine (100 mg). After 1 min, the terminal oxidant (0.4 mmol) was added. [b] Turnover number = no. of mol of product/no. of mol of barium ruthenate. [c] Based on the amount of terminal oxidant used, assuming it acts as a two-electron oxidant.

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