Liquid Phase Oxidation of Cyclo-olefins by a $PdSO_4$–Heteropolyacid Catalyst System

By HARUO OGAWA, HIDEHARU FUJINAMI, and KAZUO TAYA*
(*Department of Chemistry, Tokyo Gakugei University, Koganei-shi, Tokyo* 184, *Japan*)
and SHOUSUKE TERATANI
(*The Institute of Physical and Chemical Research, Wako-shi, Saitama* 351, *Japan*)

Summary By a $PdSO_4$–heteropolyacid($H_3PMo_6W_6O_{40}$) catalyst system in the liquid phase cyclo-olefins, particularly cyclopentene and cyclohexene, are oxidized to the corresponding ketones.

THE Wacker cycle reaction is one of the most important processes for catalytic oxidation of olefins, but it has disadvantages caused by the chlorine anion which may lead to chlorinated by-products and reactor corrosion. Recently, it was found that a heteropolyacid can oxidize palladium and that a Pd^{II} salt–heteropolyacid system can be used as a catalyst for the oxidation of ethylene[1] and but-1-ene[2] to acetaldehyde and methyl ethyl ketone, respectively. The system, however, is apt to lose its activity and gives lower turnover numbers with respect to Pd^{II}.

An attempt to obtain alicyclic ketones from cyclo-olefins using a Wacker cycle-like catalyst system, $PdSO_4$–heteropolyacid, is reported here. Five heteropolyacids, $H_3PMo_nW_{12-n}O_{40}$ (n = 0, 4, 6, 8, or 12) were prepared by a mixed-co-ordination method.[3] The acid $H_3PMo_6W_6O_{40}$ showed the highest activity for oxidation of cyclohexene among the $PdSO_4$–heteropolyacid catalyst systems examined.

The following oxidation of cyclohexene is illustrative. Palladium sulphate (5×10^{-5} mol) and the heteropolyacid $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol) were dissolved in H_2O (10 ml) and the resulting solution was shaken with oxygen under normal pressure at 30 °C for one hour. Compound (**1**) ($1{\cdot}5 \times 10^{-3}$ mol) in cyclohexane (3 ml) was then injected into the reaction vessel in which the reaction was carried out with vigorous agitation under the same conditions as those described above.

Analysis by g.l.c.† showed cyclohexanone as a product and the absence of by-products. Analysis using *trans*-decalin as an internal standard showed that cyclohexene was converted exclusively into cyclohexanone. The amount of oxygen consumed was almost half as much as that of cyclohexanone produced. These points suggest that the palladium-catalysed oxidation of the cyclo-olefins proceeded well and the heteropolyacid reoxidized palladium briskly.

The results obtained with the $PdSO_4$–$H_3PMo_6W_6O_{40}$ catalyst system are listed in the Table. The reaction requires water in the solvent system used. In the case of alcohol solvents, the reaction proceeded only in ethanol, and gave lower yields. We found that the H_2O–N-methylformamide mixture was the most effective solvent system among those examined.

Assuming the reaction scheme proposed by Urabe *et al.*,[2] one can calculate the turnovers accomplished after the reaction with respect to Pd^{II}. The largest number of turnovers accomplished was found to be about 90 in the reaction with the H_2O–N-methylformamide mixtures (see Table).

---

† Dioxan was added to the reaction mixture for analysis, because the mixture separated into aqueous and organic layers. The products were identified by comparison with authentic samples using a PEG 20M column at elevated temperatures.

TABLE. Oxidation of cyclo-olefins by $PdSO_4$–$H_3PMo_6W_6O_{40}$.[a]

Olefin	Solvent system	Reaction time/h	Yield/%	Turnovers
Cyclohexene	H_2O–cyclohexane [b]	10	0·0 [c]	0
	H_2O–cyclohexane [d]	10	0·0 [c]	0
Cyclopentene	H_2O–cyclohexane [e]	6	100	30
Cyclohexene	H_2O–cyclohexane [e]	10	70·3	21
	Ethanol [f]	7	7·3	7
	H_2O–$Pr^i{}_2O$ [e]	20	84·9	26
	H_2O–*NN*-dimethylformamide [e]	23	88·1	26
	H_2O–formamide [e]	5	23·3	7
	H_2O–*N*-methylformamide [e]	5	96·7	29
	H_2O–*N*-methylformamide [g]	24	84·7	85
3-Methylcyclohexene	H_2O–cyclohexane [h]	16	20·5 [i]	16
Cycloheptene	H_2O–cyclohexane [e]	22	10·0	3
Cyclooctene	H_2O–cyclohexane [e]	6	trace	~0

[a] All runs were conducted at 30 °C under normal pressure of oxygen. [b] Cyclohexene ($1{\cdot}5 \times 10^{-3}$ mol), $H_3PMo_{12}O_{40}$ (2×10^{-4} mol), and conc. H_2SO_4 (trace) in H_2O (10 ml) and cyclohexane (3 ml). Conc. H_2SO_4 was added to the aqueous solution in order to make the pH similar to that for the conditions of footnote e (pH 1·3). [c] No oxygen was absorbed during the reaction. [d] Cyclohexene ($1{\cdot}5 \times 10^{-3}$ mol), $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol), and conc. H_2SO_4 (trace) in H_2O (10 ml) and cyclohexane (3 ml). [e] Cyclo-olefin ($1{\cdot}5 \times 10^{-3}$ mol), $PdSO_4$ (5×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol) in H_2O (10 ml) and organic solvent (3 ml). [f] Cyclohexene (5×10^{-3} mol), $PdSO_4$ (5×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol) in ethanol (10 ml). [g] Cyclohexene (5×10^{-3} mol), $PdSO_4$ (5×10^{-5} mol), and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol) in H_2O (8 ml) and *N*-methylformamide (2 ml). [h] 3-Methylcyclohexene ($6{\cdot}6 \times 10^{-3}$ mol), $PdSO_4$ ($8{\cdot}3 \times 10^{-5}$ mol) and $H_3PMo_6W_6O_{40}$ (2×10^{-4} mol) in H_2O (10 ml) and cyclohexane (3 ml). [i] 2-Methylcyclohexanone, 7·6%; 3-methylcyclohexanone, 12·9%.

It was also found that cyclopentene was the most reactive substrate and that the yield of alicyclic ketone decreased with increasing carbon number for the olefin. 3-Methylcyclohexene gave predominantly 3-methylcyclohexanone by oxidation with the H_2O–cyclohexane solvent system.

The procedure reported here can be used for the catalytic oxidation of cyclo-olefins in the liquid phase and provides a new method for preparation of alicyclic ketones.

(*Received*, 11*th August* 1981; *Com.* 986.)

[1] K. I. Matveev, E. G. Zhizhina, N. B. Shitova, and L. I. Kuznetsova, *Kinet. Katal.*, 1977, **18**, 380.
[2] K. Urabe, F. Kimura, and Y. Izumi, Proc. 7th Intern. Cong. Catalysis (Tokyo 1980), Part B, p. 1418.
[3] J. C. Bailar, Jr., *Inorg. Chem.*, 1939, **1**, 132.