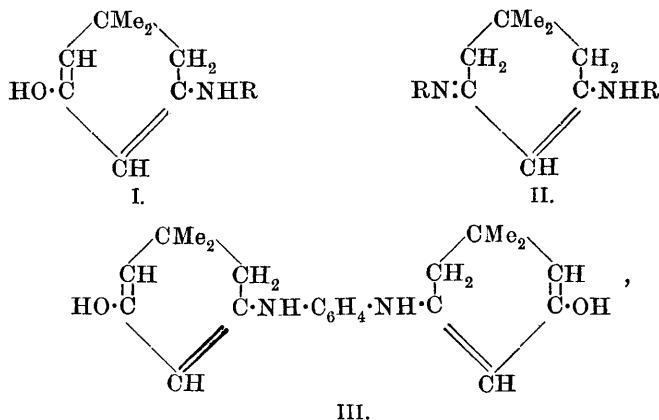


LXI.—*The Occurrence of Methane among the Decomposition Products of Certain Nitrogenous Substances as a Source of Error in the Estimation of Nitrogen by the Absolute Method.*

By PAUL HAAS, D.Sc., Ph.D.

DURING the course of the investigation of certain nitrogenous bases already described by the author (this vol., pp. 187 and 387), considerable difficulty was experienced in interpreting the analytical results. The bases, all of which are compounds of one of the three following types,

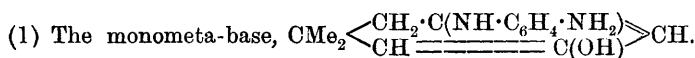


when analysed in the ordinary way in a tube filled with copper oxide, gave numbers for the percentage of nitrogen which, although agreeing fairly closely amongst themselves (compare table, p. 574),

were from 2 to 5 per cent. too high for the calculated values ; the hydrochlorides, on the other hand, gave correct values. Although the formulæ calculated from the analytical results were not in agreement with the general properties or reactions of these substances, it was not until in one case an acetyl derivative was found to give a higher percentage of nitrogen than the base from which it had been prepared that the method of analysis began to be suspected ; the gas contained in the nitrometer was accordingly analysed and found to contain methane. On consulting the literature, it was found that an isolated case of the same nature had already been recorded by Dunstan and Carr (*Proc.*, 1896, 12, 48), who observed that the alkaloid aconitine and its hydrochloride presented exactly the same anomaly as the compounds described above. Although the results contained in the present communication have been to a great extent anticipated by the above-mentioned authors, yet their paper contains no experimental details and refers only to a single substance ; in view of the importance of the question from the point of view of the reliability of the absolute method for the estimation of nitrogen, it was thought worth while to investigate the matter thoroughly, inasmuch as there was here a whole class of compounds, more than a dozen in number, which showed this abnormal behaviour.

In order to establish the presence of methane, the gas contained in the nitrometer was first washed with distilled water until the strong caustic potash had been displaced some way down the tube ; it was then transferred into an explosion burette and, after measuring, passed into a Bunte apparatus, where it was washed first with ammoniacal cuprous chloride to remove any carbon monoxide and subsequently with dilute sulphuric acid to remove ammonia ; on bringing the gas back into the explosion burette, no alteration in volume was ever observed, thus proving the absence of carbon monoxide. The oxygen, prepared by heating potassium permanganate, was introduced in requisite amount into the burette, where, after measurement, the gas was fired. After measuring the contraction on explosion, the volume of carbon dioxide was determined by absorption with caustic potash, and, after absorbing the excess of oxygen by means of an alkaline solution of potassium pyrogallate, the residual nitrogen was also measured. The volume of carbon dioxide was always found to be a little less than half the explosion contraction owing to the oxidation of some of the nitrogen ; consequently also the volume of the residual nitrogen was found to be rather less than it should have been.

The results obtained in five different cases are given below :



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(a) Analysed with cuprous chloride and lead chromate :

0.1302 gave 14.1 c.c. moist nitrogen at 18.5° and 747 mm.  $N = 12.28$ .

$C_{14}H_{18}ON_2$  requires  $N = 12.18$  per cent.

(b) Analysed with copper oxide only. Time of combustion one and a half hours.

0.1405 gave 19.3 c.c. moist nitrogen at 18° and 748 mm.  $N = 15.61$ .

Volume of gas ..... = 19.3 c.c.

„ „ mixed with oxygen... = 30.2 „

„ „ after explosion..... = 21.1 „ Contraction on explosion = 9.1 c.c.

„ „ „ absorbing carbon

dioxide = 16.8 „ Volume of carbon dioxide = 4.3 „

Residual nitrogen..... = 14.9 „

Taking the volume of methane to be equal to the volume of carbon dioxide formed and deducting this from the volume of gas originally found in the nitrometer, the volume of nitrogen becomes  $19.3 - 4.3 = 15$  c.c.: hence 0.1405 gave 15.0 c.c. of moist nitrogen at 18° and 748 mm.  $N = 12.13$  per cent.

In the remaining four examples, only the explosion contractions and the volumes of carbon dioxide and nitrogen are recorded.

(2) The monoanilide,  $CMe_2 \left\langle \begin{array}{c} CH_2 \cdot C(NH \cdot C_6H_5) \\ CH = C(OH) \end{array} \right\rangle CH$ .

(a) Analysed with cuprous chloride and lead chromate :

0.1391 gave 8.2 c.c. moist nitrogen at 21° and 758 mm.  $N = 6.79$ .

$C_{14}H_{17}ON$  requires  $N = 6.51$  per cent.

(b) Analysed with copper oxide only. Time of combustion one and a half hours.

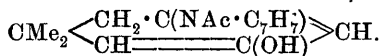
0.1725 gave 12.7 c.c. moist nitrogen at 19.5° and 758 mm.  $N = 8.43$  per cent.

Explosion contraction..... = 7.6 c.c.

Volume of carbon dioxide ... = 2.8 „ Whence  $N = 6.57$ .

„ „ residual nitrogen = 9.4 „ „  $N = 6.24$  per cent.

(3) The acetyl derivative of the monotoluidide,



(a) Analysed with cuprous chloride and lead chromate :

0.1340 gave 6.2 c.c. moist nitrogen at 22.5° and 774 mm.  $N = 5.32$ .

$C_{17}H_{21}O_2N$  requires  $N = 5.15$  per cent.

(b) Analysed with copper oxide only. Time of combustion, two hours.

0.1565 gave 10 c.c. moist nitrogen at 16° and 763 mm.  $N = 7.47$ . per cent.

In this case only an aliquot part, namely, 4.3 c.c. of gas, were analysed, the dilution being arranged to reduce the oxidation of the nitrogen to a minimum, so that the volume of carbon dioxide should be half of the explosion contraction.

Explosion contraction..... = 2.7 c.c.  
 Volume of carbon dioxide ... = 1.3 „      Whence  $N = 5.23$   
 „ „ residual nitrogen = 3.1 „      „       $N = 5.38$  per cent.

(4) The ditoluidide,  $\text{CMe}_2 \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{NH} \cdot \text{C}_7\text{H}_7) \\ \text{CH}_2 - \text{C}(: \text{N} - \text{C}_7\text{H}_7) \end{array} \text{CH}.$

(a) Analysed with cuprous chloride and lead chromate :

0.1346 gave 10.4 c.c. moist nitrogen at 21.5° and 770 mm.  $N = 8.89$ .  
 $\text{C}_{22}\text{H}_{26}\text{N}_2$  requires  $N = 8.80$  per cent.

(b) Analysed with copper oxide only. Time of combustion one and a half hours.

0.127 gave 13.3 c.c. moist nitrogen at 18° and 755 mm.  $N = 12.01$ .

Explosion contraction = 7.5 c.c.; volume of carbon dioxide = 3.6 c.c.  $N = 8.77$  per cent.

(5) *s*-Bisresorcy-*m*-phenylenediamine,  
 $\text{CMe}_2 \begin{array}{c} \text{CH}_2 - \text{C} \\ \text{CH} \cdot \text{C}(\text{OH}) \end{array} \text{CH} \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \begin{array}{c} \text{C} - \text{CH}_2 \\ \text{HC} \\ \text{C}(\text{OH}) \cdot \text{CH} \end{array} \text{CMe}_2.$

(a) Analysed with cuprous chloride and lead chromate :

0.1126 gave 7.7 c.c. moist nitrogen at 19° and 775 mm.  $N = 8.02$ .  
 $\text{C}_{22}\text{H}_{28}\text{O}_2\text{N}_2$  requires  $N = 7.95$  per cent.

(b) Analysed with copper oxide only. Time of combustion one and a half hours.

0.1376 gave 15.5 c.c. moist nitrogen at 18° and 761 mm.  $N = 13.04$ .

Explosion contraction..... = 13.0 c.c.  
 Volume of carbon dioxide ... = 5.9 „      Whence  $N = 8.06$   
 „ „ residual nitrogen = 9.3 „      „       $N = 7.82$  per cent.

In regard to the method adopted for preventing the accumulation of methane, it had been observed that the hydrochlorides of these bases behaved normally on combustion, from which it appeared that the presence of halogen had some influence, and it was found, as stated by Dunstan and Carr, that cuprous chloride when mixed with the substance made it possible to obtain correct analyses; moreover,

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since it was found (p. 576) that lead chromate was a more powerful oxidising agent for methane than copper oxide, the following modified method of analysis was employed. A layer of fused lead chromate was substituted for the usual layer of granular copper oxide, and the substance, before mixing with powdered copper oxide, was mixed with three to four times its bulk of freshly precipitated and washed cuprous chloride. Carried out in this way, perfectly correct results were obtained, the gas collected in the nitrometer being free from methane. In one case, however, that of *s*-bisresorcy-*m*-phenylenediamine, the amount of cuprous chloride mentioned above was not enough, and a correct result was only obtained on repeating the analysis with a larger bulk of the copper salt. On the other hand, a mere trace of chloride would appear to suffice in some cases, inasmuch as several of the substances gave correct results on the first analysis owing to the fact that the estimations were carried out in a tube in which hydrochloride had been previously analysed. It is probably unnecessary to use a fresh quantity of cuprous chloride each time, since (see below) cupric chloride can be substituted for the cuprous salt, but no data are available on this point. The lead chromate, on the other hand, appeared not to lose its efficiency even after a dozen or more analyses. The appended table shows the percentage of nitrogen obtained on analysing a number of these compounds when mixed with copper oxide only or when mixed with copper oxide and cuprous chloride, using lead chromate in place of granular copper oxide.

| Substance.  | Percentage of nitrogen.                             |  |
|---|---|--|
|   | Found on analysis with copper oxide only.           | Found on analysis when mixed with copper chloride and oxide. |
| Monoanilide (this vol., p. 202) .....               | 8.09, 8.55  | 6.51 6.79, 6.82  |
| Monoanilide hydrochloride ( <i>ibid.</i> )...       | 5.88  | 5.58 —   |
| Monotoluidide (this vol., p. 196)...                | 7.84, 7.87, 8.13                                    | 6.11 6.39  |
| Monotoluidide hydrochloride ( <i>ibid.</i> )        | 5.27  | 5.37 —   |
| Acetyl monotoluidide (this vol., p. 197) .....      | 5.86, 6.20  | 5.15 5.29, 5.32  |
| Ditoluidide (this vol., p. 199) .....               | 11.66   | 8.80 8.89  |
| Monometa-base (this vol., p. 389)...                | { 13.91, 14.58, 14.74, }<br>{ 14.74, 14.84, 15.32 } | 12.18 12.28, 12.30   |
| Monometahydrochloride (this vol., p. 390) .....     | 9.24  | 9.22 —   |
| Monopara-base (this vol., p. 394)...                | 13.74, 14.60  | 12.18 12.03  |
| Acetyl derivative of monometa-base                  | 12.68   | 10.29 10.27  |
| „ „ monopara-base                                   | 10.80   | 10.29 10.15  |
| <i>s</i> -Bisresorcy- <i>m</i> -phenylenediamine..  | { 10.96, 11.76, 11.99, }<br>{ 13.06, 13.26 }        | 7.95 8.02  |
| <i>s</i> -Bisresorcy- <i>p</i> -phenylenediamine... | 10.64, 10.72, 10.98                                 | 7.95 7.94  |

Subsequent experiments showed that the cuprous chloride could be replaced by cupric or lead chloride, but not by sodium chloride; it was, moreover, found that correct results could be obtained by mixing

the substance with coarsely powdered lead chromate and using a tube filled with lumps of the same material.

The following experiments illustrate the results obtained by a variety of methods of analysis. The time of heating varied from one and a half to one and three-quarter hours, being reckoned in each case from the moment of the complete expulsion of air from the tube until the last traces of gas had been collected in the nitrometer.

The Monotoluidide.—(1) Substance mixed with copper oxide and cuprous chloride. Tube filled with lead chromate.

0·1346 gave 7·6 c.c. moist nitrogen at 21° and 757 mm.  $N = 6·39$ .

(2) Substance mixed with copper oxide and cuprous chloride. Tube filled with copper oxide.

0·1326 gave 8·0 c.c. moist nitrogen at 23° and 758 mm.  $N = 6·77$ .

$C_{14}H_{17}ON$  requires  $N = 6·11$  per cent.

The Monometa-base.—(1) Substance mixed with copper oxide and cuprous chloride. Tube filled with lead chromate.

0·1302 gave 14·1 c.c. moist nitrogen at 18·5° and 747 mm.  $N = 12·28$ .

(2) Substance mixed with copper oxide and cupric chloride. Tube filled with copper oxide.

0·1251 gave 12·7 c.c. moist nitrogen at 16° and 778 mm.  $N = 12·11$ .

(3) Substance mixed with copper oxide and lead chloride. Tube filled with copper oxide.

0·1110 gave 11·7 c.c. moist nitrogen at 16·5° and 758 mm.  $N = 12·23$ .

(4) Substance mixed with copper oxide. Tube filled with copper oxide mixed with cupric chloride.

0·1220 gave 12·4 c.c. moist nitrogen at 14° and 769 mm.  $N = 12·10$ .

(5) Substance mixed with lead chromate. Tube filled with lead chromate.

0·1114 gave 11·8 c.c. moist nitrogen at 18° and 764 mm.  $N = 12·29$ .

$C_{14}H_{18}ON_2$  requires  $N = 12·18$  per cent.

(6) Substance mixed with copper oxide and sodium chloride. Tube filled with copper oxide.

0·1316 gave 15·4 c.c. moist nitrogen at 16° and 766·5 mm.  $N = 13·76$ .

With regard to the influence of the cuprous chloride, two possibilities presented themselves; either this salt was in some way able to effect the combustion of methane more completely than copper oxide alone could do or else it combined with the bases to form compounds which did not yield methane or decompose at a temperature more favourable to the combustion of methane. In order to settle this point, methane

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was passed through red-hot tubes filled with carbon dioxide and containing pure copper oxide and copper oxide mixed with cuprous chloride respectively, when it was found that, whereas in the first case as much as 43 per cent. of the gas passed over unburnt, complete oxidation was effected in the second. This shows that the action of the cuprous chloride must be attributed to its exerting some destructive influence on the methane rather than to its combining with the base, a view which gains support from the observation that lead chromate, which may be used as a substitute for cuprous chloride, also does not permit any methane passed over it to escape combustion.

The experiments were carried out as follows: an ordinary combustion tube, filled with the particular oxidising agent the action of which was to be tried, was connected in the usual manner with a hard glass tube containing sodium hydrogen carbonate for generating carbon dioxide. Between the two tubes was inserted a T-piece containing a three-way tap at its centre; the stem of the T was attached to a graduated gas burette, the lower end of which was connected by an india-rubber tube to a reservoir filled with water. From this burette, pure methane, prepared by the action of water on aluminium carbide, was introduced in a slow stream through the T-piece into the furnace, after all the air had been previously displaced by a current of carbon dioxide. When sufficient methane had been introduced into the tube, the three-way tap in the T-piece was turned so that only carbon dioxide, which had been kept bubbling all the time, entered the furnace, the stream being continued until no more gas collected in the nitrometer. By inserting a second three-way tap between the top of the burette and the tap in the T-piece, the dead space between these two could be freed from air by a current of carbon dioxide before the methane was passed through it.

The results of the experiments are given below in tabular form :

|   | Tube packed<br>with 50 cm. of<br>granular copper oxide. |            | Tube packed with<br>46 cm. of granular<br>copper oxide and<br>10 cm. of powdered<br>copper oxide mixed<br>with 4 grams of<br>cuprous chloride. | Tube<br>packed<br>with<br>60 cm.<br>of lead<br>chromate. |
|---|---|------------|--|--|
| Time occupied in passing the methane through the tube | 40 minutes  | 45 minutes | 35 minutes   | 40 minutes   |
| Volume of methane introduced into the tube .....      | 18 c.c.   | 17 c.c.    | 18.8 c.c.  | 21.7 c.c.  |
| Volume of methane collected in the nitrometer .....   | 7.8 c.c.*   | 7.6 c.c.*  | 0  | 0  |
| Percentage of methane escaping combustion .....       | 43.3  | 44.7       | 0  | 0  |

\* In each of these cases, the gas was proved to consist of methane only by exploding it with oxygen and absorbing the carbon dioxide formed with caustic potash.

In attempting to account for the formation of methane from this group of substances, it was originally thought that the phenomenon might be connected with the presence in the compounds of the grouping  $R \cdot NH \cdot R_2$ ; to test the correctness of this view, a nitrogen estimation was carried out with *p*-aminoacetanilide, a substance first prepared by Nietzki (*Ber.*, 1884, **17**, 343), and only analysed by him in the form of its platinum salt; being a substituted diamine, it was thought that it might present the same anomalies as the compounds here described; however, on analysis with copper oxide it was found to behave quite normally.

0.1233 gave 19.8 c.c. moist nitrogen at 15° and 755 mm.  $N = 18.67$ .

$C_8H_{10}ON_2$  requires  $N = 18.66$  per cent.

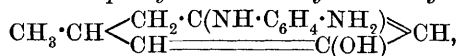
The cause of the trouble must therefore be sought in the hydro-aromatic complex, more especially as it is found that the compounds of the type III (p. 570), which contain two such complexes, give the largest amounts of methane and the lowest combustions.

In order to determine whether in this case the attachment of two methyl groups to the same carbon atom had not some special influence, it was decided to analyse an analogous substance which did not contain this grouping; accordingly, the *m*-phenylenediamine condensation product of monomethyldihydroresorcin was prepared and analysed, and was, indeed, found to give quite correct results when analysed in the usual way.

#### *Condensation of Methyldihydroresorcin with m-Phenylenediamine.*

Three and a half grams of methyldihydroresorcin and 3 grams of *m*-phenylenediamine dissolved in alcohol were heated over a water-bath for three hours. On evaporating off the alcohol, there remained a brown, syrupy residue, which, on dissolving in a mixture of alcohol and light petroleum, separated from the solution in colourless, slender prisms melting at 178.5—179.5°.

*5-Hydroxy-3-m-aminophenylimino-1-methyl- $\Delta^{3:5}$ -dihydrobenzene,*



is readily soluble in cold alcohol or acetone, slightly so in hot benzene, and insoluble in chloroform or light petroleum.

0.1355 gave 15.1 c.c. moist nitrogen at 15° and 763 mm.  $N = 13.35$ .

$C_{13}H_{16}ON_2$  requires  $N = 12.96$  per cent.

The analysis was performed in the usual way, using copper oxide only, and no methane was formed.

The combustions for carbon and hydrogen in these substances were originally performed in the ordinary way with copper oxide and a



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spiral of reduced copper gauze in air, but the results obtained by this method were too low; it was, however, found that, on substituting lead chromate for the copper oxide and carrying out the combustion in an atmosphere of oxygen with a spiral of silver gauze in place of the reduced copper, correct results could be obtained. It was, moreover, observed that the presence of a little chromium sesquioxide in the boat helped to render the combustion complete.

The following table shows the results obtained by the two methods:

| Substance.   | Percentage of carbon and hydrogen.           |                           |  |
|--|--|---------------------------|--|
|  | Combustions in<br>air with copper oxide.     | Calculated<br>percentage. | Combustions<br>in oxygen<br>with lead<br>chromate. |
| Acetylmonotoluidide.....                                 | C=73.03<br>H= 7.73                           | 75.27<br>7.75             | 74.93, 75.38<br>8.03, 8.47                         |
| Monometa-base .....                                      | C=71.10, 71.67<br>H= 8.14, 8.37              | C=73.05<br>H= 7.83        | { 73.10<br>8.48<br>73.09<br>8.01                   |
| Monopara-base .....                                      | C=71.35, 70.97<br>H= 7.75, 7.41              |                           |  |
| <i>s</i> -Bisresorecyl- <i>m</i> -phenylenedi-<br>amine. | C=71.21, 71.48, 72.79<br>H= 7.18, 7.23, 7.67 | C=75.00<br>H= 7.95        | { 74.91<br>8.56<br>74.50<br>7.95                   |
| <i>s</i> -Bisresorecyl- <i>p</i> -phenylenedi-<br>amine. | C=70.64, 71.51<br>H= 7.51, 7.73              |                           |  |

In conclusion, the author desires to express his indebtedness to Dr. H. R. Le Sueur for many useful suggestions during the course of the work.

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