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Palladium(II) Sulfate-Heteropoly Acid-catalyzed Oxidation of Cycloolefins in Liquid Phase

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Heteropoly acid (HPA) was used as an oxidant in the Wacker catalyst system. Among the catalyst systems examined, the $PdSO_4$–$H_3PMo_6W_6O_{40}$ catalyst system showed the highest activity with regard to the oxidation of cycloolefins, particularly cyclopentene and cyclohexene, to the corresponding cyclic ketones. The largest total turnover number with respect to Pd^{2+} was found to be 85 in water containing 20% *N*-methylformamide by volume. The initial rate of cyclohexene oxidation was expressed as

$$V_0 = k[\text{Cyclohexene}]^{1.0}[PdSO_4]^{1.0}[\text{HPA}]^0[O_2]^0.$$

The rate-determining step was suggested as being where cyclohexene was oxidized to cyclohexanone by Pd(II) salt. The apparent activation energy was 7.8 kcal mol^{-1} (1 cal=4.18 J). In the catalytic oxidation of cycloolefins (C_nH_{2n-2}: n=5, 6, 7, and 8), the yield of alicyclic ketone decreased as the carbon number n increased. Methyl-substituted cyclohexenes exhibited lower reactivities than cyclohexene.

The Wacker catalyst ($PdCl_2$–$CuCl_2$) is the well-established homogeneous catalyst for olefin oxidation. But there is still the need to improve the conventional Wacker catalyst, because the Cl^- anion in aqueous media causes reactor corrosion and the undesirable formation of chlorinated by-products, particularly from higher olefins. An improvement could be attained by replacing $CuCl_2$ with an oxidant which is easily reoxidized under the reaction conditions.

One candidate for the oxidant is 12-heteropoly acid, because the electrochemical reduction and oxidation of the 12-heteropolyanion proceed reversibly in acidic solutions. They are accompanied by transfer of 2,4,or 6 electrons and retention of the Keggin structure.[1] It has been reported that the redox potential of the 12-heteropoly acid which can play the role of the oxidant in the Wacker catalyst system must be in the range of 0.59—1.229 V[2] or 0.19—1.116 V[3] (*vs.* NHE); *i.e.*, the redox potential of the 12-heteropolyanion should be higher than that of the palladium redox couple Pd^{2+}/Pd^0 and lower than that of the oxygen redox couple O_2/H_2O. The highest redox potentials were measured to be 0.3 V[1] or 0.32 V[3,4] (*vs.* SCE) for $PMo_{12}O_{40}^{3-}$, and 0.50 V[3] (*vs.* SCE) for $PMo_6W_6O_{40}^{3-}$, and 0.28 V[5] (*vs.* SCE) for $PMoW_{11}O_{40}^{3-}$. These values suggest that one can substitute one of the above heteropolyanions for $CuCl_2$ as the oxidant in the Wacker catalyst system.

Recently, it was found that the 12-heteropoly acids can oxidize palladium atoms and that Pd(II) salt-heteropoly acid systems can be used as catalysts for the oxidation of ethylene[2] and 1-butene.[6] We have reported a successful attempt to obtain alicyclic ketones from cycloolefins using a $PdSO_4$–$H_3PMo_6W_6O_{40}$ catalyst system under mild conditions.[7] In this paper, details of the results are described.

Results and Discussion

Catalyst System. Figure 1 shows the initial rates of cyclohexene oxidation and amounts of cyclohexanone produced after 20 h from the start of the reaction as a function of Mo content in the $PdSO_4$–$H_3PMo_nW_{12-n}O_{40}$ catalyst series. The mixed-coordinated heteropoly acid, $H_3PMo_6W_6O_{40}$, was found to be the most active oxidant judging from the initial rate and the amount of cyclohexanone produced.

Figure 2 shows the changes of IR absorption spectra of the heteropoly acid during the oxidation. Each band is assigned according to the literature[8] as follows: 1070 cm^{-1} to P–O stretching (O_p band), 970 cm^{-1} to M=O (M: Mo and W) stretching (O_t band), and 790, 870 cm^{-1} to M–O–M vibration (O_b band). After the reaction proceeded for 20 h, the intensities of the O_p band and the O_b band decreased significantly, while the intensity of the O_t band was almost unchanged. Similar behavior in IR absorption was reported by other wokers[9—11] who concluded that these decreases in intnsity were caused by the reduction of the heteropoly compounds but the Keggin structure was still retained. The IR spectrum of the heteropoly acid used for the reaction is clearly different from those

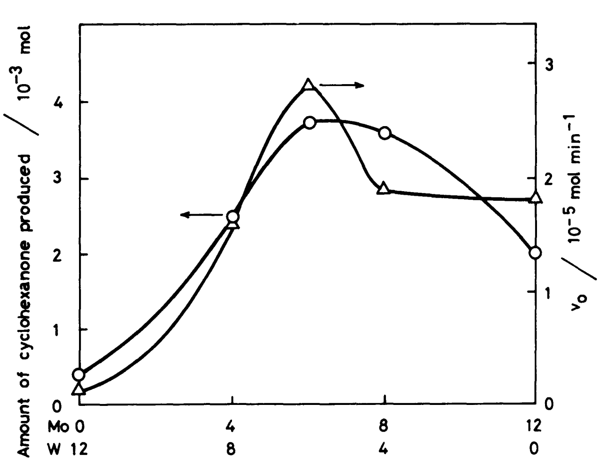

Fig. 1. Activity of $PdSO_4$–$H_3PMo_nW_{12-n}O_{40}$ catalyst system for cyclohexanone production. Each experiment was carried out at 303K for 20h under oxygen at 1 atm using cyclohexene (2.9×10^{-2} mol), $PdSO_4$ (8.3×10^{-3} mol), $H_3PMo_nW_{12-n}O_{40}$ (2.0×10^{-4} mol), and H_2O (10 ml).

of WO_3 and MoO_3. It is unlikely that the heteropoly acid decomposed to the WO_3 and MoO_3 units.

Various Pd(II) salts were tested in the oxidation of cyclohexene and 3-methylcyclohexene using $H_3PMo_6W_6O_{40}$ as the oxidant. Yields of cyclic ketones and total turnover numbers with respect to Pd^{2+} are listed in Table 1. The reaction time in Table 1 means the period of time after which no further oxidation occurred. From the standpoint of the total turnover number and the initial rate, $PdSO_4$ is the most active salt among the Pd(II) salts tested. The amount of cyclohexanone produced decreased in the following order depending upon the kind of counter anion of Pd^{2+};

$$SO_4^{2-} > NO_3^- > CH_3COO^- \geqslant Cl^-.$$

A similar order was observed in the oxidation of 1-butene.6) We then adopted $PdSO_4$–$H_3PMo_6W_6O_{40}$ as a pertinent catalyst system for the oxidation of various cycloolefins.

Rate Expression. The amount of cyclohexanone produced was equal to that of cyclohexene consumed and to half of the oxygen uptake. The material balance indicates that the overall reaction is written as

$$\text{Cyclohexene} + 1/2\ O_2 = \text{Cyclohexanone}.$$

From the temperature dependence of the initial rate, the apparent activation energy was found to be 7.8 kcal mol.$^{-1}$ The dependence of the initial rate of cyclohexanone production on the concentrations of cyclohexene and $PdSO_4$ is shown in Figs. 3 and 4, respectively. The slopes of the lines indicate that the oxidation of cyclohexene was first-order in both cyclohexene and $PdSO_4$. Under the present conditions, the initial rate was independent of the concentration of the heteropoly acid (see Fig. 5) and the partial pressure of oxygen. Accordingly, the following rate expression was obtained:

$$V_o = k[\text{Cyclohexene}]^{1.0}[PdSO_4]^{1.0}[HPA]^0[O_2]^0.$$

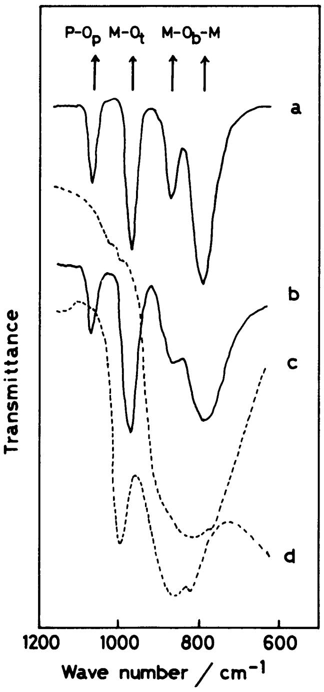

Fig. 2. IR spectra of heteropoly acid and related oxides:
a, Synthesized $H_3PMo_6W_6O_{40}$; b, $H_3PMo_6W_6O_{40}$ after 20 h of reaction; c, authentic WO_3; d, authentic MoO_3.

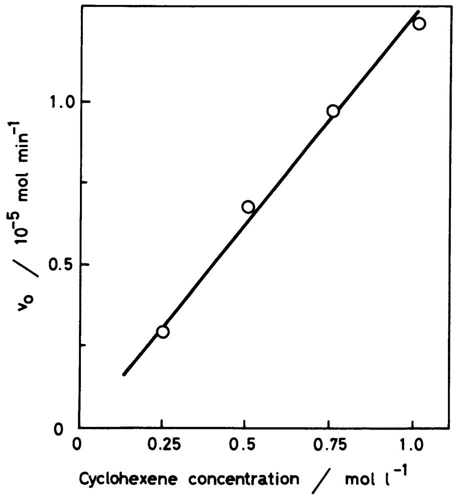

Fig. 3. Dependence of the initial rate of cyclohexanone production on cyclohexene concentration. Reaction conditions: $PdSO_4$ (5.0×10^{-5} mol) and $H_3PMo_6W_6O_{40}$ (2.0×10^{-4} mol) in H_2O (10 ml); and cyclohexene-cyclohexane solution (6 ml).

TABLE 1. ACTIVITY OF Pd(II) SALT-$H_3PMo_6W_6O_{40}$ CATALYST a)

Olefin	Pd(II) salt	Time/h	Yield/%	Total turnover number b)	$V_o/10^{-5}$ mol min^{-1}
3-methylcyclohexene c)	$PdSO_4$	16	20.5	4	0.1
	$PdCl_2$	22	1.7	0.3	—
	$Pd(NO_3)_2$	21	15.2	3	—
Cyclohexene d)	$PdSO_4$	10	70.3	21	0.37
	$PdCl_2$	24	4.1	1	0.02
	$Pd(NO_3)_2$	23	63.9	19	0.29
	$Pd(CH_3COO)_2$	24	12.1	4	0.05

a) All oxidations were carried out at 303 K under 1 atm oxygen using both cyclohexane (3 ml) and H_2O (10 ml) as solvents. b) With respect to Pd^{2+}. c) 3-Methylcyclohexene (6.6×10^{-3} mol), Pd(II) salt (8.3×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol). d) Cyclohexene (1.5×10^{-3} mol), Pd(II) salt (5×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol).

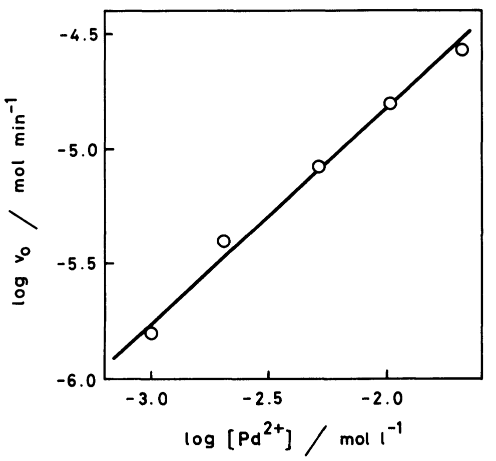

Fig. 4. Dependence of the initial rate of cyclohexanone production on $PdSO_4$ concentration. Reaction conditions: $PdSO_4$ in H_2O (10 ml), $H_3PMo_6W_6O_{40}$ (2.0×10^{-4} mol), cyclohexene (3.0×10^{-3} mol) in cyclohexane (6 ml).

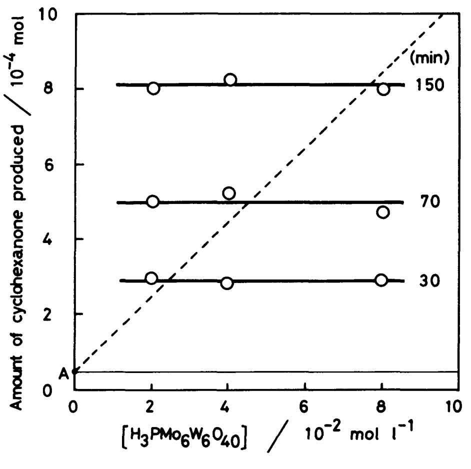

Fig. 5. Dependence of cyclohexanone production on heteropoly acid concentration. Reaction conditions: cyclohexene (3.0×10^{-3} mol) in cyclohexane (3 ml), heteropoly acid and $PdSO_4$ (5.0×10^{-5} mol) in H_2O (10 ml).

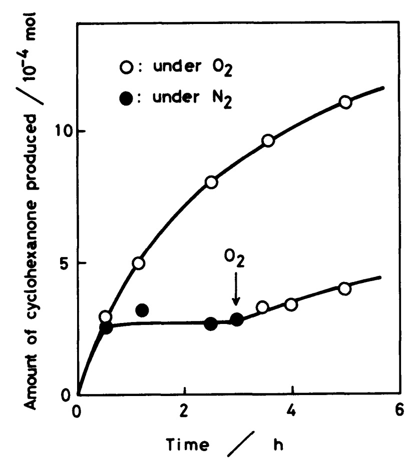

Fig. 6. Oxidation of cyclohexene under O_2 or N_2 at 1 atm. Reaction conditions cyclohexene (3.0×10^{-3} mol), $PdSO_4$ (5.0×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2.0×10^{-4} mol) in H_2O (10 ml); cyclohexane (3 ml).

Redox Cycle in the Catalyst System. In order to clarify the role of the heteropoly acid and oxygen in the oxidation of cyclohexene, the reaction was carried out under nitrogen at atmospheric pressure. The aqueous reaction mixture was degassed by bubbling nitrogen gas through it for 15 min. The reaction was then conducted for 3 h at room temperature. As shown in Fig. 6, 0.27×10^{-3} mol of cyclohexanone was produced. The amount is very close to the amount (0.25×10^{-3} mol) calculated under the assumption that all heteropoly acid molecules act as oxidants which accept two electrons each from a Pd^0 atom. When nitrogen gas was replaced by oxygen gas at this reaction stage, the oxidation started again. These facts indicate that a heteropoly acid molecule of the oxidized form oxidized a Pd^0 atom to a Pd^{2+} ion and was accompanied by transfer of two electrons. A heteropoly acid molecule of the reduced form was then easily reoxidized by molecular oxygen. From the measurements of the redox potential of $H_3PMo_6W_6O_{40}$, Izumi *et al.* concluded that two electrons were transferred in the oxidation and reduction processes.[3]

The oxidation of cyclohexene can be written as follows:

$$\text{Cyclohexene} + Pd^{2+} + H_2O \rightarrow \text{Cyclohexanone} + 2H^+ + Pd^0 \tag{1}$$

$$Pd^0 + HPA_{ox} \longrightarrow Pd^{2+} + HPA_{red} \tag{2}$$

$$HPA_{red} + 1/2O_2 + 2H^+ \longrightarrow HPA_{ox} + H_2O, \tag{3}$$

the subscripts ox and red stand for the oxidized and reduced forms, respectively. The oxidation proceeds catalytically through the redox cycles consisting of processes (1), (2), and (3).

One can confirm the passage through the redox cycles using the data shown in Fig. 5. The horizontal line through point A indicates the amount of cyclohexanone (0.05×10^{-3} mol) expected from the stoichiometric oxidation by $PdSO_4$ alone according to process (1). The dotted line indicates the amount of cyclohexanone expected from the amount of the oxidant heteropoly acid added under the assumption that processes (1) and (2) are operating. Figure 5 clearly shows that the amounts of cyclohexanone produced were above the horizontal line and exceeded the dotted line as the reaction proceeded when smaller amounts of heteropoly acid were used. These observations evidence that the redox cycles consisting of the processes (1), (2), and (3) were all operating effectively under the present conditions.

The system, $PdSO_4(0.05 \times 10^{-3}\,\text{mol})$-$H_3Mo_6W_6O_{40}$-$(0.2 \times 10^{-3}\,\text{mol})$, gave about 0.8×10^{-3} mol of cyclohexanone after 150 min of reaction. It was deduced from the values that the redox cycle of $H_3PMo_6W_6O_{40}$,

$$\begin{tikzcd} HPA_{ox} \arrow[r, bend left] & HPA_{red}, \arrow[l, bend left] \end{tikzcd}$$

turned at least 3 times. In a H_2O-*N*-methylformamide solvent, the cycle turned at least 21 times (see Table 3).

Table 2. Oxidation of cycloolefins in H_2O-cyclohexane mixture[a]

Olefin	Time/h	Yield/%	Total turnover number[b]	$V_0/10^{-5}$ mol min^{-1}
Cyclohexene[c]	10	0.0[d]	0	0
Cyclohexene[e]	10	0.0[d]	0	0
Cyclopentene[f]	6	100	30	1.25
Cyclohexene[f]	10	70.3	21	0.37
Cycloheptene[f]	22	10.0	3	0.01
Cyclooctene[f]	6	Trace	0	0
1-Methylcyclohexene[g]	8	0	0	0
3-Methylcyclohexene[g]	16	20.5[h]	4	0.1
4-Methylcyclohexene[g]	18	2.5[i]	0.5	0.003
1-Hexene[f]	10	85.9[j]	25.8	0.67

a) Each experiment was carried out at 303 K using a mixture of cyclohexane (3 ml) and H_2O (10 ml) under 1 atm oxygen. b) With respect to Pd^{2+}. c) Cyclohexene (1.5×10^{-3} mol), $H_3PMo_{12}O_{40}$ (2×10^{-4} mol), and concd. H_2SO_4 were added to the aqueous solution in order to make the pH similar to that for the conditions of footnote e (pH 1.3). d) No oxygen was absorbed during the reaction. e) Cyclohexene (1.5×10^{-3} mol), $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol), and concd. H_2SO_4 (trace). f) Olefin (1.5×10^{-3} mol), $PdSO_4$ (5×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol). g) Olefin (6.6×10^{-3} mol), $PdSO_4$ (8.3×10^{-5} mol), and $H_3PMo_6W_6O_{40}$(2×10^{-4} mol). h) 2-Methylcyclohexanone, 7.6%; 3-methylcyclohexanone, 12.9%. i) 3-Methylcyclohexanone, 1.7%; 4-methylcyclohexanone, 0.8%. j) 2-Hexanone, 75%; hexanal, 10.9%.

Oxidation of Cycloolefins. The results of the oxidation of cycloolefins were listed in Table 2. The yields of ketones in an H_2O–cyclohexane mixture decreased in the following order:

Cyclopentene > Cyclohexene > Cycloheptene > Cyclooctene,

Cyclohexene > 3-Methylcyclohexene > 4-Methylcyclohexene > 1-Methylcyclohexene.

The increase in the carbon number of the cycloolefins caused the yield of the cyclic ketones to decrease. Relative reactivities of the cycloolefins were measured by their competitive oxidation. Figure 7 shows the result of the competitive oxidation of a cyclopentene-cyclohexene equimolar mixture together with the results of the individual oxidation of cyclopentene and cyclohexene. The production of cyclopentanone was not affected by the presence of cyclohexene, while the production of cyclohexanone was inhibited by cyclopentene. After an induction period of about 3 h, cyclohexanone began to form. Competitive reactions of a cyclohexene–cycloheptene equimolar mixture and a cyclohexene–cyclooctene equimolar mixture behaved similarly; *i.e.*, the oxidation of olefin having a smaller number of carbon atoms was not retarded by the higher olefin, while the oxidation of olefin having a larger number of carbon atoms was retarded by the lower olefin.

Rate-determining Step. In the oxidation of 1-butene, Izumi *et al.*[3] suggested that process(3)determines the rate in the $PdSO_4$–$H_3PMo_6W_6O_{40}$ catalyst system. The rate expression for the cyclohexene oxidation described before suggests that process (1) is rate-determining. The shift of the rate-determining process from (3) to (1) may be due to the very low reactivities of the cycloolefins toward Pd^{2+}. This consideration is supported by the facts that the rate of process (1) decreases as the carbon number of the straight-chain olefins[12] increases and that the oxidation rate of cyclohexene was slower than that of 1-hexene (see Table 2).

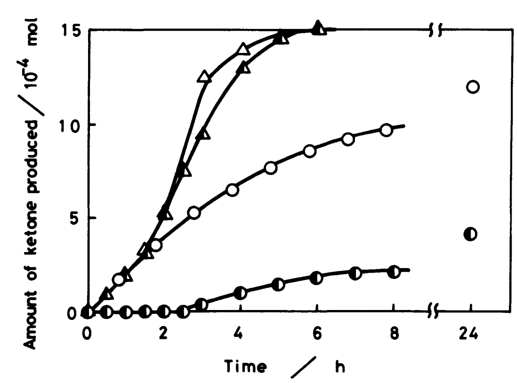

Fig. 7. Reaction profiles of oxidation of cyclopentene and cyclohexene and competive oxidation of a cyclopentene-cyclohexene equimolecular mixture: △, cyclopentanone; ○, cyclohexanone; ▲ and ◐, cyclopentanone and cyclohexanone produced in the competitive oxidation, respectively. Reaction conditions; olefin (1.5×10^{-3} mol), $PdSO_4$ (5.0×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2.0×10^{-4} mol) in H_2O (10 ml); cyclohexane (3 ml).

Cyclohexene Oxidation in Various Solvents. The oxidation of olefin with the Wacker catalyst is affected by solvating forces. Clement and Selwitz[13] described a convenient synthesis of 2-dodecanone from 1-dodecene using aqueous *N,N*-dimethylformamide solvent, and suggested that *N,N*-dimethylformamide provided more intimate contact between the olefin and the catalyst solution and also might exert a solvent effect which promoted reaction. Lloyd *et al.*[14] reported that the oxidation of cyclohexene with $PdCl_2$–$CuCl_2$ catalyst proceeded more readily in alcoholic media and most readily in media containing little or no water because of

Table 3. Oxidation of cyclohexene in various solvents[a]

Solvent system	Catalyst	Time/h	Yield/%	Total turnover number[b]
H_2O-cyclohexane[c]	$PdSO_4$-$H_3PMo_6W_6O_{40}$	10	70.3	21
Ethanol[d]		7	7.3	7
H_2O-Et_2O[c]		18	90.0	27
H_2O-$Pr^i{}_2O$[c]		20	84.9	26
H_2O-$Bu^n{}_2O$[c]		22	40.1	12
H_2O-formamide[c]		5	23.3	7
H_2O-DMF[c]		23	88.1	26
H_2O-*N*-methylformamide[c]		5	96.7	29
H_2O-*N*-methylformamide[e]		24	84.7	85
Ethanol[d]	$PdCl_2$-$CuCl_2$	22	73.8	74

a) Each experiment was carried out at 303 K, except at 293 K in H_2O-Et_2O solvent, using Pd(II) salt (5×10^{-5} mol) and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol) or Cu(II) salt (2×10^{-4} mol) under 1 atm oxygen. b) With respect to Pd^{2+}. c) Cyclohexene (1.5×10^{-3} mol), H_2O (10 ml), and organic solvent (3 ml). d) Cyclohexene (5×10^{-3} mol) and ethanol (10 ml). e) Cyclohexene (5×10^{-3} mol), H_2O (8 ml), and *N*-methylformamide (2 ml).

the greater reactivity of the alcohol-solvated Pd(II) species.

Various solvents were used for the oxidation of cyclohexene with $PdSO_4$-$H_3PMo_6W_6O_{40}$ catalyst in order to obtain cyclohexanone in good yields. The results are shown in Table 3. Each run was stopped after the time denoted in Table 3 because no further oxidation occurred thereafter. Methanol, ethanol, 2-propanol, and *t*-butyl alcohol were examined, but oxidation took place only in ethanol giving a low yield of 7.3 %. Alcohols are not suitable solvents for the present catalyst system, although $PdCl_2$-$CuCl_2$ catalyst prefers ethanol as a solvent.

In H_2O-ether solvent systems, the oxidation proceeded readily in the following order:

diethyl ether>diisopropyl ether>dibutyl ether.

Interestingly, the larger the dielectric constant of solvent is, the higher the yield of cyclohexanone becomes.

In the H_2O-formamide solvent systems examined, the H_2O-*N*-methylformamide system was the most efficient. Figure 8 shows the effect of the addition of *N*-methylformamide to water on the yield of cyclohexanone. The best yield was obtained with water containing 20% *N*-methylformamide (by volume) and the total turnover number with respect to Pd^{2+} reached 85 after 24 h of reaction. When equal volumes of *N*-methylformamide and water were employed, the yield dropped drastically. Tetrahydrofuran, sulfolane, and dimethyl sulfoxide, which are not listed in Table 3, were highly inferior to *N*-methylformamide.

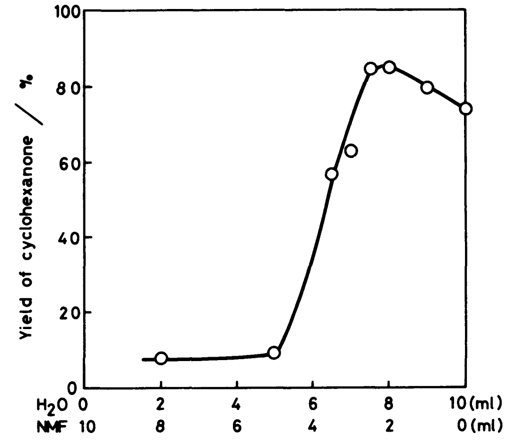

Fig. 8. Effect of addition of *N*-methylformamide (NMF) to water on the yield of cyclohexanone. Each experiment was carried out at 303K using cyclohexene (1.5×10^{-3} mol), $PdSO_4$ (5.0×10^{-4} mol), and $H_3PMo_6W_6O_{40}$ (2.0×10^{-4} mol) under oxygen at 1 atm over a 24 h period.

Life of the $PdSO_4$-$H_3PMo_6W_6O_{40}$ Catalyst. The oxidation proceeded catalytically within a certain reaction period. The reaction was inhibited by deposition of palladium metal. $PdSO_4$ or $H_3PMo_6W_6O_{40}$ was added to the reaction mixture after the inhibition, but the reaction did not proceed any more. To start the oxidation again, simultaneous addition of both $PdSO_4$ and $H_3PMo_6W_6O_{40}$ was required. The change of the IR spectra in Fig. 2 suggests that the $H_3PMo_6W_6O_{40}$ was in the reduced state after the inhibition. Calcination of the heteropoly acid in air at 673 K for 1 h restored about half of its activity. To produce a longer life for the present catalyst system, it is required that the reoxidation of the reduced heteropoly acid be activated in the course of the reaction.

Experimental

Materials. Catalysts: Pd(II) salts were used as received; $PdSO_4$ (Mitsuwa Chemicals; assay(Pd) 52.5%), $Pd(NO_3)_2$ (Wako Chemicals; assay(Pd) 45.5%) and $PdCl_2$ (Wako Chemicals; assay(Pd) 59.0%).

$H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ were purchased from Ventron Alfa Products, and used as received. Various mixed-coordinated heteropoly acids, $H_3PMo_nW_{12-n}O_{40}$ were synthesized according to the method reported.[15] It was confirmed by thermogravimetric analysis that a $H_3PMo_6W_6O_{40}$ molecule contained 10.8 molecules of water of crystallization.

Cycloolefins: Reagent grade cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, and 1-hexene were purchased from Wako Chemicals and Tokyo Kasei, and used without further purification.

Solvent: Organic solvents were all guaranteed grade except ethers (reagent grade) and were used as received.

Apparatus and Procedure. The oxidation was carried out under oxygen at atmospheric pressure using a 20 ml glass vessel reactor surrounded by a jacket in which thermostated water at 303 ± 0.1 K was circulated. A wrist-action shaker was used to achieve vigorous agitation of the reaction solution. A typical example of the oxidation of cycloolefin is illustrative. $PdSO_4$ (0.05×10^{-3} mol) and heteropoly acid (0.2×10^{-3} mol) were dissolved in water (10 ml) and the resulting mixture was allowed to settle for a day at room temperature to obtain a homogeneous solution. The solution was stirred with a magnetic stirrer under oxygen at atmospheric pressure and 303 K for 1 h in order to activate the catalyst in the solution. After the treatment, cyclohexene (1.5×10^{-3} mol) in cyclohexane (3 ml) which contained *trans*-decalin (0.3×10^{-3} mol) as an internal standard was injected into the reaction solution. The oxidation was then carried out with vigorous agitation.

Analysis of Reaction Products and Catalysts. The reaction mixtures were analyzed with a Yanagimoto Model G80 gas chromatograph. The progress of reaction was followed by glc analysis of aliquot samples and by oxygen-uptake measurements. Reaction products were identified by comparing their retention times with those of the authentic samples. To confirm the identification, gas chromatographically separated samples of the reaction products were analyzed with a JASCO infrared spectrometer, a Hitachi RMS-4 mass spectrometer, and a JEOL FX-90Q ^{1}H NMR spectrometer. Spectroscopic data are listed as below: Cyclopentanone; IR (neat) $\nu = 1745$ cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 2.07$ (8H, m, cyclopentyl); MS (8 ev) *m/z* (rel intensity), 84 (M^+;100), 85 (5.2), 56 (4.3). Cyclohexanone; IR (neat) $\nu = 1703$ cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 1.74$ (6H, m, cyclohexyl), $\delta = 2.30$ (4H, m, cyclohexyl); MS (8 ev) *m/z* (rel intensity), 98 (M^+;100), 99 (6.4), 80 (3.7). Cycloheptanone; IR (neat) $\nu = 1703$ cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta = 1.63$ (8H, m, cycloheptyl), $\delta = 2.46$ (4H, m, cycloheptyl).

Synthesized heteropoly acids were analyzed with the IR spectrometer and a Rigaku-Denki 8076D TG-DTA analyzer.

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Refereres

1) G. A. Tsigdinos and C. J. Hallada, *J. Less-Common Met.* **36**, 79 (1974).

2) K. I. Matveev, *Kinet. Katal.*, **18**, 862 (1977). K. I. Matveev, E. G. Zhizhna, N. B. Shitova, and L. I. Kuznetsova, *ibid.*, **18**, 380 (1977).

3) K. Urabe, F. Kimura, and Y. Izumi, "Shokubai" (Catalyst), Catalysis Society of Japan, **22**, 10P. (1980).

4) J. J. Altenau, M. T. Pope, R. A. Prados, and H. So, *Inorg, Chem*, **14**, 417 (1975).

5) R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, *Inorg. Chem.*, **16**, 2916 (1977).

6) K. Urabe, F. Kimura, and Y. Izumi, Proc. 7th Intern. Cong. Catalysis, Tokyo (1980), Part B, p. 1418.

7) H. Ogawa, H. Fujinami, H. Taya, and S. Teratani, *J. Chem. Soc., Chem. Commun*, **1981**, 1274.

8) C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta*, **32A**, 587 (1976).

9) M. Misono, K. Sakata, and Y. Yoneda, Proc. 7th Intern. Cong. Catalysis, Tokyo (1980), Part B, p. 1047; K. Katayama, T. Nakamura, M. Misono and Y. Yoneda, Chem. Lett., **1981**, 89.

10) K. Eguchi, Y. Toyozawa, K. Furuta, N. Yamazoe, and T. Seiyama, *Chem. Lett.*, **1981**, 1253.

11) M. Akimoto and E. Echigoya, *Chem. Lett.*, **1981**, 1759.

12) P. M. Henry, *J. Am. Chem. Soc.*, **88**, 1595 (1966).

13) W. H. Clement and C. M. Selwitz, *J. Org. Chem.*, **29**, 241 (1964).

14) W. G. Lloyd and B. J. Luberoff, *J. Org. Chem.*, **34**, 3949 (1969).

15) J. C. Bailar, *Inorg. Chem.*, **1**, 132 (1937).