In the first 3 experiments where ammonia was used much lower yields were obtained than in the last 7 similar experiments in which ammonium chloride was used.

Summary.

Methyl amines are formed only in traces when ammonia or ammonium chloride and methyl alcohol are heated without a dehydrator to as high as 303°.

Using zinc chloride as a dehydrator good yields of mono- and di-methylamines can be obtained. For example, in 8 hours at 303° (Expt. 10) yields were obtained as follows: monomethyl amine, 55%; dimethylamine, 7.5%; and trimethylamine, 1.86%, of the ammonium chloride used.

The yields increase with the amount of zinc chloride used, with increase in temperature, with increase in time of heating and with increase in ratio of methyl alcohol to ammonia.

In all cases where zinc chloride was used hydrogen was liberated due to the hydrolysis of the zinc chloride and consequent attack of the iron bomb by the hydrochloric acid formed. It was for this reason that no experiments could be carried to equilibrium.

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THE DECOMPOSITION OF NITRIC ACID IN ORGANIC NITRATIONS.

BY F. O. RICE.

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The decomposition of nitric acid in organic nitrations is a matter of some industrial importance because there is usually considerable reduction of nitric acid to oxides of nitrogen and if much nitrous oxide or nitrogen is formed there would be a serious loss of nitric acid. Nitric oxide and higher oxides can be reconverted into nitric acid by suitable condensing towers and returned to the system.

Some investigations[1] on the solution of metals in nitric acid have shown that at ordinary temperatures large amounts of nitrous oxide were present in the gases evolved. In many cases the metallic nitrate catalyzed the reduction of the acid to nitric oxide so that near the end of the reaction when there was much of the metal in solution almost pure nitrous oxide was obtained.

It seemed possible, therefore, that a similar reduction of nitric acid to nitrous oxide or nitrogen might take place in organic reactions. The

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[1] Acworth, *J. Chem. Soc.*, **28**, 828 (1875); Acworth and Armstrong, *ibid.*, **32**, 54 (1877); Freer and Higley, *Am. Chem. J.*, **15**, 71 (1893); Higley, *ibid.*, **17**, 18 (1895); Higley and Davis, *ibid.*, **18**, 587 (1896).

process selected for investigation was the nitration of phenol to trinitrophenol. The original experiments were carried out on a technical scale at one of H. M. Factories, England, but the results obtained there have since been checked and extended by laboratory scale experiments. The most difficult part of the work was in devising a fairly rapid method of analysis of the complex gas mixture from the nitrating vessel, since it changed in composition as the reaction proceeded, and the presence of nitrous oxide made it necessary to carry out the analysis in mercury absorption pipets. In one of the early experiments to determine the composition of the gas mixture 200 cc. of the gas was treated with potash to remove higher oxides of nitrogen and carbon dioxide. A considerable amount of nitric oxide was found to be present and this was removed by shaking with strong dichromate solution. There still remained about 60 cc. of gas. When this was passed over a hot platinum spiral a violent explosion occurred, the gas expanded and both oxygen and carbon dioxide appeared, neither of which was present before exploding. This behavior was finally traced to the presence of carbon monoxide and nitrous oxide. These 2 gases exploded on heating and the heat of the reaction decomposed the excess of nitrous oxide which was present, thus accounting for the expansion in volume and the presence of oxygen.

Preliminary experiments showed that the following products were given off during the course of the nitration: nitric acid vapor, nitrogen peroxide and trioxide, nitric oxide, nitrous oxide, nitrogen, carbon monoxide and carbon dioxide.

The following method was finally adopted for analyzing the gases and in ordinary working gave results correct to about 0.5%. The gases were first cooled to condense all of the nitric acid vapor; 100 cc. was then drawn into an ordinary Lunge nitrometer over mercury. This operation was done very rapidly to avoid as far as possible any condensation of higher oxides of nitrogen on the glass walls before the stopcock was closed. Two cc. of water was run into the nitrometer and shaken to remove the higher oxides of nitrogen by solution to give nitrous and nitric acids. The remaining gas was then passed into a water-jacketed measuring tube attached to a compensating tube, and the volume of gas was noted. The nitrogen trioxide and peroxide left in the 2 cc. of water in the nitrometer were estimated as nitric oxide in the usual way by addition of conc. sulfuric acid and shaking.

The gas in the measuring tube was analyzed by passing first into a special mercury pipet and adding 2 cc. of conc. potash solution. After shaking, the gas was returned to the measuring tube and the decrease in volume gave the carbon dioxide present. The gas was then returned to the pipet over the 2 cc. of potash, and pure oxygen was added in excess of that required to oxidize all of the nitric oxide present. Two cc. of strong pyrogallol solution was then run into the pipet to absorb the excess oxygen, and, after shaking, the gas was returned to the measuring tube. The diminution in volume gave the amount of nitric oxide present. The pipet was then washed out and the gas passed into it. Four cc. of ammoniacal cuprous chloride was added, and after gentle shaking the gas was returned to the measuring tube. The diminution in volume gave the amount of carbon monoxide present. The remaining gas consisted of nitrous oxide and nitrogen. The former was determined by shaking with absolute alcohol and finally several times with water. The decrease in volume gave the nitrous oxide and the residual gas was nitrogen. The following is a typical analysis of the gas from an early part of the nitration.

	Volume. Cc.
NO in nitrometer (NO_2 and N_2O_3)	5.4
Remaining gas	96.3
After removal of CO_2	52.3
After removal of NO	40.5
After removal of CO	32.4
After removal of N_2O	13.9

Other methods of analyzing the gases were also used but could not be carried out as quickly and conveniently as this one. They were used only as checks and will not be described.

Nitration Process.

In the usual methods for preparation of trinitrophenol the phenol is first mixed with about 96% sulfuric acid in the proportion of one mol of phenol to 4 or 5 times the weight of acid, and the mixture is heated to about 100° for a few hours with constant stirring. The whole of the phenol is brought to the monosulfonate stage and from 50 to 80% of it goes to disulfonate. The mixture of sulfuric acid and phenol monosulfonate and disulfonate is diluted with about $^3/_4$ of its weight of water and approximately 4 molecules of 65% nitric acid is added, the addition taking 3 to 4 hours. The initial temperature is about 75° but the heat of reaction brings the temperature rapidly to 116° which is about the b. pt. of the mixture.

Nitrations carried out by this method have been investigated very completely both on the industrial scale and in the laboratory. The method of conducting the experiments was as follows. The fumes given off from the nitrating vessel were first cooled to condense any nitric acid, which was collected and estimated. The rate of evolution of the fumes was measured by a gas flowmeter of the resistance-tube type. At intervals of a few minutes samples of the gas were drawn off and analyzed. It was found that the composition of the gases followed, approximately, the stages at which the 3 nitro groups were introduced, and the results did not differ greatly in different experiments. The following results are mean values expressed as nearest whole numbers for a large number of experiments.

	NO_2. %.	NO. %.	N_2O. %.	N. %.	CO. %.	CO_2. %.
First stage...	5.0	10	20	10	10	45
Second stage..	10.0	25	10	10	8	37
Third stage..	21.0	28	4	8	4	35

It is evident from the above figures that the greatest decomposition of nitric acid occurs during the first part of the nitration, for not only is the percentage of nitrous oxide and nitrogen highest but the rate of evolution of gas is also greatest during this period.

When the nitration was completed the contents of the nitration vessel were allowed to stand overnight, after which the picric acid was filtered off, centrifuged and weighed. The sulfuric acid present in the adhering liquid was estimated gravimetrically, and by this means the weight of pure picric acid was obtained. The filtrate, consisting of weak sulfuric acid with a little nitric and nitrous acids was also weighed, and analyzed for sulfuric acid (gravimetrically) total nitric acid (nitrometer) and oxalic acid, by neutralizing, precipitating with calcium chloride, filtering, and titrating the precipitate with standard permanganate. By heating the original filtrate (consisting mainly of weak sulfuric acid) with a little nitric acid and cooling thoroughly, a small additional amount of picric acid could usually be obtained. This was separated and weighed. The weak acid left after nitration gave the following analysis.

Sulfuric acid	45.5%
Nitric and nitrous acids	0.5% (Expressed as HNO_3)
Oxalic acid	1.6%

There were probably also small quantities of other organic nitro products in the acid, but these were not estimated. The following is the mean of 10 experiments, some being on the technical scale using a 12 kg. charge of phenol and others being small laboratory experiments. The results are calculated to a charge of 100 g. of phenol.

It will be seen from these results that less than 80% of the phenol is converted into picric acid, the remainder being broken down into oxalic acid and oxides of carbon. Only 62% of the nitric acid combines with the phenol to give picric acid. 10.2% is broken down to nitrogen peroxide and nitric oxide, and 22.2% is reduced to nitrous oxide and nitrogen, this latter representing a direct loss of fixed nitrogen in the nitration. It was found from experiment that the temperature was the main factor causing the reduction of nitric acid to nitrous oxide and nitrogen. When the temperature was kept well below 100° during the early stages of the nitration and then slowly raised to 100° until the nitration was completed, the evolution of nitrous oxide and nitrogen was very small and amounted to less than 1% of the total nitric acid present. The nitric acid was still decomposed to much the same extent, but nitric oxide was chiefly produced. It was not found possible to prevent decomposition of the phenol and even in the best experiments 20% of the phenol was oxidized away by the nitric acid.

Charge to the Nitrating Vessel.

Phenol	HNO_3	H_2SO_4.
100 g.	260 g.	427 g.

Nitric acid.	HNO_3. G.
Distilled off unchanged	7.2
Evolved as NO_2	9.3
Evolved as NO	17.3
Evolved as N_2O	36.0
Evolved as N	21.7
Contained in 187 g. of picric acid produced	154.0
Contained in second crop of picric acid produced (8 g.)	6.6
Free in 930 g. of weak acid (0.5% HNO_3)	4.6
Combined in weak acid (not estimated)	....
Total	256.7

Phenol.	Phenol.
Nitrated to picric acid	76.9
Nitrated to picric acid (second crop)	2.3
Oxidized to oxalic acid (1.6% in weak acid)	5.2
Oxidized to CO	2.4
Oxidized to CO_2	8.1
Remaining in weak sulfuric acid (not estimated)	....
Total	94.9

Sulfuric acid.	H_2SO_4.
In 930 grams of weak sulfuric acid (45.5% HSO_4)	422.0

Many experiments were performed in which the various factors, temperature, degree of sulfonation, rate of addition of acid, strength of acids, were altered but without any success. In one experiment in which ferrous sulfate was present the amount of nitrous oxide and nitrogen was much greater than usual and the yield of picric acid poor. This resembles the action of copper nitrate in causing the decomposition of nitric acid and suggests the possibility that a catalyst may be found which will have a positive effect in nitrations.

The best results were obtained when the phenol was thoroughly sulfonated (*i. e.*, converted almost entirely into disulfonate) and the temperature of the experiment was kept well below 100°, especially in the initial stages.

In a few experiments nitration was effected by adding a mixture of nitric acid and sulfuric acid to the phenol sulfonate-sulfuric acid mixture and carrying out the nitration almost at room temperature. Only nitrogen peroxide and nitric oxide were evolved and yields of picric acid slightly over 90% were obtained. Under the best conditions so far obtained almost 10% of the phenol was oxidized with consequent reduction of the nitric acid.

Conclusions.

1. A survey of the literature showed that when metals dissolved in nitric acid, nitrous oxide was produced as well as higher oxides of nitrogen. In some cases the metallic salt acted as a catalyst in the production of nitrous oxide.

2. This reduction of nitric acid to nitrous oxide may also occur in organic nitrations. In the nitration of phenol to trinitrophenol by weak nitric acid as much as 25% of the nitric acid may be reduced to nitrous oxide and nitrogen. The presence of iron salts accelerated this reduction.

3. By keeping the temperature of nitration well below 100° especially in the initial stages the formation of nitrous oxide and nitrogen may be avoided, only higher oxides of nitrogen being produced.

4. It was not found possible to nitrate phenol without causing some reduction of the nitric acid to oxides of nitrogen. The best results were obtained by sulfonating phenol almost to the disulfonate stage with 96% sulfuric acid and then nitrating at low temperatures (30°–40°) with a mixture of sulfuric and nitric acid.

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DIMETHYL-PROPYL-CARBINOL AND SOME OF ITS DERIVATIVES.

BY ANDRÉ DESCHAMPS.

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Introduction.

Originally the object of this work was to carry out an idea of M. G. C. Chavanne[1] involving the preparation of trimethyl-propyl-methane. Since Markownikoff's method is both hazardous and expensive, I attempted to prepare the compound by the action of methyl magnesium iodide upon methyl-2-bromo-2-pentane.[2] This reaction also proving impracticable, I resorted to the investigation of dimethyl-propyl-carbinol, which I had obtained as an intermediate product in the preparation of the latter substance.

Preparation of Dimethyl-propyl-carbinol.

This compound was prepared from both *n*-propyl iodide and *n*-propyl bromide by the Grignard reaction. The latter is better than that using ethylbutyrate described by Masson.[3]

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[1] G. C. Chavanne, Professor of Chemistry at University of Brussels (Belgium).

[2] Markownikoff, *Monatsh.*, **34**, 1965 (1913).

[3] Masson, *Compt. rend.*, **1901**, pp. 132–484.