Oxidation of Alkanes by Barium Ruthenate in Acetic Acid: Catalysis by Lewis Acids

Tai-Chu Lau* and Chi-Keung Mak

Department of Applied Science, City Polytechnic of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong

Barium ruthenate in acetic acid–dichloromethane oxidizes alkanes at room temperature with appreciable rates and yields; the reactions are greatly accelerated by the presence of a few equivalents of Lewis acids.

The use of high-valent transition metal oxo species as oxidants for a variety of organic functional groups is well established.[1] Most of these species are, however, unreactive toward alkanes under mild conditions; refluxing conditions are often required to oxidize unactivated C–H bonds. Over the past decade, the use of ruthenium oxo complexes as organic oxidants has become increasingly important.[2] A wide variety of ruthenium oxo complexes in oxidation states ranging from IV to VIII have been found useful for stoichiometric and catalytic oxidation of various organic functional groups. Among these complexes, only the mono-oxo species $[Ru^{V}O(N_4O)]^{2+}$, {N_4O = 2-hydroxy-2-(2-pyridyl)ethyl[bis{2-(2-pyridyl)ethyl}]amine} is able to oxidize alkanes at room temperature.[3] We report here an unusually reactive, but simple and easily prepared, ruthenium oxo system, generated by dissolving barium ruthenate(VI) in acetic acid, that readily oxidizes alkanes at room temperature.

Barium ruthenate, $BaRu(O)_2(OH)_3$, is a stable, non-hygroscopic solid that can be readily prepared from ruthenium trichloride in over 80% yield.[4] Upon adding acetic acid to its suspension in dichloromethane, the red solid gradually dissolves to give a dark-green solution. Addition of cyclohexane led to the production of cyclohexanone in 60% yield. No cyclohexanol or cyclohexyl acetate is detected by GC or GC–MS. Performing the reaction in neat acetic acid lowers the yield to 30%, while the use of acetonitrile or acetone also gave much lower yields and rates. The system is also able to oxidize linear alkanes; again ketones are produced. Oxidation of adamantane and methylcyclohexane occur predominantly at the tertiary position. As expected, the system is also effective towards the oxidation of aromatic hydrocarbons and ethers. Results are shown in Table 1. In the oxidation of triphenylphosphine to triphenylphosphine oxide and cyclohexanol to cyclohexanone, one mole of product is formed per mole of barium ruthenate used, suggesting that the system is a two-electron oxidant. The oxidation can be made catalytic by using $Bu^n_4NIO_4$ as terminal oxidant. Thus, addition of 0.01 mmol of barium ruthenate to a solution containing 0.17 mmol of $Bu^n_4NIO_4$, 1 ml cyclohexane, 1 ml acetic acid and 2 ml CH_2Cl_2 at 23 °C resulted in the production of 0.047 mmol of cyclohexanone after 24 h, corresponding to 50% yield and a turnover of 8.5 if $Bu^n_4NIO_4$ functions as a two-electron oxidant.†

Table 1 Oxidation of organic substrates by barium ruthenate in acetic acid[a]

Substrate (amount)	t/min	Product (% yield)[b]
Cyclohexane (1 ml)	240	Cyclohexanone (60)
Adamantane[c]	120	Adamantan-1-ol (95) Adamantan-2-one (3)
n-Hexane[d] (1.2 ml)	240	Hexan-2-one (20) Hexan-3-one (16)
Methylcyclohexane (1 ml)	240	1-Methylcyclohexanol (42) 2-, 3- and 4-Methylcyclohexanones (9)
Toluene (1 ml)	120	Benzaldehyde (28)
Ethylbenzene (1 ml)	20	Acetophenone (89) α-Methylbenzylacetate (4)
Tetrahydrofuran (1 ml)	30	γ-Butyrolactone (64) 2-Acetoxytetrahydrofuran (7)
Cyclohexanol (40 μl, 0.376 mmol)	30	Cyclohexanone (100)
Triphenylphosphine[c] 80 mg (0.3 mmol)	30	Triphenylphosphine (100) oxide

[a] *Reaction conditions*: temperature, 23 °C; barium ruthenate, 50 mg (0.156 mmol); CH_2Cl_2, 2 ml; acetic acid, 1 ml; unless otherwise stated. [b] Based on amount of barium ruthenate, assumimg it acts as a two-electron oxidant. [c] 3 ml CH_2Cl_2 used. [d] 0.5 ml acetic acid used.

A dark-green solid resulted upon pumping a solution of barium ruthenate in acetic acid and dichloromethane to dryness. The IR spectrum shows an intense peak at 839 cm^{-1}, characteristic of a six-coordinate *trans*-dioxoruthenium(VI) species.[5] Ba, C and and H analyses are consistent with the formula $Ba[Ru(O)_2(MeCO_2)_4].3H_2O$.‡ This solid dissolves readily back into dichloromethane and acetic acid,§ and is able to oxidize alkanes with rates and yields similar to using barium ruthenate.

The high reactivity of this system is undoubtedly due in part to the poor electron-donating ability of the acetate ligands, thus making the complex strongly oxidizing. Similar dioxoruthenium(VI) complexes[6,7] such as $[RuO_2(MeCOO)Cl_2]^-$ and $[RuO_2Cl_3]^-$, which contain more electron-donating Cl^- ligands, do not oxidize alkanes at any appreciable rates and yields.

The reactivity of the system is dramatically increased by the addition of Lewis acids (Table 2). Thus, in the presence of 5 equiv. $ZnCl_2$, the oxidation of cyclohexane is complete in less than 5 min, with also an increase in total yield to 70%. A small amount of cyclohexanol and cyclohexyl chloride is, however, produced in addition to cyclohexanone. Similar accelerating

Table 2 Effect of Lewis acid on cyclohexane oxidation by barium ruthenate in acetic acid[a]

		Products (% yield)[b]		
Lewis acid	t/min	Cyclo-hexanone	Cyclo-hexanol	Cyclohexyl chloride
$ZnCl_2$	5	65	3	3
$Zn(MeCO_2)_2$	210	56	[b]	—
$FeCl_3$	5	60	3.5	0.5
$AlCl_3$	2	[b]	[b]	3
LiCl	60	69	[b]	2
$Li(MeCO_2)$	240	64	[b]	—
$BF_3{\cdot}MeCO_2H$	5	50	[b]	—
PPh_4Cl	480	65	[b]	1.5

[a] *Reaction conditions:* temperature, 23 °C; cyclohexane, 1 ml; CH_2Cl_2, 2 ml; acetic acid, 1 ml; Lewis acid, 0.4 mmol; barium ruthenate, 0.078 mmol. Mol ratio of Lewis acid to barium ruthenate is approximately 5 to 1. [b] Not detected.

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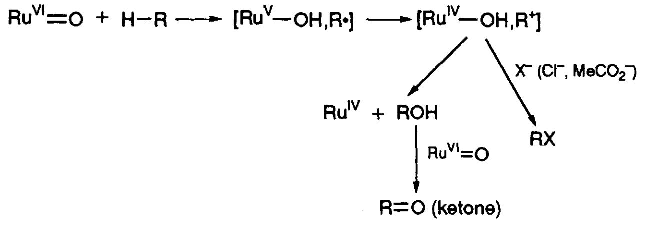
† Addition of a second quantity of periodate resulted in a lower yield of 37%, suggesting that there might be some decomposition of the ruthenium oxidant.

‡ In solution the complex may become five-coordinate by dissociation of an acetate ligand. See ref. 7.

§ A small amount of acetic acid is required for dissolving the barium salt in dichloromethane. Typically, 0.2 ml of acetic acid is added to dissolve 50 mg of the complex in 2 ml dichloromethane.



Scheme 1

effects are also observed with $FeCl_3$ and $BF_3 \cdot MeCO_2H$, though the yields are somewhat lower; while LiCl is less effective. Upon adding $AlCl_3$ a vigorous reaction occurs with the solution, resulting in immediate formation of a dark precipitate. Surprisingly, the acetate salts of zinc and lithium have virtually no effect. With PPh_4Cl, which is not a Lewis acid, the rate is actually retarded, indicating that the catalytic effect is not simply due to chloride alone. The accelerating effects are likely to be an electrophilic catalysis; electron-withdrawing by the Lewis acid through coordination to the oxo ligand: $Ru = O \rightarrow E$, would make the complex more strongly oxidizing.

The observed product distributions for the oxidation of C–H bonds and the decrease in selectivity in the presence of Lewis acids may be accounted for by the mechanism shown in Scheme 1.

The oxidation of alcohols by ruthenium oxo species is known to be much more rapid than the oxidation of alkanes.[2] Hence, under normal conditions only ketones are observed in the oxidation of secondary C–H bonds.[3] However, in the presence of Lewis acids the oxidation of alkane to alcohol may be greatly enhanced so that some alcohol can be observed as product.

Financial support from the UPGC and the Research Committee, CPHK is gratefully acknowledged.

Received, 18th December 1992; Com. 2/06720J

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