

# CATALYTIC PREPARATION OF AZOBENZENE AND ANILINE. II

BY C. O. HENKE AND O. W. BROWN

## Introduction

In our previous work we have shown that nitrobenzene is reduced by hydrogen to azobenzene in the presence of suitable catalysts.<sup>1</sup> Of a large number of catalysts studied, lead and bismuth were found to be the only catalysts which gave azobenzene in large amounts. Small amounts of azobenzene were secured with chromium, antimony and manganese while with the other catalysts a colored product was obtained, the color possibly being due to azoxybenzene and azobenzene. We have secured this formation of azobenzene with thallium as catalyst.

## Experimental Details

The apparatus used was the same as that described in our previous papers with the exception of the following minor changes. A glass combustion tube was used instead of the  $\frac{1}{2}$ " iron pipe. Also the thermometer capillary extended farther into the combustion tube than the T tube through which the hydrogen and the capillary are led into the combustion tube. This eliminates the probability of any nitrobenzene vapors being entrapped between the T tube and the combustion tube.

In our previous work the hydrogen (which was obtained in steel cylinders) was purified by passing through a heated tube filled with pieces of copper, bubbling through concentrated sulphuric acid and then passing over sticks of caustic. It then passed through the flowmeter and into the furnace. It was found, however, that small particles of sulphuric acid were mechanically carried out of the sulphuric acid bottle, through the tower containing solid caustic, through the flowmeter and

<sup>1</sup> Henke and Brown: Jour. Phys. Chem., **26**, 324 (1922).

into the furnace. Not all of the sulphuric acid particles reached the furnace. Most of them were deposited in the rubber and glass tube connections and in the caustic tower. Some, however, were deposited in the flowmeter capillary and some passed into the furnace. The small amount of acid deposited in the capillary of the flowmeter would cause it to read a little too high. It was found that these minute particles of sulphuric acid could be stopped by introducing between the caustic tower and the flowmeter a U tube filled with glass wool. The glass wool seems to effectually remove the sulphuric acid particles, for after a flowmeter had been used in this way for about three months not a trace of acid could be detected in the capillary of the flowmeter.

The method of procedure and the methods of analysis were the same as described in our previous papers.

### Experimental Results

To purify the metallic thallium it was dissolved in sulphuric acid. This solution was heated to boiling and then saturated with  $\text{H}_2\text{S}$  to precipitate any Bi, Sb, As, etc., which might be present. After standing for some time it was filtered and then boiled to remove excess  $\text{H}_2\text{S}$ . An excess of ammonia was then added to the filtrate to throw down iron and alumina and the solution again boiled and filtered. If the filtrate was not almost colorless this operation was repeated. From the clear, nearly colorless filtrate  $\text{TlCl}$  was precipitated by  $\text{HCl}$ . This was filtered out and digested with  $\text{H}_2\text{SO}_4$  with the addition of  $\text{HNO}_3$  and  $\text{HCl}$  until all the thallium was oxidized to the thallic condition. Then the digestion was continued until free from chlorine. Pure thallium hydroxide was then precipitated with ammonia, washed, filtered and dried. Twenty-one grams of the dried oxide was used as catalyst which was placed in the same part of the tube as in our previous work.

The thallic oxide was reduced by a slow current of hydrogen (1.7 liters hydrogen per hour), the temperature being raised gradually. The reduction of the oxide by hydrogen is an exothermic reaction. The heat evolved causes an increase in

temperature at that point of the catalyst column where the reduction is taking place. The reduction begins at that end of the catalyst column where the hydrogen first strikes it. As the reduction proceeded the temperature indicated by the thermocouple was kept below  $250^{\circ}$ . When, however, after about two hours, the reduction zone reached the thermocouple the temperature indicated by the thermocouple suddenly rose to  $278^{\circ}$  and after a few minutes dropped again to about  $250^{\circ}$ .

The results of experiments with this catalyst are given in Table I. In each experiment 2 cc of nitrobenzene was used, the same as in our previous work.

TABLE I.  
Temperature of catalyst— $260^{\circ}$  C.  
Rate of flow of nitrobenzene—4.1 grams per hour.

Experiment number	Hydrogen in liters per hour	Excess of hydrogen in % <sup>1</sup>	Material yield of aniline in % of theory	Material yield of azobenzene in % of theory	Total material yield in % of theory
6J4-2	14	830	2.4	68.6	70.9
7J4-2	14	830	2.0	65.3	67.3
8J4-2	7	370	2.7	78.9	81.6
9J4-2	7	370	3.4	76.0	79.4
10J4-2	3.5	130	3.4	89.9	93.3
11J4-2	3.5	130	4.0	85.5	89.5
12J4-2	1.7	13	4.3	90.2	94.5
13J4-2 <sup>2</sup>	1.7	13	2.0	51.8	53.8

From the above results thallium is a catalyst producing azobenzene almost to the exclusion of aniline. The aniline yields are without exception very low. Besides azobenzene, azoxybenzene was also produced. The amount of azoxybenzene produced was not determined.

The results of Table I are shown graphically in Fig. 1. In curve A are plotted the results of the first experiment at

<sup>1</sup> The excess of hydrogen is calculated from the amount that would be required to produce azobenzene.

<sup>2</sup> In experiment 13J4-2 10 cc of nitrobenzene was used instead of 2 cc.

each rate of flow of hydrogen while in curve B are plotted the results of the second experiment at each rate of flow of hydrogen. The result of experiment 13J4-2 is not plotted in the figure because a 10 cc portion instead of a 2 cc portion was

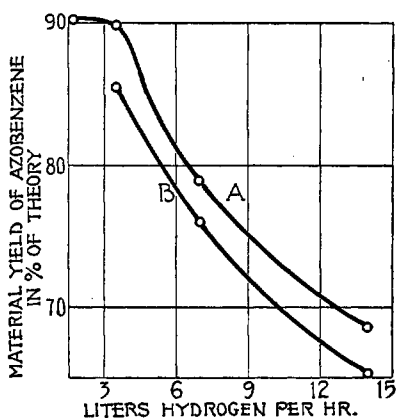


Fig. 1

used in this experiment and hence is not comparable to the others. Both curves show that each time the rate of flow of hydrogen was decreased the yield increased even to the point where the excess of hydrogen was very low. Curve B is lower than curve A. That is, the second experiment at any given rate of flow of hydrogen was lower than the first experiment. This indicates that the catalyst loses its activity with use. Then one would expect that if the first experiment had been carried out with the rate of flow of hydrogen at 1.7 liters per hour a higher total material yield than 94.5% would have been obtained.

This decrease in activity with use is probably due to the fact that thallium melts and runs together. The melting point of thallium as reported in the literature is about  $301^{\circ}$ . It was stated above that the reduction of thallic oxide by hydrogen was an exothermic reaction. With the slow rate of 1.7 liters hydrogen per hour the temperature rose from  $260^{\circ}$  to  $276^{\circ}$  when the zone of reduction reached the thermocouple. With a previous thallium catalyst in which the rate of flow of hydrogen for the reduction was 5.2 liters hydrogen per hour the temperature as indicated by the thermocouple rose from  $240^{\circ}$  to  $304^{\circ}$ . Probably with the slow rate of hydrogen each little particle when it was reduced became heated to a higher temperature than indicated by the thermocouple, probably above the melting point of thallium. Also the reduction of nitrobenzene

is an exothermic reaction. Hence when used as a catalyst probably the little particles were frequently heated above the melting point of the thallium for a short time.

This melting and running together was not encountered to such a great extent with the lead and bismuth catalysts as was pointed out in a previous paper. The lead and bismuth catalysts were frequently used  $30^{\circ}$  and even more above their melting points. Sometimes they would melt and sometimes they would not melt, probably depending on the physical condition of the oxide from which it was reduced. Of the three, thallium melts the most easily and lead the least. In this connection it is interesting to note that thallium produced practically no aniline while lead gives high yields of aniline, bismuth being intermediate. If lead adsorbs hydrogen strongly one might suppose that this adsorbed layer of hydrogen prevented the particles of lead from running together. Likewise if thallium does not adsorb hydrogen (except in small amounts) one might assume that as being sufficient reason for its melting and running together. This could be explained in an exactly similar manner if one assumed the formation of a hydride.

Our previous work with lead showed that the physical condition of the oxide from which the catalyst was made determined to a great extent whether or not it would run together. The catalyst from a coarse crystalline oxide did not run together into globules as easily as the one from a fine amorphous oxide. Thinking that this same thing might hold true in the case of thallium, some precipitated thallic oxide was treated with nitric acid and ignited, the temperature being allowed to rise to  $450^{\circ}\text{C}$ . The resulting oxide was a coarse heavy oxide, 50 grams being required to fill the trough for putting the catalyst in place while only 21 grams of the precipitated oxide were required. This catalyst after reduction was used under the same conditions as experiment 6J4-2 and gave an 89.5% yield of azobenzene and 3.5% yield of aniline. The second experiment, carried out like experiment 10J4-2,

gave an 89.9% yield of azobenzene and 6.4% yield of aniline, a result very similar to that of experiment 10J4-2. Upon examining the catalyst it was found to have melted and run together as the previous thallium catalysts.

Sabatier<sup>1</sup> states that under certain conditions platinum, when used as a catalyst in the reduction of nitrobenzene, gives some white crystals of hydrazobenzene. We have secured high yields of azobenzene with thallium, lead and bismuth as catalysts. This suggests an analogy between atomic weight and catalytic activity for when arranged in the order of their atomic weights Tl, Pb and Bi fall together, one after the other, while Pt precedes Tl by only two elements, mercury and gold. If the analogy holds these two metals should act as catalysts producing azobenzene or hydrazobenzene.

TABLE II

Rate of flow of nitrobenzene—4.4 grams per hour.

Rate of flow of hydrogen—14 liters per hour.

Excess of hydrogen—480%.

Experiment number	Temperature degrees C	Material yield of aniline in % of theory
7K2 <sup>2</sup>	260	85.9
8K2	260	54.8
10K2 <sup>3</sup>	279	90.9
11K2	298	93.2
18K2	317	90.3
19K2	336	98.3
20K2	355	99.7

A gold catalyst was prepared by dissolving 5 grams of gold in aqua regia, adding 4 grams of asbestos, and evaporating and drying. When this catalyst was used at 260° some solid red azobenzene appeared in the condenser but there was practically no aniline. In the attempt to get a more active cat-

<sup>1</sup> Sabatier: "La Catalyse," p. 112 (1913).

<sup>2</sup> In this experiment the rate of flow of nitrobenzene was 1.9 grams per hour.

<sup>3</sup> Previous to this experiment the catalyst was heated in hydrogen to 342° C.

alyst 6 grams of gold were dissolved in aqua regia as before and then boiled down several times with nitric acid. However this treatment did not remove all the chlorine. Four grams of asbestos were then added and the resulting mass dried at about 50°. This catalyst was put in the furnace and reduced at 260°. Some of the results with this catalyst are given in Table II.

In the first experiment (No 7K2) 0.185 gram of a white crystalline solid appeared in the condenser. It had a melting point of about 194° C. It was soluble in alcohol, water and dilute  $\text{NH}_4\text{OH}$  and dilute  $\text{HNO}_3$ . When dissolved in  $\text{NH}_4\text{OH}$  it gave a white precipitate upon the addition of  $\text{H}_2\text{SO}_4$ , which was soluble upon the addition of more ammonia. However the original white solid would dissolve and give a clear solution in dilute  $\text{H}_2\text{SO}_4$ . When dissolved in  $\text{HNO}_3$  it gave a white precipitate upon the addition of  $\text{AgNO}_3$  which was soluble in  $\text{NH}_4\text{OH}$ . When burned on a platinum wire it left no ash. It was probably a chlorazo or hydrazo compound.

In the second experiment only a small amount of this compound was formed. Also the aniline yield decreased a great amount indicating a decrease in activity. The first gold catalyst also decreased in activity with use, solid red azobenzene being formed in the first experiment but not in the second experiment. This indicates that gold is capable of producing small amounts of azobenzene and thus fits in the analogy, although its activity in this direction is very low.

Mercury was also tried but probably due to the fact that it is liquid at room temperature no catalytic effect was obtained. At most this analogy between atomic weight and catalytic activity is probably only one factor, for a lead catalyst can be prepared which will give 97% yields of aniline at 310° and on the other hand one can be prepared which will give 55% yields of azobenzene at 290°.

Gold is moreover capable of giving high yields of aniline, in fact almost theoretical yields, experiment 20K2 giving a 99.7% yield of aniline. However it loses its activity with use.

Thus experiment 18K2 is a little lower than 11K2 while if it had followed 11K2 it would probably have been higher.

### Summary

1. Thallium has been shown to be an excellent catalyst for reducing nitrobenzene to azobenzene, giving very little aniline.

2. The activity of the thallium decreases very rapidly with use, probably caused by its melting and running together.

3. With thallium at  $260^{\circ}\text{C}$  and 13% excess of hydrogen a material yield of 90.2% azobenzene was obtained.

4. An analogy between atomic weight and the property of acting as a catalyst in the formation of azobenzene has been pointed out.

5. Gold has been shown to have high catalytic activity for producing aniline which decreases with use. With gold as catalyst the yield of aniline at  $355^{\circ}\text{C}$  is almost quantitative.

*Laboratory of Physical Chemistry  
Indiana University, Bloomington*