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Journal of Organometallic Chemistry 493 (1995) 143–147

Journal of Organometallic Chemistry

Aerobic epoxidation with a ruthenium-porphyrin catalyst: formation of an inactive carbonyl complex ☆

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Received 7 October 1994; in revised form 30 November 1994

Abstract

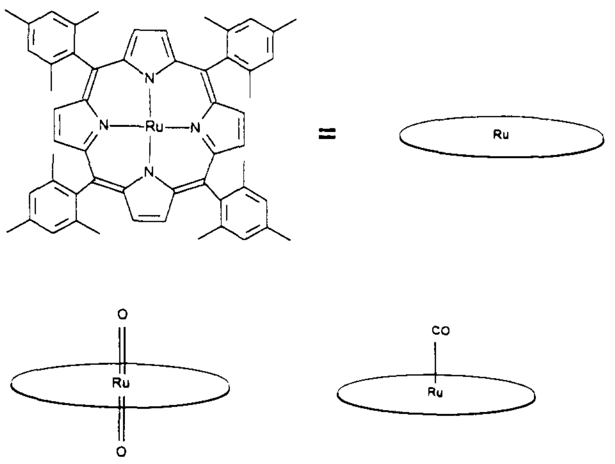
The aerobic epoxidation of linear terminal olefins such as oct-1-ene and propene can be accomplished by Ru(TMP)O_2, as catalyst with turn-overs of 40 and 36 respectively during 1 day. The catalytic activity of Ru(TMP)O_2 after this time has nearly completely vanished. The catalytic deactivation is partly due to the formation of a carbonyl species Ru(TMP)CO. About 30% of this complex relative to the amount of starting catalyst has been developed within 1 day. Ru(TMP)CO has been isolated from a catalytic reaction mixture, characterized by spectroscopic and crystallographic means and is catalytically not active. The source of CO is the alkene substrate. On-line Fourier transform IR and gas chromatography–mass spectroscopy experiments suggest a catalytic side reaction, breaking the substrate propene in presence of dioxygen into two parts: a $C_{(2)}$ moiety (acetic aldehyde, acetic acid) and as the $C_{(1)}$ moiety the CO coordinated to the ruthenium atom of a deactivated catalyst.

Keywords: Ruthenium; Porphyrin; Epoxidation; Catalyst; Crystal structure

1. Introduction

trans-Dioxo(tetramesitylporphyrinato)ruthenium(VI) (Ru(TMP)O_2) [1] (Scheme 1) is known to be a catalyst for the aerobic epoxidation of olefins. However, the catalytic activity is rather small. For activated olefins it has been found that norbornene gives only 43 turn-overs within 24 h [2]. Despite the growing interest in high valent Ru compounds as oxidation catalysts [3], very little is known about epoxidation of linear olefins and of possible deactivation routes. The earlier proposed catalytic mechanism [2] as outlined in Scheme 2 discusses only the redox levels of the central Ru. The central step is the disproportionation of the reduced catalyst, a ruthenium(IV)-monooxo species, back to the active Ru(VI) and to a Ru(II), which can be oxidized with dioxygen.

Recently, the important role of water has been described. Oxo transfer between H_2O and Ru(TMP)O_2 is easily possible [4], and a bis(hydroxy)ruthenium(IV) complex Ru(TMP)$(OH)_2$ shows at least the same catalytic activity as compared with Ru(TMP)O_2 [5]. Contrary to these observations, protic impurities as well as hydroxylic species formed by catalytic pathways have been cited as responsible for the gradual inactivation of the catalytic system [6]. The observation of the forma-



Ru(TMP)O_2 Ru(TMP)CO

Scheme 1.

☆ Dedicated to Professor Wolfgang Hilger on the occasion of his 65th birthday.

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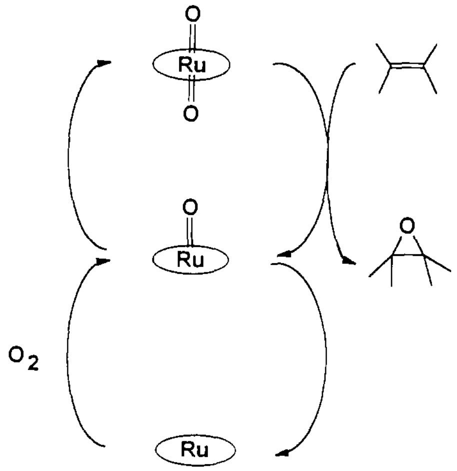
SSDI 0022-328X(95)05374-X



Scheme 2.

tion of a large amount of an unstable paramagnetic Ru porphyrin complex and traces of the carbonyl species Ru(TMP)CO [2] is not commented on with regard to its significance in a deactivation process. Only recently, it has been speculated about a build-up of catalytically inactive Ru(TMP)CO in the case of the epoxidation of styrenes; ruthenium porphyrins might act as catalysts for decarbonylation of aldehydes, which are detected as trace products during the epoxidation of styrenes. The CO formed coordinates and deactivates the catalyst [7].

We are interested in the aerobic epoxidation of propene to propene oxide and focused our investigations of the catalytic activity of Ru(TMP)O_2, especially on this reaction. We also present results for the aerobic epoxidation of the linear terminal olefin oct-1-ene which we consider as a good model for propene.

2. Experimental details

Ru(TMP)O_2 [1] and Ru(TMP)CO [8] have been prepared according to or by analogy to methods in the literature, respectively. Spectroscopic data for Ru(TMP)CO: UV–visible(CH_2Cl_2): $\lambda_{max}(\varepsilon)$, 412 (216.000), 527 (23.900) nm. ^{1}H NMR ($CDCl_3$): δ 8.49 (s, 8H), 7.26 (s, 8H), 2.61 (s, 12H), 1.93 (d, 24H) ppm. IR (CH_2Cl_2) ν(CO) 1930 cm^{-1}.

Fourier transform IR (FTIR) experiments have been carried out on a Bruker IFS 88 with spectral resolution of 4 cm^{-1} in demountable liquid cells (Perkin–Elmer) with KBr windows and a sample space of 485 μm. For isotope-labelling experiments, (1-^{13}C)-oct-1-ene (99% from Cambridge Isotope Laboratories) has been used.

2.1. Catalytic experiments

(1) The epoxidation of oct-1-ene was performed in a 100 ml flask under a pure oxygen atmosphere (1000 mbar; less than 0.2 vol. ppm CO) at ambient temperature. In a typical experiment, 9.2 mg (10 μmol) of freshly prepared Ru(TMP)O_2 was dissolved in 2.0 ml of dichloromethane; 0.3 ml of water and 112 mg (1 mmol) of oct-1-ene added and stirred. Samples were taken after 1, 6, 24 and 48 h and the products were identified with gas chromatography (GC) – mass spectroscopy (MS). The selectivity for the epoxide after 24 h is 80% based on the components detected by GC.

(2) The epoxidation of propene was performed in a 100 ml flask under atmospheric pressure (1000 mbar) in an atmosphere of propene (700 mbar) and oxygen (300 mbar; less than 0.2 vol. ppm CO) at ambient temperature. In a typical experiment, 15 mg (16 μmol) of freshly prepared Ru(TMP)O_2 was dissolved in 20 ml of 1,2-dichloroethane; 0.4 ml of water was added and stirred. As for the epoxidation of oct-1-ene, samples were taken as above and the products identified with GC–MS. The selectivity for the epoxide after 24 h is 90% based on the components detected by GC.

2.2. Isolation of a deactivated catalyst species

In a mixture of 50 ml of 1,2-dichloroethane, 8 ml of water and 9.6 ml (60 mmol) of oct-1-ene, 560 mg (0.6 mmol) of freshly prepared Ru(TMP)O_2 was stirred under a pure oxygen atmosphere (1000 mbar) at ambient temperature for 48 h. Flash chromatography with active basic alumina of the reaction mixture with dichloromethane as eluent led to an orange fraction. After evaporation and recrystallization (toluene–heptane), 150 mg (27%) of the carbonyl complex Ru(TMP)CO · H_2O results. The spectroscopic data correspond to an authentic sample. The elemental analysis (C, H, N) was correct; O_{exp}, 3.6% (O_{th}, 3.44%).

2.3. Crystal structure

The crystals were obtained by slow diffusion of heptane into a solution of toluene. A crystal of 0.5 mm × 0.3 mm × 0.1 mm was mounted into a Lindemann glass capillary. 25 reflections with $\theta > 5.3°$ were used for the determination of the cell constants on a computer-controlled diffractometer (Siemens R3m/V). The intensities were measured on the same apparatus: Mo Kα radiation; 7210 reflections ($0 < h < 32$; $-1 < k < 37$; $-10 < l < 1$); 5787 reflections with greater than $2\sigma(F)$; direct methods for solving the phase problem [9]; SHELXL-93 [10] for the parameter refinement minimizing of $\Sigma\omega(F_o^2 - F_c^2)^2$; weighting function according to the counting statistics; 572 parameters; coordinates of the hydrogen atoms calculated. The ten largest peaks of the last difference Fourier synthesis of the electron density were between 0.62 and 0.89 electrons A^{-3}.

3. Results and discussion

3.1. Catalytic activity

In preliminary experiments we reproduced the catalytic data published by Groves [2] regarding the epoxidation of the cyclic olefine norbornene. The olefine (0.5 M), dissolved together with the Ru(TMP)O_2 catalyst (0.005 M) in benzene, is converted to its epoxide with 40 ± 5 turn-overs within 20 h. A solvent screening at this early stage has shown that even weakly coordinating solvents such as acetonitrile completely block the catalytic cycle. Instead of benzene we found the chlorocarbon solvents such as dichloromethane, 1,2-dichloroethane or chlorobenzene to be the best solvents.

Interestingly, we detected an accelerating effect on the catalytic activity, if water is present in the reaction mixture. The amount of water does not seem to be important, as solvent mixtures with 1–50 vol.% of water have been tested without any difference on the catalytic behavior. We do not like to speculate about the detailed mechanistic role of water here, as this has been under investigation recently by other groups [4,5]. With our results it is unlikely that water or other protic impurities might be responsible for the catalyst's deactivation.

In the gas atmosphere of the reaction mixture, nitrogen has to be avoided as there is a negative influence of nitrogen on the catalytic activity, most probably owing to coordination of N_2 at the Ru(II) site within the catalytic cycle as known in the literature [11].

These preliminary observations define our optimized reaction conditions: chlorocarbon solvents; addition of water; exclusion of nitrogen. Under these conditions, norbornene is now converted to its epoxide with 100 turn-overs within 6 h, a significant increase in comparison with the values published so far.

Table 1
Turn-over numbers (molar amount of produced epoxide relative to the amount of used catalyst) for the epoxidation of oct-1ene and propene with the Ru(TMP)O_2 catalyst (reaction conditions are as described in Section 2)

Time (h)	Turn-over number	
	1,2-Epoxyoctane	Propene oxide
1	5.2	< 2
6	17	9.3
24	40	36
48	42	40

The conditions of the aerobic epoxidations of oct-1-ene and propene are slightly different. Oct-1-ene (0.5 M) is dissolved together with the catalyst (about 0.005 M). For attempts at propene epoxidation, the catalyst concentration is somewhat lower (about tenfold as compared with octene epoxidation) because we use more solvent to dissolve the propene in situ out of the gas atmosphere, which consists of a propene–O_2 mixture.

The catalytic activity of Ru(TMP)O_2 in a typical experiment is moderate (Table 1). The turn-over numbers with respect to the reaction time show a non-linear increase. After 24 h the activity has nearly vanished and after 48 h the catalyst was no longer active. As expected, the catalytic activity of Ru(TMP)O_2 is lower when linear olefins are used as substrates in comparison with a norbornene substrate.

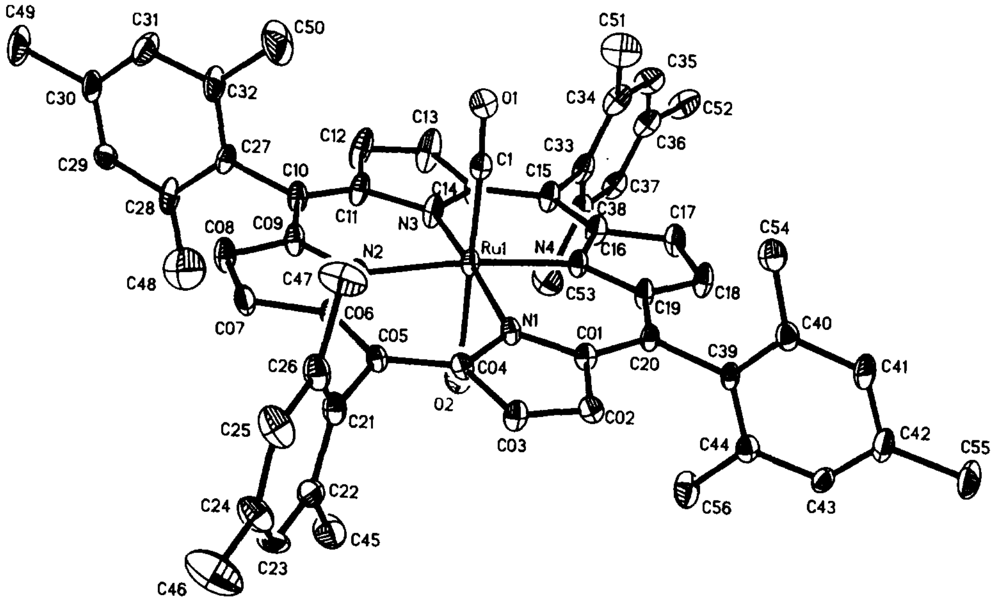


Fig. 1. Structure of Ru(TMP)CO · H_2O in the crystal.

3.2. Deactivation process: formation of a carbonyl complex

As we searched for causes for the fast deactivation process, the UV–visible spectrum of an octene epoxidation experiment after 24 h caught our attention, as its absorptions at 410 and 526 nm look comparable with the absorption spectrum of the carbonyl complex Ru(TMP)CO. Indeed, the presence of this carbonyl species can be proved by fast atom bombardment MS of the reaction mixture. A quantitative interpretation of the terminal CO vibration at 1930 cm^{-1} in the FTIR experiment after 24 h shows more than 30% of the catalyst species to be Ru(TMP)CO. We were able to isolate this species from the reaction mixture and to characterize it by spectroscopic and crystallographic methods.

The crystal structure is shown in Fig. 1; the crystal data and parameters of structure refinement are given in Table 2. The axially coordinated carbonyl ligand shows a ruthenium–carbon distance of 180.5(1.2) pm; the Ru is distorted by 13.3 pm out of the mean $N_{(4)}$ plane of the porphyrin ring. These data are comparable with known carbonyl-ruthenium porphyrins [12,13]. In the axial position *trans* to the carbonyl ligand we find the electron density attributed to a weakly coordinating water molecule, as the elemental analysis shows two oxygen atoms per molecule. The ruthenium–oxygen distance of 229.1(8) pm correlates well with the Ru–O distances of coordinated ethanol [12] or a coordinated epoxide [14].

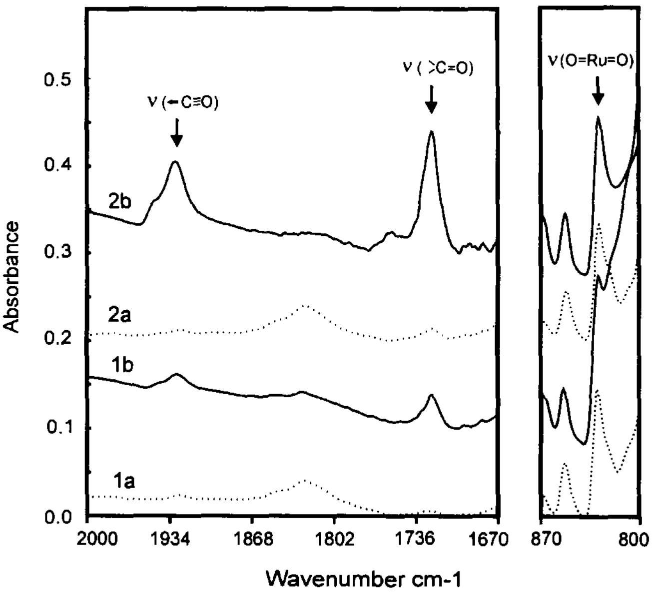


Fig. 2. Two parts (2000–1670 and 870–800 cm^{-1}) of the IR spectrum of catalyst Ru(TMP)O_2, 0.01 M in 1,2-dichloroethane under an atmosphere layer of propene (curve 1a, at the beginning of the reaction; curve 1b, after 6 h) and under an atmosphere layer of propene and oxygen (curve 2a, at the beginning of the reaction; curve 2b, after 6 h). The absorbance baseline is shifted by 0.1 units.

Table 2
Crystal data of and structure refinement data for Ru(TMP)CO · H_2O

Empirical formula	$C_{57}H_{54}N_4O_2Ru$
Formula weight	928.2
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system	Rhombic
Space group	*Pba2*
Unit-cell dimensions	
a (pm)	2440.9(3)
b (pm)	2811.8(2)
c (pm)	773.5(1)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	5.309(1)×10^9
Z	4
Density (calculated) (Mg m^{-3})	1.139
Absorption coefficient (mm^{-1})	0.334
F(000)	1.896
θ range for data collection (°)	2.21 to 28.06
Number of data	7198
Number of restraints	1
Number of parameters	572
Goodness of fit on F^2	0.900
Final *R* indices ($I > 2\sigma(I)$)	
*R*1	0.0640
*wR*1	0.1675
R indices (all data)	
*R*2	0.1162
*wR*2	0.2264
Absolute structure parameter	0.35(7)
Largest difference peak (electrons Å^{-3})	0.889, −0.494

To get an idea about the possible CO source, we dissolved the active catalyst in the pure chlorocarbon solvent under a pure oxygen atmosphere. No carbonyl species was detected within a few days. Also, ketones such as benzophenone or aldehydes as acetic aldehyde and acrolein have been proven not to react with the active catalyst under decarbonylation. The origin of the CO has been determined by the following experiment: The active catalyst Ru(TMP)O_2 was dissolved in 1,2-dichloroethane, stirred under an atmosphere of (i) pure propene or (ii) alternatively, a mixture of propene and O_2 (7 : 3, v/v), and FTIR spectra were taken. Both samples were equally concentrated in the catalyst. Curves 1a and 2a of Fig. 2 are two identical spectra at the beginning with the characteristic O=Ru=O vibration at 830 cm^{-1}. After 6 h the following have been observed.

(1) In a propene atmosphere in the presence of oxygen, the O=Ru=O absorption is still very strong. However, two additional significant bands within the carbonyl region have been developed (Fig. 2, curve 2b). The absorption at 1930 cm^{-1} can be assigned to the terminal Ru–CO vibration of the carbonyl complex Ru(TMP)CO. The absorption at 1725 cm^{-1} belongs to a carbonyl vibration of an aldehyde. The catalyst is

active. However, CO coordinated to the catalyst Ru center has been formed.

(2) In a pure propene atmosphere the C=Ru=O vibration has almost vanished; carbonyl bands have not developed (Fig. 2, curve 1b). Minor amounts of visible carbonyl absorptions might be due to the traces of oxygen present. Obviously, the catalyst has transferred once its bound oxygen, without finding a possibility for regeneration.

A significant amount of the carbonyl complex Ru(TMP)CO is only detected when propene and O_2 are present. GC–MS of a typical reaction mixture shows as side products acroleine (traces of allylic oxidation) and the $C_{(2)}$ fragments acetic aldehyde and acetic acid. The main product of the side components is acetic aldehyde. This aldehyde might also be responsible for the observed carbonyl vibration of 1725 cm^{-1} in the FTIR data as mentioned above. Surprisingly the $C_{(1)}$ components such as formic aldehyde or formic acid are missing in the GC–MS, indicating that intermediate products on the way to CO [15] cannot be detected.

As in the absence of the catalyst neither the epoxidation reaction nor the side reactions can be observed, we feel that the side reaction to the formation of CO is catalytic, also. It has to be pointed out here that Ru porphyrins are known to transform a coordinated methyl to a carbonyl group. However, the reaction pathway is not clear so far [16].

To find out which carbon atom might be the atom that forms the carbon monoxide, we carried out an isotope-labelling experiment. As with our reaction conditions it would be difficult to dose small amounts of labelled propene, we epoxidized labelled (1-^{13}C)-oct-1-ene. In this case we observed two absorptions in the terminal carbonyl region: one still at 1930 cm^{-1} due to a Ru–^{12}C vibration, but also one at 1890 cm^{-1} (with a relative intensity of 1:3 as compared with the former absorption), which can be assigned to a Ru–^{13}C vibration [16]. At least partially, the carbon atom of the formed CO derived from the first C atom of the terminal olefine.

4. Conclusion

The catalytic oxidation of propene to propene oxide with an Ru(TMP)O_2 catalyst shows rapid deactivation behavior. The active catalyst is slowly transformed into a carbonyl-ruthenium species Ru(TMP)CO, which has been crystallized out of the reaction mixture. This formed species is catalytically not active as has been proven with an authentic sample. However, we see also a faster decrease in the catalytic activity in comparison with the build-up of the carbonyl species. This indicates that more deactivation processes than that mentioned above occur. Irreversible reduction leading to an odd oxidation number of the central Ru and/or competitive inhibition by the epoxide formed are possible deactivation candidates. Clearly, more investigations are required to define the overall deactivation process better. For future chances of Ru porphyrins one can learn already that the deactivation route forming the carbonyl species is an intrinsic property of the catalyst and might be very difficult to prevent.

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