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Ruthenium-catalysed oxidation of alkanes with peracetic acid in trifluoroacetic acid: ruthenium as an efficient catalyst for the oxidation of unactivated C–H bonds

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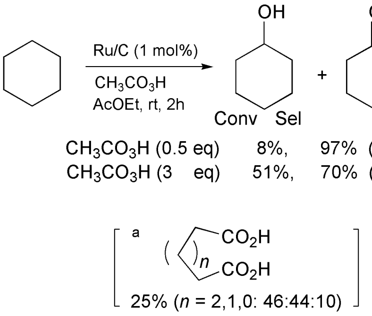
The role of ruthenium catalysts for the oxidation of alkanes with peracetic acid in trifluoroacetic acid has been confirmed.

During the course of simulation of the functions of cytochrome P-450 enzyme with transition metal complexes, we have found that transition metal-catalysed oxidations of various substrates can be performed highly efficiently.[1] In 1994 we reported that ruthenium-catalysed oxidation of alkanes with peracetic acid in ethyl acetate gives the corresponding ketones and alcohols.[2] Furthermore, the $RuCl_3$-catalysed oxidation of cyclohexane in TFA proceeds highly efficiently to give cyclohexyl trifluoroacetate and cyclohexanone with high conversion and high selectivity.[2] Recently, Moody and O'Connell reported that the oxidation of cyclohexane using urea hydrogen peroxide (UHP) in TFA without a metal catalyst gives cyclohexyl trifluoroacetate,[3] which was originally reported by Deno *et al*.[4] They obtained the rate constants ($k = 3.3 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$) for the oxidation of cyclohexane with UHP in TFA in the presence or absence of $RuCl_3$ catalyst, indicating that the system is not ruthenium dependent. They claimed our system (peracetic acid–Ru) is not ruthenium dependent. However, our system using peracetic acid is quite different from that of UHP oxidation. Here, we describe our ruthenium-catalysed oxidation of alkanes with peracetic acid, which is very fast and an efficient ruthenium dependent reaction. The kinetics show the rate is 10^5 times faster than previously reported.

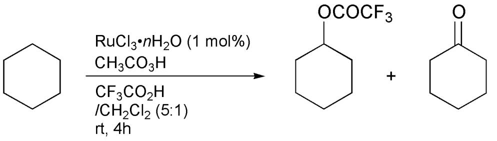
As described in our previous paper,[2] the oxidation of cyclohexane with peracetic acid in the presence of ruthenium on charcoal (Ru/C) or $RuCl_3$ (1 mol%) catalyst in ethyl acetate gives cyclohexanone along with a small amount of cyclohexanol [eqn. (1)]. No oxidation takes place without a catalyst.



(1)

Treatment of cyclohexane with 0.5 eq. of peracetic acid proceeds in the presence of Ru/C catalyst to give cyclohexanol and cyclohexanone (4 : 93) with 97% selectivity (conv. 8%). In contrast, treatment of cyclohexane with 3 eq. of peracetic acid afforded cyclohexanol and cyclohexanone (2 : 68) with 70% selectivity along with dicarboxylic acids (adipic acid–glutaric acid–succinic acid = 46 : 44 : 10), which are derived from the oxidation of cyclohexane-1,2- and -1,3-diones under the reaction conditions, with 25% selectivity (conv. 51%). Peracetic acid is quite effective for the ruthenium-catalysed oxidation of alkanes, while hydrogen peroxide does not give any oxidation product because of the decomposition of hydrogen peroxide to give O_2 and H_2O by the contact with $RuCl_3$, indicating that peracetic acid is clearly different from hydrogen peroxide in the present non-TFA system.

In order to generate more active oxo-metal species which may lead to high conversion and high selectivity for the oxidation of alkanes,[5–7] we used TFA. As described in our previous paper,[2] the $RuCl_3$-catalysed oxidation of cyclohexane with peracetic acid in a mixture of TFA and CH_2Cl_2 (5 : 1) for 4 h gave cyclohexyl trifluoroacetate and cyclohexanone with 90% selectivity (85 : 15) and 90% conversion [eqn. (2)]. However,



(2)

the same reaction in the absence of $RuCl_3$ for 24 h gave cyclohexyl trifluoroacetate only in < 3% yield.

The present catalytic oxidation can be applied to a variety of alkanes. The representative results of the ruthenium-catalysed oxidation of alkanes with peracetic acid in a mixture of TFA and CH_2Cl_2 are shown in Table 1. Both linear and cyclic alkanes can be converted into the corresponding esters of trifluoroacetic acid along with ketones. The reaction of adamantane gave adamantan-1-ol, which was formed by hydrolysis of 1-adamantyl trifluoroacetate.

Kinetic experiments on the reaction of cyclohexane with peracetic acid in TFA were carried out. In the presence of a large excess of cyclohexane, the rate was first-order with respect to

Table 1 Ruthenium-catalysed oxidation of alkanes with peracetic acid in TFA[a]

Alkane	Conversion[b] (%)	Product	Yield[c] (%)
Cyclohexane	90	Cyclohexyl trifluoroacetate	77
		Cyclohexanone	13
Cyclooctane	81	Cyclooctyl trifluoroacetate	40
		Cyclooctanone	10
Adamantane[d]	70	Adamantan-1-ol[e]	89
		2-Adamantyl trifluoroacetate	9
Norbornane[f]	90[g]	*exo*-2-Norbornyl trifluoroacetate	61
Hexane	nd	Hexyl trifluoroacetates[h]	24[b]
		Hexanones[i]	6[b]

[a] To a mixture of alkane (2.5 mmol), $RuCl_3$ (0.025 mmol), TFA (5 mL) and CH_2Cl_2 (1 mL) was added dropwise a 30% peracetic acid (5.0 mmol) solution in ethyl acetate over a period of 2 h. After stirring for 2 h, the reaction was quenched by adding 5% aqueous sodium sulfite solution. [b] Determined by GC based on the starting alkane using an internal standard (acetophenone). [c] Determined by GC based on the converted alkane. [d] TFA (5 mL), CH_2Cl_2 (10 mL) and acetic acid (5 mL) were used as a solvent. [e] 1-Adamantyl trifluoroacetate was readily hydrolyzed to give adamantan-1-ol during the work up. [f] The IUPAC name for norbornane is bicyclo-[2.2.1]heptane. [g] Not determined. [h] 2-:3-Hexyl trifluoroacetate = 45:55. [i] 2-:3-One = 34:66.

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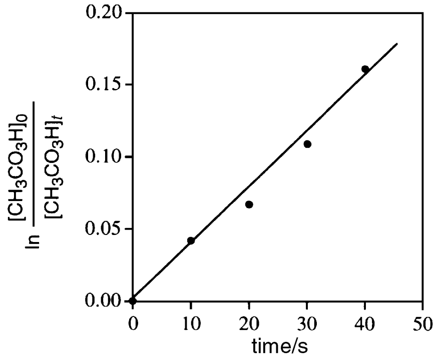

Fig. 1 Pseudo-first-order rate plot of the ruthenium-catalysed oxidation of cyclohexane with peracetic acid in the presence of TFA. Solvent, TFA–CH_2Cl_2–AcOEt = 5:1:1; [$RuCl_3$] = 7.1×10^{-4} M; [CH_3CO_3H] = 1.4×10^{-2} M; [cyclohexane] = 3.6×10^{-1} M; 20 °C; $k_{obsd} = 3.9 \times 10^{-3}$ s^{-1}.

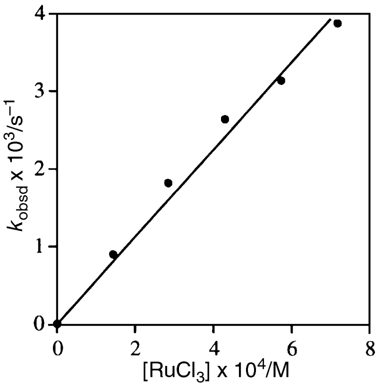

Fig. 2 Dependence of the first-order rate constants k_{obsd} on the concentration of $RuCl_3$. Solvent, TFA–CH_2Cl_2–AcOEt = 5:1:1; [CH_3CO_3H] = 1.4×10^{-2} M; [cyclohexane] = 3.6×10^{-2} M; 20 °C.

the concentration of peracetic acid (Fig. 1). The first-order rate constant increased with an increase in the concentration of $RuCl_3$ (Fig. 2), but the rate constant was independent of the concentration of cyclohexane. The rate law for the ruthenium-catalysed oxidation of cyclohexane with peracetic acid in TFA and CH_2Cl_2 was expressed by the equation ($-$d[cyclohexane]/dt = k[$RuCl_3$][CH_3CO_3H]). The second-order rate constant was determined to be $k = 5.4\ M^{-1}\ s^{-1}$. In contrast, the rate constant for the oxidation of cyclohexane without a metal catalyst is very small ($k < 10^{-6}\ s^{-1}$). These results clearly show that the oxidation of cyclohexane is catalysed by $RuCl_3$ catalyst dramatically.

Intermolecular deuterium isotope effect (k_H/k_D) of the ruthenium-catalysed oxidation of cyclohexane–cyclohexane-d_{12} in TFA was determined to be 2.9, which is smaller than the value (6.8) obtained from the same oxidation in ethyl acetate, indicating that a more reactive species is involved in the oxidation in TFA. The oxidation can be rationalized by assuming the mechanism which involves oxo-ruthenium species. The reaction of L_nRu^{III} with peracetic acid would give $L_nRu^{III}OOC(O)CH_3$ which undergoes heterolytic cleavage[8] to give the L_nRu^V=O species. Hydrogen abstraction with the oxo-ruthenium species and recombination would give an alcohol. Under the reaction conditions, an alcohol can be converted into either the corresponding trifluoroacetate or ketone. Actually, control experiments show that cyclohexanol is readily converted to a mixture of cyclohexyl trifluoroacetate and cyclohexanone under the reaction conditions.[9] The ruthenium-catalysed oxidation with peracetic acid is quite different from the oxidation with hydrogen peroxide in TFA, where electrophilic reaction of perfluoroacetic acid is involved. It is noteworthy that cyclohexanone has never been obtained from the reaction of H_2O_2–TFA.[3,4]

In summary, the oxidation of alkanes with peracetic acid in TFA proceeds efficiently in the presence of ruthenium catalyst to give the corresponding trifluoroacetic acid ester.

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