

# Alkane Oxidations by a Novel $\mu_3$ -Oxo Trinuclear Ruthenium Carboxylate Complex

Shannon Davis and Russell S. Drago\*

University of Florida, Department of Chemistry, Gainesville, Florida 32611, U.S.A.

A new  $\mu_3$ -oxo trinuclear ruthenium carboxylate catalytic system is reported which effects the air oxidation of alkanes under conditions that are much milder than possible with present commercial catalysts; the mechanism involves a radical chain process and the catalyst is proposed to initiate the reaction in addition to catalysing the hydroperoxide decomposition to ketone and alcohol.

Our studies of trinuclear carboxylate complexes have revealed their potential as oxidation catalysts. In previous work, we have shown  $[\text{Ru}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^n$  (where R = Me, Et; L =  $\text{H}_2\text{O}$ ,  $\text{PPh}_3$ ;  $n = 0, +1$ ) to be efficient catalysts for the selective oxidation of alcohols to aldehydes using molecular oxygen as the primary oxidant.<sup>1</sup> These complexes are inactive as alkene oxidation catalysts under our conditions.

More recent work from our laboratory has shown a novel trinuclear ruthenium complex containing completely fluorinated carboxylate ligands,  $[\text{Ru}_3\text{O}(\text{pfb})_6(\text{Et}_2\text{O})_3]^+$  (where pfb =  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2^-$ ), which will oxidize alkenes with  $\text{O}_2$  via a free radical pathway. These free radical reactions of alkenes have little synthetic utility. However, the high oxidation potential of complexes of fluorinated carboxylates<sup>3</sup> and the ability of this complex to catalyse the oxidation of alkenes with  $\text{O}_2$  suggested the extension of this reaction to other more interesting substrates known to be oxidized by a radical chain mechanism. One such substrate, cyclohexane, is oxidized with air industrially<sup>4</sup> at high temperatures (165 °C) and pressures (10 atm). The selective oxidation of this substrate under mild conditions is a highly desired objective, both from commercial and fundamental standpoints.<sup>5</sup> In this article, we report that the perfluorinated ruthenium trimer  $[\text{Ru}_3\text{O}(\text{pfb})_6(\text{Et}_2\text{O})_3]^+$  catalyses the oxidation of alkanes under mild conditions using  $\text{O}_2$  as the primary oxidant.

Under our reaction conditions (75 °C, 3 atm air, using 40 ml substrate, 10 ml acetonitrile solvent, and  $10^{-5}$  moles of catalyst), cyclohexane is oxidized to a 5:1 mixture of cyclohexanol and cyclohexanone (15 turnovers to alcohol/3 turnovers to ketone). Methylcyclohexane is oxidized to 1-methylcyclohexanol (~10 turnovers), 2- and 3-methylcyclohexanols (~4 turnovers), and trace amounts of 2-methylcyclohexanone. No products due to the oxidation of the methyl group were observed. *n*-Hexane in acetonitrile solvent is not oxidized; however, switching to *m*-pyrrol (1-methyl-2-pyrrolidinone) as solvent produces a 1:1 mixture of hexan-2-ol and hexan-2-one as products (corresponding to 16 turnovers) along with trace quantities of hexan-1-ol. Under these conditions, 2- and 3-methylpentane and cyclohexanol are not oxidized.

Various additives and other metal cocatalysts have been extensively studied for cyclohexane oxidations in the hope of improving yields or suppressing undesirable side reactions. Bromide ions have long been used as promoters in free radical reactions, and the addition of NaBr to the oxidations shows

the expected increase in product formation. Other studies have shown  $\text{Cr}^{\text{III}}$  enhances ketone production (primarily by increasing the rate of oxidation of cyclohexanol). While iron(III) increases alcohol production, manganese salts generally increase yields of alcohols and acids in cyclohexane oxidations, and copper has been reported to decompose alkylhydroperoxides catalytically. The effects of these additives on the ruthenium-catalysed oxidation of cyclohexane were found to follow similar trends (Table 1). The only surprising result was the complete inhibition of the reaction by the addition of Cu.<sup>2,4</sup> Since both metals are known to decompose peroxides, the bimetallic system should not have been inactive. Copper is one of the catalysts used in the oxidation of KA oil (the product mixture of ketone and alcohol) to adipic acid, so the products formed by this system may have been undetectable under the conditions of analysis used. For comparison to the ruthenium-based system, a sample of the commercial catalyst, cobalt octanoate  $[\text{Co}(\text{oct})_2]$  was tested and found to be inactive under our conditions.

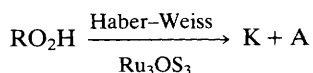
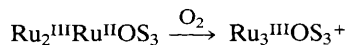
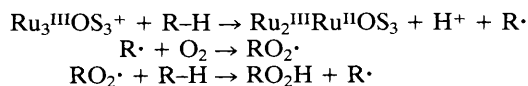
The fate of the catalyst can be easily monitored using  $^{19}\text{F}$  NMR. The NMR spectra of the catalyst before and after a typical cyclohexane oxidation show little change. FTIR of the catalyst before and after also shows little change, indicating that the catalyst is relatively stable during the oxidation.

Acetonitrile, the solvent of choice, and cyclohexane are only slightly miscible at 75 °C. The biphasic nature of the solution implies that catalysis occurs at the interface of the droplets formed as the mixture is vigorously stirred. In order to draw the catalyst into the substrate phase and thereby enhance the catalysis, sodium octanoate  $[\text{Na}(\text{oct})]$  was tried as a phase transfer reagent. The reaction rate increases with the addition of this material, but two phases still exist with little evidence of the catalyst being drawn into the substrate phase even upon addition of 4 moles of  $\text{Na}(\text{oct})$  per mole of catalyst.

Table 1. Cyclohexane oxidation studies: additives.<sup>a</sup>

Conditions	Turnovers/12 h <sup>b</sup>		Mole ratio Alcohol/ Ketone
	Alcohol	Ketone	
Standard <sup>c</sup>	14.8	3.2	4.6
$\text{Mn}^{2+}$	37.0	9.0	4.1
$\text{Br}^-$	65.1	16.2	4.0
$\text{Fe}^{3+}$	39.7	3.3	12.0
$\text{Cr}^{3+}$	150.3	45.7	3.3
$\text{Cu}^{2+}$	—	—	—
$\text{Co}(\text{oct})_2^{\text{d}}$	—	—	—

<sup>a</sup>  $10^{-5}$  moles of additive were used in combination with  $10^{-5}$  moles of catalyst. See text for details. <sup>b</sup> Turnovers = mole of product/mole of catalyst in the specified time. <sup>c</sup> Standard conditions are  $10^{-5}$  mole of catalyst ( $[\text{Ru}_3\text{O}(\text{pfb})_6(\text{Et}_2\text{O})_3]^+$ ). All cations are added as metal chloride salts. <sup>d</sup>  $\text{Co}^{\text{II}}$  octanoate, Du Pont's commercial catalyst (trade name Cobalt Hex-Cem, Mooney Chemical Co.) was employed without the ruthenium catalyst in this experiment.



Scheme 1

Previous studies have shown that while  $\text{Mn}^{\text{II}}$  stearate will catalyse alkane oxidations, the combination of  $\text{Mn}^{\text{II}}$  and potassium stearate is five times more effective<sup>6</sup> and a similar synergistic effect may be in operation here.

The addition of the free radical inhibitor benzoquinone to the reaction decreased the amount of total product formed by one third. Using AIBN (azoisobutyronitrile), a free radical initiator, with the ruthenium catalyst had no effect, while AIBN alone did not initiate the reaction. These experiments indicate the reaction is occurring *via* the expected free radical chain pathway with the ruthenium perfluorobutyrate complex catalysing the reaction under milder conditions than AIBN.

Sharpless<sup>7</sup> has published a method for titrating peroxides in organic solvents that has proven to be useful with several modifications in other biphasic catalyst systems studied in this laboratory.<sup>8</sup> A blank titration of the cyclohexane stirred for 3 h under  $\text{O}_2$  showed  $10^{-6}$  *N*-peroxides. A blank consisting of the oxidation mixture (containing all components of a typical oxidation except catalyst) run for 12 h under 3 atm air showed a peroxide concentration two orders of magnitude larger than in the starting material blank. With the ruthenium catalyst added, approximately  $10^{-3}$  *N*-peroxide is found after 12 h.

Though not impossible, we consider it unlikely that, if the complex functioned solely as a more efficient hydroperoxide decomposition catalyst, a larger steady state concentration of the hydroperoxide would result during the oxidation. These experiments suggest that the trimer is initiating the reaction to form alkylhydroperoxides. The alkyl radicals thus generated by electron or hydrogen atom transfer to the high oxidation state form of the ruthenium complex in the system probably react with  $\text{O}_2$  and additional substrate to form hydroperoxides

as intermediates in a chain reaction. The trimer then catalyses the hydroperoxide decomposition *via* a Haber-Weiss mechanism. The reduced form of the trimer could be reoxidized by  $\text{O}_2$ , reforming the initial species and continuing the cycle. This mechanism is summarized in Scheme 1, where  $\text{Ru}_3^{\text{III}}\text{O}^+$  refers to  $\text{Ru}_3\text{O}(\text{ppb})_6^+$ . Except for the metal role in the initiation step, this mechanism is similar to that previously reported.<sup>5</sup>

The support of the National Science Foundation through Grant #86 18766 is acknowledged. Mooney Chemical Company graciously donated  $\text{Co}(\text{oct})_2$ .

Received, 10th August 1989; Com. 9/03428E

## References

- 1 C. Bilgrien, S. Davis, and R. S. Drago, *J. Am. Chem. Soc.*, 1987, **109**, 3786, and references cited therein.
- 2 S. Davis and R. S. Drago, *Inorg. Chem.*, 1988, **27**, 4759.
- 3 R. S. Drago, J. R. Long, and R. Cosmano, *Inorg. Chem.*, 1982, **21**, 2196.
- 4 G. W. Parshall, 'Homogeneous Catalysis,' Wiley International Science, New York, 1980, p. 190.
- 5 C. Tolman, J. D. Druliner, M. J. Nappa, and N. Herron, 'Alkane Oxidation Studies in Du Pont's Central Research Department' in 'Activation and Functionalization of Alkanes,' ed. C. Hill, Wiley, New York, 1988.
- 6 J. E. Lyons, 'Catalytic Oxidation of Hydrocarbons in the Liquid Phase' in 'Applied Industrial Catalysis,' vol. 3, ch. 6, ed. B. E. Leach, Academic Press, New York, 1984.
- 7 Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765.
- 8 J. Ramsden, R. S. Drago, and R. Riley, *J. Am. Chem. Soc.*, 1989, **111**, 3958.