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Polyfunctional action of transition metal substituted heteropolytungstates in alkene epoxidation by molecular oxygen in the presence of aldehyde

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Abstract

Alkene epoxidation by dioxygen in the presence of isobutyraldehyde (IBA) and tetrabutylammonium salts of transition-metal-substituted heteropolyanions (HPAs), $PW_{11}MO_{39}^{n-}$ ($PW_{11}M$; $M = Co^{II}, Mn^{II}, Cu^{II}, Pd^{II}, Ti^{IV}, Ru^{IV},$ and V^V), has been studied in acetonitrile using *trans*-stilbene as a model substrate. The selectivity of epoxidation attains 95% at complete alkene conversion. The epoxide formation shows an induction period and is inhibited by 2,6-di-*tert*-butyl-4-methylphenol, indicating chain radical mechanism of the reaction. The formation of perisobutyric acid (PIBac) was detected during oxidation process after the completion of the induction period. Decomposition of PIBac as well as its interaction with *trans*-stilbene in the presence of $PW_{11}M$ has been studied. $PW_{11}M$ with $M = Co^{II}, Pd^{II},$ and Ru^{IV} greatly enhance PIBac homolytic decomposition and thus increase the rate of the degenerate branching in the chain radical process of alkene–aldehyde co-oxidation. HPAs with the other metals are much less active in PIBac decomposition and most likely catalyze the co-oxidation process by generating chain-initiating acyl radicals from IBA followed by the addition of O_2 with the formation of acylperoxy radicals responsible for epoxidation. The influence of $PW_{11}M$ on the different elementary steps of the chain radical process depends on the M nature and HPA concentration. In most cases HPAs behave as catalysts at their low concentrations and as inhibitors at high concentrations.

Keywords: Transition-metal-substituted heteropolytungstates; Alkene epoxidation; Molecular oxygen; Isobutyraldehyde; Chain radical mechanism

1. Introduction

d-Electron-transition-metal-substituted heteropolyanions (HPAs), so-called inorganic met-

alloporphyrines, attract much attention as oxidation catalysts due to the exclusively inorganic nature of their coordination sphere, which makes them stable towards oxidative degradation [1–17]. These complexes were found to catalyze alkane and alkene oxidations by various oxygen donors, such as PhIO [4–6], H_2O_2 [2,7–10], *t*-BuOOH [9,11], $NaIO_4$ [12], $NaClO$ [2] and O_2 in the presence of different reductants [13–17].

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Last years very efficient catalytic systems for alkene epoxidation based on dioxygen, branched aliphatic aldehydes and various transition metal complexes, including HPAs, have been described [14–23]. Keggin-type substituted HPAs, $PW_{11}MO_{39}^{n-}$ ($PW_{11}M$) with $M = Co(II), Mn(II),$ and $Fe(III)$ [14,15], $PMo_6V_6O_{40}^{9-}$ [16] and $PW_9O_{37}Fe_2Ni(OAc)_3^{10-}$ [17] were found to mediate this reaction. Recently we have reported that $PW_{11}M$ with $M = Ti(IV), V(V), Cu(II)$ and $Ru(IV)$ also exhibit a pronounced catalytic activity in alkene epoxidation by O_2 in the presence of isobutyraldehyde (IBA) [24]. The selectivity of epoxidation by O_2 /aldehyde/HPA system appeared to be much higher as compared to such oxidants as H_2O_2 , t -BuOOH and PhIO in the presence of HPAs [14,15,24]. Alkene–aldehyde co-oxidation, both catalyzed and uncatalyzed, has been extensively studied since the 1960s and has been established to proceed via chain radical mechanism, acylperoxy radicals being the main active epoxidizing species [25–36]. Nevertheless, impressively high selectivity observed for alkene epoxidation by O_2 in the presence of branched aliphatic aldehydes seemed to be unusual for chain radical processes. That is why heterolytic routes involving the formation of high valent metal–oxo species responsible for epoxidation were proposed by different authors [14,20–22]. Peroxy acid was suggested to be active epoxidizing reagent or precursor of metal–oxo species [14–16,20–22]. However, the fact of the inhibition of the reaction by 1,4-hydroquinone found in [16] indicated the intervention of a radical pathway. No studies were reported on alkene oxidation with peroxy acids in the presence of HPAs. So far, the mechanism of catalysis and the function of catalyst in O_2 /aldehyde/HPA systems remained far from being clear.

We extended our investigation of the epoxidation mechanism in O_2 /aldehyde/ $PW_{11}M$ systems and provide here some kinetic details which confirm our previous conclusion concerning the chain radical mechanism of this oxidation process and the radical nature of the active

epoxidizing species [24]. We have studied also both decomposition of PIBAc and its interaction with alkenes in the presence of $PW_{11}M$ ($M = Co^{II}, Cu^{II}, Mn^{II}, Pd^{II}, Ti^{IV}, Ru^{IV},$ and V^V). The possible functions of various $PW_{11}M$ in different elementary steps of the chain radical process of alkene–aldehyde co-oxidation are discussed.

2. Experimental

2.1. Materials

Acetonitrile, HPLC grade (Fluka), was used as received. Cyclohexene (Fluka) and *trans*-octene-2 (Aldrich) were passed through neutral alumina before use. *cis*-stilbene was synthesized according to [37]. Cyclohexene epoxide was purchased from Fluka, the other reference epoxides were prepared by the reaction of the corresponding alkenes with *m*-chloroperoxybenzoic acid. Isobutyraldehyde (IBA) and 2-ethylbutyraldehyde (EBA) were distilled twice under Ar and kept protected from light and air at 4°C. Its purity was controlled by GLC and 1H NMR methods. Perisobutyric acid (PIBAc) was prepared by the interaction of 90% H_2O_2 with isobutyric acid (IBAc) in the presence of 1% H_2SO_4 (conc.) according to standard procedure [38] followed by extraction with CCl_4 . The obtained solutions contained $0.7 \div 1.1$ M PIBAc and $0.8 \div 0.9$ M IBAc. The concentration of PIBAc was determined iodometrically and the molar ratio between PIBAc and IBAc was estimated from 1H NMR spectrum of the methine protons (septets with 2.69 and 2.57 for PIBAc and IBAc, respectively). 2,6-di-*tert*-butyl-4-methylphenol (ionol) was recrystallized from hexane; other reagents were of chemical or analytical grade and used without additional purification.

2.2. Heteropolytungstate catalysts

Tetrabutylammonium (TBA) salts of substituted heteropolytungstates were obtained by the

stoichiometric reaction of Na-PW₁₁O₃₉ with appropriate transition metal ion (Co(II), Fe(III), Pd(II), Ni(II) were introduced as their nitrate salts, Cu(II) and Mn(II) – as acetates; V(V) and Ru(IV) were used in the form of NaVO₃ and K₂RuCl₅OH, respectively) in aqueous solution followed by precipitation with TBABr as described in Ref. [39] and references cited therein. TBA-PW₁₁M with M = Ti(IV), Ce(IV) and Zr(IV) were synthesized from their heteropolyacids [40]. All the TBA-HPAs were dried in vacuum at 100°C for 1 h. The formation of the Keggin structure and the purity of the TBA-HPAs synthesized were confirmed by IR (solid in KBr) and ³¹P NMR spectroscopy (MeCN solutions) [39,40].

2.3. Typical oxidation procedures and product analysis

Alkene oxidation was carried out in a thermostated 20 ml Pyrex-glass reactor equipped with a stirring bar, gas supply and a reflux condenser. Molecular oxygen was passed through the reactor (2 ml/min) under atmospheric pressure. Typically, aldehyde was added to a MeCN solution (3 ml) of a catalyst ($5 \cdot 10^{-4} \div 1 \cdot 10^{-2}$ M) and an alkene (0.1 M), the reaction mixture was vigorously stirred, and GLC analysis as well as iodometric analysis was performed. The oxidation products were identified from their ¹H NMR spectra and GC-MS spectra. Yields of epoxides as well as alkene conversion were determined using GLC analysis ('Tsvet-500', FID, Ar, 2 m × 3 mm 15% Carbowax 20 M on Chromaton N-AW-HMDS, biphenyl as internal standard). Decomposition of PIBAc was carried out under Ar at 24°C as follows: 0.28 mmol of PIBAc was added to $6 \cdot 10^{-3}$ mmol of PW₁₁M dissolved in 6 ml MeCN. Aliquots were taken and analyzed by iodometric titration. The interaction of PIBAc with *trans*-stilbene was performed under Ar by the addition of 0.15 mmol of PIBAc to MeCN solution (3 ml) containing 0.15 mmol of alkene

and $3 \cdot 10^{-3}$ mmol of PW₁₁M. The reaction was monitored by GLC and iodometric analysis.

2.4. Physical measurements

GC-MS spectra were obtained using an LKB-2091 spectrometer. ¹H and ³¹P NMR spectra were recorded on an MSL-400 Bruker spectrometer. Chemical shifts, δ , were determined with respect to internal tetramethylsilane and external 85% H₃PO₄, respectively. IR and UV-VIS spectra were recorded using Specord 75 IR and Specord M-400.

3. Results and discussion

We have shown previously that co-oxidation of *trans*-stilbene with IBA efficiently proceeds under mild reaction conditions in the presence of catalytic additives of PW₁₁M with M = Co^{II}, Cu^{II}, Ti^{IV}, Ru^{IV}, and V^V [24]. *Trans*-stilbene epoxide and isobutyric acid were the main oxidation products together with small amounts of benzaldehyde. We extended our study of the catalytic properties of various PW₁₁M heteropolyanions and found that Pd(II)-substituted HPA is also very active and selective catalyst for this reaction (Table 1). At the same time PW₁₁M anions with M = Ni^{II}, Fe^{III}, Zr^{IV}, and Ce^{IV} show the results similar to that obtained in the experiment without any catalyst. The selectivity of epoxidation is high for alkenes of different structures, including those containing allylic hydrogen atoms and prone to allylic oxidation. Some data obtained with PW₁₁Pd and PW₁₁Ti catalysts are presented in the Table 1. The catalytic activity of various compounds of Ti(IV) and Pd(II) in alkene-IBA co-oxidation was first demonstrated in [22]. Invariability of IR and UV-VIS spectra of the HPAs after the reaction confirms the stability of PW₁₁M during the oxidation process. EBA can be successfully used instead of IBA. The increase of the aldehyde concentration speeds up the reaction but

decreases to some extent the selectivity of epoxide formation. In accordance with our previous results [24], the epoxidation of *cis*-alkenes proceeds in a non-stereospecific manner. This fact as well as the order of $PW_{11}M$ activity and the observed complete inhibition of the reaction by equimolar additives of ionol have led us to the conclusion that alkene oxidation by O_2 in the presence of IBA and $PW_{11}M$ has chain radical nature, acylperoxy radicals being the active epoxidizing species [24]. Below we provide new data which confirm the above conclusion and elucidate the role of $PW_{11}M$ in alkene–aldehyde co-oxidation.

Kinetic curves for *trans*-stilbene epoxide accumulation are shown in Fig. 1 and demonstrate the autocatalytic character of the reaction. When co-oxidation is carried out without addition of a catalyst, epoxidation selectively occurs but an induction period is long, and the rate of epoxidation is quite slow. It should be noted that the reaction is extremely sensitive to impurities of catalysts and inhibitors, which is typical for chain radical processes. So to obtain the reproducible value of the induction period in the blank experiment, the reaction vessel should be cleaned very thoroughly. Although the non-catalytic reaction proceeds quite slowly, it produces epoxide with high yield. Thus it is necessary to

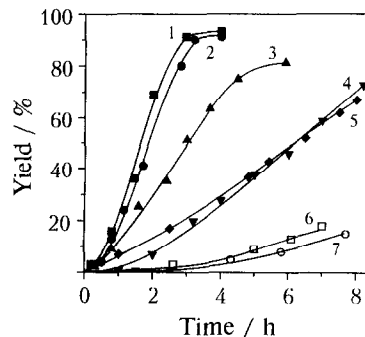


Fig. 1. Kinetic curves of *trans*-stilbene epoxide accumulation for oxidation of *trans*-stilbene (0.1 M) by O_2 (1 atm) in the presence of IBA (0.37 M) and $PW_{11}M$ ($1 \cdot 10^{-3}$ M) in MeCN at 24°C: 1 – $PW_{11}Pd$, 2 – $PW_{11}Co$, 3 – $PW_{11}Ru$, 4 – $PW_{11}Ti$, 5 – $PW_{11}V$, 6 – $PW_{11}Mn$, 7 – without catalyst.

compare the results of catalytic reactions with that of non-catalytic reaction to be sure that a catalytic effect really takes place. When the reaction is performed in the presence of $1 \cdot 10^{-3}$ M $PW_{11}M$ with $M = Co^{II}, Cu^{II}, Pd^{II}, Ti^{IV}, Ru^{IV}$, and V^V , the induction period significantly decreases (especially for HPAs with Co, Pd and Ru) and the reaction rate enhances (Fig. 1). As soon as the induction period is over, the reaction proceeds with practically constant rate. This phenomenon named ‘limiting rate’ is described for metal-catalyzed hydrocarbon autoxidation and is attributed to the attainment of a steady-

Table 1

Alkene epoxidation by O_2 in the presence of aldehyde catalyzed by $PW_{11}Pd$ and $PW_{11}Ti$ heteropolyanions^a

Catalyst	Alkene	Aldehyde	Time (h)	Alkene conversion (%)	Yield ^b of epoxide (%)
$PW_{11}Pd^{II}$	<i>trans</i> -stilbene	IBA	3.0	100	85 ^d
	<i>cis</i> -stilbene	IBA	4.0	92	79 ^d
$PW_{11}Ti^{IV}$	<i>trans</i> -stilbene	IBA	3.0	99	68 ^d
		IBA ^c	6.5	100	93 ^d
	<i>cis</i> -stilbene	EBA	3.5	98	71 ^d
		IBA	4.0	95	85 ^d
	<i>trans</i> -octene-2	EBA	3.0	95	77 ^e
	cyclohexene	EBA	4.0	98	86 ^f

^a Reaction conditions: stilbene 0.30 mmol, IBA 2.28 mmol, catalyst $6 \cdot 10^{-3}$ mmol, MeCN 3 ml, P_{O_2} 1 atm, 24°C.

^b GLC yield based on alkene consumed.

^c 1.14 mmol.

^d Exclusively *trans*-epoxide is formed, benzaldehyde being the main side product.

^e Yield of *trans*- + *cis*-epoxide (*trans/cis* ratio = 18).

^f 2-cyclohexenone is the main side product.

state concentration of intermediate hydroperoxides responsible for degenerate chain branching [25,26] and references cited therein). It is well known that peroxy acids are formed during both aldehyde autoxidation and its co-oxidation with alkenes in chain propagation acts [25–36,38,41–44]. Perisobutyric acid was detected by ^1H NMR spectroscopy during IBA oxidation by O_2 in the presence of PV_6Mo_6 [16]. We also observed the appearance of PIBAc (septet at δ 2.69 in CD_3CN) during stilbene–IBA co-oxidation after the completion of the induction period. The concentration of PIBAc indeed remains constant according to ^1H NMR and analytical measurements. Its value estimated by iodometric titration is equal to 0.02 and 0.03 M for PW_{11}Ti and PW_{11}Co , respectively. Although acylperoxy radicals are usually the main epoxidizing species in alkene–aldehyde co-oxidation processes, peroxy acids can as well produce epoxides via molecular mechanism [28,30,31,36]. The ratio of radical to non-radical epoxidation was found to increase with increasing reactivity of the olefin and with increasing olefin/aldehyde ratio [31,32]. The addition of cobalt acetate or the use of MeCN as a solvent enhances the contribution of radical epoxidation and thus results in a decrease of the stereospecificity of the reaction [36]. The exclusive formation of *trans*-stilbene epoxide from

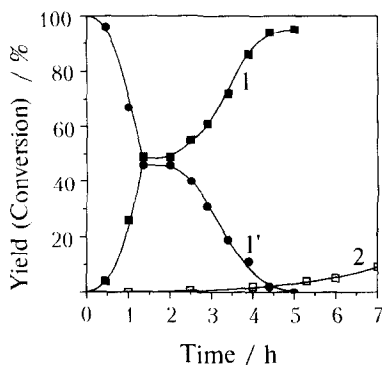


Fig. 2. Kinetic curves of *trans*-stilbene epoxide accumulation (1, 2) and *trans*-stilbene consumption (1', 2') for oxidation of *trans*-stilbene (0.1 M) by O_2 (1 atm) in the presence of IBA (0.37 M), PW_{11}Co ($1 \cdot 10^{-3}$ M) and ionol ($1 \cdot 10^{-3}$ M): 1, 1' – ionol is added after 1.35 h; 2 – ionol is added before the addition of IBA.

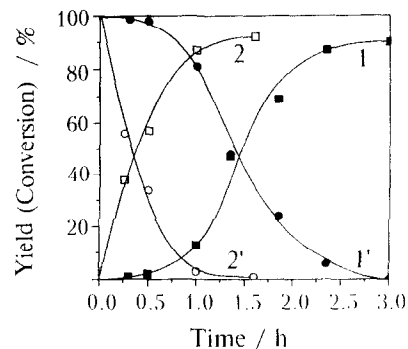


Fig. 3. Kinetic curves of *trans*-stilbene epoxide accumulation (1, 2) and *trans*-stilbene consumption (1', 2') for oxidation of *trans*-stilbene (0.1 M) by O_2 (1 atm) in the presence of IBA (0.37 M) and PW_{11}Co ($1 \cdot 10^{-3}$ M) in MeCN (3 ml): 1, 1' – with 0.05 ml CCl_4 added; 2, 2' – with addition of 0.035 mmol PIBAc in 0.05 ml CCl_4 .

cis-stilbene, which we observed for both catalyzed and uncatalyzed reactions, indicates that the role of Prilezhaev reaction in the epoxide formation is negligible in MeCN medium. To confirm this we introduced small additives of ionol, well known inhibitor of chain radical oxidation processes, into the reaction mixture at the moment when the reaction rate attained its maximum value and a steady-state concentration of PIBAc was reached. Both stilbene consumption and epoxide accumulation stopped immediately and restarted only after the complete consumption of the inhibitor (Fig. 2). When ionol was added at the beginning of the reaction, the induction period increased considerably.

In order to elucidate the role of PIBAc in the studied oxidation process, we have carried out a special experiment, in which a small additive of PIBAc was introduced into the initial reaction mixture containing PW_{11}Co catalyst. This resulted in complete disappearance of the induction period (Fig. 3). Such a change in kinetics is typical for chain radical reactions with degenerate branching when a product responsible for chain branching is added at the initial moment of the reaction [25]. Therefore we may propose that PW_{11}Co -catalyzed stilbene–IBA co-oxidation belongs to the group of chain radical pro-

Table 2
Perisobutyric acid (PIBAc) decomposition and the reaction of PIBAc with *trans*-stilbene in the presence of $PW_{11}M^a$

Catalyst	PIBAc decomposition	Oxidation of <i>trans</i> -stilbene by PIBAc	
	PIBAc conversion ^b (%)	alkene conversion ^c (%)	PIBAc conversion ^b (%)
$PW_{11}Co^{II}$	68	65	70
$PW_{11}Mn^{II}$	10	23	24
$PW_{11}Cu^{II}$	0	22	22
$PW_{11}Pd^{II}$	70	37	78
$PW_{11}Ti^{IV}$	11	24	25
$PW_{11}Ru^{IV}$	98	50	98
$PW_{11}V^V$	0	23	23
None	0	20	22

^a Reaction conditions, see Experimental section.

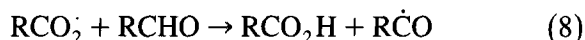
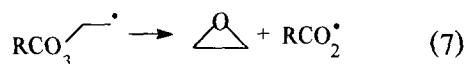
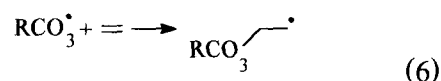
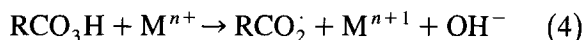
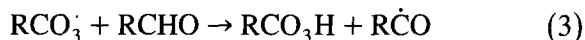
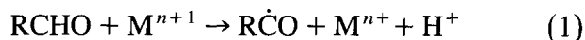
^b Determined by iodometric analysis after 2 h.

^c Determined by GLC after 2 h; *trans*-stilbene selectively converted to *trans*-epoxide.

cesses with degenerate branching. The role of degenerate branching was suggested to be not considerable in generating of active radicals during both aldehyde autoxidation and alkene–aldehyde co-oxidation [32,35,41]. To clarify this matter and the role of different HPA catalysts, we have studied decomposition of PIBAc as well as its interaction with *trans*-stilbene in the presence of various $PW_{11}M$ (Table 2). PIBAc appeared to decompose rapidly when $Co(II)$, $Pd(II)$ and $Ru(IV)$ -substituted HPAs are employed (68, 70 and 98%, respectively, in 2 h at 24°C). Note, that these HPAs are among the most active catalysts of stilbene–IBA co-oxidation. The rate of decomposition is much slower for $PW_{11}Mn^{II}$ and $PW_{11}Ti^{IV}$ whereas no decomposition of PIBAc occurs for 2 h with the other HPAs studied. $PW_{11}M$ anions, which were found to mediate effectively PIBAc decomposition, catalyze also *trans*-stilbene epoxidation with the peroxy acid (Table 2). The yields of epoxidation are high with respect to the alkene consumed and smaller with respect to PIBAc because of its competitive decomposition. The best results were obtained for $PW_{11}Co$. On the contrary, HPAs which show poor properties in PIBAc decomposition produce epoxidation yields simi-

lar to the yield of the experiment without catalyst.

The results obtained allow to propose the reaction mechanism comprising the following elementary steps of the chain radical process leading to epoxide and IBAc formation:



Acylperoxy radicals active in epoxidation are to be generated mainly via reaction (5) if the reaction is carried out in the presence of complexes which catalyze effectively a homolytic decomposition of peroxy acid. Indeed, we observed experimentally that in the case of $PW_{11}M$ with $M = Co^{II}$, Pd^{II} and Ru^{IV} the rate of epoxidation is independent on the oxygen pressure and the reaction successfully proceeds under air. When HPAs inactive in peroxy acid decomposition are used, the role of the reaction (5) in generating of active radicals should be negligible and acylperoxy radicals should appear mainly via the consecutive reactions (1) and (2). That is why a significant increase of the induction period and a decrease of the reaction rate are observed when air is used instead of O_2 . The catalytic action of HPAs inactive in PIBAc decomposition most probably is connected with

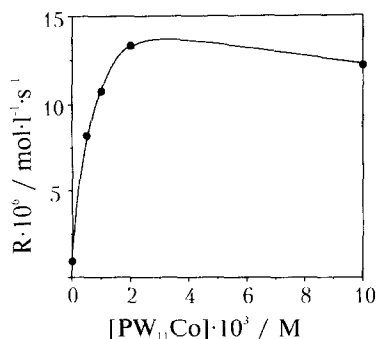
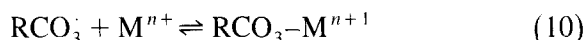


Fig. 4. Dependence of the rate of *trans*-stilbene epoxide formation on $PW_{11}Co$ concentration ($[stilbene] = 0.1$ M, $[IBA] = 0.37$ M, P_{O_2} 1 atm, $24^\circ C$).

their effect on the formation of chain-initiating acyl radicals from aldehyde via reaction (1). Invariability of UV–VIS spectra of $PW_{11}M$ during the alkene–aldehyde co-oxidation indicates that the initial oxidation state of M is regenerated in the course of reaction. Therefore M most probably acts as a catalyst rather than a classic initiator of chain radical process.

Another interesting feature of the alkene epoxidation in $O_2/IBA/HPA$ system is the phenomenon of catalyst-inhibitor inversion observed with increasing concentration of HPA. Fig. 4 demonstrates the dependence of the epoxidation rate estimated from the fast-rate portions of kinetic curves on the $PW_{11}Co$ concentration. The reaction rate increases up to about $2 \cdot 10^{-3}$ M concentration of the catalyst and then slowly decreases. Similar dependencies of oxidation rate on Co-catalyst concentration were observed in [34,43]. The dependence character is much more abrupt for $PW_{11}Ti$ and $PW_{11}V$. Thus at $1 \cdot 10^{-2}$ M concentration of $PW_{11}Ti$ the reaction practically stops, the induction period becoming infinitely long. Similar behavior is observed for $PW_{11}V$. The catalyst-inhibitor inversion, as well as ‘critical’ phenomena, are known to be the attributes of chain radical oxidation processes and are explained by the participation of a catalyst in chain termination [25,26,32,34,45,46]. For example, it was confirmed by 1H and ^{59}Co NMR that the formation of cobalt alkylperoxy complexes inhibits rather than promotes alkane

oxidation due to the capture of active RO_2 radicals [47]. Thus one more function of $PW_{11}M$ in alkene–aldehyde co-oxidation has been revealed, and reaction (10) should be added to the reactions (1)–(9):



As the dependence of epoxidation rate on $PW_{11}M$ concentration is complicated and varies with the nature of M , the orders of $PW_{11}M$ catalytic activity can differ for different catalyst concentrations. For example, at $2 \cdot 10^{-3}$ M concentration the catalytic activities of $PW_{11}Co$ and $PW_{11}Ti$ are of the same order of magnitude, however, at $1 \cdot 10^{-2}$ M the former serves still as a catalyst while the latter acts as an inhibitor. This is one of the possible reasons why different authors observed different orders of $PW_{11}M$ activity in alkene–IBA co-oxidation [14,24]. We believe that poor activity of $PW_{11}Mn^{II}$ which we observed is due to high ability of manganese to form stable acylperoxy complexes. The inhibition function of $Mn(II)$ salts in chain oxidation processes was mentioned in the literature [46].

4. Conclusion

The results obtained in this investigation prove that alkene epoxidation by O_2 in the presence of aliphatic branched aldehydes and transition-metal-substituted HPAs proceeds via chain radical mechanism, acylperoxy radicals being the active epoxidizing species. The role of heteropolyanions $PW_{11}M$ in this reaction is rather complicated. At least three functions of $PW_{11}M$ are established:

- (1) chain initiation via the reaction with aldehyde;
- (2) catalysis of the chain branching via homolytic decomposition of peroxy acid formed during aldehyde autoxidation;
- (3) chain termination due to the formation of stable complexes of active radicals with HPAs.

The relative weight of these processes depends on the nature of M and HPA concentration and determines the efficiency of a HPA-based catalytic system.

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