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Hydroxylation of Alkanes with Molecular Oxygen Catalyzed by a New Ruthenium-Substituted Polyoxometalate, [WZnRu2III(OH)(H2O)(ZnW9O34)2]11-

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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 NO + XeOF₅. NO + XeOF₅ dissolves in acetonitrile; in the ¹⁹F 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

XeOF4 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 °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, $\beta = 101.2(2)^{\circ}$, $V = 515.9(1) \text{ pm}^3$, Z = 4, $2\theta_{\text{max}} = 90^{\circ}$, $Mo_{\text{K}\alpha}$, 71.069 pm, ω scan, 4275 measured reflections of which 4169 were independent and 4150 used. Lorentz polarization correction, Difabs absorption correction [14], $\mu = 68.3 \text{ mm}^{-1}$, 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 $2.7 \,\mathrm{e}^{-} \times 10^6 \,\mathrm{pm}^{-3}$ (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

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Hydroxylation of Alkanes with Molecular Oxygen Catalyzed by a New Ruthenium-Substituted Polyoxometalate, [WZnRu₂^{III}(OH)(H₂O)(ZnW₉O₃₄)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 availibility 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 dirutheniumsubstituted polyoxometalate 1 and its use as a catalyst for the

 $[WZnRu_{2}^{III}(OH)(H_{2}O)(ZnW_{Q}O_{34})_{2}]^{11}$ 1

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 oxidaton 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 B-XW₉O₃₄ 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 measurments^[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

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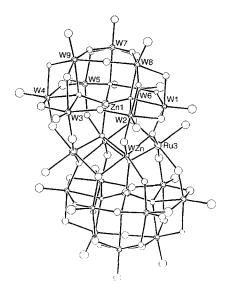


Fig. 1. Ortep drawing of the crystal structure of the anion in Na₁₁-1.

and one hydroxy ligand. Cyclic voltammetry shows a reversible Ru^{II}/Ru^{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)
c-C ₆ H ₁₂ [f] i-C ₆ H ₇ Ph [f]			
Ph ₃ CH	Ph ₂ CO (5)	Ph ₃ COH (15)	
PH ₃ CH [d] Ph ₂ CH ₃ [f]	Ph ₂ CO (11)	Ph ₃ COH (20)	
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 PRuW₁₁O₃⁴. [h] Catalyst PRuMo₁₁O₃⁴.

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 $(PRuW_{11}O_{39}^{4-},^{[16]}SiRuW_{11}O_{39}^{5-}),^{[17]}$ yielded the usual ratio of autoxidation products $(PRuMo_{11}O_{39}^{4-})$, [18] or are known to form μ -oxo dimers $((P_2W_{17}O_{61}Ru)_2O^{16-})$. [19] It would 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 Na_{11} -1·42 H_2O was prepared by adding $Ru[(CH_3)_2SO]_4Cl_2$ (4.0 g, 12.2 mmol) to a solution of $Na_{12}Zn_3$ - $(H_2O)_2Zn_2W_{19}O_{68}\cdot 46\,H_2O$ (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 $K_{11}Ru_2Zn_3W_{19}O_{68}\cdot 15\,H_2O$: $K_{6.97}$, $Ru_{3.60}$, $Zn_{3.50}$, $W_{62.32}$, $H_2O_{4.82}$; 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 $2.71\times10^{-4} \mathrm{M~Q_{11-x}Na_x^{-1}_2}$ (Q= tricaprylmethylammonium) was prepared by mixing $\mathrm{Na_{11}^{-1}_2\cdot42\,H_2O}$ (1 g) dissolved in water with tricaprylmethylammonium chloride (1 g) dissolved in 1,2-dichloroethane (10 mL), separating phases, and drying the organic phase with $\mathrm{Na_2SO_4}$. Concentrations were determined by UV-Vis spectroscopy; $\lambda_{\mathrm{max}}(c)=306\,\mathrm{nm}(50\,000\,\mathrm{M^{-1}cm^{-1}})$.

Hydroxylation reactions were carried out by holding a solution of substrate (0.25 mmol) and ruthenium polyoxometalate (0.25 μ mol, 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.

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The Crafts-Friedel Reaction: Aromatic Alkylation within the Complex Formed upon Addition of a Gaseous Arenium Ion to an Olefin**

Massimiliano Aschi, Marina Attinà, and Fulvio Cacace*

Alkylation of arenes with olefins, one of the most important industrial applications of Friedel-Crafts reactions, proceeds by preliminary protonation of the alkenes by Brønsted acids such as H(BF₃OH), H(AlCl₃OH), H₂SO₄, followed by addition of the carbenium ions formed, or their polarized complexes, to the arene [Eq. (a)]. An alternative route is conceivable, in which alkylation occurs within a complex formed upon addition of an arenium ion to the olefin [Eq. (b)].

$$C_3H_6 + HA \longrightarrow iC_3H_7 - A \xrightarrow{\delta_+ + C_6H_6} \xrightarrow{H} iC_3H_7 + A \xrightarrow{iC_3H_7}$$
 (a)

$$C_6H_7^+ + C_3H_6 \longrightarrow [C_6H_7^+ \cdot C_3H_6] \longrightarrow [C_6H_6 \cdot iC_3H_7^+] \longrightarrow 1$$
 (b)

Sequence (b) represents a distinct reaction pathway, with special kinetic and mechanistic features, only if alkylation occurs within the complex, without separation of the reagents. If, on

the contrary, the carbenium ion escapes into the medium and reacts with the arene only at some later stage, the whole sequence is tantamount to a conventional Friedel—Crafts alkylation whose only peculiarity is that the acid used to protonate the olefin is an arenium ion.

Aromatic alkylation promoted by the reaction of arenium ions with olefins was envisaged long ago by Olah, [2] but because discrimination between the alternative pathway (b) and the conventional mechanism (a) is extremely difficult in solution, further developments were blocked. We report here the first demonstration that the alkylation mechanism outlined in sequence (b) is actually operative in the gas phase and present a preliminary account of its essential features, deduced from the joint application of mass spectrometry and radiolysis. [3]

To demonstrate operation of sequence (b) in the gas phase, preliminary FT-ICR experiments were performed, where $C_6H_6D^+$ benzenium ions (m/z=80), obtained by chemical ionization of $[^{12}C]C_6H_6$ with CO/D_2 in the external ion source of the spectrometer, were driven into the resonance cell, isolated by multiple ejection techniques, and allowed to react with C_3H_6 . As expected, at the low stationary pressure (less than 5×10^{-7} Torr) of the cell, the $C_9H_{12}D^+$ ion from sequence (b) could not be detected, owing to its fast back dissociation under conditions of inefficient collisional stabilization.

However, by using a pulsed valve one can obtain, albeit for a short time (5 ms), C_3H_6 pressures up to 5×10^{-5} Torr, which allows stabilization of a fraction of the $C_9H_{12}D^+$ ions, which can thus be positively identified by accurate mass measurements (Fig. 1). Despite their low relative abundance (<5%) formation of the $C_9H_{12}D^+$ ions is significant, since it can only occur within the complex formed by the reactants. In fact, no C_6H_6 is introduced into the reaction cell, which excludes the role of any free $iC_3H_6D^+$ as a source of the $C_9H_{12}D^+$ ion observed. [4]

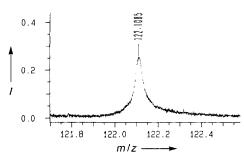


Fig. 1. Exact mass analysis of the $C_9H_{12}D^+$ adduct from the reaction of $C_6H_6D^+$ with C_3H_6 under the conditions given in the text. Relative ionic intensity in arbitrary units.

The FT-ICR results are consistent with, but do not prove the occurrence of sequence (b) since the data give no structural information, and it cannot be excluded that the $C_9H_{12}D^+$ ions observed are noncovalent complexes, like 2 and/or 3, rather than protonated cumene 1. More conclusive evidence was obtained from the radiolytic experiments (see Table 1).

In the experiments a bulk gas, for example, CH_3F at atmospheric pressure, containing small amounts of the reactants $(C_6D_6$ and $C_3H_6)$, a radical scavenger (O_2) , and a gaseous base such as $(CH_3)_2O$, is subjected to γ irradiation. According to a well-established reaction sequence. ^[5] ionization of CH_3F produces stable $(CH_3)_2F^+$ ions that react efficiently with C_6D_6 to give $C_6D_6CH_3^+$ ions. ^[6] which are largely converted by the base into $C_6D_5CH_3$, a major radiolytic product. ^[7] Those toluenium ions that escape deprotonation are available to promote iso-

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