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Selective epoxidation of cyclohexene to cyclohexene oxide catalyzed by Keggin-type heteropoly compounds using anhydrous urea–hydrogen peroxide as oxidizing reagent and acetonitrile as the solvent

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Abstract

The epoxidation of cyclohexene catalyzed by Keggin-type heteropoly compounds (HPAs) were investigated using anhydrous urea–hydrogen peroxide adduct (UHP) as an oxidant and acetonitrile as a solvent. Among a series of Keggin-type heteropoly compounds, tris(cetylpyridinium) 12-tungstophosphate (CWP) showed the highest activity. By optimizing the reaction conditions, 80% conversion of cyclohexene and 97% selectivity for cyclohexene oxide could be achieved in the UHP/CH_3CN system. When aqueous 30% hydrogen peroxide (H_2O_2, HP) was used, the cyclohexene conversion and cyclohexene epoxide selectivity were inferior to those obtained with the UHP/CH_3CN system. The reaction of UHP with CWP has been studied by UV-Vis and ^{31}P NMR spectroscopy, which has revealed that the Keggin-type heteropoly compounds CWP is degraded in the presence of excess UHP to form a considerable amount of phosphorus-containing species.

Keywords: Epoxidation; Cyclohexene; Urea–hydrogen peroxide; Keggin-type heteropoly compounds; Acetonitrile

1. Introduction

Epoxides are well known as one of the most valuable building blocks, which can be used as intermediates and precursors for chemicals production. From an industrial point of view, epoxides are largely used for the synthesis of perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc.

The epoxidation of alkenes using heteropoly compounds (HPAs) as a catalyst and aqueous hydrogen peroxide as an oxidant has been studied extensively [1–9]. The groups of Venturello [10,11] and Ishii [12–14] independently developed highly effective and mechanistically closely related polyoxometalates-based catalyst systems for alkene epoxidation by hydrogen peroxide. In recent years, the Venturello–Ishii chemistry has been investigated by several groups [15–22]. It has been shown that the epoxidation of alkenes in the Venturello and Ishii systems includes nearly identical peroxo polyoxometalate intermediates despite the use of different catalysts precursors in the two systems. Evidence has proved that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is the active species in the olefin epoxidation [22]. The major drawbacks to the Venturello–Ishii epoxidation are the use of toxic and carcinogenic chlorocarbons (chloroform and 1,2-dichloroethane) as solvents and catalyst deactivation causing difficulty in catalyst reuse [22]. The epoxidation of cyclohexene using heteropoly compounds as catalysts and aqueous hydrogen peroxide as an oxidant by non-Venturello–Ishii epoxidation systems [23–26] are not very satisfactory. The conversion of cyclohexene and selectivity for epoxycyclohexane were always relatively lower than those for the Venturello–Ishii system.

In conclusion, in some cases the use of aqueous hydrogen peroxide decreases the selectivity of the desired epoxide

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due to isomerization and hydrolysis of the epoxide and also the formation of other cleaved products. The presence of highly polar water in the system usually adversely affects difference by facilitating isomerization and hydrolysis of the desired product. Hence, it was thought that instead of aqueous hydrogen peroxide, anhydrous urea–hydrogen peroxide adduct (UHP) can be used as the oxidizing reagent for the epoxidation of cyclohexene in the presence of heteropoly compounds as a catalyst for increasing selectivity for epoxide. The use of UHP in the epoxidation of olefinic compounds over TS-1 and TS-2 redox molecular sieves has produced good epoxide yields [27,28]. A major advantage of UHP lies in its potential for releasing anhydrous H_2O_2 into solution in a controlled manner [29].

In this work, we first systematically studied the cyclohexene epoxidation by UHP over a series Keggin-type heteropoly compounds using acetonitrile as an alternative solvent. We described and discussed direct UV-Vis spectroscopic evidence to establish the evolution of the tris(cetylpyridinium)12-tungstophosphate (CWP) with different oxidants in acetonitrile solution. The reaction of UHP with CWP has also been studied by ^{31}P NMR spectroscopy, revealing that the Keggin-type heteropoly compound CWP is degraded in the presence of excess UHP to form a considerable number of phosphorus-containing species, which are the actual catalytic active species. The purpose of this work is to examine the effect of different Keggin-type heteropoly compounds, various oxidants, solvent nature, reaction time, etc. on the activity and selectivity in the epoxidation reaction. The results obtained under the most favorable conditions using UHP as the oxidizing reagent are better than those obtained with aqueous H_2O_2 (HP) under the same reaction conditions.

2. Experimental

2.1. Preparations of polyoxometalates

All solvent and chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

[Tris(cetylpyridinium)12-tungstophosphate] (CWP or $(CPB)_3[PW_{12}O_{40}]$). $H_3PW_{12}O_{40}$ (WPA) was prepared by the method of Wu [30]. The synthesis of CWP was as follows: To a solution of cetylpyridinium bromide (CPB, 5.2 mmol) in 70 ml of distilled water was added dropwise to WPA (1.7 mmol) in 10 ml of distilled water with stirring at ambient temperature to form a white precipitate immediately. After being stirred continuously for 3.5 h, the resulting mixture was filtered, washed several times with distilled water, and then dried at room temperature under vacuum for ca. 12 h. The characterization data were as follows. Elemental analysis: found (calcd) for CWP: C, 20.74 (19.96); H, 3.05 (3.03); N, 1.05 (1.11). Infrared spectra (KBr): 3425, 2923, 2851, 1633, 1486, 1464, 1173, 1080, 978, 896, 830–740, 678, 522 cm^{-1}. UV-Vis spectrum in acetonitrile at 298 K: $\lambda = 266$ nm. ^{31}P NMR (DMF): $\delta = -14.7$ ppm. These spectra data were characteristic of Keggin structure.

[Tris(cetyltrimethylammonium)12-tungstophosphate] (CWP1) and [tris(tetrabutylammonium) 12-tungstophosphate] (CWP2) were prepared in a similar manner to CWP. The quaternary alkylammonium salts used were cetyltrimethylammonium bromide and tetrabutylammonium bromide, respectively.

[Tris(cetylpyridinium)12-molybdophosphate] (CMP, or $(CPB)_3[PMo_{12}O_{40}]$). $H_3PMo_{12}O_{40}$ (MPA) was synthesized according to George [31]. CMP was prepared by a similar procedure reported previously [13]. To cetylpyridinium bromide (1.5 g) in 30 ml water was added $H_3PMo_{12}O_{40}{\cdot}nH_2O$ (2.0 g) in 20 ml water with stirring, and immediately was formed a yellow precipitate. After stirring for ca. 3 h, the resulting mixture was filtered off and then was washed several times with distilled water followed by vacuum drying for 12 h. Infrared spectra (KBr): 3399, 2917, 2850, 1633, 1486, 1468, 1175, 1063, 957, 878, 801, 681, 501 cm^{-1}.

[Quaternary alkylammonium mixed–addenda heteropolyoxometalates containing tungsten and molybdenum ($Q_3PMo_mW_{12-m}O_{40}$, $m = 4, 6, 8$)]. $H_3PMo_4W_8O_{40}$ (PMW1), $H_3PMo_6W_6O_{40}$ (PMW2), and $H_3PMo_8W_4O_{40}$ (PMW3) were synthesized by published methods [32,33]. The corresponding quaternary alkylammonium salts were prepared by a similar procedure reported above. The salts of $Q_3PMo_mW_{12-m}O_{40}$ ($m = 4, 6, 8$) were precipitated by adding an excess amount of cetylpyridinium bromide to $H_3PMo_mW_{12-m}O_{40}$ ($m = 4, 6, 8$). Infrared spectra (KBr): $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_4W_8O_{40})^{3-}$ (CPMW1): 3399, 2916, 2851, 1636, 1486, 1472, 1176, 1074, 971, 886, 802, 680, 515 cm^{-1}; $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_6W_6O_{40})^{3-}$ (CPMW2): 3416, 2915, 2849, 1635, 1487, 1470, 1177, 1067, 962, 883, 803, 683, 509 cm^{-1}; $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_8W_4O_{40})^{3-}$ (CPMW3): 3419, 2922, 2851, 1632, 1486, 1464, 1173, 1067, 963, 881, 801, 680, 508 cm^{-1}.

$[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_5(PMo_{10}V_2O_{40})^{5-}$(CPMV). $H_5PMo_{10}V_2O_{40}$ (PMV) was synthesized according to Tsigdinos and Hallado [34]. CPMV was prepared by a similar procedure reported above. Infrared spectra (KBr): 3409, 2921, 2851, 1633, 1483, 1464, 1172, 1068, 963, 879, 801, 678, 511 cm^{-1}.

$[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(VMo_{12}O_{40})^{3-}$ (CVM). This compound was synthesized by a modification of the method reported in ref [35]. 3.05 g of $Na_2MoO_4{\cdot}2H_2O$ was dissolved in 50 ml distilled water, and then 0.15 g of NH_4VO_3 beforehand dissolved in 13 ml hydrochloric acid solutions was put into the former solution. At the same time, 115 ml of ethanol was added to the mixture with stirring at room temperature. After 30 min, 6.05 g of cetylpyridinium bromide was added to the solution, and a yellow precipitate appeared immediately. After stirring for 30 min, the resulting mixture was filtered off and washed several times with distilled water followed by vacuum drying for 12 h. Infrared spectra (KBr): 3447, 2922, 2851, 1632, 1486, 1465, 1172, 957, 885, 766, 681, 579 cm^{-1}.

$[(C_4H_9)_4N]_3VMo_{12}O_{40}$ (TVM) was synthesized as above with the exception of using tetrabutylammonium bromide in place of cetylpyridinium bromide. Infrared spectra (KBr): 3457, 2926, 2855, 1718, 1467, 1379, 959, 888, 779, 617, 500 3457, 2926, 2855, 1718, 1467, 1379, 959, 888, 779, 617, 500 cm^{-1}.

$[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_4(SiW_{12}O_{40})^{4-}$(CSiW), $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_4(SiMo_{12}O_{40})^{4-}$(CSiM) 12-silicotungstic acid ($H_4SiW_{12}O_{40}$) and 12-silicomolybdic acid ($H_4SiMo_{12}O_{40}$) were synthesized by standard methods [31,36]. Their corresponding quaternary alkylammonium salts were prepared by similar procedures reported above.

2.2. Synthesis of peroxo complexes

2.2.1. Preparation of $(BuN)_3[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]$

This was based on the method described by Venturello and co-workers [10,11]. A suspension of tungstic acid (2.50 g, 10 mmol) in 7 ml of 30% aqueous H_2O_2 was stirred and heated to 60 °C until a colorless solution was obtained. To this solution, filtered and cooled at room temperature, was added 0.29 ml 98% H_3PO_4 (2.5 mmol), and the whole was diluted to 30 ml with water. To the resultant solution, 1.611 g of tetrabutylammonium bromide was added dropwise with stirring. After 20 min, the white precipitate was filtered out, washed thoroughly with water, and then air dried. Infrared spectra (KBr): 1084 and 1056 (P–O), 973 (W–O), 853 and 847 (O–O), 591 and 523 ($W(O_2)_{as,s}$); other bands at 728, 651, 576 and 550 cm^{-1}.

2.2.2. Preparation of $(CPB)_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$

This preparation was carried out according to a modification of the method reported in Ref. [37]. A solution of sodium tungstate (2.01 g, 6.1 mmol) in 15 ml water was treated with 10 ml of 30% H_2O_2. The yellow solution formed was treated with dilute HCl until it just turned colorless (pH 2.5). After the solution was allowed to stand at room temperature for 48 h, 1.17 g of cetylpyridinium bromide (3.05 mmol) was added into the solution. The precipitates obtained were filtered off, washed with ethanol, and air-dried. Infrared spectra (KBr): 967, 855, 836, 775, 617, and 554 cm^{-1}.

2.3. Characterization techniques

IR, XRD, UV-Vis, and ^{31}P NMR confirmed the formation of the Keggin structure of the free heteropoly acids. Their compositions were determined by the elemental analysis [38]. Infrared spectra of heteropoly acids and their salts were recorded on a Bruker IFS 120HR spectrometer (0.5 mm KBr pellets containing 2.5 mass% sample). X-ray powder diffraction spectra were measured on a D/Max 2400 Rigaku X-ray diffractometer with Cu Kα radiation ($\lambda = 0.1542$ nm, scan speed 2° (2θ min^{-1}). Diffuse reflectance UV-Vis spectra of solid heteropoly acids were obtained on a Shimadzu UV-240 spectrometer with $BaSO_4$ as the standard, and heteropoly compounds dissolved in acetonitrile medium were measured on a HP-8453 UV spectrometer. ^{31}P NMR spectra were recorded on a Varian Unity-300 MHz NMR spectrometer, using *N*,*N*-dimethylformamide (DMF) as the solvent; ^{31}P chemical shifts are referenced to 85% H_3PO_4 as an external standard. Chemical elemental analysis of the HPAs was done on an ICP-atomic emission spectrometer (ARL 3520 spectrometer), and C, H, and N contents were measured on a German Elementar Vario EL spectrometer.

2.4. Catalytic reactions

The catalytic reactions were performed in a 10 ml two-necked round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. Because cyclohexene autoxidizes easily in air atmosphere, it was purified by distillation and encased in a 250 ml flask sealed with a rubber septum, and then enough argon was filled into the flask in order to prevent oxidation. Catalysts, hydrogen peroxide–urea (or 30% hydrogen peroxide), and substrate were dissolved in solvent. Typically, cyclohexene (3 mmol) and 1.89 mmol of bromobenzene as an internal standard were added to the solution of catalyst (0.015 mmol), hydrogen peroxide urea (6 mmol) in 3 ml of acetonitrile. The flask was then placed in a hot oil bath at 70 °C and stirred vigorously for the required time. The reaction solution was periodically sampled by syringe and analyzed by a Perkin-Elmer XL gas chromatograph equipped with a 50 m-FFAP capillary column and FID detector. Assignments of products were made by comparison with authentic samples. Selected samples were also analyzed by GC/MC (Agilent-6890/5973N).

3. Results and discussion

3.1. Catalyst characterization

IR, XRD, UV-Vis, ^{31}P NMR, and the elemental analysis data of the 12 HPAs were compared with those of authentic samples and related literature values, clearly indicating that they do have the Keggin structure [12,39–43]. Comparison of the infrared spectra of the two peroxo complexes with the literature values showed that they were the target compounds [11,17,37].

3.2. UV-Vis absorption spectrometry

A UV-Vis study was performed, since most of the polyoxometalates have characteristic spectra in the middle of ultraviolet range. We examined the interaction between UHP (or HP) and polyoxometalates in an acetonitrile medium. Fig. 1 depicts the UV-Vis spectra of different reaction mixture

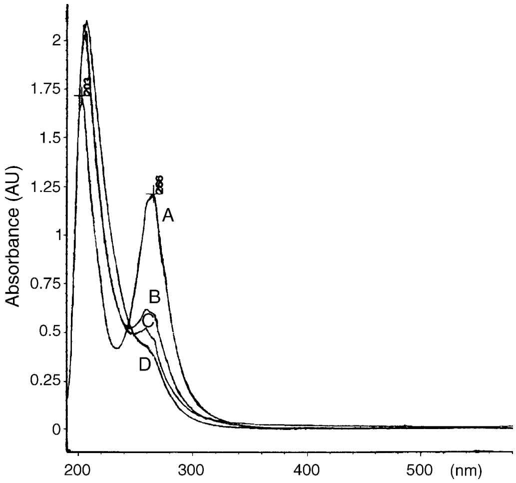

Fig. 1. UV-Vis spectra of different reaction mixture in CH_3CN. [UHP](or[HP])/CWP = 400, room temperature. CWP (A), CWP + U + HP (B), CWP + UHP (C), CWP + HP (D).

in acetonitrile. When CWP was dissolved in acetonitrile (curve A), two absorption bands were obtained. One is sharp absorption at 203 nm, which is assigned to the terminal oxygen-to-tungsten ($O_d \rightarrow W$) charge transfer absorption band. Another absorption band at 266 nm is characteristic band of the polyanionic structure in CWP, and is assigned to ligand (O_b, O_c) to metal (W) charge transfer. Pope et al. also reported that the Keggin-type HPAs based on tungsten ($PW_{12}O_{40}{}^{3-}$) have a characteristic absorption peak near 260 nm [44]. When different oxidants were added to the acetonitrile solution containing CWP, the UV-Vis absorption bands (curves B, C, and D) appeared difference. Curve B is the spectrum of the mixture of CWP/HP/U/CH_3CN ([HP]/[CWP] = 400 mol/mol, [HP] = [U]). Two absorption bands can be also seen, one is 205 nm, another is 266 nm, but the peak intensity at 266 nm has decreased much and shifts to 260 nm. These changes indicate the formation of different species by the interaction between the catalyst and HP/U, which is likely to be the mixture of peroxo anions and $PW_{12}O_{40}{}^{3-}$. Curve C is the spectra of the mixture of CWP/UHP/CH_3CN ([UHP]/[CWP] = 400 mol/mol). This curve exhibits similar types of absorptions (205 and 259 nm) in the UV-Vis region to curve B, but the intensity of the characteristic 259 nm band of the polyanionic structure in CWP reduces much compared with that of curve B. Therefore, more peroxo anions are formed. Curve D is the spectra of the mixture of CWP/HP/CH_3CN ([HP]/[CWP] = 400 mol/mol). Two absorption bands can be also seen (207 and 260 nm), whereas the characteristic 260 nm band of the polyanionic structure of CWP is very weak and almost disappears. This indicates that the degradation of CWP is very fast in the presence of large excess hydrogen peroxide.

3.3. ^{31}P NMR spectra

Previously French [17,18] and US [22] groups characterized the species in the $[H_2O_2]/H_3[PW_{12}O_{40}]$ system by UV-Vis, NMR, and Raman spectroscopy and in this case the complexes were transferred to and evaluated in organic media. Here, we observed complex time-dependent distribution of polytungstophosphate where the particular distribution depends on the ratio $[UHP]_0/(CPB)_3[PW_{12}O_{40}]_0$. An exemplary experiment using ^{31}P NMR spectra is illustrated in Fig. 2. In this study $(CPB)_3[PW_{12}O_{40}]$ was incubated with the indicated number of UHP equivalents, then the two solids mixture was dissolved in 5 ml *N,N*-dimethylformamide (DMF) at room temperature. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases (180 min). When no UHP was added to $(CPB)_3[PW_{12}O_{40}]$, the ^{31}P NMR spectra showed one peak at −14.68 ppm only, which is attributed to $[PW_{12}O_{40}]^{3-}$ [17]. The addition of UHP leads initially to the gradual conversion of $(CPB)_3[PW_{12}O_{40}]$ to a number of unidentified species (Fig. 2b–d). On the basis of preliminary Raman, ^{31}P NMR and ^{183}W NMR data, the French [17], British [37] and US [22] groups assigned these as intermediate peroxo species $[P_aW_bO_c(O_2)_d]^{x-}$. However, in the UHP/$(CPB)_3[PW_{12}O_{40}]$ system, more work needs to be done to clarify these complexes. After adding 40 eq. of UHP (b), two new signals appeared: one is at 0.920 ppm, and the other is at 1.290 ppm. But the peak intensity of $[PW_{12}O_{40}]^{3-}$ (−14.68 ppm) is much stronger than that of the two new bands, implying that the structure of $(CPB)_3[PW_{12}O_{40}]$ is still kept and hardly degraded. For the 50 eq. of UHP (c), the signal of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ (2.54 ppm) appears along with two other phosphorus-containing species with ^{31}P NMR resonances at 1.06 and −14.14 ppm, respectively. The latter is attributed to $[PW_{12}O_{40}]^{3-}$, but the peak intensity is weaker than the case (b). After the addition of 400 eq. of UHP (d), there altogether appear six lines in the ^{31}P NMR spectra pattern. The line at 2.60 ppm is attributed to $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$, and the signal of $(CPB)_3[PW_{12}O_{40}]$ (−14.22 ppm) has become very weak, suggesting that it has degraded nearly completely. Other five signals in the −8.00 to 1.20 ppm region can be attributed to phosphorous-containing species, which are probably intermediates during the degradation process in the presence of excess UHP.

In order to examine where the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ locate in the ^{31}P NMR spectra pattern, $(BuN)_3[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]$ in DMF was measured by ^{31}P NMR. As shown in Fig. 3, only one signal at 2.58 ppm is observed, proving that the signal of around 2.50 ppm is the characteristic peak of the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$.

3.4. Epoxidation of cyclohexene

3.4.1. Effect of oxidizing reagents

The effects of different sources of the oxidizing reagents and different heteropoly compounds on the cyclohexene conversion and product selectivity are given

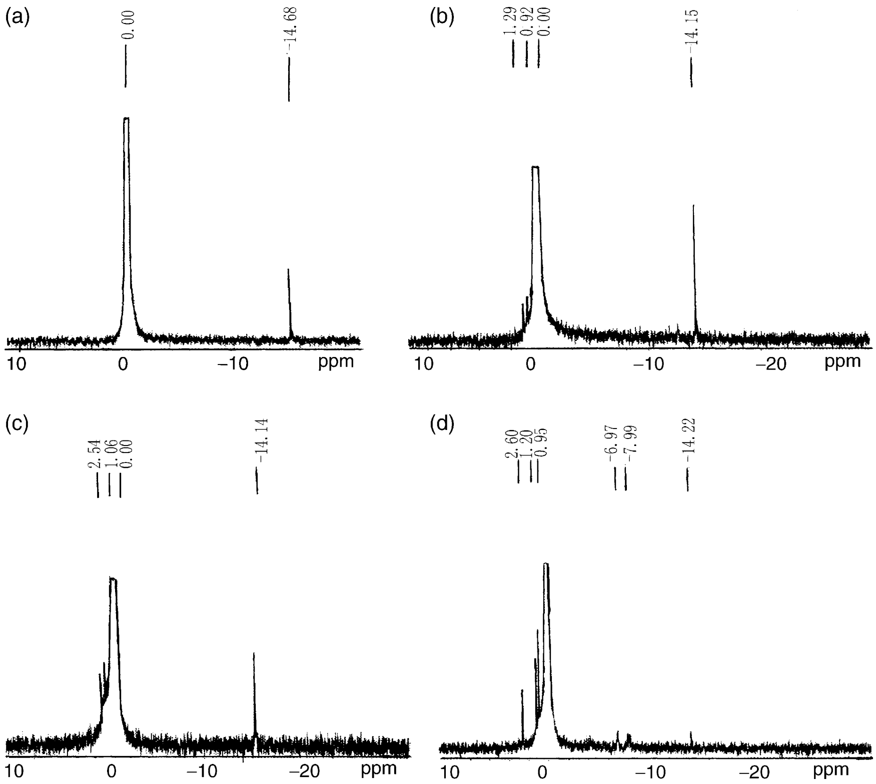

Fig. 2. ^{31}P NMR spectra of a DMF solution of $(CPB)_3[PW_{12}O_{40}]$ reacted with n equivalents of UHP, where n = (a) 0, (b) 40, (c) 50, (d) 400. Spectra are referenced to 85% H_3PO_4 as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period for each sample was constant in all cases (180 min).

in Tables 1–3, for comparative purpose. The selectivity for the desired epoxide increases when urea–hydrogen peroxide is used. Among a series of catalysts of HPAs, tris(cetylpyridinium)12-tungstophosphate (CWP) shows the

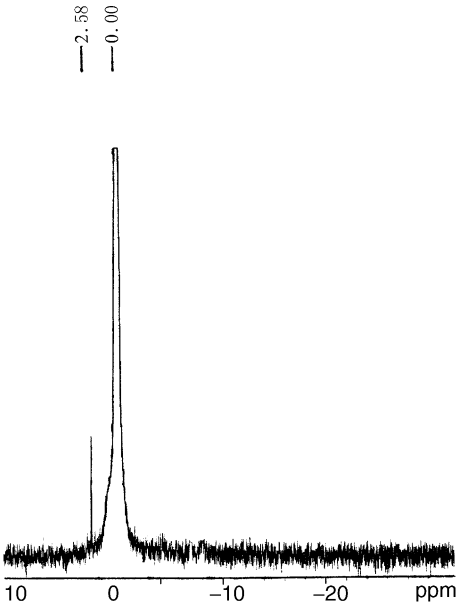

Fig. 3. ^{31}P NMR spectrum of a DMF solution of $(BuN)_3[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]$. Spectra are referenced to 85% H_3PO_4 as an external standard, 380 scans. The sum of the NMR data acquisition time and the incubation period was 180 min.

Table 1
Epoxidation of cyclohexene in the CWP, CWP1, CWP2, and CMP catalytic system[a]

Catalyst	Oxidant[b]	Conversion (mol%)[c]	TON[d]	Selectivity (mol%)[e]
CWP	UHP	50	100	91
	U + HP	49	98	85
	HP	38	75	66
	t-BuHP[f]	18	18	42
CWP1	UHP	40	80	91
CWP2	UHP	7	15	89
CMP	UHP	26	49	88
	U + HP	17	33	83
	HP	15	29	60

[a] Reaction conditions: 3 mmol cyclohexene; 6 mmol oxidant; 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 70 °C; reaction time: 3 h.

[b] UHP, urea–hydrogen peroxide adduct; HP, hydrogen peroxide (30%); U + HP, urea and hydrogen peroxide mixture (1:1, mole ratio); *t*-BuHP, *tert*-butyl hydroperoxide (65%).

[c] Conversion/theoretically possible conversion.

[d] Turnover number (TON) is given as moles of products/mol of catalyst.

[e] Selectivity for cyclohexene epoxide determined by GC analysis.

[f] 3 mmol cyclohexene; 1.5 mmol *t*-BuHP (65%); 0.015 mmol of catalyst (0.5 mol%); 5 ml acetonitrile; 1.89 mmol of bromobenzene internal standard; reaction temperature: 50 °C; reaction time: 1 h.

Table 2
Epoxidation of cyclohexene in the $Q_3PMo_mW_{12-m}O_{40}$ (m = 4, 6, 8) catalytic system[a]

Catalyst	Oxidant	Conversion (mol%)	TON	Selectivity (mol%)
CPMW1	UHP	26	53	84
	U + HP	10	20	80
	HP	7	14	70
CPMW2	UHP	26	53	84
	U + HP	27	51	86
	HP	53	100	48
CPMW3	UHP	21	42	74
	U + HP	23	46	61
	HP	60	120	45

[a] Reaction conditions: 3 mmol cyclohexene; 6 mmol oxidant; 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 70 °C; reaction time: 3 h.

Table 3
Epoxidation of cyclohexene in CPMV, CVM, TVM, CSiW, and CSiM catalytic system[a]

Catalyst	Oxidant	Conversion (mol%)	TON	Selectivity (mol%)
CPMV	UHP	8	16	51
	U + HP	5	10	30
	HP	9	17	20
CVM	UHP	14	28	61
TVM	UHP	8	16	35
CSiW	UHP	3	1	5
CSiM	UHP	7	4	6

[a] Reaction conditions: 3 mmol cyclohexene; 6 mmol oxidant; 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 70 °C; reaction time: 3 h.

highest catalytic activity. In the case of catalyst CWP and U + HP system, where urea and aqueous hydrogen peroxide solution (30%) were added separately, both the conversion and the selectivity of the desired epoxide were found to be slightly low compared the solid UHP system and significantly high in comparison to the aqueous hydrogen peroxide system. The addition of urea has a helpful effect on the selectivity of the epoxide. Probably, the urea acts not only as a dehydrating agent but also as a buffer reagent for the system, which prevents further isomerization and hydrolysis of the desired epoxide.

3.4.2. Effect of the solvent

It is well known that the nature of the solvent plays a very important role in the catalytic reactions carried out in liquid phase [45,46]. The solvent effect in the epoxidation of alkene with urea–hydrogen peroxide over HPAs has never been investigated in previous studies. To study the influence of the nature of the solvent, the epoxidation of cyclohexene with UHP using CPW as a catalyst was carried out at a fixed temperature (60 °C) in different solvents, such as acetonitrile, methanol, acetone, toluene, chloroform, and 1,2-dichloroethane. Table 4 shows the effect of solvent on cyclohexene epoxidation over the CWP/UHP system. The highest reaction activity was achieved in the system of using acetonitrile as a solvent. The results show that the catalytic performance is strongly affected by the type of solvent, but a direct correlation between solvent properties and their efficiency could not be established in any cases. Our results show that the selectivity of cyclohexene epoxide highly depends on the nature of the solvents: in aprotic solvents like acetonitrile, acetone, toluene, chloroform, and 1,2-dichloroethane, the epoxide selectivity is higher than that in protic solvent like methanol. In order to analyze the activity difference between CWP/UHP/$CHCl_3$ and CWP/UHP/CH_3CN systems, a series of experiments were carried out. At 60 °C, the solid oxidant of UHP cannot be completely dissolved in chloroform or 1,2-dichloroethane, only floating on the surface of the solvents, with a small part of the UHP dissolved in the solvents to participate in the reaction, so the efficiency of reaction is poor. While for the solvent of acetonitrile, UHP can be dissolved into the reaction system, so the conversion and selectivity are higher than $CHCl_3$, or 1,2-dichloroethane was used as the solvent.

3.4.3. Effect of HPAs and other catalysts containing tungsten

Based on the effect of solvent, we selected acetonitrile as the solvent for the epoxidation of cyclohexene using UHP as the oxidant. The data listed in Tables 1–3, CWP is the best catalyst among the 12 HPAs and that CWP1 ranks second. The reason why salts of Mo–W mixed-coordinated heteropolyoxometalates show lower catalytic activity than CWP can be explained as follows: by the interaction with UHP, $Q_3PMo_mW_{12-m}O_{40}$ (m = 4, 6, and 8) are only partially converted to the effective catalytic active species,

Table 4
Epoxidation of cyclohexene over catalyst CPW in different solvents[a]

Solvent	Dipole moment (D)	Dielectric constant (ε)	Conversion (mol%)	TON	Selectivity (mol%)
MeCN	4.03	37.5	24	48	95
MeOH	1.7	32.7	5	10	67
MeCOMe	2.85	20.7	6	12	84
MePh	0.37	2.4	5	10	86
$CHCl_3$	1.03	4.8	14	28	81
$ClCH_2CH_2Cl$		~4.0	13	27	82

[a] Reaction conditions: 3 mmol cyclohexene; 3 mmol oxidant UHP; 0.015 mmol of catalyst (0.5 mol%); 3 ml solvent; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 60 °C; reaction time: 3 h.

$\{PO_4[WO(O_2)_2]_4\}^{3-}$. So when the amounts of catalyst used are the same, CWP shows higher catalytic activity in the epoxidation. The catalytic activity of quaternary alkylammonium mixed–addenda heteropolyoxometalates containing tungsten and molybdenum (CPMW1, CPMW2, and CPMW3) show the nearly equal activity to CMP, although there is still a slight difference among them. The activity of CPMW2 is higher than the others, and CPMW3 ranks the lowest. All the catalysts of HPAs listed in Table 3 show poor catalytic activity in the epoxidation compared with the data listed in Tables 1 and 2. Among them, CSiW and CSiM show low conversion of cyclohexene and selectivity for epoxide.

The reasons why $(CPB)_3[PW_{12}O_{40}]$ has a higher activity than $(CPB)_3[PMo_{12}O_{40}]$ may be explained as follows: on the basis of previous research achievements [11,18,19,37] and our ^{31}P NMR experiments, during the catalysis process, both $(CPB)_3[PW_{12}O_{40}]$ and $(CPB)_3[PMo_{12}O_{40}]$ are degraded to form the peroxo complex $Q_3\{PO_4[MO(O_2)_2]_4\}$ and $[\{M(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ (M = W, Mo) in the presence of excess H_2O_2. The active species of $Q_3\{PO_4[WO(O_2)_2]_4\}$ and $Q_3\{PO_4[MoO(O_2)_2]_4\}$ have the same structure and coordination environment, and the differences lie in the different M–O bond order and the different state of electrons filling orbits of the central metal ion. The electron configuration of atomic tungsten (W) and molybdenum (Mo) are [Xe]$4f^{14}5d^46s^2$, [Kr] $4d^55s^1$, respectively. For the $\{PO_4[WO(O_2)_2]_4\}^{3-}$, 5d and 6s orbits are vacant, while $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ has more vacant orbits, i.e. 4f, 4d, and 5s. During the catalytic process, the alkene and the active species will form the intermediate (transitional state) in the organic phase, and the electron of the alkene will fill the vacant orbits of the metal ion complex. For $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, the electrons of the alkene can fill the vacant 4f, 4d, 5s orbits, thus the intermediate is comparatively more stable than the one formed by $\{PO_4[WO(O_2)_2]_4\}^{3-}$ only having two kinds of vacant orbits. Since the transitional state intermediate is rather stable, the transfer of active oxygen to the C=C moiety of the alkene will be retarded. Accordingly, the rate of formation epoxide catalyzed by $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ becomes slower than that of the reaction via less stable intermediate formed by $\{PO_4[WO(O_2)_2]_4\}^{3-}$. Furthermore, the O–O bonds of tungsten complex are longer than that of molybdenum complex; this seems to be essential for the facile transfer of the active oxygen [18].

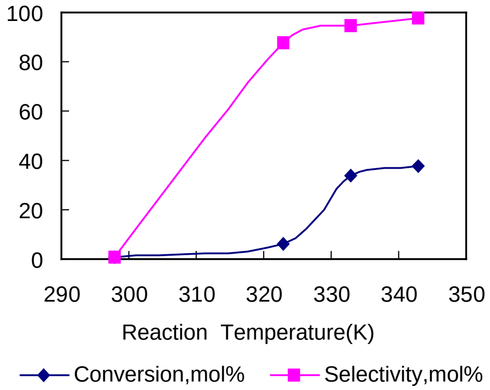

Fig. 4. Effect of reaction temperature on the epoxidation of cyclohexene. Reaction conditions: 3 mmol cyclohexene; 3 mmol oxidants UHP; 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction time: 3 h.

A series of catalysts containing tungsten were investigated in the UHP/CH_3CN and HP/CH_3CN system. The data listed in Table 5 show that all the catalysts in the UHP/CH_3CN system result in a higher selectivity for epoxide than that in the HP/CH_3CN system. This phenomena is obvious for the catalysts of $(CPB)_3[PW_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, H_2WO_4, and Na_2WO_4.

3.4.4. *Effect of reaction temperature*

We investigated the effect of reaction temperature on the epoxidation of cyclohexene. Fig. 4 shows the conversion and selectivity at different reaction temperatures and at

Table 5
Epoxidation of cyclohexene over various catalysts containing tungsten[a]

Catalyst	$[Q^+Br^-]/[W]$	Oxidant	Conversion (mol%)	TON	Selectivity (mol%)
$(CPB)_3[PW_{12}O_{40}]$	0	UHP	80	160	97
	0	HP	91	182	65
$H_3[PW_{12}O_{40}]$	0.25	UHP	96	192	85
	0.25	HP	99	198	64
$(BuN)_3{}^+[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$	0	UHP	96	192	85
	0	HP	99	198	79
$(CPB)_2{}^+[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$	0	UHP	42	84	81
	0	HP	62	124	80
H_2WO_4	0.27	UHP	23	46	64
	0.27	HP	38	76	7
Na_2WO_4	0.35	UHP	16	32	8
	0.35	HP	31	62	6

[a] Reaction conditions: 3 mmol cyclohexene; 0.75 mmol oxidants; 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; phase transfer reagent $[Q^+Br^-]$ = cetylpyridinium bromide; reaction temperature: 70 °C; reaction time: 3 h.

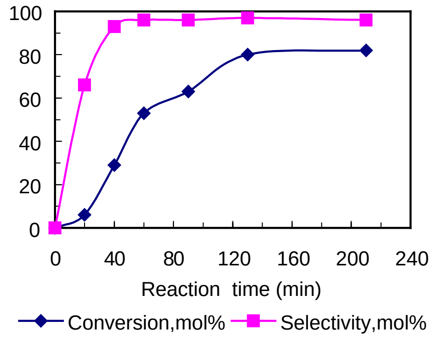

Fig. 5. Effect of reaction time on the epoxidation of cyclohexene. Reaction conditions: 3 mmol cyclohexene; 0.75 mmol UHP (cyclohexene: oxidant = 4.0); 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 70 °C.

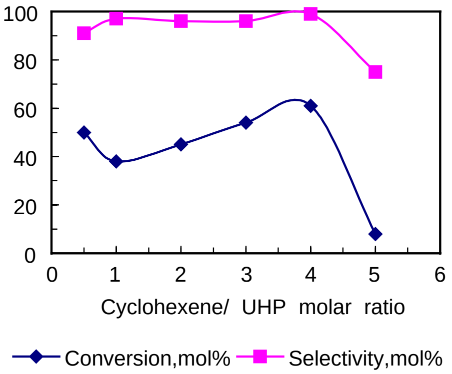

Fig. 6. Effect of cyclohexene to UHP molar ratio on the epoxidation of cyclohexene. Reaction conditions: 3 mmol cyclohexene; 0.015 mmol of catalyst (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 70 °C; reaction time: 3 h.

cyclohexene/UHP molar ratio = 1. At room temperature (25 °C), the reaction hardly happens. With increasing reaction temperature, the conversion and selectivity for epoxide increase. The selectivity (>90%) keeps nearly constant in the reaction temperature range from 50 to 70 °C, whereas the conversion increases with increasing temperature.

3.4.5. *Effect of reaction time*

In Fig. 5, the cyclohexene conversion is plotted as a function of reaction time at 70 °C (cyclohexene/UHP molar ratio 4.0). Under these reaction conditions, the conversion and selectivity simultaneously increase intensely with the continuing time. Comparatively, the increase of selectivity is more obvious than that of conversion. The conversion increases with the continuing time, and then reaches a limiting value of 80 mol% at 130 min. When the reaction time goes on, the conversion keeps at 80 mol%. The selectivity of epoxide levels off at ca. 97 mol% when 60 min elapses and keeps constant with the proceeding time.

3.4.6. *Effect of cyclohexene/UHP molar ratio*

The effect of cyclohexene/UHP molar ratio on the cyclohexene conversion and the product selectivity is shown in Fig. 6. The conversion curve decreases (from 50 to 38%) with the ratio increasing from 0.5 to 1.0, then increases (from 38 to 61%) with the increase of the ratio, finally descends greatly (from 61 to 8%) with the ratio increasing from 4.0 to 5.0. On the other hand, the selectivity first increases (from 91 to 97%) with the ratio increasing from 0.5 to 1.0, then keeps constant (ca. 97%) with the ratio from 1.0 to 3.0. When the cyclohexene/UHP molar ratio increases to 4.0, the conversion and selectivity both increase to the maximum values (61 and 99%, respectively). However, when the ratio increases to 5.0, the selectivity decreases to 75%.

The reason why the conversion and selectivity decrease at the cyclohexene/UHP molar ratio of 5 can be explained as follows: since all the reactions were carried out with the constant amount of catalyst (0.015 mmol) and substrate (3.0 mmol), with the varying the cyclohexene/UHP molar ratio, the ratio of UHP/catalyst also changes accordingly. When the cyclohexene/UHP molar ratio is 5.0, the corresponding molar ratio of [UHP]/[CWP] is 40. Fig. 2b shows that at this under this ratio [UHP]/[CWP], the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ (2.58 ppm) are not present. Only two unidentified phosphorus-containing species with ^{31}P NMR resonance peaks at 0.92 and 1.29 ppm are observed. When the cyclohexene/UHP molar ratio is 4.0, the corresponding ratio of [UHP]/[CWP] is 50. The signal of active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ (2.54 ppm) appears along with other two phosphorus-containing species with ^{31}P NMR resonances at 1.06 and −14.14 ppm, respectively (Fig. 2c). Based on the analysis of ^{31}P NMR spectra of the two reactions with the cyclohexene/UHP molar ratio of 5.0 and 4.0, respectively, the catalytic activity differences can be understood. For the former reaction system, no active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ are present. So the catalytic activity is inferior to the latter case in which the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ are produced.

Furthermore, in the range of cyclohexene/UHP molar ratio from 1.0 to 4.0, the cyclohexene conversion increases with increasing ratio mainly due to increased H_2O_2 utilization for cyclohexene oxidation. However, the selectivity of cyclohexene epoxide increases very slowly over the range.

3.4.7. *Effect of the amount of catalyst*

Fig. 7 depicts the effect of catalyst concentrations on cyclohexene epoxidation. An increase in the catalyst concentration (with respect to cyclohexene) resulted in an increase in the cyclohexene conversion initially before leveling off at ca. 53 mol%. Cyclohexene epoxide selectivity gradually decreases from the maximum value of 97 mol% to a slightly lower value of 91 mol% with increasing catalyst concentration.

3.4.8. *Epoxidation of other olefins*

Since the cyclohexene is comparatively active among various olefins, the epoxidation proceeds smoothly.

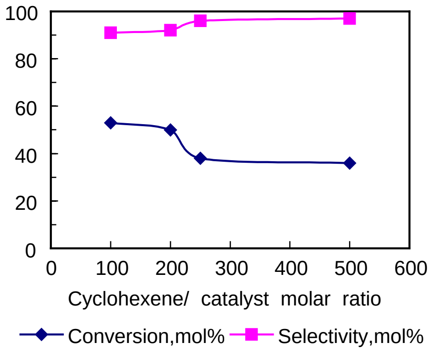

Fig. 7. Effect of catalyst concentration on the epoxidation of cyclohexene. Reaction conditions: 3 mmol cyclohexene; 6 mmol UHP; 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; reaction temperature: 70 °C; reaction time: 3 h.

What happens for the long chain linear terminal olefins and the olefin with electron-withdrawn group in this $(CPB)_3[PW_{12}O_{40}]/UHP/CH_3CN$ catalytic system? Here, 1-octene, allyl chloride and styrene were selected to test this catalytic system, and the reaction results are listed in Table 6. The conversion is only 27% for the epoxidation of 1-octene using UHP as the oxidant, but the 80% of selectivity to epoxide is still higher compared with the selectivity of 59% for the reaction using HP. For the epoxidation of styrene, using UHP also lead to a higher selectivity (60%) to epoxide compared with the 45% of selectivity for the reaction with HP. The conversion is very low in the epoxidation of allyl chloride, but the selectivity is very high with either oxidant. The conversion and selectivity for these reactions are inferior to the epoxidation of cyclohexene probably due to the electron density of the substrates. The electron densities of C=C bond of 1-octene and allyl chloride are lower than that of cyclohexene, so it is difficult for them to be attacked by the active oxygen.

Table 6
The epoxidation of alkenes under the $(CPB)_3[PW_{12}O_{40}]/UHP/CH_3CN$ system[a]

Substrate	Oxidant	Conversion (mol%)[b]	TON	Selectivity (mol%)[c]
1-Octene[d]	UHP	27	54	80
	HP	95	190	59
Styrene[e]	UHP	93	186	60
	HP	74	149	45
Allyl chloride[f]	UHP	1	2	99
	HP	2	4	99

[a] Reaction conditions: 3 mmol alkene; 0.75 mmol oxidants; 0.015 mmol of catalyst $(CPB)_3[PW_{12}O_{40}]$ (0.5 mol%); 3 ml acetonitrile; 1.89 mmol of bromobenzene as an internal standard; UHP, urea–hydrogen peroxide adduct; HP, hydrogen peroxide (30%).

[b] Conversion/theoretically possible conversion.

[c] Selectivity for epoxide determined by GC analysis.

[d] Reaction temperature: 70 °C; reaction time: 6 h.

[e] Reaction temperature: 50 °C; reaction time: 12 h.

[f] Reaction temperature: 50 °C; reaction time: 10 h.

4. Conclusions

The epoxidation of cyclohexene catalyzed by a series of Keggin-type heteropoly compounds have been carried out in CWP [tris(cetylpyridinium)12-tungstophosphate]/UHP/CH_3CN system by using anhydrous urea–hydrogen peroxide adduct (UHP) as the oxidizing reagent and acetonitrile as the solvent. Compared with aqueous hydrogen peroxide, urea–hydrogen peroxide adduct resulted in a high conversion and a very high selectivity of the desired cyclohexene epoxide. In the case of the U + HP system, both the conversion and the selectivity of the desired cyclohexene epoxide were much higher than in the aqueous hydrogen peroxide system. When aqueous hydrogen peroxide was used as an oxidant, the presence of highly polar water in the reaction system facilitates acid-catalyzed isomerization and hydrolysis of cyclohexene epoxide. The presence of urea is very important in the reaction medium. It acts not only as a dehydrating reagent but also as a buffer for the system.

^{31}P NMR spectra of a DMF solution of $(CPB)_3[PW_{12}O_{40}]$ reacted with n equivalents of UHP show that the Keggin-type heteropoly compounds $(CPB)_3[PW_{12}O_{40}]$ are degraded in the presence of excess UHP to form a considerable amount of phosphorus-containing species. Some of the species evolved from the UHP/$(CPB)_3[PW_{12}O_{40}]$ system have been identified. When the ratio of UHP/$(CPB)_3[PW_{12}O_{40}]$ is not less than 50, the active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ are produced during the incubation between UHP and $(CPB)_3[PW_{12}O_{40}]$. It is convincing that these active species of $[\{W(=O)(O_2)_2\}_4(\mu\text{-}PO_4)]^{3-}$ efficiently catalyzed the cyclohexene epoxidation in the $(CPB)_3$-$[PW_{12}O_{40}]/UHP/CH_3CN$ system.

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