HYDROGENATION OF VINYLPYRIDINES AND STYRENE IN THE PRESENCE OF THE PALLADIUM CHLORODIMETHYLSULFOXIDE COMPLEX

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The rate of hydrogenation of the vinyl group of α-, β-, and γ- vinylpyridines decreases as its distance from the nitrogen atom increases in the presence of the palladium chlorodimethylsulfoxide complex. In binary mixtures of these vinylpyridines, the γ- isomer is reduced before the other two isomers.

It has been established that the adsorbability of α-, β-, and γ-vinylpyridines on Raney nickel increases in the same order in which the rate of hydrogenation of their vinyl groups decreases [1, 2]. It seemed of interest to ascertain the dependence of the reactivity of the vinyl group on the position in the pyridine ring under conditions of homogeneous hydrogenation. The palladium chlorodimethylsulfoxide complex was used as the catalyst, inasmuch as it has been established that this catalyst is highly active and stable in hydrogenation reactions of olefins [3].

Under the selected conditions, only the vinly groups of vinylpyridines and styrene are hydrogenated; their aromatic rings are not involved. The reaction proceeds at a high rate and is zero order with respect to the compound undergoing hydrogenation (Fig. 1). The acceleration of the reaction that is observed in the first 1-2 min is associated with an increase in the concentration of the hydride formed during contact of the starting complex with hydrogen. This is confirmed by the fact that the subsequent weighed amounts of vinylpyridine (or styrene) that are added to the reaction mixture are hydrogenated from the very start at a constant rate without acceleration. The decrease in the rate of hydrogenation of the vinylpyridines does not exceed 5% when the catalyst is used again. A comparison of these results with the results obtained in [3] shows that even in the presence of a homogeneous catalyst, the C = C bond activated by conjugation with the aromatic ring is reduced at a considerably higher rate than the C = C bond of an olefin. The hydrogenation of the vinyl pyridine is inhibited to only a slight degree by the reaction product, i.e., the nitrogen atom of ethylpyridine presents almost no interference to coordination of the vinyl group of the vinylpyridine molecule in the catalyzing complex. It also follows from Fig. 1 that the rate of hydrogenation of the C = C bond of α-, β-, and γ-vinylpyridines depends on the position of the vinyl group in the pyridine ring and decreases in the order α-vinylpyridine > β-vinylpyridine, γ-vinylpyridine. > styrene. The vinylpyridine molecule is apparently coordinated not only with the vinyl group but also with the nitrogen atom. All of the vinylpyridines are reduced at a higher rate than styrene, and are saturated considerably ahead of styrene in binary mixtures with it. Under the conditions of both homogeneous catalysis and heterogeneous catalysis [1, 2], the individual γ-vinylpyridine is reduced more slowly than its α-isomer, but its hydrogenation occurs in advance in a binary mixture. γ-Vinylpyridine is apparently more strongly coordinated in the palladium com-

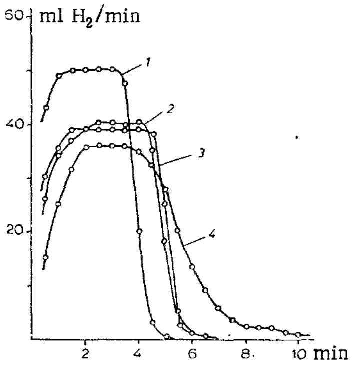

Fig. 1. Kinetic curves of the hydrogenation of α- (1), β- (2), and γ-vinylpyridines (3) and styrene (IV).

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plex during activation. In analogy with [2], it can be assumed that the vinyl group in the α-position creates steric hindrance to coordination of α-vinylpyridine by the nitrogen atom, and the competitive effect of the latter is therefore weakened. A vinyl group in the γ-position presents less hindrance to coordination of the γ-vinylpyridine molecule by the nitrogen atom, as a consequence of which, the possibility of coordination of hydrogen or of the vinylpyridine molecule at the vinyl group decreases, and the reaction is retarded.

EXPERIMENTAL

The compounds were hydrogenated in a glass, long-necked hydrogenation flask set in motion with a mechanical mixer (400-600 rpm) at 20° and hydrogen at atmospheric pressure. A 0.8-g sample of the compound to be hydrogenated and 0.025 g of the palladium complex in 20 ml of dimethyl sulfoxide were used in the experiment; hydrogen, the consumption of which was measured with a burette, was fed into the reaction vessel. The composition of the catalyzate was determined by gas–liquid chromatography with a 2 m by 4-mm column at 120°. The stationary liquid phase was polyethylene glycol-4000 (15%) on Chromosorb W with 1% NaOH. The detector was a catharometer.

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