Catalytic Properties of Heteropoly Compounds in 1,3-Butadiene Oxidation with Hydrogen Peroxide

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Abstract—The homogeneous oxidation of 1,3-butadiene (BD) in H_2O_2 –HPC–CH₃CN (HPC = heteropoly compound) solutions has been investigated. The route of the reaction depends on the nature of the metal capable of coordinating with active oxygen in the HPC. The products of radical BD oxidation (acrolein, 3-butene-1,2-diol, 2-butene-1,4-diol, furan) form in the presence of $H_{3+n}PMo_{12-n}V_nO_{40}$ (n = 1, 2) acids. 3,4-Epoxy-1-butene (EB) and acrolein + furan, which form in equal amounts in the presence of the (n-Bu₄N)₅PW₁₁O₃₉Fe(OH) salt, result, respectively, from the electrophilic addition of hydrogen peroxide to BD and from radical BD oxidation on iron–oxygen complexes in the HPC composition. The reaction carried out in the presence of (n-Bu₄N)₃{PO₄[WO(O₂)₂]₄}, (n-Bu₄N)₅Na_{0.6}H_{1.4}PW₁₁O₃₉, or (EMIm)₅NaHPW₁₁O₃₉ yields EB with high selectivity on the reacted BD basis (up to 97%) and H₂O₂ (about 100%). The formation and conversion of the phospho-

tungstate peroxo complexes $PW_n O_m^{\alpha-}$ (n = 2, 3, 4) that are active in BD epoxidation have been investigated by ³¹P NMR spectroscopy. The role of the tetrabutylammonium and ethylmethylimidazolium cations in the formation of these complexes has been demonstrated.

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The present-day common tendency to saving natural resources shifts researchers' interest to liquidphase catalytic oxidations, for these reactions occur at low temperatures and waste smaller amounts of substrate on the formation of deep oxidation products. In one of the most common types of liquid-phase oxidation systems [1-3], the catalyst is a heteropoly compound (HPC) and the stoichiometric oxidizer is 30% aqueous hydrogen peroxide. The latter is active under mild conditions, inexpensive, and convenient to handle. In the HPC $-H_2O_2$ systems, oxidative oxygen addition takes place at C=C bonds to yield an epoxide grouping. Olefin epoxidation with H_2O_2 is carried out in the presence of various HPCs containing either only Mo(VI) or W(VI) ions or, additionally, V(V), Ti(IV), Fe(III), and other transition metal ions [3-14]. The HPCs are used as soluble heteropoly acids (HPAs) or as polyoxometalate (POM) salts with organic cations in aqueous organic solutions or in two-phase mixtures. Catalysis by HPCs is based on the formation of peroxo complexes. In cyclohexene oxidation, the radical initiators present in the HPC, such as Fe(III) and Cr(III) ions, cause cyclohexene oxygenation in the allylic position along with epoxidation [3, 15]. High epoxidation selectivity for some other unconjugated olefins and high selectivity with respect to H₂O₂ reacted were achieved in the presence of disubstituted Fe(III) or V(V) silicotungstic HPCs at a very low concentration of H_2O_2 (and, accordingly, water) and a low reaction temperature with various solvents [3, 4]. Like oxidations with hydrogen peroxide on V(V), Fe(III), Cr(III), and Ti(IV) complexes [16–19], the same reactions over supported P–Mo(VI)–W(VI)–HPCs [20] take place in the presence of acid sites and may be accompanied by the cleavage of the C=C bond and the formation of the corresponding aldehydes and acids.

The liquid-phase oxidation of 1,3-butadiene and other conjugated dienes is poorly studied, as distinct from the gas-phase oxidation reactions over oxide catalysts [21–23] and epoxidation reactions over Ag/ α - Al_2O_3 [1]. The only exception is the industrial-scale synthesis of butenediol diacetate on the Pd-Te/C catalyst manufactured by Mitsubishi Co. [24]. BD is also known to be oxidizable in aqueous solutions containing Pd(II) and a strong oxidizer. With $CuCl_2$ as the oxidizer, the reaction yields crotonaldehyde [25]; under the action of a CuCl2-HCl-NaCl-NaI solution [26, 27] or a $H_9PMo_6V_6O_{40}$ solution [28], BD turns into furan. Information concerning BD epoxidation using hydrogen peroxide is limited to two publications [29, 30]. The second one provides an example of BD epoxidation in a solution of the HPC $[TBA]_{4}[\gamma-SiW_{10}O_{34}(H_{2}O)_{2}].$

In this work, we studied BD oxidation in Keggintype $HPC-H_2O_2$ systems, varying the HPC composition. The catalysts that we examined have different redox properties and different capacities to form peroxo complexes active in epoxidation reactions [31– 39]. We investigated how the BD oxidation route depends on the nature of the active metal ions of HPC, including V(V), Fe(III), Cu(II), and W(VI). The results of this study enabled us to compare the roles of radical and peroxide species of oxygen in BD oxidation.

EXPERIMENTAL

Chemicals

The following chemicals were used: $H_3PMo_{12}O_{40} \cdot nH_2O$ (reagent grade, Reakhim), unstabilized ~34% hydrogen peroxide solution (special-purity grade, Reakhim), $(C_4H_9)_4NBr$ (Reakhim), high-purity CH₃CN (brand 0, Kriokhrom), 1,3-butadiene (Aldrich), 1-butyl-3-methylimidazolium tetrafluoroborate (Aldrich), and 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich).

Preparation of Heteropoly Compounds

The commercial heteropoly acid $H_3PMo_{12}O_{40}$ · 14H₂O (H_3PMo_{12}) was purified by extraction with ether; $H_4PMo_{11}VO_{40} \cdot 13H_2O$ ($H_4PMo_{11}V$) and $H_5PMo_{10}V_2O_{40} \cdot 9H_2O$ ($H_5PMo_{10}V_2$) were obtained via a standard procedure [40].

To synthesize $[(C_2H_5)(CH_3)C_3H_3N_2]_5[PW_{11}O_{39}Cu(H_2O)]$ (EMIm-PW₁₁Cu), aqueous solutions of equimolar amounts of Na₇[PW₁₁O₃₉] (pH 4.0, 2.5 mL, 5.8 × 10⁻⁴ mol) and Cu(NO₃)₂ were mixed and an EMImBr solution (0.6 mL, 2.9 × 10⁻³ mol) was then added. The resulting precipitate was washed with water until it tested negative for Br⁻ and contained no NO₃⁻ ions (as was checked by measuring absorbance at $v_{NO_3} = 1384 \text{ cm}^{-1}$) and was then dried at 60°C.

For $C_{30}H_{57}N_{10}PW_{11}O_{40}Cu$ (M = 3314.7) anal. calcd. (%): C, 10.86; H, 1.73; N, 4.22. Found (%): C, 10.7; H, 1.80; N, 4.18.

The IR spectrum of this compound (in KBr) was consistent with the structure of the metal-substituted polyoxometalate ion $PW_{11}Cu$ [41]: v = 1100, 1058 (P–O), 952 (W=O), 884, 811, 742, 696 (W–O–W, W–O–Cu) cm⁻¹.

The compound $[(C_4H_9)(CH_3)C_3H_3N_2]_5[PW_{11}O_{39}Cu(H_2O)]$ (BMIm-PW₁₁Cu) was synthesized in the same way, but BMImBF₄ was used as the precipitant.

For $C_{40}H_{77}N_{10}PW_{11}O_{40}Cu$ (M = 3455.0) anal. calcd. (%): C, 13.9; H, 2.24; N, 4.05. Found (%): C, 13.8; H, 2.23; N, 4.01.

IR spectrum (KBr): v = 1100, 1060, 954, 883, 806, 742, 695 cm⁻¹.

The compound $[(C_4H_9)(CH_3)C_3H_3N_2]_5[PW_{11}O_{39}Fe(OH)]$ (BMIm-PW₁₁Fe) was synthesized in a similar way using Fe(NO₃)₃ and BMImBF₄ solutions.

For $C_{40}H_{76}N_{10}PW_{11}O_{40}Fe$ (M = 3446.3) anal. calcd. (%): C, 13.9; H, 2.22; N, 4.06. Found (%): C, 13.6; H, 2.25; N, 4.01.

The IR spectrum of this compound (in KBr) is consistent with the reported structure of $PW_{11}Fe$ [41]: $v = \sim 1090$ (w sh), 1063, 959, 886, 804, ~ 750 (w sh), 706 cm⁻¹.

The synthesis and identification of the salts $(n-Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ (TBA-PW₄), $(n-Bu_4N)_5Na_{0.6}H_{1.4}PW_{11}O_{39}$ (TBA-PW₁₁), and $(EMIm)_5NaHPW_{11}O_{39}$ (EMIm-PW₁₁) were described in our earlier work [42]. The synthesis of $(n-Bu_4N)_5PW_{11}O_{39}Fe(OH)$ (TBA-PW₁₁Fe^{III}) was described in [15].

1,3-Butadiene Oxidation

The oxidation of BD with hydrogen peroxide was investigated under static conditions at atmospheric pressure in the temperature range from 20 to 60°C. The reaction solution usually contained 2 mL of CH₃CN (in some cases, a mixture of CH₃CN and an imidazolium salt), 10-20 mg of an HPC (~5 μ mol), and $0.1-0.2 \text{ mL of} \sim 34\%$ aqueous H₂O₂ (1-2 mmol). A HPC sample and a solution of hydrogen peroxide in acetonitrile were placed in a temperature-controlled 28-mL Pyrex reactor fitted with two Teflon stopcocks and a magnetic stirrer. The reactor was purged with BD and sealed, and the stirrer was turned on. For measuring the volume of gas taken up, the reactor was connected via one of the stopcocks with an argon-filled measuring burette containing a sealing liquid. The second stopcock served as the sampler for GC analysis of the solution during the reaction.

The catalytic activity of the HPCs in H_2O_2 decomposition in an argon atmosphere was estimated as the amount of gas (O_2) released.

Reaction solutions were analyzed on a Kristall 2000 M chromatograph with a flame-ionization detector and an SPBTM-1000 capillary column $(0.53 \text{ mm} \times 30 \text{ m})$ in a temperature-programmed mode. The furan, acrolein, 3,4-epoxy-1-butene, 3-butene-1,2-diol, and 2-butene-1,4-diol yields were determined using the corresponding calibration relationships. Reaction products were identified by the GC-MS method. The hydrogen peroxide concentration was determined iodometrically by adding 0.1 mL of the reaction solution to 5 mL of acetic acid and 0.5 g of potassium iodide. The mixture was left standing for 10 min, 50 mL of water was then added, and the resulting solution was titrated with a 0.04 N thiosulfate solution. The organic peroxide content of the reaction products was determined in the same way, but the mix-

Entry	Temperature,	HPA	Fur	Acr	Crotonalde- hyde	1,2-diol	1,2-ox	1,4-diol	1,4-ox	<i>S</i> _{1,4} , %			
	C		μmol										
1	50	H ₃ PMo ₁₂ O ₄₀	0.15	0.86	0	0.13	0	0	0.22	27			
2	20	H ₄ PMo ₁₁ VO ₄₀	0.73	12	~0	0.90	0	1.1	1.2	19			
3	40	H ₄ PMo ₁₁ VO ₄₀	30	238	3.7	59	3.5	7.5	13	14			
4	50	H ₄ PMo ₁₁ VO ₄₀	59	282	5.1	42	3.3	15	8.4	20			
5	50	$H_5PMo_{10}V_2O_{40}$	23	99	12	17	3.0	5.0	3.3	19			

 Table 1. Yield of the products of 1,3-butadiene oxidation with hydrogen peroxide in the presence of phosphomolybdovanadic HPAs

Reaction conditions: HPA, 20 mg (~10 μ mol); CH₃CN, 2 mL; ~34% aqueous H₂O₂, 0.2 mL (2 mmol); BD atmosphere; reaction time, 2 h.

ture to be analyzed was kept for 1 h at 60° C in a nitrogen atmosphere.

RESULTS AND DISCUSSION

1,3-Butadiene Oxidation Catalyzed by $H_{3+n}PMo_{12-n}V_nO_{40}$ (n = 0, 1, 2) Heteropoly Acids

Phosphovanadomolybdic HPAs are oxidizers capable of generating radical oxygen species in the presence of H_2O_2 . An adequately studied process is the oxidation of alkylaromatic compounds in HPA $-H_2O_2$ systems [4, 31, 32, 43]. We investigated BD oxidation with hydrogen peroxide catalyzed by P-Mo-V-HPAs in CH₃CN solution. The BD oxidation products were furan, (Fur), acrolein (Acr), 3-butene-1,2-diol (1,2-diol), and 2-butene-1,4-diol (1,4-diol). Small amounts of crotonaldehyde, methyl vinyl ketone, acrylic acid, 4-vinyl-1-cyclohexene, 3-cyclohexene-1-carboxaldehvde, and, possibly, furanone were also detected. The diols could undergo further oxidation into 1,2-ox and 1,4-ox products, which, according to GC-MS data, included aldoalcohols + ketoalcohol (m/e 86) and dialdehyde + ketoaldehyde (m/e 84). Iodometric titration demonstrated that there were no peroxide compounds of BD [44] in the solution after the reaction.

In the presence of $H_3PMo_{12}O_{40}$ at 50°C, the yield of BD oxidation products was low (Table 1, entry 1). In the reaction catalyzed by the V(V)-containing acid $H_4PMo_{11}VO_{40}$, the yield of the products detectable by GC was significantly higher (Table 1, entries 2–4). The amount of products increased with an increasing temperature owing to the increasing rate of H_2O_2 decomposition catalyzed by $H_4PMo_{11}VO_{40}$. In the presence of $H_5PMo_{10}V_2O_{40}$ [45], which is a stronger oxidizer than $H_4PMo_{11}VO_{40}$, the product yield was lower (Table 1, entry 5), apparently because the products underwent further oxidation. The selectivity $S_{1,4}$ of the catalysts with respect to the formation of BD 1,4-oxygenation products (furan, 2-butene-1,4-diol, and 1,4-oxo products of its oxidation) was about 20%relative to the total amount of GC-detectable products and varied slightly from one HPA to another (Table 1). Figure 1 illustrates the kinetics of accumulation of BD oxidation products in the presence of $H_4PMo_{11}VO_{40}$. After 1 h, the formation of acrolein slowed down markedly, which was due to the high conversion of H_2O_2 (curves 1, 2). The amounts of 1,2and 1,4-diols began to decrease (curves 4, 5) because of the further oxidation of these compounds. Selectivity in terms of H₂O₂ consumed in product formation in the presence of $H_4PMo_{11}VO_{40}$ was ~40%. The low yield of the products per unit amount of hydrogen peroxide reacted is typical of the P-Mo-V-HPC catalyzed oxidation of other hydrocarbons as well, because the oxidation process is accompanied by H_2O_2 decomposition [31, 32].

Monoolefin oxidation catalyzed by vanadium(V) compounds is believed to be due to the action of the radical species

$$V^{IV} \sim 0,$$

which forms on vanadium ions [16]. It was observed [16] that oxidation by vanadium(V) picolinate peroxo complexes in CH₃CN is accompanied by the decomposition of peroxide groups with O_2 evolution. The oxidation process yielded products of monoolefin cleavage at the double bond and smaller amounts of epoxides. It was hypothesized that the epoxides were primary products and underwent further oxidation. The conversion of the olefins into epoxides followed by the hydrolysis and oxidative cleavage of the latter, which can give diols as intermediates, was also considered in the investigation of reactions on acid catalysts containing Cr–HPC or P–Mo–W–HPC [18, 20],

even though no diols were identified among the monoolefin oxidation products [17–20]. At the same time, an alternative mechanism was suggested for the radical cleavage of the double bond of the olefin in an iron salen complex; in this mechanism, O_2/H_2O or H_2O_2 molecules are involved in the catalytic cycle [17].

A specific feature of BD oxidation by hydrogen peroxide in the presence of a P–V–Mo–HPC is the formation of 1,2- and 1,4-addition products, including diols, although no significant amounts of epoxide are detected. The data available on this reaction suggest that BD oxidizes under the action of radical oxygen species coordinated to vanadium via the formation of EB as the primary product. EB is rapidly hydrated on strong Brønsted acid sites of the HPC, turning into 1,2- and 1,4-diols [46]. The subsequent oxidative conversions of the diols in the HPC–H₂O₂ system yield the complete set of products, as is shown in Scheme 1.







Interaction between 1,3-Butadiene and H_2O_2 in the Presence of Imidazolium Salts of Cu(II)and Fe(III)-Substituted Phosphotungstate Anions

Metal-substituted phosphotungstates in CH₃CN solution differ in terms of the properties they show in the catalytic decomposition of hydrogen peroxide and hydrocarbon substrate oxidation and in the formation of intermediate peroxide complexes [15, 47, 48]. We studied the conversions of H₂O₂ and BD in solutions of the following ethylmethylimidazolium and butylmethylimidazolium salts: (EMIm)₅[PW₁₁O₃₉Cu(H₂O)], (BMIm)₅[PW₁₁O₃₉Cu(H₂O)], The imidazolium salts of the [PW₁₁O₃₉Cu(H₂O)]⁵⁻ anion in CH₃CN solution, like the TBA salts [15], catalyze rapid H₂O₂ decompo-



Fig. 1. (1) Hydrogen peroxide conversion and (2–6) amounts of 1,3-butadiene oxidation products versus reaction time: (2) acrolein, (3) furan, (4) 3-butene-1,2-diol, (5) 2-butene-1,4-diol, and (6) crotonaldehyde. Reaction conditions: $H_4PMo_{11}VO_{40} \cdot 13H_2O$, 20 mg (10 µmol); ~34% aqueous H_2O_2 , 0.2 mL (2 mmol); CH₃CN, 2 mL; BD atmosphere; 50°C.



Fig. 2. Volume of oxygen released due to H_2O_2 decomposition in the presence of (1) (EMIm)₅[PW₁₁O₃₉Cu(H₂O)] and (2–4) (BMIm)₅[PW₁₁O₃₉Cu(H₂O)] in the solvents (1, 2) CH₃CN, (3) CH₃CN + 60 wt % BMImBF₄, and (4) BMImBF₄. Reaction conditions: solvent volume, 2 mL; amount of catalyst, 19 mg (5.5 µmol); ~34% aqueous H_2O_2 , 0.2 mL (1.5 mmol); 50°C.

sition with O_2 evolution (Fig. 2, curves 1, 2). This process likely occurs without the formation of intermediate oxygen complexes. Replacing part of the solvent



Fig. 3. Amounts of the resulting (1) 3,4-epoxy-1-butene and (2) acrolein as a function of reaction time in the presence of phosphotungstates: (a) TBA-PW₄ (10 mg, 5.3 μ mol), (b) TBA-PW₁₁ (20 mg, 5.1 μ mol), and (c) EMIm-PW₁₁ (17 mg, 5.0 μ mol). Reaction conditions: ~34% aqueous H₂O₂, 0.2 mL (1.9 mmol); CH₃CN, 2 mL; BD, 26 mL (1 mmol); 50°C.

with BMImBF₄ inhibits H_2O_2 decomposition (Fig. 3, curves 3, 4). Apparently, the imidazolium cation interacts rapidly with the 'OH radical [49]. In the presence of (BMIm)₅[PW₁₁O₃₉Fe(OH)], no H_2O_2 decomposition occurred in both CH₃CN and a CH₃CN + BMImBF₄ mixture, for there was no oxygen evolution.

In the experiments involving BD, H_2O_2 , and the salts of the $[PW_{11}O_{39}Cu(H_2O)]^{5-}$ anion, the oxidation products furan, acrolein, and EB formed only in trace amounts both in acetonitrile alone and in the acetonitrile + $BMImBF_4$ or acetonitrile + $BMImPF_6$ mixture. Hydrogen peroxide in this case was consumed almost entirely (Table 2, entries 1-4) via its decomposition and, possibly, other side reactions. When BD and (BMIm)₅[PW₁₁O₃₉Fe(OH)] were present in CH₃CN, the H₂O₂ conversion was low (Table 2, entries 5, 6), and so was the amount of the resulting products. In entry 6, a small amount of 1-butyl-3methyl-2,4,5-trioxoimidazolidine, an oxidation product of the BMIm⁺ cation, was detected by GC-MS. The activity of the TBA salt of the [PW₁₁O₃₉Fe(OH)]⁵⁻ anion in the hydrogen peroxide oxidation reactions is known to be due to the formation of an intermediate iron peroxo complex in the polyoxometalate anion; this complex absorbs visible light in the $18000-26000 \text{ cm}^{-1}$ range [15, 47]. We ascertained that, with the BMIm salt, this "red" complex does not form in noticeable amounts under the reaction conditions. This is the likely reason why there were no BD oxidation products.

Under the same conditions, the TBA salt of the $[PW_{11}O_{39}Fe(OH)]^{5-}$ anion catalyzed the formation of furan, acrolein, and EB (Table 2, entry 7). The other reaction products, namely, 3-butene-1,2diol, 2-butene-1,4-diol, and methyl vinyl ketone, were in minor amounts. Selectivity in terms of H_2O_2 consumed in the formation of BD oxidation products was $\sim 70\%$. No phosphotungstates free of paramagnetic Fe(III) ions were detected in the H₂O₂-containing reaction solution. (Otherwise, they would have shown themselves as narrow ³¹P NMR signals in the chemical shift range from +5 to -15 ppm.) Therefore, the observed catalytic activity should be attributed to the $[PW_{11}O_{39}Fe(OH)]^{5-}$ anion. Accordingly, the formation of EB as a product of the electrophilic oxidation of BD is due to the formation and fairly high stability of the Fe(III) peroxo complex in the HPC (Scheme 2). The rate of the hydration of the resulting EB into diols in the presence of the neutral salt $(TBA)_{5}[PW_{11}O_{39}Fe(OH)]$ was substantially lower than in the presence of the $H_{3+n}PMo_{12-n}V_nO_{40}$ acids [46]; as a consequence, EB accumulated during the reaction up to $\sim 50\%$ of the total amount of BD oxidation products. The oxidation of BD into acrolein and furan possibly includes preliminary EB hydration steps yielding 1,2- and 1,4-diols. Next, the vic-diol undergoes oxidative cleavage [50] to yield acrolein, and 1,4diol undergoes oxidative cyclization into furan. These

Entry	Catalyst	Solvent	Time h	Prod	H_2O_2			
Entry	Catalyst	Solvent	Time, ii	Fur	Acr	EB	conversion	
1	EMIm-PW ₁₁ Cu	CH ₃ CN	0.5	0	0.4	0.2	97	
2	BMIm-PW ₁₁ Cu	CH ₃ CN	0.5	0	0.4	0.4	98	
3	BMIm-PW ₁₁ Cu	$CH_3CN + 60$ wt % $BMImBF_4$	3	0.7	10.6	0	62	
4	BMIm-PW ₁₁ Cu	$CH_3CN + 34$ wt % $BMImPF_6$	1.5	0	2.3	0.9	70	
5	BMIm-PW ₁₁ Fe	CH ₃ CN	3	0.4	5.1	1.3	8	
6*	BMIm-PW ₁₁ Fe	$CH_3CN + 60$ wt % $BMImBF_4$	3	1.8	4.6	0.7	3	
7	TBA-PW ₁₁ Fe	CH ₃ CN	3	1.26	17	18	9	

Table 2. Yield of the products of 1,3-butadiene oxidation with hydrogen peroxide in the presence of salts of metal-substituted phosphotunstate anions

Note: Reaction conditions: solvent, 2 mL; catalyst, 5.5 μ mol; ~34% aqueous H₂O₂, 0.2 mL (1.66 mmol); BD atmosphere; $T = 50^{\circ}$ C. * $T = 60^{\circ}$ C.

oxidative conversions, like the similar reactions on porphyrin complexes [51], are possible owing to the

existence of different active oxygen species in the iron complexes in HPC (Scheme 2).

1,3-Butadiene oxidation with H_2O_2 catalyzed by (TBA)₅[PW₁₁O₃₉Fe(OH)]



1,3-Butadiene Oxidation with Hydrogen Peroxide Catalyzed by Phosphotungstates

The oxidation of BD with hydrogen peroxide was studied in the presence of HPCs weakly accelerating H_2O_2 decomposition and forming peroxo complexes active in electrophilic oxygen addition [33–39]. The following phosphotungstates were synthesized for this purpose: $(n-Bu_4N)_3$ {PO₄[WO(O₂)₂]₄} (TBA-PW₄), $(n-Bu_4N)_5Na_{0.6}H_{1.4}PW_{11}O_{39}$ (TBA-PW₁₁), and (EMIm)₅NaHPW₁₁O₃₉ (EMIm-PW₁₁). In this HPC series, we investigated the effects of the polyoxometalate anion and organic cation compositions on catalytic activity [42].

In acetonitrile solutions containing TBA-PW₄, TBA-PW₁₁, or EMIm-PW₁₁ and aqueous hydrogen peroxide, BD oxidized at 20–60°C into 1,2-epoxy-3butene. Acrolein, furan, and diols formed only in trace amounts (Table 3). The BD-to-EB selectivity (S_{EB}) at various temperatures and H₂O₂ conversions into the oxidation products, determined by GC, is close to 90% (Table 3).

Table 4 presents balance data for BD oxidation into EB in relation to the HPC composition and catalyst and H_2O_2 concentrations. The amount of reacted BD derived from gas uptake data was close to the amount of reacted H_2O_2 in most experiments and, within the measurement error, was consistent with the amount of the resulting products. In entries 1-7, at a fairly high H_2O_2 concentration in the solution (~1 mol/L), selectivity in terms of hydrogen peroxide consumed in BD formation (S_{H,O_2}) , defined as the ratio of the amount of BD to the amount of H₂O₂ reacted, varied with catalyst composition between 60 and 78%. The rest of the H_2O_2 apparently decomposed or reacted with the solvent [52, 53]. Reducing the H_2O_2 concentration to ~0.5 mol/L (entries 8–10) brought $S_{\rm H_{2}O_{2}}$ close to 100%. In all experiments, a high EB selectivity of \geq 90% was observed, which implied a small proportion of the radical BD oxidation products. In experiment

Entry	Catalyst	Tem- pera- ture, °C	Amount of catalyst, µmol	Amount of $\sim 34\%$ H ₂ O ₂		Product yield, mmol $\times 10^2$					$S_{\text{EB}},$	H ₂ O ₂ conver-	$S_{\mathrm{H_2O_2}},$
				mL	mmol	EB	Acr	Fur	1,2-diol	1,4-ox	70	sion, %	70
1	TBA-PW ₄	20	5.3	0.2	2.12	5.9	0.6	0.10	0.40	0.06	83	—	_
2	TBA-PW ₁₁	20	5.1	0.2	2.12	2.2	0.2	0.05	0	0	90	_	_
3	TBA-PW ₁₁	60	10	0.1	0.92	51.2	6.0	0.05	0.40	0.3	88	63	88
4	EMIm-PW ₁₁	60	10	0.1	0.86	64.5	6.2	0.20	0	0.2	91	84	90

Table 3. Yield of the products of 1,3-butadiene oxidation with hydrogen peroxide in the presence of phosphotungstates

Note: Reaction conditions: CH₃CN, 2 mL; BD atmosphere.

 Table 4. Effects of the phosphotungstate composition and catalyst and hydrogen peroxide concentrations on butadiene epoxidation

Entry	Catalyst	Amount	H_2O_2, m	nmol	BD reacted	Total amount		$S_{\mathrm{H_2O_2}},\%$
		of catalyst, µmol	initial amount	amount reacted	mmol	of products	S _{EB} , %	
1	TBA-PW ₄	5.3	1.91	0.25	0.23	0.21	93	78
2	TBA-PW ₁₁	5.1	1.91	0.12	0.09	0.09	93	67
3	EMIm-PW ₁₁	5.0	1.94	0.28	0.19	0.22	95	75
4 ^a	EMIm-PW ₁₁	2.3	1.98	0.22	0.18	0.16	94	70
5	TBA-PW ₄	2.6	1.93	0.16	0.10	0.10	86	60
6	TBA-PW ₄	11	1.99	0.46	0.24	0.33	89	63
7	TBA-PW ₄	5.3	2.79	0.22	0.13	0.18	87	71
8	TBA-PW ₄	5.3	1.01	0.13	0.14	0.15	90	~90
9	TBA-PW ₁₁	5.1	0.96	0.09	0.08	0.08	96	78
10 ^a	EMIm-PW ₁₁	2.3	1.03	0.16	0.14	0.1	97	~100
11 ^{a, b}	EMIm-PW ₁₁	5.0	0.72	0.36	0.46	0.365	98	~100
	Second cycle		0.99	0.38	0.36	0.75 ^c	98 ^d	~100 ^d

Note: Reaction conditions: \sim 34% aqueous H₂O₂; BD, 26 mL (1 mmol); CH₃CN, 2 mL; 50°C; reaction time, 2 h.

^a Reaction time of 5 h.

^b Reaction conducted in a BD atmosphere.

^c After two reaction cycles.

^d Calculated from the amounts of the resulting products and H_2O_2 consumed in two reactions cycles.

11, after 50% conversion was reached in 5 h, another reaction cycle was started by adding a new portion of H_2O_2 until its total concentration of ~0.5 mol/L and the reaction was continued for another 5 h. After the second cycle, the total amount of products was twice larger and $S_{\rm EB}$ and $S_{\rm H,O_2}$ were the same as in the first cycle.

A similar H_2O_2 consumption selectivity was observed in BD oxidation on a $[TBA]_4[\gamma-SiW_{10}O_{34}(H_2O)_2]$ catalyst in CH₃CN at a lower hydrogen peroxide concentration (0.16 mol/L) and $[BD] > [H_2O_2]$ [30]. Note for comparison that, in BD oxidation on the catalyst TS-1 [29], the BD formation selectivity $S_{H_2O_2}$ was only 46% at $[H_2O_2] = 0.23$ mol/L, much lower than in the presence of the HPC. At the same time, the activity of TS-1 was higher, namely, 193 mol EB per mole of Ti in 1 h [29] as against 110 mol EB per mole of γ -SiW₁₀ in 9 h [30] and 15–90 mol EB per mole of phosphotungstate in 2–5 h (Table 4).

Figure 3 plots kinetic curves illustrating EB accumulation and the formation of the main by-product acrolein—in the presence of the three phosphotungstates. At the early stages of the reaction (over ~1 h), the EB formation rate is higher than its steady-state value. According to their steady-state activity, the catalysts can be arranged in the following order: $(TBA)_3{PO_4[WO(O_2)_2]_4} \approx (TBA)_5Na_{0.6}H_{1.4}[PW_{11}O_{39}] <$ $(EMIm)_5NaH[PW_{11}O_{39}].$

The variation of the composition of the catalysts during the reaction was monitored by ³¹P NMR spectroscopy. This enabled us to correlate the EB formation rate with the composition of the peroxo complexes forming in the reaction solutions in the initial stage and under near-steady-state conditions. The phosphotungstate peroxo complexes forming in H_2O_2 solutions were identified in earlier works [36–39, 42]. The ³¹P NMR spectra of the reaction solutions are presented in Fig. 4. In CH₃CN containing aqueous H₂O₂, TBA-PW₄ retains its composition (spectrum a). The signal at $\delta = 3.5$ ppm is due to the peroxo complex ${PO_4[WO(O_2)_2]_4}^{3-}$. The $PW_{11}O_{39}^{7-}$ anion in TBA- PW_{11} and $EMIm-PW_{11}$ disproportionates into $\{PO_4[WO(O_2)_2]_4\}^{3-}$, $PW_{12}O_{40}^{3-}$ (spectra c, e), and polytungstate ions. Under the reaction conditions, TBA- PW_4 or TBA- PW_{11} turns mainly into the peroxo anion $\{PO_4[WO(O_2)_2]_2\}^{2-}$ ($\delta = 0.4$ ppm; spectra b, d). In the case of EMIm-PW₁₁, a large proportion of the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ complex persists and the peroxo complex PW₃O_m^{α -} is present ($\delta \approx 2$ ppm; spectra f, g).

At the early stages of the reaction (within 1 h), the amount of EB forming on each of the three catalysts correlates with the concentration of the peroxo anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ that has resulted from the reaction between the initial HPC and H₂O₂. It was demonstrated in our earlier work [42] that, even if the peroxotungstate anion $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ actually forms via phosphotungstate disproportionation [36], it is much less active toward BD. The peroxo anion $\{PO_4[WO(O_2)_2]_2\}^{2-}$ synthesized as was described by Salles et al. [37] turned out to be three times less active than $\{PO_4[WO(O_2)_2]_4\}^{3-}$. This is consistent with the fact that the activity of TBA-PW₄ in the steady state is lower by a factor of about 3. The steady-state activity of $TBA-PW_{11}$ per unit concentration ${PO_4[WO(O_2)_2]_2}^{2-}$ was two times higher than that of TBA-PW₄. This suggests that, under catalytic conditions, tungstate ions are favorable for regeneration of the more active peroxo anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$, which is rapidly consumed (Scheme 3). EMIm-PW $_{11}$ shows a higher steady-state activity because it generates larger amounts of the peroxo anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and, apparently, $PW_3O_m^{\alpha-}$.

The data listed in Table 5, obtained for the reaction catalyzed by EMIm-PW₁₁, illustrate the effect of imidazolium salts on BD oxidation with hydrogen peroxide. As the EMImBF₄ concentration was increased from 1.5 to 20%, the amount of the resulting EB decreased (entries 2, 3), while a high EB yield was attained in the presence of BMImPF₆ (entry 4). This distinction can be explained by the transformation of the catalyst in the reaction solution, as was done for the (BMIm)₃PW₁₂O₄₀ salt, which is inactive in the



Fig. 4. ³¹P NMR spectra: (a) TBA-PW₄ (10 mmol/L) in the absence of BD, (b) TBA-PW₄ 2 h after the addition of BD, (c) TBA-PW₁₁ (2.3 mmol/L) in the absence of BD, (d) TBA-PW₁₁ 2 h after the addition of BD, (e) EMIm-PW₁₁ (2.3 mmol/L) in the absence of BD, (f) EMIm-PW₁₁ 2 h after the addition of BD, (g) the same 3.5 h after the addition of BD, and (h) TBA-PW₄ solution (10 mmol/L) after prolonged storage [42] (this spectrum is presented for comparison and indicates the presence of all of the three identified peroxo complexes). Reaction conditions: $[H_2O_2] =$ 1 mol/L; CH₃CN : ~34% aqueous $H_2O_2 = 10$: 1 (vol/vol); reaction temperature of (a, h) 25 and (b–g) 50°C.

Entry	Admixture	Admixture concentration, wt %	Fur	Acr	EB	1,2-diol	1,4-diol	S %	S %	
					3 _{EB} , 70	$S_{H_2O_2}, N$				
1*	EMImBF ₄	0	0.08	0.68	15.4	0.05	0.1	94	70	
2	EMImBF ₄	1.5	0.08	0.44	8.2	0	0	94	_	
3	EMImBF ₄	20	0.04	0.22	3.8	0	0	94	96	
4	EMImPF ₆	20	0.12	0.26	13.2	0	0	97	~100	

Table 5. Effects of EMImBF₄ and EMImPF₆ admixtures on the yield of the products of butadiene oxidation with hydrogen peroxide in the presence of EMIm-PW₁₁

Note: Reaction conditions: catalyst, 2.3 μmol; (CH₃CN + EMImX), ~2 mL; ~34% aqueous H₂O₂, 0.2 mL (1.8 mmol); BD, 26 mL (1 mmol); 50°C; reaction time, 2 h.

* Reaction time of 5 h.

absence of BMImPF₆ [8]. We demonstrated that, unlike the salt of the $PW_{12}O_{40}^{3-}$ anion, the salts of the $PW_{11}O_{39}^{7-}$ anion in CH₃CN + aqueous H₂O₂ solution rapidly generate catalytically active peroxo complexes. Because the participation of water molecules is necessary for the transformation of the phosphotungstate anions, the replacement of CH₃CN in this solution with hydrophilic BMImBF₄ strongly slows down peroxo complex formation (according to NMR data), causing a decrease in the EB formation rate. Addition of hydrophobic BMImPF₆ to the CH₃CN + aqueous H_2O_2 solution does not decelerate the process, and the EB formation rate remains high. As is clear from the data presented in Table 5, the favorable effect of BMImPF₆ consists in the enhancement of EB selectivity (S_{EB}) from 94 to 97% via hampering the radical side processes. A particularly pronounced increase in EB selectivity on the H_2O_2 basis (up to ~100%) relative to the selectivity observed for the pure solvent is achieved by replacing 20% of the CH₃CN with an imidazolium salt (entries (1, 3, 4) at the equally high H_2O_2 concentration (~1 mol/L).

Transformations of the TBA-PW₁₁ catalyst (1) in a CH_3CN solution containing aqueous H_2O_2 and (2, 3) in the BD epoxidation reaction (2) at its early stages and (3) in the steady state



CONCLUSIONS

The catalytic properties of the HPCs in BD oxidation with hydrogen peroxide depend on the nature of their active metal ion—V(V), Fe(III), or W(VI). In acetonitrile + aqueous H_2O_2 solution, there is a correlation between the formation of active oxygen complexes in the catalytic system, the H_2O_2 decomposition rate, and the composition of the BD oxidation products, which include acrolein, furan, 3-butene-1,2-diol, 2-butene-1,4-diol, and EB. The acid $H_4PMo_{11}VO_{40}$ can form radical species coordinated to the vanadium ion that are active both in H_2O_2 decomposition and in radical BD oxidation yielding acrolein, furan, and 1,2- and 1,4-diols. The selectivity of the catalysts in terms of H_2O_2 consumed in the formation of oxidation products is ~40%.

The free radicals resulting from rapid H_2O_2 decomposition, which is catalyzed by the $[PW_{11}O_{39}Cu(H_2O)]^{5-}$ anion, do not yield selective BD oxidation products. The salt (TBA)₅PW₁₁O₃₉Fe(OH) shows low activity in

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 H_2O_2 decomposition and catalyze BD oxidation into both acrolein (containing furan and 1,2- and 1,4-diols) and EB owing to the formation of active iron—oxygen complexes in the HPC. The selectivity of this catalyst in terms of H_2O_2 consumed in the formation of oxidation products has a larger value of ~70%.

EB forms with high selectivity (S_{EB} of up to 97%, $S_{H_2O_2}$ close to 100%) in the presence of phosphotungstate anions, which are practically inactive in H_2O_2 decomposition. In this case, the oxidation products contain only small amounts of acrolein, furan, and 1,4- and 1,2-diols. Using the ³¹P NMR method, we were able to monitor the formation and transformation, under the reaction conditions, of $PW_nO_m^{\alpha-}$ peroxo complexes active in BD epoxidation. The imidazolium cation exerts a favorable effect on the formation of these complexes and on the selectivity of the reaction by inhibiting the side radical reactions of BD.

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