

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243821974>

Hydroxylation of Alkanes with Molecular Oxygen Catalyzed by a New Ruthenium-Substituted Polyoxometalate, $[WZnRu_2III(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$

ARTICLE in ANGEWANDTE CHEMIE INTERNATIONAL EDITION IN ENGLISH · AUGUST 1995

Impact Factor: 13.45 · DOI: 10.1002/anie.199515871

CITATIONS

73

READS

45

3 AUTHORS, INCLUDING:



Alex M Khenkin

Weizmann Institute of Science

78 PUBLICATIONS 1,825 CITATIONS

SEE PROFILE

than the fluorine atoms because of its partial double-bond character; the apical position of a pentagonal pyramid is well suited for such particularly large ligands; the nonbonding electron pair can occupy the *trans* apical position. In contrast to the central atom in BrF_6^- and XeF_8^{2-} ,^[12,13] the xenon atom in XeOF_5^- is coordinatively unsaturated. It forms intermolecular Xe–F contacts (278.4 and 298.5 pm) with two fluorine atoms of adjacent anions. This additional coordination still leaves enough space for the nonbonding lone pair. On the other hand, these intermolecular interactions are comparatively weak and have no strong structure-determining influence. We had not previously found a suitable solvent for high-resolution NMR measurements of $\text{NO}^+\text{XeOF}_5^-$. $\text{NO}^+\text{XeOF}_5^-$ dissolves in acetonitrile; in the ^{19}F NMR spectrum at -40°C a broad signal (600 Hz) is observed at $\delta = 141$; this is explained by an intermolecular fluorine exchange.

Experimental Procedure

XeOF_4 and NOF (in the approximate ratio 1:1) were condensed under vacuum (stainless steel vacuum apparatus) into a perfluoroethene–propene (Teflon–FEP) tube, which was then sealed. The liquid phase solidified slightly below room temperature to form large crystals that were partly formed by sublimation as well. Crystal structure analysis: A suitable crystal with dimensions $0.4 \times 0.4 \times 0.4$ mm was mounted at low temperature ($T = -153^\circ\text{C}$) on an Enraf–Nonius CAD4 diffractometer; space group $P2_1/n$ (no. 14), $a = 669.8(1)$, $b = 551.0(1)$, $c = 1425.1(2)$ pm, $\beta = 101.2(2)^\circ$, $V = 515.9(1)$ pm³, $Z = 4$, $2\theta_{\text{max}} = 90^\circ$, $\text{MoK}\alpha$, 71.069 pm, ω scan, 4275 measured reflections of which 4169 were independent and 4150 used, Lorentz polarization correction, Difabs absorption correction [14], $\mu = 68.3$ mm⁻¹, min./max. correction 0.73/1.10, structure solved with the program SHELXS-86 [15], structure refinement with SHELXL-93 [16], 83 parameters, $R_1 = 0.0296$, $wR_2 = 0.0806$, extinction coefficient 0.0114(9), residual electron density $2.7 \text{ e}^- \times 10^3 \text{ pm}^{-3}$ (80 pm from xenon atom). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-58969.

Received: March 15, 1995 [Z77981E]

German version: *Angew. Chem.* **1995**, *107*, 1772–1773

Keywords: fluorine compounds · xenon compounds

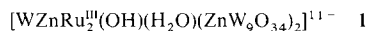
- [1] J. F. Martins, E. B. Wilson, Jr., *J. Mol. Spectr.* **1968**, *26*, 410–417; *J. Chem. Phys.* **1964**, *41*, 570–571; E. J. Jacob, H. B. Thompson, L. S. Bartlett, *J. Mol. Struct.* **1971**, *8*, 383–394.
- [2] A. G. Robiette, R. H. Bradley, P. N. Brier, *J. Chem. Soc. D* **1971**, 1567–1568.
- [3] A. J. Edwards, P. Taylor, *J. Chem. Soc. Dalton Trans.* **1975**, 2174–2177.
- [4] H. Selig, *Inorg. Chem.* **1966**, *5*, 183–186; D. E. McKee, C. J. Adams, A. Zalkin, N. Bartlett, *J. Chem. Soc. Chem. Commun.* **1973**, 26–28; D. E. McKee, C. J. Adams, N. Bartlett, *Inorg. Chem.* **1973**, *12*, 1722–1725; R. J. Gillespie, G. J. Schrobilgen, *ibid.* **1974**, *13*, 2370–2374.
- [5] K. O. Christe, *Inorg. Chem.* **1972**, *11*, 1215–1219; A. R. Mahjoub, A. Hoser, J. Fuchs, K. Seppelt, *Angew. Chem.* **1989**, *101*, 1528–1529; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1526–1527.
- [6] J. H. Holloway, V. Kaucic, D. Martin-Rovet, D. R. Russell, G. J. Schrobilgen, H. Selig, *Inorg. Chem.* **1985**, *24*, 678–683; G. J. Schrobilgen, D. Martin-Rovet, P. Charpin, M. Lance, *J. Chem. Soc. Chem. Commun.* **1980**, 894–897.
- [7] A. R. Mahjoub, K. Seppelt, *Angew. Chem.* **1991**, *103*, 309–311; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 323–324.
- [8] R. D. Burbank, G. R. Jones, *J. Am. Chem. Soc.* **1974**, *96*, 43–48.
- [9] H. H. Rupp, K. Seppelt, *Angew. Chem.* **1974**, *86*, 669–670; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 612–613; K. Seppelt, H. H. Rupp, *Z. Anorg. Allg. Chem.* **1974**, *409*, 331–337; K. Seppelt, N. Bartlett, *ibid.* **1977**, *436*, 122–126; G. J. Schrobilgen, J. H. Holloway, P. Granger, C. Brevard, *Inorg. Chem.* **1978**, *17*, 980–987.
- [10] K. O. Christe, D. A. Dixon, J. C. P. Sanders, G. J. Schrobilgen, S. S. Tsai, W. W. Wilson, *Inorg. Chem.* **1995**, *34*, 1868.
- [11] G. J. Moody, H. Selig, *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 319–320.
- [12] A. R. Mahjoub, A. Hoser, J. Fuchs, K. Seppelt, *Angew. Chem.* **1989**, *101*, 1528–1529; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1526–1527; A. R. Mahjoub, X. Zhang, K. Seppelt, *Chem. Eur. J.* **1995**, *1*, 261–265.
- [13] S. W. Peterson, J. H. Holloway, B. A. Coyle, J. M. Williams, *Science* **1971**, *173*, 1238–1239.
- [14] N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158–166.
- [15] G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, **1986**.
- [16] G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, **1993**.

Hydroxylation of Alkanes with Molecular Oxygen Catalyzed by a New Ruthenium-Substituted Polyoxometalate, $[\text{WZnRu}_2^{\text{III}}(\text{OH})(\text{H}_2\text{O})(\text{ZnW}_9\text{O}_{34})_2]^{11-}$

Ronny Neumann,* Alexander M. Khenkin, and Mazal Dahan

The utilization of dioxygen in liquid-phase oxidation of hydrocarbons is currently an important research goal due to its availability and its benign effect on the environment. Since dioxygen has a triplet ground state, direct oxidation of organic compounds is not possible. Common modes of dioxygen “activation” thus include a) formation of hydrocarbon radicals leading to formation of reactive hydroperoxides by free-radical autoxidation mechanisms,^[1] b) photoexcitation of dioxygen to form highly reactive singlet oxygen,^[2] c) use of dioxygen as a secondary oxidant in metal-ion-catalyzed mechanisms as in Wacker-type processes,^[3] and d) reductive cleavage of transition-metal dioxygen complexes to form highly active metal–oxo intermediates as in manganese porphyrins^[4] and the various Gif systems.^[5] A more desirable mode of activation would be the direct use of dioxygen to elicit oxygenation without formation of hydrocarbon radicals, or use of photoexcitation or reducing agents. A few such examples exist including alkene epoxidation with ruthenium porphyrins^[6] and alkane hydroxylation with perfluorinated iron porphyrins,^[7] although recently evidence has been put forward claiming that the latter is a free-radical autoxidation.^[8]

In this paper we report on the preparation of a diruthenium-substituted polyoxometalate **1** and its use as a catalyst for the



hydroxylation of alkanes such as adamantane with molecular oxygen at atmospheric pressure. Hydroxylation takes place almost *exclusively* at the tertiary carbon positions. This regioselectivity indicates that the oxidation is not a typical free-radical autoxidation and that the ruthenium-substituted polyoxometalate activates molecular oxygen in a non-radical pathway. Supportive of this conclusion are the findings that adamantane is more reactive than triphenylmethane, that the reaction is not inhibited by the presence of alkyl-radical scavengers such as *tert*-butylcatechol, and that oxidation with hydroperoxides (required intermediates in autoxidations) yield significantly different reaction selectivities.

The polyoxometalate may be viewed as a dimer of a truncated Keggin structure having a “belt” of W, Zn, and Ru cations sandwiched between the two $\text{B-XW}_9\text{O}_{34}$ trivacant Keggin fragments (Fig. 1). This new ruthenium polyoxometalate is isostructural with other similar transition-metal-substituted compounds reported^[9,10] and used previously.^[11] Temperature-dependent magnetic susceptibility measurements^[12] and the EPR spectrum^[13] of the polycrystalline solid both support the X-ray analysis, indicating that the polyoxometalate should be viewed as a compound with two hexacoordinate ruthenium(III) centers at the designated terminal positions with one labile aqua

[*] Dr. R. Neumann, Dr. A. M. Khenkin, M. Dahan
Casali Institute of Applied Chemistry, Graduate School of Applied Science
The Hebrew University of Jerusalem, Jerusalem 91904 (Israel)
Telefax: Int. code + (26) 528250
e-mail: ronny@vms.huji.ac.il

[**] This research was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities. We thank Dr. Shmuel Cohen for the crystallographic analysis.

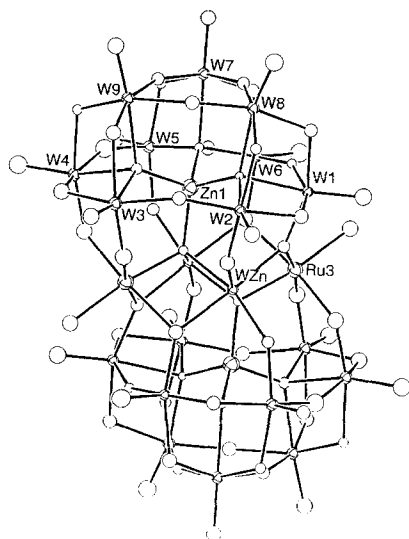


Fig. 1. Ortep drawing of the crystal structure of the anion in $\text{Na}_{11}\text{-1}$.

and one hydroxy ligand. Cyclic voltammetry shows a reversible $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ oxidation at + 0.38 V.

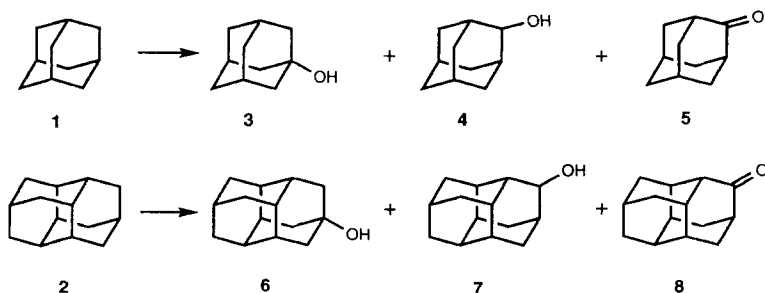
The results of the oxidation reactions are summarized in Table 1. Substrates such as adamantane (**1**) and congressane (**2**)

Table 1. Hydroxylation of alkanes catalyzed by ruthenium polyoxometalate [a].

Substrate	Products (mol product/mol catalyst)			
1 [b]	3 (103–118)	4 (trace)	5 (trace)	
1 [c]	3 (369)	4 (trace)	5 (3)	
1 [d]	3 (92)	4 (trace)	5 (trace)	
1 [e]	3 (trace)	4 (trace)	5 (trace)	
1 [c, e]	3 (38)	4 (2)	5 (13)	
2	6 (87)	7 (trace)	8 (trace)	
2 [d]	6 (78)	7 (trace)	8 (trace)	
<i>c</i> - C_6H_{12} [f]				
<i>i</i> - $\text{C}_6\text{H}_5\text{Ph}$ [f]				
Ph_3CH	Ph_2CO (5)	Ph_3COH (15)		
Ph_2CH [d]	Ph_2CO (11)	Ph_3COH (20)		
Ph_2CH_2 [f]				
1 [g]	3 (trace)	4 (trace)	5 (trace)	
1 [h]	3 (156)	4 (22)	5 (37)	

[a] See Experimental Procedure. [b] Range for five reactions. [c] Reaction time 7 days. [d] 1 mmol *tert*-butylcatechol added. [e] No catalyst; conversion in % $\times 10$. [f] No reaction. [g] Catalyst $\text{PRuW}_{11}\text{O}_{39}^{4-}$. [h] Catalyst $\text{PRuMo}_{11}\text{O}_{39}^{4-}$.

having both tertiary and secondary saturated carbon atoms that bear hydrogen atoms react virtually only at the tertiary position yielding 1-adamantanol (**3**) and 1-congressanol (**6**). Very little alcohol or ketone is formed at the secondary carbon.^[14]



Further confirmation of this trend can be seen in the complete inactivity of alkanes with only secondary carbon centers such as cyclohexane and diphenylmethane. Under free-radical conditions, normal ratios of oxidation at tertiary vs. secondary positions is 3:1. Furthermore, addition of the alkyl-radical scavenger, *tert*-butylcatechol, even at four times the amount of alkane substrate, caused only a very slight decrease in catalytic activity.^[15] Additionally, alkylaromatic compounds such as cumene and triphenylmethane, known to be relatively highly reactive to free-radical autoxidations, were inactive or only slightly active in the presence of the disubstituted ruthenium polyoxometalate. Finally, oxidations with of adamantane with *tert*-butylhydroperoxide yielded a ratio of oxidation tertiary/secondary of 6.7:1. Assuming similar regioselectivity of all tertiary hydroperoxides, this result would also seem to indicate that adamantane hydroperoxide, the expected intermediate in an autoxidation pathway, is not an intermediate in the oxidation with molecular oxygen. Other ruthenium-substituted polyoxometalates reported in the literature were inactive ($\text{PRuW}_{11}\text{O}_{39}^{4-}$,^[16] $\text{SiRuW}_{11}\text{O}_{39}^{5-}$,^[17] yielded the usual ratio of autoxidation products ($\text{PRuMo}_{11}\text{O}_{39}^{4-}$,^[18] or are known to form μ -oxo dimers ($(\text{P}_2\text{W}_{17}\text{O}_{61}\text{Ru})_2\text{O}^{16-}$).^[19] It would be presumptuous at this stage to give a mechanistic explanation for our findings; however, a variety of explanations ranging from formation of caged hydrocarbon radicals within **1** to formation of active ruthenium-oxo intermediates is to be explored. The mechanistic uncertainty, however, does not detract from the importance of the discovery of a new mode of dioxygen activation in the hydroxylation of alkanes by use of a novel "oxidatively stable"^[20] ruthenium-substituted polyoxometalate.

Experimental Procedure

The ruthenium-disubstituted polyoxometalate $\text{Na}_{11}\text{-1} \cdot 42\text{H}_2\text{O}$ was prepared by adding $\text{Ru}[(\text{CH}_3)_2\text{SO}]_4\text{Cl}_2$ (4.0 g, 12.2 mmol) to a solution of $\text{Na}_2\text{Zn}_3(\text{H}_2\text{O})_2\text{W}_{10}\text{O}_{68} \cdot 46\text{H}_2\text{O}$ (23 g, 3.9 mmol) in water (10 mL) at 90 °C under argon. The solution was stirred at this temperature for 18 h, then cooled, and opened to air. When 2 g of KCl was added to the brown solution, 10.9 g of the desired compound precipitated. The product was recrystallized twice from hot water. Overall yield: 24%; anal. calcd for $\text{K}_{11}\text{Ru}_2\text{Zn}_3\text{W}_{10}\text{O}_{68} \cdot 15\text{H}_2\text{O}$: K 6.97, Ru 3.60, Zn 3.50, W 62.32, H_2O 4.82; found K 7.06, Ru 3.56, Zn 3.24, W 61.30, H_2O 4.69. Single crystals for X-ray analysis were obtained by recrystallizing 0.12 g of the potassium salt in 10 mL of 0.5 M NaCl solution.

A stock solution of $2.71 \times 10^{-4}\text{ M}$ $\text{Q}_{11-1}\text{Na}_4\text{-1}_2$ (Q = tricaprilmethylammonium) was prepared by mixing $\text{Na}_{11}\text{-1}_2 \cdot 42\text{H}_2\text{O}$ (1 g) dissolved in water with tricaprilmethylammonium chloride (1 g) dissolved in 1,2-dichloroethane (10 mL), separating phases, and drying the organic phase with Na_2SO_4 . Concentrations were determined by UV-Vis spectroscopy: $\lambda_{\text{max}}(\epsilon) = 306\text{ nm}(50000\text{ M}^{-1}\text{cm}^{-1})$.

Hydroxylation reactions were carried out by holding a solution of substrate (0.25 mmol) and ruthenium polyoxometalate (0.25 μmol , 0.1 mol%) in 1,2-dichloroethane (0.5 mL) under dioxygen (10 mL, approximately 0.45 mmol) at atmospheric pressure at 80 °C for 24 h. After cooling, reaction mixtures were analyzed unambiguously by GLC with two different columns using reference samples; the product identity was crosschecked by GLC-MS.

Received: February 1, 1995

Revised version: April 3, 1995 [Z 7677 IE]

German version: *Angew. Chem.* **1995**, *107*, 1740–1742

Keywords: oxygen activation • polyoxometalates • ruthenium compounds

- [1] R. A. Sheldon, J. K. Kochi, *Metal Catalysed Oxidation of Organic Compounds*, Academic Press, New York, **1981**.
- [2] H. H. Wassermann, R. W. Murray, *Singlet Oxygen*, Academic Press, New York, **1978**.
- [3] G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, 2. ed., Wiley, New York, **1992**, p. 138.
- [4] I. Tabushi, *Coord. Chem. Rev.* **1988**, *86*, 1.
- [5] D. H. R. Barton, E. Csuhi, N. Ozbalik, *Tetrahedron* **1990**, *46*, 3743.
- [6] J. T. Groves, R. Quinn, *J. Am. Chem. Soc.* **1985**, *107*, 5790.

