Asymmetric Hydrogenation of C=O Double Bond with Modified Raney Nickel. XIV

Yoshiharu Izumi and Toshio Ninomiya

Division of Organic Chemistry, Institute for Protein Research, Osaka University, Kita-ku, Osaka

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In the course of the studies of the asymmetric hydrogenation reaction, many kinds of optically-active amino and hydroxy acids have been used as the modifying reagents of Raney nickel catalysts.[1] It has been found that two functional groups, carboxyl and amino or hydroxy groups, are essential in a modifying reagent in order to produce a strong asymmetric activity of the catalyst; that is, the derivative formation of these functional groups of modifying reagents, for example, the acylation of the amino and hydroxy groups or the esterification of carboxyl groups, gives a catalyst which has a lower asymmetric activity than the catalyst modified with the original amino or hydroxy acids.[2] This fact and the physical and physicochemical evidence suggest that the carboxyl and amino or hydroxy groups of the modifiying reagents take part in the binding to the catalyst by chelation, so it seems that these functional groups are indispensable to the adsorption of the modifying reagents on the catalyst surface.

When the metal amino acid chelates are used as the modifiying reagents, all the amino acid molecules on the catalyst surface can adsorb as nickel chelates, so the metal amino acid chelates are expected to have special properties as modifying reagents.

In the present experiment the abilities of the metal chelates of several optically-active amino acids used as modifying reagents were tested. These investigations were carried out with catalysts modified with aqueous or methanolic solutions; the results are summarized in Table 1.

Table 1. Asymmetric activities of the catalysts modified with metal chelates

Modifying solution	$[\alpha]_D^{20}$ of methyl 3-hydroxybutyrate
$[Ni(L\text{-}Val)_2]\cdot 2H_2O$ in MeOH (1% soln.)	−4.21
$[Ni(L\text{-}Ala)_2]\cdot 4H_2O$ in MeOH (1% soln.)	−0.18
$[Ni(L\text{-}Ala)_2]\cdot 4H_2O$ in H_2O (1% soln.)	+0.86
$[Cu(L\text{-}Ala)_2]$ in H_2O (1% soln.)	−0.50
$[Ni(L\text{-}Glu)]\cdot 2H_2O$ in H_2O (1% soln.)	−4.00
L-Val in H_2O (2% soln.)	−2.31[*1]
L-Ala in H_2O (2% soln.)	+1.08[*1]
L-Glu in H_2O (2% soln.)	−3.46[*2,*3]

Substrate: methyl acetoacetate 0.15 mol
Hydrogenation temperature: 60°C
Modifying temperature: 0°C

[*1] Y. Izumi, M. Imaida, H. Fukawa and S. Akabori, This Bulletin, **36**, 155 (1963).

[*2] Y. Izumi, M. Imaida, H. Fukawa and S. Akoabri, *ibid.*, **36**, 21 (1963).

[*3] Obtained at pH 5.0.

Three points are noticeable in Table 1. The first is the fact that the asymmetric activities of the catalysts modified with the metal chelates of the optically-active amino acids are rather higher than those modified with their original amino acids. The second is the fact that the asymmetric activity depends on the solvent used in the modification of the catalyst; that is, the aqueous solution and the methanolic solution of $[Ni(L\text{-}Ala)_2]\cdot 4H_2O$ give an opposite asymmetric direction to the catalyst. The third is the finding that the modification with the aqueous solution of $[Cu(L\text{-}Ala)_2]$ gives the catalyst with an asymmetric direction opposite to that of the catalyst modified with the aqueous solution of $[Ni(L\text{-}Ala)_2]\cdot 4H_2O$.

The detalis of this investigation will be published after the descriptions of our physical and physicochemical investigations of the adsorption of amino acids on the nickel surface.

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1) Part XII of this series: Y. Izumi, S. Tatsujmi and M. Imaida, This Bulletin, **42**, 2373 (1969); Part XIII: Y. Izumi, S. Tatsumi, M. Imaida and K. Okubo, *ibid.*, **43**, 566 (1970).

2) Y. Izumi, M. Imaida, H. Fukawa and S. Akabori, This Bulletin, **36**, 155 (1963).