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Mononitration of Cumene

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Cumene was produced in large amounts during World War II as a blending agent for aviation gasoline. This production ceased at the end of the war, but some fields of chemical utilization should be available. Nitration is the first step in making many chemical products.

Cumene was nitrated with a yield of 94.5% mononitrocumene using a 2 to 1 ratio of sulfuric acid to hydrocarbon, acid concentration 81%, and 20% excess nitric acid at 15° C.

A new theory of aromatic nitration which considers the nitryl ion, NO_2^+, as the nitrating agent has been used to develop a new series of process variables for aromatic nitration to replace the concept of dehydrating value of sulfuric acid. The ratio of acid to hydrocarbon and the initial concentration of the sulfuric acid (on a nitric acid–free basis) replace the dehydrating value of sulfuric acid as a process variable. The advantage of this new concept is shown. The orientation of the entering nitro group is shown to be 24% in the ortho position and 76% in the para position, contrary to a report that the orientation changes from essentially ortho to completely para when the temperature of nitration changes from 0° to 45° C.

BEFORE World War II, cumene (isopropylbenzene) was a relatively rare aromatic hydrocarbon, produced in limited quantities for special uses. However, its use as a high-octane blending agent in aviation gasoline during the war brought about a spectacular increase in its production—from 400 barrels per day in May 1942 to 15,000 barrels per day in December 1944 (*19*). The end of the wartime emergency resulted in a sharp decrease in demand, and it was felt that some investigation of the utilization of cumene as a chemical raw material was needed. As nitration is one of the important reactions used to introduce functional groups into the aromatic nucleus, a study of this unit process applied to cumene would give important information concerning an initial step in chemical utilization. The work of Sterling and Bogert (*26*) had indicated that the temperature of nitration has an unusually strong effect on the position taken by the entering nitro group, and a thorough study of this particular process should make some contribution to the theory of orientation in the benzene nucleus.

After some exploratory work, it was decided to attempt a new approach to the study of the nitration process, using the fundamental data now available on the kinetics and mechanism of the nitration reaction. In the past few years a considerable amount of fundamental data has been published on nitration, and it is believed that the present work presents the unit process of nitration in a new light and will lead to generalizations not heretofore recognized.

THEORY OF AROMATIC NITRATION

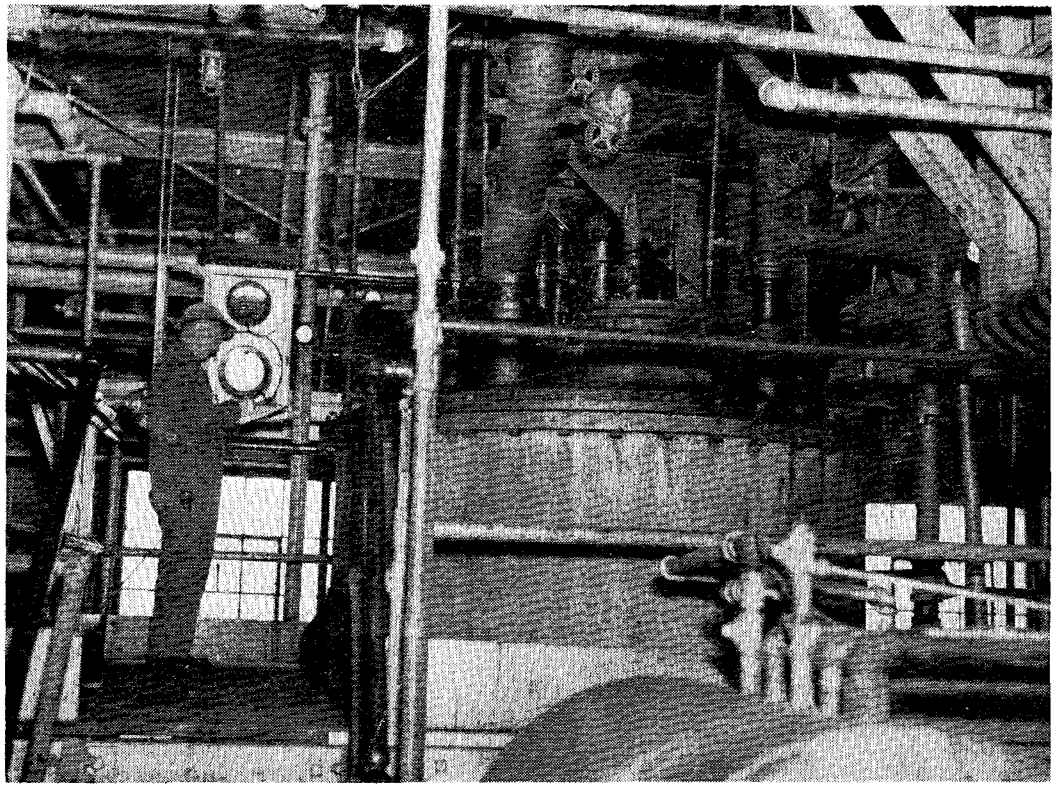
The basic mechanism of the process of aromatic nitration has been the subject of intermittent investigation and controversy for many years. The earliest proposal as to the mechanism was made by Kekule (*18*) and supported by others (*1, 30*), on the basis of the addition of nitric acid to ethylenic linkages; it held that the nitric acid added to the "double bond" of the benzene structure to yield a nitrohydrin which was then dehydrated by strong acids to yield the nitro compound. More recently, on the basis of a reinvestigation of the addition of nitric acid to alkenes, Michael (*22*) and Michael and Carlson (*23*) proposed a slightly different mechanism for the nitration reaction. This mechanism involves the addition of nitric acid to the hydrocarbon in an aldolization reaction, followed by a loss of water to form the nitro compound.

The essential common feature of the two mechanisms outlined is the concept of the function of the sulfuric acid as a dehydrating agent. This has led to the usual method of presenting process data on nitration reactions, in which the dehydrating value of sulfuric acid (D.V.S.) is used to indicate the composition of the mixed nitration acid (*14*). Dehydrating value is defined as the ratio of the weight of sulfuric acid present to the weight of water present at the end of the nitration reaction, assuming a theoretical yield of nitro compound.

These mechanisms lead to an implicit belief that the sulfuric acid serves only to combine with one of the products of reaction, thus driving the equilibrium toward completion of the reaction. However, Gilman (*12*) presents data indicating that the nitration reaction is irreversible and there is no equilibrium to be so affected; and it has been shown (*11*) that nitration will not take place in the presence of phosphoric acid or phosphorus pentoxide, although these materials have a higher affinity for water than does sulfuric acid. These data, and many other lines of evidence, indicate that a more thorough study of the fundamental characteristics of the nitration reaction is necessary.

Recently, Gillespie and Millen (*11*) published an extensive review of the literature on nitration reactions, and summarized the results of a long-term investigation of the reaction by a group of British workers. The mechanism proposed involves direct electrophilic displacement of a hydrogen atom on the benzene nucleus, in the form of a hydrogen ion, by the nitryl ion, NO_2^+, a suggestion originally made by Euler (*8*) in 1901.

Gillespie and Millen consider the sulfuric acid (or other strong acid) only as an ionizing medium in which the reaction takes place, and which is a strong proton donor. The presence of the nitryl ion is supported by the spectroscopic data of Chedin (*6*), whose data on the mixed acid system are presented by Gillespie and Millen (*11*) in the form of curves of constant amount of nitryl ion in gram-moles per 1000 grams of mixed acid on a



Nitrator and Control Equipment at the Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

triangular diagram of the system sulfuric acid–nitric acid–water. This diagram is reproduced in Figure 1.

Cryoscopic techniques have been used by Gillespie and coworkers (*9*) to show that the NO_2^+ ion is formed in solutions of nitric acid in strong sulfuric acid; Bennett, Brand, and Williams (*3*) have obtained data on the migration of nitric acid to the cathode during electrolysis in oleum solution, which also support this concept. Goddard and coworkers (*13*) have isolated a salt of the nitryl ion, nitryl perchlorate, as a pure crystalline solid of definite composition.

After several earlier investigators had been unsuccessful, Martinsen (*20, 21*), in 1904, was able to determine values of the rate constants for nitration reactions in sulfuric acid. More recently, British workers (*2–4, 10, 17*) and Westheimer and Kharasch (*29*) have obtained data on the kinetics of nitration reactions. Most of this work has been done in homogeneous solution and for the nitration of difficultly nitrated materials, because of experimental difficulties in measuring the rate of a mononitration reaction. Westheimer and Kharasch (*29*) have estimated that the second-order rate constant for the mononitration of toluene is 10,000,000 times that for the nitration of mononitrotoluene.

The kinetic data on nitration in sulfuric acid indicate that the reaction is of the second order. The outstanding characteristic which all the data have in common is the fact that the rate constants for the nitration of all the substances studied are a function of the initial sulfuric acid concentration. As the initial concentration of the sulfuric acid solvent is increased, the rate constants pass through a maximum in the range of 88 to 93% sulfuric acid. The rate increases sharply from that at low concentrations to the maximum and then shows a less-pronounced decrease toward 100% acid. Two typical curves, for the nitration of nitrobenzene and of dinitromesitylene at 25° C., are shown in Figure 2.

On the basis of all the available information on nitration reactions, Gillespie and others (*10*) have formulated the following mechanism for the reaction:

I. Formation of NO_2^-

$$2HNO_3 \underset{2}{\overset{1}{\rightleftarrows}} H_2NO_3^+ + NO_3^-$$

1 and 2 are fast reactions

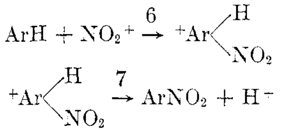
$$H_2SO_4 + HNO_3 \underset{4}{\overset{3}{\rightleftarrows}} H_2NO_3^+ + HSO_4^-$$

3 and 4 are fast reactions

$$H_2NO_3^+ \xrightarrow{5} NO_2^+ + H_2O$$

5 is a slow reaction

II. Entrance of NO_2^+ into Aromatic Nucleus



$$ArH + NO_2^+ \xrightarrow{6} {}^+Ar\begin{matrix}H\\NO_2\end{matrix}$$

6 is a slow reaction

$${}^+Ar\begin{matrix}H\\NO_2\end{matrix} \xrightarrow{7} ArNO_2 + H^+$$

7 is a fast reaction

Steps 1 and 3 are supported by the fact that both nitrate and bisulfate ions decrease the rate of the over-all reaction without affecting the reaction order.

APPLICATIONS TO UNIT PROCESS OF NITRATION

The large mass of accumulated evidence in favor of the nitryl ion mechanism and the now well-established kinetics of the nitration reaction necessitate a reappraisal of the present concepts of this important unit process. First, a new fundamental process variable is defined: the sulfuric acid concentration. This concept must replace the dehydrating value of sulfuric acid for it is now recognized that sulfuric acid does not function as a dehydrating agent in the reaction. It has already been shown that the concentration exerts an appreciable effect on the rate of reaction, and that the effect is very general, the concentration for which the maximum rate is obtained being approximately the same for similar compounds. The initial acid concentration and the dehydrating value of sulfuric acid are not directly related, as it is possible to obtain any desired dehydrating value of sulfuric acid simply by changing the total amount of sulfuric acid at

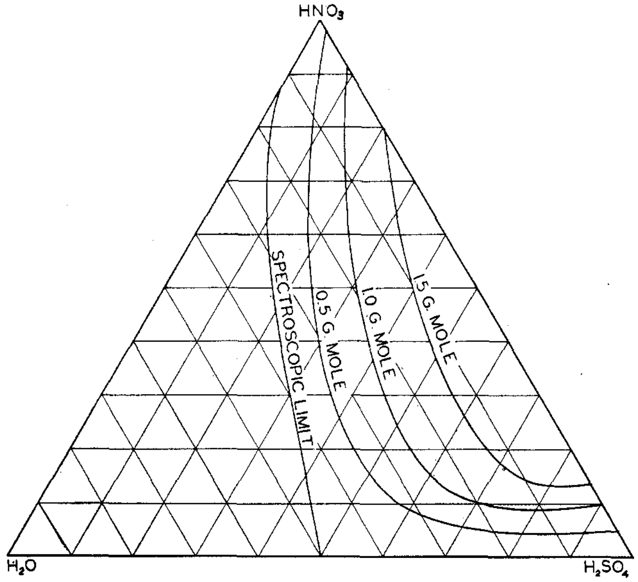


Figure 1. Constant Amount of Nitryl Ion per 1000 Grams of Mixed Acid of Indicated Composition

constant concentration. The sulfuric acid concentration is defined as the percentage by weight of sulfuric acid in the total initial mixed acid on a nitric acid-free basis, care being taken to include the water introduced with the nitric acid. It is desirable economically to operate at or near the concentration of maximum rate, but the use of as dilute a mixed acid as possible is necessary in order to reduce the cost of refortifying the recycled acid. Thus, it is necessary to have information on the effect of solvent concentration on the yield obtainable over a wide range of concentrations.

Another variable of major economic interest is the amount of mixed acid used per unit of hydrocarbon. Experimentally, it is simpler to vary the amounts of sulfuric acid and of nitric acid separately, thus giving two more process variables: the amount of sulfuric acid per unit of hydrocarbon, and the amount of nitric acid used over that required stoichiometrically.

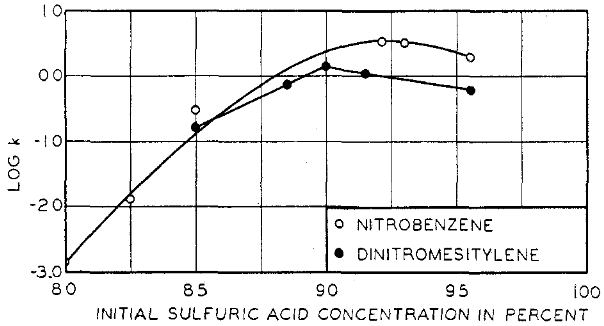


Figure 2. Effect of Initial Sulfuric Acid Concentration on Second-Order Rate Constants for Nitration of Nitrobenzene and Dinitromesitylene at 25° C.

Data of Westheimer and Kharasch (29)

The temperature of nitration is a process variable of particular theoretical and practical interest. At low temperatures, the oxidation side reactions in a nitration may be minimized with consequent gain in yield. However, the rate of the main reaction is decreased at low temperatures according to the general rule for the effect of temperature on reaction rate, and also because the solvating power of the sulfuric acid is greatly increased by the lower temperatures. The increase in solvation results in a decreased concentration of the free hydrocarbon, and thus a reduction in the rate of reaction. Furthermore, the cost of refrigeration to obtain the necessary low temperatures must be considered. At higher temperatures, increased rates of reaction may be realized, and the cost of cooling the mixture may be decreased by the use of cooling water at ordinary temperatures, but only with the risk of encountering extremely active side reactions which render such operation undesirable. Finally, although the time of reaction is of particular economic importance, for most process studies the important information may be obtained using a constant reaction time, provided the time is kept within reasonable limits.

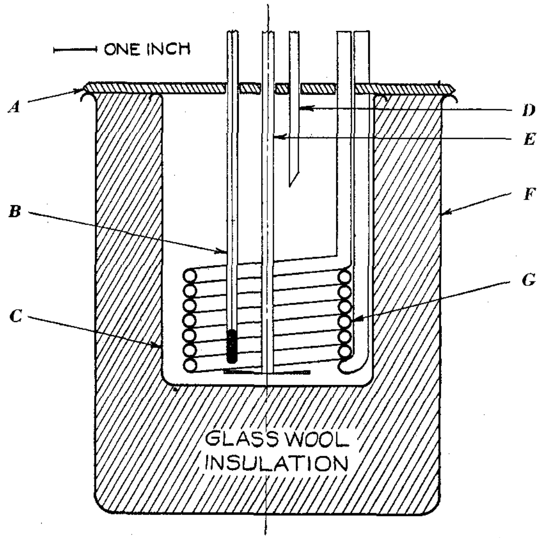


Figure 3. Nitrator

A. **Asphalt-asbestos board sheathed with 22-gage stainless steel**
B. **Thermometer**
C. **2-liter stainless steel beaker**
D. **Mixed acid tube**
E. **Stirrer shaft**
F. **6-liter stainless steel beaker**
G. **Cooling coil, 7 turns of $^{1}/_{4}$-inch stainless steel tubing, $3^{3}/_{8}$ inches in inside diameter**

To summarize, the process variables indicated as important by the new concept of the unit process of nitration are: the solvent (sulfuric acid) concentration, the amount of sulfuric acid per unit of hydrocarbon, the amount of excess nitric acid, the reaction temperature, and the time of reaction.

PREVIOUS WORK

The previous work and available data on the process conditions for the nitration of cumene are summarized in Table I.

The only large scale nitration of cumene is that of Vavon and Callier (*28*), who determined the best values of the physical constants of the nitro compounds, using acetyl nitrate as the nitrating agent. Later work was in connection with the preparation of sterols (*15*, *26*) or ultraviolet absorption spectra (*5*). Nitrocumene can be obtained by the nitration of 1,3- and 1,4-diisopropylbenzenes (*24*), in which one isopropyl group is eliminated. This has been shown to be a common reaction during nitration of polyalkylated benzenes (*7*, *25*).

Unusual results are reported by Sterling and Bogert (*26*), who nitrated cumene with mixed acids. When the reaction was carried out below 20° C. the product contained 21% 2-nitro- and 79% 4-nitrocumene. However, if the reaction was conducted at 40° to 50° C., a yield of 77% 4-nitrocumene was obtained "essentially free from 2-nitro and only a small amount of higher boiling compounds. Much of the unreacted cumene was recovered." This change in orientation with almost complete

Table I. Summary of Literature Process Data on Nitration of Cumene

	Hydrocarbon		Nitration Mixture			
Authors		Grams		Grams	Conditions	Yields
Vavon and Callier (*28*)	Cumene	150	Nitric acid (1.5)[a] Acetic acid Acetic anhydride	90 110 110	Room temp. 1 day, 45° C., 6 hours	About 90% over-all recovery
Vavon and Callier (*28*)	Cumene	2 kg.	Acetyl nitrate, 10% excess		Below 30° C. plus 2 hours	500 g. 2-nitro 1800 g. 4-nitro (83% yield; 22% 2-, 78% 4-nitro)
Haworth and Barker (*15*)	Cumene	50	Nitric acid Sulfuric acid	50 100	5–10° C., 2 hours	5 g. 2-nitro 62 g. 4-nitro
Sterling and Bogert (*26*)	Cumene	100	Nitric acid (1.42)[a] Sulfuric acid (1.84)[a]	86 120	Below 20° C. plus 2 hours	18 g. 2-nitro 67 g. 4-nitro 7 g. dinitro
Sterling and Bogert (*26*)	Cumene	100	Nitric acid (1.42)[a] Sulfuric acid (1.84)[a]	63 125	40–50° C.	112 g. 4-nitro (77%)
Newton (*24*)	1,3-Diisopropylbenzene		Nitric acid (96%) 1.24–2.05 equivalents		45–50° C., allowed to stand 24 hours	70.5% 4-nitrocumene 24.0% nitrodiisopropylbenzene
Newton (*24*)	1,4-Diisopropylbenzene		Nitric acid (96%) 1.24–2.05 equivalents		45–50° C., allowed to stand 24 hours	15.1% 4-nitrocumene 10.5% nitrodiisopropylbenzene

[a] Specific gravity of acid.

elimination of the 2-nitro compound is most unusual and calls for further investigation.

APPARATUS AND MATERIALS

The nitrator used in this investigation is shown in Figure 3.

The nitrating vessel itself was a 2-liter stainless steel beaker placed inside a 6-liter beaker of the same material with the space between the containers packed with fine glass wool. This packing served to insulate the reaction mixture from fluctuations in the room temperature, and glass wool was chosen because of its resistance to the action of the strong acids used.

The cooling coil was made by forming stainless steel tubing $^{1}/_{4}$ inch in inside diameter into a close-wound helical coil, 7 turns 3.375 inches in inside diameter, with the straight ends of the tubing turned parallel to the axis of the helix, so as to reach above the top of the nitrator and allow attachment of the rubber tubing used for circulation of the cooling medium through the coil. The coil was placed in the nitrator as shown and was supported about 0.5 inch above the bottom of the nitration vessel by the coolant supply and discharge tubes to allow circulation of the reaction mixture and to prevent trapping of a portion between the coil and the vessel wall.

The cover shown in the figure was used for the first 28 runs, but for the remainder of the work a cover made from Plexiglas methyl methacrylate plastic was used. The area immediately over the inner nitrating vessel in the bottom of the plastic cover was protected by a circle of 16-gage stainless steel sheet, which was drilled in the same manner as the cover and, in addition, was furnished with two rectangular openings symmetrically located with respect to the stirrer shaft. These openings were made the same size as a standard microscope slide, and a glass slide was cemented over them to protect the plastic from the hydrocarbon splashed from the nitrator. One opening was used for illumination and the other for observation of the reaction mixture through the clear plastic and glass slide. This eliminated the danger of splashing strong mixed acids into the worker's face. Although this system was very useful, the plastic was slowly attacked in spite of the glass slides; and observation was impossible after only a few runs.

In order to obtain the best possible emulsification and contact between the heterogeneous phases present in the nitrator, a standard laboratory mixer with a shaft speed of 4000 r.p.m. was used for agitation. The agitator itself was a three-bladed propeller-type stirrer with a blade circle diameter of 1.5 inches and a 0.375-inch shaft; the entire assembly was of stainless steel.

The mixed acid addition tube of the nitrator was a standard glass thistle tube with the open end under a 250-ml. dispensing buret and the small tube passing down through the cover of the nitrator. The rate of addition of the mixed acid could be observed as it dripped from the tip of the buret and was controlled by the stopcock on the buret.

The temperature of the nitration mixture was determined with an ASTM cloud and pour thermometer with a range of from −50° to 50° C., graduated in single degrees.

The conventional steam-distillation apparatus, using live steam from the laboratory lines, proved to be so time-consuming that another method was necessary. The procedure evolved apparently is not described in the literature. The apparatus is shown in Figure 4.

A 5-liter round-bottomed boiling flask with three standard-taper ground-glass necks was used, the center neck being a 45/50 joint and the two side necks 24/40. A standard Dean and Stark moisture trap, as used in the determination of the moisture content of fibrous materials (*27*), furnished with ground-glass joints and a stopcock for removal of the contents of the trap, was placed in the center neck of the flask and a Friedrich condenser was attached at the top of the trap.

In operation, a batch of crude nitro compound washed once with water was placed in the flask and about 1 liter of water was added. Using a mixture of $^{1}/_{4}$-inch porcelain Berl saddles and a few chips of Teflon sheet for boiling stones, this mixture could be made to boil steadily and with a minimum of bumping, in spite of the immiscibility of the liquids. This amounted to a codistillation of the nitro compounds with water, with the entire vapor mixture being condensed, the nitro compound separating from the water and settling to the bottom of the

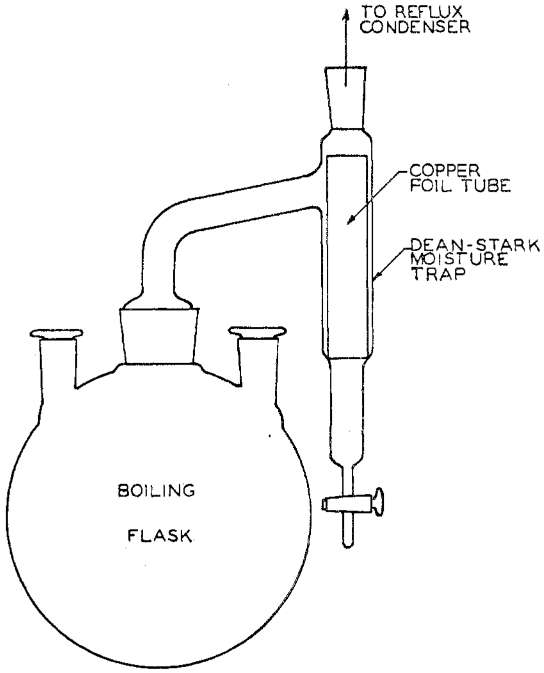


Figure 4. Steam Distillation Apparatus

Rolled copper foil tube inserted in moisture trap and supported by shoulder

trap, and the water overflowing back into the boiling flask. It was found necessary to place a tube rolled from copper foil in the trap, reaching above the liquid level, in order to prevent the droplets of oil held on the surface by the interfacial tension from flowing back into the flask before they became large enough to settle out. In this manner, using electric hot plates for heating, the product from one nitration could be steam-distilled for about 30 hours with almost no attention beyond an occasional drawing off of the accumulated nitro compound layer from the trap.

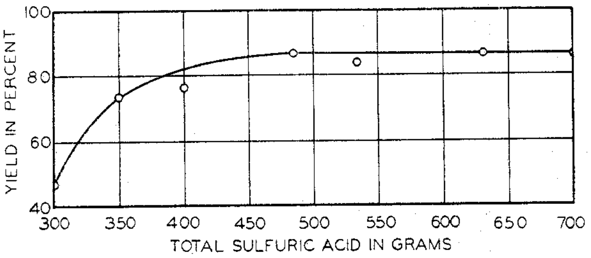


Figure 5. Effect of Amount of Sulfuric Acid on Yield

15° C., 86.4% sulfuric acid, 10% excess nitric acid, reaction time 2 hours
Nitration of 250 grams of cumene

Cumene was obtained from the Shell Oil Co. as a cumene aviation alkylate. The only treatment given was fractional distillation at very high reflux ratio through a 1.5 × 36 inch column packed with $^1/_4$-inch Raschig rings (about five theoretical plates). Approximately 5% (by volume) of the charge was distilled before the temperature reached the boiling point of cumene at the prevailing atmospheric pressure, and 70 to 75% was distilled at a constant temperature. This middle fraction was used without further treatment, as successive treatments with sulfuric acid did not improve the physical constants over those obtained for the distilled, but untreated, material.

The mixed acids were prepared from reagent grade concentrated sulfuric and nitric acids, fuming nitric acid, and oleum.

NITRATION PROCEDURE

In a nitration run 250 grams of cumene were weighed and placed in the nitrator. The cover and other auxiliaries were then assembled on the nitrator and cooling was begun with the agitator operating. Cooling was continued until the temperature was at least 10° C. below the temperature at which the nitration was to be run, and in all cases below 20° C. When the cumene was cooled to the desired temperature, the nitrator acid was run in from the buret; and the cumene and acid were emulsified as well as possible. The nitrator acid contained about 60% of the total sulfuric acid used for the run, and for concentrations below 86.4% sulfuric acid (nitric acid–free basis) contained all the water which had to be added to the mixed acid. For concentrations above this figure, the nitrator acid was either concentrated sulfuric acid or a mixture of concentrated sulfuric acid with oleum. Details are given below. The 86.4% concentration is the solvent concentration resulting from mixing 500 grams of 97% sulfuric acid with 206 grams of 70% nitric acid and was chosen for consistency in the method of preparation of the acids.

After the cumene and the nitrator acid had been emulsified, the buret was closed and the mixed acid placed in it. This mixed acid consisted of all the nitric acid used, together with the remainder of the sulfuric acid necessary to make up a total mixed acid of the desired concentration. Both the nitrator acid and the mixed acid were cooled to approximately 0° C. in a refrigerator before using.

By the time the mixed acid had been placed in the buret, any heat effect which had occurred as a result of the emulsification of the nitrator acid and the cumene had been overcome by the cooling system, and the addition of the mixed acid was begun. The rate of addition was controlled at 3 to 5 ml. of acid per minute so as to require about 1 hour for the complete addition of the mixed acid. During this time the temperature of the reaction mixture was controlled manually by starting and stopping the coolant flow. The time, buret reading, and temperature were recorded at 5-minute intervals.

For nitration at 15°, 25°, and 35° C., ice water was used to cool the reaction mixture, and at 10° C., a calcium chloride brine which had been pumped over ice. The low temperature runs at 0° and −10° C. required the use of solid carbon dioxide for cooling. The solid carbon dioxide was crushed, wiped free of frost with a cloth, and dropped directly into the nitrator, with the cover and cooling coil removed. For the one run at 45° to 50° C. no cooling was necessary; the temperature was controlled by the rate of addition of the mixed acid.

After all the mixed acid had been added, stirring and temperature control were maintained until the allotted time for the run had elapsed. The reaction mixture was then poured over ice and diluted to a total volume of approximately 4 liters. The resulting mixture was poured into separatory funnels and the crude nitro compounds, which were heavier than the diluted acid, were allowed to separate and then were decanted. A steam distillation, using the procedure described, was then performed without neutralization of the mixture, as it was found that a neutralizing wash resulted in a significant decrease in the yield. The portion of the steam distillate which was heavier than water was taken as 100% mononitrocumene, on the basis that the initial light ends would be unreacted cumene, while polynitrated materials would have such low vapor pressures as to be distilled only in negligible amounts. The Dean and Stark trap performed the functions of both a receiver and a separatory funnel, so that at the end of the distillation the remainder of the nitro compounds was run from the trap, dried over Drierite, then decanted and weighed. The mononitrocumene so obtained was a light yellow oil, free from turbidity, which slowly changed through deep red to a dark brown color on exposure to light.

After a number of exploratory runs, the procedure described was fixed and a total of 66 nitration runs was made.

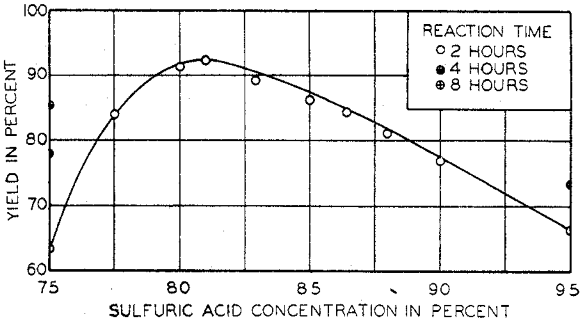


Figure 6. Effect of Sulfuric Acid Concentration on Yield

15° C., 500 grams of sulfuric acid, 10% excess nitric acid
Nitration of 250 grams of cumene

RESULTS

A summary of the data obtained for the nitration of cumene is given in Table II. The first 26 runs were exploratory in nature; the basis taken was primarily the work of Sterling and Bogert (*26*), combined with the concept of dehydrating value of sulfuric acid. It was not found possible to duplicate their work, and attempts at nitration at the temperature and acid compositions described by them resulted only in almost complete oxidation of the cumene. In addition, the strong effect of the nitration temperature on the relative amounts of the two isomers was not found. By a trial and error method, however, a set of experimental conditions under which cumene could be nitrated in about 87% yield was found:

Sulfuric acid (97%)	500 grams
Nitric acid (70%)	206 grams
Cumene	250 grams
D.V.S.	4.25

In addition to the amounts of reactants given, the solvent concentration was calculated to be 86.4% sulfuric acid, the reaction time was 2 hours, and the reaction temperature was from 0° to 25° C.

The results of the systematic process study are shown in Table II, beginning with run 27.

The effect on the yield of varying the amount of sulfuric acid used is shown in Figure 5, where all other conditions are held con-

TABLE II. SUMMARIZED DATA AND RESULTS

Run No.	Temp., ° C.	Nitrator Acid		Mixed Acid			Total H_2SO_4, Grams	H_2SO_4,[a] %	D.V.S.	Excess HNO_3, %	Reaction Time, Hours	Product	
		97% H_2SO_4, grams	Water, grams	70% HNO_3, grams	97% H_2SO_4, grams	Water, grams						Grams	Yield, %
4	15	1000[b]	...	321[b]	...	...	970.0[c]	88.5	...	...	2	255.0[c]	43.2
6	15	600[d]	...	430[d]	...	...	582.0[c]	80.0	1.55	14.9	2	311.7[c]	45.4
8	15	600[d]	...	430[e]	600[c]	...	582.0[c]	80.0	1.55	14.9	2	306.9[c]	44.5
9[f]	15	600[d]	...	430[d]	...	...	582.0[c]	80.0	1.55	14.9	2	420.7[c]	61.0
10	25	300	...	206	200	...	485.0	86.4	4.25	10.0	2	266.7	77.4
11	25	300	...	206	200	...	485.0	86.4	4.25	10.0	2	118.8	33.3
12	25	300	...	206	200	...	485.0	86.4	4.25	10.0	2	253.0	73.1
13	10	300	...	206	200	...	485.0	86.4	4.25	10.0	2	260.7	75.5
14	10	300	...	206	200	...	485.0	86.4	4.25	10.0	2	267.0	77.1
15	45	300	...	206	200	...	485.0	86.4	4.25	10.0	2	Very small	
16	0	300	...	206	200	...	485.0	86.4	4.25	10.0	2	268.9	77.6
17	0	300	...	206	200	...	485.0	86.4	4.25	10.0	2	318.7	92.1
18	0	300	...	206	200	...	485.0	86.4	4.25	10.0	2	299.0	86.5
19	15	300	...	206	200	...	485.0	86.4	4.25	10.0	2	274.0	78.2
20	15	300	...	206	200	...	485.0	86.4	4.25	10.0	2	268.0	77.5
21	25	300	...	206	200	...	485.0	86.4	4.25	10.0	2	257.0	74.4
22	−10	300	...	206	200	...	485.0	86.4	4.25	10.0	..	Freezing	
23	25	300	...	206	200	...	485.0	86.4	4.25	10.0	2	242.8	70.0
24	25	300	...	206	200	...	485.0	86.4	4.25	10.0	2	226.0	65.4
25	10	300	...	206	200	...	485.0	86.4	4.25	10.0	2	271.2	78.5
26	10	300	...	206	200	...	485.0	86.4	4.25	10.0	2	255.6	74.0
27	15	132.5	38.5[g]	206	88.8	25.6[g]	283.0	83.1	2.97	10.0	2	276.7	80.2
28	15	222.0	18.3[g]	206	148.6	12.3[g]	392.0	86.8	4.03	10.0	2	299.7	86.9
29	15	360.0	...	206	240.0	13.2	585.0	86.4	4.51	10.0	2	253.8	73.5
30	15	48.5	122.8[g]	206	32.4	81.7[g]	300.0	86.4	3.53	10.0	2	157.7	46.7
31	15	166.5	74.2[g]	206	110.9	49.6[g]	400.0	86.4	3.96	10.0	2	264.0	76.3
32	15	91.4	114.5[g]	206	60.9	76.5[g]	350.0	86.4	3.77	10.0	2	251.6	73.4
33	15	230.0	38.5[g]	206	152.4	26.7[g]	440.0	86.4	4.11	10.0	2	233.3	68.0
34	15	330.0	...	206	220.0	6.2	533.5	86.4	4.39	10.0	2	288.2	84.0
35	15	390.0	...	206	260.0	19.2	630.5	86.4	4.60	10.0	2	297.6	87.0
36	15	433.1	...	206	288.7	26.6	700.0	86.4	4.75	10.0	2	207.8	87.0
37	15	300.0	...	206	200.0	...	485.0	86.4	4.26	10.0	2	298.1	87.0
38	15	246.2	57.6[g]	206	164.2	38.4[g]	500.0	88.0	4.72	10.0	2	257.3	75.0
39	15	300.0	...	150.8[h]	215.5	56.6	500.0	86.4	4.26	10.0	2	289.5	84.5
40	15	300.0	10.0	206	215.5	...	500.0	85.0	3.96	10.0	2	295.4	86.2
41	15	300.0	25.8	206	215.5	...	500.0	82.9	3.61	10.0	2	306.0	89.3
42	15	300.0	...	150.8[h]	215.5	49.5	500.0	90.0	5.36	10.0	2	263.8	77.0
43	15	300.0	89.4	206	215.5	...	500.0	75.0	2.44	10.0	2	217.1	63.3
44	15	300.0	...	150.8[h]	215.5	46.0	500.0	88.0	4.72	10.0	2	277.8	81.1
45	15	300.0	...	150.8[h]	215.5	4.2	500.0	95.0	7.81	10.0	2	227.9	66.5
46	15	300.0	67.8	206	215.5	...	500.0	77.5	2.71	10.0	2	288.3	84.1
47	15	300.0	89.4	206	215.5	...	500.0	75.0	2.45	10.0	4	267.4	78.0
48	15	300.0	39.9	206	215.5	...	500.0	81.0	3.23	10.0	2	316.3	92.2
49	15	300.0	47.7	206	215.5	...	500.0	80.0	3.08	10.0	2	312.8	91.3
50	15	300.0	89.4	206	215.5	...	500.0	75.0	2.45	10.0	8	292.1	85.2
51	15	300.0	45.5	187.3	215.5	...	500.0	81.0	3.23	0.0	2	295.7	86.4
52	15	300.0	34.2	225	215.5	...	500.0	81.0	3.23	20.0	2	323.7	94.5
53	15	300.0	28.7	263.5	215.5	...	500.0	81.0	3.23	30.0	2	323.9	94.5
54	15	300.0	...	150.8[h]	215.5	4.2	500.0	95.0	7.81	10.0	4	252.1	73.6
55	15	300.0	83.8	225	215.5	...	500.0	75.0	2.45	20.0	2	274.9	82.6
56	15	300.0	...	164.7[h]	215.5	45.2	500.0	88.0	4.72	20.0	2	293.5	85.7
57	15	300.0	...	164.7[h]	215.5	3.6	500.0	95.0	7.81	20.0	2	160.8	46.9
58	25	300.0	83.8	225	215.5	...	500.0	75.0	2.45	20.0	2	274.9	82.6
59	25	300.0	34.2	225	215.5	...	500.0	81.0	3.23	20.0	2	314.5	91.8
60	25	300.0	...	164.7[h]	215.5	45.2	500.0	88.0	4.72	20.0	2	262.2	76.5
61	25	300.0	...	164.7[h]	215.5	3.6	500.0	95.0	7.81	20.0	2	199.4	58.2
62	35	300.0	83.8	225	215.5	...	500.0	75.0	2.45	20.0	2	304.5	88.9
63	35	300.0	34.2	225	215.5	...	500.0	81.0	3.23	20.0	2	314.6	92.0
64	35	300.0	...	164.7[h]	215.5	45.2	500.0	88.0	4.17	20.0	2	255.7	74.7
65	35	300.0	...	164.7[h]	215.5	3.6	500.0	95.0	7.81	20.0	2	216.5	63.2
66	15	300.0	34.2	225	215.5	...	500.0	81.0	3.23	20.0	4	321.1	93.6

[a] H_2SO_4/(grams H_2O + grams H_2SO_4).
[b] Cumene added to mixed acid in nitrator.
[c] 500 grams cumene used.
[d] Acids added to cumene.
[e] Cumene and H_2SO_4 emulsified, HNO_3 added.
[f] 40 ml. Turkey red oil added.
[g] Oleum, 26% free SO_3.
[h] 95.6% HNO_3.

stant at those found in the exploratory work. On the basis of these data a constant amount of sulfuric acid, 500 grams (100% basis), was chosen for the remainder of the work.

The effect of the solvent concentration on the yield at constant temperature, sulfuric acid, and nitric acid is shown in Figure 6. This curve has almost the same shape as the curves of reaction rate constant versus solvent concentration (Figure 2). The optimum sulfuric acid concentration is 81%, considerably below that for the monohydrate of sulfuric acid. This is emphasized by Figure 7, in which the data shown in Figure 6 are plotted as a

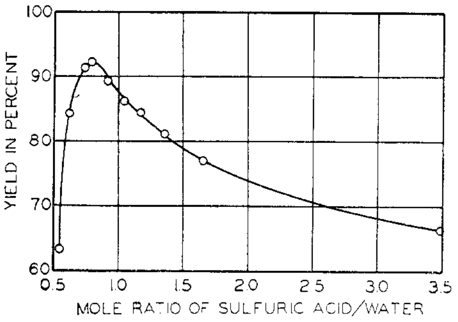


Figure 7. Effect of Sulfuric Acid–Water Mole Ratio on Yield

15° C., 500 grams of sulfuric acid, 10% excess nitric acid, reaction time 2 hours
Nitration of 250 grams of cumene

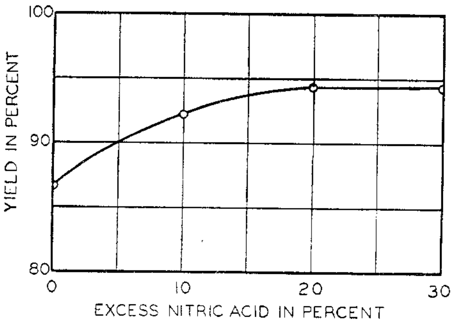


Figure 8. Effect of Excess Nitric Acid on Yield

15° C., 81% sulfuric acid concentration, 500 grams of sulfuric acid, reaction time 2 hours
Nitration of 250 grams of cumene

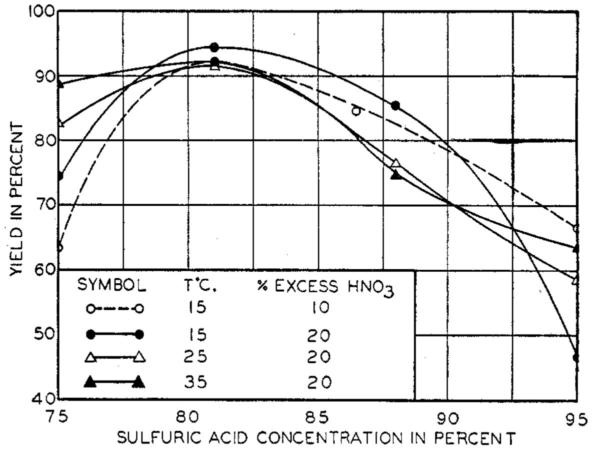


Figure 9. Effect of Sulfuric Acid Concentration and Temperature on Yield

Nitration of 250 grams of cumene with 500 grams of sulfuric acid, reaction time 2 hours

function of the mole ratio of sulfuric acid to water and only for the 2-hour reaction time. In none of the experiments with 10% excess nitric acid was there any evidence of polynitration. Unreacted *p*-cymene was recovered from the reaction products, confirming the kinetic effect already pointed out (Figure 2). The tarry material present did not contain any crystalline dinitrocumene and probably resulted from decomposition of the hydrocarbon by the severe oxidizing conditions undoubtedly existing in the concentrated mixed acid.

With the optimum solvent concentration found and with the minimum amount of sulfuric acid necessary fixed, the amount of excess nitric acid over the amount required stoichiometrically was varied at the optimum conditions previously fixed and at a constant temperature of 15° C. In Figure 8 it may be seen that the amount of nitric acid affects the yield very strongly up to 20% excess, or a mole ratio of nitric acid–cumene of 1.20, after which there is no further increase.

In order to study the effect of the nitration temperature as completely as possible, a series of nitrations was carried out. The reaction temperatures chosen were 15°, 25°, and 35° C., and four runs were made at each temperature for concentrations of 75, 81, 88 and 95%, with the minimum amounts of sulfuric and nitric acids, and a constant reaction time of 2 hours. Figure 9 shows that the optimum concentration remains unaffected by the temperature, while the reduction in yield that occurs at low concentrations apparently is purely the result of slow reaction in these solvents. At high concentrations the major effect of temperature is to accelerate side reactions, as the changes are irregular. However, at very high concentrations the kinetic effect is important, as may be seen from Figure 10, in which the temperature is taken as one variable and the concentration as a parameter. Dinitration products were isolated from the steam distillation residue from the nitration at 15° C. with 20% excess nitric acid at 95% acid concentration.

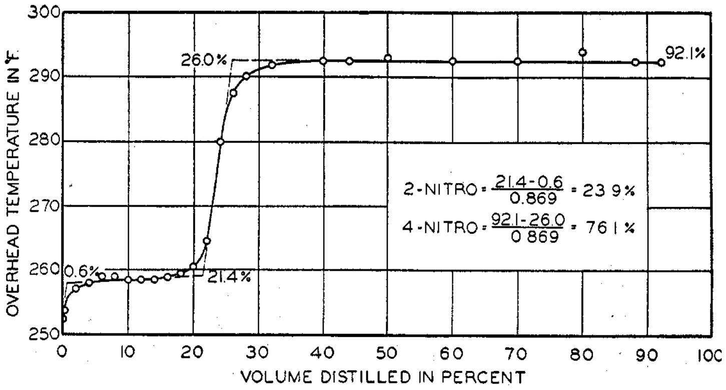


Figure 11. Distillation Curve for Product from Run 37

At 13.3 mm. mercury pressure

Attempts to analyze the reaction products by spectrophotometric methods were unsuccessful, but the optical densities of the products were so nearly constant as to indicate that the powerful effect of temperature on the position taken by the nitro group reported by Sterling and Bogert (*26*) does not exist, although it is probable that there is a small effect, as has been shown by Holleman (*16*) for the mononitration of toluene. It is also likely that very severe nitration conditions might give rise to a product in low yield which is predominantly 2-nitrocumene, as it was found during the characterization of the nitro compounds that the 2-nitro isomer resisted oxidation by chromic acid for 2 hours at the reflux temperature, while the 4-nitrocumene was easily oxidized to *p*-nitrobenzoic acid.

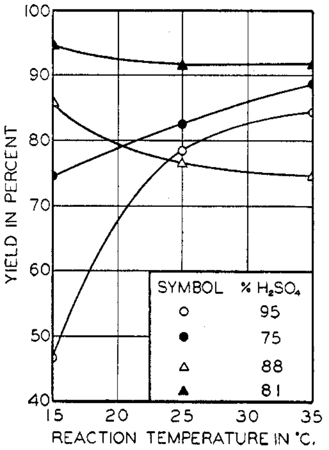


Figure 10. Effect of Temperature and Sulfuric Acid Concentration on Yield

500 grams of sulfuric acid, 20% excess nitric acid, 2 hours reaction time
Nitration of 250 grams of cumene

An analysis of the product was obtained by fractional distillation at low pressure through a 54 inch × 20 mm. column packed with 1/8-inch stainless steel helices and having about 30 theoretical plates at atmospheric pressure. No exact evaluation of the fractionating power of the column was carried out, as it was intended for operation at 10 to 15 mm. mercury pressure. The distillation curve obtained for the product from nitration run 37 is shown in Figure 11. The orientation so obtained is about 24% 2-nitrocumene and 76% 4-nitrocumene.

TABLE III. PHYSICAL PROPERTIES OF NITROCUMENES

Compound	2-Nitrocumene	4-Nitrocumene
Boiling point, ° C.	111.1–111.4/9.2 mm.	128.3–128.9/12.8 mm.
Refractive index, n_D^{20}	1.52420	1.53465
Density, d_4^{20}, g./ml.	1.0848	1.0852

Samples of each of the two isomers of nitrocumene obtained were prepared by successive fractionation of the combined products from several nitrations in the vacuum column described. The nitro compounds were characterized by oxidation of the isopropyl group with chromic acid at reflux and by reduction to the corresponding cumidines. The boiling points at reduced pressure, the refractive indexes by the dipping refractometer, and the densities of the nitrocumenes are shown in Table III.

REDUCTION OF NITROCUMENES

Because the most important use of nitro compounds is in the manufacture of the corresponding aromatic amines, an investigation of the reduction process was undertaken. A process was developed by which the steam distillate from the nitration process could be reduced in almost quantitative yield. This process is also applicable to the reduction of either of the two mononitrocumenes separately.

Reduced iron (200 grams of iron metal powder reduced by hydrogen, National Formulary) and 250 ml. of water were placed in a 3-liter round-bottomed, three-necked boiling flask having standard-taper ground-glass necks, with a handful of porcelain Berl saddles added for boiling stone. A Friedrich reflux condenser was then attached to one of the side necks of the flask and a 250-ml. separatory funnel to the center neck. The mixture was heated to boiling, the heater was turned off, and 20 ml. of concentrated hydrochloric acid were added to etch the iron. After 2 to 3 minutes 200 grams of mixed nitro compounds were added and the mixture was cautiously heated until the reaction began. There was a short period of vigorous reaction, after which 250 ml. of concentrated hydrochloric acid were allowed to drop into the reaction mass from the separatory funnel. All the acid was added at the end of 1 hour and the mixture was continued in active refluxing until a total time of 2 hours had elapsed from the addition of the nitro compounds. The mixture was poured into a 5-liter round-bottomed flask, the reduction flask was washed with a little dilute (10%) hydrochloric acid, and the washings were added to the distillation flask. The mass was made basic to litmus with 50% sodium hydroxide and diluted with water to a total volume of approximately 3 liters. A condenser was attached, the flask was heated with a Glas-Col mantle, and distillation was begun. Additional water was added at intervals to maintain the volume at about the original value, and distillation was continued until no turbidity could be observed in the distillate, which occurred when the total volume distilled was about 2.5 liters.

The distillate was placed in separatory funnels and the oily layer separated. The water layer was extracted three times with ether and the extract was combined with the separated amine. At this point, the amine was a clear orange-yellow oily liquid. The ether-amine solution was then dried over Drierite and the ether was evaporated on the steam bath. The yield was about 160 grams, or about 98% of the theoretical yield, 163.8 grams. The final product was dark red in color and had the characteristic odor of aromatic amines.

The particle size of the iron used was found to be the controlling factor in obtaining good yields in the reduction. The yield obtained was an inverse function of the average particle size. Use of iron filings of the finest available degree of pulverization resulted in yields of the order of 75 to 85% under the same conditions for which the reduced iron gave almost quantitative results.

Reduction of the crude nitro compound product without steam distillation required essentially the same conditions as those described, except that the great excess of hydrochloric acid is not necessary. Use of only 50 ml. of acid with all other conditions the same gave a violent reaction and almost quantitative yields. However, as the boiling points of the two amines differ by only about 1° C. over a wide range of pressures, the recommended procedure is for separation and reduction of the nitro compounds.

SUMMARY

The effects of the various process variables on the yield obtainable in the nitration of cumene with mixed nitric and sulfuric acids have been studied. The methods used in this investigation are proposed as general methods for the study of the nitration of any aromatic hydrocarbon. Their development was based on a new concept of the unit process of aromatic nitration derived from recent fundamental studies of the nitration reaction. The maximum yield obtained was 94.5%, using 250 grams of cumene, 500 grams of sulfuric acid, solvent concentration 81%, and 20% excess nitric acid, at 15° C.; and the orientation obtained was approximately 24% ortho and 76% para at temperatures from 15° to 35° C.

A purified nitration product from the nitration of cumene can be reduced to the amines in almost quantitative yield, using iron and hydrochloric acid for the reduction. The maximum yield of 98% was obtained using 200 grams of nitrocumene, 200 grams of reduced iron, 250 ml. of water, and 270 ml. of hydrochloric acid, at reflux for 2 hours. As the separation of the amine isomers is more difficult than the separation of the nitrogen compounds, the process conditions were developed for the reduction of purified 2- and 4-nitrocumenes.

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