SHORT COMMUNICATIONS

Asymmetric Hydrogen with Modified Raney Nickel. VII

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It has been reported from our laboratory[1] that Raney nickel catalyst, modified with aqueous solutions of optically active 2-amino and 2-hydroxycarboxylic acids, shows an asymmetric hydrogenation activity in the hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate, and that optically-active dihydroxy dicarboxylic acids, such as D- or L-tartaric acid, and their *C*-alkyl-substituted derivatives are very effective in the asymmetric modification.

The present paper will describe the asymmetric activity of Raney nickel modified with (+)-1, 2-dihydroxycyclohexane-1, 2-dicarboxylic acid,* which is a sort of *C, C'*-disubstituted tartaric acid. The asymmetric activity of the catalyst in the hydrogenation of methyl acetoacetate to methyl 3-hydroxybutyrate was measured as described in a previous paper.[1]

When Raney nickel was modified at 0°C with an aqueous solution of the acid, its asymmetric activity was greatly influenced by the pH of the modifying solution, as is shown in Fig. 1, this influence being quite different from those of catalysts obtained on modifications with tartaric acid, *C*-methyl- and *C, C'*-dimethyltartaric acid.[1] Optimum asymmetric activities were observed at pH 5—7; this pH range approximately corresponds to the pH-jumping region of the neutralization curve of the acid, as is shown in Fig. 2. However, there was a very great diminution in activity at pH values below pH 5. It is likely that both carboxyl groups of the modifying reagent are adsorbed upon the nickel metal under acidic conditions, while at pH 5—7, one of them is desorbed completely from the metal and forms a massive steric hindrance, which then regulates the approach of methyl acetoacetate to the catalyst. Further details will be reported in the near future.

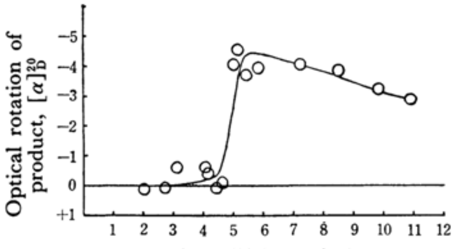

Fig. 1. Modification with (+)-1, 2-dihydroxycyclohexane-1, 2-dicarboxylic acid.

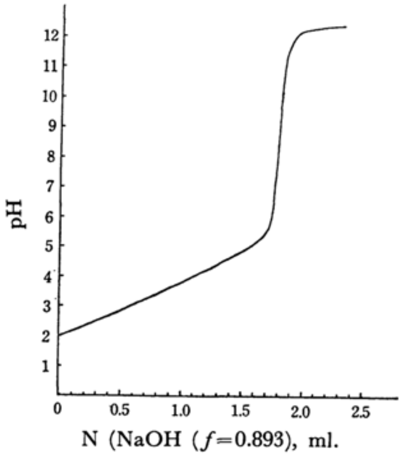

Fig. 2. Neutralization curve of 1% acid solution with N NaOH.

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* The preparation of this hydroxy acid will be reported in this Bulletin in the near future.

1) Part V; Y. Izumi, S. Tatsumi, M. Imaida, Y. Fukuda and S. Akabori, This Bulletin, **38**, 1206 (1965); Part VI; Y. Izumi, S. Tatsumi, M. Imaida, Y. Fukuda and S. Akabori, ibid., in press.