

XXXVI.—*The Action of Nitric Acid on Unsaturated Hydrocarbons. The Action of Nitric Acid on Acetylene.*

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THE action of nitric acid, in contrast to nitrogen peroxide, on unsaturated (non-aromatic) hydrocarbons has not yet been thoroughly examined. Such references as are found in the literature indicate that complete oxidation to oxalic acid or carbon dioxide usually occurs. Baschieri (*Atti R. Accad. Lincei*, 1901, [v], **9**, i, 391) and Testoni and Mascarelli (*ibid.*, 1902, [v], **10**, i, 442; *Gazzetta*, 1903, **33**, ii, 319), on examining the action of fuming nitric acid on acetylene, obtained, however, a mixture of complex substances, the constitution and even the composition of which were not with certainty elucidated. J. Schmidt (*Ber.*, 1901, **34**, 619), who prepared from stilbene and nitrogen dioxide a dinitrostilbene, suggested that this behaviour foreshadows the manner of reaction with acetylene.

We have examined the interaction of nitric acid and acetylene under varying conditions of concentration, of temperature, and in the presence of metallic salts, in the first instance to ascertain whether tetranitromethane or substances such as nitroform, which could be easily converted into tetranitromethane by nitration, were produced. This quest has been highly successful, and thus a source of tetranitromethane, which has a certain usefulness as a high explosive, from inexpensive materials has been obtained.

Acetylene is absorbed with very great ease by absolute nitric acid, or by mixtures of nitric acid and sulphuric acid. With dilution of the nitric acid, the rate of interaction, and hence the readiness of the absorption, decreases. Rise of temperature and the presence of the catalyst (mercury salt) cause an increase in the rate of the interaction and readiness of absorption. In these comparative statements of the readiness of absorption, it is to be understood that the method of bringing the gas and the liquid into contact is unchanged. Obviously intimate intermingling of a gas and a liquid will promote absorption and interaction, and may lead to as ready an absorption by a dilute acid at low temperature as is with less efficient mixing only found at more favourable temperatures and concentrations of the acid.

The reaction is accompanied by a small development of heat. On the scale of our experiments, the temperature was kept thereby at 5—8° above the laboratory temperature.

The products of the interaction of acetylene and nitric acid are various; and the nature and the proportion of these products is largely determined by the concentration of the acid, by the temperature, and by the presence of a catalyst or of sulphuric acid.

The Italian investigators (*loc. cit.*) isolated from the interaction of acetylene and nitric acid (D 1.52; the proportions are not stated) at low temperatures small quantities of different solid products, some neutral and some acid, which were frequently explosive. Nitroform was also found among the products.

Omitting the products of reduction of nitric acid, the reaction yields nitroform and certain substances, which can be converted into tetranitromethane, carbon dioxide (and a trace of carbon monoxide), and other substances—among them sometimes oxalic acid ("O.S." in the tables)—which cannot be converted into tetranitromethane; the latter may predominate in certain circumstances, such as high or low concentration of the nitric acid or low temperature. Of the antecedents of tetranitromethane, nitroform usually amounts to about 75—85 per cent., and the others to about 15 per cent. Of the metals which we have tried as catalysts, only mercury causes a marked increase of the proportion of nitroform, etc., and at the same time reduces to a very small proportion the by-products which do not yield tetranitromethane. In fact, the reaction is simplified, and the acetylene is quantitatively represented by nitroform, etc., and carbon dioxide. Table I summarises the results of experiments, which illustrate the effect of concentration of acid, temperature, presence of mercury nitrate, or of sulphuric acid.

Under "t.n.m." in the table is the quantity of tetranitromethane (as a percentage of the acetylene reacting) which can be obtained from the product by a treatment described later. This quantity is a convenient measure of the extent to which nitroform and the other antecedents are produced under given conditions. If 2 moles of tetranitromethane were formed from one of acetylene, "t.n.m." would amount to 1508 per cent. in a quantitative yield, or if 1 mole of acetylene yields one of tetranitromethane, which is far more probable, 754 per cent.

TABLE I.

A. Varying Concentration of Nitric Acid. Temperature, 15°.

| Experiment. | Percentage of nitric acid. | C ₂ H ₂ absorbed by 100 grams of nitric acid. Litres. | "t.n.m." as percentage of C ₂ H ₂ absorbed. |
|-------------|----------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------|
| 1..... | 100.0 | 1.610 | 75.5 |
| 2..... | 97.5 | 1.516 | 163.0 |
| 3..... | 95.0 | 1.296 | 238.0 |
| 4..... | 90.0 | 1.097 | 160.0 |
| 5..... | 85.0 | 0.546 | 158.0 |
| 6..... | 70.0 | 1.043 | 37.4 |

B. Sulphuric Acid present. Temperature, 15°.

| Experiment. | H ₂ SO ₄ /HNO ₃ . | C ₂ H ₂ absorbed per 100 grams of nitric acid. Litres. | CO ₂ evolved per 100 grams of nitric acid. Litres. | CO ₂ /C ₂ H ₂ by volume. | "t.n.m." as percentage of C ₂ H ₂ absorbed. | "O.S." as a percentage. |
|-------------|----------------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------------|-------------------------|
| 7..... | 0.11/1 | 1.336 | 0.295 | 0.25/1 | 148.5 | 77.9 |
| 8..... | 0.5 /1 | 1.41 | 0.137 | 0.09/1 | 0.0 | 95.6 |
| 9..... | 0.5 /1 | 1.615 | 1.092 | 0.67/1 | 129.0 | 57.8 |
| 10..... | 2.6 /1 | 1.774 | 0.17 | 0.1 /1 | 0.0 | 95.9 |

In Experiment 9, 0.33 per cent. of mercuric nitrate was present. In Experiments 6 and 10 the temperature was 30°.

C. Mercuric Nitrate present, 0.66 per cent. Temperature, 15°.

| Experiment. | Percentage of nitric acid. | C ₂ H ₂ absorbed by 100 grams of nitric acid. Litres. | CO ₂ evolved per 100 grams of nitric acid. Litres. | CO ₂ /C ₂ H ₂ by volume. | "t.n.m." as percentage of C ₂ H ₂ . | "O.S." as a percentage. |
|-------------|----------------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|-------------------------|
| 11..... | 90 | 1.490 | 2.27 | 1.52/1 | 204 | 9.82 |

D. Temperature Varied.

| T°. | Percentage of nitric acid. | C ₂ H ₂ absorbed by 100 grams of nitric acid. Litres. | CO ₂ evolved per 100 grams of nitric acid. Litres. | CO ₂ /C ₂ H ₂ by volume. | "t.n.m." as percentage of C ₂ H ₂ . | "O.S." as a percentage. |
|-----------|----------------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|-------------------------|
| 12... —3° | 95 | 1.20 | 0.54 | 0.394/1 | 104 | 61.0 |
| 13... 15 | 95 | 1.296 | 1.04 | 0.8 /1 | 238 | 44.0 |
| 14... 30 | 95 | 1.49 | 1.565 | 1.05/1 | 331 | 25.4 |

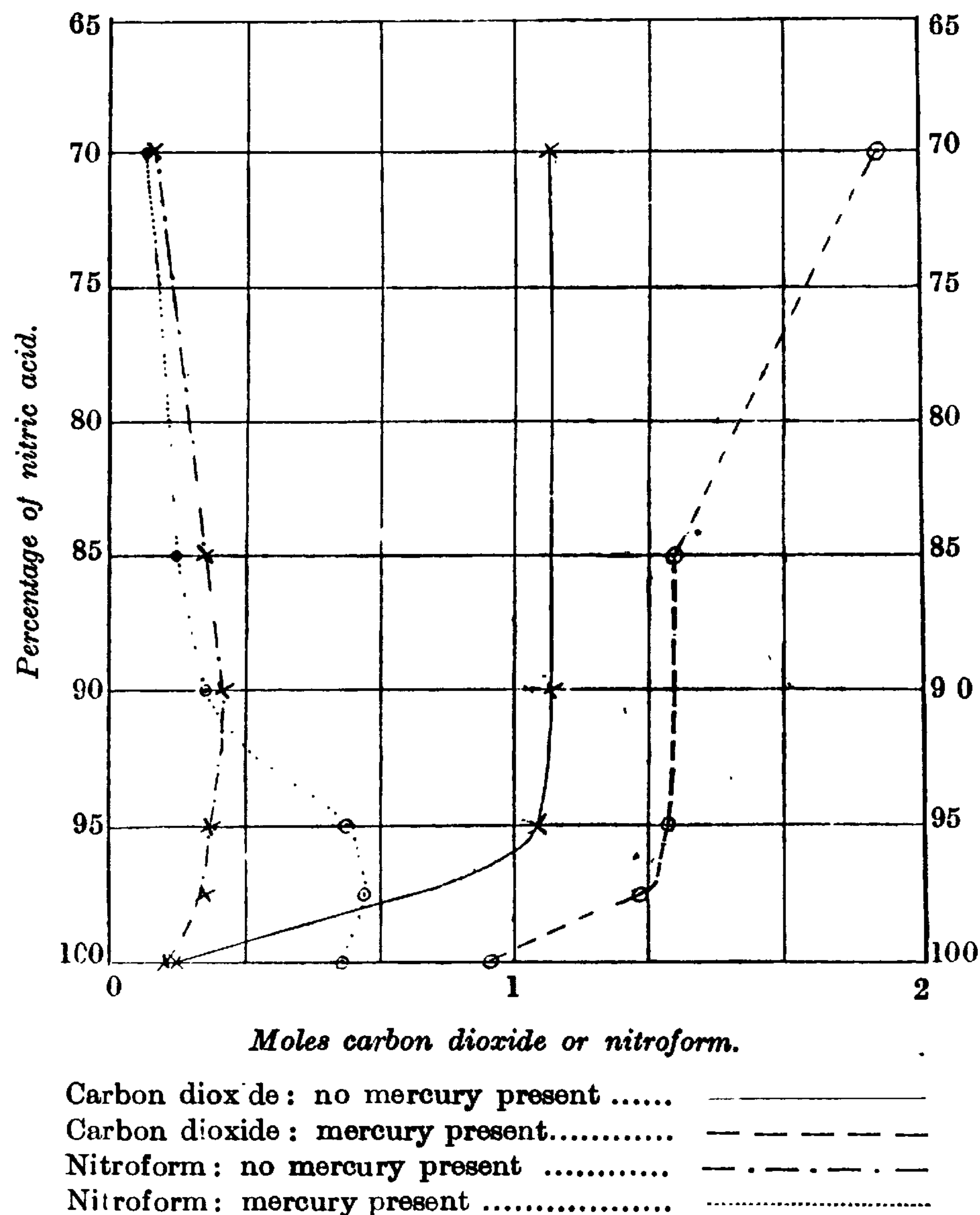
E. Mercuric Nitrate, 0.3—0.66 per cent. Temperature, 30°.

| | | | | | | |
|---------|-----|-------|------|--------|-----|-----|
| 15..... | 95 | 1.571 | 2.22 | 1.41/1 | 523 | 0.0 |
| 16..... | 100 | 3.456 | 4.87 | 1.4 /1 | 410 | 2.4 |
| 17..... | 70 | 0.581 | 1.1 | 1.91/1 | 47 | 1.9 |

It will be seen that both a high concentration (in the absence of mercury salt) and a low concentration of nitric acid are unfavourable to the formation of nitroform and the other antecedents of

tetranitromethane. The optimum concentration is about 95—97 per cent. Obviously in the interaction of nitric acid and acetylene the acid becomes diluted, and the yield will only be a maximum when a small quantity of acetylene is absorbed by this acid (Expt. 15). To obtain the maximum quantity of nitroform (and tetranitromethane) in one operation the absorption of 3.5—3.7 litres of

FIG. 1.



acetylene by 100 grams of "100 per cent." nitric acid, to which 0.33 gram of mercury nitrate has been added, is best (Expt. 16). The yield of nitroform is then about 14.2 grams, and of tetranitromethane 16.7 grams (or 410 per cent.). At the lower concentrations (70 per cent.) of nitric acid, oxidation to carbon dioxide increases; the ratio $\text{CO}_2 : \text{C}_2\text{H}_2$ (by volume, molar) approaches, and in Expt. 17, under the influence of mercury nitrate, nearly

reaches 2 : 1. The dependence of the products of the reaction on the concentration of the nitric acid is well shown in Fig. 1. This indicates first the volume of carbon dioxide for one volume of acetylene, plotted against the concentration of nitric acid, (a) when no mercury salt has been added, (b) when mercury salt is present, and secondly the moles of nitroform for one mole of acetylene under similar different conditions; about 1 litre of acetylene has reacted with 100 grams of nitric acid.

Effect of the Presence of Various Metallic Salts.

The effect of the presence of small quantities of salts of platinum, silver, uranium, copper, and mercury on the reaction between nitric acid and acetylene has been examined. The metals were added as nitrates, except platinum, which was in the form of chloroplatinic acid. The quantities used were molar equivalents of the amount of the mercury nitrate required to form a 0.33 per cent. solution. In 95 per cent. nitric acid solution was complete, or nearly complete, except with platinum, when a heavy, yellow precipitate appeared and remained throughout. With copper a precipitate appeared during the reaction. Table II summarises the results. The nitric acid was diluted to 95 per cent., and the temperature was 30°.

TABLE II.

| Experi- ment. | Metal. | C_2H_2 absorbed by 100 grams of nitric acid. Litres. | CO_2 evolved per 100 grams of nitric acid. Litres. | Percent- age of C in C_2H_2 as a per- centage of C_2H_2 . | Percent- age of C in C_2H_2 becoming "t.n.m." | Percent- age of C in C_2H_2 becoming CO_2 . | Percent- age of C in C_2H_2 becoming "O.S." |
|------------------|--------|----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 18 | Pt | 2.68 | 2.25 | 203 | 13.5 | 41.8 | 44.7 |
| 19 | Ag | 2.73 | 2.20 | 221 | 14.7 | 49.3 | 36.0 |
| 20 | Ur | 2.60 | 3.32 | 222 | 14.9 | 63.6 | 21.5 |
| 21 | Cu | 2.55 | 2.64 | 371 | 24.2 | 51.5 | 24.3 |
| 22 | Hg | 3.02 | 4.38 | 453 | 29.18 | 70.81 | 0.0 |
| 23 | None | 2.81 | 2.72 | 341 | 22.6 | 49.0 | 28.4 |

Mercury stands alone in having a markedly favourable effect on the rate of interaction, and hence on the readiness of absorption. Again, mercury is the only metal of those examined which exerts a beneficial influence on the production of nitroform and hence tetranitromethane. All the metals, save copper, favour oxidation of the acetylene, at the expense of the production of nitroform, etc.; uranium is peculiarly active in this respect. The experiment in which mercury is present stands out in that "other substances" are absent. Platinum has the opposite effect, and causes an increase in the proportion of by-products.

The proportion of mercury is important; the most favourable proportion lies below 1 per cent. Table III summarizes the results of experiments made with the object of ascertaining exactly the best proportion, which is obviously 0.3—0.4 per cent.

TABLE III.
Temperature, 30°.

| Ex- peri- ment. | Per- cent- age of nitric acid. | Hg(NO ₃) ₂ as per- centage. | C ₂ H ₂ ab- sorbed by 100 grams of nitric acid. Litres. | CO ₂ evolved per 100 grams of nitric acid. Litres. | Percent- age “t.n.m.” of C ₂ H ₂ as a per- centage of C ₂ H ₂ . | Percent- age of C in C ₂ H ₂ be- coming “t.n.m.” CO ₂ . | Percent- age of C in C ₂ H ₂ be- coming “O.S.” |
|-----------------------|-----------------------------------------------|----------------------------------------------------------|-------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| 24..... | 95.0 | 0.66 | 3.06 | 4.39 | 383 | 25.4 | 3.1 |
| 25..... | 95.0 | 0.33 | 3.02 | 4.38 | 453 | 29.2 | 0.0 |
| 26..... | 95.0 | 0.33 | 1.55 | 1.62 | 552 | 37.1 | 0.2 |
| 27..... | 97.5 | 0.28 | 3.16 | 4.34 | 429 | 28.5 | 3.3 |
| 28..... | 95.0 | 0.165 | 3.03 | 3.83 | 431 | 28.6 | 8.2 |
| 29..... | 95.0 | 0.0 | 2.81 | 2.72 | 341 | 22.6 | 28.4 |

The mercury salt appears to have more than one effect on the interaction of acetylene and nitric acid, and at different concentrations as well as at different temperatures one or other of these effects may be the more marked.

The most characteristic effect is the elimination of products other than the precursors of tetranitromethane or carbon dioxide. These products have been grouped together under “other substances,” but two important groups can be distinguished. In the first place, when the nitric acid is highly concentrated, substances are produced in considerable quantity which do not on further treatment—“nitration”—yield tetranitromethane. These are probably the substances isolated by Mascarelli and his co-workers. Thus we find that with 100 per cent. nitric acid at 14° “O.S.” may represent 86 per cent. of the acetylene absorbed, but in the presence of a mercury salt at 30° “O.S.” is reduced to zero. The large increase in the yield of tetranitromethane from less than 100 per cent. in the first experiment to 460 per cent. in the second shows that the effect of a mercury salt is to cause the substitution of precursors of tetranitromethane for these other substances.

In less concentrated nitric acid, about 95 per cent., another effect becomes apparent. Now in the absence of mercury an important by-product is oxalic acid [Ca(CO₂)₂, H₂O gave CaCO₃=69.15. Calc., CaCO₃=68.50 per cent.], which can be readily isolated from or estimated in the product. When 1.5 litres of acetylene are absorbed by 100 grams of nitric acid (95 per cent. at 30°), as much as 25 per cent. of the acetylene appears as oxalic acid. If a mercury salt is

present, however, only a very small quantity of oxalic acid is found, and there is a correspondingly large increase in the carbon dioxide. Direct experiment shows that a mercury salt does not cause the oxidation of oxalic acid by nitric acid, and it seems probable, therefore, that now, in the presence of mercury salt, some intermediary other than oxalic acid is directly oxidised to carbon dioxide.

The presence of a mercury salt also modifies the reaction of acetylene with a mixture of nitric acid and sulphuric acid. A comparison of experiments 8 and 9 (table I) demonstrates this effect. It will be seen that the precursors of tetranitromethane are only produced in the presence of a mercury salt, and, further, that concurrently there is more oxidation of the acetylene.

The mercury salt is without effect on the conversion of primary products of the interaction of acetylene and nitric acid into tetranitromethane, for addition after the absorption of the acetylene does not affect the yield of tetranitromethane in the subsequent treatment. The mercury salt then determines only the course of the primary interaction.

Formation of Nitroform and other Precursors of Tetranitromethane.—In order to account for the formation of tetranitromethane in the interaction of diacetylorthonitric acid, acetyl nitrate or nitric acid and acetic anhydride, Pictet and Genequand (*Ber.*, 1903, **36**, 2225) suggested that nitroform, which they isolated, or even trinitroacetic acid, precedes tetranitromethane. The formation of tetranitromethane by the nitration of nitroform had earlier been demonstrated by Schischkov (*Annalen*, 1861, **119**, 248), who used a mixture of nitric and sulphuric acids.

Nitroform, as its characteristic ammonium salt, can easily be isolated from the product. The estimation in the complex acid mixture is not so simple; but after removal of the “nitrous acid” by ammonium nitrate the nitroform can be distilled in a current of steam or extracted with ether, and then titrated in the distillate or extract with alkali hydroxide, or, better, with permanganate.

The quantity of nitroform thus determined does not represent more than 85—87 per cent. of the tetranitromethane which can be obtained from the product, and is in some circumstances less. No want of accuracy which can be detected in the method of estimation of the nitroform will account for this discrepancy between the quantities of nitroform and tetranitromethane.

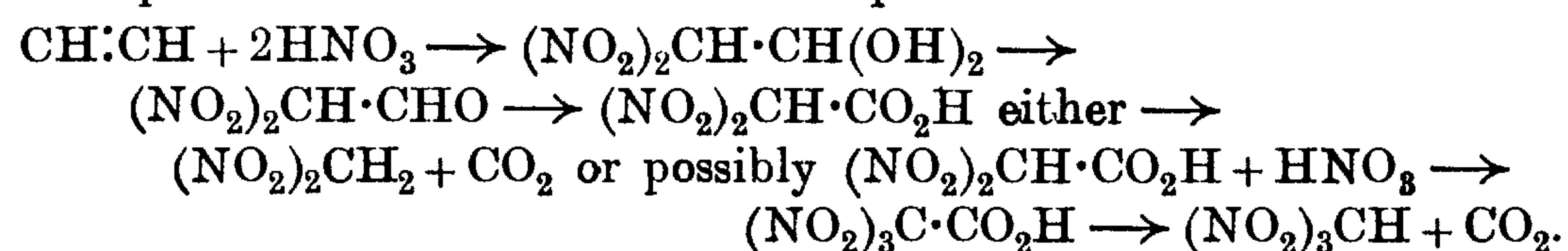
Clear evidence that the product contains substances other than nitroform which yield tetranitromethane when heated with sulphuric acid is adduced by the following experiment. The product was obtained by passing acetylene into 95 per cent. nitric acid at

30°, 0.33 per cent. of mercuric nitrate being present. The nitroform found in a portion of the fresh product was equivalent to 15.6 grams of tetranitromethane, whereas the product yielded 20 grams. An equal portion of the product was heated at 85° for two hours before treatment with sulphuric acid. The yield of tetranitromethane in this portion was now 16.6 grams, and the nitroform therein was equivalent to 15.3 grams.

The yield of tetranitromethane also falls off, rapidly at first, if the product is kept for some time at the ordinary temperature, whereas the decomposition of nitroform in the product, which is also observed, is very much slower.

Obviously substances which can yield tetranitromethane have been destroyed by heating or keeping the product. It is clear that they have not been converted into nitroform, for the quantity of nitroform is approximately unchanged and, it is to be noted, after the heating, is nearly equivalent to the tetranitromethane.

The formation of nitroform from acetylene and nitric acid can be represented as the result of a simple addition:



(The addition of nitrogen peroxide is not considered.)

Dinitromethane very readily reacts with nitrous acid (Duden, *Ber.*, 1893, **26**, 3003), yielding the *isonitroso*-compound, which under the conditions would probably be oxidised to nitroform, thus:



The *isonitroso*-compound does not appear usually to be present in the product, for in normal experiments there is no marked indication of the blood-red colour which it yields with alkalis (Duden, *loc. cit.*). At lower dilutions of nitric acid, however, this reaction is obvious on rendering the product alkaline.

When nitroform is produced by the routes indicated above, one mole of acetylene yields one mole of nitroform and one mole of carbon dioxide; hence as a maximum only 50 per cent. of the carbon of the acetylene would become nitroform.

EXPERIMENTAL.

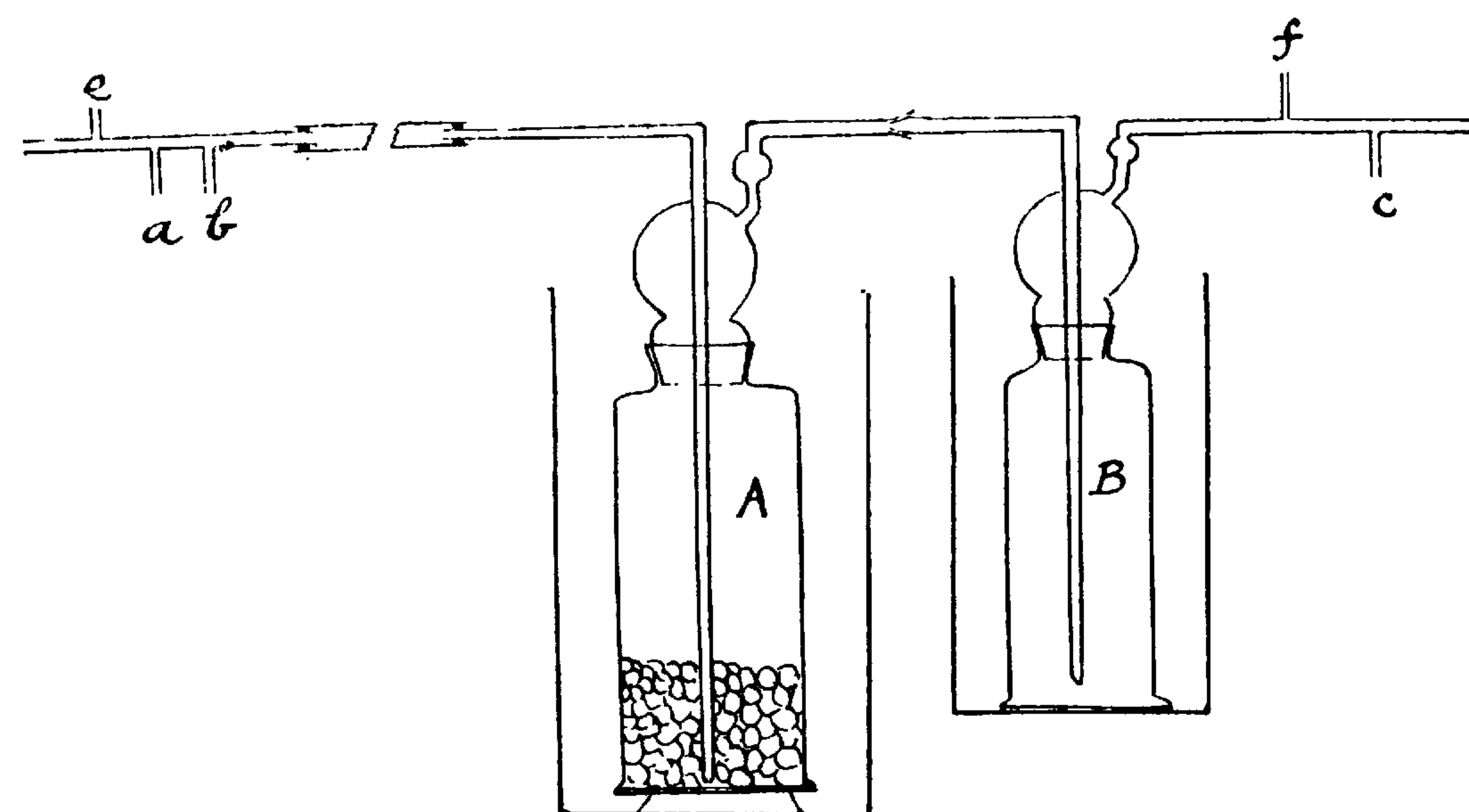
The essential parts of the apparatus are shown in Fig. 2. Acetylene is absorbed so readily, at least by sufficiently concentrated nitric acid at moderate temperatures, that the Drechsel bubbler (A), in which the end of the inlet tube is somewhat con-

stricted, serves as the reaction vessel; the bubbles of gas are broken by a layer of glass beads. This bubbler, which is nearly full, is immersed in a bath maintained at a constant temperature, usually 30°.

The second bubbler (B), which is placed in a cooling-bath, contains 30 c.c. of sulphuric acid (96—97 per cent.); all the oxides of nitrogen coming from (A) are absorbed in (B). No nitrous or nitric oxides have been found in the gas, which passes through the sulphuric acid. Safety devices for meeting a development of negative pressure or a sudden positive pressure are placed at *a*, *b*, and *c*. Samples of gas for analysis can be drawn off from the pipe line at *e* and *f*.

The acetylene, which was not purified, was dried by calcium

FIG. 2.



chloride. In this apparatus, good absorption (more than 90 per cent. under the best conditions) was obtained up to a speed of 400 c.c. per hour. Usually the speed was considerably less, about 150—200 c.c. per hour.

The nitric acid was prepared from a crude, fuming nitric acid ($D_{15} 1.5$), which contained much iodine as iodic acid, by distilling from an equal weight of sulphuric acid. The distillate had $D_{15} 1.545$; the acid contained 2.2 per cent. of "nitrous acid," as determined by potassium permanganate.

Mercuric nitrate (0.5 gram:0.33 per cent.) is placed in the bubbler, then water (7.5 c.c. when a 95 per cent. nitric acid is used), and finally the nitric acid (138.6 grams=90 c.c.). The mercuric nitrate dissolves completely; the quantity of 95 per cent. nitric acid just given will dissolve 1.2—1.3 grams at the ordinary

temperature. Absolute nitric acid dissolves very little mercuric nitrate which, at the beginning of the experiment, is in suspension, but dissolves later.

It is not advantageous to pass more than 4.5—4.6 litres of acetylene into *A*, although when absolute nitric acid is used this may be increased to 5 litres. As the reaction proceeds, the nitric acid is diluted; not only is the reaction then more tardy, and hence the absorption poorer, but oxidation of the acetylene, and hence the evolution of carbon dioxide, becomes more prominent. At the early stages of the reaction, very little gas leaves (*A*); later, oxides of nitrogen and carbon dioxide are evolved, towards the end of the experiment vigorously.

The results of typical experiments are summarised in table IV.

TABLE IV.

In all experiments, 0.33 per cent. of mercury nitrate was present.

| Ex- peri- ment. | Per- cent- age of nitric acid. | C ₂ H ₂ absorbed by 100 grams of nitric acid. Litres. | Nitro- form. Grams. | CO ₂ evolved by 100 grams of nitric acid. Litres. | Percent- age of C ₂ H ₂ as a per- centage of C ₂ H ₂ . “t.n.m.” | Percent- age of C in C ₂ H ₂ be- coming “t.n.m.” | Percent- age of C in C ₂ H ₂ be- coming CO ₂ . | Percent- age of C in C ₂ H ₂ be- coming “O.S.” |
|-----------------------|-----------------------------------------------|-----------------------------------------------------------------------------------------------|---------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| 30..... | 95.0 | 3.068 | 10.3 | 4.38 | 436 | 28.94 | 71.04 | 0.0 |
| 31..... | 97.5 | 3.163 | 10.5 | 4.34 | 430 | 28.8 | 68.5 | 2.3 |
| 32..... | 100.0 | 3.456 | 11.0 | 4.87 | 410 | 27.6 | 70.5 | 2.4 |
| 33..... | 100.0 | 2.883 | 9.9 | 4.07 | 448 | 29.73 | 70.3 | 0.0 |

Preparation of Nitroform.—The product is diluted 1 to 10, and then the nitrous acid removed by ammonium nitrate, 20 grams to 100 c.c. of the diluted product. The nitroform is then extracted by ether, preferably in a continuous apparatus. The ethereal extract is concentrated and added to alcoholic ammonia or alcoholic potassium hydroxide, when the salt crystallises out. From 100 grams of the product prepared under the best conditions, about 15 grams of the crude ammonium salt can be obtained.

Analysis of the Product; Nitroform, Nitrous and Nitric Acids.—The estimation of nitrous acid cannot be made directly on the product, for other substances which reduce permanganate are present. Two procedures have been followed. The permanganate titre of the product diluted 1 in 10 is determined; then either the nitrous acid is removed by aspiration or by boiling with ammonium nitrate (Gailhat, *J. Pharm. Chim.*, 1900, [vi], 12, 9; Gerlinger, *Zeitsch. angew. Chem.*, 1902, 14, 1250; they both use ammonium chloride). In the aspiration, it is not necessary to remove the whole of the nitrous acid, which is a very lengthy process. At a

given temperature and with a given air current, the percentage loss of nitrous acid from the solution follows the well-known law, and is independent of the initial concentration. At 16°, with the rate of air current 0.1 litre per minute, trials with known solutions of nitrous acid at various concentrations in aqueous nitric acid, and with known solutions of nitroform and nitrous acid in 7—8 per cent. nitric acid, show that 73.3 (72.8—73.9) per cent. of nitrous acid disappear in one hour. After the partial removal of the nitrous acid by aspiration or the complete removal by ammonium nitrate, the residual permanganate titre is determined, whence the “nitrous acid” can be calculated. Determinations of the nitrous acid made by these two methods agree fairly well, but the method of aspiration is probably the more trustworthy.

Determination of Nitroform.—Nitroform can be titrated in aqueous solution by alkali hydroxide in the presence of phenolphthalein (Hantzsch and Rinckenburger, *Ber.*, 1899, 32, 631). We have devised a method, depending on the reduction of permanganate in the presence of sulphuric acid, which will be discussed more fully in another place. Recently, Erich Schmidt (*Ber.*, 1919, 52, [B], 400) has described a procedure in which nitron is used as precipitant; this we have not yet tested, nor would it be easily applicable to our conditions, owing to the presence of nitric acid.

The product contains, besides nitrous acid and nitroform, other substances (for example, oxalic acid) which reduce permanganate. After removal of the nitrous acid, the nitroform may be extracted with ether and then titrated, or, preferably, distilled off and titrated with permanganate.

The following is a typical analysis: 2—5 c.c. of the “product” are added to 18—45 c.c. of *N/2-N*-alkali hydroxide; 5 c.c. are diluted with 10—15 c.c. of water, and 2—3 grams of ammonium nitrate added. The mixture is gently boiled for several minutes (five to ten), and then diluted to 100 c.c., acidified with 5—10 c.c. of 10 per cent. sulphuric acid, and distilled until the distillate is colourless (thirty minutes). The distillate may be collected in water or *N/10*-alkali; it is finally titrated with *N/10*-KMnO₄. One c.c. of *N/10*-KMnO₄ is equivalent to 151/80,000 = 0.0019 gram of nitroform.

After destruction of nitrous acid and extraction of nitroform by ether, the residue still reduces permanganate. The reduction is but small under conditions most favourable for the preparation of nitroform or tetranitromethane. Some, and sometimes most, of the reduction of the permanganate by the residue is to be attributed to oxalic acid.

A rough estimate of the nitric acid in the product can be made

by deducting from the total alkali titre the alkali titre equivalent to the permanganate titre of the diluted product. As this deduction does not amount to more than 10 per cent. of the total alkali titre, a rough estimate of the nitric acid remaining is possible.

In a typical experiment, in which 4.27 litres of acetylene were absorbed by 138.6 grams of nitric acid (diluted to 95 per cent.), about 75 grams of nitric acid remained in the product, which weighed 123.5 grams. Deducting nitric acid, nitrous acid, and nitroform, the water in the product comes to 30 grams.

Analysis of Gases evolved during the Interaction of Acetylene and Nitric Acid.—The gas coming from the bubbler (*B*) is collected over a neutral, saturated calcium chloride solution in a large vessel of known capacity; the last part of the gas in an experiment is measured in a graduated vessel. Both carbon dioxide and acetylene are less readily soluble in saturated calcium chloride than in other saline solutions; at 14°, carbon dioxide has a solubility of 0.1 in 1, and acetylene 0.08 in 1, by volume.

The gas evolved during the heating of the product with sulphuric acid was collected in a similar manner. The liquid nearly filled the flask, which was ground on to a narrow condenser tube; this tube was carried on as a delivery tube for the evolved gas.

Table IV shows the large volumes of gas (carbon dioxide) collected. Nine-tenths, or rather more, are evolved during the interaction of acetylene and nitric acid when mercury is present, and the remainder during the heating with sulphuric acid. In the absence of mercury, 2/3—3/4 of the gas passes off at the first stage, and 1/4—1/3 at the second stage. These ratios strictly apply only to the carbon dioxide, which, however, largely predominates, especially in the first stage, less exactly to the total gas. The gas consists in the main of carbon dioxide with small percentages of acetylene and carbon monoxide, and traces of air. The gas given off in the heating contains much oxygen (up to 40—50 per cent.) from the interaction of nitric and sulphuric acids.

The gas was analysed in a "Bone and Wheeler" apparatus. The acetylene was absorbed by a 5 per cent. solution of potassium bromide saturated with bromine; the absorption is somewhat slow towards the end, but complete. After removal of the bromine vapour by the alkaline reagent, the carbon monoxide is absorbed by the ammoniacal cuprous chloride reagent. We have tested exhaustively this procedure on known mixtures of gases, and found it quite accurate. Usually, the gas of the first stage will contain: $\text{CO}_2 = 75\text{--}80$, $\text{C}_2\text{H}_2 = 5\text{--}6$, $\text{CO} = \text{at most } 1$ per cent.

Preparation of Tetranitromethane.—Originally, tetranitro-

methane was prepared by Schischkov (*loc. cit.*) from trinitroacetonitrile. Later, it was obtained in the exhaustive nitration of aromatic hydrocarbons (Will, *Ber.*, 1914, **47**, 704; Claessen, D.R.-P. 184229) by the action of diacetylorthonitric acid or acetyl nitrate on acetic anhydride (Pictet and Genequand, *loc. cit.*; Pictet and Khotinsky, *Compt. rend.*, 1907, **144**, 210), or from nitrogen pentoxide on acetic anhydride (Schenck, D.R.-P. 211198, 211199), or from nitric acid on acetic anhydride (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 224057; Berger, *Compt. rend.*, 1910, **151**, 813; Chattaway, T., 1910, **97**, 2099).

In preparing tetranitromethane from a hydrocarbon by exhaustive nitration, it is obvious that a low proportion of hydrogen to carbon, such as obtains in benzene, naphthalene, or acetylene, is desirable in order to economise nitric acid. Not only does the oxidation of a large proportion of hydrogen entail a corresponding loss of nitric acid, but the nitrating agent becomes diluted with water, and hence less efficient. On these grounds, benzene or its derivatives, or naphthalene derivatives, or acetylene are the most suitable substances. For various reasons, acetylene would be an excellent source of tetranitromethane. Whilst only some 4—5 per cent. of benzene nitrated can be converted into tetranitromethane, it has been shown in the foregoing that some 37 per cent. of the acetylene appears as this substance under suitable conditions.

The product from the interaction of acetylene and nitric acid contains very little tetranitromethane. If it is heated or first mixed with phosphoric oxide, sulphuric acid, or fuming sulphuric acid and then heated, tetranitromethane is formed.

A satisfactory procedure, in which all the nitroform is converted into tetranitromethane and the maximum yield is obtained, is to mix the product from 90 c.c. of 100 per cent. nitric acid with 190—380 grams of sulphuric acid or sulphuric acid containing 25 per cent. of sulphur trioxide. The sulphuric acid is added to the product, and care is taken that the temperature does not rise. The sulphuric acid from the bubbler (*B*), which contains a little nitroform, is also introduced. The mixture may be then directly distilled, but it is preferable to heat it, finally to 90—95°, under reflux until gas ceases to be evolved; this operation usually occupies about four hours. For reasons given in the foregoing, it is important that the product is mixed with sulphuric acid as soon as possible after the passage of the acetylene. That this mixture should then be kept for some time before heating or distilling is immaterial.

On cooling, much of the tetranitromethane will appear as an

oil, or even crystals; it may be collected by means of carbon tetrachloride or petroleum, but isolation by distillation is simplest.

The effect of certain variations in this procedure may be noted. The proportion of sulphuric acid may even be reduced below the limits given in the foregoing without producing any considerable diminution in the yield. Even if the proportion $\text{H}_2\text{SO}_4:\text{HNO}_3=0.75:1$ by weight, the yield of tetranitromethane is only reduced by 10 per cent. The heating or the distillation of such a mixture is, however, attended with risk, as sudden decomposition, with evolution of gas, may ensue.

The addition of 20—25 grams of nitric acid to the mixture of the product and sulphuric acid before heating or distilling leads to an improvement of the yield (some 10 per cent.), especially if the conditions have otherwise been unfavourable; for example, if an excessive volume of acetylene has been passed into the nitric acid, or the temperature has been low, or the nitric acid too dilute. Under the conditions outlined in the foregoing, such addition of nitric acid has little, if any, effect.

As examples of the operation, the two following may be cited. The largest quantity of tetranitromethane (23.2 grams: 410 per cent. on the acetylene) in one operation was obtained by passing 5 litres into 138.6 grams (90 c.c.) of absolute nitric acid at 30° with 0.55 gram of mercuric nitrate in suspension. A better yield, of 453 per cent., was obtained by passing 4.6 litres into the same quantity of nitric acid diluted with water to 95 per cent. at the same temperature and with the same quantity of mercuric nitrate in solution; the weight of tetranitromethane isolated was 22.3 grams.

The Purification and Properties of Tetranitromethane.—The crude material, after washing with water, is nearly colourless, and melts at $13.4\text{--}13.5^\circ$. Thorough washing with dilute aqueous sodium carbonate does not change the melting point. After partial freezing and pouring off the remaining liquid three times, the substance melted at 13.75° , and the melting point was not raised by further fractionation. It has $D_{15.8}^{15.8}$ 1.65009.

