Nature of the reactive intermediates from the titanium-induced activation of hydrogen peroxide: Studies using ^{1}H and ^{17}O NMR

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Abstract

Using ^{17}O and ^{1}H NMR, peroxotitanium species formed in the reaction of TiO(acac)$_2$ and Ti(OEt)$_4$ with H$_2$O$_2$ in CHCl$_3$ were characterized. Dinuclear μ-oxo, μ-peroxo complex [Ti(acac)$_2$]$_2$O(O$_2$) was prepared via reaction of TiO(acac)$_2$ with H$_2$O$_2$ in CHCl$_3$. This complex is inert towards alkenes oxidation. When Ti(OEt)$_4$ reacts with an equimolar amount of 95% H$_2$O$_2$ in CHCl$_3$ at 293 K, ca. 75% of the initial titanium complex converts to the oligomeric peroxotitanium species, containing no alkoxo ligands, ca. 20% of titanium exists in solution in the form of dinuclear μ-oxo, μ-peroxo complexes of the type [Ti(OEt)$_2$L$_2$]$_2$O(O$_2$), where L is solvent or EtOH, and 3–5% in the form of mononuclear peroxo complexes of the type Ti(O$_2$)(OEt)$_2$L$_2$. Oligomeric and dinuclear peroxotitanium species were inert towards alkenes and phenol; in contrast mononuclear ones oxidize cyclohexene at 293 K predominantly into cyclohexene oxide and phenol into a 1:3 catechol/hydroquinone mixture. Peroxo complex Ti(O$_2$)(OEt)$_2$L$_2$ is the first peroxotitanium complex active towards oxidation of organic substrates.

Keywords: Peroxo complexes; Titanium; Epoxidation; NMR spectroscopy

1. Introduction

Recently it was shown that titanium silicates, exhibiting a pentasil structure particularly, can be used for a number of industrially important oxidations of organic substrates with an aqueous or aqueous–alcohol solutions of hydrogen peroxide [1–7]. These findings have aroused considerable interest to the structure and reactivity of peroxotitanium compounds. However, con-

trary to what has been observed in the case of molybdenum or vanadium [8,9], all peroxotitanium compounds isolated until recently were unreactive towards organic substrates (olefins, allylic alcohols, cyclic ketones or sulfides). Peroxotitanium complexes with picolinato, hydroxyquinolino, hydroximato and porphyrino ligands were studied [10,11].

To elucidate factors governing the reactivity of peroxotitanium compounds, we undertook studies of the peroxotitanium species formed in the reaction of titanyl acetylacetonate (TiO(acac)$_2$) and titanium(IV) ethoxide (Ti(OEt)$_4$) with H$_2$O$_2$ in CHCl$_3$.

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It was previously shown that dialkyl sulfides can be oxidized to the corresponding sulphoxides with hydrogen peroxide in the presence of catalytic amounts of $TiO(acac)_2$ in aqueous ethanol at 293 K [12].

2. Experimental

Cyclohexene, chloroform were purified by standard procedures. Deuterated chloroform was purchased and used without additional purification. Hydrogen peroxide 30% was concentrated in vacuo up to 60–95% and titrated with $KMnO_4$ just before experiments. $TiO(acac)_2$ was synthesized by the procedure described in [13] $Ti(OEt)_4$ (Aldrich) was distilled before use.

2.1. Synthesis of $[Ti(acac)_2]_2O(O_2)$ (1)

A 2.62 g (0.01 mmol) amount of $TiO(acac)_2$ was dissolved in 50 ml of $CHCl_3$. After that 0.358 g (0.01 mmol) of 95% H_2O_2 were added dropwise. The solution was stirred for 10 min, then it was filtered and concentrated in vacuo to ca. 10 ml. Addition to 100 ml of pentane gave a precipitate that was collected by filtration, washed with pentane, and air-dried to give 1 as a yellow powder (1.629 g, 0.003 mmol, 60%). ^1H-NMR, $CDCl_3$, δ 1.88 (6H, s), 1.97 (6H, s), 2.11 (6H, s), 2.13 (6H, s), 5.62 (2H, s), 5.66 (2H, s) ppm; ^{17}O-NMR, δ 350 (8O, br s, $\Delta\nu_{1/2}$ = 3 kHz), 828 (1O, s, $\Delta\nu_{1/2}$ = 140 Hz). Anal. Calcd. for $C_{20}H_{28}O_{11}Ti_2$: C, 44.44; H, 5.18; Ti, 16.78. Found: C, 42.46; H, 4.97; Ti, 17.63.

For iodometric titration 0.540 g (0.001 mmol) of 1 were dissolved in 5 ml of glacial acetic acid, then 2 ml of a saturated solution of NaI in glacial acetic acid were added; the solution obtained was stored for 15 min and diluted with 10 ml of water. A 0.1 N solution of $Na_2S_2O_3$ with starch as indicator was used for titration at 293 K. 1.57–1.61 mmol of peroxide were determined in 1 g of complex 1 (0.85–0.87 mol of peroxide per mol of complex 1). Thus, complex 1 includes one peroxo group per two titanium atoms.

2.2. Reaction of H_2O_2 with $Ti(OEt)_4$

A 2.28 g (0.01 mmol) amount of $Ti(OEt)_4$ was dissolved in 15 ml of $CHCl_3$. After that 0.358 g (0.01 mmol) of 95% H_2O_2 were added dropwise with intensive stirring. The obtained solution was used for ^1H and ^{17}O NMR measurements.

2.3. Nuclear magnetic resonance measurements

^{17}O and ^1H NMR spectra were recorded at 54.043 and 400.13 MHz, respectively, using pulsed FT-NMR technique, on a Bruker MSL-400 NMR spectrometer. Compounds with a natural abundance of magnetic isotopes were used in all the NMR studies. ^{17}O NMR spectra were recorded with cylindrical 10 mm tubes (sample volume 1.3–1.5 cm^3). A high power probe head was used for the ^{17}O NMR measurements to increase sensitivity. The field homogeneity was adjusted by shimming on the ^2H resonance of D_2O. The following operating conditions were used for ^{17}O NMR measurements: sweep width 80000 Hz; spectrum accumulation frequency 100 Hz; number of scans 500000–1500000. The data were accumulated with 2 K data points in the time domain and were transformed with an optimal exponential multiplication of 50–100 Hz. Chemical shifts were calculated in ppm with positive values in the low field direction with respect to the reference: TMS for ^1H, H_2O for ^{17}O. The error in measuring the ^{17}O chemical shift values was ± 1 ppm for line widths below 500 Hz and ± 10 ppm for line widths around 3 kHz.

3. Results

3.1. Characterization of the dinuclear μ-oxo, μ-peroxo complex $[Ti(acac)_2]_2O(O_2)$ (1)

It was found that $TiO(acac)_2$ converts into peroxo complex 1 upon interaction with ca.
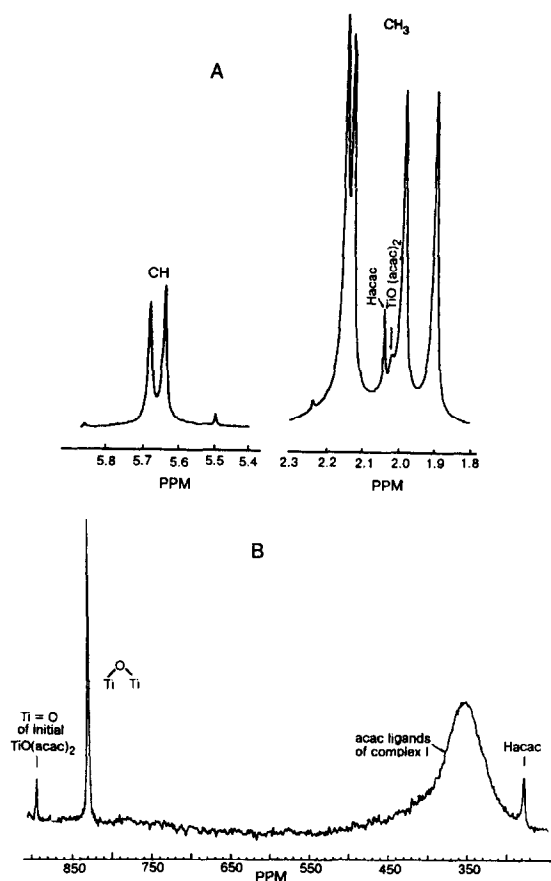
Fig. 1. (A) ^{1}H and (B) ^{17}O NMR spectra of a 0.2 M solution of complex 1 in CDCl$_3$ at 293 K.

equimolar amount of 95% H_2O_2 in $CHCl_3$ at 293 K (see Experimental Part). The ^{1}H NMR spectrum of complex 1 in $CDCl_3$ shows six signals with relative intensities 1:1:3:3:3:3 (at 5.68, 5.64, 2.14, 2.12, 1.98, 1.90 ppm) from two sets of two non-equivalent acetylacetonato ligands (Fig. 1a). Two of the lines are attributed to the CH protons (1:1), and four to the CH_3 protons (3:3:3:3) of the acetylacetonato ligands. Note that the initial TiO(acac)$_2$ exhibits in the ^{1}H NMR spectrum two resonances with relative intensities 1:6 (at 5.64 and 2.01 ppm, CDCl$_3$) from CH and CH_3 protons of the two equivalent acetylacetonato ligands.

^{17}O NMR spectrum of complex 1 exhibits two resonances with relative intensities 1:8 at

828 ppm ($\Delta\nu_{1/2} = 140$ Hz) and 350 ppm ($\Delta\nu_{1/2} = 3$ kHz) (Fig. 1b).

The resonance at 828 ppm can be attributed to Ti–O–Ti oxygen atom. The resonance at 350 ppm belongs to acetylacetonato ligands of complex 1. Based on the relative intensities of the ^{17}O NMR resonances (1:8) it is natural to suppose that complex 1 contains a dinuclear fragment [Ti(acac)$_2$]$_2$O with a μ-oxygen atom. According to results of iodometric titration (see Experimental Part), one peroxo group corresponds to two titanium atoms in complex 1. The most probable structure of complex 1 is [Ti(acac)$_2$]$_2$O(O$_2$) with bridging oxo and peroxo groups. Nonequivalence of the CH and CH_3 protons of acetylacetonato ligands (Fig. 1a) is in agreement with the supposed structure of complex 1. The lack of the direct observation of the peroxo group of complex 1 with ^{17}O NMR spectroscopy (natural abundance of the ^{17}O isotope) is caused by the large width of its resonance. The width of the resonance of the peroxo group of the mononuclear complex Ti(O$_2$)(Pic)$_2$ is 3.2 kHz [14]. The width of the corresponding resonance in the dinuclear complex 1 would be even larger.

Complex 1 isolated as solid can be stored for a months at 293 K in air. When dissolved in $CHCl_3$, it slowly decays with characteristic time of 2 h at 333 K. The decay product is the initial complex TiO(acac)$_2$. Complex 1 was inert towards cyclohexene and trans-stilbene at 333 K in $CHCl_3$.

At the same time the catalytic system TiO(acac)$_2$ + H_2O_2 has been reported to oxidize sulfides to the corresponding sulphoxides in EtOH [12]. ^{1}H and ^{17}O NMR spectra show that complex 1 predominates in this catalytic system only at small amounts of H_2O_2([H$_2$O$_2$] $\approx$ [TiO(acac)$_2$]). Further increase of H_2O_2 concentration gives rise to conversion of all acetylacetonato ligands of complex 1 to free acetylacetone and products of its oxidation (predominantly acetic acid). Thus possible active peroxotitanium species of the catalytic system TiO(acac)$_2$ + H_2O_2 in EtOH contain no acety-

lacetonato ligands. However, products of acetylacetone oxidation complicate the interpretation of the ^{1}H and ^{17}O NMR spectra and characterization of these peroxotitanium species. The catalytic system $Ti(OEt)_4 + H_2O_2$ appeared to be more adequate for this goal.

3.2. The reaction of Ti(OEt)₄ with H₂O₂

^{1}H NMR spectrum of the 0.7 M solution of $Ti(OEt)_4$ in $CHCl_3$ exhibits a broad signal at 4.2 ppm ($\Delta\nu_{1/2} = 40$ Hz) arising from CH_2 protons of the coordinated OEt groups (for comparison, CH_2 protons of free ethanol exhibits quartet at 3.74 ppm in this solvent, $J = 7$ Hz). The signal corresponding to CH_3 protons of $Ti(OEt)_4$ (triplet at 1.33 ppm, $J = 7$ Hz) practically coincides with that of free ethanol in this solvent. After the addition of 95% H_2O_2 (to make its concentration 0.7 M, 293 K) to the previous sample no pronounced decomposition of H_2O_2 is observed, while the colorless solution becomes yellow. According to ^{1}H NMR, in the course of this reaction the initial $Ti(OEt)_4$ disappears and a number of new titanium complexes is formed (Fig. 2).

The most intense resonance in the Fig. 2 belongs to the CH_2 protons of the free ethanol. Besides the multiplets denoted by the letters A, B and C and arising from CH_2 protons of three types of titanium complexes are observed (Fig. 2). Further, these complexes will be referred as complexes A, B and C. The liberation of ethanol (Fig. 2) testifies that a predominant part of the titanium converts into the complexes containing no OEt ligands, via the reaction of $Ti(OEt)_4$ with H_2O_2. Integration of the resonances in Fig. 2 shows that ca. 75% of titanium contains no OEt or other organic ligands and ca. 25% exists in solution in the form of complexes A, B and C, containing OEt ligands. The concentration of complex A does not exceed 3–5% of the total titanium in solution.

The corresponding resonances of the methyl protons of complexes A, B and C overlap with each other and yield no information.
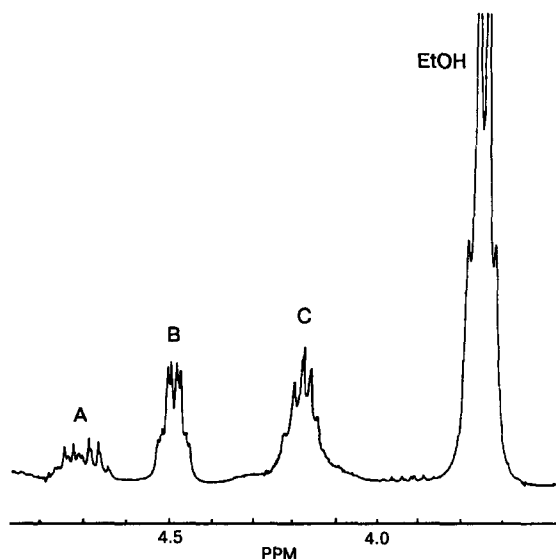

Fig. 2. ^{1}H NMR spectrum of a 0.7 M solution of $Ti(OEt)_4$ in $CDCl_3$ 5 min after the addition of 95% H_2O_2 ([H_2O_2] = 0.7 M) at 293 K.

Complexes A, B, C are rather stable and do not change their concentration for five hours at 293 K.

^{17}O NMR spectrum of the sample of Fig. 2 exhibits a weak resonance at 592 ppm ($\Delta\nu_{1/2} = 150$ Hz) and an intense resonance due to free ethanol.

The integration of the lines in the ^{17}O and ^{1}H NMR spectra of the sample of Fig. 2 shows that the resonance at 592 ppm in the ^{17}O NMR spectrum can belong to complex C or complex B.

When 80% H_2O_2 is used instead of 95% H_2O_2 as the starting reagent, the formation of complex A is not observed and the relative concentration of complex B decreases (the ratio [B]:[C] changes from 1:1 to 1:2).

It is very important to note that the addition of cyclohexene (to make [C_6H_{10}] = 1 M) to the sample of Fig. 2 at 293 K gives rise to a very rapid disappearance of the signals of complex A and to a parallel increase of the resonance (at 3.02 ppm) of cyclohexene oxide. GC analysis showed that cyclohexene oxide is the main product of cyclohexene oxidation (selectivity of ca. 70%). Complexes B and C were inert to-

wards cyclohexene. Complex A reacts rapidly with phenol at 293 K to give catechol and hydroquinone in 1:3 ratio ([A] = 0.01 M, [PhOH] = 0.1 M, $CHCl_3$).

4. Discussion

4.1. Characterization of the peroxotitanium species formed in the reaction of $Ti(OEt)_4$ with H_2O_2

4.1.1. Complex A $(Ti(O_2)(OEt)_2L_2)$

Complex A is active towards cyclohexene and phenol oxidation. Hence, one of its ligands contains activated oxygen atom. The role of such a ligand can be played by peroxo (O_2^{2-}), hydroperoxo (OOH^-) or alkylperoxo $(OOEt^-)$ moiety. The multiplet corresponding to CH_2 protons of the OEt ligands of complex A, consists of four quartets (at 4.71, 4.72, 4.68 and 4.67 ppm, $J = 7$ Hz) denoted by triangles, squares, points and crosses, respectively (Fig. 3). The relative integral intensities of quartets are 2:1:2:1. Very likely this pattern belongs to a set of isomers of the peroxo complex $Ti(O_2)(OEt)_2L_2$, where L is EtOH or solvent ($CHCl_3$). Possible isomers of $Ti(O_2)(OEt)_2L_2$ are shown in Fig. 4. The isomer I has a relative statistical weight of 4, and isomers II and III have one of 1.

The OEt groups of the isomers II and III are equivalent, and those of isomer I are not (Fig.
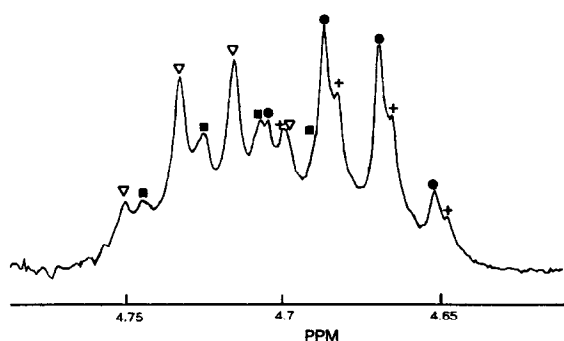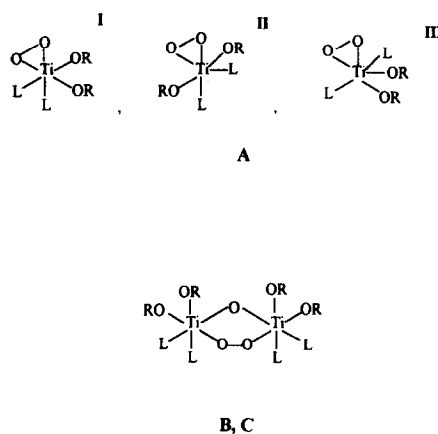

Fig. 4. Possible structures of peroxotitanium species.

4). Thus, the CH_2 protons of isomer I would exhibit in the ^1H NMR spectrum two quartets of equal intensities, and those of isomers II and III would display one quartet. If we suppose that all the isomers are present in solution with equal probability, then four quartets with relative integral intensities 2:1:2:1 would actually correspond to complex A in solution. Two quartets (2:2) belong to isomer I (relative statistical weight 4). One quartet (1) is attributed to isomer II (relative weight 1), and the other quartet (1) belongs to isomer III (relative weight 1). The assignment of the observed pattern 2:1:2:1 to the other possible intermediates $Ti(OEt)_3OOH$ or $Ti(OEt)_3(OOEt)$ seems far less probable. These species would exhibit more isomers and more complex patterns in the ^1H NMR spectra. Thus, most probably, complex A is the peroxo complex of $Ti(O_2)(OEt)_2L_2$ type.

4.1.2. Complexes B and C

The CH_2 protons of the OEt ligands of complexes B and C exhibit in the ^1H NMR spectrum doublets of quartets ($J = 7$ Hz, Fig. 2). Thus, they contain two sets of nonequivalent OEt ligands. The resonance at 592 ppm, corresponding to complex B or C in the ^{17}O NMR spectrum can be attributed to the Ti–O–Ti oxygen atom. Tentatively, by analogy with complex $[Ti(acac)_2]_2O(O_2)$ (1), we suppose that complexes B and C are dinuclear μ-oxo, μ-peroxo

Fig. 3. ^1H NMR spectrum of complex A in $CDCl_3$: characteristic pattern of CH_2 protons.

bridged species. One of the possible structures is shown in Fig. 4. Similar to complex **1**, complexes B and C are inert towards alkenes.

4.1.3. Oligomeric peroxotitanium species

The integral intensity of the resonance of free ethanol in the ^{1}H NMR spectrum of Fig. 2 shows that ca. 75% of titanium exists in solution in the form of complexes containing no ethoxy or other organic ligands. Probably, these complexes are oligomeric peroxo species of the type
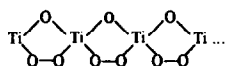

In agreement with this hypothesis, the solution of Fig. 2 converts to the glassy state, when storing for two days at 293 K. When reaction of Ti(OEt)$_4$ with H$_2$O$_2$ is carried out in ether as a solvent, the polymeric peroxotitanium species precipitate. The precipitate is unsoluble in water and organic solvents. The addition of an excess of acetylacetone to the sample of Fig. 2 gives rise to the conversion of oligomeric species to the complex **1**. Oligomeric peroxotitanium species are inert towards cyclohexene. We have not succeeded in detection of the ^{17}O NMR spectrum of the oligomeric peroxotitanium species. This detection, most probably, is complicated by the increase of the widths of the ^{17}O NMR resonances with the growth of the size of molecule, typical for quadrupole nuclei [15].

4.2. Nature of the reactivity of peroxotitanium complex A (Ti(O$_2$)(OEt)$_2$L$_2$)

Complex A (Ti(O$_2$)(OEt)$_2$L$_2$) is the first example of a peroxotitanium complex which can selectively epoxidize alkenes. The unreactivity of the peroxotitanium complexes isolated until now is most probably caused by the decrease of the electrophilicity of coordinated peroxo groups under influence of strong σ-donor ligands [16]. All isolated peroxotitanium complexes contained such ligands. Alkoxo ligands in the com-

plex A provide high reactivity of coordinated peroxo group. However, the homogeneous Ti(OEt)$_4$ + H$_2$O$_2$ catalytic system is ineffective in the epoxidation of alkenes. This is the result of the conversion of the active mononuclear peroxo titanium species A into inert dimeric and oligomeric ones. When titanium is incorporated in the zeolite framework, the problem of oligomerization is avoided.

Let us now discuss possible intermediates of oxidation with titanium silicalites as catalyst. Notari [1] and Huybrechts et al. [3] have suggested that a titanium peroxo species of type 1 are active intermediates.
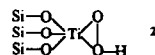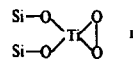
On the basis of the inactivity of the isolated peroxotitanium compounds and the effects of the solvents, bases and acids on kinetics, other authors have suggested that the intermediate of the type **2** is an active center of oxidation [5–7]. From our results of this work we can conclude that monoperoxo complexes of titanium with appropriate ligands can be active in the selective epoxidation of alkenes and phenols, and peroxo species of the type 1 can in principle be active intermediates of oxidation. The effects of solvents, bases and acids on kinetics can be explained by their coordination to the active intermediate of type 1.

5. Conclusions

Using ^{1}H and ^{17}O NMR, peroxotitanium species formed in the reaction of TiO(acac)$_2$ and Ti(OEt)$_4$ with H$_2$O$_2$ in CHCl$_3$ were characterized. Dinuclear μ-oxo, μ-peroxo titanium complex [Ti(acac)$_2$]$_2$ O(O$_2$) was isolated and characterized with ^{1}H, ^{17}O NMR and iodometry.

This complex was inert towards alkenes. When $Ti(OEt)_4$ reacts with an equimolar amount of 95% H_2O_2 in $CHCl_3$, the main part of titanium (95%) occurs in solution in the form of dinuclear and oligomeric peroxotitanium species inert towards organic substrates, and a small part (3–5%) in the form of mononuclear peroxotitanium species $Ti(OEt)_2(O_2)L_2$ active towards cyclohexene epoxidation and phenol hydroxylation.

Acknowledgements

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