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# HOMOGENEOUS HYDROGENATION OF ALKENES BY THE COMPLEX OF POLYACRYLIC ACID WITH RHODIUM(III)

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The complex of polyacrylic acid with rhodium(III) functions as a homogeneous catalyst for the hydrogenation of terminal alkenes in methanol solution at 30°C under an atmospheric pressure of hydrogen. The triethylammonium salt of the complex is effective for the hydrogenation of internal alkenes as well as terminal alkenes.

The complex of polyacrylic acid with rhodium(III) has been found to be a very active catalyst for the homogeneous hydrogenation of a number of alkenes in methanol solution.

A bitter orange-colored solution of $RhCl_3.3H_2O$ (0.1 or 0.2 mmol), NaOH (40 mmol), and polyacrylic acid, degree of polymerization 2560, (40 mmol as monomer unit) in methanol (100 ml)-water (100 ml) was refluxed under nitrogen for ca. 8 hr. The solution became brownish-dark green. The solution was filtered from a trace of black precipitate formed during refluxing to yield the sodium salt of polyacrylic acid-rhodium complex (the PAA-Rh-Na complex) in methanol-water solution. The filtrate was passed through a 20×2.5 cm. column of cation exchange resin, Amberlite IR-120(H) (Rohm and Haas) and washed with water until the washing was no longer acidic. The obtained polyacrylic acid-rhodium complex solution was evaporated to concentrate under reduced pressure, and dissolved into methanol (twice the volume of the concentrated solution). The methanol solution was added to a large excess of ether to precipitate the polymer complex. The dark green precipitate was washed with ether and dried at 35°C in vacuo for ca. 5 hr resulting in the polyacrylic acid-rhodium complex (the PAA-Rh-H complex)(yield, 95.0% based on polyacrylic acid).

Alkylammonium salts of the polymer complex were prepared as follows. The obtained polyacrylic acid-rhodium complex solution mentioned above was neutralized with an equimolar amount of n-propylamine or triethylamine before evaporation, and filtered. The filtrate was evaporated to concentrate under reduced pressure, and dissolved into methanol (twice the volume of the concentrated solution). The methanol solution was added into a large excess of ether. The dark green precipitate was washed with ether and dried at 35°C in vacuo for ca. 5 hr(yield, for n-propylammonium salt of the complex, 88.6%; for triethylammonium salt of the complex, 70.2% based on polyacrylic acid). Hydrogenation of substrates was carried out using a Hershberg type catalytic hydrogenation apparatus[1)] equipped with an Eyela Shaker (Tokyo Rikakikai Co.) for a constant agitation of a reaction vessel (200-ml. glass flask) which was immersed in a water bath kept at a constant temperature. High purity hydrogen gas (Takachiho Co.) adjusted to atmospheric pressure was passed through a 50×1.4 cm. column of silica gel before admission to the reaction vessel. The reaction products were analyzed by glpc with a 5 m column of diethylene glycol contained $AgNO_3$ or a 2 m column of polyethylene glycol contained $AgNO_3$.

In the methanol-water solution of the PAA-Rh-Na complex obtained under refluxing, alkenes are found to be hydrogenated in the homogeneous state at 30°C under an atmospheric hydrogen pressure. The PAA-Rh-Na complex in methanol-water solution precipitates when the concentration of methanol increases to about 60% in volume.

Table 1. Rates of Hydrogenation of Hex-1-ene by Complexes of Polyacrylic Acid with Rh(III); hex-1-ene concentration, 0.4 mol/l; total volume of reaction mixture, 50 ml; temp., 30 ± 0.05°C; $H_2$ pressure = 76 cmHg - vapour pressure of solvent media.

| Complex | Ligand/Rh (molar ratio) | Rh(mmol) | Solvent | Initial hydrogen uptake in ml/min at s.t.p. |
|---|---|---|---|---|
| PAA-Rh-Na | 200 | 0.04 | $MeOH-H_2O$[a)] | 3.04 |
| PAA-Rh-H | " | 0.0346[b)] | MeOH | 4.00[c)] |
| " | 400 | 0.0173[b)] | " | 5.40[d)] |

a) Reaction mixture contains 20 ml $H_2O$. b) Calculated value, 500 mg complex was used. c) Heterogeneous hydrogenation. d) 5.40 ml/min = $8.03\times10^{-5}$mol/l sec.

The PAA-Rh-H complex dissolves in methanol and/or water to give brownish-dark green solutions when the molar ratio of monomeric residue of the ligand to Rh(III)(ligand/Rh molar ratio) of the complex is more than about 400, and functions as a homogeneous catalyst for the hydrogenation of a number of alkenes. Though the PAA-Rh-H complex of which ligand/Rh molar ratio is less than about 200 does not solve in both methanol and water, the complex functions in the heterogeneous state as a catalyst for the hydrogenation of alkenes in these solvents. The rates of hydrogen uptake for the hydrogenation of hex-1-ene catalyzed by the PAA-Rh-Na and the PAA-Rh-H complexes are given in Table 1.

It can be seen from Table 1 that the polymer-rhodium complexes are much more active than a rhodium complex with monomeric ligand, $Rh_2(OCOCH_3)_4$ complex, which gives initial rates of hydrogen uptake, $2.28\times10^{-5}$mol/l sec in dimethylformamide and $5.10\times10^{-6}$mol/l sec in ethanol, for the hydrogenation of hex-1-ene at the conditions; catalyst concentration, 5.0 mmol/l; substrate concentration, 1.0 mol/l; temp., 30°C; atmospheric $H_2$ pressure.[2)] For example, the catalytic activity per rhodium atom of the PAA-Rh-H complex becomes about 120 times as much as that of $Rh_2(OCOCH_3)_4$ in dimethylformamide on the assumption that the initial rate of hydrogen uptake is first order in the catalyst concentration and substrate concentration.

The alkylammonium salts of polyacrylic acid-rhodium complex well dissolve in methanol and/or water to give brownish-dark green solutions, and function as excellent hydrogenation catalysts as shown in Table 2. Comparing Table 2 with 1 for the hydrogenation of hex-1-ene, it is found that the alkylammonium salts of polyacrylic acid-rhodium complex are much more active than the PAA-Rh-Na and the PAA-Rh-H complexes. For example, The catalytic activity of the PAA-Rh-n-PA complex is about three times as much as that of the PAA-Rh-H complex.

As shown in Table 2, the alkylammonium salts of polyacrylic acid-rhodium complex are very active for the hydrogenation of straight chain terminal and internal alkenes, certain substituted ethylene, straight diene, and cyclic monoene. The catalytic behaviors of the alkylammonium salts of polyacrylic acid-rhodium complex for the substrates such as trans-internal alkenes, e.g. trans-hex-2-ene and dienes, e.g. hexa-1,5-diene are different from that of the $Rh_2(OCOCH_3)_4$ complex which is not active for these substrates.[2)] On the other hand, the polymer complexes are much less active for the hydrogenation of alkynes than for that of alkenes and not active for the hydrogenation of other functional groups such as

Table 2. Rates of Hydrogenation of Substrates by Alkylammonium salts of Complex of Polyacrylic Acid with Rh(III)(500 mg, ligand/Rh molar ratio=200); substrate concentration, 0.4 mol/l; total volume of reaction mixture, 50 ml; temp., 30 ± 0.05°C; $H_2$ pressure = 76cmHg - vapour pressure of solvent media.

| Complex | Solvent | Substrate | Initial hydrogen uptake in ml/min at s.t.p. |
|---|---|---|---|
| PAA-Rh-n-PA[a)] | MeOH | Hex-1-ene | 14.1 |
| | $MeOH-H_2O$[b)] | " | 2.31 |
| | MeOH | trans-Hex-2-ene | 2.59 |
| | " | cis-Hex-2-ene | 4.42 |
| | " | Oct-1-ene | 13.0 |
| | " | Hexa-1,5-diene | 7.52 |
| | " | Styrene | 11.3 |
| | " | Mesityl oxide | 5.24 |
| | " | Dimethyl itaconate | 11.8 |
| | " | Itaconic acid | 2.15 |
| | " | α-Acetamidocinnamic acid | c) |
| | " | Cyclohexene | 3.67 |
| | " | Cyclohexa-1,3-diene | 1.88[d)] |
| | " | Hex-1-yne | 1.10 |
| | " | Hex-1-yne-3-ol | 0.47 |
| PAA-Rh-TEA[e)] | " | Hex-1-ene | 12.7 |
| | " | trans-Hex-2-ene | 9.15 |
| | " | Mesityl oxide | 11.7 |
| | $MeOH-H_2O$[b)] | " | 3.88 |
| | MeOH | Hex-1-yne | 1.08 |

a) n-Propylammonium salt of the complex of polyacrylic acid with rhodium(III).

b) Reaction mixture contains 20 ml $H_2O$.

c) No hydrogenation observed.

d) Substrate concentration, 0.2 mol/l.

e) Triethylammonium salt of the complex of polyacrylic acid with rhodium(III).

carbonyl and aromatic groups.

Glpc analysis of the organic reaction products arising from hex-1-ene indicated that n-hexane was produced. Small amounts of isomerization products during hydrogenation of alkenes were also found. For example, in the case of hex-1-ene, trans-hex-2-ene (about 5% in maximum value), cis-hex-2-ene (about 1.5% in maximum value), trans-hex-3-ene (about 1.0% in maximum value), and a trace of cis-hex-3-ene were detected in the reaction mixture. However, they were hydrogenated completely to hexane for further hydrogenation. In the case of oct-1-ene, trans- or cis-hex-2-ene as substrate, small amounts of isomerized alkenes were also found during the hydrogenation to alkane.

The catalytic activities of polymer complexes are found to depend on the sort of alkylamines used, notably for the hydrogenation of internal alkenes. For example, as shown in Table 2, the PAA-Rh-TEA complex is much more active than the PAA-Rh-n-PA complex for the hydrogenation of trans-hex-2-ene and mesityl oxide. Using the PAA-Rh-TEA complex as catalyst, however, hydrogen uptake was scarcely observed for the hydrogenation of a bulky internal alkene, α-acetamidocinnamic acid.

The PAA-Rh-n-PA complex hydrogenates more easily dimethylitaconate and mesityl oxide than itaconic acid in contrast with the catalytic behaviors of the silk-rhodium catalyst which is much more active for the hydrogenation of the C=C double bonds in the compounds of the type C=CHCOOH such as maleic acid than for the hydrogenation of the C=C double bonds attached to an ester group or conjugated with a carbonyl group.[3)]

Though the addition of a small amount of water (0-0.2 mol/l) in the reaction mixture caused a slight increase in the rate of hydrogen consumption, the rate decreased considerably when a large amount of water (about 40% in volume) was added to the methanol used as solvent as shown in Table 2. The addition of a small amount of acid (e.g. $CH_3COOH$) to the catalytic system resulted in a slight decrease in the reaction rate.

Preliminary kinetic results, using hex-1-ene as substrate and the PAA-Rh-TEA complex as catalyst at the same conditions of temperature and pressure as given in Table 2 suggest that the reaction is first order in catalyst concentration. The dependence on olefin concentration changes from first order to zero order as the olefin concentration increases.

The visible absorption spectrum of the PAA-Rh-H complex in methanol, $\lambda_{max}(\varepsilon)$

589 mμ (445) and in water, $\lambda_{max}(\varepsilon)$ 588 mμ (402), which was found close to that of rhodium(11) acetate,[4] did not change on the addition of alkenes and/or molecular hydrogen to the solution and remained unchanged throughout the course of the reaction.

The polymer complexes are quite stable and can be stored for a long period (more than half a year) without loss of activity on storage as the methanol solutions, and have a distinct advantage that the presence of oxygen does not cause any marked decrease in catalytic activity. At the completion of hydrogenation of the substrates, the polymer complexes can be easily recovered in the solution or in the solid state, and reused without any appreciable loss in activity.

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