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Studies on styrene oxidation reaction catalyzed by ruthenium substituted polyoxotungstates: kinetics and phase transfer effect

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Abstract

A series of ruthenium substituted polyoxotungstates were used to catalyze the cleavage oxidation of styrene. Under all experimental conditions investigated, reaction products were benzaldehyde and benzoic acid. Kinetic studies showed that these reactions were consecutive reactions consisting of first oxidizing styrene into benzaldehyde and then oxidizing the benzaldehyde into benzoic acid. In this work, the first oxidation step was carefully studied. It has been shown to be first order with respect to substrate and catalysts but zero order with respect to NaIO_4 under the conditions studied. The activation energies of the first oxidation catalyzed by different polyanions are closely similar to one another, but the value of pre-exponential factors, differed by orders of magnitudes. Such differences could possibly be accounted for by the phase transfer effect as experiments showed that lowering the concentration of phase transfer reagent for low distribution ratio ($C_{\text{aq}}/C_{\text{org}}$) catalysts would enhance the pre-exponential factor value and selectivity of the reaction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of novel and effective catalysts for the selective oxidation of alkenes is currently of considerable interest. In the early 1980s, studies on metalloporphyrins showed that these kinds of compounds manifest high initial activity and selectivity. However, the catalytic activity quickly deteriorates due to the instability of the organic ligands under

oxidizing environments. This drawback has substantially hindered their practical application in chemical engineering processes. One approach to solve this problem has been to synthesize fairly expensive haloporphyrins, that are resistant to oxidation [1,2], another approach is to use substituted polyoxometalates that are regarded as porphyrin analogues in inorganic chemistry. In such a scheme, vacant polyoxometalates acting as porphyrins coordinate with a variety of transition metal cations to form a series of substituted compounds [3–5]. These compounds, acting as the porphyrins, may combine with oxygen or form high valent coordination compounds so as to

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effect the stoichiometric transfer of oxygen in the same ways as the metalloporphyrins but they are fairly stable towards oxidation [6,7].

Research works on substituted polyoxometalates catalyzed reaction revealed that the reaction selectivity mainly relied on two factors: one is the property of the inserted transition metal cations; the other is the characteristic of the oxidants. While the inserted metal cations present in lower valency states, the reactions using O_2 or H_2O_2 as oxidant always follow the radical chain mechanism which are induced by $M-O_2$ intermediates [8]. Otherwise high valent metal cations usually lead to oxygen transfer reactions which are catalyzed by $M=O$ intermediates. In the cases involving strong oxidants such as $PhIO$, $NaIO_4$ and $BuOOH$, the inserted metal cations were often oxidized to high valency and the reactions proceed via oxygen transfer mechanism; in some cases, the alkene cleavage compounds were also observed.

Recently, catalysis studies on second or third period row metal cation substituted polyoxometalates are getting more and more popular due to the exciting discovery that $Ru(II)$ -porphyrin displays good catalytic activity and selectivity on alkene epoxidation reaction [10]. But most of the published works dealt with the empirical experimental data of such reactions only [11–13]. We have noted that Neumann reported one of the very few mechanisms in this field, concerning the styrene cleavage reaction catalyzed by $Ru(H_2O)SiW_{11}O_{39}$ [8,9]. In his mechanism, Neumann described that styrene reacted with oxidized catalysts to form a metalcyclohexane which through molecular rearrangement in the rate determining step yielded the final cleavage products, benzaldehyde. We have carefully studied the kinetics of styrene cleavage reaction catalyzed by a series of ruthenium-substituted compounds and particularly the influence of the phase transfer reagent on this reaction.

2. Experimental

2.1. Material

All chemical reagents were analytical grade and used without further purification. The $\alpha-K_5SiW_{11}$ -

$Ru(H_2O)O_{39}$, $\alpha-K_4PW_{11}Ru(H_2O)O_{39}$, $K_7P_2W_{17}Ru(H_2O)O_{61}$ and $K_8P_2W_{17}Pt(H_2O)O_{61}$ were prepared by published methods and identified by IR and ^{183}W NMR spectra [13,14]. The related tetra-*n*-butyl ammonium salts were prepared by adding a solution of *n*- NBu_4Cl (1.846 mol/l) to the aqueous solution of corresponding polyoxotungstates.

2.2. Measurements

IR spectra were recorded on a Nicolet 5DX FT infrared spectrophotometer using KBr pellets. UV–VIS spectra were measured on a Shimadzu UV-240 spectrophotometer using 1.0 cm quartz cells. ^{183}W NMR spectra were run on a Bruker MSL-300 NMR spectrometer using saturated Na_2WO_4 in D_2O as external standard. The products of the catalysis reaction were detected by a HP-6890 GC-MS and each nonacid compound was qualified by a 103G GLC using TCD as the detector. The content of benzoic acid was obtained by photometric method [15].

2.3. Typical procedure for the oxidation reaction

The cleavage oxidation reaction was carried out as following: the ruthenium substituted polyoxotungstate (tetra-*n*-butyl ammonium salt, 0.008 mmol) and styrene (4 mmol) were dissolved in 20 ml of 1,2-dichloroethane and mixed with 20 ml aqueous solution of $NaIO_4$ (2 mol/l) at $60 \pm 0.5^\circ C$. The two-immiscible solutions were vigorously stirred, samples were taken at appropriate intervals and analyzed by GLC. Peaks were standardized by using available reference compounds. The catalysts were recovered by ether precipitation at the end of the reaction and reused for several times, and no activity decline was observed.

2.4. Typical procedure for benzaldehyde oxidation reaction

The ruthenium substituted catalysts (0.008 mol) and benzaldehyde (0.22 ml) was dissolved in 20 ml of 1,2-dichloroethane and mixed with 20 ml aqueous solution of $NaIO_4$ (2 mol/l) at $60 \pm 0.5^\circ C$. The experiment was then carried out in the same manner as given in the foregoing descriptions. The decrease of

Table 1
Highest selectivity in benzaldehyde under 100% conversion of styrene^a

Catalyst	Time to reach 100% conversion (min)	Conversion (%)	Selectivity(%)	
			Benzaldehyde	Benzoic acid
Q ₄ PW ₁₁ Ru	60	100	83.1	15.4
Q ₇ P ₂ W ₁₇ Ru	60	100	83.5	17.2
Q ₅ SiW ₁₁ Ru	45	100	96.4	4.4
Q ₈ P ₂ W ₁₇ Pt	–	20.4	13.8	6.6

^a The reactions were carried out at 60°C. Conversion of the reaction catalyzed by Q₈P₂W₁₇Pt did not attain 100% after 120 min. Selectivity results were reported at this time interval.

benzaldehyde was measured by GLC at appropriate intervals.

2.5. Determination of catalyst distribution at various *t*-butylammonium additions.

To a 15 ml aqueous solution of ruthenium substituted polyoxotungstate (1×10^{-3} mol/l) different volume of the aqueous solution of *n*-NBu₄Cl (1.846 mol/l) was added in order to adjust the ratio between *n*-NBu₄⁺ and polyanion. This aqueous solution was stirred with 15 ml 1,2-dichloroethane and heated at proper temperature in a sealed tube for 2 h. Two phases were separated. The content of the polyanion in different phase was measured by photo-

metric method using 245 nm as the detecting wavelength.

3. Results and discussion

3.1. Oxidation of styrene catalyzed by different ruthenium substituted polyoxometalates

All ruthenium-substituted polyoxometalates irrespective of their foregoing vacant polyoxotungstates, displayed essentially high catalytic activity and selectivity (Table 1) under the same reaction conditions. But while ruthenium was replaced by platinum, the catalytic activity dramatically declined. It is thus clearly indicated that the catalytic activity of

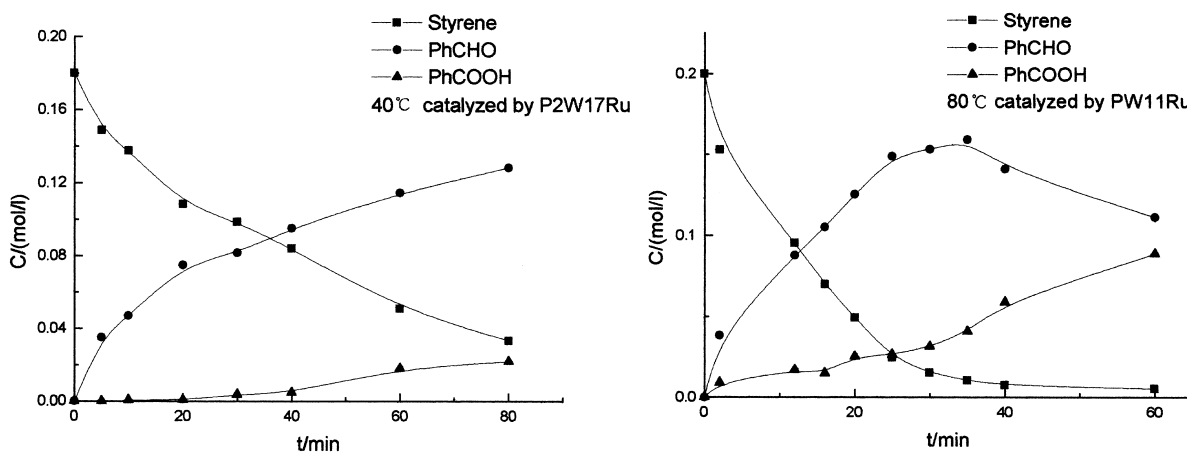


Fig. 1. The relationship between the concentration of the substrate, benzaldehyde, benzoic acid and reaction time.

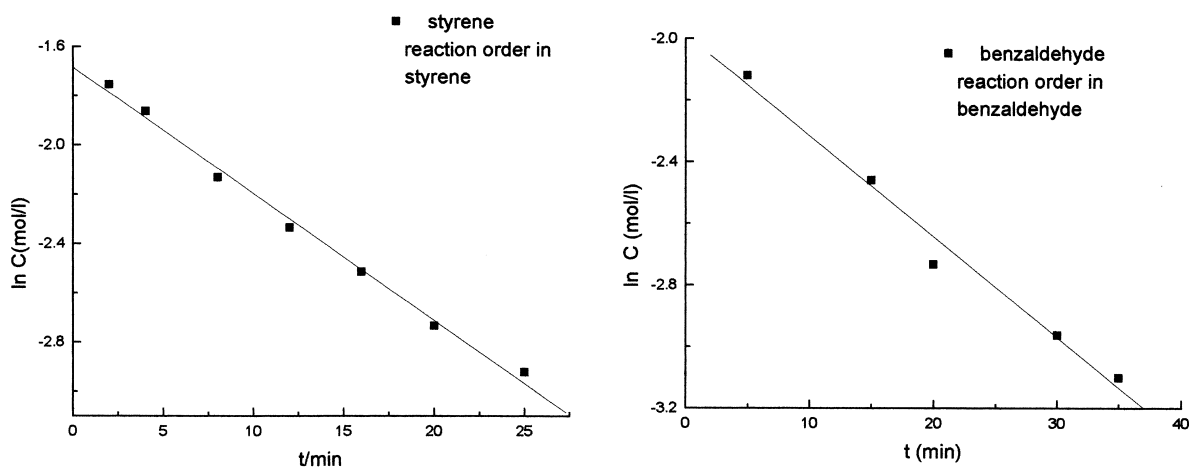


Fig. 2. The reaction profile for the oxidation of styrene and benzaldehyde.

such metal substituted polyoxometallates is mainly dictated by the nature of the metal atom.

In an attempt to investigate the course of reaction, reaction mixtures were sampled at certain time intervals and analyzed. Unlike Newman's work, in our experiments both benzaldehyde and benzoic acid were present. In order to approximately ascertain the nature of the reaction, a careful examination of the relationship between the concentration of the substrate, benzaldehyde, benzoic acid and reaction time was carried out. Two typical plots were shown in (Fig. 1). At low temperatures, the speed of benzoic acid formation increased along with the accumulation of benzaldehyde in the system and at high temperatures a maximum concentration of benzaldehyde was observed. Such results strongly suggest that it could possibly be a consecutive reaction, consisting of first oxidizing styrene into benzaldehyde and then further oxidizing benzaldehyde into benzoic acid and both oxidations are catalyzed by

the same ruthenium substituted polyoxometallates [16].

3.2. Kinetic study of the reactions catalyzed by ruthenium substituted polyoxometallates

Kinetic study of the catalytic reaction was then performed by using the decrease of the substrate to evaluate the kinetics of the first oxidation that we were interested in. Further oxidation of benzaldehyde into benzoic acid was studied by separated experiments according to the reaction conditions given in the experimental section. In order to keep the quasi-zero order in oxidants, great excess of NaIO_4 was used in both experiments. Fig. 2 indicates that both oxidations are first order reactions no matter which one of the three compounds was used as the catalyst. Data fitting is highly satisfactory as evidenced by their calculated r -values ranging from 0.99 to 0.999. This may serve to definitely clarify the first order

Table 2

The value of the experimental rate coefficient

Catalyst	$K_{40^\circ\text{C}} (\text{min}^{-1}) (M_{\text{cat}} (\text{mol}))$		$K_{60^\circ\text{C}} (\text{min}^{-1}) (M_{\text{cat}} (\text{mol}))$		$K_{80^\circ\text{C}} (\text{min}^{-1}) (M_{\text{cat}} (\text{mol}))$	
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2
$\text{Q}_4\text{PW}_{11}\text{Ru}$	0.0209 (1.54×10^{-5})	0.0017	0.0560 (1.75×10^{-5})	0.0045	0.105 (1.90×10^{-5})	0.0095
$\text{Q}_7\text{P}_2\text{W}_{17}\text{Ru}$	0.0198 (1.58×10^{-5})	0.0026	0.0512 (1.63×10^{-5})	0.0060	0.0608 (1.30×10^{-5})	0.0085
$\text{Q}_5\text{SiW}_{11}\text{Ru}$	0.0228 (7.19×10^{-6})	0.0018	0.0339 (4.6×10^{-6})	0.0033	0.0779 (6.12×10^{-6})	0.0081

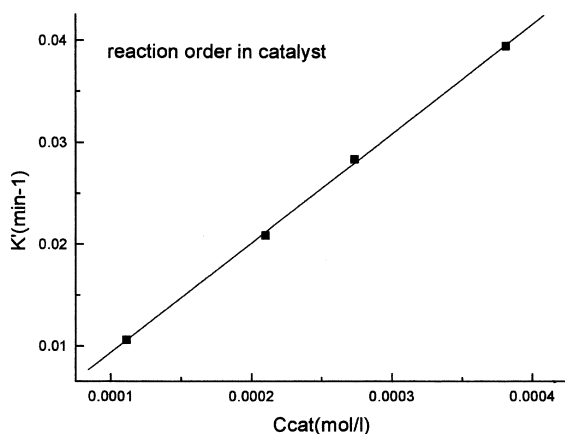


Fig. 3. The profile for the catalyst.

consecutive reaction mechanism and k_{exp} value of both oxidation steps could be obtained by experimental data simulation (c.f. Eqs. (1) and (2)). They are listed in Table 2.

$$[\text{styrene}] = C_{\text{styrene}} \times \exp(-k_{\text{exp1}} t) \quad (1)$$

$$[\text{benzaldehyde}] = \left[\frac{k_{\text{exp1}}}{k_{\text{exp2}} - k_{\text{exp1}}} \right] \times C_{\text{styrene}} \times \left[\exp(-k_{\text{exp1}} \times t) - \exp(-k_{\text{exp2}} \times t) \right] \quad (2)$$

Comparing the rate coefficient values of both steps, it could be observed that the first step was almost 10 times faster than the second step. This is how, the high selectivity of the catalysts in their preferential oxidation of the substrate was attained. In order to get the actual rate law of the first step, the reaction order in catalysts were studied (Fig. 3). The results also followed the first order in these catalysts

and the rate law of the first oxidation step was summarized as following: rate = $k[\text{catalyst}][\text{styrene}]$.

Table 3 gives the actual rate coefficient of the first catalyzed oxidation reaction at temperature ranging from 40 to 80°C. These data were processed according to Arrhenius equation to give the value of the activation energy and pre-exponential factor which were listed in Table 3. It can be found that the activation energy of the reactions catalyzed by the three compounds are not far apart from one another though the values of pre-exponential factor are dramatically different.

The similarity of the activation energy among the catalyzed reactions implies that all of the reactions followed the same mechanism which uses ruthenium as the active site. But the difference in pre-exponential factor value can be attributed to other factors that influence the efficient collision between the substrate and the oxidized catalysts in the organic phase. Because the reaction is a double-phase reaction, it will be shown later that this difference can well be explained in terms of the respective solubilities of the oxidized and reduced forms of the catalyst in the two phases.

3.3. Phase transfer effect

Fournier et al. stated that *t*-alkylammonium salts of polyanions usually form cation-anion aggregates in organic solvents even in dilute solutions. The formation of the lipophilic and nearly uncharged aggregates could well explain the ability of the ammonium salts of polyoxometalates to dissolve in weak polar solvents such as CCl_4 , CHCl_3 and CH_2Cl_2 [17]. In our experiments, three tetrabutylammonium salts of polyanions both in original and

Table 3

The actual rate coefficient, pre-exponential factor and activation energy value of ruthenium substituted polyoxometalates

Catalyst	$K_{40^\circ\text{C}}$ ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)	$K_{60^\circ\text{C}}$ ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)	$K_{80^\circ\text{C}}$ ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)	Ea (kJ mol^{-1})	In A ($\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$)
$\text{Q}_4\text{PW}_{11}\text{Ru}$	24.7	63.9	110	34.5	16.5
$\text{Q}_7\text{P}_2\text{W}_{17}\text{Ru}$	25.1	62.8	93.3	30.5	15.0
$\text{Q}_5\text{SiW}_{11}\text{Ru}$	50.0	134.8	245.1	36.7	18.1
$\text{Q}_{1.6}\text{K}_{2.4}\text{PW}_{11}\text{Ru}$	53.0	134.2	240.0	34.8	17.5

Table 4

The distribution ratio of the ruthenium substituted polyoxotungstate^a

Complex	K ₄ PRuW ₁₁ O ₃₉			K ₅ SiRuW ₁₁ O ₃₉		K ₇ P ₂ W ₁₇ RuO ₆₁	
N _Q /Z _p	0.40	1.01	2.00	0.49	0.98	1.96	1.00
C _{Q(aq)} /C _{Q(org)}	1.87 ^b	0.65	0.24	3.94	1.03	0.77	0.13
	0.85 ^c	0.37	0.17	1.52	0.75	0.36	0.13
	0.31 ^d	0.21	0.11	0.77	0.55	0.32	0.12

^a N_Q/Z_p is the ratio between the amount of *n*-NBu₄⁺ (in mol) and the charge of the substituted polyoxotungstates.^b Measured at 313 K.^c Measured at 333 K.^d Measured at 353 K.

Table 5

The relationship between anion charge/surface area ratio and their distribution ratio in organic and aquatic phase

Compound	Anion charge	Anion surface area (nm ²) ^a	Charge surface area ratio	Distribution ratio (313 K)
SiRuW ₁₁	-5	11.8	-0.42	1.03
PRuW ₁₁	-4	11.8	-0.34	0.65
P ₂ RuW ₁₇	-7	21.9	-0.31	0.13

^a The anion surface area is calculated by the method mentioned below: the Keggin and Dawson type anions are assumed to be cylinder and their surface area are calculated by the equation of $2\pi R^2 + 2\pi RH$ [18].

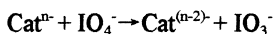
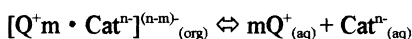
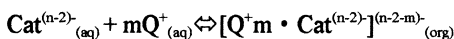
oxidized form were involved. Table 4 listed the distribution ratio (C_{aq}/C_{org}) of the three compounds in their reduced forms. It could be seen that the distribution ratio of the same compound varied with temperature and the content of the phase transfer reagent. Table 5 indicates that surface charge density of these compounds varies inversely as their respective distribution ratios.

Since *t*-butylammonium is a large cation compared with the anion itself, spacial configuration does not allow all the negative charges of the reduced anion with high surface charge to be fully

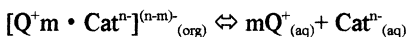
compensated by the positive lipophilic sphere formed by *t*-butylammonium cations. Their aggregates would always carried several negative charges. This would hinder their entrance into the organic phase.

In a real catalysis system, both original and oxidized polyanions were carried into the organic phase by the *t*-butylammonium cations, but more of the oxidized catalyst would be carried over as they have fewer charges than their original forms. Here we would attempt to propose a mechanism for the phase transfer effect that was not covered by Neumann. Since all the catalysts, in their original forms, have

Stage 1

*in aqueous solution*

Stage 2



Scheme 1. The double phase oxidation mechanism of the reaction.

Table 6
Benzaldehyde selectivity enhancement after tuning the N_Q/Z_p ratio of $Q_4PW_{11}Ru$

Catalyst	Time to reach 100% convergent (min)	Benzaldehyde selectivity (%)
$Q_4PW_{11}Ru$	60	83.1
$K_{2.4}Q_{1.6}PW_{11}Ru$	45	93.3

notable solubility in aqueous solutions (Table 4), it would be more reasonable to presume that the catalysts were oxidized in the aqueous phase while the substrate was oxidized by the high-valency catalyst which was transferred into the organic phase by phase transfer reagent. This was summarized in Scheme 1.

In this scheme, a suitably high solubility in aqueous phase of the original or the reduced form of the catalyst is preferred. Or else the low concentration of the original catalysts in aqueous phase would accordingly reduce the amount of oxidized catalyst formed per unit time. This would further reduced the steady state concentration of the oxidized catalysts in organic phase thereby lowering the rate of the effective collision between substrates and oxidized catalysts and finally, leading to the small value of pre-exponential factor as shown for $Q_7P_2W_{17}Ru$ and $Q_4PW_{11}Ru$. Since the solubility of the original catalyst in aqueous solution is the key-factor in fixing the pre-exponential value, adjusting the phase transfer concentration would be capable of accordingly adjusting the pre-exponential factor of both $PW_{11}Ru$ and $P_2W_{17}Ru$. Such a consideration has been definitely verified by tuning the N_Q/Z_p ratio of $PW_{11}Ru$ to 0.4, so that the distribution ratio of $Q_2K_2PW_{11}Ru$ could be made close to that of $Q_5SiW_{11}Ru$ (Table 4). The pre-exponential factor value of the reactions under such circumstances is therefore closer to that of the $Q_5SiW_{11}Ru$ (Table 3).

Since the activation energies of the reactions were no more than 40 kJ, the pre-exponential factor may substantially effect the value of rate coefficients especially at low temperatures. In most case, low

temperature may suppress other reactions requiring higher activation energies so that reaction selectivity is significantly improved. By tuning the concentration of the phase transfer reagent, it is possible to realize the selective synthesis of benzaldehyde at low temperatures. This has been verified by the catalytic behavior of $Q_{1.6}K_{2.4}PW_{11}Ru$ at 40°C (cf. Table 6).

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