Oxidation of alkanes by TBHP in the presence of soluble titanium complexes

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Abstract

The oxidation reaction of alkanes by *t*-butylhydroperoxide (TBHP) in the presence of titanium alkoxides produced the corresponding alcohols and ketones. The feature of this reaction was different from titanosilicate, although the tetra-alkoxide structure of titanium alkoxides is similar to titanosilicate. Other titanium complexes with titanyl or peroxo-titanium groups were not effective. This oxidation reaction proceeded in radical mechanism. *t*-Butoxyl radical formed from TBHP and titanium alkoxide started the radical reaction. The evolution of oxygen (the decomopsition of peroxide) and the abstraction of hydrogen from alkane to form alkyl radical occurred competitively. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alkane oxidation; Titanium alkoxide; *t*-Butylhydroperoxide; Radical reaction; Titanosilicate

1. Introduction

Titanium complexes are good reagents or catalysts for the oxidation of organic compounds such as alkenes. Sharpless oxidation of allylic alcohols is a typical example [1,2]. On the other hand, titanosilicate (TS-1 is a representative one) and related compounds have been actively studied as well as titanium complexes for the catalysts of the oxidation reactions in liquid phase [3], especially for the epoxidation of alkenes [4–15]. Some of these solid catalysts also realized the oxidation of alkanes [16–20].

There are many debates on the mechanism of the oxidation reaction using titanosilicates [3,6,14,16,20,21]. As they are heterogenous cat-

alysts, it is comparatively difficult to reveal what happens under the actual reaction conditions. Recently some model titanium complexes of titanosilicate using Feher's silsequioxanes [22,23] were reported to be effective for the epoxidation of alkenes [24–27]. These studies are regarded as frontier works of the model of titanosilicate and titanium-loaded silica catalysts. On the other hand, the oxidation of alkanes using titanium complexes with peroxide has scarcely been reported. As long as we know, only one paper [28] briefly referred to the reaction of alkanes as a side-reaction of epoxidation. The active studies on the functionalization of alkanes by many researchers [29–33] indicated that it is one final goal of chemistry. Titanosilicate seems to give us a chance to find out a goal of this. Therefore, revealing the basic features of titanium complexes for the oxidation of alka-

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nes is one approach to this chemistry. In this paper, we wish to report a detailed study of the reaction of alkanes and peroxides in the presence of some soluble titanium complexes in organic solvents. We also want to discuss the comparison of this oxidation reaction with that of titanosilicates.

2. Experimental

Almost materials we employed in this paper were commercial available and used without further purification. All solvents were dried before utilization. The CH_2Cl_2 and cyclohexane solutions of *t*-butylhydroperoxide (TBHP) were prepared by a described method [34]. The concentration of peroxide in the solution was determined by a common iodometric titration. The identification of gas generated was performed by GC with TCD detector. UV–Vis spectrum was measured by Jasco V-560 spectrometer.

The reaction of alkanes with TBHP and titanium complex was carried out by the following procedure. To the solution of a titanium complex (0.4 mmol) and an alkane (10 mmol) in a solvent (2 ml) was added a solution of TBHP (about 1 ml for fixing the amounts of TBHP at 5 mmol) at room temperature under nitrogen atmosphere. The solution was not degassed because the evolution of oxygen during the reaction was observed as mentioned after. After 1 h, the conversion of TBHP was determined using a small amount of the solution by the common iodometric titration. The resulting solution was treated by the aqueous solution of $Na_2S_2O_3$ to decompose the remained peroxide. After the extraction of organic compounds with a small amount of diethylether, the yields of the products were determined by capillary GC (SHIMADZU GC-17A) with internal standard. The identification of the products was performed both by the retention time in GC compared with the commercial available standard compounds and by GC-MS (SHIMADZU GCMS QP-5000).

3. Results and discussion

3.1. Reaction of alkanes with TBHP in the presence of titanium alkoxides

Titanium tetra-alkoxide was selected as a titanium complex, because it is the commonest titanium alkoxide well used in organic syntheses, and has four titanium oxygen bonds like as titanium in titanosilicate. Table 1 summarizes the results of the reaction of cyclohexane with TBHP in the presence of titanium tetra-alkoxides. Cyclohexanol and cyclohexanone were obtained in approximately same yields based on titanium used in the case of titanium tetra-isopropoxide at room temperature (run 1). No product was obtained in the absence of the alkoxide (run 2). Other titanium alkoxides, tetra-ethoxide (run 7) and tetra-*n*-butoxide (run 8) slightly decreased the yields of products. Acetonitrile was the best solvent in this study. When the additional solvent was not used (cyclohexane solvent), the selectivity of cyclohexanol increased (run 6). In the case of HMPA (hexamethylphosphoric triamide) solvent, no product was obtained and no conversion of TBHP was observed (run 4). It seems that HMPA formed six-coordinated titanium. The use of cyclohexane solution of TBHP instead of its CH_2Cl_2 solution had little influence on the result (run 9). Although *t*-butyl peroxide was obtained in 5 ~ 10% yields in almost cases, this peroxide was inert to this oxidation reaction (run 12). *t*-Butylperoxycyclohexane, which was reported to be form in the previous paper [28], was scarcely detected in this case. Titanium tetra-1,1,1,3,3,3-hexafluoro-isopropoxide obtained in situ from titanium tetra-isopropoxide and 1,1,1,3,3,3-hexafluoro-isopropanol, had less activity (run 11). In addition, *m*-CPBA (*m*-chloroperbenzoic acid) afforded no product in spite of its complete conversion (run 10). In general, the efficiency of peroxide such as H_2O_2 and TBHP, represented by the ratio of the consumed peroxide for the oxidation of alkanes in the total conversion of peroxide, is important in the reac-

Table 1
Oxidation of cyclohexane by *t*-butylhydroperoxide in the presence of titanium complexes

Run	Ti complex	Oxidant[a]	Solvent	Conversion of oxidant (%)[b]	Yield (%)[c]	
					Cyclohexanol	Cyclohexanone
1	$Ti(OPr^i)_4$	TBHP	MeCN	74	47	45
2	–	TBHP	MeCN	10	~ 0	~ 0
3	$Ti(OPr^i)_4$	TBHP	CH_2Cl_2	77	28	26
4	$Ti(OPr^i)_4$	TBHP	HMPA	< 1	~ 0	~ 0
5	$Ti(OPr^i)_4$	TBHP	AcOH	48	22	7
6	$Ti(OPr^i)_4$	TBHP	Cyclohexane[d]	80	56	29
7	$Ti(OEt)_4$	TBHP	MeCN	68	32	20
8	$Ti(OBu^n)_4$	TBHP	MeCN	68	38	27
9	$Ti(OPr^i)_4$	TBHP[e]	MeCN	50	40	41
10	$Ti(OPr^i)_4$	mCPBA	MeCN	> 99	~ 0	~ 0
11	$Ti[OCH(CF_3)_2]_4$	TBHP	MeCN	61	32	25
12	$Ti(OPr^i)_4$	*t*-BuOO-*t*-Bu	MeCN	~ 0	~ 0	~ 0

Ti complex/cyclohexane/oxidant = 0.4/10/5 mmol, solvent 2 ml, room temperature, 1 h, N_2 atmosphere.
[a] Solution of TBHP in CH_2Cl_2.
[b] Determined by iodometric titration.
[c] Based on titanium complex.
[d] 3 ml.
[e] Solution of TBHP in cyclohexane.

tion of titanosilicate. This efficiency in the case of TS-1 is around 60% [16]. However, the maximum efficiency of TBHP in this reaction is about 10% (run 1).

The observation of this reaction was very characteristic. In the almost cases, after a few minutes of the addition of TBHP solution the reaction proceeded exothermically with the evolution of gas and the colorless solution became yellow. The solution was still transparent visually. The gas formed was identified as oxygen (O_2) by GC. The reaction feature in the case of *m*-CPBA was similar. However, white solid (*m*-chlorobenzoic acid) was formed immediately after the evolution of gas. Chlorobenzene was also observed by GLC to indicate that the decomposition of *m*-CPBA occurred. These observations were not reported in the case of TS-1.

Some improvements of the reaction conditions were attempted to enhance the yield of products, and the results are summarized in Table 2. The reaction at higher temperature was examined, because the alkane oxidation using TS-1 is generally carried out at higher tempera-

ture (over 60°C). However, higher reaction temperature (60°C) afforded the products in lower yields with approximately complete conversion of TBHP (run 3). At lower temperature (2°C) the yields of the products also decreased considerably in spite of the slight decrease of the conversion of TBHP (run 2). Therefore, it seems that room temperature is the most suitable for this reaction. MS-4A or dicyclohexylcarbodiimide (DCC) were added as H_2O-remover, because H_2O can be formed as a by-product of the oxidation and titanium alkoxide is very sensitive to it. Furthermore, in the case of Sharpless oxidation the addition of molecular sieve was very effective to enhance the yield of product [34]. However, MS-4A decreased the yields of products (run 6) and DCC had no remarkable effect to this reaction (run 7). In the case that TBHP was added dropwise, the yields of the products decreased considerably (run 8). Although the dropwise addition of titanium tetraisopropoxide did not influence the yields (run 9), the utilization of much amounts of titanium alkoxide (4 mmol) depressed the reaction and white solid (TiO_2) was formed (run 5). These

Table 2
Influences of reaction conditions on oxidation of alkanes

Run	Temperature (°C)	Time (min)	Ti amount (mmol)	Additive	Method of addition	Conversion of oxidant[a] (%)	Yield (%)[b]	
							Cyclohexanol	Cyclohexanone
1	rt	60	0.4	–	one portion	74	47	45
2	2	60	0.4	–	one portion	65	25	30
3	60	60	0.4	–	one portion	94	11	23
4	rt	5	0.4	–	one portion	64	38	39
5	rt	60	4.0	–	one portion	78	~ 0	~ 0
6	rt	60	0.4	MS-4A[c]	one portion	83	11	7
7	rt	60	0.4	DCC[d]	one portion	64	37	50
8	rt	60	0.4	–	dropwise[e]/TBHP	35	21	20
9	rt	60	0.4	–	dropwise[e]/Ti(OPr^i)$_4$	61	40	39

Ti(OPr^i)$_4$/cyclohexane/TBHP = 0.4/10/5 mmol, MeCN 2 ml, room temperature, 1 h, N_2 atmosphere.
[a] Determined by iodometric titration.
[b] Based on Ti(OPr^i)$_4$.
[c] 0.5 g.
[d] Dicyclohexylcarbodiimide: 1 mmol.
[e] 10 min.

results indicated that diluted titanium alkoxide was necessary to achieve this oxidation reaction. Although our modifications were not comprehensive, it seems that this reaction is not catalytic essentially, because all yields of the products based on titanium were under 100%. This observation is also different from the reported one in titanosilicate.

The same reactions of other hydrocarbons are shown in Table 3. In the case of ethylbenzene, only the reaction at benzyl-position occurred (run 1). The reaction of *n*-hexane gave four products. The yields of products reacted at 2-position (2-hexanol and 2-hexanone) were completely in accord with those at 3-position (3-hexanol and 3-hexanone) (run 2). No reaction at primary carbons took place. It is well-known that the reaction of adamantane is advantageous to determine the reaction mechanism of alkane oxidation [35,36]. As adamantane was hard to dissolve in acetonitrile, benzene was used instead of it. In this reaction (run 3), 1-adamantanol was obtained in 44% yield in contrast to the modest yields of 2-adamantanol and 2-adamantanone. Thus, the preferential functionalization of adamantane at tertiary carbon was confirmed. Moreover, the addition of Galvinoxyl as a radical scavenger to the reaction of cyclohexane drastically inhibited the re-
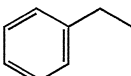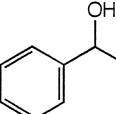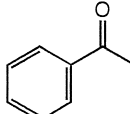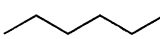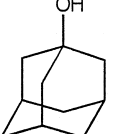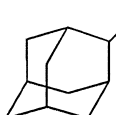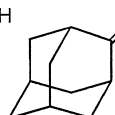
action. TBHP scarcely converted (3%) and no product was obtained. All these results suggested that a radical reaction proceeded in this case.
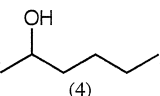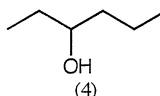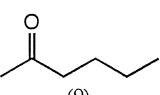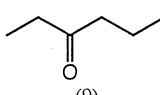
3.2. Mechanistic discussion of the reaction of alkanes with TBHP and titanium alkoxide

Many groups studying the alkane oxidation using TS-1 and its analogues [16–21] unanimously claimed that a radical type reaction realizes the oxidation of alkanes, although there are still many debates on the detailed mechanism. As mentioned before, this reaction by TBHP with titanium alkoxide was also thought to proceed in radical mechanism. However, its reaction features are considerably different from TS-1. The reaction was exothermic with the evolution of oxygen and the color of the solution changed. The result only after 5 min, when the fever became calm and the evolution of oxygen was no longer observed, was approximately in accord with after 1 h (run 4 in Table 2). Therefore, the reaction almost completed during the drastic period until 5 min. This observation was also distinct from the reaction of TS-1.

Scheme 1 shows a representative proposed mechanism of alkane oxidation by H_2O_2 using

Table 3
Oxidation of hydrocarbons using TBHP and Ti(OPr^i)$_4$

Run	Hydrocarbon	Products (Yield / %)[a]		
1		(24)	(24)	
2		(4)	(4)	
		(9)	(9)	
3[b]		(44)	(7)	(7)

Ti(OPr^i)$_4$/hydrocarbon/TBHP = 0.4/10/5 mmol, MeCN 2 ml, room temperature, 1 h, N$_2$ atmosphere.
[a] Based on Ti(OPr^i)$_4$.
[b] Benzene (5 ml) was used instead of MeCN as solvent.

TS-1 [16]. In this case, titanyl group and peroxotitanium group are essential intermediates in the catalytic cycle. Other researchers also mentioned that they are very important or active [3,19]. The reaction of cyclohexane with TBHP in the presence of titanium (IV) oxide acetylacetonate bearing a titanyl group showed the low conversion of TBHP (30%) and no formation of
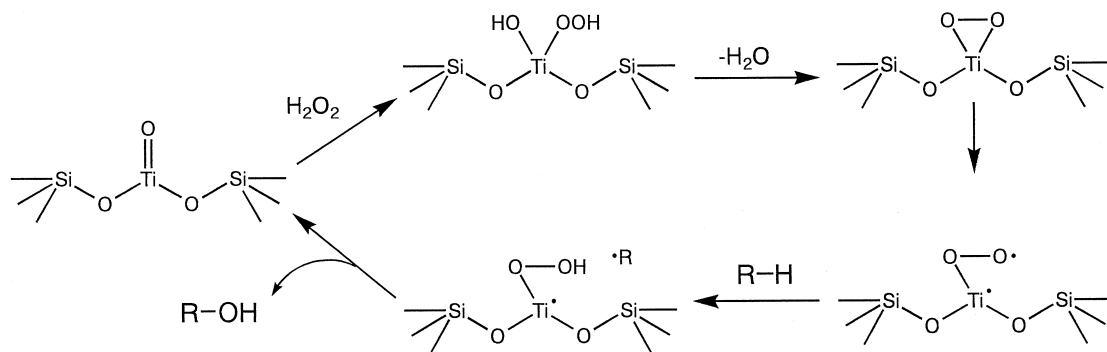
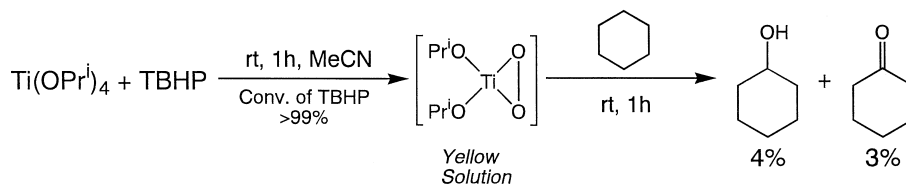Scheme 1. A proposed mechanism of oxidation of alkanes using TS-1.

the oxidation products (cyclohexanol and cyclohexanone). Although this titanyl compound was not the best model of titanosilicate, it is unlikely that the titanyl group is the reactive species for the oxidation of alkanes in this reaction.

The peroxo-titanium group is also regarded as an important intermediate in the reaction of TS-1. It is well-known that four-valent titanium readily forms peroxo-titanium compound with hydroperoxide and the color of these compounds is clear yellow [37–39]. It is also often reported that the color of TS-1 after used for the oxidation reaction became yellow because of the formation of peroxo-titanium [21,40]. Furthermore, the color of the resulting solution in this reaction was yellow. The UV–Vis spectrum of this yellow solution showed the absorption at 361 nm, which was in accordance with reported one assigned to peroxo-titanium in titanosilicate [40]. This showed that a peroxo-titanium type compound formed during the reaction. Therefore, the reaction of this peroxo-titanium species with cyclohexane was suggestive to reveal the mechanism of this reaction (Scheme 2).

Titanium tetra-isopropoxide was reacted with TBHP prior to the addition of cyclohexane. After 1 h when the color of the solution changed to yellow and TBHP converted completely, cyclohexane was added. After stirring at room temperature for 1 h, the formation of cyclohexanol and cyclohexanone were slight. From this observation, it seems that the peroxo-titanium species obtained in this reaction was not an active species. In conclusion, neither titanyl and peroxo-titanium group were excluded as active species in the oxidation reaction using TBHP

and titanium alkoxide. The peroxo-titanium compound observed here was only an inert by-product.

From all these observations, a plausible mechanism of the oxidation reaction of alkanes with TBHP and titanium alkoxide is shown in Scheme 3. The exchange of alkoxy groups on titanium occurs at the first stage, because the OH proton in TBHP is acidic ($pK_a = 12.8$) [41]. This step is well-known in the Sharpless oxidation [1]. In the case of epoxidation, one oxygen in t-butylperoxide (O–O-t-Bu) group readily reacts with a double bond of an alkene. The considerable yield of epoxide has already been reported in the reaction of cyclohexene [28]. However, in the case of alkane oxidation, there are no functional group in the reaction mixture. The intermediate **1** bearing two t-butylperoxide groups produces *tert*-butoxyl radical **3** with the formation of peroxo-titanium compound (**2**) which has yellow color. When the radical **3** reacts with alkane, the abstraction of hydrogen forms the corresponding alkyl radical **4**. This radical **4** gives the corresponding alcohol with TBHP and ketone by further oxidation. It is natural that the tertiary carbon reacted preferentially to the primary and the secondary carbons and that Galvinoxyl inhibited the reaction. However, the radical **3** also reacts with TBHP to generate oxygen and to form *tert*-butanol and *tert*-butyl peroxide. This side-reaction is predominant because the reaction of the t-butoxyl radical **3** with TBHP is considerably facile compared with the reaction with alkane. Consequently, the total yield of the products was about 90% even in the highest case.

Scheme 2. Reactivity of peroxo titanium complex obtained from TBHP and Ti(OPr^i)$_4$.
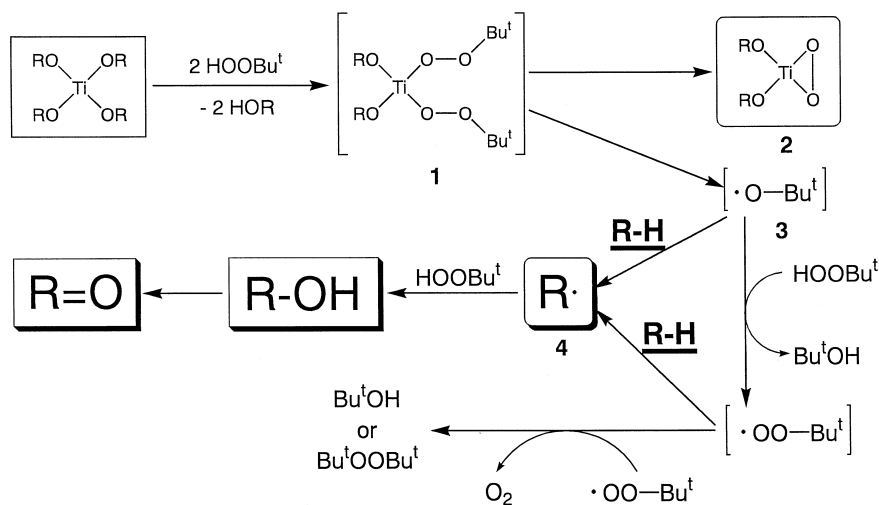
Scheme 3. A plausible reaction mechanism of oxidation of alkanes using TBHP and titanium alkoxide.

3.3. Comparison of the alkane oxidation between titanium alkoxide and titanosilicate

Although the local structure of titanium in titanosilicates must be a kind of titanium alkoxide, the features of the reaction we studied were perfectly different from those of titanosilicates. In addition, the same type of reaction with benzene formed no phenol and benzene was recovered completely, although the transformation of benzene to phenol was reported in titanosilicates [42]. It is thought that the electron density of titanium in titanosilicates is lower than titanium alkoxide because of electron-withdrawing siloxy group. However, titanium tetra-1,1,1,3,3,3-hexafluoro-isopropoxide with high electron-withdrawing group had less activity (run 11 in Table 1). Titanium-triethanol-aminato-isopropoxide formed from titanium tetra-isopropoxide and triethanol amine [43,44] with tridentate alkoxide ligand resulted in neither conversion of TBHP nor formation of oxidation products. Furthermore, the titanium complex with diethyl tartrate, which is famous as the reagent for Katsuki–Sharpless asymmetric epoxidation [1,2] and whose structure was identified as six coordinated titanium [45], had no activity in the reaction of alkanes. Titanium in titanosilicates is thought to be fixed in the sil-

ica-matrix, being forced to be the tetrahedral coordination. It seems that this coordination state is hard to change even when it reacts with peroxy compounds such as H_2O_2 and TBHP. On the other hand, the coordination state of titanium tetra-alkoxide was alterable. Therefore, not only the electronic circumstance but also the coordination one of titanium are seem to be essential factors for the specific reactivity of titanosilicates. The studies using other titanium complexes as model compounds of titanosilicates are now under investigation.

4. Conclusion

The oxidation of alkanes by TBHP was effected in the presence of titanium tetra-alkoxides. TBHP and titanium tetra-alkoxide form *t*-butoxyl radical, which performs the competitive reaction with between alkane and TBHP. The abstraction of hydrogen from alkane is more difficult than the reaction with TBHP. Consequently, the total yields of oxidized products and the efficiency of TBHP were low. Thus, it was revealed that the fundamental reaction manner of titanium alkoxides, whose coordination state is not fixed tightly, was different from that of titanosilicates. Therefore, the spe-

cific reaction behaviors of titanium in titanosilicate must be derived from the characteristic situation of titanium in silica-matrix.

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