584. *Hydrogenation of Oximes with Platinum Metal Catalysts.*

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The rate of hydrogenation of cyclohexanone oxime in presence of various platinum catalysts in several solvents has been determined. The course of the hydrogenation is discussed.

THIS paper deals with the low-pressure hydrogenation of oximes in presence of palladium, platinum, rhodium, and ruthenium on carbon of high surface area. Low-pressure hydrogenation of oximes has been reported only infrequently[1] and confined mainly to Raney nickel catalysts. No report comparing the rate of reduction of an oxime by various platinum metal catalysts has been made.

In Table 1 the rates of hydrogenation of cyclohexanone oxime in various solvents are given. All reactions were continued, except when the rate was very slow, until two mols. of hydrogen had been absorbed, whereupon the reaction generally ceased abruptly. No cyclohexane was formed under the conditions used, except in methanol. With a few interesting exceptions the rates were of zero order over almost the entire reaction, or in very slow reactions, over the smaller range examined. This order implies a simplicity that does not, in fact, exist. In water, the major product is cyclohexanol and not cyclohexylamine. Despite the complexity of the reaction, the observed rate must be the rate of reduction of the oxime, and not of some intermediate product. The alcohol arises by hydrolysis of the imine and not by hydrolysis of the oxime and reduction of the ketone. Oximes are hydrolysed very slowly in water,[2] and in the time required for complete reduction

TABLE 1. *Rate of hydrogenation (ml. of* H_2 *per min.) of cyclohexanone oxime* (400 *mg.*) *in various solvents* (100 *ml.*) *with various catalysts* (300 *mg.*) *at* 25°.

Solvent	5% Pd	5% Rh	5% Ru	5% Pt
AcOH	0·5	1·9	0·2	8·0
Water	0·5	10·2	1·5, 5·2 *	†
0·5M-NaOH, aq.	0·5	22·8	3·2, 8·0 *	†
0·5M-HCl, aq.	0·45	2·1	0·2	24·0
Methanol	0·7	5·3	0·3	0·7
Dioxan	0	0	0	0

* The first and second portion respectively of the hydrogenation.
† Catalyst poisoned rapidly.

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[1] Iffland and Teh-Fu Yen, *J. Amer. Chem. Soc.*, 1954, **76**, 4180; Buckley, *J.*, 1947, 1494.

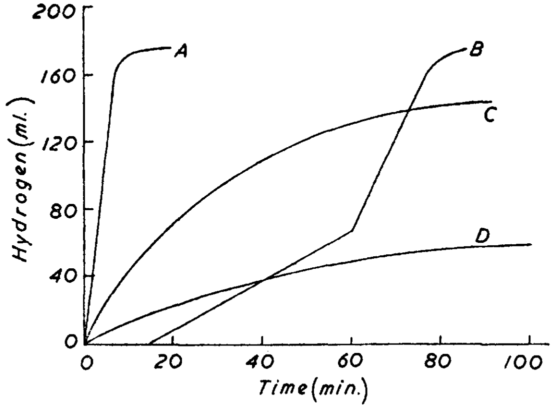
[2] Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937.

no measurable amount of hydroxylamine, determined by titration, is formed. Cyclohexanol was not formed by catalytic dehydrogenation of cyclohexylamine to the imine,[3] for under the conditions of the experiments cyclohexylamine was recovered unchanged.

The effect of solvent on reaction rate is marked. Dioxan, a solvent frequently used for high-pressure reductions, is worthless at low pressures. In methanol the rate is convenient only when rhodium is the catalyst, and in acetic acid only when it is platinum.

In methanol a slow, partial hydrogenolysis occurred that ceased before the third mol. of hydrogen was absorbed. Cyclohexyl alcohol and cyclohexylamine both resisted hydrogenolysis under the conditions employed. Cyclohexanone ketal, a probable product of the reaction, did undergo a slow hydrogenolysis. Although ketones do not usually form ketals under these conditions,[4] cyclohexanone (and probably its imine) form a ketal readily with methanol.[5]

The rate of hydrogenation in water is sharply dependent on pH, except with palladium catalysts. In neutral solution hydrogenation with platinum begins fast but becomes slower and virtually ceases after 75% of the theoretical absorption. The decline in rate is probably due to poisoning by cyclohexylamine. In acid solution, where the amine could be converted into the ammonium salt, the reaction is fast and of zero order. The rate curve was virtually unchanged when 400 mg. of cyclohexylamine hydrochloride were added initially, but the catalyst was poisoned immediately when 300 mg. of the free amine were added (see Figure). A similar observation has been made with hydrogenation of unsaturated amines over platinic oxide.[6]



Hydrogenation of cyclohexanone oxime.
A, Pt *in* 0·6N-HCl.
B, Ru *in* H_2O.
C, Pt *in* H_2O.
D, Pt *in* H_2O plus *cyclohexylamine.*

The activity of a rhodium catalyst is also affected greatly by pH, but the reason is less clear in this case. The absorption rate changes from 2·1 ml./min. in 0·5N-hydrochloric acid to 22·8 ml./min. in 0·5N-sodium hydroxide. Oximes behave as both acids and bases,[2] and the change in rate may reflect a change in the structure of the ion undergoing reduction. A parallel, though smaller, change in rate with pH has been observed in the reduction of nitrobenzene with rhodium,[7] and it was suggested then, to account for this pH dependence, that rhodium ionizes hydrogen heterolytically.

Palladium catalysts show very little variation in rate with changing environment, and in no case are they particularly active for reduction of oximes. The rate of reduction of nitrobenzene by palladium, very fast, is also insensitive to pH, which led to the suggestion [7] that palladium, unlike rhodium, ionizes hydrogen homolytically.

[3] Yura, Nakao, and Goto, *J. Chem. Soc. Japan*, 1952, **55**, 337.

[4] Post, " The Chemistry of Aliphatic Orthoesters," ACS Monograph 92, Reinhold Publ. Corp., New York, 1943, chapter 3.

[5] McCoy, Baker, and Gohlke, *J. Org. Chem.*, 1957, **22**, 1175.

[6] Devereux, Payne, and Peeling, *J.*, 1957, 2845.

[7] Hernandez and Nord, *Experientia*, 1947, **3**, 12.

Ruthenium catalysts exhibit a rather unusual rate curve (see Figure). The rate is essentially of zero order until reaction is about 60% complete, then the curve changes abruptly to a faster zero-order one. This reaction was repeated six times with varying ratios of catalyst to substrate and with different catalysts. The break-point always occurred at 60—63% completion. Sometimes, but not always, there was an initial induction period, as indicated in the Figure. Once this induction period lasted 180 minutes. Variable, and occasionally lengthy, induction periods are characteristic of the ruthenium catalyst and have caused many excellent ruthenium catalysts to be discarded. There seems to be no correlation between the length of the induction period and the rate of hydrogenation (unpublished results from our laboratories).

Although most of the reductions lead to zero-order rate curves, hydrolysis occurs concomitantly with hydrogenation and cyclohexanol usually predominates in the products. In Table 2 the yield of cyclohexylamine in various solvents is given. Those conditions that lessen the opportunity for hydrolysis of imine give increased yields of amine. Ammonia has been used previously to increase the yield of primary amine at the expense of secondary amine,[8] but in the present work its beneficial effect seems to arise mostly from its competition with water in nucleophilic attack on the imine: $\mathrm{X{:}NH} + \mathrm{NH_3} \longrightarrow \mathrm{X(NH_2)_2} \xrightarrow{\mathrm{H_2}} \mathrm{NH_3} + \mathrm{X}\left\langle {}^{\mathrm{H}}_{\mathrm{NH_2}} \right.$. The yield of secondary amine was in all cases less than a few per cent. Surprisingly, the yield of secondary amine seemed equally as large in the dilute solutions of the kinetic experiments, during which the dicyclohexylamine formed a complex with cyclohexanol and floated on top of the solution as white flakes, m. p. 48°.[9] The lack of dependence of yield of secondary amine on the concentration of the reactants suggests that alkylation occurs on a saturated catalyst surface. This suggestion has been made to account for the fact that in the hydrogenation of nitriles the yield of secondary amine is increased only slightly by prior addition of primary amine to the nitrile solution.[10]

TABLE 2. *Yield (%) of cyclohexylamine formed from cyclohexanone oxime (10 g.) in various solvents with rhodium catalysts (5 g.; 5% on carbon).*

Solvent	Yield	Solvent	Yield
Water, 400 ml.	25	Methanol, 100 ml.	48
0·125M-NaOH, 400 ml.	29	Ethanol, 100 ml.	55
Conc. aq. NH_3, 400 ml.	77	Methanol, saturated with NH_3, 100 ml. ...	82

EXPERIMENTAL

The catalysts were commercial preparations manufactured by Engelhard Industries of 5% reduced metal on carbon of high surface area (Norit). Ruthenium catalysts were reduced immediately before use by shaking them in solvent under hydrogen (1 atm.) for 1 hr., after which the flask was flushed with nitrogen and the substrate added. The other catalysts were used directly as received. Electrolytic hydrogen and " reagent grade " solvents were used without further purification. Cyclohexanone oxime, m. p. 88°, was purified by recrystallization from ethanol.

In the rate measurements, the hydrogen consumption was measured over a small change in pressure by a differential manometer with sensitive strain gauges and an electronic recording potentiometer. Rate measurements were made at room temperature and an initial pressure of 1 atm. with 300 mg. of catalyst, 400 mg. of substrate, and 100 ml. of solvent. During the experiment the pressure fell 5—10%. Agitation by shaking was sufficiently vigorous to eliminate contribution of hydrogen transport to the reaction rates.

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[8] Reeve and Christian, *J. Amer. Chem. Soc.*, 1956, **78**, 860.

[9] Winans, *ibid.*, 1939, **61**, 3591.

[10] Juday and Adkins, *J. Amer. Chem. Soc.*, 1955, **77**, 4559.