Catalytic Vapor-Phase Nitration of Benzene...

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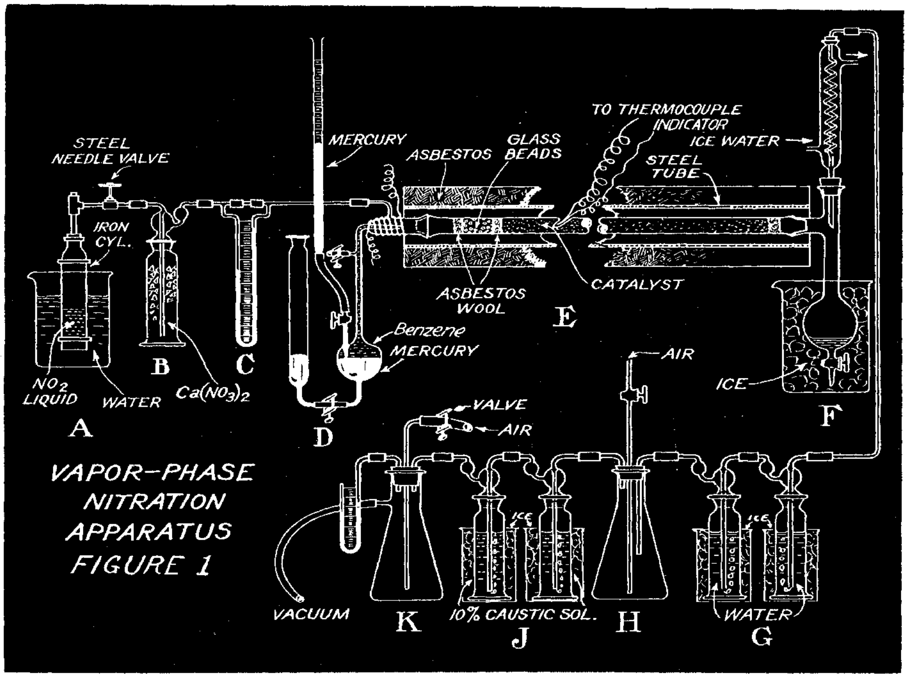

VAPOR-PHASE NITRATION APPARATUS FIGURE 1

NITROGEN dioxide as a nitrating agent has been the subject of numerous publications, and its present availability by the oxidation of ammonia has increased interest in the field. Reactions of nitrogen dioxide with liquid benzene have been described (*1*, *6*, *9*, *19*), but nitrobenzene was not produced in quantity without by-products, and the results may well be expressed in the words of one of the later papers, "We have detected very little evidence of the utility of nitrogen dioxide as a nitrating agent." More satisfactory nitrations resulted when anhydrous chlorides (*16*, *17*), and also sulfuric acid (*13*, *14*), were used together with nitrogen dioxide.

Nitration of benzene is normally carried out using a mixture of sulfuric and nitric acids. The present paper describes a vapor-phase process using nitrogen dioxide as the nitrating agent at atmospheric pressure and about 310° C. and silica gel as catalyst. The conversion of benzene to nitrobenzene can be brought to 80 per cent but only by use of excess nitrogen dioxide. Nitric oxide formed as a by-product can readily be recovered for re-use as nitrogen dioxide by air oxidation.

In this investigation benzene was nitrated in the vapor phase with nitrogen dioxide using silica gel as a catalyst with yields ranging from 0 to 83 per cent with respect to benzene. The conditions would, if desired, permit the recovery of the excess of each of the starting materials for re-use. By-products of nitrobenzene were not formed in objectionable amounts.

Previous vapor-phase nitration work recorded in the literature consists essentially of a German patent (*7*), in which the nitrogen oxides are absorbed by a metallic oxide and the resulting solid salt brought in contact with hot benzene vapor; an article by Menke (*10*), which describes the passage of a mixture of benzene and nitrogen dioxide over heated bismuth oxide or through mercury vapor; and finally an article by Shoruigin and Topchiev (*18*), which appeared after the present work was well under way. The latter authors reported that, when 40 grams of benzene and 200 grams of nitrogen dioxide, independently vaporized in streams of carbon dioxide, were brought together at 55° to 60° C. in the presence or absence of ultraviolet light for a short vapor-phase contact and then condensed, within a period of 2 hours, 20 grams of mononitrobenzene resulted. The nitrations were apparently noncatalytic.

Silica gel in several cases has showed its value as a catalyst for reactions in which water issues as a product of the reaction. Thus Brown and Reid (*5*) found silica gel to be a vapor-phase alkylation catalyst in their work on the combination of alcohols with ammonia and aniline. The esterification of acetic acid with ethyl alcohol has been performed in a similar fashion with high conversion efficiencies by Milligan, Chappell, and Reid (*11*). Since water would be expected to be a product in the type of nitration reaction under consideration, the use of silica gel as a catalyst for the vapor-phase nitration of benzene by nitrogen dioxide suggested itself at the beginning of the present investigation. Preliminary experiments soon showed that nitrobenzene was in fact formed in the presence of silica gel. The gel did not appreciably aid nitration of benzene by nitrogen dioxide in the liquid phase. Copper oxide, dehydrated bauxite, precipitated aluminum oxide, magnesium oxide, cerium oxide, and other oxides used in the preliminary experiments gave no appreciable vapor-phase nitration under conditions for which silica gel permitted very definite nitration. Following this initial work, a larger apparatus was built and the function of silica gel as a nitration aid was singled out for investigation.

Materials

Nitrogen dioxide was prepared by the usual method of dropping concentrated nitric acid on warm powdered arsenious oxide. Water and nitric acid were removed by fractional condensation.

Benzene with a boiling range between 80° and 82° C. and toluene with a range between 110° and 112° C. were used.

The most satisfactory nitrations were obtained and most of the experimental work was done with an active gel that is ordinarily used for the physical dehydration of gases. It was a 14-mesh material and will be called "silica gel A." Another gel, designated "silica gel B" and generally used in water purification by filtration, was less active in catalyzing the nitration of benzene. It was a 6–10 mesh gel.

Bauxite from British Guiana was used in a 5-6 mesh size. The bauxite contained titanium oxide, iron oxide, silicon dioxide, and water in addition to aluminum oxide.

An activated alumina, 8–14 mesh, and ordinarily employed in the physical drying of gases, was used in one nitration experiment.

Analytical Methods

NITRO GROUP. In the analysis for the nitro group, the titanous chloride titration method was used (*8*). The titanous chloride was standardized against recrystallized *p*-nitraniline and checked against potassium dichromate. Each analysis was carried out under nitrogen in order to avoid the oxidation of titanous ion by air. The average deviations for pairs of determinations varied between 1 and 2 per cent.

NITROGEN DIOXIDE. Nitrate and nitrite ions that are formed when nitrogen dioxide is absorbed in a caustic soda solution were separately determined. The total nitrogen dioxide absorbed was calculated by its equivalence to the sum of these ions. Oxidation with an excess of standard potassium permanganate solution and back-titration with standard ferrous sulfate served to determine nitrite ion. The nitrate ion was determined by the method of Bowman and Scott (*4*). The 0.35 *M* ferrous sulfate solution was standardized against C. P. potassium nitrate.

Apparatus

The final arrangement of the vapor-phase nitration apparatus is shown in Figure 1. It was designed to permit gaseous nitrogen dioxide and vaporized benzene to flow together at controlled individual rates, to mix, to pass through the catalyst held at a fixed temperature, and finally to provide for the collection of condensable and volatile products:

A, *B*, and *C* were the nitrogen dioxide supply, drying, and measuring devices, respectively. In order to maintain a positive pressure of nitrogen dioxide, even at high vaporization rates, the iron cylinder containing it was immersed in a stirred water bath at 30° C. The vaporized oxide passed from the cylinder at a rate controlled by a steel needle valve to a gas absorption bottle filled with fused and crushed calcium nitrate. An orifice meter served to measure the nitrogen dioxide flow. Several interchangeable orifices that were used with this meter were separately calibrated for different flow rates with nitrogen dioxide, which was absorbed in caustic solution and analyzed. A heavy petroleum oil (Nujol) was used as the indicating fluid in the meter. Since the oil appeared to be attacked mildly by nitrogen dioxide, it was renewed after every run. The nitrogen oxide flowed from the meter to the vaporizer where it met a stream of vaporized benzene.

Apparatus *D* controlled the rate of benzene flow into the vaporizer. The benzene was displaced from its reservoir by mercury dropped from the buret at a timed rate. Since the head of mercury changed in the buret as a run proceeded, an adjustment of the microstopcock was necessary from time to time in order to maintain a constant benzene flow. The leveling tube, shown on the left arm of *D*, was used to bring the benzene level into the vaporizer at the beginning of a run. During an experiment the mercury in this leveling tube was separated from that in the benzene reservoir by means of a pinch clamp. The benzene reservoir was filled when necessary through a side opening on the capillary tube which led from the benzene reservoir to the vaporizer. The side tube was closed during an experiment.

The benzene vaporizer was heated electrically to a sufficiently high temperature so that all benzene flowing into it was immediately and entirely volatilized. The benzene and the nitrogen dioxide flowed from the vaporizer into the reaction tube through a ground-glass joint by means of which these two parts were connected.

The reaction tube was a straight, Pyrex glass tube, 162 cm. long and 2.8 cm. in diameter. Both ends terminated in ground-glass joints. The gaseous reaction mixture, when passing through the tube, first met a plug of asbestos wool, then a 25-cm. section of glass beads which preheated the gases. Next they passed through another asbestos plug, then through 110 cm. of catalyst, and a final asbestos plug. The glass reaction tube slid into the steel tube core of the electrically heated furnace, *E*. Although especially made, the tube furnace was the usual design.

The temperature of the catalyst bed was measured with a chromel-alumel thermocouple, the tip of which was inserted into a thin-walled internal glass well which, in turn, was fitted at the center of the Pyrex reaction tube. The thermocouple leads were taken out between the steel tube of the furnace and the glass reaction tube. The couple was calibrated together with its millivoltmeter indicator at the boiling points of water, naphthalene, and sulfur, and at the melting point of aluminum. The cold junction was kept in cracked ice during all operations.

Benzene, nitrated benzene, and some nitrogen dioxide condensed in *F* after leaving the reaction chamber. In order to make the condensation reasonably complete, the collector bulb was packed in ice, and a stream of ice water was run through the spiral condenser. All nitric oxide and some nitrogen dioxide passed through this condenser to the absorption train *G*, *H*, *J*, *K*; *G* and *J* were cooled by ice. All of this nitrogen dioxide and a small portion of the total nitric oxide were absorbed by water in *G*. The yellow color of the former oxide was removed by these water absorbers. The unabsorbed nitric oxide flowed into the oxidizer, *H*, in which it met an air stream drawn in by suction applied at the end of the train. The nitric oxide was converted to nitrogen dioxide and tetroxide in the oxidizer. These higher oxides were absorbed in a 10 per cent caustic solution in *J*. A visual test for the completeness of the oxidation and absorption of the nitric oxide was the lack of yellow color in the vacuum flask, *K*.

The various parts of the nitration apparatus, with the exception of the ground-glass joints already mentioned, were connected with pieces of heavy-walled rubber tubing. Since nitrogen dioxide decomposes rubber, it was necessary to replace the rubber connections after every run.

Operating Procedure

The procedure and technic used in making the nitrations are shown by a typical run. The temperature at the center of the silica gel catalyst bed during the experiment was 310° C. This was kept constant within 3° by proper adjustment of furnace resistances. Benzene was passed into the apparatus at the rate of 0.5 cc. per minute. The flow of nitrogen dioxide was adjusted so that 2 molecules of the dioxide for every molecule of benzene were passed into the reaction chamber. In this run 31.1 grams of nitrogen dioxide flowed into the apparatus together with 26.4 grams of benzene in 1 hour. At the end of the run, nitrogen was passed through the catalyst bed for an additional hour to sweep out the reactants.

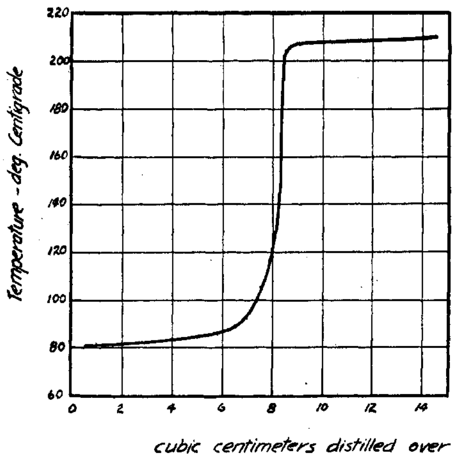

FIGURE 2. TYPICAL DISTILLATION CURVE OF PRODUCTS OF VAPOR-PHASE NITRATION OF BENZENE

The liquid product was washed free of condensed nitrogen dioxide with a 10 per cent caustic solution followed by a water wash. The caustic and wash solutions were later analyzed for their equivalent nitrogen dioxide content. The quantity of organic product was volumetrically measured and found to be 26 cc. Two portions of this organic condensate were analyzed for nitro compound with titanous chloride solutions, and 12.54 grams of nitro product as mononitrobenzene were found. Based on the benzene which entered the reaction chamber, the conversion was 30.1 per cent.

All of the caustic wash and water wash solutions were combined and analyzed for nitrite and nitrate ions. These were equivalent to all of the nitrogen dioxide which came from the reaction chamber plus a small amount of nitric oxide which also dissolved in the water absorbers.

The caustic absorber solution, *J*, was in like manner analyzed for nitrite and nitrate ions. These were equivalent to all the nitric oxide which came from the reactor minus the small amount which dissolved in absorbers *G*.

An over-all nitrogen dioxide balance can be made for this experiment:

Grams NO_2 into apparatus	31.10
Grams NO_2 accounted for:	
Grams in nitrobenzene	4.70
Grams in absorber *G* as nitrite	0.14
Grams in absorber *G* as nitrate	2.46
Grams in absorber *J* as nitrite	14.50
Grams in absorber *J* as nitrate	6.73
Total grams NO_2 accounted for	28.53
Per cent recovery, (28.53/31.10) × 100	91.8

Such a nitrogen dioxide balance was performed on twelve experiments, and the average recovery in this series was 92.0 per cent. Individual balances as high as 98 per cent were obtained. The losses may be attributed mainly to a lack of complete absorption of the nitrous gases and also to reactions leading to nitrophenols and other by-products.

Compound Formed

The compound formed by the interaction of benzene and nitrogen dioxide produced a dye when reduced, diazotized, and coupled with β-naphthol. This showed it to be a nitro compound, but not whether it was mono- or dinitrobenzene. To clarify this point, distillation curves were made of products prepared at three different times in the investigation. They were all similar. Figure 2 shows the distillation curve made from 15 cc. of product and is typical. The catalyst temperature during this run was 310° C. The analysis for mononitrobenzene by titration showed a 36.0 per cent conversion. The conversion can also be calculated from Figure 2, and gives about 34.6 per cent by distillation analysis. This agrees reasonably well with the chemical analysis.

Nitrophenols formed in any of the experiments were removed from the main nitrobenzene product with the caustic wash. In the case of all experiments conducted below 330° C., the caustic wash appeared light in color. In the experiments conducted above 330° C., more nitrophenol formed since the caustic solution turned a deep red.

Space Velocity and Space Time Yield

In all heterogeneous catalytic reactions, space velocity is an important prime variable. The manner of expressing space velocity varies. In this work the unit, grams of benzene per gram of catalyst per hour, was chosen.

The temperature of the catalyst bed during the experiments on space velocity was 310° C.; 320 grams of silica gel A were used. The molar ratio of benzene to nitrogen peroxide was maintained constant at 0.5. The total flow was varied and its effect on the conversion by benzene to nitrobenzene was observed. The data are summarized in Table I.

TABLE I. EFFECT OF SPACE VELOCITY ON PERCENTAGE CONVERSION AND SPACE TIME YIELD

Run No.	Grams Benzene per Hr.	Grams NO_2 per Hr.	Per Cent Conversion	Space Velocity ($\times 10^{-2}$)	Space Time Yield ($\times 10^{-2}$)
29	6.6	7.8	44.7	2.06	0.97
28	13.2	15.6	45.4	4.12	1.87
36	26.4	31.1	33.0	8.25	2.72
27	52.8	62.3	19.1	16.50	3.15

The rapid fall in the percentage conversion of benzene to nitrobenzene with an increase in space velocity greater than 4.1 grams of benzene per gram of gel per hour indicates that equilibrium was not achieved in the reaction. Since all other experiments in this research were made with space velocities larger than that value, it may be concluded that this is a study of non-equilibrium vapor-phase nitration.

At the lowest space velocities the percentage conversion reaches an apparently constant value. This might indicate that equilibrium does obtain at those low flow rates. Whether the equilibrium is a true one was not tested by a study of the reverse reaction. From the large negative free energy of nitration reactions, it would be suspected, however, that the equilibrium conversion should be much greater. The standard free energy change for the simplest nitration reaction,

$$C_6H_6 + 3/2\ NO_2 = C_6H_5NO_2 + 1/2\ NO + 1/2\ H_2O$$

when all reactants and resultants are in the gaseous phase is $F_{298} = -32{,}708$. The equilibrium constant under those conditions is of the order of 1.0×10^{24}. This indicates that at true equilibrium the nitration reaction is approximately complete. (The free energy and equilibrium constant could not be calculated at the actual reaction temperature because of the lack of necessary heat capacity data. The free energy of nitrobenzene at 25° C. was calculated by the method given by Parks and Huffman, *12*).

No less important than space velocity is space time yield. The latter quantity is the space velocity multiplied by the percentage conversion. In this case the space time yield is expressed in grams of benzene converted per gram of catalyst per hour. The space time yield for several space velocities within the operation range of the apparatus is given in Table I. The space time yield is shown to increase with increasing space velocity as would be expected.

Reactant Concentrations

As might be expected, the percentage conversion of benzene to nitrobenzene was found to be a function of the ratio of nitrogen dioxide to benzene vapors. The experimental results are presented in Table II. The temperature of the catalyst in all experiments of this series was 310° C. The space velocity with respect to benzene was not kept entirely constant. In the first five experiments listed, the space velocity was 8.25×10^{-2} gram of benzene per gram of gel per hour. In order to obtain a sufficiently high nitrogen dioxide proportion experimentally, it was necessary to cut the space velocity in the last two experiments to 4.12×10^{-2} gram of benzene per gram of gel per hour.

TABLE II. EFFECT OF REACTANT PROPORTIONS ON CONVERSION OF BENZENE TO MONONITROBENZENE

Run No.	Grams Benzene per Hour	Grams NO_2 per Hour	Mole Fraction of NO_2	Per Cent Conversion to Nitrobenzene	
				Benzene	NO_2
26	26.4	8.1	0.34	8.3	42.7
25	26.4	15.6	0.50	16.0	15.8
19	26.4	31.1	0.67	33.3	16.7
20	26.4	39.0	0.72	36.0	14.3
21	26.4	46.7	0.75	44.3	14.8
24	13.2	39.0	0.83	73.5	10.5
23	13.2	54.5	0.88	83.6	..

Figure 3 is a plot of the data in the last three columns of Table II. It shows graphically the rapid rise in the conversion of benzene to nitrobenzene with an increase in the proportion of nitrogen dioxide and a decline in the conversion of nitrogen dioxide to nitrobenzene with increase in nitrogen dioxide proportion.

It is probable that the two highest conversion points on the curve would have been somewhat lower had it been possible to maintain the same space velocity as in the remaining experiments.

Temperature

All experiments performed to determine the effect of temperature on the conversion of benzene to mononitrobenzene were conducted with a constant benzene-nitrogen dioxide molecular ratio and a constant space velocity. The value of the former was 0.5, and that of the latter 8.25×10^{-2} gram of benzene per gram of gel per hour. The length of each experiment was one hour and the same 320 grams of silica gel A were used in all runs. Table III contains a summary of the essential data, which are plotted in Figure 4.

TABLE III. EFFECT OF TEMPERATURE ON CONVERSION OF BENZENE TO MONONITROBENZENE

Run No.	Catalyst Temp., ° C.	Per Cent Conversion	Average
30	255	15.2	
32	282	26.1	
19	310	33.3	31.9
33	310	30.1	
36	310	33.0	
39	310	31.0	
34	330	30.2	30.0
35	330	29.7	
37	380	13.8	

The experimental study of the temperature variable leads to several conclusions:

1. The temperature-conversion curve for the nitration curve of benzene under the selected concentration and flow conditions has a maximum at 310° C.
2. In order to drive the nitration product from the silica gel in a continuous manner, the temperature of the gel should be above about 280° C. Thus, it was found that, on raising the temperature of the silica gel after a nitration at 255° C., a large quantity of nitrobenzene formed at 255° was released. A nitration performed at 282° showed by a subsequent elevation in temperature that no very appreciable amount of nitrobenzene was retained by the gel at that temperature.
3. Oxidation by-products are formed above about 330° C. The conversion efficiency to the nitro derivative is then lowered. Thus it was found that, although nitration at 330° discolored the catalyst slightly, it did not impair its activity which was measured by another nitration with the same gel at 310°. The conversion at 310° was 33 per cent which checked previous experiments at that temperature. However, a nitration at 380° allowed considerable side reaction to take place as was shown by the passage of yellowish white fumes from the apparatus, by the dark brown color of the caustic wash of the product, and by a darkening of the gel. The conversion of benzene to nitrobenzene at 380° was only 13.8 per cent. The coated catalyst was then used in another nitration at the standard 310° temperature, and this time the conversion was low—22.4 per cent instead of the normal 32 per cent for a 310° nitration. Thus the activity of the catalyst was impaired by operation at an elevated temperature.
4. If the temperature of the silica gel is raised so high that it becomes coated with decomposition products, the gel can be restored to its original activity by an air oxidation treatment. Thus the coating on the gel after the 380° run mentioned above was completely removed by blowing air through the gel at 485° C. After this oxidation treatment the gel was again used as a catalyst in a 310° nitration run. A conversion of 31 per cent at this latter temperature indicated that the silica gel had regained its original activity.
5. At four different points in the investigation, nitrations were performed under the same set of conditions—i. e., temperature, 310° C.; benzene-nitrogen dioxide ratio, 0.5; space velocity, 8.25×10^{-2}. A mean value of 31.9 per cent conversion for the four experiments with an average deviation of 1.4 per cent serves as an estimate of the over-all experimental and analytical precision.

Nitration Reaction

Most of the data in this work were not taken under equilibrium conditions. Consequently they cannot be applied to a calculation of the equilibrium constant of the proper stoichiometrical equation for the nitration. They can be used, however, to test the type of reaction that is occurring. A first assumption is that the over-all reaction is:

$$2C_6H_6 + 3NO_2 = 2C_6H_5NO_2 + NO + H_2O$$

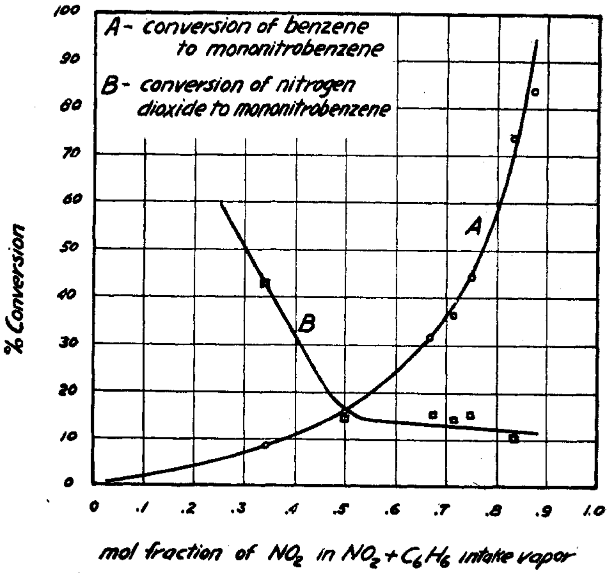

FIGURE 3. EFFECT OF REACTANT PROPORTIONS ON CONVERSION OF BENZENE AND OF NITROGEN DIOXIDE TO MONONITROBENZENE AT 310° C.

If that is true, then nitric oxide as well as nitrobenzene should appear in the product owing to reduction and nitration reactions. In examining the data for these two products, there must be taken into consideration the fact that nitrogen dioxide dissociates into nitric oxide and oxygen at elevated temperatures:

$$NO_2 = NO + 1/2\ O_2$$

This latter reaction will also cause nitric oxide to appear in the product. The amount can be evaluated since Bodenstein (*3*) determined the equilibrium constant. At 310° C. the dissociation is 34 per cent. Since this is a comparatively slow reaction, the time of passage of nitrogen dioxide through the apparatus should theoretically be taken into consideration. But the velocity constants worked out by Bodenstein apply only in a homogeneous reaction and not at the surface of silica gel at which this reaction is accelerated. For the purposes of calculation, then, equilibrium will be assumed to have been achieved. That is a conservative procedure in this case.

If nitrogen dioxide alone is passed through silica gel at 310° C., it will dissociate 34 per cent to give nitric oxide and oxygen. If the nitration of benzene causes the reduction of a further amount of nitrogen peroxide to nitric oxide, this latter amount should be detected in addition to that due to the primary thermal dissociation. The data in Table IV show that such an excess does occur (Table II gives other data).

TABLE IV. NITRIC OXIDE PRODUCTION IN NITRATION OF BENZENE AT 310° C.

1 Run No.	2 NO_2 Intake *Grams*	3 NO Formed by Thermal Dissociation (Calcd.) *Grams*	4 NO Absorbed in Caustic Soln. *Grams*	5 (4 − 3) NO Formed in Nitration (Calcd.) *Grams*	6 Nitrobenzene Formed by Nitration *Grams*	7 Ratio NO to Nitrobenzene *Moles*
19	31.1	6.90	10.28	3.38	13.9	1.0
20	39.0	8.65	14.05	5.40	15.0	1.5
21	46.7	10.37	17.30	6.93	18.7	1.5
24	39.0	8.65	14.20	5.55	15.3	1.5
25	15.6	3.46	6.07	2.61	6.6	1.6
26	8.1	1.80	3.64	1.84	3.5	2.2
27	31.1	6.90	11.76	4.86	7.9	2.5
28	15.6	3.46	6.74	3.28	9.5	1.4
33	31.1	6.90	13.86	6.96	12.5	2.3

Column 3, Table IV, shows the calculated maximum number of grams of nitric oxide that can appear in the product owing to thermal dissociation. The fourth column presents the grams of nitric oxide that came from the apparatus and were absorbed.

The differences between the values of the third and fourth columns presumably are the numbers of grams of nitric oxide, fifth column, that are formed by the nitration reaction. The ratio of the number of moles of nitric oxide calculated to be formed in the nitration reaction to the moles of nitrobenzene is given in column 7. The ratios were much larger than would be expected by the stoichiometric equation already postulated.

These results show that nitric oxide is formed as one of the products when benzene is nitrated by the use of nitrogen dioxide. If thermal equilibrium alone were considered, the mole ratio at 310° would be (34/66 =) 0.52. The experimental ratios for the same nine runs mentioned in Table IV varied considerably and are not included in the table, but all were much larger than 0.52.

The formation of nitric oxide would be important if the exit gases were recycled. Then the reduced oxide of nitrogen would need to be reoxidized to nitrogen dioxide before again entering the cycle. It would otherwise act as in inert gas.

Effect of Air

All experiments on vapor-phase nitration of benzene mentioned thus far were conducted with nitrogen dioxide and benzene alone. It was considered of interest to determine the effect of adding air to these two reactants. The conditions of the standard run, previously referred to, were maintained for comparative purposes:

Catalyst temp., ° C.	310
Benzene per hour, grams	26.4
Nitrogen dioxide per hour, grams	31.1
Time of run, hour	1

Without the addition of air, the conversion under these conditions was an average of 31.9 per cent.

Under standard conditions 1.13 cubic feet of air were passed into the apparatus in addition to the other reactants. The products condensed well. The exit gases were much darker than in the regular experiments, which indicated a reoxidation of nitric oxide to some extent by the air. Definite signs of the formation of phenolic compounds were evident. The alkali wash of the liquid product was very dark brown instead of the usual yellow. The catalyst darkened during the run. The conversion of benzene to nitrobenzene was 21.0 per cent, which is 10 per cent lower than that obtained in the runs without air.

The experiment seems to indicate that the addition of air to benzene and nitrogen dioxide increases the amount of side reaction in vapor-phase nitration. The lowering of the yield may be due to a change of the effective time of contact of the normal reactants by the addition of air.

Life of Catalyst

One bed of silica gel was used as a catalyst in a long series of experiments. These varied over a wide range of temperature, flow, and composition conditions. After one of these experiments it was necessary to oxidize the gel in order to reactivate it. The gel was in use for a total of 33 hours of actual experimental time. During this period 362 grams of nitrobenzene were formed on the 320-gram bed of gel. The catalyst was as active when discarded as when new. Its nitration activity as well as its heat of adsorption with respect to liquid water appeared to be the same when finally removed from the apparatus as when initially placed there.

Explosion Hazards

The literature (*2*, *15*) cites two serious explosions that have been due to nitrogen dioxide. In 1917 in Zschornewitz, Germany, in a nitric acid plant toluene and nitrogen dioxide mixed in the liquid phase and exploded. A similar explosion occurred in Bodio, Switzerland, in 1921. After a failure of

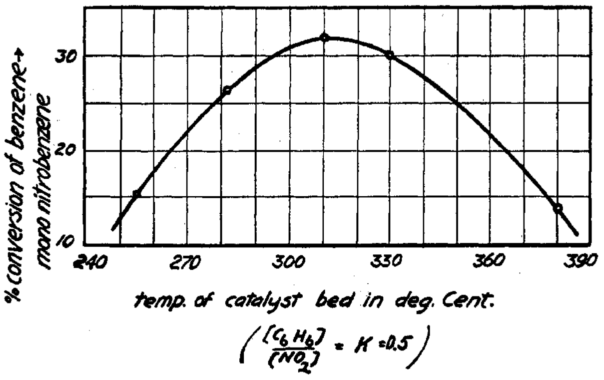

FIGURE 4. EFFECT OF TEMPERATURE ON CONVERSION OF BENZENE TO MONONITROBENZENE

Molecular benzene–nitrogen dioxide ratio, 0.5; space velocity, 8.25 × 10^{-2} gram of benzene per gram of gel per hour equipment, plant operators there tried to separate benzine and nitrogen dioxide, and they detonated.

Explosion difficulties in this present work with benzene were limited to one of the preliminary experiments. Fine glass wool was used in the form of plugs in the reaction tube. After several minor detonations, the apparatus was taken apart, and the glass wool plugs, and these plugs alone, were black with a carbon deposit. It appeared that oxidation was catalyzed by the surface of the glass wool. Long-fiber asbestos was substituted for the glass wool and no further explosion difficulties were met in the remainder of the benzene nitration experiments.

Catalysts

The results of nitrations with different catalysts are summarized in Table V.

TABLE V. EFFECTIVENESS OF DIFFERENT CATALYSTS

(Temperature, 310° C.; time, one hour; reactants, 26.4 grams benzene and 31.0 grams nitrogen dioxide)

Run No.	Catalyst		Main Product Formed	Conversion to Mononitrobenzene
	Grams			%
19, 33, 36, 39	320	Silica gel A	Nitrobenzene	31.9
47	380	Silica gel B	Nitrobenzene	4.6
52	290	Granular pumice	Nitrobenzene	0.5
53	300	TiO_2 on pumice	Nitrobenzene	1.1
50, 51	480	Dehydrated bauxite	Diphenyl + ammonia	0.0
48	500	Activated alumina	Diphenyl	1.0

Silica gel A is a dehydrating gel and was used in most experiments in this investigation. Silica gel B was designed for use in water purification. The greater activity of the former gel than the latter with respect to the catalysis of benzene nitration suggests that the former has a greater surface per unit weight than the latter. Relative heats of adsorption of the two gels were measured, and the heat of adsorption of silica gel A was found to be twice as great as that of silica gel B. This property correlates with the hypothesis that the more active catalyst has the greater area.

The very low catalytic activity of granular pumice in vapor-phase nitration as compared to a good silica gel clearly shows that the reaction of benzene with nitrogen dioxide on the surface of the latter is a heterogeneous, specifically catalyzed reaction.

Titanium dioxide precipitated on granular pumice from titanous sulfate solution by ammonia and followed by air oxidation and heating at 350° C. showed itself to be an inefficient nitration catalyst.

An interesting reaction took place on dehydrated and activated bauxite when benzene and nitrogen dioxide were passed over it with the conditions specified in Table V. No nitration took place. Instead, the nitrogen dioxide was reduced to ammonia, and diphenyl resulted as a second product. Activated alumina in a manner similar to bauxite permitted diphenyl to be formed as a product. A small amount of nitrobenzene in addition to the diphenyl was formed on the alumina.

Nitration of Toluene

The greater part of the nitration experiments dealt with the nitration of benzene. It was considered worth while to try the vapor-phase method with toluene. Silica gel A was the catalyst, and 31 grams each of toluene and nitrogen dioxide were used. With this flow ratio the molecular ratio of nitrogen dioxide to toluene was 2.

Since a patent (7) on nitration, previously referred to, indicated that toluene could be nitrated at a temperature about 70° C. higher than benzene, 380° was chosen for this experiment at the start. A mild explosion led to a lowering of the temperature to 310° and finally to 275° C., at which temperature the run was completed. A nitro analysis showed that a conversion of 6.8 per cent of the toluene to nitrotoluene had occurred.

This experiment appeared to show that toluene is more reactive than benzene in the presence of nitrogen dioxide, and therefore a lower temperature of nitration must be chosen.

On the other hand, the nitrotoluenes have a higher boiling point than nitrobenzene and as a consequence need a higher gel temperature in order that the toluene product may be distilled off. These opposing requirements leave a smaller temperature interval in which nitration can be achieved in the case of toluene than of benzene.

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