

A Ruthenium Heteropolyanion as Catalyst for Alkane and Alkene Oxidation

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A ruthenium heteropolyanion, $\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{5-}$, has been synthesized which catalyses the liquid phase oxidation of alkanes and alkenes with various primary oxidants including potassium persulphate, sodium periodate, *t*-butyl hydroperoxide, and iodosylbenzene; the activity and selectivity vary with the oxidant used.

Liquid phase oxidation of hydrocarbons such as alkenes and alkanes which requires the activation of the relatively inert carbon–hydrogen bond has received a great deal of research attention over the past few years. The traditional transition metal compounds co-ordinated with organic ligands generally used as catalysts are often degraded owing to their susceptibility to self-oxidation. Robust catalysts stable to oxidation are therefore desirable and one such family includes transition metal substituted heteropolyanions,¹ compounds consisting of transition metals co-ordinated in an entirely inorganic metal–oxo framework. Most applications of heteropolyanions in liquid phase oxidations involve catalysts with complete Keggin² structures such as $\text{PW}_{12}\text{O}_{40}^{3-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$, or substituted lacunary type anions such as $\text{SiM}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{q-}$ where M is a transition metal such as Fe^{III} , Mn^{III} , Co^{II} , or Cu^{II} . Specific examples of the use of complete heteropolyanions as liquid phase oxidation catalysts include the epoxidation and oxidative cleavage of alkenes with hydrogen peroxide,^{3–5} the synthesis of benzoquinones from phenols,⁶ the oxidation of secondary alcohols to ketones,^{3,7} and the oxidation of alkynes.⁸ Lacunary heteropolyanions have been used to catalyse the epoxidation of alkenes with iodosylbenzene,⁹ the hydroxylation of alkanes with *t*-butyl hydroperoxide,¹⁰ and the synthesis of *N*-alkylacetamides and alkyl halides from alkanes.¹¹

We report here on the preparation of a ruthenium lacunary substituted heteropolyanion, $\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}^{5-}$, and the use of this ruthenium polyoxotungstate as a catalyst for the oxidation of alkenes and alkanes with various primary oxidants. The reactivity and selectivity of the oxidations are found to be strongly influenced by the oxidant used indicating different catalytic pathways in each case. The ruthenium heteropolyanion was synthesized by a procedure analogous to that used for the preparation of a similar rhodium heteropolyanion¹² by adding $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (1.05 mmol) to an aqueous solution (100 ml) containing $\text{K}_8\text{SiW}_{11}\text{O}_{39}^{13}$ (1 mmol) at 80 °C. The brown-black solution was left at this temperature for 30 min and then cooled to 50 °C whereupon methanol (80 ml) was added to precipitate a sticky ruthenium compound. The solid was triturated with acetone and a fine black powder was collected, yield 70%. Elemental analysis† of the product using atomic absorption for potassium and ruthenium,¹⁴ gravimetric analysis of silicon as SiO_2 and tungsten as the 8-hydroxyquinolinotungstate, and thermogravimetric analysis for water indicates a compound with the molecular formula, $\text{K}_5\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39} \cdot 15\text{H}_2\text{O}$. The heteropolyanion was made soluble in organic solvents by replacing the potassium cation with the tetra-*n*-hexylammonium cation, yielding $[(\text{C}_6\text{H}_{13})_4\text{N}]_5\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$ (**1**), yield 95%.‡

Four different oxidants, *t*-butyl hydroperoxide, potassium persulphate (Oxone), sodium periodate, and iodosylbenzene were used in the oxidation of alkanes and alkenes as summarized in Table 1 and Table 2 respectively. The heteropoly compound (**1**) is an effective catalyst with all four oxidants; however activity and product selectivity differ significantly depending on the primary oxidant used. The oxidations by *t*-butyl hydroperoxide (TBHP) show high activity but low selectivity to identifiable products. In alkane oxidation selectivity to oxygenation was about 45–50%, the ratio of oxygenation at tertiary vs. secondary carbons was low (2.5:1), and alcohols and ketones were formed in almost equivalent amounts. In the oxidation of alkenes allylic oxidation was prominent for cyclohexene (45% selectivity) whereas for oct-1-ene where allylic oxidation is more difficult almost no oxygenated products were identified. The more active styrene gave a variety of oxygenated products. All reactions were accompanied by non-productive decomposition of TBHP to oxygen and *t*-butyl alcohol.

Table 1. Oxidation of alkanes catalysed by $[(\text{C}_6\text{H}_{13})_4\text{N}]_5\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$.^a

(A) Substrate: adamantane		Product yield ^b , %			
Oxidant	t/h	2-ol	2-one	1-ol	Other ^c
KHSO_5	1 ^d	2.2	17.6	35.9	—
KHSO_5^e	5	2.4	2.5	9.6	—
NaIO_4	7	—	1.1	21.3	—
NaIO_4^e	24	—	—	—	—
PhIO	4	1.0	2.6	7.0	—
PhIO ^e	4	0.2	0.6	1.6	—
Bu^tOOH	2 ^f	2.2	2.8	12.7	18.3
Bu^tOOH^e	5	0.2	0.2	1.2	—

(B) Substrate: cyclohexane		Product yield ^b , %		
Oxidant	t/h	Alcohol	Ketone	Other ^c
KHSO_5	3	—	17.7	5.1
KHSO_5^e	5	—	<0.1	<0.1
NaIO_4	4	—	2.7	—
NaIO_4^e	8	—	—	—
PhIO	5	0.2	2.3	—
PhIO ^e	8	—	—	—
Bu^tOOH	3 ^f	6.3	6.9	10.3
Bu^tOOH^e	8	0.4	1.2	—

^a Reaction conditions: 1 mmol of substrate, 5 mmol of oxidant (for KHSO_5 2.5 mmol Oxone; Bu^tOOH tech., 70%), 0.002 mmol of $[(\text{C}_6\text{H}_{13})_4\text{N}]_5\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$, 5 ml of 1,2-dichloroethane, temp. 60 °C. In reactions with KHSO_5 and NaIO_4 the oxidant was dissolved in 5 ml of water and 0.02 mmol of Bu_4NHSO_4 was added as phase transfer agent. ^b Yields are based on starting substrate, and were determined by g.l.c. analysis using authentic samples as references on a FFAP 10 m \times 0.53 μm capillary column. ^c Other products were not identified. ^d Addition of 2 mmol of KHSO_5 after 2 h gave a 78.4% total conversion of adamantane. ^e Control reaction carried out in the absence of the ruthenium heteropolyanion. ^f The conversion of Bu^tOOH was complete.

† For $\text{K}_5\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39} \cdot 15\text{H}_2\text{O}$, calc. (found) K: 6.0% (6.0%), Si: 0.9, (0.7), Ru: 3.1 (3.0), W: 62.05 (60.8), H_2O 8.8 (8.5).

‡ Analysis of the organic cation; for $[(\text{C}_6\text{H}_{13})_4\text{N}]_5\text{SiRu}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}$, calc. (found) C: 30.7% (29.3%), H: 5.7 (5.5), N: 1.5 (1.1).

Table 2. Oxidation of alkenes catalysed by $[(C_6H_{13})_4N]_5SiRu(H_2O)W_{11}O_{39}^{5-}$ ^a

(A) Substrate: cyclohexane					Product yield ^b , %	
Oxidant	t/h	Epoxide	2-enone	2-enol	Adipic acid ^c	Other ^d
KHSO ₅	3	—	—	—	78(64) ^e	<0.1
KHSO ₅ ^f	3	—	—	—	5(2) ^e	—
NaIO ₄	3	—	—	—	15.2	34.8 ^g
NaIO ₄ ^f	8	—	—	—	—	—
PhIO	4	4.1	5.6	2.1	1.2	3.3
PhIO ^f	4	0.1	0.2	0.1	—	—
Bu ^t OOH	1 ^h	—	28.7	1.3	—	25.2
Bu ^t OOH ^f	7	—	4.7	2.1	—	5.1

(B) Substrate: oct-1-ene			Product yield ^b , %	
Oxidant	t/h	1,2-Epoxide	Heptanoic acid	Other ^d
KHSO ₅	4	10.3	30.1	18.5 ⁱ
NaIO ₄	4	—	1.8	—
PhIO	6	5.4	9.8	7.8
Bu ^t OOH	4	—	<0.1	10.3

(C) Substrate: styrene				Product yield ^b , %		
Oxidant	t/h	PhCHO	PhCO ₂ H	PhCH(O)CH ₂	PhCH ₂ CHO	Other ^d
KHSO ₅	2	3.3	95	—	—	—
NaIO ₄	2	98	—	—	—	—
PhIO ^j	2	21.2	5.1	3.8	3.1	—
Bu ^t OOH ^j	2	14.4	4.2	1.0	2.8	9.5

^a Reaction conditions: as for Table 1. ^b Yields as for Table 1. ^c Determined by g.l.c. using PhBr as external standard. ^d Other products were not identified. ^e Isolated yield from the aqueous phase. ^f Control reaction carried out in the absence of the ruthenium heteropolyanion. ^g Adipaldehyde, CHO(CH₂)₄CHO, was the product. ^h The conversion of Bu^tOOH was complete. ⁱ Octan-2-ol was the product. ^j Reactions carried out with 1 mmol of oxidant.

Potassium persulphate may be considered analogous to TBHP as it is also a hydroperoxide; however, the results of the oxidation reactions were considerably different. In the oxidation of adamantane the ratio of oxygenation at tertiary vs. secondary carbons was low (1.8 : 1), as for TBHP, but there were no side products and adamantan-2-ol was formed in only a small amount. Oxidation of the less active cyclohexane gave cyclohexanone along with some unidentified products. Alkene oxidation is typified by oxidative bond cleavage yielding the corresponding acid. For oct-1-ene the intermediate epoxide was quite stable and acid-catalysed hydration (Oxone in water is highly acidic) of the double bond was significant. As in the case of TBHP the ruthenium heteropolyanion catalysed the decomposition of persulphate to potassium hydrogen sulphate and oxygen, and this competed with the oxidation of the substrate.

In oxidations with Oxone and TBHP the organic phase retained the original brown-black colour of (1), whereas addition of sodium periodate and iodosylbenzene turned the catalyst colourless pointing to different oxidation states of the ruthenium cation. Sodium periodate was found to be a very selective oxidant. The finding that adamantane was oxidized almost exclusively at the tertiary position coupled with the relative inertness of cyclohexane clearly demonstrates that alkane oxidation at tertiary carbons is feasible with almost no oxidation at secondary or primary positions. This trend of organic substrate sensitivity carries over into alkene oxidation where one finds that oct-1-ene is almost inert and active substrates are oxidatively cleaved quite selectively to aldehydes. Iodosylbenzene was the least active oxidant overall and for oxidation of alkanes similar in product distribution to potassium persulphate. In the oxidation of alkenes iodosylbenzene gave the entire range of oxidation reactions including epoxidation, bond cleavage, and allylic oxidation in addition to the formation of unidentified products.

The reactivity and varying product distributions in the oxidation of alkanes and alkenes by the four different oxidants used show that the ruthenium heteropolyanion, SiRu-(H₂O)W₁₁O₃₉⁵⁻, is a versatile and robust catalyst for the oxygenation of hydrocarbons.

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