

the same two stages really exist, but that iron catalyzes the secondary reaction so that it is practically instantaneous.

Reactions.

It has long been known that perchloro-mercaptan can be reduced by silver dust,¹ iron and acetic acid,² or stannous chloride, or tin and hydrochloric acid³ to thiophosgene, according to the reaction $CSCl_4 + SnCl_2 \longrightarrow CSCl_2 + SnCl_4$. When this reduction was tried with zinc and hydrochloric acid the perchloro-methyl-mercaptan disappeared completely; apparently it was reduced to methane, which escaped as gas. With iron and hydrochloric acid, a mixture of thiophosgene and carbon tetrachloride is obtained. When perchloro-methyl-mercaptan was refluxed with iron filings it gave nothing but carbon tetrachloride. An attempt to replace one of the chlorine atoms by fluorine failed. When perchloro-methyl-mercaptan was refluxed with zinc fluoride the inner tube of the condenser was rapidly and deeply etched, and the product was nearly pure carbon tetrachloride.

Summary.

A convenient method of preparing perchloro-methyl-mercaptan with yields as high as 65% has been worked out, and some of the reactions of this compound have been studied.

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THE RÔLE OF MERCURIC NITRATE IN THE "CATALYZED" NITRATION OF AROMATIC SUBSTANCES.⁴

[FIRST PAPER.]

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When nitric acid containing mercury in solution acts upon benzene, or upon certain of its derivatives, nitro groups are introduced, but some other reaction or series of reactions also occurs; one of the hydrogen atoms of the aromatic nucleus is replaced by an hydroxyl group, and the product is a nitrated phenol. Benzene, for example, warmed with ordinary commercial nitric acid in which mercuric nitrate has been dissolved, produces nitrobenzene and picric acid, the latter in such yields that this

¹ Rathke, *Ann.*, **167**, 204 (1873); Klason, *Ber.*, **20**, 2377 (1887).

² Klason, *ibid.*, **20**, 2380 (1887).

³ Klason, *ibid.*, **20**, 2380 (1887); Kern and Sandoz, *Jahresber.*, **1887**, p. 2545; *Mont. sci.* [4] **1**, 1328 (1887).

⁴ The funds for this investigation were provided by a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance.

process can compete favorably with the other processes for the preparation of picric acid from benzene, *viz.*, through chlorobenzene, or through benzene sulfonic acid and phenol. Since Wolfenstein and Boeters¹ patented the process in 1908 various modifications and even other "catalysts" have been suggested,² but no investigation of the course of the reaction, or of its mechanism, appears to have been made.

At first sight, the most plausible hypothesis to account for the formation of picric acid directly from benzene would seem to be the supposition that the benzene is first nitrated, that the nitro group renders the hydrogen atom in the *ortho* position to it labile and active, and that this hydrogen atom is then oxidized to an hydroxyl group—so producing a nitrophenol which is subsequently nitrated to picric acid. We have tested this hypothesis in a number of ways, and have found it to be inadequate.

Commercial nitric acid containing sufficient mercuric nitrate converts benzene completely into nitrobenzene and picric acid, while the same nitric acid in the absence of mercury salts leaves a large part of the benzene unaffected. Dil. nitric acid of about 10% strength boiled with benzene in the presence of mercuric nitrate produces considerable 2,4-dinitrophenol, while it yields scarcely enough nitrobenzene to be detected by its odor. The simple nitration of benzene, therefore, requires a higher concentration of nitric acid than does the formation from benzene, in the presence of mercuric nitrate, of dinitrophenol or picric acid.

Increasing concentrations of nitric acid, even if mercuric nitrate is present, result in decreasing yields of picric acid. At a concentration of nitric acid in the neighborhood of 70% and above, the yield of picric acid is so poor as to render the process impracticable. The yields of mono- and dinitrobenzene, however, are good. We find that picric acid is oxidized and destroyed by boiling with strong nitric acid. The fact that experiments with strong acid in the presence of mercuric nitrate gave good yields of nitrohydrocarbons indicates that whatever picric acid may have been formed (and conceivably oxidized) was less than the amount which is produced with less concentrated acid. The production of picric acid is, therefore, not due merely to the oxidizing action of the nitric acid.

When nitric acid containing dissolved mercuric nitrate was boiled for 4 hours with nitrobenzene, under conditions which would produce picric acid from benzene itself, more than half of the nitrobenzene was recovered along with a small amount of dinitrobenzene, and no evidence was found that any picric acid had been produced. There was no yellow color.

¹ *D. R. P.*, 194,883, 1908.

² Wolfenstein and Boeters, *D. R. P.*, 214,045, 1909; Ramy, *Brit. pat.*, 125,461, 1918; MacDonald and Calvert, *Brit. pats.*, 126062, 126084, and 126675-6, 1918; Brewster, *Brit. pat.* 131,403, 1919.

When pure *m*-dinitrobenzene was treated in the same way, about 82% of it was recovered, and mercury oxalate was isolated from the mother liquors. Pure samples of *s*-trinitrobenzene and of 2,4,6-trinitrotoluene were treated in the same way, and the substances were recovered in practically theoretical amount. No picric acid could be found in any of the experiments. The losses by destructive oxidation were least in the cases of those substances which contained the largest number of nitro groups. The results indicate definitely that the presence of mercuric nitrate does not encourage the oxidation of the hydrogen atoms of a nitrated aromatic nucleus, and the conclusion is justified that the reaction, benzene-to-picric acid, does not depend upon the primary formation of a nitro compound. The hydrogen atoms of *s*-trinitrobenzene are so active that a lukewarm aqueous solution of potassium ferricyanide oxidizes the substance to picric acid.¹ Trinitrotoluene is oxidized in the same fashion; while, with a solution of chromic acid in sulfuric acid at ordinary temperatures, it is oxidized readily in another mode to yield trinitrobenzoic acid. The recovery of both of these substances in quantitative amounts from mixtures in which they had been subjected to vigorous treatment with nitric acid in the presence of mercuric nitrate, seems to establish definitely that the mercury in these reactions does not play the rôle of an *oxidizing catalyst*.

Two experimenters prepared dinitrobenzene from nitrobenzene, each according to the method which is described in Gattermann's laboratory manual and each according to the same method except that a mol equivalent of mercuric nitrate was present in the reaction mixture. Both obtained smaller yields in the experiments where mercury was used—a result which seems to indicate that mercury does not catalyze the introduction of nitro groups.

By working with substituted benzenes, we had hoped that the orientation of the groups in the substituted picric acids which would be formed would make possible some inference as to which groups were the first to enter the molecule. From toluene and chlorobenzene we have obtained² respectively trinitro-*m*-cresol and trinitro-*m*-chlorophenol. These results would seem to indicate that the nitro group or groups, here occupying the *ortho*- and *para*-positions, were the first to be introduced, but the evidence which has been given above indicates that such cannot possibly be the case. The surprising formation of *meta*-substituted hydroxyl compounds from toluene and from chlorobenzene seemed to us to indicate that the hydroxyl group and at least one nitro group are probably intro-

¹ Hepp, *Ann.*, 215, 344 (1882).

² An experiment with phenol yielded picric acid, not trinitro-resorcinol, as might be expected, probably because phenol nitrates so readily that the other reaction had no chance to occur. In this experiment the phenol was dissolved in nitrobenzene and boiled with nitric acid and mercuric nitrate.

duced simultaneously, and that the course of the reaction probably involves the intermediate formation of a complex molecular compound.

We find that an increase in the amount of mercury increases the yield of picric acid. This would not be the case if the mercury were a true catalyst acting simply "by presence." The graph showing the relation between the amount of mercury and the yield of picric acid rises continuously, but the yield of picric acid is not directly proportional to the amount of mercury—a fact which is readily understood in the light of the consideration that 2 reactions, the other leading to the formation of nitrobenzene, are competing for the material. When the mercury amounts to a mol equivalent or more, considerable quantities of mercury picrate and dinitrophenolate are precipitated in the reaction mixture, and the mass is difficult to handle.

The hypothesis that the mercury takes real part in the reaction which leads to the formation of picric acid is supported by the appearance of the reacting mass. When benzene is added to a solution of mercuric nitrate in commercial nitric acid, the acid layer rapidly takes on a deep brown color and becomes nearly black if it is kept cool. Very little nitrogen peroxide is given off by the cold mixture. When it is warmed, red fumes come off abundantly and the dark color of the solution disappears. By working at low temperatures, we have succeeded in preparing picric acid and dinitrophenol under conditions where practically no nitrobenzene is produced. We have made a quantitative study of the gases which are evolved, and find that nitrogen peroxide is evolved abundantly during the first hour of heating, but that it falls off rapidly in amount, and that further application of heat results in the slow but regular evolution of nitric oxide formed by the destructive oxidation of the picric acid. In one experiment, in which 20 g. of benzene was used, we isolated 8 g. of a black substance, evidently a complex intermediate compound, which contains mercury and which yields picric acid when it is heated with nitric acid. This intermediate will be studied further.¹

The evidence now at hand indicates that benzene reacts with a solution of mercuric nitrate in nitric acid to form a highly colored complex compound. When the mixture is warmed, this compound is attacked by the nitric acid, regenerating mercuric nitrate, liberating nitrogen peroxide, and producing 2,4-dinitrophenol. We have found no evidence of the *o*-nitrophenol which Wolfenstein and Boeters claim is formed. On further heating of the mixture, the dinitrophenol is nitrated to picric acid which is in part oxidized to carbon dioxide and destroyed.

Sulfuric acid interferes with the reaction and reduces the yields of picric acid to little or nothing. This may perhaps mean that the complex

¹ Studies are now going on in this laboratory of the reaction of nitric acid on naphthalene in the presence of mercury nitrate. Nitro-naphtholes are formed.

compound of mercuric sulfate with an aromatic substance is different in its properties from the complex compound with mercuric nitrate, different to the extent that it now makes the aromatic nucleus susceptible to easy oxidation—and may perhaps explain the action of the mercury catalyzer in the well-known process for the preparation of phthalic anhydride from naphthalene. The matter will be investigated.

Mercury is the only "catalyzer" which we have found for this reaction.¹ Lead, copper, silver, arsenic, aluminum, manganese, vanadium, cerium and uranium do not appear to act, and aluminum and manganese do not appear to "promote" the action of the mercury.

Discussion of Experiments.

All experiments, unless otherwise noted, were carried out in round-bottom Pyrex flasks equipped with a sealed-on water-jacketed condenser. The mercuric oxide or nitrate was dissolved in the nitric acid, the benzene was added, and the mixture was heated on the sand-bath at such rate that it bubbled regularly and gently, and that red fumes did not come off too abundantly. At the end of the heating, the mixture was treated with an equal volume of water and steam-distilled. Unchanged benzene and nitro-benzene came over first. These were separated by fractional distillation. It was found that the nitrobenzene which was obtained in this way always contained considerable dinitrophenol and required to be purified by shaking with aqueous sodium carbonate before it was suitable for use as a reagent. After the nitrobenzene had been driven over in the steam distillation, the dinitrobenzenes and 2,4-dinitrophenol came over with the distillate. The dinitrobenzenes came over before most of the dinitrophenol, but the separation was far from complete. 2,4-Dinitrophenol is definitely volatile with steam, about half a gram comes over with a liter of distillate. It forms low melting mixtures with dinitrobenzene and the mixtures are volatile with steam. It is perhaps such mixtures as these that Wolfenstein and Boeters took to be *o*-nitrophenol. We have isolated from the products of our experiments all 3 of the dinitrobenzenes. The separation of these isomers by fractional crystallization is very troublesome, and, after we had shown that all 3 of them and no other substances were present in the dinitrobenzene of certain experiments, we did not trouble to work up the others. The residue left from the steam distillation generally contained a little precipitated mercury salt; it was filtered hot and deposited crystals of picric acid on cooling. The mother-liquors were generally evaporated somewhat for a second crop of picric acid, and, in certain cases, were extracted with ether for the complete recovery of product.

A mixture in the proportions recommended by Wolfenstein and Boeters, 400 g. of benzene, 50 g. of mercuric nitrate, and 625 g. of commercial nitric acid (sp. gr. 1.396, 64.25%), was warmed on the water-bath but the reaction became so vigorous that it was necessary to cool the mixture. It was finally heated for 9 hours on the water-bath, at the end of which time red fumes had practically ceased to come off. The mixture yielded 207.2 g. of benzene, 38 g. of nitrobenzene, 17 g. of crude 2,4-dinitrophenol (m. p. 100–105°), and 125 g. of crude picric acid (m. p. 118°). No evidence was found of any dinitrobenzenes except the little which was present as an impurity in the dinitrophenol. 30 liters of distillate was collected.

Relatively more acid gave a much better yield. 200 g. of benzene, 600 cc. of nitric acid (sp. gr. 1.42) and 10 g. of mercuric oxide boiled on the sand-bath for 7 hours yielded 41 g. of benzene, 61.3 g. of nitrobenzene, 105 g. of picric acid (m. p. 121°), and 4 g. of a

¹ Copper and silver have been patented as catalyzers, and manganese and aluminum as "promoters."

mixture which was found to consist of about equal parts of *m*-dinitrobenzene and of 2,4-dinitrophenol, along with some *p*-dinitrobenzene. All of the substances were identified by "mixed melting points" with known specimens. Two g. of 2,4-dinitrophenol, m. p. 114–115°, and 0.5 g. of pure *p*-dinitrobenzene, m. p. 172–173°, were isolated. The *p*-dinitrobenzene was identified by mixed melting point with a sample prepared synthetically by the action of nitric acid on quinone dioxime.

To examine the effect of dilute acid, 100 g. of benzene was boiled for 5 hours with a mixture of 100 cc. of nitric acid (sp. gr. 1.40) and 500 cc. of water in which 10 g. of mercuric oxide had been dissolved. The first appearance of yellow color was in the aqueous layer, but the benzene evidently extracted this color, for, at the end of the experiment, the benzene layer was a deep yellow while the aqueous layer was only a pale lemon-yellow. The aqueous layer contained a slight amount of precipitate, evidently a basic dinitrophenolate. There were no red fumes in the flask at any time, but there was evidence of nitrogen peroxide in the upper part of the condenser. The reaction mixture yielded 76 g. of benzene, 2 g. of crude dinitrophenol (m. p. 106°) and about half a gram of an oil which smelled like nitrobenzene. On standing in the laboratory, this oil evaporated in part and left a few brown crystals, too small in amount to be studied.

Effect of Acid Concentration.—A series of experiments was carried out to determine how the product varies with variation in the concentration of the nitric acid. Nitric acid was prepared of about the desired strength, its density determined with an hydrometer, and the percentage composition ascertained from tables. Three hundred cc. of the prepared acid was taken, 2 g. of mercuric oxide was dissolved in it, and the mixture was boiled for 2 hours with 20 g. of benzene. A period of 2 hours was chosen because we feared that a longer period might result in considerable losses by oxidation. The mixture was diluted with 600 cc. of water and worked up as has been described. Results are shown in the following table, where the figures indicate grams of material isolated. "None" means that none was isolated. The results, of course, are only roughly quantitative. The dinitrobenzene of these experiments was largely the *meta* compound.

Nitric acid. %	Benzene. G.	Nitrobenzene. G.	Dinitrobenzene. G.	Dinitrophenol. G.	Picric acid. G.
100.0	None	None	28.0	None	None
78.6	None	10.0	10.0	None	None
62.5	None	10.0	0.3	Trace	12.0
40.9	4.6	4.0	None	0.3	4.0
20.6	14.6	Trace	None	0.5	None

Action with Compounds Already Containing Nitro Groups.—24.6 g. (0.20 mol) of an especially purified sample of nitrobenzene, b. p. 210–210.5°, which had been shaken with aqueous sodium carbonate solution and fractionated, was boiled for 4 hours with 300 cc. of nitric acid (1.40) in which 43.6 g. of mercuric oxide (slightly more than a mol equivalent) had been dissolved. 13.2 g. of nitrobenzene was recovered, together with 4 g. of dinitrobenzene from which a quantity of the *meta* derivative was isolated and identified.

Thirty-three and six-tenths g. of pure *m*-dinitrobenzene (0.20 mol) was treated in precisely the same way. At the end of the heating the mixture was diluted with water and the precipitated dinitrobenzene was filtered off and dried, 27.5 g., m. p. 90.5°. The practically colorless filtrate was extracted with ether, and the ether extract yielded a product which after recrystallization from alcohol, amounted to less than half a gram and melted at 88° to 90°. The aqueous solution left from the ether extraction was allowed to stand for a week and deposited 2.0 g. of well-formed yellow crystals which were identified as mercuric oxalate. This substance does not melt, but deflagrates

when heated. It explodes when struck with the hammer. It gives a sublimate of mercury when ignited. It dissolves in aqueous nitric, hydrochloric or sulfuric acid. Its solution in hydrochloric acid gives a black precipitate with ammonium sulfide, and with calcium chloride a white precipitate insoluble in ammonia. Its solution in aqueous sulfuric acid discharges the color of permanganate instantly in the cold.

Twenty-one and three-tenths g. of pure *s*-trinitrobenzene (0.10 mol.) was boiled for 4 hours with 300 cc. of nitric acid (sp. gr. 1.40) in which 21.6 g. of mercuric oxide had been dissolved. The mixture was poured into ice-water and the precipitate collected and dried, amounted to 20 g. of trinitrobenzene, m. p. 121.5°. The ether extraction of the filtrate yielded a residue which without recrystallization gave an additional 0.6 g., m. p. 120°.

A similar experiment with 22.7 g. of 2,4,6-trinitrotoluene gave at once 21.1 g., m. p. 80.8°, and an additional 0.7 g., m. p. 80.5°, from the ether extract. These trinitrohydrocarbons appear perfectly resistant to the oxidizing action of hot commercial nitric acid.

Reaction with Toluene.—The reaction with toluene is decidedly more vigorous than that with benzene and requires to be cooled during its early stages. Oxides of nitrogen, arising evidently from the oxidation of the methyl group of the nitrated compounds, continue to come off for a long time, and a much longer heating, than with benzene, is needed to bring the reaction to completion.

Two hundred g. of toluene and 600 cc. of nitric acid (sp. gr. 1.40), in which 10 g. of mercuric oxide had been dissolved were heated together under a reflux condenser for 12.5 hours on the water-bath at 65° to 85°, for 2 hours at 85° to 95°, for 1 hour at 95°, and finally for 7 hours on the sand-bath. The reaction mixture yielded 48 g. of toluene, b. p. 109° to 115°, about 15 g. of *o*-nitrotoluene, about 12 g. of *p*-nitrotoluene, 8.8 g. of *p*-nitrobenzoic acid, and 6 g. of trinitro-*m*-cresol, together with about 60 g. of other solid material. As this other solid material appeared to contain nothing but *p*-nitrobenzoic acid, trinitro-*m*-cresol, and mercury salt, it was not subjected to the tedious fractional crystallization. The *p*-nitrobenzoic acid was identified by its own melting point, 233° to 234°, and by that of its methyl ester, 94° to 95°. To prepare the methyl ester, a solution of the substance in absolute methyl alcohol was chilled in the freezing mixture and saturated with dry hydrogen chloride. After the mixture had stood in a stoppered vessel overnight, it was poured out for spontaneous evaporation, and the residue was recrystallized from methyl alcohol to constancy of melting point. The large quantity of *p*-nitrobenzoic acid indicates that much *p*-nitrotoluene had been formed and was subsequently oxidized by the hot nitric acid, so producing the long-continued evolution of oxides of nitrogen. *o*-Nitrobenzoic acid was not isolated, but must undoubtedly have been present. The trinitro-*m*-cresole was identified by a mixed melting point determination (107°), with a pure sample obtained from French sources. (Cresylite, St. Chamas.)

Reaction with Chlorobenzene.—The reaction with chlorobenzene is much less vigorous than that with benzene. At the end of 10 hours' boiling, the chlorobenzene layer, while highly colored, still floated on the acid, and red fumes were still given off slowly from the top of the condenser. One hundred g. of chlorobenzene was boiled for 10 hours with 300 cc. of nitric acid (sp. gr. 1.40), in which 5 g. of mercuric oxide had been dissolved. The reaction mixture yielded 57.6 g. of chlorobenzene (boiling within 2°), 7.6 g. of *p*-nitrochloro-benzene, m. p. 83°, 4 g. of an unidentified oil, b. p. 229–233°, which is possibly *o*-nitrochloro-benzene, and 1.5 g. of a pure pale yellow, crystalline material which we believe we have identified as trinitro-*m*-chlorophenol. This substance, recrystallized from alcohol to constancy of melting point, melts at 112–113°. The reported melting point of trinitro-*m*-chlorophenol is 119°. It liberates carbon dioxide from an aqueous solution of sodium carbonate. Chlorine determinations by the

method of Carius gave chlorine 13.18% and 13.05%, while that calculated for $C_6H_5O_7N_3Cl$ is 13.31%. The nitrogen determination was difficult, for the material, in spite of all precautions, always exploded in the combustion tube. The best determinations gave nitrogen 16.51% and 15.15%, while that calculated for $C_6H_5O_7N_3Cl$ is 15.95%.

Effect of Mercury Concentration.—A systematic series of experiments was performed for the purpose of determining the effect on the yield of picric acid of varying amounts of mercuric nitrate. For 20 g. of benzene (0.256 mol) a very large excess of nitric acid was taken—300 cc. of nitric acid of sp. gr. 1.40—in order to avoid the presence of lower nitrated phenols and in order that only benzene, nitrobenzene, and picric acid need be sought in the products of the reaction. A few g. of dinitrobenzene, however, was also formed in each experiment. The amount of mercuric oxide was varied from 0.1 g. to 55.4 g. which is more than the molecular proportion. In each experiment the heating was continued for 4.5 hours at such a rate that the evolution of red fumes was never violent. As more and more mercury was used, the reaction mixture seemed to require less and less heating; but, since 4.5 hours' heating in the experiment with 2 g. of mercury oxide was sufficient to produce the virtual cessation of red fumes, this time was chosen as the duration of the heating in all of the experiments. The reaction mixture in each case was worked up for *practically pure products*, nitrobenzene boiling between 205° and 210°, and picric acid melting above 121°. The results of these experiments, similar in all respects except in the amount of mercury, are shown in the following table.

Mercury. G.	Oxide. Mols.	Products.									Total % ac- counted for.
		Picric acid.			Nitrobenzene.			Recovered benzene.			
		G.	Mols.	%.	G.	Mols.	%.	G.	Mols.	%.	
0.1	0.00046	0.0	0.0	0.0	10.2	0.084	32.7	8.1	0.11	42.9	75.6
0.5	0.0023	4.3	0.0184	7.2	16.4	0.134	54.0	0.0	0.0	0.0	61.2
1.0	0.0046	7.0	0.0306	11.8	13.7	0.112	43.7	0.0	0.0	0.0	55.5
2.0	0.0093	14.1	0.062	24.2	10.2	0.0821	32.1	0.0	0.0	0.0	56.3
5.0	0.023	14.7	0.064	25.0	10.0	0.0812	31.7	0.0	0.0	0.0	56.7
10.0	0.046	14.7	0.064	25.0	5.1	0.041	16.0	0.0	0.0	0.0	41.0
55.4	0.263	19.3	0.084	32.7	10.2	0.084	32.7	0.0	0.0	0.0	65.4

These results are plotted in Fig. 1.

The yield of picric acid increases continuously as the amount of mercury increases but the increase is not in direct proportion. An increase in the amount of mercury produces at first a very rapid increase in the yield of nitrobenzene, but the effect soon

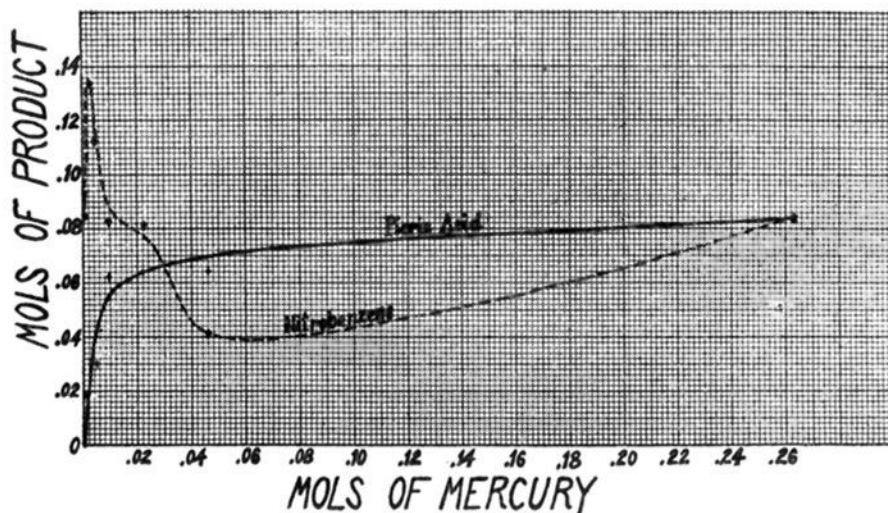


Fig. 1.

disappears; and, above a relatively small concentration of mercury, the yield of nitrobenzene decreases. The variations in the yield of picric acid indicate clearly that the mercury enters into the reaction which leads to the formation of picric acid. The more ready formation of picric acid when the concentration of mercury is highest removes benzene rapidly from the sphere of the simple nitration reaction and accounts adequately for the dropping off in the yields of nitrobenzene. The early and rapid increase in the yield of nitrobenzene and the subsequent dropping off seemed at first to be difficult to explain, but was clarified by later experiments. The intermediate compound which is first formed between benzene and mercury nitrate is presently attacked by the nitric acid with the production of nitrogen peroxide which acts on other benzene which is present to convert it into nitrobenzene. The amount of nitrobenzene which results is proportional to the amount of nitrogen peroxide and is hence proportional to the amount of intermediate compound and to the amount of mercury. The curves which show the relation between mercury concentration and the yields of picric acid and of nitrobenzene at first rise at very nearly the same rate. At high concentrations of mercury the rate of formation of picric acid becomes so rapid that the benzene is quickly removed from the sphere of action of the nitrogen peroxide.

The yields in the case where the amount of mercury was slightly in excess of the molecular equivalent were surely affected by the fact that in this mixture large quantities of mercuric picrate and dinitrophenolate were early precipitated. If this precipitation had not occurred, the yield of picric acid would undoubtedly have been larger and the yield of nitrobenzene smaller. In this same experiment about 0.2 g. of a *p*-dinitrobenzene was isolated and identified by mixed melting point with a specimen prepared synthetically.

Study of the Gaseous Products.—In the process as usually carried out in a flask equipped with an open reflux condenser, the total yield of the various products is not sufficient to account for all of the benzene. Moreover, it is difficult to infer the precise nature of the gaseous products of such experiments or to decide whether destructive oxidation occurs. Experiments were, therefore, undertaken in which the gaseous products were collected and analyzed, in the hope that the results would show us something about the course of the reaction and would indicate whether destructive oxidation occurs and to what extent.

The reaction was carried out in an apparatus of such sort that the gaseous products were forced to pass through wash bottles containing sodium hydroxide solution for the absorption of nitrogen peroxide and of carbon dioxide, and thence into a large glass bottle where the unabsorbed gas (nitric oxide) was collected and measured. A 2-liter Pyrex flask was used for the reaction mixture. In the first experiments, this was equipped with a rubber stopper, painted with collodion, and carrying in addition to the reflux condenser a dropping funnel through which the benzene and nitric acid were introduced and through which nitrogen gas (from a warm solution of sodium nitrite and ammonium chloride) was blown in until all air had been swept from the apparatus. But the corrosive action of the gases proved too strong for the rubber stopper, and the apparatus which was finally adopted was that which is illustrated below.

Rubber connections were inevitable in order that access might be had afterwards to the reaction mixture: they were used only in the cool parts of the apparatus, the ends of the tubes were brought together and joined with pressure tubing which was wired on, and fresh rubber connections were used for each run. The apparatus naturally contained air at the beginning of each run; when the run was completed, the apparatus was allowed to stand overnight until constancy of temperature had been restored, and the volume of unabsorbed gas in the gas-measuring bottle was taken as the volume of nitric oxide produced during the run. If the air originally in the apparatus had been entirely swept over into the gas collecting bottle and if only nitric oxide remained in the

reaction flask at the end of the run, then the volume of gas in the bottle would be precisely equal to the volume of nitric oxide which was produced. Experiments in the apparatus which was filled with nitrogen showed that nitrogen peroxide was the principal product during the first part of the reaction. Since this displaces the air without reacting with it, and since the gases evolved toward the end of the reaction are at least in large part nitric oxide, the volume of the gases in the gas measuring bottle may be taken as a sufficiently precise measure of the nitric oxide which was produced.

Standard sodium hydroxide solution (about 4 *N*), the carbonate and hydroxide content of which had previously been determined, was used in the safety bottle and in the 2 wash-bottles.

The volume was measured accurately; about 800 cc. was generally taken. At the end of the run, the liquid in the several bottles was brought together, the bottles were rinsed, the entire liquid was diluted to a convenient volume in a volumetric flask, and analyzed. Carbonate was determined gravimetrically by precipitation as barium carbonate, and carbon dioxide was calculated. Total alkalinity was determined by titrating the sample, from which the carbonate had been precipitated, with standard hydrochloric acid using phenolphthalein as an indicator. Methyl orange was found to be unsuitable for use with solutions containing nitrites. Nitrite was determined by adding a known volume of the solution to an excess of permanganate, acidified with 10% sulfuric acid and heated to 50–60°, adding standard oxalic acid solution in excess, and titrating back with standard permanganate. From the amount of nitrite, the amount of nitrogen peroxide was calculated, allowing 2 molecules of nitrogen peroxide for each molecule of nitrous acid, in accordance with the equation $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$. Knowing the total alkalinity, the amount of nitrous acid which had been formed from the nitrogen peroxide, and the amount of nitric acid which had been formed from the same source, it was possible to calculate the amount of nitric acid which had been carried over as such along with the gases of the reaction.

A certain amount of benzene was always carried along with the gases, and lost. In some cases the issuing gases contained so much benzene that they were combustible. At first the expedient was tried of cooling the trap or safety bottle with a freezing mixture of ice and salt, but no visible benzene was condensed and the attempt to prevent all losses of benzene was abandoned.

In each experiment 20 g. of benzene was used along with 90 g. of mercuric nitrate (about 10% excess of the molecular quantity) and a large excess of conc. nitric acid, usually 500 cc. The mercuric nitrate was dissolved in the acid, and most of the mixture was introduced into the reaction flask through the long tube. The benzene was added, and then finally the rest of the acid. The reaction mixture rapidly took on a brown color and warmed up; the reaction started spontaneously and red fumes were produced. The mixture was then heated on the sand-bath at such rate that the evolution of gas was regular, and the heating was continued for the desired interval of time. At the end of the run the apparatus was allowed to come to equilibrium and the gas volume was measured. The reaction mixture was then diluted with water and steam distilled, and the residue was worked up for total picric acid either by extracting directly with

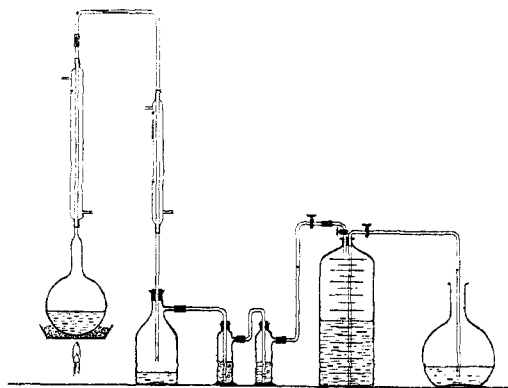


Fig. 2.

ether, or by collecting the first crop of crystals and extracting the mother liquors with ether.

In the first experiment, where the apparatus had been previously filled with nitrogen gas, the mixture was heated on the sand-bath. It rapidly darkened in color and finally became black while a vigorous evolution of reddish-brown fumes of nitrogen peroxide was maintained. The production of brown fumes seemed to reach a maximum in about half an hour, after which it gradually diminished. The liquid in the first wash-bottle was completely neutralized, and some evidence was obtained which indicated a reaction between nitrogen peroxide and an aqueous acid solution of nitrous acid leading to the formation of nitric oxide, perhaps thus, $\text{HNO}_2 + \text{NO}_2 = \text{HNO}_3 + \text{NO}$, but that matter was not investigated.

In another experiment, with the final type of apparatus, the evolution of gas was rapid, while the mixture was heating up and continued rapid for about half an hour. It then fell off markedly and continued finally at a practically constant rate. The attempt was considered to continue the heating until the color of the reaction mixture should fade to a pure yellow, but the color was still a deep orange at the end of 12 hours and gas was coming off. This behavior indicated the probability of a reaction between nitric acid and picric acid, and later experiments verified the conclusion.

The results of several experiments are shown in the following table. The dinitrobenzene of these experiments was apparently a mixture of the *ortho* and *meta* compounds. None of the *para* compound was isolated. The *o*-dinitrobenzene was isolated in considerable quantity and was identified by mixed melting point with a sample of Kahlbaum's material.

	I.	II. ^a	III.	IV.	V.
Duration of heating, hours.....	12	3	4	6
Nitrobenzene, g.....	22.5	10.2	8.4	1.0
Dinitrobenzene, g.....	18.3	4.1	5.8	13.0
Picric acid, g.....	8.2	10.4	20.0	15.1	13.8
Nitric oxide, g.....	1.4	8.8	9.0	11.0
Nitrogen peroxide, g.....	1.21	29.2	55.1	62.4
Nitric acid in gases, g.....	19.15	12.0	37.8	19.7
Carbon dioxide, g.....	1.35	3.2	13.9	14.1
Benzene accounted for in nitro compounds, %.....	68	89	76	68	56
Benzene accounted for on CO ₂ , %.....	2	4	20	21
Total benzene accounted for, %.....	91	80	88	77

^a In Expt. II the mixture was allowed to react spontaneously. It quickly changed from water-white to yellow, gradually deepened through orange and red, and finally became black. It was noticeably warm in 3 minutes and soon became warm enough to boil the benzene. Red fumes were evolved rapidly and the reaction appeared to reach its height at the end of 30 minutes. When it had quieted, the reaction mixture was worked up at once.

The results indicate that the longer the period of the boiling the greater the losses due to destructive oxidation. During the heating considerable benzene is also carried away by the gases as such, and is lost. The yields of nitrobenzene decrease as the boiling is longer (and the amount of carbon dioxide is greater)—a result which indicates that nitrobenzene is destroyed by the boiling. Later experiments showed that picric acid is also destroyed by boiling with nitric acid. The carbon dioxide of these experiments, therefore, arises from the oxidation of both nitrobenzene and picric acid. The ratio, carbon dioxide to oxides of nitrogen, is evidently much smaller than it would be if these gases arose from the complete destructive oxidation of an aromatic compound.

In later experiments where picric acid was destroyed by boiling with nitric acid, attempts to identify oxalic acid in the reaction product were not successful. In the experiment (above) where dinitrobenzene was boiled with nitric acid, mercuric oxalate was found. From the evidence at hand it therefore appears probable that the boiling with nitric acid oxidizes a part of the picric acid completely to carbon dioxide and a part of the nitrobenzene to oxalic acid.

Oxidation of Picric Acid by Nitric Acid.—Twenty g. of pure picric acid and 500 cc. of conc. nitric acid were introduced into the flask and the apparatus was arranged for the determination of gaseous products. The boiling was continued for 3 hours. The mixture became noticeably darker just before boiling commenced, and the reaction was very vigorous when boiling had been attained, after which it fell off, but nitric oxide and nitrogen peroxide continued to be evolved as long as the heating was continued. The residue was steam distilled, but no volatile matter came over, and 8 g. of picric acid was recovered. 12 g. of picric acid (0.052 mol) was destroyed and yielded 2000 cc. of nitric oxide at 30° (2.5 g. or 0.083 mol), 41.4 g. of nitrogen peroxide (0.900 mol) and 8.9 g. of carbon dioxide (0.202 mol). The amount of carbon dioxide is almost precisely $\frac{2}{3}$ of the amount which would be produced by the complete oxidation of 12 g. of picric acid, but the discrepancy is perhaps explained by the difficulty of the carbonate determination and by the impossibility of recovering all of the undestroyed picric acid.

A similar experiment in the presence of a mol equivalent of mercuric nitrate gave practically the same result. Here also the mercury does not appear to be an oxidizing catalyst.

A series of experiments was carried out in which picric acid was boiled for varying durations of time with nitric acid of varying concentrations. In each case the reaction mixture was diluted with water, steam-distilled, and extracted with ether for the recovery of picric acid. In the experiment with fuming nitric acid (97% HNO_3) the steam distillation yielded a few drops of a heavy slightly yellowish oil with marked lachrymatory properties, evidently tetranitro-methane. No volatile product from the steam distillation was obtained in any of the other experiments. In one series of experiments, 20 g. of picric acid was boiled for 3 hours with nitric acid of varying concentrations. In the other, 20 g. of picric acid was boiled with 300 cc. of nitric acid (sp. gr. 1.42) for varying time intervals. The results are tabulated below.

Effect of HNO_3 . Concentration 3 hours.		Effect of Time. Nitric Acid, sp. gr. 1.42.	
Nitric acid.	Picric acid recovered.	Time.	Picric acid recovered.
97%	1.0 gram	30 minutes	15.8 grams
60%	15.0 grams	2 hours	11.9 grams
40%	19.5 grams	4 hours	7.8 grams
		6 hours	6.4 grams

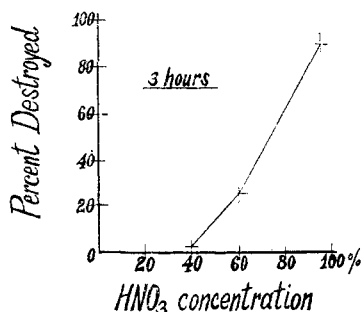
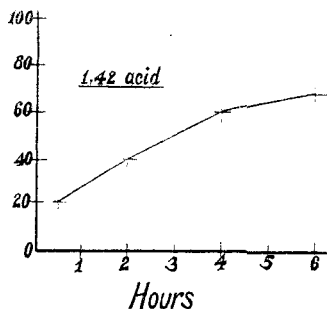


Fig. 3.—Destruction of picric acid by boiling nitric acid.

Taking the amount of picric acid which was not recovered as the amount which was destroyed, these results are plotted.

Reaction at Lower Temperature.—Since the experiments in which the gases were analyzed demonstrated that considerable losses due to destructive oxidation were caused by boiling the mixture, it seemed worth while to investigate what yields could be obtained by operating at lower temperatures. The results showed also that heating is not necessary, and that picric acid is formed when the reaction goes on at room temperature.

The same amounts of benzene, mercuric nitrate, and nitric acid were used as in the earlier experiments.

(a) The materials were introduced into a 5-liter flask, (affording large surface of contact between the benzene and the acid layer), which was stoppered loosely and set aside in ice water. The ice melted slowly and the system gradually attained the temperature of the room. The mixture turned black as usual and oxides of nitrogen filled the flask, but the pressure of the gases was not great enough to blow out the stopper. After standing for 80 hours at room temperature, the mixture was diluted with water and worked up.

(b) Mixture allowed to react for 60 hours without any application of heat or of cold.

(c) Mixture allowed to react spontaneously until reaction slackened, then heated for an hour, then stopped by diluting with ice water.

(d) Mixture allowed to react spontaneously for 6 hours with occasional shaking, then stopped by diluting with ice water. The black mixture was extracted with ether, and it was noticed that a black solid separated at the junction of the 2 layers. About 8 g. of this material was collected, and the low yield of picric acid in this experiment is doubtless connected with the fact that this substance was removed. In the usual procedure this black substance is without doubt decomposed during the course of the steam distillation. It resembles coke when it is dry and can readily be powdered between the fingers. In the flame it burns with marked intumescence. If heated in a test-tube it deflagrates and gives a sublimate of mercury. When warmed with nitric acid, it goes into solution, abundant red fumes are given off, and dinitrophenol is formed (isopurpurate test).

(e) Mixture was allowed to warm up slightly and was then cooled so that it was kept between room temperature (about 30°) and 50° for 18 hours.

	A.	B.	C.	D.	E.
Nitrobenzene, g.	17.4	12.0	14.0	13.0	18.5
Dinitrobenzene, g.	7.0
Dinitrophenol, g.	2.5	3.0	5.0	3.0
Picric acid, g.	21.1	17.5	14.0	6.0	7.5
Total benzene accounted for.	97%	74%	75%	62%	79%

These experiments substantiated the conclusions of the earlier ones. They also showed that the reaction which leads to the formation of the highly colored intermediate compound takes place spontaneously and produces a rise of temperature. The heat so produced, of simply standing for a longer time in the presence of nitric acid, is sufficient to provoke the formation of picric acid from the intermediate compound.

Effect of Sulfuric Acid.—Experiments were carried out with 20 g. of benzene, 3 g. of mercuric oxide, and 300 cc. of nitric acid (sp. gr. 1.40) in the presence of varying amounts of sulfuric acid. In each case the mercuric oxide was dissolved in the nitric acid, then the sulfuric acid, respectively (1) 1 g.; (2) 10 g., and (3) 50 g. of sulfuric acid, c. p., sp. gr. 1.84, was added, then the benzene, and the mixture was finally boiled gently for 4.5 hours. In Expt. 1 the mixture immediately turned yellow on adding the benzene,

in (2) it turned orange; and in (3) it turned red. In (2) and (3) a film of purple colored material was observed in the necks of the flask. In (3) red fumes were given off immediately in abundance, and (3) was the first to quiet down. Experiments 1 and 2 evolved red fumes more gradually, in such fashion that it was perfectly apparent that the rate and vigor of the oxidation was greater the greater the amount of sulfuric acid which was present. Nitrobenzene was obtained in each case, 13.8, 13.8 and 9.0 g., respectively; and *m*-dinitrobenzene was identified in the solid product in each case. No picric acid was isolated, but there was distinct yellow color in the product of each experiment, and the yellow color was most intense in the case where the least sulfuric acid had been used. The results indicate that sulfuric acid either hinders the formation of picric acid by the action of mercuric nitrate or provokes the destructive oxidation of the aromatic material, and indicate that an investigation of the action of sulfuric acid on aromatic compounds in the presence of mercury salts might lead to results of considerable theoretical interest.

Investigations will be continued of the action of naphthalene with nitric acid in the presence of mercuric nitrate, of the action with naphthalene, benzene, etc., of sulfuric acid in the presence of mercuric sulfate, and of the black intermediate compound which we have found to be formed in the reaction which leads to the production of picric acid.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

MERCURI-ORGANIC DERIVATIVES: II. NITROBENZENE MERCURY COMPOUNDS; AN INDIRECT METHOD OF MERCURIZING ORGANIC COMPOUNDS.

BY MORRIS S. KHARASCH¹ AND LYMAN CHALKLEY, JR.

Received November 19, 1920.

Theoretical Part.

Some time ago, one of us became interested in the study of the mercurization of aromatic compounds and its relation to the various theories of substitution in the benzene nucleus. It is well known that at the present time no theory explains satisfactorily all the known facts about substitution. The Crum Brown and Gibson rule of substitution is merely an empirical generalization which is not rigidly correct, and does not suggest the mechanism of the reaction. In the last few years, some theories have been advanced to explain orientation in the benzene nucleus from an electronic point of view. Of the latter the structure formulas of benzene proposed by Fry² and by Vorländer³ deserve most consideration. The two differ in the following respects. Fry assumes the existence in benzene of hydrogen atoms alternately positive and negative, as in Formula I,

¹ This work was carried out under the direction of Kharasch, National Research Fellow in Organic Chemistry.

² Fry, *THIS JOURNAL*, **35**, 863 (1915); and other papers.

³ Vorländer, *Ber.*, **52B**, 263 (1919).