

# Epoxidation of cyclohexene catalyzed by transition-metal substituted $\alpha$ -titanium arsenate using *tert*-butyl hydroperoxide as an oxidant

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## Abstract

Epoxidation of cyclohexene, using transition-metal substituted  $\alpha$ -titanium arsenate { $\alpha$ -TiMAs, where M=Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III)} as a catalyst and dry *tert*-butyl hydroperoxide as an oxidant, was studied. In the epoxidation reaction, cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone. It was found that the reactivity of the epoxidation reaction decreased in the order  $\alpha$ -TiRuAs >  $\alpha$ -TiMnAs >  $\alpha$ -TiFeAs >  $\alpha$ -TiCrAs >  $\alpha$ -TiCoAs >  $\alpha$ -TiCuAs. A maximum selectivity for epoxidation of cyclohexene (89.89%) was observed for  $\alpha$ -TiRuAs/dryTBHP system after 4 h of reaction when concentrations of the catalyst and the substrate were 0.20 and 20 mmol, respectively. The competitive epoxidation of cyclic olefins were studied and the reactivity-order in the relative rates of epoxidation of cyclic olefins was found to decrease in the order norbornene > cyclooctene > cyclohexene > cyclopentene. The mechanism for epoxidation of cyclohexene catalyzed by  $\alpha$ -TiMAs/dryTBHP system is proposed.

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## 1. Introduction

The direct oxidation of hydrocarbons is a field of academic and industrial importance. The epoxidation of olefins, using metal catalyzed system, plays a central role in the selective and partial oxidation of both saturated and unsaturated hydrocarbons to useful products. Complexes of various transition-metals, viz. Fe, Cr, Ru, Mn, Cu, Co, etc., are used in homogeneous catalytic systems for epoxidation of olefins to study model systems for cytochrome P-450 [1–13]. However, heterogeneous catalytic systems are better than similar homogenous catalytic systems in terms of separation of reaction products from the catalyst [16–22]. In the process of heterogenization of homogeneous catalysts, complexes are affixed to surfaces of polymers and such polymer-supported transition-metals are used as catalysts in epoxidation of olefins [22]. The ion-exchange method of catalyst immobilization on layered compounds is simpler compared to the procedures required for at-

tachment of complexes to polymers [23]. Based on cation exchange, polymer-supported catalysts are also developed [24], however the thermo-oxidative instability of the polymer under reaction conditions and the poor mechanical properties of the organic support are the main drawbacks of these systems [25]. In this regard also, the ion-exchange method of catalyst immobilization on layered compounds is better because it provides temperature- and solvent-stable inorganic layered exchangers of known structure as support [23]. Transition-metal substituted  $\alpha$ -zirconium phosphate is used as a catalyst in epoxidation of olefin mainly because  $\alpha$ -zirconium phosphate has a structure with zeolite type cages and it behaves as a cation exchanger [26]. The compound  $\alpha$ -titanium arsenate is a cation exchanger [27] and it has a layered structure similar to that of  $\alpha$ -zirconium phosphate [28]. The group 4B arsenates form layered compounds of two types: the  $\alpha$  type, having relatively small interlayer spacing (7.77 Å), and the  $\gamma$  type, having larger interlayer spacing (~11 Å) [28]. The preparation and ion exchange properties of  $\alpha$ -titanium arsenate, {Ti(HAsO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O}, is examined [27,29]. The ion exchange properties of layered titanium arsenate as weak acid cation exchanger are studied [30]. Weak acid cation

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exchanger containing transition-metals, Mo, V, and Ti, are used for epoxidation of alkenes by organic hydroperoxides as oxidant [31]. Therefore, it is interesting to investigate the immobilization of catalytically active transition-metal ions on  $\alpha$ -titanium arsenate and potential of transition-metal substituted supports as catalysts in epoxidation of olefins. *tert*-Butyl hydroperoxide (TBHP) is one of the best sources of oxygen atoms for a variety of organic oxygenations because of economics, selectivity and safety [32] and product isolation is also significantly easier [33]. However, commercially available TBHP, which is widely used in industrial production of epoxides, contains (by weight) 70% TBHP and 30% H<sub>2</sub>O. The epoxidation of cyclohexene is inhibited by water [34] and  $\alpha$ -titanium arsenate ( $\alpha$ -TiAs) is strongly hydrolyzed in aqueous medium [28]. Therefore, dry TBHP is better than aqueous TBHP as an oxidant in the epoxidation of cyclohexene by transition-metal substituted  $\alpha$ -titanium arsenate.

In this paper, we are reporting synthesis and catalytic behavior of transition-metal substituted  $\alpha$ -titanium arsenate ( $\alpha$ -TiMAs) {where M = Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III)} in the epoxidation of cyclohexene using dry TBHP as an oxidant.

## 2. Experimental

### 2.1. Starting materials

Sodium arsenate (E. Merck), 15% (w/v) titanate chloride solution (BDH) and six transition-metal salts, viz. copper acetate, cobaltous chloride, manganous acetate, ferric chloride, chromium chloride and ruthenium chloride (all E. Merck) were of reagent grade. The starting olefins, viz. cyclohexene, cyclopentene, cyclooctene, and norbornene (all E. Merck) were checked by gas chromatography (G.C.) to ensure that no oxidation products were present in the substrate. Whenever oxidation products were found, the olefins were purified by literature procedure [35]. All the olefins were stored at  $-20^{\circ}\text{C}$ . The solution of dry TBHP in benzene was obtained by careful azeotropic distillation of the aqueous 70% commercial solution (E. Merck) according to the procedure described by Sharpless et al. [32]. Benzene (E. Merck), used as solvent, was purified by a known method [36]. The strength of dry TBHP was estimated by a known procedure [32]. The reference sample of epoxide was prepared by the standard procedure [37].

Analytical gas chromatography was carried out on a gas chromatograph (Chromatography and Instruments Company (CIC), Baroda, India) with dual flame ionization detector (FID) and an attached XY recorder. Differential scanning calorimetry (DSC) studies of hydrogen form of  $\alpha$ -titanium arsenate ( $\alpha$ -TiH<sub>2</sub>As) and transition-metal substituted  $\alpha$ -titanium arsenate ( $\alpha$ -TiMAs) were done on a differential scanning calorimeter (Polymer Rheometric Ltd., UK) at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The electron spin resonance

(ESR) spectrum was recorded at R.S.I.C., Indian Institute of Technology-Mumbai, India. The *g* value is reported relative to a 2,2-diphenyl-1-picrylhydrazil (dpph) standard with  $g = 2.0036$ .

### 2.2. Preparation of catalysts

The catalysts were prepared in two steps, described below:

- (1) In the first step,  $\alpha$ -TiH<sub>2</sub>As, { $\alpha$ -Ti(HAsO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O}, was synthesized by a known procedure [27].
- (2) In the second step, hydrogen of  $\alpha$ -TiH<sub>2</sub>As was substituted by a transition-metal ion, M, where M stands for six transition-metal ions, viz. Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III), to synthesize  $\alpha$ -TiMAs.

For preparation of  $\alpha$ -TiCuAs, stock solution of copper acetate (0.1 N) was prepared and initial pH of the solution was measured on a digital pH meter (PC DPL-KOTA, INDIA). Then 100 ml of the solution was vigorously stirred with 1.0 g of  $\alpha$ -TiH<sub>2</sub>As by a magnetic-stirrer for 1 h. During stirring, the pH of the solution was measured at an interval of every 10 min to monitor change in the pH value. The uptake of copper ion is determined from the change in pH value and constancy of pH is an indication of attainment of equilibrium [38]. After attainment of equilibrium, the solution was filtered. The filtered solid was added to a fresh solution (100 ml) of copper acetate and the process was repeated again. The process was repeated until there was no further change in pH of the solution. The total uptake of copper ion is the sum of uptakes of copper ion in each trial. The cation exchanger, so obtained, was filtered and washed with distilled water. Finally, it was dried in an oven at  $40^{\circ}\text{C}$ .

For preparation of  $\alpha$ -TiCoAs,  $\alpha$ -TiMnAs,  $\alpha$ -TiFeAs,  $\alpha$ -TiCrAs and  $\alpha$ -TiRuAs, stock solutions of cobaltous chloride (0.1 N), manganous acetate (0.1 N), ferric chloride (0.1 N), chromium chloride (0.1 N) and ruthenium chloride (0.005 N) were prepared, respectively, and the remaining procedure in each case was same as described in the case of  $\alpha$ -TiCuAs.

### 2.3. Catalytic epoxidation of cyclohexene

Epoxidation of cyclohexene was carried out in a three-necked round bottom flask (100 ml) under nitrogen atmosphere. Nitrogen was flushed for 10 min through the flask, which was loaded with benzene (10 ml), cyclohexene (20 mmol), catalyst ( $\alpha$ -TiMAs, 0.2 mmol) and dodecane (an internal standard, 0.1 ml). After nitrogen flushing, TBHP (4 mmol) was added and the contents of the flask were heated at  $80^{\circ}\text{C}$  on a magnetic hot plate for 4 h with continuous stirring. After completion of the reaction, the contents of the flask were cooled in an ice-bath and the catalyst was filtered out. The filtered catalyst was analyzed by ESR. In the filtrate, 10 ml of freshly prepared 10% solution of sodium sulfite was added drop by drop under constant stirring to destroy unreacted TBHP. The products

were extracted with ether and then dried using anhydrous magnesium sulphate. These products were analyzed by gas chromatography using XE-60 as column at 120 °C.

#### 2.4. Catalyst concentration

The effect of catalyst concentration on the epoxidation of cyclohexene was studied by changing the concentration of the catalyst ( $\alpha$ -TiRuAs) from 0.1 to 0.5 mmol. The reactions were carried out by taking catalyst ( $\alpha$ -TiRuAs), cyclohexene (20 mmol), TBHP (4 mmol) and dodecane (0.1 ml) in benzene (10 ml) under nitrogen atmosphere. The contents of the flask were heated at 80 °C for 4 h with continuous stirring. After completion of the reactions, the products were extracted and analyzed in the same way as done in the case of epoxidation of cyclohexene.

#### 2.5. Substrate concentration

The effect of cyclohexene concentration was studied by taking catalyst ( $\alpha$ -TiRuAs, 0.2 mmol), TBHP (4 mmol), dodecane (0.1 ml) and six different concentrations of cyclohexene (1, 5, 10, 15, 20 and 25 mmol) in benzene (10 ml) under nitrogen atmosphere. The contents of the flask were heated at 80 °C for 4 h with continuous stirring. After completion of the reactions, the products were extracted and analyzed in the same way as done in the case of epoxidation of cyclohexene.

#### 2.6. Competitive epoxidation of cyclic olefins

The competitive epoxidation of cyclic olefins, viz. cyclopentene, cyclohexene, cyclooctene, and norbornene were studied by mixing cyclohexene (20 mmol), another cyclic olefin (20 mmol), catalyst ( $\alpha$ -TiRuAs, 0.4 mmol), TBHP (8 mmol), and dodecane (0.1 ml) in benzene (10 ml) in a three-necked round bottom flask (100 ml) under nitrogen atmosphere. The contents of the flask were heated at 80 °C for 4 h with continuous stirring. After completion of the reaction, the products were extracted in the same way as extracted in the case of epoxidation of cyclohexene. Two columns XE-60 (at 120 °C) and Carbowax-20M (at 90 °C) of the gas chromatograph were used to analyze the products.

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

The catalysts ( $\alpha$ -TiMAs), where M = Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III), were prepared by exchanging surface protons (hydrogen ions) from  $\alpha$ -TiH<sub>2</sub>As with corresponding transition-metal ion. The total number of released hydrogen ions [H<sup>+</sup>] in the exchange reaction determined the total uptake of transition-metal ions on the surface of  $\alpha$ -TiH<sub>2</sub>As. The number of hydrogen ions [H<sup>+</sup>] released in the exchange reaction in each trial was calculated from pH value of the metal solution at equilibrium. The process of attaining equilibrium was repeated until the subsequent pH change was negligible and the total uptake of transition-metal ions is determined from the total change in the pH value in all trials [38].

In case of catalyst  $\alpha$ -TiCuAs, the final pH value of the copper acetate solution was 2.87 in the first trial. Thus, [H<sup>+</sup>] =  $1.348 \times 10^{-3}$  M/l ( $6.74 \times 10^{-5}$  moles per 50 ml). The weight of the sample ( $\alpha$ -TiH<sub>2</sub>As) was 1.0 g, thus  $6.74 \times 10^{-5}$  moles per 50 ml is equal to 0.067 m eq./g. Five such trials were required after which change in pH was negligible. In the last trial, the sample was kept in the solution for overnight to observe any change in the pH value. The data for these trials are given in Table 1. The total uptake of copper metal ions in  $\alpha$ -TiCuAs, obtained by summing uptakes of copper ions in five trials, was 0.128 m eq./g. Similarly, the total uptake of metal ions in other five catalysts, viz.  $\alpha$ -TiCoAs,  $\alpha$ -TiMnAs,  $\alpha$ -TiFeAs,  $\alpha$ -TiCrAs and  $\alpha$ -TiRuAs were estimated as 0.074 m eq./g, 0.013 m eq./g, 1.124 m eq./g, 0.367 m eq./g and 0.575 m eq./g respectively (Table 1).

DSC studies of  $\alpha$ -TiH<sub>2</sub>As showed two endotherms at 175 and 550 °C, which is in consistent with the earlier observation [27]. Endotherm at 175 °C was due to loss of external water molecules while endotherm at 550 °C was due to loss of one more water molecule due to condensation. In case of  $\alpha$ -TiMAs, only one endotherm at 175 °C was observed. The absence of the endotherm at 550 °C indicated absence of any replaceable H<sup>+</sup> ion. These results confirm that hydrogen form of titanium arsenate is converted into transition-metal substituted titanium arsenate.

Table 1  
Transition-metal ions uptake of  $\alpha$ -titanium arsenate ( $\alpha$ -TiH<sub>2</sub>As)

Metal ions	Trial no.												Total uptake (meq./g)
	1		2		3		4		5		6		
	pH	Uptake (meq./g)	PH	Uptake (meq./g)	pH	Uptake (meq./g)	pH	Uptake (meq./g)	pH	Uptake (meq./g)	pH	Uptake (meq./g)	
Cu(II)	2.87	0.067	3.24	0.029	3.50	0.016	3.67	0.011	4.01	0.005	4.01	0.000	0.128
Co(II)	3.01	0.049	3.30	0.025	3.30	0.000	–	–	–	–	–	–	0.074
Mn(II)	3.75	0.008	3.99	0.005	3.99	0.000	–	–	–	–	–	–	0.013
Fe(III)	2.19	0.322	2.24	0.288	2.27	0.269	2.31	0.245	2.31	0.000	–	–	1.124
Cr(III)	2.29	0.256	2.92	0.060	3.28	0.026	3.30	0.025	3.30	0.000	–	–	0.367
Ru(III)	2.51	0.154	2.54	0.144	2.55	0.141	2.57	0.136	2.57	0.000	–	–	0.575

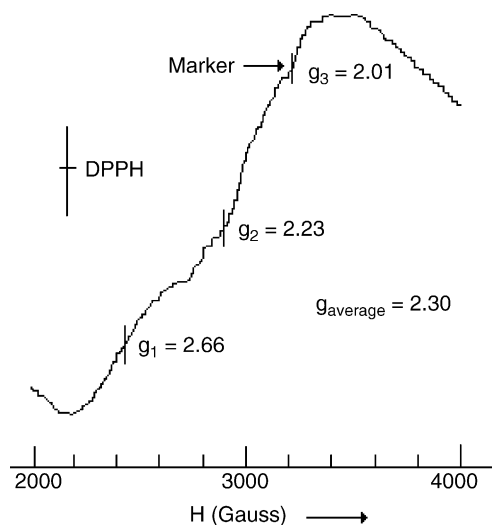
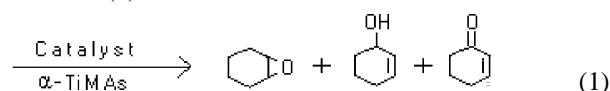
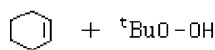


Fig. 1. ESR spectrum of Ru(III) of  $\alpha$ -TiRuAs.



The ESR spectrum of randomly oriented powder sample of  $\alpha$ -TiRuAs was taken before and after catalytic reactions at room temperature. The ESR spectrum of  $\alpha$ -TiRuAs, taken before catalytic reaction, showed a broad signal, Fig. 1. The three 'g' values,  $g_1$ ,  $g_2$  and  $g_3$ , obtained were 2.66, 2.23 and 2.01, respectively, and the average 'g' value was 2.30. Thus, the oxidation state of ruthenium was three and there was rhombic distortion in  $\alpha$ -TiRu(III)As [39,40]. The ESR spectrum of  $\alpha$ -TiRuAs, taken after catalytic reaction, did not show any typical ESR signal indicating absence of Ru(III) species.

### 3.2. Epoxidation of cyclohexene

The epoxidation of cyclohexene using  $\alpha$ -TiMAs/TBHP system was studied under atmospheric air as well as under nitrogen. It was observed that cyclohexene was oxidized to cyclohexene oxide (epoxide), cyclohexenol (alcohol) and cyclohexenone (ketone) in the epoxidation reaction. The yield of epoxide was more in the epoxidation reaction under nitrogen compared to that under atmospheric air. Similar observation is reported in the epoxidation reaction with

$\text{CrO}_3$ /TBHP system [10]. The epoxidation reaction is inhibited by water while accelerated by nondonor polar solvents [34] and azeotropically dried solution of TBHP in benzene is very stable to storage [41]. Thus, instead of commercial TBHP (70% in water), dry TBHP in benzene was used as the oxidant in the epoxidation of cyclohexene. The yields of the products were based on the internal standard (dodecane) and the consumption of TBHP was determined iodometrically.

Six  $\alpha$ -TiMAs catalysts [M = Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III)] and  $\alpha$ -TiH<sub>2</sub>As were separately tested in similar experimental conditions for epoxidation of cyclohexene. In the study, it was found that all the six  $\alpha$ -TiMAs catalysts were active for the epoxidation of cyclohexene with dry TBHP as an oxidant whereas  $\alpha$ -TiH<sub>2</sub>As was catalytically inactive. Therefore, the exchange of transition-metal ion with hydrogen converted a non-catalyst,  $\alpha$ -TiH<sub>2</sub>As, into active catalysts for the epoxidation of cyclohexene. The catalytic epoxidation of cyclohexene, catalyzed by  $\alpha$ -TiMAs/dryTBHP system can be explained by the reaction (1):

The formation of cyclohexenol and cyclohexenone in the epoxidation reaction suggest that a free radical pathway is operative [42].

The selectivity of the epoxide (cyclohexene oxide) is a measure of the reactivity of the catalyst ( $\alpha$ -TiMAs). The percentage-conversion of the substrate and the percentage-selectivity of the products in the epoxidation reaction are calculated as

$$\text{substrate conversion (\%)} = \left[ \frac{\text{substrate converted (moles)}}{\text{substrate used (moles)}} \right] \times 100$$

$$\text{product selectivity (\%)} = \left[ \frac{\text{product formed (moles)}}{\text{substrate converted (moles)}} \right] \times 100$$

The catalytic performances of the six catalysts in terms of conversion of cyclohexene (%) and selectivity of the epoxide (%) are given in Table 2. The reactivity of the six catalysts in the epoxidation reaction decreased in the following

Table 2  
Epoxidation of cyclohexene catalyzed by  $\alpha$ -TiMAs/dryTBHP system

S. no.	Catalyst	Conversion of cyclohexene (%)	Selectivity of epoxide (%)	Selectivity of cyclohexenol (%)	Selectivity of cyclohexenone (%)
1	$\alpha$ -TiCuAs	4.36	62.11	34.56	3.33
2	$\alpha$ -TiCoAs	5.17	63.02	34.98	3.00
3	$\alpha$ -TiMnAs	18.65	86.09	12.71	1.20
4	$\alpha$ -TiFeAs	11.90	78.24	19.95	1.81
5	$\alpha$ -TiCrAs	10.11	79.47	18.80	1.73
6	$\alpha$ -TiRuAs	18.41	89.89	8.99	1.12

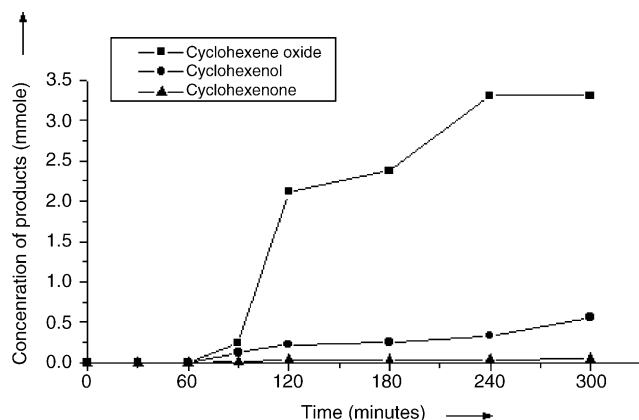
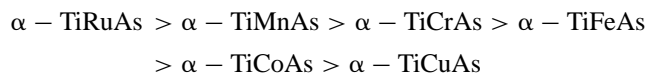


Fig. 2. Kinetics of epoxidation of cyclohexene catalyzed by  $\alpha$ -TiRuAs/dryTBHP system.

order:



It is observed that the conversion of cyclohexene was a maximum (18.65%) in case of  $\alpha$ -TiMnAs however the selectivity of epoxide was not a maximum (86.09%) due to considerable formation of other products (13.91%). In case of  $\alpha$ -TiRuAs, the conversion of cyclohexene was not the maximum (18.41%) but the selectivity of epoxide was the maximum (89.89%) due to minimum formation of other products (10.11%). Therefore,  $\alpha$ -TiRuAs is the best catalyst for the epoxidation of cyclohexene. The catalytic activity of  $\alpha$ -TiRuAs is examined in detail. A study of the catalytic behavior of  $\alpha$ -TiRuAs is also interesting because relatively little attention has been devoted to ruthenium as an epoxidation catalyst compared to other transition metals, viz. iron and manganese, though ruthenium is a potentially interesting epoxidation catalyst due to its ability to form a variety of high-valent oxo complexes [12].

The kinetics of cyclohexene epoxidation using  $\alpha$ -TiRuAs/dryTBHP system was monitored at different time-intervals, Fig. 2. It was observed that initial 1 h was the induction period of the catalyst for epoxidation reaction during which no product formation took place and the reaction was complete in 4 h after which no further epoxide formation took place. The conversion of cyclohexene and the selectivity of

products were estimated at different times. The percentage conversion of cyclohexene kept on increasing continuously with time. The percentage formation of cyclohexenol and cyclohexenone were a maximum in first 1.5 h and then it decreased with time. The percentage selectivity of epoxide reached a maximum (89.89%) after 4 h and then started decreasing. After completion of epoxidation reaction, the catalyst was filtered out and its ESR spectrum confirmed demetallation of the  $\alpha$ -TiRuAs. The demetallation produced free metal ions, which increased homolytic decomposition of TBHP, which in turn increased the selectivity of cyclohexenol and cyclohexenone. Due to increase in selectivity of cyclohexenol and cyclohexenone, the selectivity of cyclohexene oxide decreased. Leaching of metal ions from the support is one of the major drawbacks of supported catalysts [43], however, some metal-leaching is observed in several catalytic systems [13–18].

### 3.3. Effect of catalyst concentration

The effect of the concentration of catalyst,  $\alpha$ -TiRuAs, in the epoxidation of cyclohexene using dry TBHP as an oxidant was studied and the results are given in Table 3 and Fig. 3. It was observed that the selectivities of cyclohexene oxide, cyclohexenol and cyclohexenone were different at different concentrations of the catalyst. At 0.20 mmol concentration of the catalyst, the selectivity of cyclohexene oxide was a maximum (89.89%), while selectivity of other products was a minimum (cyclohexenol=8.99% and cyclohexenone=1.10%). Similar observation is reported in case of Fe (SALEN)Cl/PhIO system [2]. It was also observed that with change of concentration of the catalyst, the change in the selectivity of cyclohexenone was relatively lesser than that of other products.

### 3.4. Effect of substrate concentration

The effect of the concentration of cyclohexene (substrate) in the epoxidation reaction of cyclohexene using  $\alpha$ -TiRuAs/dryTBHP system was studied. The results of the conversion of cyclohexene, selectivity of products for different concentrations of cyclohexene are summarized in Table 4 and plotted in Fig. 4. The concentration of cyclohexene was varied from 1 to 25 mmol and it was observed that the yield of all the products increased with increase

Table 3

Effect of concentration of catalyst on the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiRuAs/dryTBHP system

S. No.	Concentration of catalyst (mmol)	Conversion of cyclohexene (%)	Selectivity of epoxide (%)	Selectivity of cyclohexenol (%)	Selectivity of cyclohexenone (%)
1	0.10	16.11	89.45	9.34	1.21
2	0.20	18.41	89.89	8.99	1.12
3	0.30	19.65	83.20	15.30	1.50
4	0.40	19.91	81.86	16.51	1.63
5	0.50	19.96	81.38	16.96	1.66

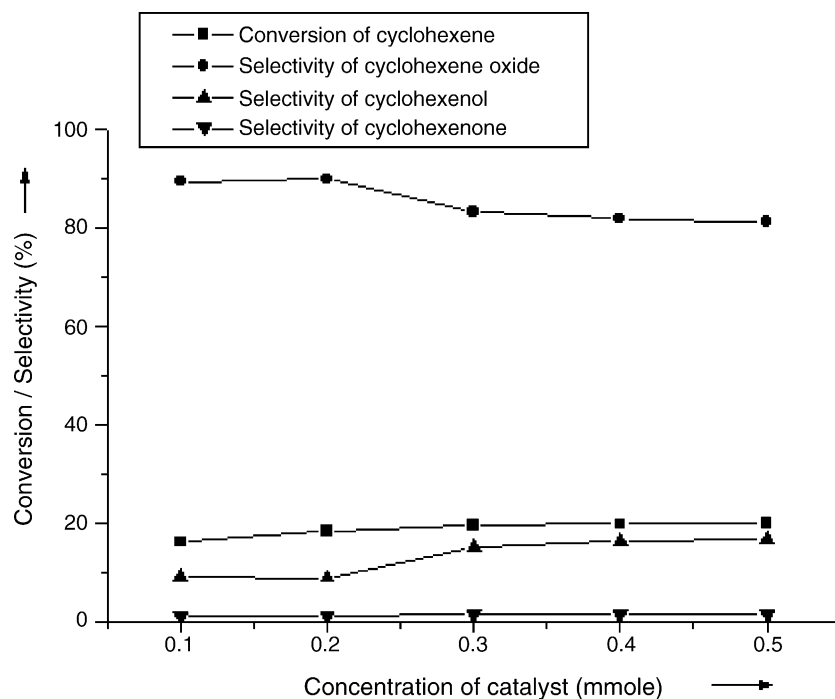


Fig. 3. Effect of concentration of catalyst on the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiRuAs/dryTBHP system.

Table 4

Effect of concentration of substrate on the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiRuAs/dryTBHP system

S. no.	Concentration of substrate (mmol)	Conversion of cyclohexene (%)	Selectivity of epoxide (%)	Selectivity of cyclohexenol (%)	Selectivity of cyclohexenone (%)
1	1.00	2.00	81.45	15.29	3.26
2	5.00	3.78	83.38	13.51	3.11
3	10.00	5.08	84.45	12.60	2.95
4	15.00	12.47	88.41	12.19	1.40
5	20.00	18.41	89.89	8.99	1.12
6	25.00	19.55	84.66	13.68	1.66

in concentration of cyclohexene. The selectivity of cyclohexene oxide reached a maximum (89.89%) for 20 mmol concentration of cyclohexene.

### 3.5. Effect of water on selectivity of epoxide

In the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiRuAs/TBHP (70% in water), the conversion of cyclohexene was 18.43% and the selectivity of the epoxide was 78.64%, when the concentrations of catalyst and substrate were 0.20 and 20 mmol, respectively. In similar experimental conditions by use of dry TBHP in benzene as the oxidant, the conversion of cyclohexene was almost the same (18.41%) while the selectivity of the epoxide was more (89.89%).

### 3.6. Competitive epoxidation

The relative rate of the epoxidation of cyclic olefins, viz. cyclopentene, cyclohexene, cyclooctene, and norbornene were studied using  $\alpha$ -TiRuAs/dryTBHP system and the

results are summarized in Table 5. The order of reactivity of cyclic olefins decreased in the order, norbornene > cyclooctene > cyclohexene > cyclopentene. The higher rates of epoxidation with norbornene and cyclooctene compared to cyclohexene indicate that the olefin is not rigidly coordinated to the metal center during epoxidation. Had olefin been coordinated to metal center, than the rate of epoxidation of olefin having a carbon atom number higher than cyclohexene would have been lower, contrary to observation with  $\alpha$ -TiRuAs/dryTBHP system. Hydrogenation of olefins using  $\text{RhCl}(\text{PPh}_3)_3$  showed that the rate of

Table 5

Competitive epoxidation of cyclic olefins catalyzed by  $\alpha$ -TiRuAs/dry-TBHP system

S. no.	Substrate	Relative ratio of epoxide
1	Cyclopentene	0.53
2	Cyclohexene	1.00
3	Cyclooctene	1.19
4	Norbornene	2.00

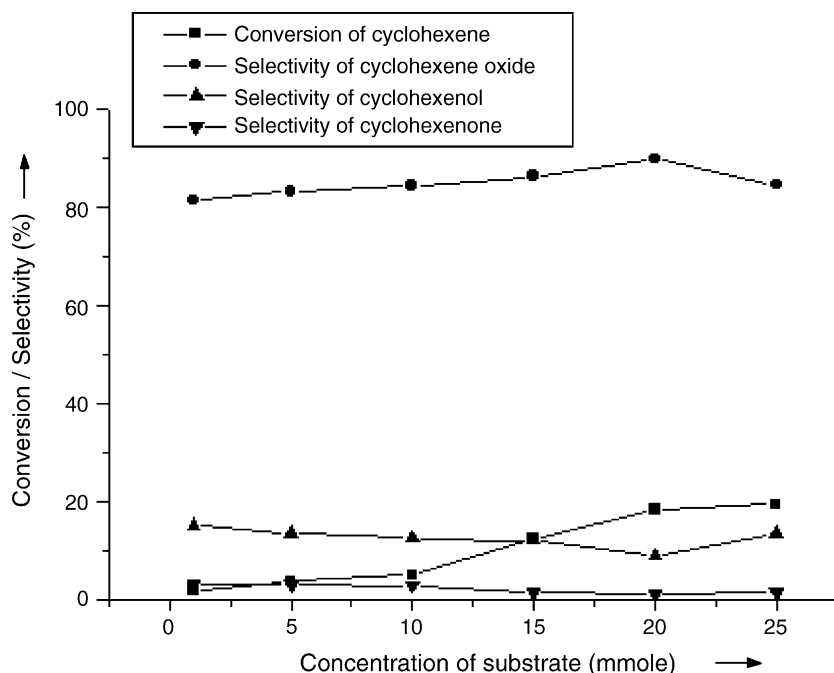


Fig. 4. Effect of concentration substrate on the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiRuAs/dryTBHP system.

hydrogenation decreased with increasing olefin ring size  $C_5 > C_6 > C_7 > C_8 > C_9$  as coordination of olefin to the metal center takes place in the transition state [44]. Higher rates of epoxidation for norbornene and cyclooctene have been observed for Fe(SALEN)Cl/PhIO and Mn(SALEN)NCS/PhIO catalytic systems [2,8]. It suggests that the conformation, the bond angle strain and the torsional strain play important roles in governing the relative rates of the epoxidations of the cyclic olefins.

### 3.7. Mechanism

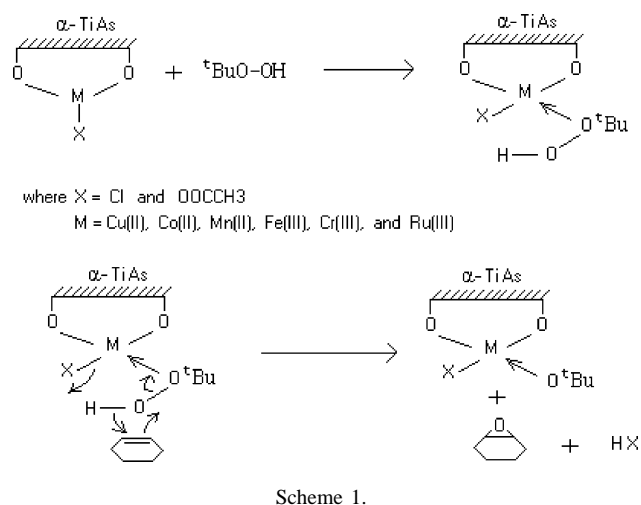
On the basis of the experimental observations, a mechanism is proposed which explains the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiMAs/dryTBHP system. The following observations are noticed in the epoxidation of cyclohexene catalyzed by  $\alpha$ -TiMAs/dryTBHP system:

- The selectivity for epoxidation is high in the beginning.
- The catalytic activity decreases after a certain time.
- The byproducts of the reaction are cyclohexenol and cyclohexenone.

The mechanism of epoxidation of cyclohexene catalyzed by  $\alpha$ -TiMAs/dryTBHP system is described in Scheme 1.

According to the Scheme 1, initial complex formation between metal catalyst ( $\alpha$ -TiMAs) and *tert*-butyl hydroperoxide renders the peroxidic oxygen more electrophilic and hence more labile to attack by an olefinic double bond. The remaining *tert*-butoxy ( $O^{\cdot t}Bu$ ) radical is a worse leaving group as far as the catalytic reaction is concerned. Cyclohexene reacts with *tert*-butoxy radical to form cyclohexenol,

which further oxidizes to cyclohexenone. Thus, epoxidation by  $\alpha$ -TiMAs/dryTBHP system involves two competing reactions, viz. and (a) epoxidation and (b) homolytic decomposition of TBHP. The results on catalytic epoxidation demonstrate that the performance of transition-metal substituted inorganic ion exchangers depend on the relative rates of metal catalyzed epoxidation and metal catalyzed decomposition of TBHP. In case of metal catalyzed epoxidation, the high selectivity of epoxidation is obtained due to the electrophilic attack on the olefin that involves heterolytic mechanism [46]. The transition-metal ion (M), which is present on the surface of the heterogeneous catalyst ( $\alpha$ -TiMAs), provides selectivity for the epoxidation and also suppresses the side products, which are formed due



to homolytic decomposition of TBHP. The observation of the highest relative rate of epoxidation by norbornene in competitive epoxidation of cyclic olefins confirms that complex formation takes place between metal catalyst and TBHP. If olefin had coordinated to the metal catalyst in the epoxidation reaction then a reverse order of relative rate of epoxidation would have been observed [44]. Demetallation of the supported catalyst decreases the catalytic activity after four hours in the epoxidation reaction [3,45] while increases metal-catalyzed homolytic decomposition of TBHP [46,47]. The products formed in this reaction are cyclohexenol and cyclohexenone.

In the proposed mechanism, the introduced transition-metal ions act as the active sites for oxygen transfer and the reactivity of oxygen transfer depends on the strength of metal–oxygen (M–O) bond. Thus the catalytic inactiveness of the hydrogen form of titanium arsenate,  $\alpha$ -TiH<sub>2</sub>As, can be explained by the absence of active sites for oxygen transfer [26]. Analogous mechanisms are suggested for epoxidation of cyclohexene catalyzed by molybdenum [46], boron [47] and titanium supported on silica [48].

#### 4. Conclusions

Six transition-metal substituted titanium arsenate catalysts,  $\alpha$ -TiMAs [M = Cu(II), Co(II), Mn(II), Fe(III), Cr(III) and Ru(III)], were synthesized and studied with dry TBHP as an oxidant for epoxidation of cyclohexene. A maximum selectivity for epoxidation of cyclohexene (89.89%) was observed for  $\alpha$ -TiRuAs/dryTBHP system after 4 h of reaction when concentrations of catalyst and substrate were 0.20 and 20 mmol, respectively. A mechanism is proposed, which satisfactorily explains the catalytic activity of the  $\alpha$ -TiMAs/dryTBHP system for the epoxidation of cyclohexene.

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