Pergamon

Tetrahedron Letters 39 (1998) 1353–1356

TETRAHEDRON
LETTERS

Ruthenium Colloids: A New Catalyst for Alkane Oxidation by tBHP in a Biphasic Water-Organic Phase System.

Franck Launay, Alain Roucoux and Henri Patin*

Laboratoire de Chimie Organique et des Substances Naturelles
associé au CNRS - Ecole Nationale Supérieure de Chimie de Rennes
Avenue du Général Leclerc - 35700 Rennes (France).

Received 15 September 1997; accepted 15 December 1997

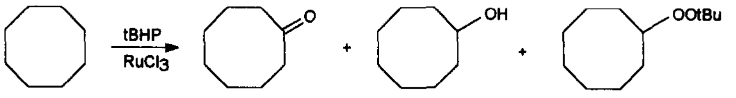
Abstract : *Efficient and highly selective conversion of cyclooctane into cyclooctanone is obtained under pure biphasic conditions through t-butylhydroperoxide activation by the in situ formation of colloidal ruthenium species arising from $RuCl_3$, $3H_2O$. Model extension experiments to other cycloalkanes are also discussed.* © 1998 Elsevier Science Ltd. All rights reserved.

Hydrocarbon oxidation by oxygen catalyzed by soluble cobalt complexes is still one of the largest scale applications of homogeneous catalysis.[1] However, kinetic stability and low reactivity of alkanes require such drastic reaction conditions that high conversion and selectivity cannot be achieved simultaneously. Consequently, the search for reactions catalyzed by transition metal derivatives under milder conditions has received a great deal of interest.[2] To date, considerable efforts have been made to reproduce the performance of Cytochrome P450[3] or Methane MonoOxygenase enzymes[4] by building up various kinds of complexes based either on iron or exogeneous elements like ruthenium.[5] These approaches are extremely useful but often hampered by oxidative degradation of the organic ligands. Recently alternative models were explored such as catalysis on zeolites or other inorganic supports[6] and dispersions of colloidal metal oxides.[7] An original approach consisted in mixing two reverse microemulsions containing respectively the oxidant (H_2O_2 or tBHP) and the metallic salt leading rapidly to catalytically active colloidal particles. Very encouraging results have been obtained particularly because of the better control of peroxide consumption. However water or *tert*-butyl alcohol production lead to evolution of the system towards emulsions and we later found that the amphiphilic molecules used in the formulation could have opposite effects: a good protection of the colloidal aggregates against collapsing but the lowering of their catalytic activity.[8] We have now found that with other transition metals such as ruthenium, no additives were necessary.

In the present paper, we describe the results obtained in a pure biphasic system (water and organic phase *i.e.* the alkane to be oxidized) with ruthenium trichloride (colloid precursor) and tBHP as the oxygen source. The results of some typical experiments are listed in Table 1. The biphasic system is made of a vigorously stirred mixture of cyclooctane (a model alkane in this preliminary study) and an aqueous solution of $RuCl_3$ to which tBHP is added quickly at room temperature under air or if required oxygen or argon. After 3 h (almost total consumption of the oxidant) the GLC analysis[9] of the organic layer is performed after decantation and/or extraction by diethylether if needed. Cyclooctanone **1** is always the major product (entry 1); various amounts of cyclooctanol **2** and *tert*butylperoxycyclooctane **3** are also characterized. By analogy with the formation of an iron(III) species,[8] ruthenium trichloride is rapidly transformed into colloidal particles which remain in the aqueous phase after removal of the organic layer. This aqueous phase retains its catalytic properties (being recycled up to four times under similar conditions) without loss of activity and selectivity (**1/2/3**). We observed that addition of surfactants (Aerosol-OT: entry 2)[10] or polyanions[11] (triphenylphosphine oxide n-trisulfonate sodium salts : entry 3) have no effect on the catalytic activity. Thus, contrary to the iron case[8,11] the colloidal ruthenium species do not need external antiaggregants. This suggests that tertiobutylate residues may be present on the particles surface in sufficient amounts to prevent their collapsing and favor contact ruthenium colloids with the lipophilic substrate but with no excess in order to maintain an appropriate level of hydrophilicity. Detailed investigation of the catalyst's nature is under way.

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(97)10834-6

Table 1: Ruthenium colloids catalyzed oxidation of cyclooctane with tBHP[a]



1 2 3

Entry	Conditions	Products (mmol) 1	2	3	ratio one/ol	ratio 1/3	Efficiency[b] (%)	T.O.N.
1	A[d]	1.90	0.55	0.27	3.4	7.0	54	160
2	A[e]	1.80	0.30	0.33	6.0	5.5	50	143
3	A[e]	1.90	0.64	0.36	3.0	5.3	56	171
4	B	4.90	0	1.10	∞	4.5	29	200
5	A[f]	1.60	0.50	0.30	3.2	5.3	47	142
6	A[f]	2.40	0.13	0.40	19	6	62	173
7	A[f]	2.80	0.13	0.40	22	7	72	196
8	A[g]	1.70	0.30	0.20	5.7	8.5	46	130
9	A[g]	0.09	0.16	0.14	0.6	0.6	6	23
10	A[g]	1.00	0.34	0.21	2.9	4.8	30	92
11	A[g]	0.00	0.05	0.09	-	-	02	09

a) Reaction conditions are either (A) cyclooctane (57 mmol); aqueous $RuCl_3$, $6H_2O$ 0.025 M (0.017 mmol); tBHP 70% (8.6 mmol) or (B) cyclooctane (12.5 mmol); aqueous $RuCl_3$, $6H_2O$ 0.025 M (0.030 mmol); tBHP 70% (37.5 mmol). All runs were carried out at 20°C (0°C for B) and under air unless otherwise stated (3 hours). b) % Eff.= (2 R=O + R-OH + R-OOtBu) / tBHP. c) T.O.N.: moles of products per moles of catalyst. d) Oxidations run with the aqueous phase recovered after the first attempt still exhibited similar efficiencies and product distributions during at least four other cycles. e) Results for the reactions conducted either in reverse microemulsion (entry 2) or in emulsion (entry 3) after the addition of Aerosol-OT (20% in cyclooctane) or TPPTS (molar ratio TPPTS/Ru = 10). f) Experiments performed under anaerobic conditions with degassed solvents and reagents (entry 5) or aerobic conditions with oxygen : 1 atm (entry 6) and 10 atm (entry 7). g) Entries 8, 9, 10, 11 correspond respectively to the addition of carbon tetrachloride (1 mL), dimethyl sulfide (650 μL), acetonitrile (200 μL) or EtOH (5 mL) to the standard conditions (entry 1).

Very good yields can be obtained for instance by increasing the amount of tBHP (entry 4) or under an oxygen atmosphere (entries 6 and 7). In those conditions, the selectivity in the formation of ketone versus alcohol improves considerably. Starting under anaerobic conditions (entry 5), the system is less efficient; however one part of the oxidant introduced is transformed into oxygen (authentified by GLC analysis[12]), justifiying that the other experiments were conducted under aerobic conditions. Actually the best results (entry 7) are obtained under oxygen pressure, which favours the ketonisation process versus alcohol and dialkylperoxide productions.

At the very beginning of the reaction (tBHP addition) the mixture becomes blue, indicating the presence of Ru (II) species and then turns to red as long as tBHP is not entirely consumed. These observations militate in favor of the occurence of a Haber-Weiss decomposition of tBHP leading to tertiobutylperoxy and tertiobutoxy radicals with the concomittant disproportionation effect producing tertiobutanol and oxygen. The formation of $tBuO^{\bullet}$ and $tBuOO^{\bullet}$ are in good agreement with the participation of a radical pathway leading to **3** and eventually to cyclooctylhydroperoxide (not detected by GLC analysis)(Scheme1). However, this radical process is not the only one as shown by the results obtained in the presence of a radical scavenger (entry 8). Addition of acetonitrile (entry 10)[13] or dimethylsulfide (entry 9) have a much larger influence especially on the production of cyclooctanone.

$$2\,\mathrm{tBuOO}^{\bullet} \longrightarrow 2\,\mathrm{tBuO}^{\bullet} + \mathrm{O_2} \;;\; \mathrm{tBuO}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{tBuOH} + \mathrm{R}^{\bullet}$$
$$\mathrm{R}^{\bullet} + \mathrm{O_2} \longrightarrow \mathrm{ROO}^{\bullet} \;;\; \mathrm{ROO}^{\bullet} + \mathrm{tBuOO}^{\bullet} \longrightarrow \mathrm{O_2} + \mathrm{ROOtBu}$$
$$\mathrm{ROO}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet} \;;\; \mathrm{R}^{\bullet} + \mathrm{O_2} \longrightarrow \mathrm{ROO}^{\bullet}$$

Scheme 1 : radical reactions occuring in the process (R = cyclooctyl)

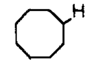
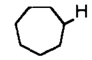
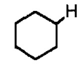
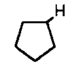
The efficient inhibition observed in the presence of Me_2S suggests that ruthenium oxo species of high oxidation level (Scheme 2) are the most effective catalysts for ketonisation.[14] Measurement of the primary Kinetic Isotope Effect (KIE = 12 for cyclohexane versus cyclohexane-d_{12}) is consistent with the C-H bond activation in the rate determining step by such oxo species.[15] Although quantification of tertiobutanol production could not be effected by GLC we have checked that even in large excess this alcohol does not affect the efficiency of the reaction contrary to methanol or ethanol which were probably oxidized into aldehydes (entry 11). In the presence of low molecular weight primary alcohols no alkane transformation was observed. Other oxidizing systems based on $RuCl_3$-tBHP have been described for efficient conversions of various alcohols into carbonyl derivatives.[16] However, kinetic studies of our reaction show that ketone **1** and alcohol **2** are formed independently and we have checked that in our conditions, compound **2** is very slowly oxidized.

$$\left.\begin{array}{l} \mathrm{Ru^{(III)}} + \mathrm{tBuOOH} \longrightarrow \mathrm{tBuOH} + \mathrm{Ru^{(V)}{=}O} \\ \mathrm{Ru^{(II)}} + \mathrm{tBuOOH} \longrightarrow \mathrm{tBuOH} + \mathrm{Ru^{(IV)}{=}O} \end{array}\right| \xrightarrow[\mathrm{O_2}]{\mathrm{RH}} \text{products}$$

Scheme 2 : formation of oxo ruthenium species (R=tBu ; cycloalkyl).

Finally, we have extended this cycloalkane functionalization to other substrates. The standard oxidation of cycloheptane (entry 12), cyclohexane (entry 13), cyclopentane (entry 14) was carried out at room temperature and the influence of cycloalkane size was studied by comparison with cyclooctane (entry 1) as model (Table 2). The results show that that cycloheptane and cyclooctane give similar results and appear to be three times more reactive than cyclohexane. Undoubtedly, carbon-hydrogen bond activation decreases with the cycle size in agreement with the poor turnover number of cyclopentane (compare entries 1 and 12 with entries 13 and 14).

Table 2: Functionalization of various cycloalkanes [a]

Entry	Substrate R-H	Products (mmol)			Efficiency[b] (%)	T.O.N.
		R=O	R-OH	R-OOtBu		
1		1.90	0.55	0.27	54	160
12		2.05	0.83	0.30	61	187
13		0.71	0.31	0.09	21	66
14		0.45	0.16	0.06	13	40

a) Reaction conditions: substrate (57 mmol); aqueous $RuCl_3, 6H_2O$ 0.025 M (0.017 mmol); tBHP 70% (8.6 mmol). All runs were carried out at 20°C. b) % Eff.= (2 R=O + R-OH + R-OOtBu) / tBHP. c) T.O.N.: moles of products per moles of catalyst.

Our results shed light on new interesting aspects of biphasic catalysis where the active species is able to functionalize hydrocarbons under mild conditions with high effciency and conversion rates at the surface of polynuclear aggregates. More detailed studies on the colloidal particles and on the mechanistic aspects of this reaction, actually in progress, will allow us to improve the understanding of this new biphasic system for C-H bond activation by taking into account very recent results on the distinction between radical and other types of activation in the field of Gif chemistry.[17]

Acknowledgment

We thank Sir Derek Barton (Texas A & M University) for helpful comments.

References and Notes

1 (a) Parshall, G.W.; Ittel, D.D. *Homogeneous Catalysis,* Wiley and Sons, New York, **1992**; (b) Schuchardt, U.; Carvalho, W.A.; Spinace, E.V. *Synlett* **1993**, *10*, 713-718.

2 (a) Davies, J.A. et al., *Selective Hydrocarbon Activation: Principle and Progress*, VCH, New York, **1994**; (b) Sheldon, R.A.; Kochi, J.K. *Metal Catalyzed Oxidations of Organic compounds*, Academic Press, New York, **1991**, 17-31.

3 (a) Sheldon, R.A.(Ed.) *Metalloporphyrins in catalytic oxidations*, Dekker, M.; New York, **1994**, 1-27; (b) Ortiz de Montellano, P.R.(Ed.) *Cytochrome P450: Structure, Mechanism and Biochemistry*, Plenum, New York, **1995**; (c) Newcomb, M.; Le Tadic-Biadatti, M.H.; Chestney, D.L.; Roberts, E.S.; Hollenberg, P.F. *J. Am. Chem. Soc.*, **1995**, *117*, 12085-12091; (d) Sono M.; Roach, M.P.; Coulter, E.D.; Dawson, J.H. *Chem. Rev.*, **1996**, *96*, 2841-2887.

4 (a) Shteinman, A.A. *Russ. Chem. Bull.*, **1995**, *44*, 975-984; (b) Rabion, A.; Chen, S.; Wang, J.; Buchanan, R.M.; Seris, J.L.; Fich, R.H. *J. Am. Chem. Soc.*, **1995**, *117*, 12356-12357; (c) Nguyen, C.; Guajardo, R.J.; Mascharak, P.K. *Inorg. Chem.*, **1996**, *35*, 6273-6281; (d) Kodera, M.; Shimakoshi, H.; Kano, K. *Chem. Commun.*, **1996**, 1737-1738; (e) Nivorozhkin, A.L.; Girerd, J.J. *Angew. Chem. Int. Ed. Engl. Tr.*, **1996**, *35*, 609-615; (f) Que Jr., L.; Dong, Y. *Acc. Chem. Res.*, **1996**, *29*, 190-196; (g) Que Jr., L.; Ho, R.Y.N. *Chem. Rev.*, **1996**, *96*, 2607-2624; (h) Wallar, B.J.; Lipscomb, J.D. *Chem. Rev.*, **1996**, *96*, 2625-2657; (i) Barton, D.H.R.; Hu, B.; Taylor, D.K.; Rojas Wahl, R.U. *J. Chem. Soc., Perkin Trans.*, **1996**, *2*, 1031-1041.

5 (a) Goldstein, A.S.; Drago, R.S. *J. Chem. Soc., Chem. Commun.*, **1991**, 21-22; (b) Bressan, M.; Morvillo, A.; Romanello, G. *J. Mol. Catal.*, **1992**, *77*, 283-288; (c) Murahashi, S.I.; Oda, Y.; Naota, T. *J. Am. Chem. Soc.*, **1992**, *114*, 7913-7914; (d) Murahashi, S.I.; Oda, Y.; Naota, T.; Kuwabara, T. *Tetrahedron Lett.*, **1993**, *34*, 1299-1302; (e) Bressan, M.; Forti, L.; Morvillo, A. *Inorg. Chim Acta*, **1993**, *211*, 217-220; (f) Murahashi, S.I.; Naota, T.; Komiya, N. *Tetrahedron Lett.*, **1995**, *36*, 8059-8062; (g) Groves, J.T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.*, **1996**, *118*, 8961-8962.

6 (a) Balkus Jr, K.J.; Eissa, M.; Levado, R. *J. Am. Chem. Soc.*, **1995**, *117*, 10753-10754; (b) Newmann, R.; Khenkin, A.M. *Chem. Commun.*, **1996**, 2643-2644; (c) Battioni, P.; Cardin, E.; Louloudi, M.; Schöllhorn, B.; Spyroulias, G.A.; Mansuy, D.; Traylor, T.G. *Chem. Commun.*, **1996**, 2037-2038.

7 (a) Briffaud, T.; Larpent, C.; Patin, H. *J. Chem. Soc., Chem. Commun.*, **1990**, 1193-1194; (b) Larpent, C.; Patin, H. *J. Mol. Catal.*, **1992**, *12*, 315-329.

8 (a) Launay, F.; Patin, H. *New J. Chem.*, **1997**, *21*, 247-256; (b) Launay, F. *Thesis University of Rennes, France*, **1995**.

9 The reaction products were quantified on Carlo Erba FTV 4000 Chromatograph equipped with AT1 column (30m * 0.25mm). Organic layer aliquots were diluted with a diethylether solution of naphtalene (internal standard).

10 Bis(2-ethylhexyl)sulfosuccinate de sodium.

11 Larpent, C.; Patin, H. *J. Mol. Catal.*, **1988**, *44*, 191-195.

12 Oxygen is detected on Delsi Chromatograph equipped with CTR I column.

13 (a) Lau, T.C.; Che, C.M.; Lee, W.O.; Poon, C.K. *J. Chem. Soc., Chem. Commun.*, **1988**, 1406-1407; (b) Taube, H. *Coord. Chem. Rev.*, **1978**, *26*, 33-45.

14 (a) Menage, S.; Vincent, J.M.; Lambeaux, C.; Chottard, G. ; Gret, A.; Fontecave, M. *Inorg. Chem.*, **1993**, *32*, 4766-4773; (b) Leising, R.A.; Kim, J.; Perez, M.A.; Que, L. *J. Am. Chem. Soc.*, **1993**, *115*, 9524-9530. (c) Menage, S.; Vincent, J.M.; Lambeaux, C. ; Fontecave, M. *J. Mol. Catal.*, **1996**, *113*, 61-75. (d) Kim, J. ; Kim, C.; Harrison, R.G.; Wilkinson, E.C.; Que Jr., L. J. Mol. Catal., **1997**, 117, 83-89.

15 (a) Groves, J.T.; Nemo, T.E. *J. Am. Chem. Soc.*, **1983**, *105*, 6243-6248; (b) Goldstein, A.S.; Beer, R.H.; Drago, R.S. *J. Am. Chem. Soc.*, **1994**, *116*, 2424-2429 and references included; (c) Murahashi, S.I. *Angew. Chem. Int. Ed. Engl. Tr.*, **1995**, *34*, 2443-2465.

16 Agarwal, D.D.; Jain, R.; Sangha, P.; Rastogi, R. *Indian J. Chem.*, **1993**, *32B*, 381-382.

17 Barton, D.H.R.; Launay, F. ; Le Gloahec, V.N. ; Li, T. ; Smith, F. *Tetrahedron Lett.*, **1997**, *38*, 8491-8494.