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Epoxidation of Some Olefins with Hydrogen Peroxide Catalyzed by Heteropolyoxometalates

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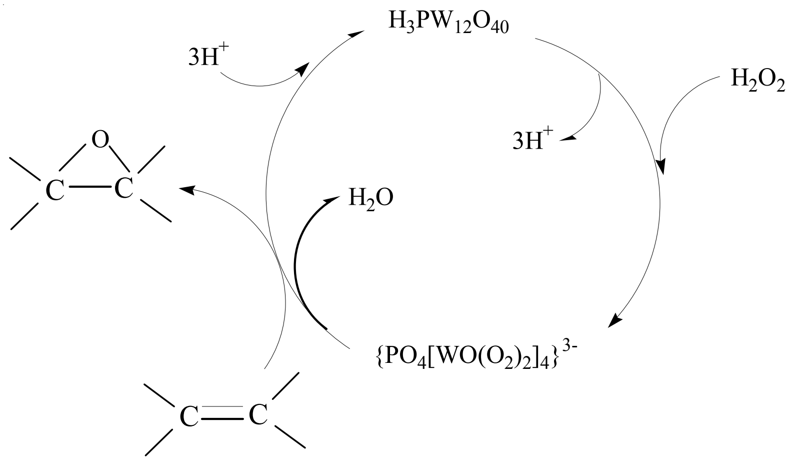
Catalytic epoxidation of some olefins was carried out with 34 % hydrogen peroxide in the presence of a variety of heteropolyoxometalates. Results have shown that dodeca-tungstophosphoric acid ($H_3PW_{12}O_{40}$) is the most successful polyoxometalate evaluated in terms of both olefin conversion and epoxide selectivity. Whereas, dodecamolybdophosphoric acid, $H_3PMo_{12}O_{40}$ and other substituted heteropolyoxometalates have revealed low catalytic activity.

Key Words: Catalytic epoxidation, Hydrogen peroxide, Olefins.

INTRODUCTION

The oxidation of organic substrates with aqueous hydrogen peroxide has attracted considerable attention from the viewpoint of industrial technology and academic synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle[1]. For instance, extensive attention has been devoted for a long time to the direct epoxidation of olefins by aqueous hydrogen peroxide[2]. In recent years, it has been reported that olefins can be epoxidized by molybdenum and tungsten derivatives as catalysts with dilute hydrogen peroxide under phase transfer conditions. Epoxidation of olefins, oxidative cleavage of olefins and *vicinal* diols, ketonization of alcohols and diols and conversion of alkynes into epoxy ketones have been achieved by hydrogen peroxide oxidation catalyzed by heteropolyoxometalates having a phase-transfer agent[3]. Among a wide variety of heteropolyoxometalates, heteropoly acids (HPA) such as 12-molybdophosphoric acid (MPA) or 12-tungstophosphoric acid (WPA) are often used not only for the oxidation of organic substrates but also for many acid-catalyzed reactions, because they possess the dual catalytic functions of oxidizing ability and strong acidity[4].

In this paper, the author wishes to present the results of oxidation of some saturated and unsaturated hydrocarbons with H_2O_2 in the presence of a variety of heteropoly acids and transition metal-substituted polyoxometalates. Scheme-I illustrates the overall catalytic oxidation of alkenes with hydrogen peroxide in the prsence of $H_3PW_{12}O_{40}$.



Scheme-I. Overall oxidation of alkenes with hydrogen peroxide catalyzed by $H_3PW_{12}O_{40}$

EXPERIMENTAL

Olefins, hydrogen peroxide 34 %, cetyl-pyridinium chloride and other solvents were commercially available and their purity were monitored by gas chromatography. All products were characterized by comparing their spectral and physical data with those of known samples. Purity of the substances and progress of the reactions were monitored by TLC on silica gel or by gas chromatography. GLC analyses were performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector using 25 m × 0.25 mm CPB 5-20 capillary columns. The heteropolyoxometalates $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $(TBA)_3PMo_{12}O_{40}$, $Na_3PW_9Mo_3O_{40}$, $H_{14}P_5W_{30}O_{110}$, $Na_3PW_{12}O_{40}$, $Na_6P_2Mo_{18}O_{62}$, $K_6P_2W_{18}O_{62}$ and $(TBA)_7PW_{11}O_{39}$ were prepared and characterized according to literature procedures[5].

Synthesis of $Na_3PW_{12}O_{40}·7H_2O$: $Na_2WO_4·2H_2O$ (30 mmol, 10 g) was slowly added to 20 mL of distilled water and the mixture was warmed to 60°C with complete stirring. Then, H_3PO_4 85 % (15 mmol, 1 mL) and HCl (100 mmol, 8 mL) were added and the resulting mixture was stirred for 1 h. The white afforded precipitate was washed with water and was recrystallized twice from hot water.

Synthesis of $Na_2HPMo_{12}O_{40}·14H_2O$: To 420 mL of a 2.85 M aqueous solution of Na_2MoO_4 were added successively 6.8 mL of 85 % H_3PO_4 and 284 mL of 70 % HClO. The disodium salt was precipitated from the yellow lukewarm solution. After the mixture was cooled to room temperature, the microcrystalline powder was filtered and air-dried. Recrystallization in a mixture of 40 mL Et_2O/200 mL H_2O gave 180 g of greenish microcrystals.

Synthesis of $H_3PMo_{12}O_{40}\cdot 14H_2O$: $H_3PMo_{12}O_{40}\cdot 14H_2O$ was obtained from an aqueous solution of $Na_2HPMo_{12}O_{40}\cdot 14H_2O$ (250 g/200 mL), acidified by 50 mL of 12 M HCl and extracted by Et_2O (400 mL). The heavy layer (300 mL), added with half its volume of water, gave yellow crystals after desiccation (190 g).

Synthesis of $(TBA)_3PMo_{12}O_{40}$: A 10 g quantity of $H_3PMo_{12}O_{40}\cdot 14H_2O$ was dissolved in 20 mL of water; a 5 g quantity of $[(n\text{-}C_4H_9)_4N]Br$ (TBABr) was dissolved in 50 mL of CH_2Cl_2 and the mixture was poured into the molybdophosphate solution with vigorous stirring. Three phases were formed: a yellow solid one, a lower liquid one (CH_2Cl_2), yellow coloured and an aqueous upper one, poorly coloured. The solid was washed with Et_2O, providing 8.5 g of product. A further yield of 2.5 g was obtained by addition of Et_2O to the CH_2Cl_2 phase. Recrystallization was performed in CH_2Cl_2.

Synthesis of $Na_7PW_9MO_2O_{39}$: $Na_5HPW_9O_{34}\cdot 24H_2O$ (11 g) is dissolved in an aqueous mixture of sodium molybdate (20 mL, 1 F) and HCl (16 mL, 1 F). Then hydrochloric acid (about 12 mL, 1 F) is added drop wise until the pH lies between 6 and 6.5. The sodium salt $Na_7PW_9Mo_2O_{39}\cdot 19H_2O$ is precipitated out by addition of solid sodium chloride.

Synthesis of $Na_3PW_9Mo_3O_{40}$: Quantities of dioxane (20 mL), aqueous hydrochloric acid (30 mL, 5.45 F) and aqueous sodium molybdate (10 mL, 1 F) are mixed. Upon addition of $Na_7PW_9Mo_2O_{39}\cdot 19H_2O$ (10 g) to this solution, the yellow salt $Na_3PW_9Mo_3O_{40}\cdot 25H_2O$ precipitates out. This compound, unstable in aqueous solution, is stable in hydro-organic mixtures, as water-dioxane, 1:1 in volume.

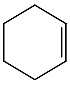
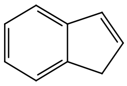
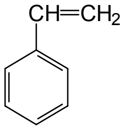
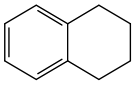
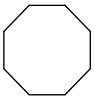
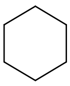
General procedure for epoxidation of olefins: To the stirred solution of heteropoly acid (*ca.* 0.052 mmol), n equivalents of CPC (n = charge on polyanion) and 34 % H_2O_2 (20 mmol) in chloroform (20 mL) was added olefin (9 mmol) and the mixture was allowed to react under refluxing temperature. Progress of the reaction was followed by the aliquots withdrawn directly from the reaction mixture, analyzed by gas chromatography using internal standard or by TLC using ethyl acetate and hexane (1/10) mixture. After completion of the reaction, the partially precipitated catalyst was separated by filtration, the filtrate was treated with a solution of 10 % sodium hydrogen sulfite to decompose unreacted H_2O_2 and then with 10 % sodium hydroxide. The product was extracted with chloroform. Pure product was obtained by distillation or by silica gel column chromatography (hexane:ethyl acetate, 10:1-2, eluent). Spectral data of each product were compared with those of authentic samples and the literature values.

RESULTS AND DISCUSSION

A practical route for direct epoxidation of olefins by aqueous H_2O_2 which is environmentally clean and relatively easy to handle, through the use of a suitable catalyst, is desirable. Ishii and Venturello have been achieved heteropolyoxometalates under the synergism of phase-transfer catalysis for the oxidation of olefins, alcohols and diols with dilute H_2O_2[6]. Now, in continuation of the past investigations and in order to ascertain the scope of the oxygenation, various saturated and unsaturated hydrocarbons were oxidized with hydrogen peroxide by using different heteropolyoxometalates.

Table-1 describes oxygenation of some olefins and various alkanes with H_2O_2 catalyzed by $H_3PW_{12}O_{40}$ in CH_2Cl_2-H_2O two-phase system under air at reflux. In a control experiment without any catalyst no epoxidation of cyclohexene was observed over the same or prolonged reaction time.

TABLE-1
OXYGENATION OF SOME SATURATED AND UNSATURATED HYDROCARBONS WITH H_2O_2 CATALYZED BY $H_3PW_{12}O_{40}$†

Substrate	Conversion (%)	Yield (%)	Time (h)	TOF (h^{-1})‡
	85	85	2.5	58.500
$CH_3(CH_2)_3CH{=}CH_2$	65	65	2.5	44.500
	25	24	3.5	11.800
	25	17	4.0	7.650
	3	3	4.0	1.350
	4	4	4.0	1.800
	2	2	4.0	0.990

†Olefin (9 mmol) was allowed to react with 34 % H_2O_2 (20 mmol) in the presence of catalyst (0.052 mmol), n equivalents of CPC (n = charge on polyanion), in chloroform (20 mL) under air at 60°C for the required time.

‡Turnover frequency (TOF) is calculated by the expression [product]/[catalyst] × time (h^{-1}).

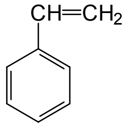
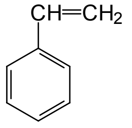
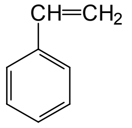
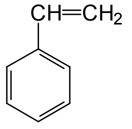
Cyclohexene has provided cyclohexene oxide with 85 % conversion and 100 % selectivity under air after 2.5 h; whereas, indene, as a two-substituted olefin, has produced only 25 % of epoxide after 3.5 h. To the best of our knowledge, epoxidation of linear alkenes is one of the most important transformations in organic synthesis and more of the introduced catalytic methodologies failed to epoxidize mono-substituted linear alkenes efficiently. Therefore, the epoxidation of 1-hexene is examined in our catalytic oxidation system. Results showed that 1-hexene was also reactive in this oxygenation system. It has provided 65 % of conversion with complete selectivity in the presence of $H_3PW_{12}O_{40}$ under the reaction conditions reported here after 2.5 h. Noteworthy, $H_3PMo_{12}O_{40}$ has led to distinctly lower catalytic activity in the epoxidation of 1-hexene. It has produced only 15 % of 1-hexene oxide under the same reaction conditions introduced for $H_3PW_{12}O_{40}$ after 24 h.

Styrene oxide is an important intermediate in organic process industry and it can be produced by epoxidation of styrene amongst other routes. The current work was examined the epoxidation of styrene to styrene oxide by using a synergism of heteropoly acids and phase-transfer catalysts under the so-called Ishii-Venturello chemistry. Present oxygenation system has revealed low reactivity for epoxidation of styrene. Styrene resulted in 25 % of conversion after 4 h. Styrene oxide (17 %) was the major product and benzaldehyde (8 %) was the minor product of this oxygenation. It should be mentioned that all the produced styrene oxide was converted into benzaldehyde in longer reaction times or by addition of higher amounts of hydrogen peroxide.

Earlier several attempts on the oxygenation of cycloalkanes and aryl alkanes with $H_3PW_{12}O_{40}$ under air were led to a little success. Cyclooctane, cyclohexane and tetralin were exposed to the oxidation under air. But they have provided < 4 % of a mixture of their corresponding alcohols and ketones after 4 h. However, studies on the oxygenation of alkanes by means of simple and cheap heteropolyoxometalates as catalysts to afford higher conversions under aerobic reaction conditions are under investigation. Finally, it should be noted that sodium periodate was unable to oxidize the mentioned olefins in the presence or absence of $H_3PW_{12}O_{40}$ under the reaction conditions reported here.

Table-2 introduces the results of oxygenation of some olefins with hydrogen peroxide catalyzed by some different substituted Keggin-type heteropolyoxometalates under aerobic conditions at reflux. Findings have shown that $H_3PW_{12}O_{40}$ was the best catalyst among the examined catalysts for the epoxidation of the introduced alkenes. Thereafter, $Na_3PW_9Mo_3$, $Na_2K_5PW_{11}O_{39}$ and its tetra-*n*-butylammonium salt, $(TBA)_7PW_{11}O_{39}$, have shown better results in the epoxidation of 1-hexene under similar reaction

TABLE-2
EPOXIDATION OF SOME OLEFINS WITH H_2O_2 CATALYZED BY SOME DIFFERENT HETEROPOLYOXOMETALATES†

Catalyst	Substrate	Conversion (%)	Yield (%)	Time (h)	TOF (h^{-1})‡
$Na_3PW_9Mo_3O_{40}$	$CH_3(CH_2)_3CH{=}CH_2$	31	31	24	2.230
$Na_3PW_9Mo_3O_{40}$		15	10	24	0.721
$K_4SiW_9Mo_2O_{39}$	$CH_3(CH_2)_3CH{=}CH_2$	10	10	24	0.721
$K_5Na_2PW_{11}O_{39}$		10	3	24	0.216
$K_5Na_2PW_{11}O_{39}$	$CH_3(CH_2)_3CH{=}CH_2$	30	30	24	2.160
$(TBA)_7PW_{11}O_{39}$	$CH_3(CH_2)_3CH{=}CH_2$	25	25	24	1.800
$(TBA)_7PW_{11}O_{39}$		15	10	24	0.721
$H_3PMo_{12}O_{40}$	$CH_3(CH_2)_3CH{=}CH_2$	15	15	24	1.080
$H_3PMo_{12}O_{40}$		5	3	10	0.519
$Na_6P_2Mo_{18}O_{62}$	$CH_3(CH_2)_3CH{=}CH_2$	12	10	8	2.160

†Olefin (9 mmol) was allowed to react with 34 % H_2O_2 (20 mmol) in the presence of catalyst (0.052 mmol), n equivalents of CPC (n = charge on polyanion), in chloroform (20 mL) under air at 60ºC for the required time.
‡Turnover frequency (TOF) is calculated by the expression [product]/[catalyst] × time (h^{-1}).

conditions. These catalysts have afforded 31, 30 and 25 % of their corresponding epoxides, respectively, under air after 24 h. Other catalysts introduced in Table-2, have revealed less catalytic activity in the epoxidation reactions.

Eventually, it seems that different reactivity patterns observed for the epoxidation of alkenes should be explained considering reactivity of the olefin toward oxidation, acid strength of the catalyst, oxidation potential of the metal center in catalyst and steric hindrandrances in the approach of the substrate to the catalytically active oxidizing species[7].

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