UDC 542.941.4 + 547.74.82.83

LIQUID PHASE HYDROGENATION OF SOME HETEROCYCLIC NITROGEN COMPOUNDS OVER RUTHENIUM CATALYSTS

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 2, pp. 239-242, 1966

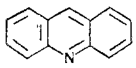
Results are given for the hydrogenation of some heterocyclic nitrogen compounds (pyrrole, pyridine, indole, quinoline, and acridine) and certain derivatives of them in the liquid phase under pressure, in the presence of ruthenium catalysts. The results obtained indicate that these catalysts are very effective, making it possible to obtain high yields of the corresponding saturated compounds. In the cases of quinoline and acridine, depending on the temperature, double bonds in the polycyclic systems can be selectively hydrogenated.

Catalytic hydrogenation of heterocyclic nitrogen compounds (pyrrole, pyridine, quinoline, etc) gives valuable products, which find application in preparation of special dyes, pharmaceutical preparations, solvents, some kinds of polymers, etc (see, for example, [1, 2, 3]).

The literature contains relatively little information about methods of hydrogenating heterocyclic nitrogen compounds. Still it is known that many of them are rather difficult to hydrogenate, that drastic conditions and active catalysts are needed, and that in several cases hydrogenation is complicated by side reactions.

Table 1

Hydrogenation of Some Heterocyclic Nitrogen Compounds over Ruthenium Catalysts

Starting material	Catalyst	Run temp., °C	Initial hydrogen pressure atm	Reaction product	Yield, %
Pyridine	RuO_2	70	85	Piperidine	97
	Ru/C	80	110	″	89
	Ru/silica gel	100	95	″	98
α-picoline	RuO_2	100	97	α-Pipecoline	97
Ethyl nicotinate	RuO_2	150	75	Ethyl hexahydronicotinate	60
Quinoline	RuO_2	120	93	Decahydroquinoline	98
	Ru/silica gel	140	90	Tetrahydroquinoline	97.5
Acridine 	RuO_2	100	90	Dihydroacridine	98.5
	RuO_2	180	110	Tetradecahydroacridine	60
Pyrrole	RuO_2	110	105	Pyrrolidine	80.6
Indole	RuO_2	150	80	Octahydroindole	78.5

The first successful work on the hydrogenation of pyrrole was that of Adkins [4], who obtained about a 45% yield of pyrrolidine using a nickel catalyst at 180°. No positive results were obtained when attempts were made to hydrogenate pyrrole homologs over platinum and palladium. Rhodium [6] proved to be an effective catalyst, making it possible to obtain almost quantitative yields of pyrrolidine.

A more detailed study was made of the hydrogenation of pyridine and its derivatives. Pyridine could be successfully hydrogenated over nickel catalysts using temperatures about 200° C and hydrogen pressure about 200 atm [7]. There is information regarding hydrogenation of pyridine and its homologs over platinum catalysts under mild conditions [8]. Investigation of rhodium catalysts showed that pyridine and its derivatives are hydrogenated by them under mild conditions, but that they are rapidly poisoned [9].

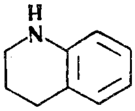
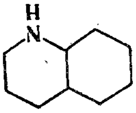
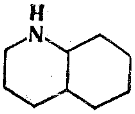
There are only a few papers [10-13] dealing with the hydrogenation of quinoline, acridine, and indole, and in these it is mentioned that quite drastic conditions are needed even when using active catalysts such as Raney nickel and platinum. Usually the yields of hydrogenation products are low.

Some papers indicate an undoubted potential value for ruthenium catalysts. For example, high yields of piperidine and its homologs were obtained by hydrogenating the corresponding pyridine over a ruthenium catalyst [12].

Research carried out by some of the present authors [14-17] showed that ruthenium catalysts are generally quite effective for hydrogenating organic nitrogen compounds. It is known that generally a nitrogen functional group in a compound has an adverse effect on the activities of nickel, platinum, and a number of other hydrogenation catalysts.

Table 2

Selective Hydrogenation of Quinoline over RuO_2

Temperature, °C	Initial hydrogen pressure	Reaction product	n_D^{20}	Yield, %
80	82		1.5935	97.5
120	90		1.4920	98.0
200	105		1.4930	99.0

In the course of systematic research on the catalytic properties of ruthenium in progress at Saratov State University, methods of making some catalysts were developed, and their behaviors when hydrogenating many aromatic compounds, and heterocyclic nitrogen and oxygen compounds investigated [14-23].

The present paper deals with liquid-phase hydrogenation of some heterocyclic nitrogen compounds (pyrrole, pyridine, quinoline, etc) over ruthenium catalysts [18, 20], and the experimental results obtained are set out in Table 1.

Hydrogenation of pyridine group compounds. It is seen from Table 1 that the ruthenium catalysts used are highly active for hydrogenation of pyridine, α-picoline, and ethyl nicotinate. Thus even at a temperature of the order of 50°, pyridine is hydrogenated to piperidine. A higher temperature, 80-100°, makes it possible to prepare piperidine quickly, and in quantitative yields.

α-Picoline is smoothly hydrogenated to α-pipecoline, but as was to be expected, introduction of a methyl group hinders hydrogenation, and cuts its speed.

Some experiments on the hydrogenation of ethyl nicotinate made it possible to show that the presence of an ester group hinders pyridine ring hydrogenation even more, the reaction rate starting to be appreciable only at 150°.

Quinoline hydrogenation. Hydrogenation of quinoline takes place at various temperatures with a high degree of selectivity. Thus at 80-90°, tetrahydroquinoline is formed, above 120°, only decahydroquinoline, and raising the temperature to 200° does not result in any practical decrease in the decahydroquinoline yield (Table 2).

Hydrogenation of quinoline over a 5% ruthenium on silica gel required higher temperatures and was less selective. Thus at 90-140° the main product was tetrahydroquinoline contaminated with quinoline, while at much higher temperatures it was decahydroquinoline.

Acridine hydrogenation. Preliminary experiments showed that acridine is hydrogenated over ruthenium dioxide at 100° to a quantitative yield of acridane. The solvent used was methanol. Higher temperatues lead to formation of a mixture comprising acridine at various stages of reduction. Tetrahydroacridine is obtained in adequately high yield (60%) above 170°.

Pyrrole hydrogenation. Pyrrole was hydrogenated over RuO_2 and Ru/C catalysts. The yield of pyrrolidine attained 80%. Here ruthenium catalysts were rather more active than platinum and palladium ones, so that ruthenium catalysts can be regarded as the ones to use for hydrogenating pyrrole and its derivatives.

Indole hydrogenation. Experiments on liquid phase hydrogenation of indole, carried out using ruthenium dioxide, showed that at 150° indole is readily converted in 78.5% yield to perhydroindole.

Experimental

Preparation of catalysts [14, 18, 19]. Ruthenium dioxide was prepared by decomposing the hydroxide of quadrivalent ruthenium at high temperature. $Ru(OH)_4$ was prepared from K ruthenate. The 5% Ru/C and 5% Ru/silica gel catalysts were prepared by applying ruthenium hydrochloride from aqueous ethanolic solution to active charcoal or silica gel.

Typical hydrogenation procedure. The compound to be hydrogenated was charged, with or without solvent, into a rotating autoclave, followed by the catalyst, and then the hydrogen. The particular temperature was maintained with an EPV-1-11A electronic potentiometer. The hydrogen uptake was read on a MKD type manometer. When the calculated quantity of hydrogen had been taken up, the autoclave was emptied, the catalyst filtered off, and after distilling off the solvent, the products distilled under reduced pressure. Reaction products were identified by boiling points, refractive indices, and, in isolated cases, by elementary analytical data and IR spectroscopy.

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7 December 1964

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