THE CATALYTIC ACTIVITY OF REDUCED COPPER CHROMATE AND OF VANADIUM OXIDE IN THE REDUCTION OF NITROCOMPOUNDS*

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Introduction

The ability of finely divided platinum to promote certain oxidations was discovered by Davy and Doebereiner at the beginning of the nineteenth century. Near the latter part of the same century Sabatier and his co-workers began an extensive investigation of catalysis in the field of organic chemistry. Since that time numerous experiments have been carried out in many different laboratories, showing that a great number of diversified chemical reactions can be promoted by the use of suitable catalysts.

Since 1920, a series of investigations have been made in this laboratory, concerning the ability of finely divided metals and oxides to catalyze the reduction of nitrocompounds by hydrogen. This article gives the results of an investigation of the catalytic activity of reduced copper chromate and of vanadium oxide in the reduction of nitrobenzene to anilin. The activity was measured by the yields of amines and by the impurities which were present in the anilin.

Apparatus and Method of Procedure

The catalytic furnace used in this investigation was a horizontal type with an electrically heated bath consisting of lead-tin eutectic alloy, 75 atomic per cent of tin. The catalyst tube was an iron pipe, thirty inches in length and one inch in diameter. The design of the furnace and the method of operation are described in a previous publication[3] from this laboratory

The ends of the catalyst tube were covered with a thick layer of asbestos to retard the leakage of heat and to prevent the condensation of the products in the delivery tube. The products were condensed in an air-cooled glass condenser. The excess hydrogen passed downward through a condenser drain tube and bubbled through 100 cc. of 1:1 HCl in a graduated liter flask. This was to prevent the escape of uncondensed anilin.

The catalyst was introduced into the furnace through an opening made by unscrewing the delivery tube. By means of a metal boat with a calibrated handle, a catalyst column ten inches long was placed inside the furnace. The outer end of this column was five and one-half inches inside the heating jacket of the furnace.

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[3] J. Phys. Chem., **34**, 2651-2665 (1930).

The temperature was measured by means of a copper constantan (advance) thermocouple which was inserted in a well surrounded by the metallic bath. This was calibrated against a standard thermocouple whose tip was placed inside the catalyst tube, five and one-half inches inside the heating jacket. During the calibration, air was passed through the furnace at the rate of 14 liters per hour.

Two cubic centimeter samples, measured by means of a calibrated pipette, were introduced into the furnace through a glass capillary. This capillary extended far enough into the catalyst tube to insure that the nitrobenzene was vaporized and would be carried over the catalyst by the hydrogen. The rate of flow of the nitrobenzene was regulated by means of a variable pressure which was obtained by changing the height of a mercury column, as described by Brown and Henke.[1] The rate of flow of hydrogen was measured by a calibrated flowmeter.

While the furnace was being heated to the desired temperature before an experiment and during the cooling which followed the completion of a series of runs, a current of hydrogen was continually passed through the furnace.

The hydrogen was allowed to flow for forty minutes, at the same rate as that used during the experiment, after the last of the nitrobenzene had entered the furnace. The amount of material still remaining in the furnace was very small and practically constant. Since the experiments were carried out without a time interval between them, this error was eliminated from all except the first run of a series.

After the furnace was "washed" with hydrogen 1:10 HCl was used to wash the products from the condenser into the graduated liter flask containing the 100 cc. of 1:1 HCl. This sample was then diluted to one liter and 100 cc. aliquot portions were titrated with tenth molar sodium nitrite solution. (This solution was standardized against pure catalytic ortho amido phenol.) Twenty cubic centimeters of conc. HCl were added before titrating. Starch iodide paper was used as an external indicator.

At room temperature the reaction is as follows:

$$C_6H_5NH_2 + HNO_2 \longrightarrow C_6H_5OH + N_2 + H_2O$$

If the temperature is low the following reaction occurs:

$$C_6H_5NH_2 \cdot HCl + HNO_2 \longrightarrow C_6H_5N_2Cl + 2H_2O$$

Since both reactions use the same amount of nitrous acid per mol of anilin the titration can be made at room temperature. Any other amines present would produce an error but this would be less than that introduced by purifying the anilin and weighing it.

All the yields given in this article are the average of from two to four consecutive experiments. The first run of each series is not included since it is generally either high or low, depending upon the previous history of the catalyst. The maximum variation of yields from these consecutive experiments is within one-half of one per cent.

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[1] J. Phys. Chem., **26**, 161, 272 (1922).

The quality of the anilin was investigated by collecting one run at each point of investigation. Part of this was let stand exposed to light for several days and the color changes noted. Part was placed on a watch glass in a drying oven at about 80°C. After the anilin had evaporated the glass was examined for solid residue.

In order to purify the nitrobenzene, it was shaken with sodium carbonate solution, removed from the mixture by steam distillation, separated from the water in the distillate by decantation and dried with anhydrous calcium chloride. It was then distilled while in contact with fresh drying agent. The central constant boiling portion was redistilled. The middle portion of this distillate was used in this investigation.

The commercial hydrogen was purified by passing over red-hot copper, bubbling through concentrated sulphuric acid, passing through a caustic tower and then through a glass-wool filter.

Part I

Reduced Copper Chromate as a Catalyst

Preparation of the Catalyst

One hundred grams of Mallinckrodt's potassium dichromate were dissolved in about three liters of distilled water. Enough potassium hydroxide was added to convert the salt to potassium chromate. One hundred fifty grams of J. T. Baker's C. P. copper nitrate were dissolved in one and one-half liters of water. This solution was added to the potassium chromate solution while stirring rapidly. The precipitate was washed three times by decantation and then washed well on a Büchner funnel. It was then dried in an oven for about two days at 80°C. The lumps were then ground into a coarse powder (through a ten mesh screen) and stored in a stoppered bottle until needed.

All copper chromate catalysts were prepared in the following manner unless otherwise specified. Fifteen grams of copper chromate were placed in the catalyst tube and reduced at 360°C. for one hour with a rate of flow of hydrogen of 14 liters per hour.

Experimental Part

The data given in Table I show the effect of the rate of flow of nitrobenzene on the yield of amines.

Twenty runs were made before the above data were taken. Nitrobenzene was fed into the furnace at the rate of 3.55 grams per hour in these preliminary experiments. A new catalyst does not give constant yields during the first few runs.

Slow rates of flow of nitrobenzene produced a red-colored product. Tar-like substances condensed in the furnace exit-tube. The red color of the product and the tar gradually disappeared as the rate of flow of the nitrobenzene was increased.

TABLE I

Catalyst—reduced copper chromate.
Rate of flow of hydrogen—14 liters per hour.
Temperature—310°C.

Nitrobenzene Gms. per hr.	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
2.4	975	96.6
2.9	810	97.0
3.55	660	97.5
4.75	495	97.4
7.3	320	97.2
10.8	220	96.6

The best yields and the best products were obtained when 3.5 to 4.75 g. per hour of nitrobenzene were fed into the furnace. This anilin was clear with only a faint green color. Only a faint trace of solid residue remained when a small portion was evaporated on a watch glass. The sample which was titrated remained water white after titration. Many of the impurities gave colored products with sodium nitrite in the presence of hydrochloric acid. This showed that these substances were absent.

A deep green color replaced the green tint as the rate increased beyond 4.75 g. of nitrobenzene per hour. This color seemed to appear when the catalyst was being overloaded. This could be done either by feeding the nitrobenzene into the furnace too rapidly or by shortening the time of contact by increasing the rate of flow of the hydrogen. Anilin which had this deep green color reddened rapidly on standing in the light. The conditions under which the green appeared indicate that it was probably due to some intermediate reduction compound of nitrobenzene.

The figures given in Table II show the effect of the rate of flow of hydrogen on the yield of amines.

TABLE II

Catalyst—reduced copper chromate.
Rate of flow of nitrobenzene—3.55 g. per hour.
Temperature—310°C.

Hydrogen in liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
25	1180	96.7
20	940	97.7
14	660	98.3
10	470	98.8
5	235	98.7
3	140	98.3

Fifteen runs were made before the above data were taken.

The best yields and products were obtained when the rate of flow of hydrogen was ten liters per hour. When slower rates were used, the anilin had a reddish tint which darkened to a deep red on standing over night. When faster rates were used, the product had a deep green color. Here, again, this color appeared when the catalyst was overloaded.

The results given in Table III show the effect of temperature on the yield of amines.

TABLE III

Catalyst—reduced copper chromate.
Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of hydrogen—10 liters per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin
381	86.4	297	98.4
349	94.3	282	98.1
333	96.9	246	96.0
310	98.8	237	80.9
		217	43.2

The product had a burnt orange color at high temperatures. This color gradually disappeared as the temperature was lowered. After four runs at 310°C., the product was clear and the only color was a faint tinge of green. Below 310°C., the green gradually darkened.

Below 310°C., the yield of anilin decreased as the temperature became less. Two things indicate that this was due to a decrease in the activity of the catalyst. The first was the appearance of the green color. The second was the appearance of nitrobenzene in the products. One method of detecting its presence was by its odour. Another was by the characteristic taste of nitrobenzene that one obtained from the vapors while pipetting aliquot samples for titration. Below 246°C., a black tarry amorphous precipitate appeared in the hydrochloric acid solution. It also appeared in the delivery tube of the furnace. Nitrobenzene, highly colored with impurities, collected at the bottom of the solution of anilin-hydrochloride.

Above 310°C., the yield of anilin also decreased. Apparently, since no nitrobenzene was found in the products, this decrease in yield was not due to too little activity but rather to too much activity on the part of the catalyst. Above 400°C., the volume of the condensed liquid products decreased rapidly. When operating at these high temperatures, a white smoke poured out of the delivery tube of the furnace. This smoke condensed neither in the air-cooled glass condenser nor in the 1:1 HCl in the graduated liter flask but was carried out into the air by the excess hydrogen.

Traces of products, probably due to consecutive reactions, increased with the temperature (above 310°C.). At 381°C. enough diphenylamine was produced to give a slight precipitate when the anilin-hydrochloride solution was diluted to one liter. At temperatures below 381°C., there was enough of the secondary amine present to give the solution a purple color after titration with sodium nitrite. After two or three runs were made at 297 to 282°C., no test for diphenylamine could be obtained. After running at temperatures in the neighborhood of 400°C., several runs were necessary before the product failed to give a test for this secondary amine when the temperature of the furnace was maintained at 310°C.

The curves in Fig. 1 show the relation between the temperature and the yield of amines with a reduced copper chromate, a copper and a chromium catalyst. The data for the copper and chromium were obtained from previous publications[1] from this laboratory.

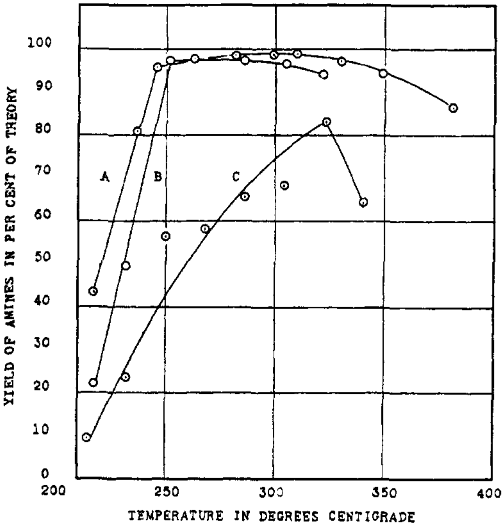

FIG. 1

Curve A shows the yields obtained over a reduced copper chromate catalyst. The yields for a copper catalyst are plotted in curve B and for chromium in curve C.

It is seen, from the curves, that the action of the reduced copper chromate catalyst more closely resembles that of copper than of chromium. The products also indicated this.

Three catalysts were prepared from copper chromate. Fifteen grams were used in each case. The first was heated in a current of hydrogen, 14 liters per hour, at 360°C. for one hour. The second was heated in a current of hydrogen, 14 liters per hour, at 460°C. for one hour. The third was first heated in a current of air at 460°C. for two hours and then heated in a current of hydrogen, 14 liters per hour, at 360°C. for one hour. The three catalysts

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[1] J. Phys. Chem., **26**, 161, 272 (1922).

were run at 310°C. until constant yields were obtained. The rate of flow of nitrobenzene was 3.55 g. per hour. The rate of flow of hydrogen was 14 liters per hour. The first catalyst produced 98.7 per cent of anilin. The second gave yields which averaged 96.5 per cent and the third produced 99 per cent of anilin. This shows that the yield of anilin can be decreased by heating the catalyst in hydrogen at 460°C. The anilin produced by such a catalyst is opaque. Previous heating in air at 460°C. seemed to have little effect on the yield and quality of the anilin. The products obtained by the use of the first and third catalysts were clear and almost white. The only color was a faint trace of green. There was only a slight trace of solid residue remaining after the anilin was removed by evaporation at about 80°C. The solution of anilin-hydrochloride remained water white after titration with sodium nitrite. The anilin, without purification by distillation, when protected from the light would remain without any appreciable color change for three or four days. At the end of three weeks, it was still clear but had acquired a light red color.

Anilin produced under unfavorable conditions was opaque and not clear. This was due to finely divided impurities in suspension. The addition of two drops of nitrobenzene to 2 cc. of anilin will produce a red color in a few minutes. This explains why the anilin which contained traces of nitrobenzene was red. Other impurities were produced at high temperatures which also gave the product a red color.

PART II

The Catalytic Activity of Vanadium Oxide in the Reduction of Nitrocompounds

A few experiments, using a lower oxide of vanadium as a catalyst, were carried out[1] in this laboratory in 1922. The maximum yield of anilin obtained by the reduction of nitrobenzene was 88 per cent of theory. The following experiments were carried out to investigate the activity of this catalyst.

The catalysts were prepared by the ignition of ammonium meta-vanadate, C. P., purchased from the S. W. Shattuck Chemical Co., Denver, Colorado.

The effect of the rate of flow of hydrogen on the yield of amines is shown by the results given in Table IV.

TABLE IV

Catalyst—15 g. V_2O_5 reduced in hydrogen (é).
Rate of flow of nitrobenzene—3.55 g. per hour.
Temperature—403°C.

Hydrogen in liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
20	940	80.8
14	660	83.9
10	470	79.5

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[1] J. Phys. Chem., **26**, 283 (1922).

(*e*) *Preparation of the catalyst.* Ammonium meta-vanadate was placed in a porcelain dish and ignited in an electric muffle at 275°C. for three hours. During the heating the catalyst was stirred frequently. The muffle was provided with two openings for the circulation of air. The resulting black powder was placed in a cold catalytic furnace. The temperature was gradually raised to 460°C. where it was maintained for two and one-half hours. During this time, hydrogen was passed through the furnace at the rate of 14 liters per hour. The catalyst was probably a lower oxide of vanadium.

Fifteen runs were made with this catalyst at 403°C. before the data for Table IV were taken. Constant results were not obtained during the first runs. The product from these first runs was green and no precipitate could be detected in the anilin-hydrochloride solution. The color became lighter after the first few runs and a precipitate containing diphenylamine appeared in the 1:1 HCl in the liter flask. No precipitate appeared in the glass condenser since this secondary amine is somewhat soluble in anilin.

The diphenylamine was identified by the following properties:

1. It was almost insoluble in dilute acids and its solubility increased with the concentration of the acid. It was soluble in concentrated hydrochloric or concentrated sulphuric acid.

2. When sodium nitrite or some other oxidizing agent was added to its solution in concentrated sulphuric acid an intense blue color appeared. At lower concentrations, varying shades of color from blue to light purple appeared.

3. The crystals were flat plates. The melting point was not sharp but was from 55° to 65°C. This was due to impurities and to decomposition products caused by the exposure of the amine to the air and to traces of HCl which was used to remove the anilin.

4. When the crystals were moistened with dilute hydrochloric acid they turned blue on exposure to the air for a few hours.

The presence of this secondary amine introduced an error in the determination of amines, since one mol of diphenylamine combines with the same amount of nitrous acid as one mol of anilin. When the solution of anilin in 1:1 HCl was diluted to one liter, part of the dissolved diphenylamine precipitated. Most of the precipitate was in a state of fine division and remained in suspension. Since part of the secondary amine was still in solution no attempt was made to remove the rest by filtration. Even under the most favorable conditions for the production of diphenylamine less than five per cent of it was produced. When the conditions were favorable for the production of anilin this error was less than one-tenth of one per cent. The presence of the precipitate made the end point of the titration rather slow since more of the precipitate dissolved as that in solution was removed by the titration. In acid solution, the following reaction takes place during titration.[1]

$$(C_6H_5)_2NH + HNO_2 \longrightarrow (C_6H_5)_2N \cdot NO + H_2O$$

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[1] Bernthsen and Sudborough: "Text-book of Organic Chemistry," 404 (1930).

The best yield of amines was obtained with this catalyst when hydrogen was passed into the furnace at the rate of 14 liters per hour. When a rate of ten liters per hour was used the precipitate of diphenylamine increased. When samples of the anilin were taken most of this secondary amine was dissolved in the solvent, but part of it remained in suspension. This caused the solution to be opaque. The sample darkened rapidly. This was more noticeable when it was exposed to a strong light.

The production of diphenylamine seems to be a consecutive reaction and not a side reaction. If a catalyst promotes consecutive reactions, then increasing the time of contact with the catalyst should increase the amount of the substances which are formed by the consecutive reactions. This fact and the results shown in Table IV and Table V lead the authors to believe that the production of the diphenylamine is a consecutive reaction. It probably takes place in the following manner.

$$2\ C_6H_5NH_2 \longrightarrow (C_6H_5)_2NH + NH_3$$

Diphenylamine was produced in all of the experiments listed in Table IV. When the rate of flow of hydrogen was increased to twenty liters per hour the yield of both anilin and diphenylamine decreased.

The effect of nitrogen on the activity of vanadium oxide is shown in the results given in Table V.

TABLE V

Catalyst—15 g. of reduced V_2O_5, prepared in the same manner as described following Table IV

Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of gas—14 liters per hour.
Temperature—403°C.

Nitrogen Liters per hour	Hydrogen Liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
0	14	660	83.8
4	10	470	80.8
10	4	190	73.7

In this case, the rate of flow of the gases was kept constant and the partial pressure of the hydrogen was varied. The effect which the nitrogen had on the adsorption of the hydrogen and the nitrobenzene is not known. This should be specific and should depend on the nature of the catalyst used and on the other substances present. The yield of amines was decreased by the presence of the nitrogen. If the variation in the amount of hydrogen made any change in the amount of diphenylamine produced, this difference was too small to be detected by inspection of the precipitate.

The data given in Table VI show the effect of temperature on the activity of a vanadium oxide catalyst.

Table VI

Catalyst—15 g. of reduced V_2O_5, prepared as previously described.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—3.55 g. per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yields of amines in percent of theory. Calculated as anilin
489	35.1	403	81.3
442	61.0	393	75.0
425	66.9	368	54.7
413	75.1	336	30.2

Fifteen runs were made with this catalyst at 403°C. before the data for Table VI were taken. All anilin produced above 393°C. contained diphenylamine. The amount increased as the temperature increased. No clear aniline was produced with a vanadium oxide catalyst prepared in this manner. The opacity of the aniline was due to impurities which were in suspension.

The anilin was black when the temperature was allowed to drop a few degrees below 403°C. A tarry product condensed in the delivery tube of the furnace. It was this substance which produced the color in the anilin. Tests showed that this tar was only slightly soluble in alcohol, ether or gasoline, but was fairly soluble in anilin. When several runs were made at lower temperatures the formation of this tar decreased rapidly but never ceased entirely. This was very similar to the action of reduced copper chromate at temperatures below 246°C. As the amount of tar produced decreased the black color of the product gradually changed to red. The red color was probably due to traces of nitrobenzene in the product. The amount of nitrobenzene increased as the temperature decreased. When the catalyst was used at temperatures as low as 336°C. large drops of nitrobenzene collected at the bottom of the anilin-hydrochloride solution. The catalytic activity of this catalyst, at temperatures below 403°C. seems to decrease as the temperature decreases. The red color of the anilin produced at low temperatures is similar to the color produced when nitrobenzene is added to anilin.

Although nitrobenzene was found in the products at lower temperatures, none was detected in the mixture at higher temperatures. Products from consecutive reactions, such as diphenylamine appeared at higher temperatures but they did not appear when the catalyst was used at lower temperatures.

Experiments were conducted to determine the effect of heating the V_2O_5 in air at 400°C. before it was reduced in hydrogen. After the V_2O_5 was heated in a current of air at 400°C. for one hour, 15 g. of the material were placed in the catalyst tube and reduced by heating in hydrogen for two and one-half hours at 460°C. The rate of flow of hydrogen was 14 liters per hour. Fifteen runs were made before the data were taken. The yields from this catalyst are shown in Table VII.

TABLE VII

Catalyst—15 g. of reduced V_2O_5.
Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of hydrogen—14 liters per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin
415	80.8	398	86.8
408	87.7	378	77.2
403	89.3	360	67.9

The results in Table VII show that heating to 400°C. in air increased the production of anilin. Less diphenylamine was produced by this catalyst than by the ones prepared by heating in air to only 275°C. The anilin produced by the use of this catalyst was opaque due to impurities in suspension.

A catalyst was prepared by heating ammonium meta-vanadate in air at 450°C. for one hour. Fifteen grams of the V_2O_5 produced were placed in a catalytic furnace and heated in a current of hydrogen, fourteen liters per hour, at 460°C. for two and one-half hours.

A study of the effect of the rate of flow of nitrobenzene on the yield of amines was made with this catalyst. Table VIII shows the results obtained. Fifteen runs were made before the data for this table were taken.

TABLE VIII

Catalyst—reduced V_2O_5.
Temperature—403°C.
Rate of flow of hydrogen—14 liters per hour.

Nitrobenzene Gms. per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
2.37	970	90.9
2.85	805	91.3
3.55	660	91.7
4.90	480	91.8
7.10	330	88.3

The color of the anilin was a cherry red when slow rates of feed of nitrobenzene were used. The purple color due to the reaction of diphenylamine and sodium nitrite, appeared in the solution of anilin-hydrochloride after the titration had been made. Tarry substances condensed in the delivery tube of the furnace.

As faster rates were used, the product gradually lost its red color. When 7.1 g. per hour of nitrobenzene were fed into the furnace the product was a yellowish green. The color as well as the decrease in the yield of amines indicates that the catalyst was overloaded.

The anilin produced when 3.5 to 4.9 g. per hour of nitrobenzene were fed into the furnace was almost clear. A test for diphenylamine could be obtained by evaporating the anilin at about 80°C. and dissolving the solid residue in a few drops of concentrated sulphuric acid. The addition of a drop of sodium nitrite solution produced a deep blue color.

Discussion of Results

When the flow of nitrobenzene was kept constant, the furnace maintained at the most favorable temperature and the rate of flow of hydrogen was varied, an intermediate rate was found to give the highest yield of amines in per cent of theory. A high velocity of the hydrogen seemed to cause incomplete reduction. In the horizontal furnace, the contact between the reacting gases and the catalyst is brought about by the diffusion of the gases and convection currents. The heat of reaction and, possibly, the heat of adsorption cause the temperature of the catalyst to become higher than that of the rest of the furnace. The heat of reaction in the reduction of nitrobenzene to anilin is 98.8 Calories per mol. The vapors in contact with the wall of the furnace also become hotter than the rest. This difference in temperature causes the convection currents. The concentration of the nitrobenzene vapor in the original gaseous mixture is decreased next to the catalyst since it, in addition to part of the hydrogen, is continually being removed by the chemical reaction. This would cause diffusion of the nitrobenzene toward the catalyst. Probably, a high velocity would carry some of the nitrobenzene vapor through the furnace without its being in contact with the catalyst.

When the velocity of the vapors was too low there was too long a contact with the catalyst, which reduced the yield of anilin. The red color and the opacity of the products, neither of which was due to nitrobenzene or anilin, indicate that the decrease in yield was due to the formation of other compounds. When a vanadium oxide catalyst was used one of these compounds was shown to be diphenylamine.

In addition to velocity, the ratio of nitrobenzene to hydrogen is a factor which must be considered in the production of anilin. When the rate of flow of hydrogen was kept constant and the amount of nitrobenzene was varied an intermediate rate of flow of nitrobenzene was found to be the most favorable for the production of anilin. (See Tables I and VII). When low rates of flow of nitrobenzene were used, the product was red and opaque. A tar-like substance with a high boiling point condensed in the delivery tube of the furnace. When sufficiently high rates were used nitrobenzene could be detected in the products. Thus, low rates favor the formation of impurities in the anilin while high rates cause incomplete reduction of the nitrobenzene. The most favorable rate of flow of nitrobenzene and of hydrogen depends upon the amount and the nature of the catalyst used.

The effect of the temperature has been described following Tables III and VI.

When these catalysts, which had been working under favorable conditions for the production of anilin, were used at sufficiently low temperatures a large quantity of tarry substances appeared in the products. However, the amount of tar decreased with each successive run until only a trace remained. In the case of reduced copper chromate, the temperature drop required was about 70°C. below the most favorable temperature for the production of anilin. When vanadium oxide was used a drop of about 15°C. was sufficient to promote the formation of these tars.

Conclusion

I. The highest yield of amines obtained with a reduced copper chromate catalyst was 99 per cent of theory. This yield was obtained at 310°C. with a flow of hydrogen of 14 liters per hour and a rate of flow of nitrobenzene of 3.55 g. per hour. The catalyst used was prepared by heating copper chromate in air at 460°C. and then reducing it in a current of hydrogen, 14 liters per hour, at 360°C.

II. The highest yield of amines obtained with a reduced vanadium oxide catalyst was 91.8 per cent of theory. This yield was obtained at 403°C. with the rate of flow of nitrobenzene 4.9 g. per hour. The rate of flow of hydrogen was 14 liters per hour. The catalyst was prepared by igniting ammonium meta-vanadate in air at 450°C. for one hour. Fifteen grams of the vanadium pentoxide produced were placed in a cold catalytic furnace and heated in a current of hydrogen, 14 liters per hour, at 460°C. for two and one-half hours.

III. Diphenylamine was shown to be one of the products which was produced by both catalysts. Vanadium oxide was shown to be a better catalyst than reduced copper chromate for the production of diphenylamine.

IV. The substitution of nitrogen for part of the excess hydrogen was shown to decrease the yield of amines when a vanadium oxide catalyst was used.

V. Reduced copper chromate was shown to be a better catalyst for the production of anilin than vanadium oxide. The ability of reduced copper chromate to promote the production of a high grade anilin was shown.

VI. The relative amounts of nitrobenzene and hydrogen, the velocity of the gases as they passed over the catalyst and their temperature were shown to be important factors in the production of secondary products.

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