Selective *cis* Hydrogenation of *o*-Xylene and 1,2-Dimethylcyclohexene over Osmium and Iridium Catalysts

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Detailed studies by Siegel and his coworkers[1] on the stereochemistry of hydrogenation of isomeric xylenes and their tetrahydro derivatives indicated that a considerable amount of *trans* isomer was contained in the products from hydrogenation of isomeric xylenes with Adams platinum catalyst and also that desorption of the tetrahydro derivatives from the catalyst surface would be responsible for the formation of the *trans* isomer. Actually, the presence of such desorbed intermediates in the hydrogenation products has later been observed by Hartog and Zwietering[2] with nickel, rhodium and ruthenium catalysts and also by Siegel *et al.*[3] with platinum and rhodium catalysts.

The *trans* isomer was also formed in a considerable amount (18.2% at 25°C under 1 atm in acetic acid) in the platinum-catalyzed hydrogenation of 1,2-dimethylcyclohexene[4] which is expected to yield only *cis*-1,2-dimethylcyclohexane by simple *cis* addition of hydrogen.

In the study of the stereochemistry of hydrogenation of *o*-xylene and its tetrahydro derivatives with other platinum metals, it has been found that hydrogenation of *o*-xylene and 1,2-dimethylcyclohexene with osmium and iridium catalysts yield *cis*-1,2-dimethylcyclohexane with high stereospecificity. Thus, formation of the *trans* isomer was only 3.2 and 1.4% when *o*-xylene was hydrogenated over osmium and iridium catalysts in isopropyl alcohol at 25°C under one atmosphere of hydrogen.[5] The *trans* isomer was formed even in a smaller amount in the hydrogenation of 1,2-dimethylcyclohexene (1.9 and 1.3% in isopropyl alcohol and 1.4 and 1.1% in *t*-butyl alcohol, respectively with osmium and iridium metals). It is to be noted that formation of the *trans* isomer (15.0 and 17.6%) in hydrogenation of 2,3-dimethylcyclohexene with osmium and iridium catalysts as much as with the other platinum metals. Hydrogenation of *m*- and *p*-xylene with osmium and iridium catalysts also gave the *trans* isomer in a much smaller amount than with other platinum metals (9.6 and 10.3% for *m*-xylene; 18.3 and 11.1% for *p*-xylene), although the hydrogenation was less stereospecific than in the case of *o*-xylene.

The selective-formation of *cis*-1,2-dimethylcyclohexane from *o*-xylene may be explained either by selective formation of 1,2-dimethylcyclohexene as the intermediate or by only slight desorption of the intermediate 2,3-dimethylcyclohexene from the catalyst surface. The maximum amounts of 1,2- and 2,3-dimethylcyclohexene in the reaction mixture during the course of the hydrogenation over iridium were only 0.3 and 0.02%, respectively.[6] Only a slight extent of the desorption of 2,3-dimethylcyclohexene formed on the catalyst surface will explain the selective formation of *cis* isomer. The results seem to indicate that the *cis* addition of hydrogen to unsaturated hydrocarbons during a single period of residence on the catalyst surface may largely occur over osmium and iridium catalysts.[7]

The catalyst metals used in this study were prepared by the reduction of corresponding metal hydroxides (Ru, Rh, Ir) or metal oxides (Os) in water followed by a thorough washing with distilled water.

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[1] For references, see S. Siegel, *Advan. Catal.*, **16**, 123 (1966).

[2] F. Hartog and P. Zwietering, *J. Catal.*, **2**, 79 (1963).

[3] S. Siegel, V. Ku and W. Halpern, *ibid*, **2**, 348 (1963); S. Siegel and V. Ku, Proc. 3rd Intern. Congr. Catalysis, North-Holland Publishing Company, Amsterdam (1965), p. 1199.

[4] S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082 (1960).

[5] Yamamoto *et al.* reported that ruthenium gave the least amount of *trans* isomer in the vapor phase hydrogenation of *o*- and *p*-xylene with Group VIII metal catalysts other than osmium [(*Chem. Pharm Bull.* (Tokyo), **15**, 752 (1967)].

[6] The maximum amounts of 1,2- and 2,3-dimethylcyclohexene in hydrogenation of *o*-xylene were 3.9 and 1.0% over ruthenium catalyst and 0.84 and 0.18% over rhodium catalyst. *Cf.* Refs. 2 and 3.

[7] It was reported that only 2% of *trans*-decalin was formed in deuteration of $\Delta^{9,10}$-octalin with an iridium-carbon catalyst at 25°C under 360 to 400 psig deuterium, while hydrogenation of tetralin with the same catalyst gave 7.5% of *trans*-decalin at 25°C under 1000 psig hydrogen [A. W. Weitkamp, *Advan. Catal.*, **18**, 1 (1968)].