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Cyclodextrin-Palladium Chloride. New Catalytic System for Selective Oxidation of Olefins to Ketones

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Terminal olefins are oxidized to ketones in high yields under mild conditions using palladium chloride and cyclodextrins as catalysts in two-phase systems; cyclodextrins show substrate selectivity.

Cyclodextrins(CDs) form inclusion compounds with various organic molecules[1] and they have been extensively studied as a model of enzymes.[2] However, in most of the reactions reported CDs are not catalysts and so their applications to organic syntheses have been limited. Previously we reported that CDs form inclusion compounds with some organometallic complexes.[3] Now we found a system in which CDs function as catalysts and show marked substrate selectivity. Here we report the first example of the use of CDs as inclusion catalysts for effecting reactions catalysed by transition metal complexes in aqueous-organic two-phase systems.

We have examined the behavior of CDs in the oxidation of terminal olefins to the corresponding methyl ketones. Although ethylene can be oxidized to acetaldehyde by $PdCl_2$ in an aqueous system (Wacker reaction), higher α-olefins

$$R\text{-}CH{=}CH_2 + O_2 \xrightarrow[H_2O,\ 1\ atm.]{PdCl_2\text{-}CuCl_2,\ CD} RCOCH_3$$

are oxidized to methyl ketones only very slowly or not oxidized in entirely aqueous solutions of $PdCl_2$. Now we have found that on addition of CD into this system, terminal olefins are smoothly oxidized under mild conditions to give the corresponding methyl ketones in high yields and that cyclodextrins show substrate selectivity.

In a typical experiment, dec-1-ene (25 mmol) was added to an aqueous solution of α-CD (1.0 mmol), $PdCl_2$ (1.0 mmol), and $CuCl_2$ (10 mmol) at 75 °C. When oxygen was bubbled through an aqueous solution and stirred vigorously, decan-2-one was obtained in 76% yield. No oxidation products were obtained without α-CD.

The results on the oxidation of some long-chain olefins by the present catalytic system are summarized in Table 1 and illustrated in Fig. 1, which shows that the yield of ketones depends strongly on the substrate employed and high yields are obtained with the substrates having C8—C10 structures. The yield

Table 1. Oxidation of olefins to methyl ketones

Olefin	Temp °C	Time h	Yield %
Oct-1-ene	65	10	76
Non-1-ene	60	8	62
Dec-1-ene	75	10	76
Dodec-1-ene	80	10	13
Tetradec-1-ene	85	10	9
Oct-2-ene	60	8	2

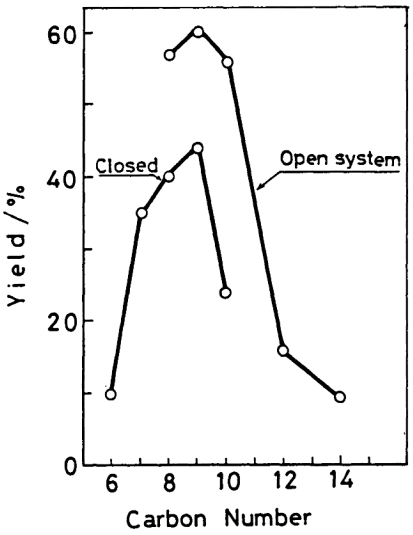

Fig. 1. Effects of carbon number on the yields of ketones. Open system, 70 °C, 8 h. Closed system, 60 °C, 8 h, 1 atm.

suddenly drops when the carbon number of the substrate exceeds ten, indicating that the CD-$PdCl_2$ system shows high substrate-selectivity. Essentially no reactions of internal olefins were observed under the present conditions.

It should be noted that α-CD is effective as catalyst and it can be recovered simply by cooling the solution and can be reused. β-CD is also effective as the catalyst and shows similar selectivity. The metal catalyst can be reused without any reduction in yields. Oxygen can be replaced by air.

Recently, Alper et al. reported that the reaction was carried out in two-phase systems with quaternary ammonium salts as phase transfer catalysts and CCl_4 as solvent.[4] In our system isolation of the products from catalysts or solvent is quite easy because no organic solvents are required, and the CD and $PdCl_2$ catalysts are soluble only in an aqueous phase.

One possible pathway of the reaction may be the initial formation of CD complexes with substrates. CD extracts substrates from the organic phase allowing them to form complexes with $PdCl_2$. Then the substrates undergo oxidation to yield ketones. Unlike with the phase transfer catalysts generally used, such as quaternary ammonium salts, the reaction proceeds in the aqueous phase in our system.

The results show that this new system consisting of cyclodextrin and $PdCl_2$ is effective and selective catalysts for oxidation of long-chain α-olefins to ketones in a two-phase system and that separation of the products from catalysts or solvents is quite easy.[5,6]

References
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