[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Promoter Effect of Platinic Chloride on Raney Nickel. II. Effect of Alkali on Various Groups[1,2]

BY JULIAN R. REASENBERG,[3] EUGENE LIEBER AND G. B. L. SMITH

In 1936, Lieber and Smith[1] found that small amounts of platinic chloride, added to Raney nickel catalyst just prior to the start of the reduction, produced a marked enhancing effect on the activity of the catalyst at low hydrogen pressures. This was distinguished from the catalytic activity of equivalent quantities of platinic chloride alone and of Adams platinum oxide *alone* and *in combination* with active Raney nickel. The platinic chloride was found to be without activity, while the addition of Adams catalyst in an amount equal to the platinic chloride was without effect on the activity of the Raney nickel. Further comparison between platinum plated on inactive metals and of Adams platinum oxide indicated that the enhancing effect obtained on adding platinic chloride to active Raney nickel was *markedly* beyond that which could be expected on the basis of the quantity of platinum metal involved.

At about the same time, Delépine and Horeau[4] reported that the several metals of the platinum family, when deposited on Raney nickel, had a strong promoter action in the reduction of the carbonyl group, especially when small amounts of alkali were present.

The work of Lieber and Smith[1] and of Delépine and Horeau[4] differ in several particulars. In the former, the maximum promoter effect is obtained when the platinic chloride is added to the catalyst and hydrogen acceptor in solution *immediately before* the start of the reduction, while in the latter work the Raney nickel is *plated* with the platinum and is washed before adding it to the reduction mixture. Furthermore, while Lieber and Smith found that addition of alkali retarded the activity of the catalyst in the reduction of nitroguanidine, Delépine and Horeau report that a maximum enhancement of activity of the promoted nickel for the reduction of the carbonyl group is obtained only after alkali is added. Lastly the French authors describe the preparation of the Raney nickel catalyst from an alloy containing 30% nickel and 70% aluminum while the common Raney alloy obtained in this country and used by Lieber and Smith contains 50% nickel and 50% aluminum.

It was, therefore, the object of this work (1) to study and compare the two methods of promoting Raney nickel with platinum, (2) to study the effect of alkali on the reduction of various groups and (3) to compare the activities of Raney catalysts prepared from alloys of varying compositions of nickel and aluminum as well as to study the effect of other substituent groups on the reduction of the aromatic nitro radical.

Experimental Section

Apparatus, Catalysts and Materials.—The apparatus for the reductions was the same as that used previously.[5] The Raney alloy, used to prepare the active catalyst by the method of Adkins and Covert,[6] contained 50% nickel and 50% aluminum and was ground to pass through a 150-mesh screen. An alloy having the composition 30% nickel–70% aluminum was also studied. The chloroplatinic acid was made by dissolving platinum metal (containing a little iridium) in aqua regia and the concentration of the solution was adjusted to 10% platinum by weight. The alkali solution was 10 *M* sodium hydroxide.

Procedure.—The order of addition of reagents to the reduction flask was as follows: hydrogen acceptor (washed in with the solvent, 95% ethyl alcohol), catalyst, solvent up to volume, and lastly, promoter, alkali or both. The following conditions were kept constant. The rate of shaking was maintained at 190 oscillations per minute. One-twentieth of a mole of hydrogen acceptor was used in each experiment. The ratio of catalyst to hydrogen acceptor was fixed so that there was present 3.0 g. of catalyst per 0.1 mole of hydrogen to be absorbed. The ratios of promoter and alkali to catalyst were fixed at 0.25 and 2.0 millimoles, respectively, per 3.0 g. of nickel. Ethyl alcohol was used throughout as a solvent except in the case of nitroguanidine, where water was used and the total volume of reduction solution was 120 ml. The reductions were all performed at room temperature and atmospheric pressure.

Effect of Alloy Composition on Catalyst Activity.—The two active nickel catalysts studied were prepared from the 30 and the 50% nickel Raney alloys. The hydrogen

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(1) For the first communication in this series see Lieber and Smith, THIS JOURNAL, **58**, 1417 (1936).

(2) Part of this paper was presented at the 94th meeting of the American Chemical Society at Rochester, N. Y., in September, 1937.

(3) This paper is abstracted from part of the thesis submitted by Mr. Reasenberg to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science in Chemistry in June, 1938.

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

(5) Lieber and Smith, THIS JOURNAL, **57**, 2479 (1935).

(6) Adkins and Covert, *ibid.*, **54**, 4116 (1932).

acceptors were maleic acid, benzaldehyde, methyl ethyl ketone, nitroguanidine and nitrobenzene. The catalysts studied were: (a) nickel, (b) nickel with platinic chloride (added just prior to the start of the experiment), (c) nickel and alkali, (d) nickel and promoter followed by alkali and (e) nickel and alkali followed by promoter. The data obtained from the active nickel catalyst prepared from the 50% nickel alloy are summarized in Table I. In no case was there any appreciable difference found in the activity of the catalyst prepared from the 30% nickel alloy.

TABLE I

EFFECT OF ALKALI AND CHLOROPLATINIC ACID ON THE RATE OF REDUCTION OF VARIOUS GROUPS WITH RANEY NICKEL

Hydrogen acceptor		Catalyst *a*	*b*	*c*	*d*	
Maleic acid	(1)	74[f]	97	85	131	109
Benzaldehyde	(2)	20	114	42	113	86
Methyl ethyl ketone	(3)	0	0	17	81	55
Nitroguanidine	(4)	36	57	29	49	...
Nitrobenzene	(5)	115	261	0	119	0
o-Nitrotoluene	(6)	159	242	67	246	224
m-Nitrotoluene	(7)	125	240	39	145	138
p-Nitrotoluene	(8)	65	235	19[g]	151	146
o-Nitraniline	(9)	115	174	137	211	194
m-Nitraniline	(10)	109	243	13[g]	49	50
p-Nitraniline	(11)	41	155	44	179	123
o-Nitrophenol	(12)	319	398	301	340	351
m-Nitrophenol	(13)	90	334	192	342	328
p-Nitrophenol	(14)	42	98	52	182	168
o-Nitrophenetole	(15)	227	373	20[g]	310	323
m-Nitrophenetole	(16)	60	346	5[g]	198	73
p-Nitrophenetole	(17)	23	212	18[g]	249	253

[a] Raney nickel alone. [b] Promoted nickel. [c] Nickel and alkali. [d] Nickel, platinic chloride and alkali added in that order. [e] Nickel, alkali and platinic chloride. [f] All of the figures refer to an average rate of reduction expressed in ml./100 sec. [g] The average rate is something less than the number shown.

Effect of Alkali on the Reduction of Various Groups.—In addition to the hydrogen acceptors studied above, the effects of alkali and the order of addition of alkali to the promoted catalyst (from the 50% nickel alloy) were studied on a series of substituted nitrobenzenes. These derivatives were the methyl, amino, hydroxy and ethoxy substituted nitrobenzenes in the ortho, meta and para positions. The results are tabulated in Table I. All of the rates are expressed in ml. per 100 sec. and are calculated from the absorption of the *first half of the theoretical hydrogen required* for purposes of comparison. In every case the reduction was carried to *completion* for the promoted catalyst (catalyst *b* of Table I) and the percentage yield of product determined. Figure 1 shows some typical rate data for the whole period of reduction using the promoted catalyst.

Comparison of Promoting Methods.—Three parallel experiments were performed using 5.2 g. of nitroguanidine with water (120 ml.) as solvent and 3.0 g. of Raney nickel. Experiment (a) contained 0.25 millimole of platinic chloride added just before the start of the reduction; (b) contained the same amount of platinum deposited by the method of Delépine and Horeau[4]; and (c) contained no promoter at all. The rates in ml. per 100 sec. were: (a) 33.3, (b) 22.2 and (c) 23.2.

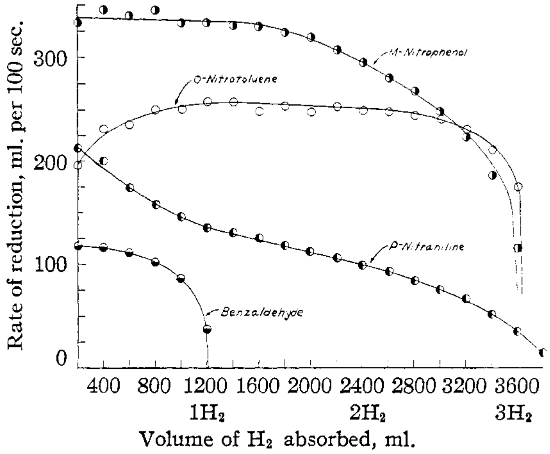

Fig. 1.—Typical reduction curves with promoted nickel.

Isolation and Identification of Products.—The products were isolated as amine hydrochlorides by separating the catalyst on a Büchner funnel, passing dry hydrogen chloride through the alcoholic solution of the amine, and purifying. The amines which did not have readily identifiable hydrochlorides were characterized as acyl derivatives. The quinone dichlorimide of *p*-phenylenediamine was prepared by treating a water solution of the amine with a 10% solution of bleaching powder. The analytical data are shown in Table II.

TABLE II

ANALYTICAL DATA

Cpd.[a]	Product	% yield	Derivative	M .p., °C.[b]
(5)	Aniline	75	Acetyl	114.8
(6)	*o*-Toluidine	81	Hydrochloride	214
(7)	*m*-Toluidine	92	Acetyl	65.3
(8)	*p*-Toluidine	93	Hydrochloride	240
(9)	*o*-Phenylenediamine	80	1,2-Dibenzoyl	303
(10)	*m*-Phenylenediamine	98	1,3-Diacetyl	189
(11)	*p*-Phenylenediamine	95	Dichloroquinonimide	122
(12)	*o*-Aminophenol	93	Acetyl	204
(13)	*m*-Aminophenol	97	Hydrochloride	230
(14)	*p*-Aminophenol	83	Hydrochloride	306 dec.
(15)	*o*-Phenetidine	71	Acetyl	77.5
(16)	*m*-Phenetidine	89	Acetyl	96.5
(17)	*p*-Phenetidine	91	Hydrochloride	235

[a] See Table I for the name of the compound. [b] All melting points are corrected.

Effect of Concentration of Platinic Chloride and Nickel Chloride on the Reduction of Nitrobenzene.—In all of the experiments described in this section 0.05 mole of nitrobenzene dissolved in 120 ml. of ethanol was used as the hydrogen acceptor. Figure 2 shows the effect of the concentration of chloroplatinic acid on the rate of reduction, the weight of Raney catalyst being 4.5 g. The average rates were based on the first half (1.5 molecular equivalents of hydrogen) of the reduction. The effect of nickel chloride on the rate of reduction, with the weight of catalyst kept constant, is also shown.

From the equation for the reaction between the promoter and Raney nickel[1]

$$3Ni + H_2PtCl_6 \longrightarrow H_2 + Pt + 3NiCl_2$$

it can be seen that three moles of nickel chloride are equivalent to one mole of chloroplatinic acid. The rates are calculated from the absorption of the first 600 ml. of hydrogen.

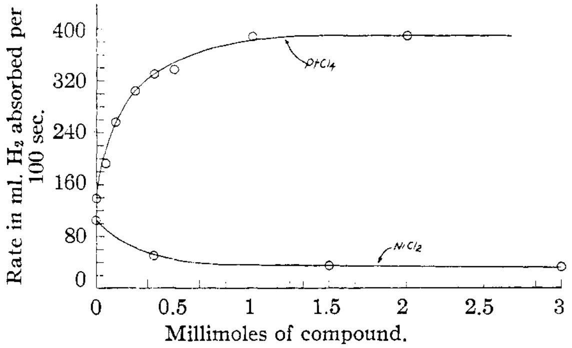

Fig. 2.—Effect of concentration of $PtCl_4$ and $NiCl_2$ on rate of reduction of nitrobenzene.

Reproducibility of Results.—A number of the experiments described in Table I were repeated. The results could be reproduced within ±5%. In those cases where a repeated trial did not agree with the previous determination, a sufficient number of additional experiments were performed to justify the deletion of the least reliable result by means of the average mean deviation.

Nitrobenzene was used as a standard in testing each new preparation of catalyst. On the basis of rates of reduction of nitrobenzene with each sample of catalyst, all the preparations of Raney nickel had activities within 12% of each other. The activity of the catalyst decreased with age.

Discussion

Platinum, deposited on Raney nickel by the method of Delépine and Horeau, does not increase the activity of the catalyst for the reduction of nitroguanidine. The difference in activities of the platinum promoted nickels prepared by the two methods is probably due to a diffusion of the platinum, plated by the method of Delépine and Horeau, below the surface of the nickel. Such a solid solution takes time and might occur during the lapse of time between the platinizing of the catalyst by this method and its use in a reduction.

The effect of alkali on the activity of the catalyst varies with the compound studied. The addition of three millimoles of sodium hydroxide inhibits completely the reduction of nitrobenzene and this same poisoning effect is noted to a lesser extent in all of the other neutral nitro compounds studied. On the other hand, the presence of alkali is indispensable for the reduction of methyl ethyl ketone under the conditions described above and this enhancing effect is noticed to a lesser extent in the reduction of benzaldehyde and some of the basic or acidic nitro compounds. No generalization on the effect of alkali on the reduction of nitro compounds with Raney nickel can be made because of the limited number of examples studied.

The promoter effect of platinic chloride on Raney nickel reductions is observed in every case studied. The increase in activity of the catalyst as observed from the rates varies from 25 to 800%.

Although it would seem that a catalyst prepared from an alloy having a higher percentage composition of aluminum would have a greater activity because of finer dispersion of nickel through the alloy, this is not the case as illustrated by the reductions with catalysts prepared from alloys of 30 and 50% nickel. It would seem from the above that the activity of Raney nickel is dependent on some surface characteristic in addition to surface area or particle size.

It is interesting to note that in every instance studied the position of the substituent group as well as its nature has a strong effect on the rate of reduction of the nitro radical. For any particular series, the ortho substituted compound invariably reduced the fastest and the para, the slowest.

The shape of the curve in Fig. 2 showing the effect of the concentration of chloroplatinic acid on the rate of reduction may be explained in one of two ways. The presence of the plateau in the curve may be offered as evidence in favor of the "active center" theory of catalysis by explaining that at the beginning of the plateau the platinum has promoted all of these centers or the rate of reduction corresponding to the plateau is the maximum rate of solution of hydrogen into the solvent under the conditions of the experiment (speed of shaking, pressure, etc.). Additional work is being done in this Laboratory at the present time to determine which explanation is the more probable.

Summary

1. Chloroplatinic acid added to the catalyst just before the start of the reduction is a strong promoter for catalytic hydrogenation with Raney nickel at atmospheric pressure and room temperature.

2. There is no difference in activity of a Raney nickel catalyst prepared from an alloy containing 30% nickel and one from an alloy of 50% nickel.

3. Alkali is a poison in the reduction of nitrobenzene and the other neutral substituted aromatic nitro compounds, nitrotoluene and nitro-

phenetole. It enhances the rate of reduction of methyl ethyl ketone, benzaldehyde and certain of the nitranilines and nitrophenols.

4. Ortho substituted aromatic nitro compounds will reduce faster than the corresponding meta compounds which in turn will reduce faster than the para.

5. Nickel chloride is a poison for the reduction of nitrobenzene.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reaction of Sulfur with Some of the Halogenated Derivatives of Diphenyl Sulfide

BY J. H. BILLMAN[1] AND GREGG DOUGHERTY

Krafft and Vorster[2] described the reaction which takes place when unsubstituted diphenyl sulfide is heated with sulfur at 260°. The following equation will summarize their results

$$\mathrm{C_6H_5SC_6H_5} + \mathrm{S} \longrightarrow \mathrm{C_6H_5SSC_6H_5} \qquad (1)$$

An essential point is that the sulfur, entering the unsubstituted diphenyl sulfide molecule, takes up a position adjacent to the sulfur atom already present.

When halogen substitution products of diphenyl sulfide were heated with sulfur a marked reaction took place over the range 240–270°. The principal products were halogen substitution products of benzene, polymeric material of varying composition containing halogen and sulfur in addition to carbon and hydrogen. The sulfur was present as sulfide, disulfide and polysulfide linkages. Also a considerable quantity of unchanged halogenated diphenyl sulfide was always found among the products regardless of the reaction time. The compounds studied and the halogenated benzene derivatives formed were

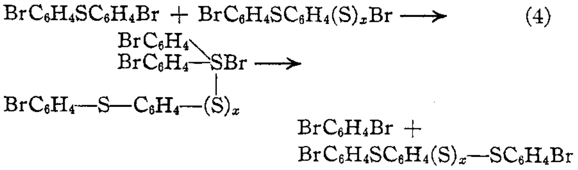
p,p'-Dibromodiphenyl sulfide ⟶ *p*-Dibromobenzene
p-Bromodiphenyl sulfide ⟶ *p*-Dibromobenzene and bromobenzene
p,p'-Dichlorodiphenyl sulfide ⟶ *p*-Dichlorobenzene
p-Chlorodiphenyl sulfide ⟶ Chlorobenzene
p,p'-Chlorobromodiphenyl sulfide ⟶ *p*-Dibromobenzene and *p*-chlorobromobenzene (2)

It was also found that the reaction could be extended to molecules of the type X—C_6H_4—E—C_6H_4—X where X is halogen and E is an atom or group easily replaced by sulfur or converted to sulfur during the reaction. Thus dichlorodiphenyl oxide and dichlorodiphenyl sulfoxide, both known to satisfy the above conditions, gave positive results while dibromodiphenylamine and dichlorodiphenylmethane yielded no halogenated benzenes when heated with sulfur.

It is obvious that the reaction here must be far more complex than that given by Krafft and Vorster for the simple sulfide. A hypothesis which best accounts for all the products obtained is one which assumes that the reaction proceeds through the intermediate formation of a sulfonium compound, with subsequent splitting of that compound into simpler molecules. The most probable course involves first the addition of one or more atoms of sulfur to form an aryl sulfur halide

$$\mathrm{BrC_6H_4SC_6H_4Br} + x\mathrm{S} \longrightarrow \mathrm{BrC_6H_4SC_6H_4(S)_{\mathit{x}}Br} \qquad (3)$$

This compound unlike an aryl halide is very reactive and at once forms a sulfonium salt with an adjacent sulfide molecule



$$\mathrm{BrC_6H_4SC_6H_4Br} + \mathrm{BrC_6H_4SC_6H_4(S)_{\mathit{x}}Br} \longrightarrow \begin{array}{l} \mathrm{BrC_6H_4} \diagdown \\ \mathrm{BrC_6H_4{-}SBr} \\ \qquad | \\ \mathrm{BrC_6H_4{-}S{-}C_6H_4{-}(S)_{\mathit{x}}} \end{array} \longrightarrow \mathrm{BrC_6H_4Br} + \mathrm{BrC_6H_4SC_6H_4(S)_{\mathit{x}}{-}SC_6H_4Br} \qquad (4)$$

Finally the complex breaks at the temperature of the reaction to give the dibromobenzene and an unsymmetrical polysulfide. There is an analogy to this method of sulfonium salt formation in the work of Scott and Klingen,[3] who obtained the diiodide of trimethylsulfonium iodide from sulfur and methyl iodide. Also the type of decomposition postulated, *i. e.*, the formation of a halide and a sulfide different from those used in forming the sulfonium complex, has been reported frequently in the literature. In order to test the proposed mechanism phenylsulfur chloride was mixed with dibromodiphenyl sulfide and heated over the temperature range ordinarily used.

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[1] From a thesis submitted by J. H. Billman in partial fulfillment of the requirement for the degree of Doctor of Philosophy at Princeton University.

[2] Krafft and Vorster, *Ber.*, **26**, 2813 (1893).

[3] Scott and Klingen, *Proc. Chem. Soc.*, 156 (1904).