

β -CYCLODEXTRIN AND HYDRIDOPENTACYANOCOBALTATE CATALYZED SELECTIVE HYDROGENATION OF α,β -UNSATURATED ACIDS AND THEIR DERIVATIVES

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Summary: Hydrogenation of the double bond of α,β -unsaturated acids, esters, anhydrides, amides, and nitriles occurs in good to excellent yields using in situ generated $\text{HCo}(\text{CN})_5^{-3}$, and β -cyclodextrin as the phase transfer catalyst. Hydrolysis of the acid derivative usually accompanies double bond reduction.

One of the most intensively investigated research areas in recent years concerns the influence of β -cyclodextrin on organic reactions¹. Some of these studies have focussed on the use of the cyclic amylose as a phase transfer agent²⁻⁴. Of particular value are those reactions involving metal catalyzed oxidation⁵ and reduction. Concerning the latter, β -cyclodextrin is an effective phase transfer agent for the hydrogenation of conjugated dienes to monoolefins catalyzed by the hydridopentacyanocobaltate anion, the process usually proceeding by 1,2-addition of hydrogen to the diene⁶. Reduction of the double bond of α,β -unsaturated acids and their derivatives is a useful organic transformation. We now wish to report the application of β -cyclodextrin for the $\text{HCo}(\text{CN})_5^{-3}$ mediated hydrogenation of such substrates.

Treatment of cinnamic acid with hydrogen, $\text{HCo}(\text{CN})_5^{-3}$ [generated from CoCl_2 , KCN, KCl, and H_2], 0.9 N KOH, and β -cyclodextrin, for one day at room temperature and one atmosphere, affords 3-phenylpropionic acid in 80% yield [all yields reported herein are of pure, isolated materials]. The ratio of reactant/ $\text{HCo}(\text{CN})_5^{-3}$ / β -cyclodextrin was 1.0/0.2/0.055. Potassium chloride is beneficial for the reaction, as repetition of the cinnamic acid experiment without KCl gave 3-phenylpropionic acid in 49% yield. Note that lower product yields were realized at higher or lower concentrations of base or phase transfer agent.

The hydrogenation reaction was utilized for the reduction of a series of unsaturated acids and their derivatives, and the results are listed in Table 1. Several reactions were accelerated by running them at 70°C rather than at room temperature. The high yield reduction of acrylic acid (81%) and methacrylonitrile (80% - the yield was 16% when no β -cyclodextrin was used) are especially noteworthy, since previous attempts to effect $\text{HCo}(\text{CN})_5^{-3}$ catalyzed hydrogenation of these substrates under homogeneous conditions gave mixtures of monomeric and dimeric products in the case of acrylic acid⁷, while attempts to effect reduction of methacrylonitrile were unsuccessful⁸. Hydrolysis of the nitrile to the acid occurred when methacrylonitrile was reacted at 70°C. 2-Methylpropionic acid was obtained in fine yield by use of methacrylic acid or its methyl ester or amide as reactants. Although the reduction of fumaric acid proceeded in low yield, maleic anhydride and cinnamonitrile afforded reduction products in reasonable yields.

The following general procedure was used: to a stirred mixture of 1.0 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.275 mmol of β -cyclodextrin in 5 mL of 0.9 N KOH was rapidly added (pressure-equalizing dropping funnel), under hydrogen, a 5 mL solution of 0.9 N KOH containing 5.2 mmol of KCN and 2.20 mmol of KCl. After 30 minutes, 5.0 mmol of the substrate was added, and the reaction mixture was stirred under hydrogen [see Table 1 for reaction times and temperatures]. Work-up was effected by neutralization using 10% HCl, followed by extraction with ether. The ether extract was dried (MgSO_4) and distilled, or subjected to rotary evaporation followed by recrystallization.

TABLE 1

β -Cyclodextrin and $\text{HCo}(\text{CN})_5^{-3}$ Catalyzed Reduction of α,β -Unsaturated Acids and Derivatives

Reactant	Reaction time, hr.	Temp., °C	Product, % ^a
Cinnamic acid	24	r.t.	$\text{PhCH}_2\text{CH}_2\text{COOH}$, 80
Acrylic acid	24	70	Propionic acid, 81
Methacrylic acid	24	r.t.	2-Methylpropionic acid, 89
Fumaric acid	48	70	Succinic acid, 23
Maleic anhydride	48	70	Succinic acid, 65
Methyl methacrylate	24	r.t.	2-Methylpropionic acid, 87
Methacrylamide	48	r.t.	2-Methylpropionamide, 22 2-Methylpropionic acid, 19
	24	70	2-Methylpropionamide, trace 2-Methylpropionic acid, 77
Methacrylonitrile	24	70	2-Methylpropionic acid, 80
Cinnamonitrile	24	70	3-Phenylpropionic acid, 51 3-Phenylpropionamide, 21 3-Phenylpropionitrile, 3

^aYields are of isolated, pure products which were identified by comparison of physical and spectral data with authentic materials.

In conclusion, the β -cyclodextrin - $\text{HCo}(\text{CN})_5^{-3}$ system is an effective one for the hydrogenation of α,β -unsaturated acids and their derivatives affording products in good to excellent yields. The reaction occurs under mild conditions, and is simple in execution and work-up.

Acknowledgement

We are grateful to the Natural Sciences and Engineering Research Council of Canada, and to British Petroleum, for support of this research.

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