

A NOVEL POLYMER-RHODIUM COMPLEX AS HYDROGENATION  
CATALYST OF ALKENES

Yoshio NAKAMURA and Hidefumi HIRAI\*

The Noguchi Institute, 8-1, Kaga 1-Chome, Itabashi-Ku, Tokyo 173

\*Dept. of Industrial Chemistry, Faculty of Engineering,  
The University of Tokyo, Bunkyo-Ku, Tokyo 113

A polymer-rhodium complex prepared from rhodium(III) chloride and styrene-divinylbenzene copolymer with iminodiacetic acid groups is found to catalyze the heterogeneous hydrogenation of alkenes in polar solvents at 30°C under an atmospheric hydrogen pressure. The polymer complex hydrogenates selectively the ethylenic double bonds in the alkenes with carbonyl and aromatic groups. The rates of hydrogenation of alkenes by the polymer complex are found to be markedly affected by the steric hindrance of the substrates.

The complexes of polyacrylic acid and cross-linked polyacrylic acid with rhodium(III) were found to catalyze the homogeneous and heterogeneous hydrogenation of unsaturated compounds at 30°C under an atmospheric hydrogen pressure.<sup>1,2)</sup> We now wish to report that the reflux of a styrene-divinylbenzene copolymer with iminodiacetic acid groups binding rhodium(III) ion in methanol-water solution yields a pale yellow-green polymer-rhodium complex which functions as an active heterogeneous catalyst for the hydrogenation of alkenes exhibiting a great sensitivity to the substrate structure.

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  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (0.5 mmol) in methanol (50 ml) was added to water (100 ml) contained Chelex 100 in the disodium salt form (50 ml, 35 meq. as carboxyl group) and the solution was stirred at 25°C for 1 hr. Then 15 ml of 1N HCl aq. solution was added to the solution containing resin parti-

cles converting the resin into the monosodium salt form in order to bind rhodium (III) ion, and the solution was stirred for 3 hr. After decantation to remove a small amount of brown substance like alga formed during stirring, the yellow resin particles containing rhodium(III) ion were added to water (200 ml) contained 20 meq. of NaOH to reconvert the yellow resin into the disodium salt form. Then the yellow particles were refluxed in methanol (50 ml)-water (50 ml) solution under a nitrogen atmosphere for ca.8 hr to yield pale yellow-green particles of polymer-rhodium complex (the Chelex 100-Rh complex). The polymer-rhodium complex was 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.<sup>2)</sup> The reaction products were analyzed by glpc using several columns as given in the previous paper.<sup>2)</sup>

Under refluxing in pure water instead of in the methanol-water solution, the particles containing rhodium(III) ion remains yellow with scarce catalytic activity for the hydrogenation of hex-1-ene. Under refluxing in the methanol-water solution, the yellow particles in the monosodium salt form yield black particles which are active for the hydrogenation of hex-1-ene, but the reaction solution becomes dark brown during the hydrogenation. This result may be due to the liberation of the rhodium metal reduced under refluxing. On the other hand, the pale yellow-green particles of the Chelex 100-Rh complex obtained under refluxing of the yellow particles in the disodium salt form mentioned above are exceedingly stable and active for hydrogenation of alkenes at room temperature under an atmospheric

Table 1. Dependence of Rate of Hydrogenation of Hex-1-ene on the Form of Iminodiacetic Acid Groups of Chelex 100-Rh Complex; Rh, 0.091 mmol<sup>4)</sup>; substrate concentration, 0.4 M; solvent, MeOH; total reaction mixture, 50 ml; temp., 30 ± 0.05°C; H<sub>2</sub> pressure = 760 mmHg - vapour pressure of solvent media.

Form of iminodiacetic acid	Volume of complex in MeOH (ml)	Initial hydrogen uptake in ml/min at s.t.p.
Disodium salt form	7.4	12.0
Monosodium salt form	6.4	13.0
Acid form	6.0	3.0

hydrogen pressure.

The Chelex 100-Rh complexes in the monosodium salt form and acid form were obtained by adding 1 N HCl aq. solution to water (200 ml) contained the Chelex 100-Rh complex in the disodium salt form. The catalytic activities of these complexes were examined for the hydrogenation of hex-1-ene. As shown in Table 1, the Chelex 100-Rh complex in the monosodium salt form is the most active. The activity of the acid form complex is very small in contrast to the result obtained for the cross-linked polyacrylic acid-rhodium complex, the IRC-84-Rh complex, where the acid form is about twice as active as the sodium salt form.<sup>3)</sup> In the present study, the catalytic behavior of the Chelex 100-Rh complex in the monosodium salt form will be investigated in detail. Hereafter the Chelex 100-Rh complex means the polymer-rhodium complex in the monosodium salt form.

Some straight and substituted alkenes, and hex-1-yne were hydrogenated at 30°C under an atmospheric hydrogen pressure by the Chelex 100-Rh complex. As can be seen from Table 2, terminal alkenes are much more easily hydrogenated than internal alkenes. Substitution of alkene markedly interferes with hydrogenation, presumably by increasing steric hindrance to approach to the C=C bond. For example, the rate of the hydrogenation of hex-1-ene becomes about 30 times as much as that of 2,3-dimethylbut-2-ene. This high sensitivity of the Chelex 100-Rh complex to substitution is in marked contrast to the IRC-84-Rh complex<sup>2)</sup> and a rhodium-active carbon catalyst (Japan Engelhard Co., Rh/C). The rates of the hydrogenation of hex-1-ene relative to that of 2,3-dimethylbut-2-ene catalyzed by the IRC-84-Rh complex and the Rh/C under the conditions as given in Table 2 were found to be 4.6 and 1.7, respectively.

As shown in Table 2, unsaturated esters such as dimethylmaleate are much more easily hydrogenated than unsaturated acids such as maleic acid. Addition of 1 N aq. NaOH solution (20 ml) or triethylamine (20 mmol) to the catalytic system containing maleic acid (10 mmol) as a substrate scarcely caused enhancement of the rate of hydrogenation.

Though the Chelex 100-Rh complex functions as an excellent catalyst for the hydrogenation of alkenes, the complex catalyst is much less active for the hydrogenation of alkynes and not active for the hydrogenation of carbonyl and aromatic groups. For example, styrene and hex-5-ene-2-one were hydrogenated selectively on vinyl group to give ethylbenzene (yield, 100%) and n-butylmethyl ketone (yield,

99.5%) respectively, and no further hydrogen uptake was observed.

In the case of styrene, one of terminal alkenes, the observed slow rate of hydrogen uptake may be attributed to a specific interaction of aromatic ring with the complex. Addition of the Chelex 100-Rh complex to the solvents such as benzene and toluene made the polymer complex yellow-green, and addition of styrene (0.4 M) to the catalytic system caused a marked decrease in the rate of hydrogenation of hex-1-ene in methanol.

Migration of double bonds for the hydrogenation of alkenes catalyzed by the Chelex 100-Rh complex appears to be markedly retarded compared with the results obtained for the IRC-84-Rh complex.<sup>5)</sup> After half hydrogenation using the Chelex 100-Rh complex as catalyst, hex-1-ene yielded trans-hex-2-ene (6.0%), cis-hex-2-ene (1.5%), trans-hex-3-ene (1.5%), and a trace of cis-hex-3-ene.

Cyclic alkenes are also smoothly hydrogenated using the Chelex 100-Rh complex

Table 2. Rates of Hydrogenation of Various Substrates by Chelex 100-Rh Complex; catalyst, 6.4 ml in MeOH; Rh, 0.091 mmol; solvent, MeOH.<sup>a)</sup>

Substrate	Initial hydrogen uptake in ml/min at s.t.p.
Hex-1-ene	13.0
Dec-1-ene	10.4
trans-Hex-2-ene	6.9
2-Methylpent-1-ene	7.4
2-Methylpent-2-ene	0.81
2,3-Dimethylbut-2-ene	0.41
Maleic acid	2.5
Dimethyl maleate	12.6
Dimethyl itaconate	5.5
Hex-5-ene-2-one	12.3
Mesityl oxide	1.6
Styrene	2.0
Hex-1-yne	0.26

a) Other conditions as given in Table 1.

as catalyst. However, some substituted cycloalkenes and conjugated dienes are slowly hydrogenated. As can be seen from Table 3, the Chelex 100-Rh complex is very sensitive to the environment of the double bond. The rate of hydrogenation of 4-methylcyclohexene is about 40 times as much as that of 1-methylcyclohexene. The rates of the hydrogenation of 4-methylcyclohexene relative to that of 1-methylcyclohexene catalyzed by the IRC-84-Rh complex and the Rh/C under the conditions as given in Table 3 were found to be 4.0 and 1.2, respectively. For an excellent homogeneous complex,  $\text{RhCl}(\text{PPh}_3)_3$ , the rate of the hydrogenation of cyclohexene relative to that of 1-methylcyclohexene is reported to be about 35 in ethanol-benzene solution.<sup>6)</sup>

Table 3 shows a decrease in rate as the ring size of cyclic monoene increases. This ring size effect obtained for the Chelex 100-Rh complex on the rate becomes larger than that reported for a phosphinated polymer-rhodium(1) complex.<sup>7)</sup> Cycloocta-1,3-diene is unexpectedly easily hydrogenated from the ring size effect on the rate found in a series of cyclic monoene, yet cyclooctene is well known to be slowly hydrogenated.<sup>8)</sup> In contrast to the hydrogenation of the conjugated system of cycloocta-1,3-diene, that of cyclohexa-1,3-diene is very slowly hydrogenated. The cyclohexa-1,3-diene result may be due to stable complex formation with the diene. Indeed, in the presence of the diene (0.4 M), the rate of hydrogenation

Table 3. Rates of Hydrogenation of Various Cyclic Alkenes by Chelex 100-Rh Complex.<sup>a)</sup>

Substrates	Initial hydrogen uptake in ml/min at s.t.p.
Cyclopentene	14.2
Cyclohexene	13.4
4-Methylcyclohexene	9.9
1-Methylcyclohexene	0.25
Cyclohexa-1,3-diene	0.88
Cyclooctene	1.4
Cycloocta-1,3-diene	7.9
Cyclododecene	1.3

a) Conditions as given in Table 2.

of hex-1-ene was decreased to about one-fourteenth.

The polymer complex functions as an active hydrogenation catalyst in a variety of polar solvents. Alcohols were found to be the best solvents for the catalytic activity. On the other hand, in dimethyl sulfoxide, the activity of the complex was entirely suppressed. Though the presence of oxygen gas results in a lowering of the rate of hydrogenation of alkenes, the activity of the Chelex 100-Rh complex can be completely recovered by the treatment with an atmospheric hydrogen for about 20 min.

The Chelex 100-Rh complex is slightly less active than the IRC-84-Rh complex,<sup>2)</sup> and the sensitivity of the former to the substrate structure is found to be much more enhanced than that of the latter. At present, detailed information of the structure of the polymer complex is not known; nevertheless, the advanced sensitivity found in the catalytic behavior of the Chelex 100-Rh complex may be attributed to a stable and rigid chelate structure formed by imino and carboxyl groups. The particles of the Chelex 100-Rh complex are found to be quite stable and to remain pale yellow-green throughout the course of reaction. At the completion of the reaction, the particles of the polymer complex can be easily recovered and reused without any appreciable loss in activity.

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