tion to a trichloro-acetate was noted, we believe this offers a very quick method of determining qualitatively the purity of dichloro-acetic acid.

TABLE II

BEHAVIOR OF DICHLORO-ACETIC ACIDS WITH ANILINE

Source	Ppt.	M. p., °C.	Recryst.	M. p., °C.	By-product
Coleman-Bell	Pale yellow	115–118	Yellow	122	Yellow
Merck	Pink	95–102	Yellow	118–122	Yellow
Eastman	Yellow	114–117	Orange	118–121	Orange
Kahlbaum	White	122	White	122	None

We wish to thank Mr. R. D. Norton for his assistance in testing the commercial preparations of dichloro-acetic acid and for reëxamination of some of the salts.

Summary

1. The dichloro-acetates and trichloro-acetates of methylaniline, *o*-chloro-aniline, 2,4-dichloro-aniline, benzidine, *o*-anisidine and *p*-aminophenol were prepared.

2. Identical products were obtained in cold and hot solutions and also when two moles of acid were used instead of one.

3. No salt formation occurred with dimethylaniline.

4. The purity of dichloro-acetic acid was quickly noted by its reaction with pure aniline. In the samples examined, one made from chloral gave a pure white salt at once; other acids gave a yellow compound in addition to the white salt.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE REDUCTION OF AROMATIC NITRO COMPOUNDS TO AMINES WITH HYDROGEN AND PLATINUM-OXIDE PLATINUM BLACK AS A CATALYST. XIV[1]

BY ROGER ADAMS, F. L. COHEN AND O. W. REES[2]

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Though the catalytic reduction of aromatic compounds to aromatic amines by means of hydrogen and platinum or palladium colloid or black has been frequently used, no systematic study has been made to deter-

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[1] (a) Voorhees with Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers with Adams, *ibid.*, **45**, 1071 (1923); (c) **46**, 1675 (1924); (d) **47**, 1047 (1925). (e) Adams and Shriner, *ibid.*, **45**, 2171 (1923); (f) **46**, 1683 (1924). (g) Kaufmann with Adams, *ibid.*, **45**, 3029 (1923). (h) Pierce with Adams, *ibid.*, **47**, 1098 (1925). (i) Kern and Shriner with Adams, *ibid.*, **47**, 1147 (1925). (j) Heckel with Adams, *ibid.*, **47**, 1712 (1925). (k) Tuley with Adams, *ibid.*, **47**, 3061 (1925). (l) Adams and Garvey, *ibid.*, **48**, 477 (1926). (m) Hiers and Adams, *Ber.*, **59**, 162 (1926).

[2] This communication is an abstract of a portion of theses submitted by F. L. Cohen and O. W. Rees, in partial fulfilment of the requirements for the degree of Master of Science in Chemistry, at the University of Illinois.

mine the effects of changes in the laboratory conditions, such as character of solvent, temperature or presence of foreign materials upon the rate of reduction. This investigation was undertaken to study these factors, using platinum-oxide platinum black as the catalyst, and a variety of simple aromatic nitro compounds in the hope of obtaining sufficient information to make possible immediate selection of approximately the most efficient conditions for the reduction of any aromatic nitro compound not previously studied. A large portion of the work has been carried out with nitrobenzene, although sufficient experiments have been completed with substituted nitrobenzenes to show that they give analogous results.

It is well known that the rate of reduction is increased by the increase of the amounts of catalyst up to a certain limit. The preliminary experiments[3] in this investigation indicated that 0.2 g. of catalyst for reducing 0.1 mole of nitro compound in 150 cc. of solvent with hydrogen at 2 to 3 atm. pressure was the maximum amount needed for a very rapid reduction (10–11 minutes). Larger amounts than this did not increase the rate of reduction appreciably; smaller amounts caused the expected decrease in the rate of reduction, though much smaller amounts of catalyst (0.05 g.) could be used and a quantitative reduction still be obtained (about 60 minutes). By raising the temperature of the reaction mixture, the reductions took place at an increased rate but quantitative experiments were not made. In all the experiments except where otherwise mentioned the same volume of solvent (150 cc.), the same amount of nitro compound (0.1 mole) and 0.2 g. of platinum oxide were used and the reduction was carried out under an initial pressure of 2.5–3 atm. and an initial temperature of 25–30°.

Various dilutions of ethyl alcohol with water were first studied as solvents. The results are given below, the figures in parentheses following the various percentages of alcohol representing the time in minutes for the absorption of the amount of hydrogen required to give the corresponding amine: 100% (10); 95% (11); 85% (15); 75% (30); 65% (46); 50% (64).

Since the nitrobenzene was not completely soluble in alcohol of 75% strength or lower, the data given are not directly comparable. However, the heat of reaction at the beginning of these reductions was sufficient to cause the complete solution of the remainder of the nitrobenzene within four or five minutes. It is a fair conclusion, therefore, that the presence of more than 10% of water in the ethyl alcohol slows down the rate of reduction.

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[3] Actual times are given in most cases to illustrate the relative rates of reduction. When it was necessary to prepare new catalyst, this was always tested in reduction of nitrobenzene before using. In a different apparatus where minor changes are necessarily present, the exact times may vary slightly more or less from the figures given here, but the relative times will remain the same.

In place of ethyl alcohol, methyl, *n*-propyl, *n*-butyl and *iso*-amyl were studied. No appreciable difference in the rate within experimental error was found when methyl or propyl alcohols were substituted in place of ethyl alcohol, but with butyl and amyl alcohols the time of reduction was increased in the first case by about 25%, and in the second case by approximately 50%. The probability is that the higher molecular weight alcohols would be even less satisfactory.

Reductions in ethyl acetate proceeded as rapidly as in 95% ethyl alcohol. Acetone was almost as satisfactory and can be classed as an excellent solvent for these reductions. It is probable that with substances which are more slowly reduced than nitro compounds, the acetone would itself be reduced somewhat and thus interfere with quantitative results. Dry ether was not entirely satisfactory, owing to the fact that the platinum catalyst tended to collect on the sides of the flask. Reduction did take place completely but the time required was three to four times that necessary with the other solvents already mentioned. With glacial acetic acid as solvent, the reduction took place nearly six times as slowly as with alcohol. Acetic acid, therefore, should be used only when it is a particularly desirable solvent for the substance to be reduced. These results with acetic acid check with those found in the study of the reduction of other compounds with platinum-oxide platinum black, namely, that acetic acid is usually not a preferred solvent. This is rather surprising, since glacial acetic acid has been proved an excellent if not the best solvent for catalytic reductions, using platinum black made by the formaldehyde and alkali method. It is, of course, possible that by this process a small amount of alkali is occluded in preparing platinum black and that this is removed by the acetic acid.

The effect of the presence of certain types of substituting groups upon the rate of reduction of the nitro group was studied. The *o*-, *m*- and *p*-nitrotoluenes, the *o*- and *p*-nitrochlorobenzenes, the *o*-, *m*- and *p*-nitrobenzoic acids, *p*-nitro-anisole and *p*-nitro-phenol were reduced under exactly analogous conditions to those used in the reduction of nitrobenzene, in approximately the same time. *Ortho* substitutions which might be expected to slow down the reduction had absolutely no effect. The methyl *o*-, *m*- and *p*-nitrobenzoates were reduced even more rapidly than nitrobenzene and the same was true of α-nitronaphthalene. Although complete experiments were not made with these substituted compounds using solvents other than alcohol, many experiments with these solvents were performed and in every instance analogous results were obtained to those expected from the study of the same solvents in the reduction of nitrobenzene.

In the case of the *o*- and *p*-nitrochlorobenzenes it was observed that if the reductions were allowed to run as long as hydrogen was absorbed, about four molecular equivalents of hydrogen reacted. The reaction mixtures then contained certain amounts of cyclohexylamine hydrochloride which was isolated and identified. On the other hand, if the reductions were stopped as soon as three moles of hydrogen were absorbed, chloro-anilines were obtained in about 85% yields.

The effect of the presence of foreign substances upon the rate of reduction of nitrobenzene and one or two derivatives has been studied. As basic nitrogen compounds tend to poison a catalyst, it was expected that the presence of a little hydrochloric acid might increase the rate of reduction by combining with the amine as it was formed. The addition of hydrochloric acid in quantities up to 0.1 mole to the reaction mixture caused a diminution in the rate of reduction which was only slight and which could be accounted for by the dilution of the alcohol. Upon addition of 0.15, 0.2, 0.25 and 0.3 mole of hydrochloric acid in the form of 20% acid, the time required was, respectively, 22, 43, 80 and finally 110 minutes. Such an increase in the time cannot be accounted for merely by dilution and it must be concluded that appreciable quantities of hydrochloric acid slow the reduction.

The addition of 0.1 mole of acetic acid slightly lowered the rate of reduction (16 minutes) and larger amounts, 0.15 and 0.2 mole of acetic acid, caused an additional diminution in the rate (25 and 29 minutes, respectively).

Sodium hydroxide has a distinct poisoning effect, as little as 0.025 mole in the form of a saturated solution entirely preventing the reduction. On the other hand, 0.1 mole of sodium carbonate in the form of a saturated solution had merely a retarding effect, complete reduction taking place in about 20 minutes. Zinc acetate had a much greater poisoning effect, 0.001 or even 0.0005 mole allowing only a very slight absorption of hydrogen to take place. On the other hand, with 0.0002 mole, the amine formed quantitatively in 90 minutes, and with 0.0001 mole in 44 minutes.

Ferrous sulfate had only a slight effect, since 0.001 mole increased the time of reduction only slightly (to 15 minutes) and even 0.01 mole increased the time of reduction only from 11 to 32 minutes. Analogous results were found with substituted nitrobenzenes in the presence of ferrous sulfate and zinc acetate.

Manganese chloride (0.00005 mole) added to a nitrobenzene reduction required 35 minutes, and 0.0001 mole about 42 minutes. Mercuric acetate (0.0001 mole) increased the time only very slightly, while 0.001 mole increased it only to about 30 minutes, though there was a five- or six-minute lag before the reduction started.[4]

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[4] Results from duplicate experiments when poisons were added varied somewhat and in a few instances varied considerably in the time of reduction. Without poisons no such difficulty was encountered.

A study of the reduction of certain substances containing both nitro and olefin groups was made. When *m*-nitrobenzalacetophenone and *m*-nitrobenzalacetone were reduced in alcohol in the usual way using, however, 0.1 g. of catalyst to slow somewhat the rate of reduction, only 3 moles of hydrogen was absorbed with the quantitative reduction of the nitro group to the amine. Similar results were obtained with ethyl *m*-nitrocinnamate although a little more than 3 moles of hydrogen was absorbed in this case. On the assumption that the amines, because of their basicity, poisoned the platinum as a catalyst toward the reduction of the olefin groups, other experiments were made in which 0.15 mole of acetic acid was added to the reduction mixture. Under these conditions, the absorption of hydrogen proceeded until both the nitro and olefin groups were completely reduced, though as might be expected the reduction of the nitro group was slowed considerably by the presence of acetic acid.

An attempt was made by adding foreign substances to the reduction mixture of *m*-nitrobenzalacetophenone and *m*-nitrobenzalacetone to poison the catalyst toward the reduction of the nitro group and not toward the olefin linkage. Since sodium hydroxide had such a marked poisoning effect on the catalyst toward the reduction of the nitro group in nitrobenzene, and not toward the reduction of the olefin linkage, in various olefins it was added to the reaction mixture. The presence of 0.1 mole of sodium hydroxide completely poisoned the catalyst and no reduction took place.

In order to obtain some insight into the mechanism of the action of the alkali, a study was made of the reduction of a mixture of two individual compounds, one containing an olefin group and the other a nitro group.

The reduction of a mixture of 0.1 mole of safrol and 0.1 mole of nitrobenzene in 150 cc. of alcohol with 0.2 g. of catalyst was studied. Complete reduction of both molecules took place in 16 minutes. A similar experiment, when the reduction was stopped after 3 moles of hydrogen was absorbed (11 minutes), showed that most of the nitrobenzene had been reduced. The presence of 0.1 mole of sodium hydroxide was previously shown to prevent completely the reduction of nitrobenzene; on the other hand, this same amount of alkali allowed the reduction of safrol in 45 minutes. The addition of 0.1 mole of sodium hydroxide to the mixture of compounds entirely prevented the reduction. It seems probable that the sodium hydroxide has reacted with the nitrobenzene to give a compound or compounds poisonous to the catalyst. More experiments, however, are necessary in order to be sure of such a conclusion.

Unusual results were obtained with zinc acetate. The reduction of 0.1 mole of nitrobenzene was slowed by the presence of 0.0002 mole of zinc acetate from 11 to 90 minutes, though 0.1 mole of safrol was reduced under similar conditions in 10 minutes. A mixture of these same amounts of nitrobenzene and safrol with 0.0002 mole of zinc acetate absorbed 4 moles of hydrogen in 50 minutes. In this case the presence of the safrol actually aided the reduction of the nitrobenzene. A series of experiments similar to the last two mentioned has been planned to demonstrate, if possible, in the mechanism of the action of promoters and poisons in catalytic reductions, whether the action is upon the substance to be reduced or upon the catalyst.

Experimental Part

The apparatus and catalyst were the same as described in previous papers in this series.

The solid materials used in the reductions were purchased as pure as possible and then recrystallized to constant melting point. The poisons added were of commercial C. P. grade and were dissolved in the smallest amount of water before being added to the reduction mixture. The liquids were distilled, and the material boiling over a range of 0.5° was saved for reductions.

The reduced substances were isolated by filtration of the platinum, addition of slightly more than the calculated amount of hydrochloric acid, and evaporation to crystallization of the amine hydrochloride.

As the isolation of the reduction products from the *m*-nitrobenzalacetophenone and *m*-nitrobenzalacetone was slightly different from that of the simpler products, more details are given below.

***m*-Aminobenzalacetophenone,** $NH_2C_6H_4CH{=}CHCOC_6H_5$.—After reduction, the catalyst was filtered and the alcohol solution evaporated to a volume of about 30 cc. A small amount of dil. hydrochloric acid was added, a small portion of insoluble matter that separated was filtered off and the solution boiled with a little Norite to remove the color. The resulting solution was cooled in ice, and concd. hydrochloric acid was added to precipitate the hydrochloride. The melting point of this amine hydrochloride was 185–195° (with decomposition). The free base was obtained by action of the sodium carbonate solution and was purified by crystallization from benzene. The yield was over 90%; m. p.,[5] 155–156°.

***m*-Aminobenzylacetophenone,** $NH_2C_6H_4CH_2CH_2COC_6H_5$.—After reduction the catalyst was filtered, the solvent evaporated to 20 cc., dil. hydrochloric acid was added, a small amount of tarry material filtered, and the filtrate made alkaline with sodium carbonate. The free amine which separated as an oil was redissolved in hydrochloric acid and precipitated as the amine hydrochloride by the action of concd. hydrochloric acid. By repeating this procedure once more the base came down as a solid. It was purified by dissolving in benzene and adding low-boiling petroleum ether until a slight cloudiness appeared. Upon slow crystallization yellow crystals separated; m. p., 64–65°.

Anal. Subs., 0.2484: CO_2, 0.7304; H_2O, 0.1462. Calcd. for $C_{15}H_{15}ON$: C, 79.95; H, 6.71. Found: C, 80.19; H, 6.86.

The acetyl derivative melted at 97–99°.

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[5] Rupe and Porai-Koschitz [*Z. Farben-Ind.*, **5**, 317 (1906)] give 159°.

***m*-Aminobenzalacetone,** $NH_2C_6H_4CH{=}CHCOCH_3$.—The procedure was the same as for the *m*-aminobenzalacetophenone and the free amine was isolated as an oil. It was refluxed with benzoyl chloride in order to obtain a solid derivative. This melted[6a] at 122–124° after crystallization from alcohol.

***m*-Aminobenzylacetone,** $NH_2C_6H_4CH_2CH_2COCH_3$.—The product was isolated as the amine hydrochloride, converted into the amine and benzoylated, thus yielding a product which, upon crystallization, melted[6b] at 93–95°.

Summary

1. The relative rates of reduction of nitrobenzene and substituted nitrobenzenes in various solvents are given.
2. The effect of acids, alkalies and various salts upon the rates of reduction of nitrobenzene and certain substituted nitrobenzenes is discussed.
3. It has been shown that *m*-nitrobenzalacetophenone and *m*-nitrobenzalacetone are reduced in alcohol to the corresponding amino compounds quantitatively and no further absorption of hydrogen takes place. If, on the other hand, a small amount of acetic acid is present, sufficient hydrogen is absorbed to give the reduction of the olefin as well as the nitro groups.
4. Competitive experiments on unsaturated compounds in the presence of certain poisons and promoters are given.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE CATALYTIC REDUCTION OF DI- AND TRIPHENYLAMINES WITH HYDROGEN AND PLATINUM-OXIDE PLATINUM BLACK. XV[1]

BY G. S. HIERS AND ROGER ADAMS

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The catalytic reduction of certain aromatic amines by means of platinum-oxide platinum black and hydrogen was recently described.[2] This work has been extended to the reduction of diphenylamine and triphenylamine with the formation of dicyclohexylamine and tricyclohexylamine, respectively.

The tricyclohexylamine is of particular interest because it represents that class of tertiary amines in which three secondary carbon atoms are attached to the nitrogen. Although it is reported in the literature that tri-*iso*propylamine[3] and tri-*sec.*-butylamine were obtained in very

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[6] Miller and Rohde [*Ber.*, **23**, 1886 (1890)] give (a) 125°, (b) 94–95°.

[1] Previous articles in this field are listed in a footnote in Article No. XIV, THIS JOURNAL, **49**, 1093 (1927).

[2] Hiers and Adams, *Ber.*, **59**, 162 (1926).

[3] Mailhe, *Compt. rend.*, **141**, 114 (1905).