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SELECTIVE HYDROGENATION OF CONJUGATED DIOLEFINS TO MONOOLEFINS CATALYZED BY A POLYMER-PALLADIUM COMPLEX

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A polymer-palladium complex prepared from palladium(II) chloride and styrene-divinylbenzene copolymer with iminodiacetic acid groups is found to catalyze the selective hydrogenation of conjugated diolefins to monoolefins at 30°C under an atmospheric hydrogen pressure.

The complex of styrene-divinylbenzene copolymer with iminodiacetic acid groups with rhodium(III) was found to catalyze the heterogeneous hydrogenation of olefins at 30°C under an atmospheric hydrogen pressure.[1)] We now wish to report that the complex prepared from palladium(II) chloride and styrene-divinylbenzene copolymer with iminodiacetic acid groups functions selective hydrogenation of conjugated diolefins to monoolefins at 30°C under an atmospheric hydrogen pressure.

A chelating resin with iminodiacetic acid groups attached to a styrene-divinylbenzene copolymer matrix, Chelex 100 (200-300 mesh, Bio. Rad. Laboratories) was used as a polymeric ligand. A solution of $PdCl_2.2H_2O$ (0.5 mmol) in methanol (50 ml) was added to water (100 ml) contained Chelex 100 in the monosodium salt form (50 ml, 35 meq. as carboxyl group) and the solution stirred at 25°C for 1 hr. Then the yellow resin particles contained palladium(II) ion were added to water (200 ml) containing 20 meq. of NaOH to convert the monosodium salt form of the yellow resin into the disodium salt form and the yellow resin particles were refluxed in methanol (50 ml)-water (50 ml) solution under nitrogen ca. 6 hr to yield pale yellow green particles of polymer-palladium complex. The particles of polymer-palladium complex were washed with degassed methanol and stored in degassed methanol. Hydrogenation of substrates under an atmospheric hydrogen pressure was carried out using the apparatus and the procedure described in the previous paper,[2)] and the reaction products were analyzed by glpc.

Under refluxing in the methanol-water solution, the yellow particles in the monosodium salt form remains yellow with a very small catalytic activity for the hydrogenation of 1,3-cyclooctadiene. On the other hand, the pale yellow green particles of the Chelex 100-Pd complex obtained under refluxing of the yellow resin particles in the disodium salt form mentioned above are exceedingly active for the hydrogenation of conjugated diolefins at room temperature under an atmospheric hydrogen pressure.

The Chelex 100-Pd complexes in the monosodium salt form and acid form were also obtained by the addition of 1 N HCl aq. solution to the water (200 ml) containing the Chelex 100-Pd complex in the disodium salt form. The examination of the catalytic properties of these complexes for the hydrogenation of 1,3-cyclooctadiene in methanol revealed that the Chelex 100-Pd complex in the monosodium salt form is the most active and gives cyclooctene in the highest yield. In the present letter, the catalytic behavior of the Chelex 100-Pd complex in the monosodium salt form (the Chelex 100-Pd complex) for the hydrogenation of olefins will be reported in detail.

Some terminal and internal olefins, and polyolefins were hydrogenated in methanol at 30°C under an atmospheric hydrogen pressure by the Chelex 100-Pd complex. As shown in Table 1, terminal olefins are much more easily hydrogenated than internal olefins. On the other hand, conjugated dienes, even the dienes with the internal C=C double bonds such as hexa-2,4-diene are much more smoothly hydrogenated than internal olefins and terminal olefins. Conjugated cyclic dienes are also more easily hydrogenated than corresponding cyclic monoolefins and unconjugated dienes. Especially, cycloocta-1,3-diene are quite easily hydrogenated compared with the corresponding cyclic monoene, cyclooctene. The rate of hydrogenation of cycloocta-1,3-diene is more than 100 times that of cyclooctene. The rates of the hydrogenation of cycloocta-1,3-diene relative to those of cyclooctene catalyzed by a Chelex 100-Rh complex[1)] and by a palladium-active carbon catalyst (Kojima Chemical Co. Ltd.) were found to be about 6 and 10, respectively. The high catalytic activity of the Chelex 100-Pd complex to the hydrogenation of conjugated diolefins indicates that

Table 1. Rates of Hydrogenation of Various Substrates by Chelex 100-Pd Complex; catalyst, 7.4 ml in MeOH; Pd, 0.125 mmol[3)]; substrate concentration, 0.2 M; solvent, MeOH; total reaction mixture, 50 ml; temp., 30 ± 0.05°C; H_2 pressure = 760 mmHg - vapour pressure of solvent media.

Substrate	Initial hydrogen uptake in ml/min at s.t.p.
Hex-1-ene	10.6
Dec-1-ene	9.4
trans-Hex-2-ene	2.1
2-Methylpent-2-ene	0.29
Haxa-2,4-diene	22.1
2-Methylbuta-1,3-diene	17.8
Cyclohexene	2.38
Cyclooctene	0.21
Cyclohexa-1,3-diene	14.1
Cycloocta-1,3-diene	22.5
Cycloocta-1,5-diene	4.5
Cyclohepta-1,3,5-triene	0.98

selective hydrogenation of polyolefins to monoolefins can be achieved using the polymer-Pd complex as catalyst.

Table 2 shows the results of hydrogenation of some conjugated diolefins catalyzed by the Chelex 100-Pd complex in methanol. The products in the table are the products when the equivalent mole of hydrogen to that of charged olefin was absorbed and the hydrogenation rate began to decrease, besides the case of the hydrogenation of cyclohexa-1,3-diene.[4] As shown in Table 2, the conjugated dienes can be hydrogenated to the corresponding monoolefins with high selectivity using the Chelex 100-Pd complex as catalyst. Unconjugated dienes are hydrogenated to monoolefins with less selectivity than those for the conjugated dienes. In the case of cyclohexa-1,3-diene, appreciable disproportionation of the diene to benzene and cyclohexene is observed during the course of hydrogenation. Judging from the facts that the concentration of trans-hex-3-ene found in the reaction products of hexa-2,4-diene as shown in Table 2 was very high compared with that produced by the

Table 2. Selective Hydrogenation of Conjugated Diolefins by Chelex 100-Pd Complex; Pd, 0.125 mmol; substrate concentration, 0.2 M; solvent, MeOH.[a]

Substrate	Reaction time (min)	Products (%)
Hexa-2,4-diene[b]	16	trans-Hex-2-ene (46.0) cis-Hex-2-ene (13.5) trans-Hex-3-ene (34.0) cis-Hex-3-ene (3.0) Hexane (3.5)
2-Methylbut-1,3-diene	19[52]	2-Methylbut-1-ene (19.8)[5.8] 3-Methylbut-1-ene (17.2) 2-Methylbut-2-ene (58.1)[82.4] 2-Methylbutane (4.9)[11.8]
Methylsorbate	20	Methyl-2-hexenoate (83.7) Methyl-3-hexenoate (7.5) Methyl-4-hexenoate (6.1) Methylcaproate (1.9)
Cyclohexa-1,3-diene	6	Cyclohexene (55.8) Cyclohexane (3.2) Benzene (41.0)
Cycloocta-1,3-diene	15	Cyclooctene (99.2) Cyclooctane (0.8)
Cycloocta-1,5-diene	215	Cycloocta-1,5-diene (3.7) Cyclooctene (92.9) Cyclooctane (3.4)

a) Other conditions are given in Table 1. b) Trans-trans, 70% and trans-cis, 30%.

isomerization reaction[5] of tran- or cis-hex-2-ene, and that 2-methylbut-1-ene and 3-methylbut-1-ene were also found together with 2-methylbut-2-ene in the course of hydrogenation of 2-methylbut-1,3-diene, the hydrogenation reaction of conjugated dienes catalyzed by the Chelex 100-Pd complex may include both 1:2 and 1:4 addition of hydrogen to substrates.

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REFERENCES AND NOTES

1) Y. Nakamura and H. Hirai, Chemistry Letters, 1975, 809.
2) Y. Nakamura and H. Hirai, Chemistry Letters, 1974, 645.
3) Palladium content in the polymer complex was calculated from the charged quantity since no appreciable loss of palladium was found in the course of preparation of the complex.
4) In the case of cyclohexa-1,3-diene, the products in Table 2 were obtained when hydrogen uptake approached to about 22 mol % of charged diene and the hydrogenation rate began to decrease.
5) Trans-Hex-3-ene (10% in maximum) was found in the course of hydrogenation of trans- or cis-hex-2-ene catalyzed by the Chelex 100-Pd complex.

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