Baeyer–Villiger rearrangement catalysed by titanium silicate molecular sieve (TS-1) / H_2O_2 system

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Received 5 March 1996; accepted 29 March 1996

Titanium silicate molecular sieve TS-1 has been found to be an efficient catalyst for Baeyer–Villiger (BV) oxidation of cyclic and aromatic ketones under triphase conditions (solid catalyst along with two immiscible liquid reactants in the absence of any cosolvent), using dilute H_2O_2. Reactions studied are the oxidation of cyclohexanone and acetophenone. Whereas in the case of cyclohexane, ε-caprolactone, a BV product along with hydroxy and diketones is formed, in the case of acetophenone, phenyl acetate, a BV product along with *o*- and *p*-hydroxyacetophenone is formed. The acidic nature of titanium peroxo species, stabilised by water, is proposed to be responsible for such reactions under triphasic reaction conditions.

Keywords: Baeyer–Villiger; titanium silicate molecular sieve; oxidation; rearrangement; titanium peroxo; triphase

1. Introduction

Titanium silicate molecular sieves, well known heterogeneous oxidation catalysts using dilute H_2O_2 as oxidant, are attracting increasing attention of researchers, both from academia and industry [1]. Recently, we have observed [2] a significant enhancement of activity and para selectivity in the hydroxylation/oxidation of various hydrophobic organic compounds over crystalline, microporous, titanium silicate, TS-1, using dilute H_2O_2 (30 wt%, aq) as oxidant under triphasic reaction conditions (solid catalyst + organic substrate + aqueous H_2O_2) over the conventionally used biphase conditions (solid catalyst + single liquid phase in the presence of a cosolvent). Baeyer–Villiger (BV) rearrangement, induced by peroxyacid [3] or H_2O_2/Lewis acid [4] system, organometallics [5] and metalloenzymes [6], is an important reaction for synthesising esters and lactones from acyclic and cyclic ketones, respectively. Now we report, for the first time, TS-1/H_2O_2-induced BV oxidation and aromatic hydroxylation of acetophenone to phenyl acetate and *o*- and *p*-hydroxy acetophenone (which is an important raw material in pharmaceutical industry) and cyclohexanone to ε-caprolactone, hydroxyketones and diketones under mild acidic conditions in the absence of any cosolvent (i.e. triphase).

2. Experimental

TS-1 (Si/Ti = 29) was synthesised according to the known conventional procedure [7] and thoroughly characterised by well known techniques like XRD, IR, UV-VIS and SEM to ascertain that it is free from any crystalline or amorphous impurities. The size of TS-1 crystallites was 0.2–0.3 μm. Catalytic reactions were carried out in a two-neck glass reactor at 80°C. In a typical experiment 1.0 mmol of ketone was taken with 1.0 mmol of H_2O_2, 20 wt% catalyst and 2.5 mmol of H_2O (in triphase as a dispersion medium) or CH_3CN (in biphase as cosolvent). The effect of the addition of a small amount of extra acid (0.1 mmol of H_2SO_4, catalytic amount) was also studied. The products were analysed and identified through capillary gas chromatographs (HP 5880 and Simadzu GC-17A), GCMS (Simadzu 14A-QP 2000A) and FTIR.

3. Results and discussion

Table 1 presents the results obtained in the BV oxidation of cyclohexanone. The conversion is significantly higher along with higher selectivity for ε-caprolactone in the triphase (compared to biphase) system (entry 1 vs. 2). Further, in the presence of a small catalytic amount of added acid (commonly used in BV oxidation) the conversion as well as the selectivity to ε-caprolactone increases considerably (entry 1 vs. 3). Under biphase conditions and in the absence of acid, very little reaction (ca. 5% conversion) with no ε-caprolactone was observed. Apart from ε-caprolactone, a Baeyer–Villiger oxidative rearrangement product, other products were hydroxyketones and diketones, cyclohexene and corresponding epoxide.

In table 2, the results of BV oxidation of acetophenone are recorded. Like the oxidation of cyclohexanone,

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Table 1
Oxidation of cyclohexanone over TS-1 [a]

Entry	System	Phase [b]	Conv. [c] (mol%)	Product selectivities (mol%)			
				ε-caprolactone	hydroxyketone	diketone	cyclohexene + epoxide
1	TS-1/H_2O_2/H^+	tri	64.0	45.2	17.0	14.0	23.8
2	TS-1/H_2O_2/H^+	bi	30.2	28.4	25.5	31.0	15.1
3	TS-1/H_2O_2	tri	31.0	19.6	31.3	33.6	15.5
4	TS-1/H_2O_2	bi	5.0	–	64.0	36.0	–

[a] Reaction conditions: substrate : $H_2O_2 = 1 : 1$, catalyst TS-1 (Si/Ti = 29) 20 wt% with respect to substrate, temp. 353 K.

[b] tri = solid catalyst + two immiscible liquid phases (organic substrate + H_2O_2 in water); bi: solid catalyst + one homogeneous liquid phase (organic substrate + aq H_2O_2 + CH_3CN as cosolvent).

[c] Maximum conversion achieved during the reaction after 6 h reaction time.

discussed above, in this case also under triphase (vis-à-vis biphase) condition along with added acid, higher conversion of acetophenone and selectivity for phenyl acetate, which is a BV rearrangement product (entries 1 and 3), were observed. Further, the presence of added acid significantly enhances both the conversion and ester selectivity (entry 1 vs. 2). Under biphase conditions very little (< 6%) and no conversion was observed in the presence and absence of added acid, respectively (entries 3 and 4). The ester, so formed, undergoes acid hydrolysis, producing phenol (PH) (and its further oxidation products like catechol (CA) and hydroquinone (HQ)) and acetic acid (AA). The other major reaction, only under triphase conditions with added acid, is the direct hydroxylation of acetophenone to give quite important products namely, *o*- and *p*-hydroxyacetophenone (32%), which are the raw materials for *o*- and *p*-acetamol, respectively. The formation of hydroxyl acetophenones (particularly the *o*-isomer) is also possible due to the acid catalysed Fries rearrangement of the initially formed BV product phenyl acetate. To check this point, phenyl acetate was taken as substrate and the reaction was carried out under identical conditions. Interestingly, around 70% of the substrate converted into the corresponding hydrolysed products, phenol and acetic acid. No *o*- and *p*-hydroxyacetophenone were detected, indicating feasibility of hydroxyacetophenone as a result of direct hydroxylation of acetophenone. This is further supposed by the fact that, when the reaction was carried out in the absence of any catalyst and cosolvent (i.e. acetophenone + H_2O_2 + H_3O^+), nearly 5% conversion was achieved (with the formation of *o*-hydroxyacetophenone and no *p*-hydroxyacetophenone), whereas no reaction was observed in the presence of cosolvent acetonitrile and in absence of catalyst (entry 6, table 2).

It is interesting to note that, even in the absence of catalyst (blank experiment entry 6, table 2), the presence of cosolvent CH_3CN completely suppresses the reaction compared with that in the presence of water (two immiscible liquid phases). Another interesting observation is the formation of *o*- and *p*-hydroxyacetophenone, particularly the *p*-isomer, which is not formed in the blank experiment (entry 5, table 2). It seems that, under triphase conditions, the TS-1/H_2O_2 system can also favour hydroxylation of the deactivated aromatic ring. Bellussi and Fattore [8] have reported that TS-1 exhibits Brønsted acidity in the presence of H_2O_2, due to the formation of titanium peroxo species ($\equiv$Ti–O–O···H, scheme 1, species II) stabilised by a protic solvent like water (scheme 1, species III) and alcohols. However, this acidity is solvent dependent [8]. Under triphase conditions, TS-1 seems to act, both as oxidation and Brønsted

Table 2
Baeyer–Villiger rearrangement and hydroxylation of acetophenone over TS-1/H_2O_2 system [a]

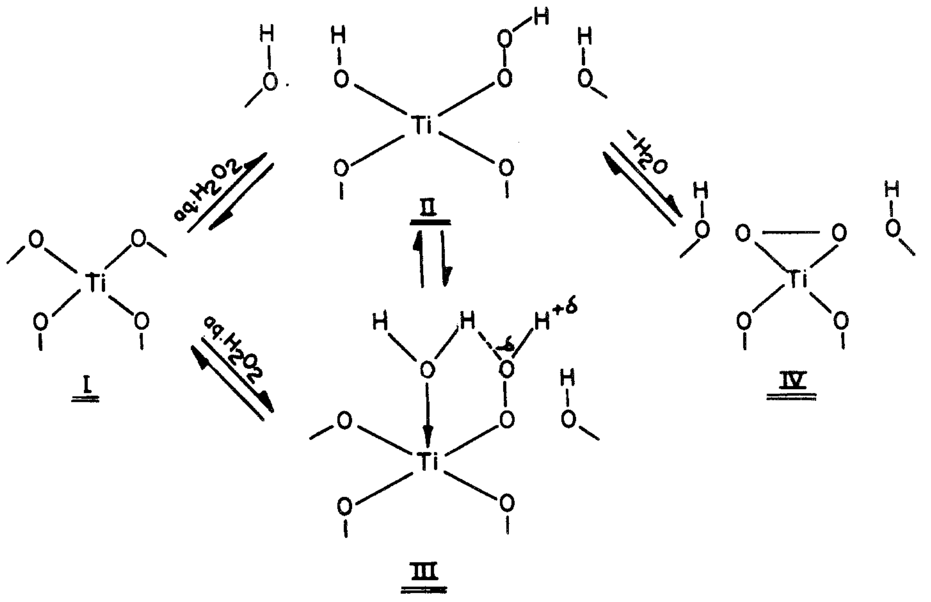
Entry	System	Phase [b]	Conv. [c] (mol%)	Product [d] selectivities (mol%)						
				5	6	7	PH	CA	HQ	AA
1	TS-1/H_2O_2/H^+	tri	31.0	49.7	16.6	16.0	7.0	1.0	1.1	8.6
2	TS-1/H_2O_2	tri	7.0	27.0	2.8	5.6	12.6	7.4	12.3	32.3
3	TS-1/H_2O_2/H^+	bi	6.1	61.0	–	–	4.6	10.8	4.4	19.0
4	TS-1/H_2O_2	bi	–	–	–	–	–	–	–	–
5	blank/H_2O_2/H^+	bi [e]	5.5	31.8	6.9	–	24.9	2.8	3.5	30.1
6	blank/H_2O_2/H^+	mono [f]	–	–	–	–	–	–	–	–

[a–c] Same as given in table 1 except that the reaction time was 12 h.

[d] Products 5, 6 and 7 as given in scheme 2.

[e] Two liquid phases (substrate + H_2O_2 in water).

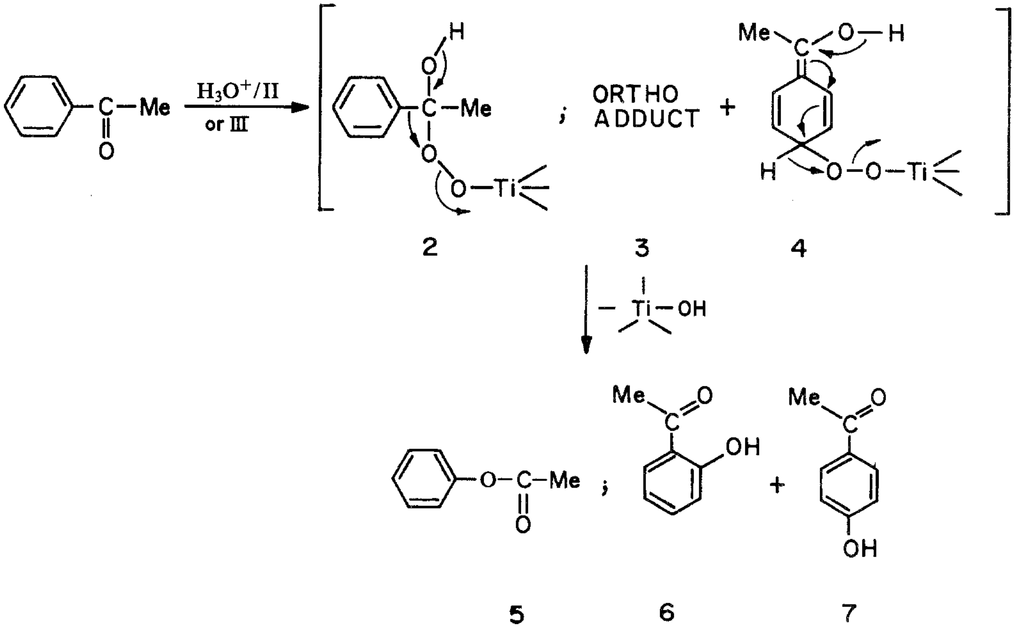
[f] One liquid phase (substrate + H_2O_2 in water + CH_3CN as cosolvent).



Scheme 1.

acid catalyst. That is why, even in the absence of any added acid, TS-1 in triphase conditions (entry 2, table 2) exhibits the formation of ester and aids its hydrolysis. The "≡Ti–O–O···H" moiety, stabilised in the presence of water, is proposed to attack, through nucleophilic oxygen, the *o*- and *p*-positions (which are partially deactivated by the presence of the electron-withdrawing CH_3CO–group) forming *o*- and *p*-hydroxyacetophenones.

A plausible reaction path in the oxidation of acetophenone taken as representative is depicted in scheme 2. The species **II** may act as a nucleophile, particularly in the presence of water (species **III**, scheme 1) under triphase conditions, to attack the electron deficient carbonium ion produced after the initial protonation step, thus forming **5** via a plausible intermediate **2** through the migration of the phenyl [9] group. Similarly, the species **II** can also attack the partially electron deficient *o*- and *p*-positions of the deactivated aromatic ring of acetophenone, thus producing *o*- and *p*-hydroxyacetophenones (species **6** and **7** via species **3** and **4**, respectively). The significantly higher activity of TS-1 under triphase, compared to biphase conditions, can be attributed to the highly hydrophobic nature of TS-1 [2], where an organic solvent, when present (as in the biphase conditions), will favourably compete with the substrate for the diffusion and adsorption at the active sites. Whereas, under the triphase conditions, the organic substrate will not face such



Scheme 2.

diffusional competition with water in TS-1 [2]. Further, the higher Brønsted acidity of the TS-1/H_2O_2 system in the presence of water [8] (vis-à-vis CH_3CN) may also be responsible for higher yields of BV rearrangement products in triphase.

4. Conclusions

TS-1, in the absence of any organic cosolvent (triphase), with dilute H_2O can facilitate the Baeyer–Villiger rearrangement of aromatic and cyclic ketones to the corresponding ester and lactones respectively. Addition of extra acid (a few drops) further increases the yield of BV product. The titanium peroxo species stabilised by the presence of the protic solvent is proposed to be responsible for such reactions under triphase conditions.

Acknowledgement

AB and PK thank CSIR, New Delhi for granting Senior Research Fellowships. The authors thank Dr. P. Ratnasamy, Director, NCL, Pune and Dr. T.S.R. Prasad Rao, Director IIP, Dehradun for helpful discussions, and encouragement.

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