the precipitated magnesium hydroxide and mercury from azobenzene. Even after repeated extraction by boiling with methyl alcohol the precipitate showed red crystals when dried and examined with a magnifying glass.

No evidence of the production of hydrazobenzene was obtained, and it was at first supposed that this was due to the use of practically the theoretical amount of the reducing agent, since in other respects the magnesium amalgam resembled sodium amalgam in its action. Additional work with larger amounts of the amalgam, however, showed that even then no hydrazobenzene was formed.

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THE REDUCING ACTION OF MAGNESIUM AMALGAM UPON AROMATIC NITRO COMPOUNDS.

By Thomas Evans and Harry S. Fry.

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Evans and Fetsch[1] reduced nitrobenzene with magnesium amalgam, and as some of the reductions attempted by them with ethyl alcohol as a solvent gave unsatisfactory results, it was deemed advisable to investigate the reduction of nitrobenzene in both ethyl and methyl alcohol.

Finding that the nature of the products of the reduction were dependent upon the nature of the solvent, the concentration and time, a more extended study of the subject was made.

Nitrobenzene in Ethyl Alcohol.—Twenty-five grams of nitrobenzene were dissolved in 1¼ liters of 93 per cent. ethyl alcohol at 15° in a glass cylinder 10 cm. in diameter, and 30 cm. high, provided with a mechanical agitator. An amount of coarsely powdered magnesium amalgam, theoretically sufficient to convert the nitrobenezene into aniline, was then added in small portions to the violently agitated solution. At each addition there was a rapid evolution of hydrogen, accompanied by a precipitation of magnesium hydroxide and mercury in a fine state of division. The solution darkened slightly and the temperature rose from 15° to 45° during the reaction. When all the amalgam had been decomposed and the temperature began to fall the thinly fluid, green-

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[1] See preceding article.

ish gray reaction-mixture was transferred to a flask provided with a return condenser and heated fifteen hours on a water-bath.

The alcohol was then distilled off and the residue dried at water-bath temperature. The light yellow mass so obtained was repeatedly extracted with boiling ligroin, and the combined extracts concentrated to 30 cc. After standing twelve hours the solution had solidified to a mass of light red needles. While the substance was crystallizable from ether it was found impossible to remove all traces of the ligroin with this solvent. Purification was finally accomplished by dissolving in a small quantity of methyl alcohol and inducing crystallization by directing a stream of dry air on to the surface of the solution until a few crystals formed, when crystallization proceeded rapidly. These were filtered off and recrystallized in the same manner. The crystals proved to be azoxybenzene, melting-point 38°. The yield was 18 grams, or 89.9 per cent. of the theoretical.

Metadinitrobenzene in Ethyl Alcohol.—Fifty grams *m*-dinitrobenzene were dissolved in 2½ liters of 90 per cent. ethyl alcohol, and 869 grams of 5 per cent. magnesium amalgam, sufficient to reduce the dinitrobenzene to phenylene diamine, added, as described in the preceding reduction.

The darkening of the solution and the rise in temperature were more marked than in the reduction of nitrobenzene. When no further action of the amalgam was perceptible, the brownish red reaction-mixture was heated for fifteen hours on the water-bath. The boiling liquid and accompanying solid were poured upon a large Büchner filter and suction applied. As the filtrate cooled, a light brown flocculent substance separated; this was filtered off and the filtrate concentrated, yielding more of the same compound.

The residue upon the original filter was extracted by boiling alcohol until a colorless extract was obtained. The compound was so insoluble that fifteen extractions with 500 cc. of alcohol were necessary to dissolve it all out.

Purification was effected by repeated recrystallization from alcohol. The purified compound consistd of light tan-colored, microscopic needles, slightly soluble in ether, somewhat more soluble in benzene, toluene and in boiling alcohol, and readily soluble in chloroform. The melting-point was 141°-142°.

These properties agree very well with those of *m*-dinitroazoxybenzene, as given by Klinger and Pitschke.[1]

For more complete identification a nitrogen determination was made. This gave 19.34 per cent. N; calculated, 19.48 per cent.

Additional evidence as to the identity of the substance was obtained by converting it into the corresponding oxyazo compound. For this purpose 5 grams of the reduction product were heated with 50 cc. of concentrated sulphuric acid for one hour at 140°. After cooling, the dark red solution was poured into 500 cc. of water, which precipitated a light yellow flocculent substance. This was filtered off and recrystallized from alcohol, in which it is sparingly soluble. The oxyazo compound dissolved in caustic alkali solutions with a deep red color and was reprecipitated upon addition of dilute acids. The melting-point was 172°-173°, which is that of *m*-dinitroxyazobenzene.

A nitrogen determination gave 19.30 per cent. N; calculated, 19.48 per cent.

This, in connection with the properties already cited, is conclusive evidence that metadinitrobenzene in excess of ethyl alcohol is reduced to metadinitroazoxybenzene by 5 per cent. magnesium amalgam. The yield was 30 grams, or 70 per cent. of the theoretical.

Orthonitrotoluene in Ethyl Alcohol.—Twenty-five grams of *o*-nitrotoluene were dissolved in 1250 cc. of ethyl alcohol and 300 grams of 5 per cent. magnesium amalgam added in the manner already described. The resultant yellow reaction mixture was heated on the water-bath for fifteen hours, the alcohol distilled off and the residue dried at water-bath temperature. It was then repeatedly extracted with boiling ligroin until a colorless extract was obtained. The combined extracts were concentrated to 50 cc. and set aside. In the course of three of four days a considerable quantity of dark orange monoclinic prisms had crystallized out. One of these measured 2.5 x 1 cm. x 2.5 mm. After filtering off the large crystals the filtrate was concentrated on the water-bath until a dark oil remained. This was dissolved in a small amount of absolute alcohol. The solution was evaporated cold by directing a blast of dry air upon its surface, stirring rapidly at the same time.

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[1] *Ber. d. chem. Ges.*, **18**, 2552 (1885).

Small, light yellow needle-like crystals separated out in a short time: these were filtered off, washed with alcohol, and the process repeated with the filtrate and washings. This treatment of the mother-liquor was continued as long as crystals were obtained. The substance was purified by recrystallization from absolute alcohol. The substance is readily soluble in all the ordinary organic solvents and melts at 59°-60°. This, in connection with other properties, identifies it as orthoazoxytoluene. The yield was 10 grams, or 50 per cent. of the theoretical. The red oily mother-liquor was distilled with steam and gave 9 grams of unchanged *o*-nitrotoluene.

Paranitrotoluene in Ethyl Alcohol.—Twenty-five grams of *p*-nitrotoluene were dissolved in 1250 cc. of ethyl alcohol and 300 grams of 5 per cent. magnesium amalgam added, as in the other cases. The product was then heated on the water-bath for fifteen hours, the alcohol distilled off and the dried residue extracted with ligroin. The extract yielded yellowish red crystals upon evaporation. These were purified by recrystallization from methyl alcohol. When pure they formed hair-like yellow crystals, melting at 75°, and readily soluble in all the usual organic solvents. These properties identify the reduction product as *p*-azoxytoluene. Yield, 18 grams, or 90 per cent. of the theoretical. The nitro-compounds were next reduced in dilute methyl alcohol in the same way.

Nitrobenzene in Methyl Alcohol.—Twenty-five grams of nitrobenzene were dissolved in 1250 cc. of 95 per cent. methyl alcohol and treated with 300 grams of 5 per cent. amalgam. After the addition of a few portions of the amalgam it was apparent that its action with methyl alcohol was different from that with ethyl alcohol. No precipitation of magnesium hydroxide occurred, but the larger pieces of the amalgam collected at the bottom of the cylinder and were soon dissolved by the liberated mercury. The temperature rose from 15° to 45° in twenty minutes, and the solution became reddish yellow. When about one-half of the amalgam had been added, the reaction-mixture began to thicken, and was soon of the consistency of a thick gelatinous syrup.

This became much thicker as the last portions of the amalgam were added. The temperature at this time was 50°. The contrast between this yellow, gelatinous solution and the gray, thinly fluid one obtained with ethyl alcohol was striking, and was explained by the supposition that a methylate of magnesium was formed in the one instance and that no corresponding ethylate was produced in the other. This will be referred to later. The odor of nitrobenzene was still distinct in the reaction-mixture after all the amalgam had been added, but after heating on the water-bath for fifteen hours was no longer discernable.

During the long heating the solution changed in color from light orange-yellow to deep orange-red and became more thinly fluid. The methyl alcohol was then distilled off, leaving a granular orange-colored residue. This was dried in a dish at water-bath temperature, and repeatedly extracted with boiling ligroin. The combined extracts were concentrated to 30 cc. by distillation. After several days beautiful red plates crystallized out; these were recrystallized from methyl alcohol in order to remove the ligroin, and were found to melt sharply at 68°, the melting-point of azobenzene. The yield was 15.5 grams, or 88.5 per cent. of the theoretical.

Metadinitrobenzene in Methyl Alcohol.—Twenty-five grams of *m*-dinitrobenzene were dissolved in 1250 cc. of methyl alcohol (95 per cent.), and 450 grams of amalgam were used for the reduction. During the action of the amalgam the formation of the gelatinous solution was again noted and the colorless solution became chocolate-brown. As in the reduction of the nitrobenzene, the temperature rose to 50°. During the subsequent heating on the water-bath the reaction-mixture became darker and more thinly fluid. The mixture, while still boiling, was poured on to a large Büchner filter, connected with a filter-pump. The dark red filtrate was then heated on the water-bath to distil off the methyl alcohol, and left a residue of 11 grams of an almost black oil. The precipitate on the Büchner filter was dried and then dissolved in 300 cc. of glacial acetic acid, leaving the mercury unattacked. After filtration to remove the last of the mercury, the deep red solution was poured into 2 liters of water, whereupon a voluminous brown precipitate was formed. This was filtered off, washed with water and recrystallized from alcohol. Its melting-point was 140°-142°. This and its other properties identified it as *m*-dinitroazoxybenzene. The yield was 11 grams, or 54.4 per cent. of the theoretical. The filtrate from which it was separated was found to consist of a solution of magnesium acetate, slightly colored by traces of organic matter. The tarry oil obtained from the original alcoholic solution seems to contain the corresponding azo compound, but its separation and purification have proved to be so difficult that it has not been positively identified.

Orthonitrotoluene in Methyl Alcohol.—Twenty-five grams of *o*-nitrotoluene were dissolved in 1250 cc. of methyl alcohol and 300 grams 5 per cent. amalgam added in the customary manner. The gelatinous solution was formed, and upon heating this for fifteen hours it became more thinly fluid, and changed from light yellow to orange-red in color. After distilling off the alcohol and drying the residue, this was extracted with ligroin. The concentrated extract was allowed to stand for several days, when a mass of red, monoclinic prisms crystallized out. These crystals varied in length from 2 mm. to 10 mm. They were filtered off, washed with methyl alcohol and dried; melting-point, 55°. The filtrate was mixed with methyl alcohol, evaporated with a blast of air, and yielded small crystals of the same melting-point. This product agrees with the *o*-azotoluene of Klinger and Pitschke[1] in its properties. The yield was 12.5 grams, or 66.5 per cent. of the theoretical.

Paranitrotoluene in Methyl Alcohol.—Twenty-five grams of *p*-nitrotoluene were dissolved in 1250 cc. of methyl alcohol and reduced with 300 grams of the 5 per cent. amalgam, in the usual manner. Even after fifteen hours heating on the water-bath the odor of *p*-nitrotoluene was still strong, showing that the reduction was incomplete. Notwithstanding this, the alcohol was distilled off, the residue dried and extracted with ether. Evaporation of the ether left 19.5 grams of light yellow, greasy-looking crystals. These were dissolved in ethyl alcohol, and upon evaporation of the solution with a blast of air a quantity of rather short and thick orange-colored prisms was obtained. These were filtered off and upon recrystallization were obtained in the form of slender orange needles, melting at 144°. They were *p*-azotoluene.[2] Yield, 4.5 grams, or 23.9 per cent. of the theoretical.

The filtrate from the *p*-azotoluene was evaporated to expel the alcohol, leaving a red oil, weighing 15 grams, which was dis-

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[1] *Ber. d. chem. Ges.*, **18**, 2555 (1885).

[2] Janovsky and Werigo: *Jahresb.*, 1864, p. 527.

tilled with steam. The distillate had the odor of *p*-nitrotoluene, while the non-volatile part was odorless. The distillate was extracted with ether, the solvent evaporated, leaving reddish yellow crystals, which, upon repeated recrystallization from alcohol, became almost colorless and melted at 54°. This was unchanged *p*-nitrotoluene and weighed 9.5 grams.

The residue from the steam distillation was also extracted with ether, evaporated to dryness and the yellow crystalline mass recrystallized from ethyl alcohol. In this way fine, light yellow crystals, melting at 75°, were obtained. The yield was 5.5 grams, or 22.2 per cent. of the theoretical yield of *p*-azoxytoluene. The result of this reduction was *p*-azotoluene, 23.9 per cent.; *p*-azoxytoluene, 22.2 per cent.; while 38 per cent. of the original *p*-nitrotoluene was recovered unchanged.

In summing up the reductions in dilute methyl alcohol it is seen that nitrobenzene and *o*-nitrotoluene yield the corresponding azo-compounds, while *p*-nitrotoluene yields both azo- and azoxytoluene. The chief exception to the behavior of the other nitro-compounds was found to be *m*-dinitrobenzene, which gave 54.37 per cent. of the theoretical quantity of *m*-dinitroazoxybenzene. The extreme unsolubility of this compound may explain why more of it was not reduced to the corresponding azo-derivative.

A summary of the various reductions with 5 per cent. amalgam and dilute solutions is given in the following table:

Nitro-compound.	Solvent.	Reduction-product.	Theoretical yield. Per cent.
Nitrobenzene . . .	Ethyl alcohol.	Azoxybenzene.	89.9
	Methyl alcohol.	Azobenzene.	88.53
Metadinitrobenzene	Ethyl alcohol.	Metadinitroazoxybenzene.	70.00
	Methyl alcohol.	Metadinitroazoxybenzene.	54.37
Orthonitrotoluene	Ethyl alcohol.	Orthoazoxytoluene.	50.00
	Methyl alcohol.	Orthoazotoluene.	66.50
Paranitrotoluene .	Ethyl alcohol.	Paraazoxytoluene.	90.00
	Methyl alcohol.	Paraazoxytoluene.	22.22
		Paraazotoluene.	23.90

It being evident that methyl alcohol tended to cause the reduction to go to the azo-derivative, while the reduction in ethyl alcohol gave azoxy-derivatives when carried out in dilute solution, the next step in the investigation was to ascertain the cause of this difference in the behavior of the two alcohols.

It was noted that when methyl alcohol was used as a solvent the addition of a magnesium amalgam produced a thick gelatinous syrup, which was absent when ethyl alcohol was used. This, naturally, suggested the thought that methylate of magnesium was formed, and that upon boiling this with a reducible compound it was oxidized to formate of magnesium.

Magnesium Methylate.—Absolute methyl alcohol was prepared from Kahlbaum's best methyl alcohol by prolonged heating over quick lime, followed by distillation and subsequent digestion with anhydrous barium oxide until a yellowish solution was produced and final distillation of this product over more barium oxide.

Two hundred grams of 5 per cent. magnesium amalgam were added to 500 cc. of absolute methyl alcohol in a 1-liter flask, which was provided with a return condenser and heated on the water bath until no evolution of hydrogen was perceptible. The solution was very thick and looked gray, owing to suspended solid matter and finely divided mercury. It was poured, while still boiling, onto a large Büchner filter and suction applied. A clear liquid of syrupy consistency and of a faint yellow color filtered through; after standing over night it deposited a mass of semitransparent, prismatic crystals, from 5 to 10 mm. long.

These crystals were very soft and jelly-like in consistency; upon agitating the flask they broke up to form a pulverulent jelly. This was filtered off on the pump and washed with methyl alcohol. Upon drying at 100° the mass became a white granular powder which, when heated on platinum foil, burned for a short time with a flame like that of alcohol, leaving a white residue which proved to be magnesium oxide. From this it was clear that the magnesium of the amalgam had reacted with the methyl alcohol to form a product soluble therein. After drying the compound for two hours longer at 110° the percentage of magnesium oxide was determined.

Weight of substance.	Calculated MgO in $Mg(OCH_3)_2$. Per cent.	Found MgO. Per cent.
0.7456	46.69	45.50
0.6373	....	45.49

The percentage of magnesium oxide in magnesium hydroxide

71.42, hence we are justified in concluding that the compound formed is not magnesium hydroxide.

If a drop of solution of the supposed magnesium methylate in methyl alcohol be added to 2 cc. or 3 cc. of water, magnesium hydroxide is thrown down as a thick gelatinous precipitate. The reaction is accompanied by the liberation of heat, and is analogous to that which occurs when methylate of sodium or potassium is treated with water.

Magnesium methylate is decomposed upon heating, forming the oxide. It absorbs carbon dioxide from the air, as was proved by exposing the dry compound to the atmosphere and then treating with dilute hydrochloric acid, when an appreciable amount of carbon dioxide was evolved. Magnesium methylate is slightly hygroscopic.

These results agree essentially with those of Szarvasy, who prepared magnesium methylate from magnesium nitride and methyl alcohol, and also by heating magnesium ribbon and the corresponding alcohol under pressure.

Magnesium Ethylate.—Two hundred and fifty cc. of absolute alcohol, contained in a 00 cc. flask with return condenser, were treated with 10 grams of 10 per cent. amalgam. Little or no reaction was apparent until heat was applied. Heating was continued for one hour and a half, when the amalgam was apparently intirely decomposed.

The boiling solution and insoluble matter were poured onto a Büchner filter and suction applied. The colorless filtrate was vaporated to dryness and left a very small residue, showing that the ethylate of magnesium was either insoluble in alcohol or had been decomposed by the heat. The residue upon the Büchner was vashed free from alcohol with absolute ether and the ether removed by heating under diminished pressure on the water-bath. the residue was gray, owing to finely divided mercury. This was collected as completely as possible by agitating the flask and poured off. A considerable quantity of the mercury remained, however. Upon treating a small quantity of the gray powder with n equal volume of water there was a vigorous reaction with volution of heat. Upon adding more water and boiling, ethyl alcohol distilled off, and the solution became gelatinous owing to the formation of magnesium hydroxide. This would indicate that magnesium ethylate was present in the insoluble residue, obtained by the action of hot absolute alcohol upon magnesium amalgam.

Upon subjecting the supposed ethylate to dry distillation a liquid distillate was obtained which smelled strongly of acroleïn, and reduced ammoniacal silver nitrate in the cold, and restored the color to fuchsin aldehyde reagent.

This would indicate that the reason the reductions go one step farther in dilute methyl alcohol than in dilute ethyl alcohol is that while the magnesium methylate is soluble in the corresponding alcohol, and, consequently, easily oxidized to the formate, the ethylate is insoluble in ethyl alcohol and, consequently, has a much weaker reducing action.

In confirmation of the reducing action of the methylate 25 grams of nitrobenzene were dissolved in 1 liter of methyl alcohol and 300 grams of 5 per cent. amalgam added in the customary manner, and the reaction product worked up without boiling To this end the methyl alcohol was distilled off *in vacuo*, the residue dried on the water-bath and extracted in the usual manner Both azoxy- and azobenzene were obtained, the former in large quantity, showing that the chief product of the reduction, due to the amalgam, is azoxybenzene, and that this is reduced to azobenzene when boiled with a solution of the methylate of magnesium.

The results obtained with dilute solutions being different from those obtained by Evans and Fetsch with 10 per cent. magnesium amalgam, and more concentrated solutions it was deemed advisable to repeat their experiments. Accordingly, 10 grams of nitrobenzene were dissolved in 250 cc. of 95 per cent ethyl alcohl in a flask provided with a return condenser, and a quantity of 1 per cent. amalgam theoretically sufficient to reduce the nitrobenzene to aniline, namely, 60 grams, was added in three portion first 30 grams and then two portions of 15 grams each. The reaction was not very energetic upon the addition of the first po tion, but became so upon heating the solution to boiling. As the reaction became less violent, the remaining portions of the amalgam were added. When hydrogen was no longer evolved, the reaction product was filtered and the residue extracted with boiling alcohol. The extracts yielded 5 grams of azobenzene, 67.50 per cent. of the theory. Evaporation of the mother-liquid gave 3 grams of a dark red oil with a decided isonitrile odor. This odor was noticed to a slight extent in all the reductions of nitrobenzene.

Paranitrotoluene in Concentrated Solution.—Ten grams of *p*-nitrotoluene dissolved in 250 cc. of 95 per cent. alcohol and reduced in the manner just described, with 53 grams of 10 per cent. amalgam gave 4 grams *p*-azotoluene, melting-point 144°, equal to 52.2 per cent. of the theory, and 3.5 grams of *p*-azoxytoluene, melting-point 54°, or 42.5 per cent. of the theoretical.

It is probable that the reason for the more marked reducing action of the amalgam in the concentrated hot solution is that the magnesium ethylate is, in part, oxidized as it forms, while if the reduction be carried out in the cold the ethylate precipitates and is not affected by the subsequent boiling.

NOTE.

Note on the Amount of Moisture Remaining in a Gas after Drying with Phosphorus Pentoxide.—My earlier[1] paper on this subject stated that the amount of moisture left in a gas by this drying agent is something like a milligram in 40,000 liters. It is now possible to make the approximation somewhat closer. In order to explain the advance in precision it will be convenient to refer to the parallel case of sulphuric acid.

If air is passed through sulphuric acid it retains some water and takes up some vapor of sulphur trioxide. It is easy to determine the sum of these two quantities, and easy to determine the quantity of sulphur trioxide. The difference of these quantities gives the amount of aqueous vapor left unabsorbed. The quantities concerned are so large, in the case of sulphuric acid, that volumes of a few hundred liters of gas are sufficient to give a tolerable accuracy to the determinations.

Phosphorus pentoxide leaves so little water vapor that an experiment, lasting four months and dealing with 4,300 liters, only gave a quantity 0.1 mg. for the sum of water and of phosphorus pentoxide vapor. This result was published in the hope that it might be found useful, although the amount of pentoxide vapor

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[1] *Am. J. Sci.*, **34**, 199 (1887); Fresenius: *Ztschr. anal. Chem.*, **27**, 1.