The Hydrogenation of Nitro Compounds with Raney Nickel Treated with Chloroplatinic Acid and with Alkali[1]

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In a series of studies of hydrogenation with Raney nickel, Smith and co-workers[5-8] have shown that chloroplatinic acid added to a Raney nickel–acceptor–ethanol mixture just prior to the introduction of hydrogen is a more effective promoter of the liquid phase hydrogenation of nitro compounds in the Parr hydrogenator than is platinized Raney nickel prepared by the method of Delépine and Horeau.[9]

Smith, et al., also found that a small amount of alkali retarded the activity of Raney nickel in the hydrogenation of nitrobenzene and the other neutral nitro compounds that they studied and to promote the activity of this catalyst in the reduction of certain nitroanilines and nitrophenols.

Furthermore, Reasenberg, Lieber and Smith,[7] found the ortho compounds to be reduced more readily by Raney nickel than were the corresponding meta and para isomers.

It was the purpose of this research to extend the study of the hydrogenation of nitro compounds, and by so doing to obtain additional information as to the influence of molecular structure upon the reactivity with Raney nickel, and upon Raney nickel treated with chloroplatinic acid and with alkali.

Experimental

The apparatus, catalyst, general procedure and method of expressing results was that used by the previously mentioned workers.[5-8] The equipment contained approximately 400 ml. of hydrogen at atmospheric pressure and room temperature. This volume was increased to 600 ml. as each charged manometer containing 200 ml. of hydrogen at atmospheric pressure was introduced into the system. Under these conditions the volume changes as well as the slight variations in pressure associated with the measurement of the gas consumed in a manually equalized mercury column are common to each hydrogenation, and is considered a constant factor in the determination of the rate of reaction. The hydrogen acceptor (0.05 mole) was introduced into the reaction chamber with the aid of a small portion of 95% ethanol. The weighed catalyst was then

added and in certain experiments followed in order by the addition of 0.375 millimole of chloroplatinic acid or 3 millimoles of sodium hydroxide or both and the contents made up to 150 ml. with ethanol. This volume of ethanol was sufficient to dissolve the acceptor completely and constituted one-third of the volume of the reaction chamber. The rate of reaction was followed by recording the time for consumption of successive 200 ml. of hydrogen at atmospheric pressure and room temperature, while the reaction vessel was being shaken at a rate of 190 oscillations per minute.

The weight of catalyst used in each experiment was that amount that would give an average rate of hydrogen consumption of 195 ± 5% ml. per 100 seconds, with nitrobenzene under the conditions described above.

The precision of the catalyst weighing was increased by pressing out the catalyst rapidly between several folds of filter paper and transferring the pressed out catalyst to a small tared beaker containing a small amount of ethanol.

The procedure of adjusting the quantity of catalyst in accordance with its reactivity toward the hydrogenation of nitrobenzene compensated for some variations in the activity of the several catalyst preparations used during the study, and a small decreasing activity observed as the catalyst aged. This weight of catalyst ranged from 3.0 to 3.8 g., and was readily determined by making a few preliminary runs and utilizing the fact that the rate of reaction with nitrobenzene is directly proportional to the amount of catalyst.[10,11]

All hydrogenations were carried out in duplicate. The resultant rate of hydrogenation for each compound was reproducible well within 10%.

The nitro compounds obtained from supply houses as well as those synthesized especially for this study were subjected to a variety of purification procedures before use. In each case the coincidence of the physical constants with the literature values were used as the criteria of purity.

The reaction chamber was meticulously cleaned between each run since it was observed that traces of contaminants such as traces of reaction products and of acids used in cleansing had a significant effect upon the reaction rate.

Under the conditions of these experiments the rate of consumption of hydrogen in the reduction of all of the mononitro and in some of the dinitro compounds is approximately constant throughout each reaction (Fig. 1). As in the case of the previously mentioned papers from this laboratory, the average number of ml. of hydrogen consumed per 100 seconds over the first half of the reaction, termed the "half rate," is used to express the rate of the reaction. Although this rate of absorption of hydrogen is a convenient means of expressing the comparative reactivity, it is also true that any such numerical expression of reactivity is at best only a semi-quantitative term since in these experiments a small temperature rise was usually encountered during each reaction. This temperature rise consisted of a barely detectable increase in the case of the slow reactions and an increase amounting to about 10° in the case of the very fast reactions. These temperature changes are not considered to invalidate the comparison of the relative rates of reaction obtained in these experiments, since the majority of the reactions take place at a characteristic constant rate (Fig. 1).

In the reduction of the polynitro compounds the average rate of hydrogen consumption is of little significance since in these reactions in which the theoretical quantity

(1) Presented in part before the Division of Organic Chemistry at the Pittsburgh meeting of the American Chemical Society, September, 1943.

(2) This paper is abstracted in part from the thesis submitted by Mr. Samuelsen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in June 1943, and (3) in part from two theses submitted by Mr. Garik in partial fulfillment of the requirements for the degree of Batchelor of Science and for the degree of Master of Science, respectively, to the faculty of the Polytechnic Institute of Brooklyn.

(4) U. S. Naval Ordnance Test Station (R. D. & T.), Inyokern, California.

(5) Lieber and Smith, THIS JOURNAL, 57, 2435 (1935).

(6) Lieber and Smith, ibid., 58, 1417 (1936).

(7) Reasenberg, Lieber and Smith, ibid., 61, 384 (1939).

(8) Skolnik, Reasenberg, Lieber and Smith, ibid., 63, 1192 (1941).

(9) Delépine and Horeau, Compt. rend., 201, 1301 (1935); 202, 995 (1936); Bull. soc. chim., [5] 4, 31 (1937).

(10) E. Lieber, Thesis, Polytechnic Institute of Brooklyn.

(11) G. S. Samuelsen, Thesis, Polytechnic Institute of Brooklyn.

of hydrogen was consumed the rate varied greatly throughout the reaction and in several instances was so slow that the reaction may be considered as not taking place. For this reason numerical values are not used to denote the reactivity of these compounds.

Following each reduction the product was isolated and at least two derivatives prepared in order to establish the identity of the products. In all of the hydrogenation reactions in which the theoretical quantity of hydrogen was consumed, the primary amine was obtained in a yield that approached 100%.

Discussion

These experiments confirm the general understanding that Raney nickel is an active catalyst for the liquid phase hydrogenation of both aliphatic and aromatic nitro compounds. The reaction, in equipment similar to the Parr unit, although limited to rather small quantities has the advantage of proceeding under such mild conditions that only rarely are side reactions or structural changes encountered and in consequence the reactions are usually complete.

Examination of the collected results (Table I) reveals that substitution in the aromatic nitro compounds by aliphatic side chains contribute to the completeness of the reaction, while the presence of functional groups such as hydroxy and amino groups usually, but not always, interferes with the reaction.

TABLE I

SUMMARY OF RESULTS

Mono nitro compounds	Catalysts			
	a	b	c	d
Nitromethane	69	114	84	149
Nitroethane	115	215	133	286
1-Nitropropane	103	207	100	283
2-Nitropropane	71	169	80	287
Nitrobenzene	200	330	0	144
o-Nitroethylbenzene	24	285	250	406
p-Nitroethylbenzene	32	479	157	394
2-Nitro-p-cymene	81	388	210	403
Nitrodurene	236	411	x	x
Nitromesitylene	217	340	310	481
2-Nitro-1,4-dimethylbenzene	121	451	213	554
5-Nitro-1,3-dimethylbenzene	123	523	1	x
4-Nitro-2-aminotoluene	125	479	55	286
6-Nitro-2-aminophenol	i	i	i	i
1-Nitro-2-methylanthraquinone	45	175	1—	x
Dinitro compounds				
o-Dinitrobenzene	80	450	0	80
m-Dinitrobenzene	1—	584	0	133
p-Dinitrobenzene	1—	436	1—	x
2,4-Dinitrotoluene	302	612	0	0
2,4-Dinitrophenetole	367	654	0	200
3,5-Dinitro-o-cresol	539	559	545	560
2,4-Dinitrophenylhydrazine	100	400	220	285
2,4-Dinitrophenol	422	581	424	584
2,6-Dinitrophenol	i	i	i	i
2,4-Dinitroaniline	409	427	159	292
4,6-Dinitro-2-aminophenol	i	i	i	i
3,5-Dinitrosalicylic acid	i	i	i	i
1,5-Dinitronaphthalene	298	520	180	257
1,8-Dinitronaphthalene	450	454	0	0

Trinitro compounds

2,4,6-Trinitro-1,3-dimethyl-5-t-butylbenzene	Rapid, complete, slight promotion by platinum and alkali
2,4,6-Trinitrobenzoic acid	Incomplete, not promoted
2,4,6-Trinitrophenol	Incomplete, promoted slightly by platinum
2,4,6-Trinitro-m-cresol	Incomplete, not promoted

The values are the observed half-rates, expressed as ml. of hydrogen absorbed per 100 seconds. Catalysts: (a) Raney nickel, (b) Raney nickel and platinum, (c) Raney nickel and alkali, (d) Raney nickel, platinum and alkali. The variable rate of consumption of hydrogen recorded in the hydrogenation of 2,4,6-trinitro-1,3-dimethyl-5-t-butylbenzene is not suited for the determination of the half rate. The term (i) (incomplete reaction) in this table indicates that an appreciable reaction was recorded before the absorption of hydrogen ceased. The designation x is used where lack of material prevented the carrying out of the reaction.

There is some confirmation of the observation of Reasenberg that the ortho substituted nitro compounds hydrogenate more readily than the meta and para isomers. This may well be an example of the so called "ortho effect," used by Birtles and Hampson[12] and others[13,14] to explain the numerous experimental findings wherein the ortho member was at variance with its isomers.
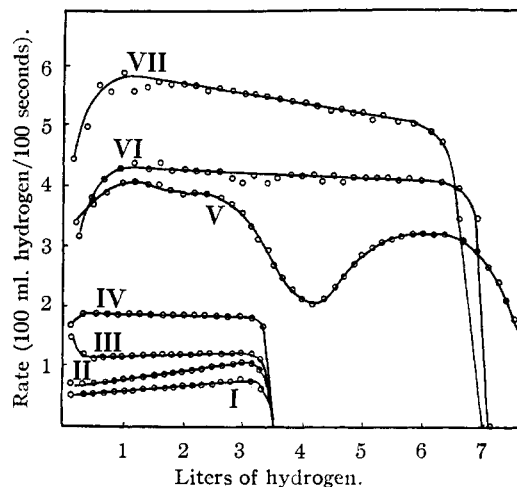

Fig. 1.—I, Nitropropane-1; II, nitropropane-2; III, 2-nitro-1,4-dimethylbenzene; IV, nitrobenzene; V, 2,4,6-trinitro-1,3-dimethyl-5-t-butylbenzene; VI, 2,4-dinitroaniline; VII, 3,5-dinitro-o-cresol.

The ease of hydrogenation of the ortho nitro group is particularly noticeable in the reduction of several of the polynitro compounds and probably accounts for the fact that the ortho amine can frequently be isolated as an intermediate.

(12) Birtles and Hampson, J. Chem. Soc., 10, 987 (1937).
(13) G. N. Lewis and G. T. Seaborg, THIS JOURNAL, 62, 2122 (1940).
(14) G. W. Wheland and A. A. Danish, ibid., 62, 1125 (1940).

The majority of the ortho substituted nitro compounds that do not hydrogenate readily are of the type known to exist as a chelated structure.

Platinum introduced as chloroplatinic acid acts as a true promoter, since through its action all nitro compounds that are hydrogenated with Raney nickel are hydrogenated more readily, while the platinum does not initiate reactions with compounds which are not hydrogenated by the catalyst alone.

The addition of a small amount (3 millimoles) of alkali to the reaction mixture usually retards the hydrogenation of nitro compounds. Contrary to the conclusion of Reasenberg this poisoning action is not limited to the neutral compounds. A few of the reactions with nitro compounds are promoted by the addition of alkali to the Raney nickel. This is particularly true in the case of the reduction of the nitroalkanes.

The fact that the addition of platinum tends to oppose the poisoning action of alkali gives support to the idea that the action of both alkali and platinum are probably at the catalyst surface, and not due to the effect of the small amount of these substances upon the nitro compound undergoing reduction.

Summary

Data on the relative rates of hydrogenation with Raney nickel, and with Raney nickel treated with chloroplatinic acid and with alkali of 32 nitro compounds are presented.

Under the mild conditions of these experiments, the primary amine was obtained in almost quantitative yield. No evidence of the formation of intermediate compounds was observed.

The action of chloroplatinic acid and of alkali in the quantities used in these experiments and added just prior to the introduction of the hydrogen into the system, appears to exert their effect upon the catalyst surface rather than upon the nitro compound being hydrogenated.

The Addition of Acetic Anhydride to Benzalaniline. The Perkin Reaction in the Nitrogen System[1]

BY HENRY S. ANGEL AND ALLAN R. DAY

Although many writers have commented on the similarities in chemical behavior of the carbonyl group ($-\overset{|}{C}=O$) and the Schiff base linkage ($>C=N-$), there is little work reported on the Perkin reaction in the nitrogen system. Kalnin[2] heated benzalaniline, acetic anhydride and anhydrous potassium carbonate at 180° for fifteen minutes. He isolated a very small amount of cinnamic acid (4.3%) from the reaction mixture. He did not isolate any intermediates and the mechanism which he proposed appears to be highly improbable.[3]

Passerini and Macentelli[4] heated benzalaniline with acetic anhydride for several minutes and isolated a forty per cent. yield of an addition product which they formulated as

$$\left[\begin{array}{c} C_6H_5CH=\overset{|}{N}-C_6H_5 \\ \overset{|}{C}OCH_3 \end{array}\right]^+ {}^-OOCCH_3$$

$$I$$
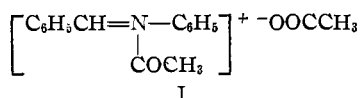
This formula was proposed because of the ease with which the compound hydrolyzed to form acetanilide, benzaldehyde and acetic acid.

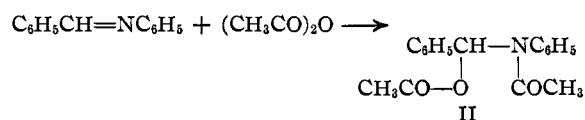Later workers formulated the addition product differently. Ekeley, Swisher and Johnson[5] formulated the reaction as

$$C_6H_5CH=NC_6H_5 + (CH_3CO)_2O \longrightarrow$$

$$\begin{array}{cc} C_6H_5CH-NC_6H_5 \\ | \quad\quad | \\ CH_3CO-O \quad COCH_3 \end{array}$$

$$II$$

Snyder, Levin and Wiley[6] accepted this formulation of the addition product but suggested a different course for its formation. Since the presence of acetic acid improved the yield of addition product, they proposed that the first step involves the addition of acetic acid to the double bond between carbon and nitrogen. This is followed by reaction with acetic anhydride to form the N-acetyl derivative (II). If this course of reaction were the correct one, one would assume that if the addition were carried out in the presence of acetic acid, benzoic acid and sulfuric acid, respectively, three different adducts might be obtained. Actually it is shown, in the present investigation, that the same adduct is formed in each case. Thus the acid must function solely as a catalyst for the addition of the anhydride to the Schiff base.

Previous workers apparently failed to notice the possibility of an aldol-type addition of the acetic anhydride to benzalaniline. Such an addition would be acid catalyzed and may be shown as

(1) From the Ph.D. Dissertation of Henry S. Angel.

(2) Kalnin, Helv. Chim. Acta, 11, 977 (1928).

(3) Kalnin assumed that the carbon-hydrogen bond of the aldehyde group adds across the double bond of the enol form of the anhydride.

(4) Passerini and Macentelli, Gazz. chim. ital., 58, 64 (1928).

(5) Ekeley, Swisher and Johnson, ibid., 62, 81 (1932).

(6) Snyder, Levin and Wiley, THIS JOURNAL, 60, 2025 (1938).