

A Pronounced Catalytic Activity of $\text{PW}_{11}\text{CoO}_{39}^{5-}$ for Epoxidation of Alkenes
by Molecular Oxygen in the Presence of Aldehyde

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The epoxidation of cyclohexene, 1-decene, and styrene by molecular oxygen in the presence of aldehydes such as isobutyraldehyde and pivalaldehyde was efficiently catalyzed at 303 K by mono-cobalt-substituted Keggin-type heteropolytungstate.

The strong acid or oxidizing properties of heteropolyanions and sometimes their unique basicity induce a lot of studies on the heterogeneous and homogeneous catalysis.¹⁾ An additional attractive and important aspect of the heteropolyanions is the inherent stability toward the oxygen donors or molecular oxygen itself.^{2,3)} Therefore, for example, heteropoly compounds are useful catalysts for the liquid-phase oxidations of alcohols,⁴⁾ alkenes,⁵⁾ alkynes,⁶⁾ β -unsaturated acids,⁷⁾ *vic*-diols,⁸⁾ phenol,⁹⁾ and amines¹⁰⁾ with hydrogen peroxide, epoxidation of alkenes and the oxygenation of alkanes with iodosylbenzene or *t*-butyl hydroperoxide,^{2,11)} and allylic oxygenation of cyclohexene by molecular oxygen.¹²⁾ There appears no report on the epoxidation of alkenes with molecular oxygen on heteropoly compounds.

The epoxidation of alkenes has become important both in industrial process and organic synthesis because epoxide is one of the most useful synthetic intermediates. Many catalysts such as ruthenium, molybdenum, and titanium complexes have been reported to be active for the reaction with peracids or peroxides since the pioneering work of Hawkins.¹³⁾ Although the catalytic epoxidations with molecular oxygen under mild conditions are rewarding goals, only a little is known of the reaction.^{14,15)} In this communication we wish to report the first example of aerobically induced catalytic epoxidation of alkenes on a mono-cobalt-substituted heteropolytungstate species and the pronounced catalytic activity.

The tetra-*n*-butylammonium salts of the transition-metal-substituted heteropolytungstate complexes, $\{\text{PW}_{11}(\text{M}^{n+})\text{O}_{39}\}^{(7-n)-}$ ($\text{M} = \text{Co}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Mn}^{2+}$; denoted by $\text{PW}_{11}\text{-M}$) were prepared by the slight modification of the method reported in Ref. 16. The formation of Keggin structure and the composition were confirmed by IR and/or ^{31}P NMR and the elemental analysis, respectively. Bis[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato] nickel ($\text{Ni}(\text{dmp})_2$) and iron ($\text{Fe}(\text{dmp})_3$) were prepared according to the Ref. 15 and the formation was confirmed by the elemental analysis and IR spectra.

The reaction was performed as follows unless otherwise stated: The catalyst (0.25 μmol) was introduced in a sealable glass vial (40 cm^3) containing a magnetic stir bar and 3 cm^3 of the appropriate solvent. The 250 μmol of the substrate, cyclohexene, styrene, and 1-decene and aldehyde (1000 μmol) were added to the solution, and the vial was sealed. Then 1 atm O_2 was introduced to the system. The reaction vessel was placed at 303 K and vigorously stirred. The reaction vessel was removed from the bath every 10 - 30 min to refill the tube with 1 atm O_2 . The reaction solution was periodically sampled by syringe and analyzed by gas chromatography together with NMR.

The time course of cyclohexene oxidation by molecular oxygen on $PW_{11}\text{-Co}$ in the presence of isobutyraldehyde is shown in Figure 1. The major product was cyclohexene oxide and small amounts of 2-cyclohexen-1-ol and 2-cyclohexen-1-one. Isobutyraldehyde was oxidized to isobutyric acid. The amounts of cyclohexene oxide, 2-cyclohexen-1-one, and 2-cyclohexen-1-ol after 1 h were 82 μmol , 13 μmol , and 7 μmol , respectively, and the ratio showed little change with time. Further addition of isobutyraldehyde and cyclohexene gave identical catalytic activities and no structural change in $PW_{11}\text{-Co}$ was observed by IR and UV. The results prove that $PW_{11}\text{-Co}$ was stable under the conditions employed.

The catalytic oxygenation of cyclohexene in the presence of various catalysts in acetonitrile is shown in Table 1. Each reaction system was homogeneous. The main product was cyclohexene oxide and small amounts of 2-cyclohexen-1-ol and 2-cyclohexen-1-one were observed. Without any $PW_{11}\text{-M}$ catalysts the conversion was less than 4%. The conversion level on $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{-PW}_{12}\text{O}_{40}$ was almost the same as that of the blank experiment, suggesting that the transition metals introduced are active centers. $PW_{11}\text{-Co}$ was the most active for the reaction among the mono-transition-metal-substituted polyanions and the order of the activities were $PW_{11}\text{-Co} \gg \text{-Mn} \geq \text{-Fe} > \text{-Cu} \geq \text{-Ni}$.

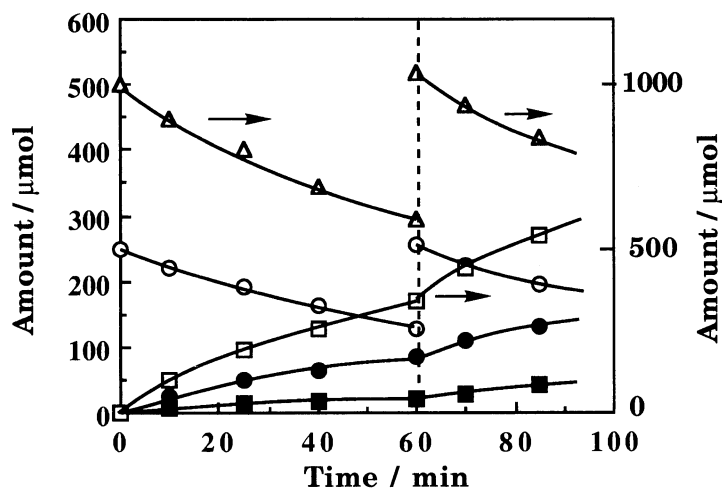


Fig. 1. Time course of cyclohexene oxidation by molecular oxygen on $PW_{11}\text{-Co}$ in the presence of isobutyraldehyde in acetonitrile at 303 K.

○, cyclohexene; ●, cyclohexene oxide; ■, 2-cyclohexen-1-one + 2-cyclohexen-1-ol; Δ, isobutyraldehyde; □, isobutyric acid. $PW_{11}\text{-Co}$, 0.25 μmol ; cyclohexene, 250 μmol ; isobutyraldehyde, 1000 μmol ; PO_2 , 1 atm; acetonitrile, 3 cm^3 . Dashed line indicates the addition of cyclohexene and isobutyraldehyde.

Table 1. Oxidation of Cyclohexene on $PW_{11}\text{-M}$

M in $PW_{11}\text{-M}$	Products/ μmol			
	Cyclohexene oxide	2-Cyclohexene-1-one	2-Cyclohexene-1-ol	Isobutyric acid
Co	82	13	7	355
Mn	28	7	3	119
Fe	25	5	3	104
Cu	11	5	<1	49
Ni	10	1	<1	42
Blank	9	2	2	37

$PW_{11}\text{-M}$, 0.25 μmol ; cyclohexene, 250 μmol ; isobutyraldehyde, 1000 μmol ; PO_2 , 1 atm; solvent (acetonitrile), 3 cm^3 ; reaction time, 1 h.

In addition, $\text{PW}_{11}\text{-Co}$ was the most active among Co-containing catalysts and the order of the catalytic activities in the system of cyclohexene (250 μmol) + O_2 (1 atm) + isobutyraldehyde (1000 μmol) + catalyst (10 μmol) was $\text{PW}_{11}\text{-Co} > \text{Co}_3\text{O}(\text{OAc})_6 > \text{Co}(\text{OAc})_2 > \text{CoCl}_2$ with the relative yields of cyclohexene oxide in acetonitrile after 1 h of 1.0 : 0.76 : 0.68 : 0.62, respectively. The fact suggests that the presence of $\text{PW}_{11}\text{O}_{39}^{7-}$ lacunary heteropolytungstate enhances the activity. The enhancement of the catalytic activity of Ir^+ upon the support on polyanion was also observed.¹²⁾ The above results show that $\text{PW}_{11}\text{-Co}$ was the most active for the epoxidation of cyclohexene among the mono-transition-metal-substituted polyanions and Co-containing catalysts.

Hill and Brown reported that $\text{PW}_{11}\text{-Co}$ and -Mn were active among various transition metal-based catalysts for the epoxidation of alkenes with iodosylbenzene in acetonitrile.²⁾ For the comparison, the epoxidations of cyclohexene (250 μmol) on $\text{PW}_{11}\text{-Co}$ (0.25 μmol) in acetonitrile were carried out in the systems of O_2 (1 atm)+isobutyraldehyde (1000 μmol), N_2 (1 atm)+iodosylbenzene (1000 μmol) and N_2 (1 atm)+hydrogen peroxide (1000 μmol). The ratio of the cyclohexene oxide yield after 1 h was 1.0:0.24:0, respectively, and the present system gave the highest yield. This fact also shows the effectiveness of the present system for the epoxidation.

Next, the effects of aldehydes and solvents on the activity of $\text{PW}_{11}\text{-Co}$ are investigated. The order of the effectiveness of the aldehydes for the epoxidation of cyclohexene on $\text{PW}_{11}\text{-Co}$ in acetonitrile was pivalaldehyde > isobutyraldehyde >> butyraldehyde $\approx$ acetaldehyde > valeraldehyde > benzaldehyde. The catalytic activity of $\text{PW}_{11}\text{-Co}$ was also solvent dependent decreasing as follows: Chloroform $\geq$ dichloromethane > 1,2-dichloroethane $\geq$ acetonitrile > *N,N*-dimethylformamide > dimethyl sulfoxide, with the relative yields of cyclohexene oxide after 1 h of 11:10:8:7:1:0, respectively.

The turnovers and selectivities of $\text{PW}_{11}\text{-Co}$ for the epoxidation of cyclohexene, 1-decene, and styrene were compared with those of $\text{Ni}(\text{dmp})_2$ and $\text{Fe}(\text{dmp})_3$, which have recently been reported by Mukaiyama et al. to be very active for the epoxidation.¹⁵⁾ As shown in Table 2, it is remarkable that the turnovers of $\text{PW}_{11}\text{-Co}$ for the epoxidation of cyclohexene, styrene, and 1-decene were greater than those of $\text{Ni}(\text{dmp})_2$ and $\text{Fe}(\text{dmp})_3$. In addition, the selectivities to the corresponding epoxides, cyclohexene oxide, 1,2-epoxy-decane, and styrene oxide, were comparable to or higher than those of $\text{Ni}(\text{dmp})_2$ and $\text{Fe}(\text{dmp})_3$: 1-Decene was selectively oxidized to 1,2-epoxy-decane on $\text{PW}_{11}\text{-Co}$ and the yield reached 61% after 69 h. In the oxidation of styrene, styrene oxide and benzaldehyde were obtained in 64% and 36% selectivity, respectively. Thus, it is clear that $\text{PW}_{11}\text{-Co}$ more efficiently catalyzed the epoxidation than $\text{Ni}(\text{dmp})_2$ and $\text{Fe}(\text{dmp})_3$.

The reaction mechanism is now under investigation; it might involve the peracids as intermediates because the formation of perisobutyric acid was confirmed in the present oxidation system by ^1H NMR.

Table 2. Epoxidation of Alkenes on $\text{PW}_{11}\text{-Co}$, $\text{Ni}(\text{dmp})_2$, and $\text{Fe}(\text{dmp})_3$ at 303 K

Alkene	Catalyst turnover ^{a)}		
	$\text{PW}_{11}\text{-Co}$	$\text{Ni}(\text{dmp})_2$	$\text{Fe}(\text{dmp})_3^{\text{b)}$
Cyclohexene	328 (80) ^{c)}	204 (65)	76 (86)
Styrene ^{d)}	48 (64)	8 (37)	4 (44)
1-Decene	116 (> 95)	72 (68)	

Catalyst, 0.25 μmol ; alkene, 250 μmol ; isobutyraldehyde, 1000 μmol ; PO_2 , 1 atm; acetonitrile, 3 cm^3 ; 1 h. a) Mol epoxide formed / mol catalyst used. b) The solvent was 1,2-dichloroethane and the other condition was the same as above. c) Numbers in parentheses are the selectivities to the epoxides (mol epoxide formed/mol substrate consumed). d) The amount of styrene oxide was estimated by the sum of itself and phenylacetaldehyde isomerized in the g.c. column.

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