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ROOM TEMPERATURE EPOXIDATION OF ALKENES WITH HYDROGEN PEROXIDE CATALYZED BY HETEROPOLYOXOMETALATE

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ABSTRACT

Keggin-type heteropolyoxometalates have been explored as catalysts for the epoxidation of alkenes at room temperature. Alkenes have been catalytically oxidized to the corresponding epoxides using mild and environmentally benign hydrogen peroxide as terminal oxidant. For vanadium(V)-substituted heteropolyoxometalates $[H_{x-2}PV_xW_{12-x}O_{40}]^{5-}$ (x = 4 for **POM 1** and 6 for **POM 2**), the efficiency of the catalyst towards epoxidation of alkenes is found to be dependent on the amount of vanadium atoms present in the POM catalyst and also on the nature of the reaction medium.
Key Words: Heteropolyoxometalate,Catalysis, Epoxidation, Alkene, Hydrogen Peroxide.

INTRODUCTION

Epoxidation of alkenes is of great significance, because epoxides play a significant role as useful intermediates in various organic syntheses[1]. Moreover, epoxides are also used in the production of drugs, paints, epoxy resins, pesticides and food additives[2]. Although catalytic epoxidation processes with various oxidants have been developed, a non-catalytic chlorohydrin process and homogeneously catalyzed processes in presence of ROOR$^/$ or RC(=O)OOH as oxidant are well-known[3-5]. But these processes have major drawbacks from the environmental as well as economical point of view. Therefore, the development of efficient routes for catalytic epoxidation under mild conditions using inexpensive terminal oxidants remains as an important challenge in synthetic chemistry. Recently, catalytic epoxidation reaction in presence of hydrogen peroxide (H_2O_2) as terminal oxidant has attracted much attention[6-13] because:

(i)   It generates only water as a side product.
(ii)   It contains the largest amount of active oxygen species among the known oxidants, and
(iii)   It is inexpensive and not harmful to use than ROOR$^/$ or RC(=O)OOH[14].

This makes H_2O_2 the ideal oxidant from the viewpoint of green chemistry[15, 16].

Polyoxometalates (POMs) are the polyoxoanions of the early transition metals and exhibit several characteristic features that make them suitable for applications in the fields of catalysis, biology, medicine, materials, electrochemistry, and photochemistry[17-19]. Among them, POMs play a significant role in the field of catalysis because their acidic and redox properties can be controlled at atomic or molecular levels[20-24]. Moreover, the inherent stability of POMs toward different terminal oxidants like dioxygen and hydrogen peroxide makes them attractive in catalysis. Accordingly the catalytic activity of POMs has received significant attention towards homogeneously catalyze selective oxidation reactions in presence of terminal oxidants. Various H_2O_2-based epoxidation reactions catalyzed by POMs have been developed[25-30].
Herein, we wish to report the room temperature epoxidation of alkenes catalyzed by heteropolyoxometalate $[H_{x-2}PV_xW_{12-x} O_{40}]^{5-}$ (x = 4 for **POM 1** and 6 for **POM 2**) with mild and benign

H_2O_2 as terminal oxidant. The effect of a number of vanadium atoms in the heteropolyoxometalates towards alkene epoxidation has also been studied in this work.

EXPERIMENTAL

Materials and Methods
Chemicals used for the synthesis, alkenes used as substrates and the internal standard (pentafluoroiodobenzene) were purchased from Sigma Aldrich and were used directly. Solvents were distilled prior to epoxidation reaction following the known procedure[31]. The active oxygen content of H_2O_2 (as ~30% solution in water) was measured by the iodometric method. The analysis of the catalytic product was performed by Perkin-Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column). The identification and quantification of the products were done from the response factors of standard product samples.

Syntheses of Catalysts
Potassium salt of the heteropolyoxometalates
Potassium salt of the heteropolyoxometalates, $K_5[H_{x-2}PV_xW_{12-x}O_{40}]$ (x = 4 and 6), were prepared following the known procedure[32].

Tetra-n-butylammonium (TBA) salt of the heteropolyoxometalates
Tetra-n-butylammonium (TBA) salt of the heteropolyoxometalates, $[(C_4H_9)_4N]_5[H_{x-2}PV_xW_{12-x}O_{40}]$ (x = 4 for **POM 1** and 6 for **POM 2**) were synthesized and characterized according to the published method[33].

General Procedure for Epoxidation Reaction
Catalytic epoxidations were performed under a nitrogen atmosphere in small screw-capped vials fitted with PTFE septa. In a typical reaction, the alkene substrate and the catalyst were dissolved in 2 mL of solvent saturated with nitrogen. The epoxidation reaction was initiated by the addition of 2 mM of H_2O_2 and the reaction mixture was stirred at room temperature by using the magnetic bar. The reaction mixture was analyzed periodically by GC. At the end of the reaction, an aliquot of 1 µL from the reaction mixture was directly injected into a capillary column of a preheated GC after adding a standard solution of pentafluoroiodobenzene (PFIB) as an internal standard. The reaction products were identified and yield was measured by comparison of the response factors of standard product samples as usual.

RESULTS AND DISCUSSION

Catalytic Epoxidation of alkenes with H_2O_2
The TBA-salt of the heteropolyoxometalates (**POM 1** and **POM 2**) have been explored as catalysts for the epoxidation of a group of alkenes at room temperature with environmentally benign H_2O_2 as oxidant under a nitrogen atmosphere.

Epoxidation of Cyclooctene
The catalytic activity of TBA-salt of heteropolyoxometalates has been examined initially in the epoxidation of cyclooctene, chosen as a model substrate, by H_2O_2 at room temperature (Scheme-1).
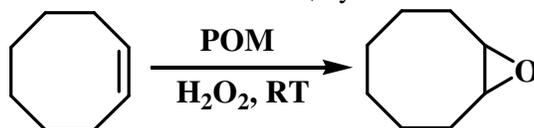
Scheme-1:Catalytic epoxidation of cyclooctene at room temperature.

Effect of Solvent on the Catalytic Epoxidation Reaction
Solvent plays a crucial role in the epoxidation of alkenes catalyzed by heteropolyoxometalates. The role of solvent in the catalytic epoxidation reaction was examined by performing the reaction in the solvents,

viz., dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN) and a mixture of acetonitrile and dichloromethane. Table-1 shows the **POM 1** catalyzed epoxidation of cyclooctene with H_2O_2 in various solvent systems. All the reactions were carried out at least thrice, and the yields of epoxides reported represent the average obtained. The other parameters such as the concentration of substrate, catalyst,and H_2O_2 were kept constant in each solvent system.

Table-1: Room temperature epoxidation of cyclooctene by **POM 1** in different solvents[a].

Entry	Solvent	Yield[b] (%)
1	CH_2Cl_2	4
2	CH_3CN	5
3	CH_3CN/CH_2Cl_2 (2:1, *v/v*)	10
4	CH_3CN/CH_2Cl_2 (1:1, *v/v*)	22
5	CH_3CN/CH_2Cl_2 (1:2, *v/v*)	8

[a]Reaction condition: cyclooctene (100 mM), catalyst (50 µM), H_2O_2 (2 mM) in 2 mL solvent, 4 h. [b]Yields are based on the concentration of the oxidant.

The results reveal that epoxidation of cyclooctene strongly depends on the nature of the solvent. The catalyst was almost inactive in CH_2Cl_2 and CH_3CN. As it can be obtained from Table-1, a mixed solvent of CH_3CN and CH_2Cl_2 in the 1:1 ratio (*v/v*) proves to be an effective solvent for the cycloocteneepoxidation in terms of epoxide yield.

Nature of Catalyst
After choosing the best solvent system for the epoxidation reaction using **POM 1** as catalyst, epoxidation of cyclooctene was next studied with **POM 2** as catalyst under identical reaction conditions. The results are compiled in Table-2.

Table-2: Room temperature epoxidation of cyclooctene by **POM 2** in different solvents[a].

Entry	Solvent	Yield[b] (%)
1	CH_2Cl_2	7
2	CH_3CN	8
3	CH_3CN/CH_2Cl_2 (2:1, *v/v*)	14
4	CH_3CN/CH_2Cl_2 (1:1, *v/v*)	36
5	CH_3CN/CH_2Cl_2 (1:2, *v/v*)	10

[a]Reaction condition: cyclooctene (100 mM), catalyst (50 µM), H_2O_2 (2 mM) in 2 mL solvent, 4 h. [b]Yields are based on the concentration of the oxidant.

It was found that cyclooctene was not epoxidized at all in the absence of POM catalyst under the similar reaction conditions showing that POMs have significant contribution in the epoxidation reaction.Moreover, the catalytic activity depends on the number of vanadium atoms in the catalyst. The epoxidation of cyclooctene with both the catalysts suggested that **POM 2** exhibited better catalytic activity in terms of epoxide yield than **POM 1** in all the solvents used. This suggested that a number of vanadium atoms in the heteropolyoxometalate catalyst plays a key role in the epoxidation by H_2O_2. Fig.-1 shows the percentage yield of epoxide in different solvents by both the catalysts.

Epoxidation of 1-Octene
The notable feature of the present catalytic system is that non-activated terminal alkenes could be efficiently transformed to the corresponding epoxides in moderate yields. To examine the scope of the present epoxidation with regard to non-activated terminal alkenes, epoxidation of 1-octene was examined by TBA salt of POM (**POM 1** and **POM 2**) with H_2O_2 under nitrogen atmosphere (Scheme-2).
Like cyclooctene, here also, a mixed solvent of CH_3CN and CH_2Cl_2 in the 1:1 ratio (*v/v*) afforded maximum epoxide yield. The epoxidation of 1-octene results 1,2-epoxyoctane in 17% conversion with

POM 1/H_2O_2 and in 26% with **POM 2**/H_2O_2. Here also, **POM 2** exhibits better catalytic efficiency in terms of epoxide yield than **POM 1**.
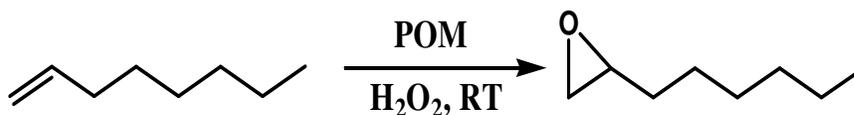
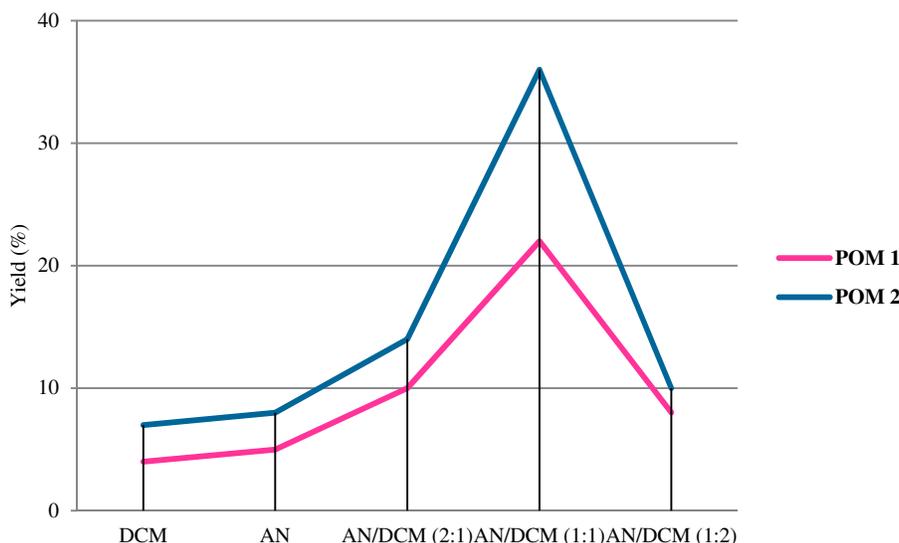Scheme-2: Catalytic epoxidation of 1-octene at room temperature.

Fig.-1: the Relative yield of epoxide for cyclooctene epoxidation by **POM 1** and **POM 2**, where DCM and AN stand for dichloromethane and acetonitrile respectively.

Epoxidation of Other Alkenes

The scope of the present epoxidation reaction catalyzed by TBA salt of POM (**POM 1** and **POM 2**) with regard to other alkenes such as norbornene and dihydronaphthalene using environmentally benign H_2O_2 as oxidant was also examined under a nitrogen atmosphere at room temperature with the same reaction conditions. Among the CH_2Cl_2, CH_3CN and a mixed solvent of CH_3CN and CH_2Cl_2, 1:1 mixture of CH_3CN and CH_2Cl_2 (*v/v*) was selected as the reaction medium because better conversion in the catalytic reaction in terms of epoxide yield was achieved. The results are compiled in Table-3.

Table-3: Room temperature epoxidation of alkenes by POM catalysts[a].

Entry	Substrate	Catalyst	Product	Product Yield (%)[b]
1		**POM 1**		48
2		**POM 2**		62
3		**POM 1**		56
4		**POM 2**		66

[a]Reaction condition: substrate (100 mM), catalyst (50 µM), H_2O_2 (2 mM) in 2 mL solvent, 4 h. [b]Yields are based on the concentration of the oxidant.

As shown in Table-3, norbornene is regiospecificallyoxidized to its *exo*-epoxide only. **POM 2** with a greater number of vanadium atoms catalyzes the oxidation of norbornene with the yield of 62%; however, the conversion decreases to 48% when **POM 1** is used as catalyst (Table-3, entries 1, 2).

The present POM/H_2O_2 system also efficiently catalyzes the epoxidation of dihydronaphthalene at room temperature (Table-3, entries 3, 4). Here also **POM 2** appears as a better catalyst than **POM 1**. By using **POM 2**, dihydronaphthalene is transformed to the corresponding epoxide with 66% yield whereas the yield decreases to 56% using **POM 1** as a catalyst. Thus, at room temperature, **POM 2** exhibits better catalytic activity than **POM 1** towards the epoxidation of alkenes at room temperature in presence of H_2O_2 as the terminal oxidant.

Comparison of Efficiency of the Catalysts in the Epoxidation Reaction
The efficiency of heteropolyoxometalate catalysts with a different number of vanadium atoms (**POM 1** and **POM 2**) has also been examined. It has been found that a number of vanadium atoms in the POM catalysts has significant contribution in the epoxidation reaction by H_2O_2. It can be seen from the epoxidation of various alkenes (like cyclooctene, 1-octene, norbornene,anddihydronaphthalene) that the epoxide yield has been substantially increased when heteropolyoxometalate with a greater number of vanadium atoms (**POM 2**) was used as a catalyst.

CONCLUSION
The epoxidation of alkenes has been achieved at room temperature by heteropolyoxometalates as catalysts (**POM 1** and **POM 2**) in presence of environmentally benign H_2O_2 as terminal oxidant. The choice of the reaction medium plays a significant role in the catalytic epoxidation reaction. Remarkable improvement in epoxide yield has been observed in a mixture of acetonitrile/dichloromethane (1:1, *v/v*) than in pure acetonitrile or in pure dichloromethane. The notable feature of the present catalytic system is that non-activated 1-octene has been efficiently epoxidized in moderate yield. The room temperature epoxidation of various alkenes under mild and environmentally friendly conditions seems promising for practical purposes.

ACKNOWLEDGEMENT

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