

ditions, no *E* to *Z* isomerization and no rearrangement of the exocyclic double bond occurred [exo methylene protons **5a-d** δ 4.14-4.98 and 4.89-4.98; *E* internal for **5a-d** δ 5.57-5.72 (*J* = 16 Hz) and 5.93-6.16 (*J* = 16 Hz)].

The palladium-catalyzed cyclization of other substrates bearing different functional groups by the coupling of various organostannane and electrophilic termini is being explored.

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The Selective Oxidation of Primary Alcohols to Aldehydes by O₂ Employing a Trinuclear Ruthenium Carboxylate Catalyst

Carl Bilgrien, Shannon Davis, and Russell S. Drago*

Department of Chemistry, University of Florida
Gainesville, Florida 32611

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Though many reports describe trinuclear ruthenium carboxylates as catalysts,¹ none of these systems utilize dioxygen as the primary oxidant. We have found Ru₃O(O₂CR)₆L₃ⁿ (R = CH₃ or C₂H₅; L = H₂O or PPh₃; n = 0, +1) to be an efficient catalyst for the selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones by O₂ under mild conditions.

Ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, *tert*-butyl alcohol, and cyclohexanol were investigated as substrates. The primary alcohols were oxidized more rapidly than secondary alcohols, while tertiary alcohols were unreactive under the conditions employed. Typical oxidations utilized 50 mL of substrate/solvent, 1 mL of a ketone standard, and generally were 10⁻³ M in catalyst. Reactions were run in a 65 °C oil bath under an initial pressure of 40 psi of dioxygen and monitored over a 12- or 24-h period by GC and GCMS. At 25 °C, ethanol was not oxidized while *n*-propyl alcohol was oxidized only slightly. All the other substrates except *tert*-butyl alcohol were oxidized at 65 °C. Increasing the temperature to 100 °C increased the rate of the reaction but also increased the rate of catalyst deactivation. No induction period was observed in these reactions and in all cases the oxidations were 100% selective for the carbonyl product. Further oxidation of product aldehydes to acids was not observed, and acetal or ketal formation was only observed when acetaldehyde was formed in ethanol solution. Several different ruthenium carboxylate complexes were found to be effective catalysts. The mixed-valence, neutral carboxylates, Ru₃O(prop)₆(H₂O)₃ (prop = CH₂CH₂CO₂⁻) and Ru₃O(prop)₆(PPh₃)₃, were slightly more active^{2a} than their cationic congeners, Ru₃O(OAc)₆(H₂O)₃⁺ and Ru₃O(prop)₆(H₂O)₃⁺.

For mechanistic studies we chose the Ru₃O(prop)₆(H₂O)₃⁺-catalyzed oxidation of isopropyl alcohol. This catalyst was pre-

pared by using a modification of the original synthesis.³ Liquid chromatography on a Sephadex gel was used instead of precipitating the complex from a solution of the crude carboxylate. Three bands resulted which were characterized by elemental analysis, IR, NMR, and UV-visible spectroscopy. The middle fraction corresponded most closely⁴ to the complex reported by Wilkinson and was the only catalytic fraction.

The trinuclear complex was compared with two monomeric ruthenium compounds reported to catalyze alcohol oxidations. Hydrated ruthenium trichloride has been reported to oxidize secondary alcohols at 100 °C and 1 atm of O₂, albeit slowly.⁵ The other compound studied, RuCl₂(PPh₃)₃, has been used to dehydrogenate secondary alcohols to ketones and primary alcohols to aldehydes and acetal mixtures under a variety of conditions.⁶ The trinuclear carboxylate complex is as selective as either RuCl₃·(H₂O)_x or RuCl₂(PPh₃)₃ and approximately 10 times more active.^{2b}

UV-visible spectroscopy has been very informative in determining the active species in solution. Since no induction period is observed for this reaction, either the trinuclear carboxylate is the active catalytic species or it is a precursor that converts rapidly to the active species in solution. A distinct color change is observed when an alcoholic solution of the catalyst is heated to 43 °C under an inert atmosphere; the changes in the spectra correspond to the conversion of the ruthenium(III,III,III) to the ruthenium(III,III,II) complex as reported by Wilkinson.³ However, if ketone were produced during this reduction, the amount produced (assuming a stoichiometric conversion either per mole of catalyst or per mole of ruthenium) was too small to be detected by GC. This change is reversible; the addition of either O₂, 30% H₂O₂, or air to the warm alcohol solution immediately oxidizes the (III,III,II) to the (III,III,III) species. The color change corresponding to the reduced (III,III,II) complex is not observed under our catalytic conditions (40 psi O₂); however, this complex could be a transient species.

Attempts to characterize the spent catalyst were unsuccessful. After 1000 turnovers were achieved (143 h), the UV-vis spectrum showed essentially no change in the catalyst. The solid recovered after 135 turnovers (43 h) contained a small amount of unidentified impurity, but both ¹H NMR and FTIR confirmed the presence of starting material. None of these results identify the nature or the nuclearity of the active species in solution.

To eliminate the possibility of a free radical chain mechanism, several reactions were carried out with use of free radical initiators and free radical traps. ABMP (2,2'-azobis(2-methylpropionitrile)), a free radical initiator, was used in place of the catalyst and produced insignificant amounts of product after 12 h. The addition of the free radical trap, benzoquinone, to a typical oxidation with catalyst present had no effect on the reaction.

A dual GC analysis (using FID and TCD detectors) of an isopropyl alcohol reaction revealed that for every mole of acetone produced, 1 mol of water was formed. Monitoring the O₂ consumption revealed that 2 mol of product were formed for every mole of O₂ consumed, indicating the four-electron reduction of O₂ to H₂O. One four-electron step seemed unlikely; two two-electron steps with H₂O₂ as an intermediate are more probable, even though identification of H₂O₂ in the reaction mixture was unsuccessful. Added H₂O₂ is rapidly consumed with accelerated carbonyl formation and thus would not be expected to exist in appreciable concentrations during the catalysis.

Isopropyl alcohol oxidations catalyzed by Ru₃O(prop)₆(H₂O)₃⁺ exhibit a slight rate dependence upon acidity. Brønsted acids, HClO₄ and CF₃SO₃H, had an inhibiting effect as did Cu(II) and Zn(II). Isopropyl alcohol oxidation was accelerated by sodium

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(2) Isopropyl alcohol oxidation under standard conditions. Turnover numbers (t.o.) = (mmol of product)/(mmol of catalyst). (a) Ru₃O(OAc)₆(H₂O)₃⁺, 270 t.o./24 h; Ru₃O(prop)₆(H₂O)₃⁺, 254 t.o./24 h; Ru₃O(prop)₆(H₂O)₃, 764 t.o./24 h; Ru₃O(prop)₆(PPh₃)₃, 904 t.o./24 h. (b) Ru₃O(prop)₆(H₂O)₃⁺, 112 t.o./12 h; RuCl₃, 5.5 t.o./12 h (3 × 10⁻³ M catalyst); RuCl₂(PPh₃)₃, 12 t.o./12 h.

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(4) Anal. Calcd: C, 28.49; H, 4.68; N, 0.00. Found: C, 27.34; H, 4.32; N, 0.44. ¹H NMR δ 2.18 (q, 2 H, anion), 1.42 (q, 12 H, bridge), 1.08 (t, 3 H, anion), 0.80 (t, 18 H, bridge).

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ethoxide but inhibited by 2,6-lutidine, while addition of NaOH precipitated the catalyst. Gagné and Marks have reported⁷ oxidative dehydrogenation of alcohols catalyzed by ruthenium complexes of 1,3-bis(2-pyridylimino)isindolines. The necessary addition of strong base in their oxidations was attributed to base-promoted disproportionation⁸ of Ru(III): $2\text{Ru(III)} \rightleftharpoons \text{Ru(II)} + \text{Ru(IV)}$. Catalysis with the triruthenium carboxylates may involve intramolecular disproportionation, precluding the need for base promotion. Unique to this system, however, is the redox role of the ancillary metal centers⁹ and the possible participation of the central μ_3 -oxygen atom. More detailed mechanistic and kinetic studies are under way.

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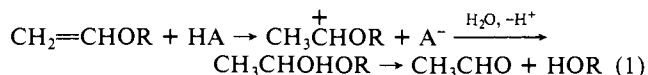
Reexamination of the Alleged Vinyl Ether Hydrolysis Reaction of 9-Methoxy-1-oxacyclonon-2-ene: Disproof of Reversible Carbon Protonation

R. A. Burt, Y. Chiang, W. K. Chwang, A. J. Kresge,*
T. Okuyama, Y. S. Tang, and Y. Yin

Department of Chemistry, University of Toronto
Toronto, Ontario M5S 1A1, Canada

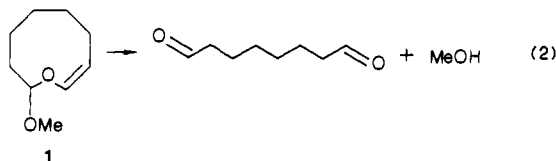
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The conventional reaction mechanism for acid-catalyzed hydrolysis of vinyl ethers consists of rate-determining proton transfer from catalyst to substrate followed by rapid hydration of the cation so formed and further fast decomposition of the ensuing hemiacetal, eq 1. This reaction scheme is based upon a sizeable body



of evidence obtained by examining a number of different substances,¹ and the reaction has acquired the status of a prototype process; it has been used to provide detailed information not only about the proton-transfer process but also on the hydration of carbon-carbon double bonds.

Some time ago an exception to this general mechanism was claimed for the case of 9-methoxy-1-oxacyclonon-2-ene (**1**).² The hydrolysis of this substance to suberaldehyde, eq 2, appeared to



occur by reaction of its vinyl ether functional group through the

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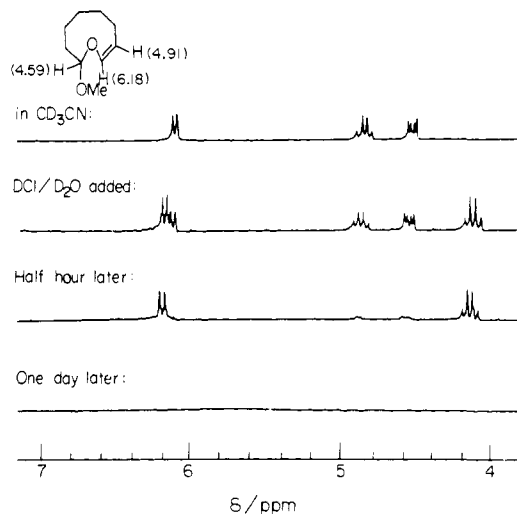


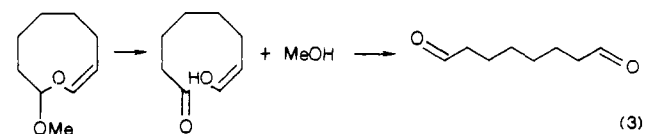
Figure 1. Proton NMR spectral changes occurring during the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene; spectra measured at 200 MHz in CD_3CN and in 10:1 $\text{CD}_3\text{CN}/0.1 \text{ M DCl-D}_2\text{O}$ solutions.

mechanism of eq 1 when the reaction was carried out in dilute hydrochloric acid solutions. In acetic acid buffers, however, buffer catalysis became saturated as buffer concentration increased, and the hydronium ion isotope effect, which was normal ($k_{\text{H}^+}/k_{\text{D}^+} > 1$) in hydrochloric acid solutions, became inverse ($k_{\text{H}^+}/k_{\text{D}^+} < 1$). This behavior was taken to indicate that carbon protonation had become reversible in the presence of a sufficient concentration of buffer base and that some subsequent step was then rate determining.

We have searched, in vain, for other examples of reversible carbon protonation in the hydrolysis of vinyl ethers.³ We now report that this phenomenon is absent in the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene as well.

The hydrolysis of vinyl ethers may be monitored by following the change in strong UV absorbance at 200-220 nm which is characteristic of carbon-carbon double bonds bearing oxygen substituents. We have found that in the case of 9-methoxy-1-oxacyclonon-2-ene this change is biphasic: there is an initial increase followed by a somewhat slower decrease. This process is accompanied by a corresponding biphasic change in the NMR spectra of reaction mixtures (Figure 1): upon addition of a small amount of aqueous acid to an acetonitrile solution of 9-methoxy-1-oxacyclonon-2-ene, the original vinyl proton signals at 6.18 and 4.91 ppm are replaced by a new set at 6.22 and 4.16 ppm, and these new signals then disappear leaving this region of the spectrum bare. Similar changes occur with wholly aqueous solutions, and these are accompanied by the appearance of signals attributable to aldehyde protons at 9.66 ppm and aldehyde hydrate methine protons at 5.02 ppm.

This emergence of a new set of vinyl proton NMR signals means that the hydrolysis of 9-methoxy-1-oxacyclonon-2-ene cannot be occurring through initial hydrolysis of its vinyl ether group, for that would lead to a simple monophasic loss of the original vinyl group signals without production of a new set. Initial hydrolysis of the acetal function, on the other hand, would give an enol with a new vinyl group (eq 3); enols, moreover, are known to have vinyl



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