[CONTRIBUTION NO. 31 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. VI. Promoter Action of Platinic Chloride on Raney Nickel Catalyst

BY EUGENE LIEBER AND G. B. L. SMITH

Introduction

While investigating the effect of small amounts of impurities on the activity of the Raney nickel catalyst for the hydrogenation of nitroguanidine,[1] the further results of which will be reported in another paper, it was found that platinic chloride had a very marked enhancing action.

Nickel catalysts have been rather extensively studied with respect to the promoter action obtained when foreign substances are introduced into the catalyst mass and are summarized by Ellis.[2] Combinations of the platinum and nickel group catalysts have received attention as well as platinum and palladium deposited on other metals.[3] Of these Ginsberg and Ivanov[3e] have prepared active catalysts by adding *in situ* solutions of platinum or palladium chloride (the latter as Na_2PdCl_4) to powdered non-catalytically active metals. More recently, Delépine and Horeau[4] have described the enhancement of the activity of Raney nickel catalyst by platinum deposited from a solution of "alkaline platino-chloride" on the Raney nickel. The enhanced activity was manifested (for the reduction of ethyl acetoacetate) only after the addition of alkali.

In the hydrogenation of nitroguanidine it was observed that the addition of small quantities of platinic chloride very greatly increased the rate of reduction. It was in general found that this effect could be extended with even more marked results to other organic types. Table I summarizes these results, the details of which are given in the experimental section.

TABLE I

ADDITION OF PLATINIC CHLORIDE TO RANEY NICKEL

Hydrogen acceptor	Absorption rate, ml. H_2/min. Raney Ni	Raney Ni + $PtCl_4$
Nitroguanidine	28.4	51.4
Castor oil	35.8	125.8
Linseed oil	24.4	67.0
Nitrobenzene	18.4	165.6
Benzaldehyde	10.2	67.6

Experimental

Method.—The catalytic hydrogenations were carried out at one atmosphere pressure and at room temperature; the general procedure was the same as used previously.[1] The test mixtures were as follows: 5.2 g. (0.05 mole) of nitroguanidine, suspended in water as a solvent, 2.5 g. (or multiple of that quantity) of Raney nickel catalyst or non-catalytic metal powder. Just prior to the beginning of the hydrogenations, varying volumes of an aqueous solution of platinic chloride were added. The hydrogen adsorption rates were followed for a period of thirty minutes.

Concentration of Platinic Chloride.—Keeping the ratio of catalyst to hydrogen acceptor constant, the concentration of platinic chloride was varied from 0.034 to 0.680 g. (0.1 to 2.0 millimoles) per 100 ml. of solvent. The results are summarized graphically in Fig. 1.

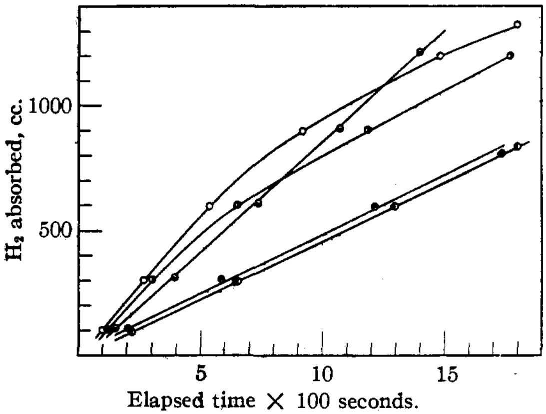


Fig. 1.—Variation in $PtCl_4$ concentration: ● Raney; ○ Raney + 2 millimoles $PtCl_4$; ◑ Raney + 1 millimole $PtCl_4$; ◒ Raney + 0.25 millimole $PtCl_4$; ◐ Raney + 0.13 millimole $PtCl_4$.

Variation in Catalyst Mass.—In this series of experiments the concentration of platinic chloride was maintained at 0.075 g. (0.25 millimole) per 100 ml. of solvent and the ratio of catalyst to nitroguanidine was varied from 0.25 to 1.0. It was found here that the greatest effect was with the smallest ratio of catalyst to nitroguanidine. The effect of adding 0.25 millimole of platinic chloride (48 mg. of platinum) to 0.50 g. of Raney nickel catalyst per gram of nitroguanidine gives a rate of hydrogenation equal to that obtained when the ratio of catalyst to nitroguanidine is 1.12.

The Reaction between Raney Nickel Catalyst and Platinic Chloride.—Certain facts concerning the promoter action of platinic chloride on Raney nickel catalyst are

---

[1] Lieber and Smith, THIS JOURNAL, **67**, 2479 (1935).

[2] Ellis, "Hydrogenation of Organic Substances," 3d ed., D. Van Nostrand Co., New York, 1930.

[3] (a) Dewar and Liebmann, U. S. Patent 1,268,692 (1918); (b) Ueno, *J. Chem. Ind.* (*Tokyo*), **21**, 898 (1918); (c) Paal and Wendisch, *Ber.*, **56**, 4011 (1913); (d) Paal and Karl, *ibid.*, **56**, 3069 (1913); (e) Ginsberg and Ivanov, *J. Russ. Phys.-Chem. Soc.*, **62**, 1991 (1930).

[4] Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935); see *C. A.*, **30**, 1776 (1936). This paper came to the attention of the authors after this article was prepared for publication but before submission to the Editor.

revealed in the following experiments. Absorption of hydrogen in ml. of hydrogen in thirty minutes by 5.2 g. of nitroguanidine in 100 ml. of water and the catalyst (a) 1 millimole (0.337 g.) of platinic chloride alone, (b) an amount of Adams platinum oxide catalyst equal to 0.337 g. of platinic chloride, (c) a mixture of 2.5 g. of Raney nickel and platinum oxide equal to 0.337 g. of platinic chloride, (d) 2.5 g. of Raney nickel catalyst and (e) 2.5 g. of Raney nickel and 0.337 g. of platinic chloride, are (a) 0, (b) 537, (c) 796, (d) 851 and (e) 1222. These data indicate that platinic chloride is without activity and that the addition of Adams catalyst in an amount equal to the platinic chloride does not increase the activity of Raney nickel.

Thirty-four hundredths gram of platinic chloride was added to a suspension of 2.5 g. of Raney nickel catalyst in 100 ml. of water and the mixture was allowed to stand with occasional shaking for forty-five minutes. The mixture became opalescent during the first few minutes of contact but on standing the colloidal material settled and a clear green supernatant solution resulted. The clear solution was decanted, the remaining "catalyst" mass was washed several times by decantation, and the combined solutions were diluted to a volume of 200 ml. The nickel was determined in aliquot portions by weighing as nickel dimethylglyoxime: found 0.23, 0.25 g.; calcd. on the basis of equation

$$3Ni + PtCl_6^{-} + 2H^+ \longrightarrow Pt + 3Ni^{++} + H_2 + 6Cl^- \quad (I)$$

0.20 g. The solution was strongly acid and contained *no platinum*. The catalyst mass treated as described above had an activity *no greater* than the ordinary Raney nickel catalyst without platinum.

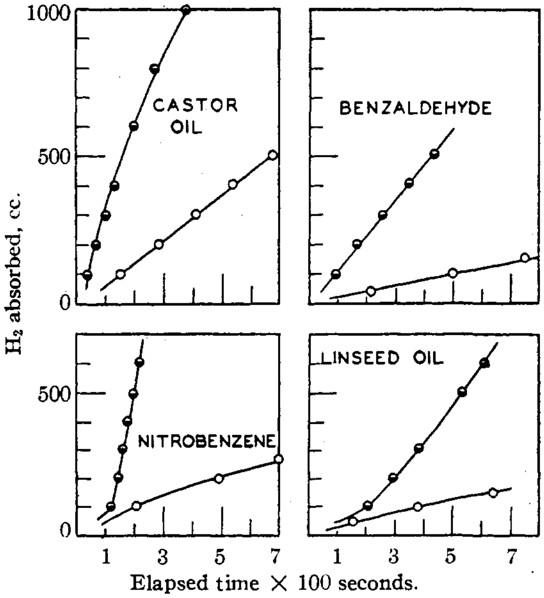


Fig. 2.—Promoted hydrogenations: ○ Raney nickel; ● promoted Raney nickel.

In order to determine the possible effect of the several components present the following experiments were performed. In each case 5.2 g. of nitroguanidine was suspended in 100 ml. of water.

	Catalyst	Adsorption ml. H_2/min.
1	2.5 g. Raney nickel	28.4
2	2.5 g. Raney nickel and 0.34 g. $PtCl_4$ added just before start of reduction	51.4
3	0.34 g. of $PtCl_4$ deposited as Pt on 2.5 g. Raney nickel and catalyst mass washed free of ions	29.0
4	As (3) with addition of 3 millimoles of nickel as Ni^{++}	22.7
5	As (3) with addition of 2 millimoles of HCl	26.6
6	2.5 g. of Raney nickel with 2 millimoles of HCl	5.4
7	2.5 g. of Raney nickel with 1 millimole of Ni^{++}	9.1

The addition of alkali (potassium hydroxide) sufficient to neutralize the acidity, produced in catalyst (2) above, decreased its activity 50–60%.

The nickel catalyst, which consists of nickel dispersed on kieselguhr, was prepared according to the method of Adkins and Cramer[5] and was tested for its catalytic activity with and without the addition of platinic chloride. There was no promotor action due to platinic chloride.

Platinic Chloride and Non-Catalytic Metal Powders.—The non-catalytic metal powders tested comprised Raney alloy (50% nickel), iron, aluminum and tungsten, using 0.337 g. (1 millimole) of platinic chloride the absorption rates obtained in ml. of H_2 per minute were 15.4, 8.0, 13.9 and 0.0, respectively. Using 0.075 g. (0.25 millimole) of platinic chloride with non-catalytic Raney alloy and catalytic Raney nickel the hydrogen absorption rates were 3.0 and 51.4 ml. of H_2 per minute, respectively.

Platinic Chloride Promotor Action on the Hydrogenation of Castor Oil, Nitrobenzene, Benzaldehyde and Linseed Oil.—In this series of experiments the solvent was 100 ml. of 95% ethanol; 0.25 g. of Raney nickel per gram of hydrogen acceptor (except for raw linseed oil where 0.1 g. of Raney nickel per gram of material was used) and 0.075 g. (0.25 millimole) of platinic chloride added just prior to the start of the reduction. The quantities of substances hydrogenated were 25 g. of castor oil, 25 g. of linseed oil, 12.5 g. of nitrobenzene and 10.5 g. of benzaldehyde. The reductions were carried out first with Raney nickel alone and then Raney nickel with platinic chloride. The data are summarized in Fig. 2 and Table I.

Discussion of Results

The action of platinic chloride on Raney nickel catalyst is open to several interpretations. It may be defined as a promoter action based upon the definition of Pease and Taylor[6] as the "activation of a catalyst by a small quantity of a relatively active substance." The examination of the reaction between platinic chloride and Raney nickel shows that we are dealing with reaction (I) and it is possible that the observed rates of hydrogenation are the result of the simultaneous activity of nickel and platinum. However, this re-

---

(5) Adkins and Cramer, THIS JOURNAL, 52, 4349 (1930).

(6) Pease and Taylor, *J. Phys. Chem.*, 24, 241 (1920).

action apparently must take place during the reduction with hydrogen, *i. e.*, the promotor effect is manifested when platinic chloride is added just before the hydrogenation is started. The interpretation of the results is further complicated by the fact that in adding platinic chloride, poisons for the nickel catalyst are added, although it should be pointed out that using non-catalytically active metals, or completely plating out the platinum and removing the poisons resulted in completely reduced activity. Further, the type of catalytically active nickel appears to be a factor. On a weight basis, reduced nickel on kieselguhr is hundreds of times as active as is Raney nickel,[7] however, addition of platinic chloride to such a catalyst under the same conditions as Raney catalyst (temperature, pressure of hydrogen and ratio of catalyst to hydrogen acceptor) had no effect on its activity.

On the other hand, however, the effect is not limited to the hydrogenation of a single substance (nitroguanidine), as is often the case in promoter catalysis. It has, indeed, been applied even more successfully to the hydrogenation of castor oil, linseed oil, nitrobenzene and benzaldehyde.

The application of the Raney nickel–platinic chloride catalyst to the hydrogenation of various types of organic compounds, as well as a more detailed investigation of the effects involved particularly with respect to other noble metal salts, is in progress in this Laboratory and will be reported in a subsequent paper.

Summary

Small amounts of platinic chloride added to Raney nickel catalyst immediately before the beginning of the hydrogenation have a definite and pronounced enhancing action which is not limited to the hydrogenation of nitroguanidine but is apparently applicable to the reduction of many types of organic compounds.

BROOKLYN, NEW YORK RECEIVED MARCH 26, 1936

---

(7) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

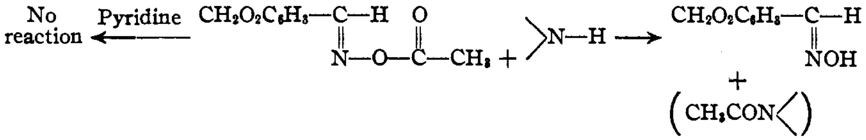
The Reactions of Aldoxime Derivatives with Bases. III. The Reactions of Geometrically Isomeric Acetyl-3,4-methylenedioxybenzaldoximes with Certain Amines

BY CHARLES R. HAUSER AND EARL JORDAN[1]

In continuation of our investigations[2] of the reactions of acyl-aldoximes with bases, a study has been made of the reactions of the two isomers of acetyl-3,4-methylenedioxybenzaldoxime with certain primary, secondary and tertiary amines.

It has been found that when the α-isomer is dissolved in *n*-butylamine, aniline, piperidine or diethylamine, and allowed to stand for a short time, it is converted into the corresponding α-aldoxime in yields of 90–99%; apparently these reactions are quantitative. On the other hand, the acetyl-α-aldoxime may be heated in pyridine solution at 97–100° for an hour and then recovered practically unchanged; also, it is relatively stable in triethylamine solution. The yields of aldoxime and recovered acetyl-α-aldoxime are given in Table I.

The reaction of acetyl-α-3,4-methylenedioxybenzaldoxime with a primary or secondary amine may be represented as an aminolysis,[3] thus[4]



$$\text{No reaction} \xleftarrow{\text{Pyridine}} \begin{array}{l}\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{—C—H}\quad\text{O}\\ \qquad\qquad\quad\;\; \| \qquad\;\; \| \\ \qquad\qquad\quad\;\text{N—O—C—CH}_3\end{array} + \;>\!\text{N—H} \longrightarrow \begin{array}{l}\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{—C—H}\\ \qquad\qquad\qquad\quad\;\|\\ \qquad\qquad\qquad\;\;\text{NOH}\end{array} + \left(\text{CH}_3\text{CON}\!<\right)$$

The tertiary amines have no hydrogen atom attached to nitrogen and consequently are not capable of bringing about this reaction. The other possible decomposition, the elimination of acetic acid from the acetyl-α-aldoxime to form nitrile,[5] might occur very slowly in triethylamine solution at the boiling point of the

---

(1) This is from a portion of a thesis presented by Earl Jordan in partial fulfilment of the requirements for the Ph.D. degree at Duke University.

(2) See (a) Hauser and Sullivan, THIS JOURNAL, **55**, 4611 (1933); (b) Hauser and Jordan, *ibid.*, **57**, 2450 (1935); (c) Hauser, Jordan and O'Conner, *ibid.*, **57**, 2456 (1935).

(3) This reaction is analogous to an ammonolysis of an ester; it is possible that the primary or secondary amine attacks the carbonyl group of the acetate, perhaps forming an intermediate addition compound which decomposes to form aldoxime and amide; the latter, however, has not been isolated.

(4) For references to evidence that α-aldoximes have the *syn* configuration, see note 2b.

(5) Although the acetyl-β-aldoxime in the presence of a base eliminates acetic acid to form nitrile much more readily than the α-isomer, it is possible for the latter, under certain conditions, to form nitrile or the corresponding acid; see reference 2b.