# 290. *The Kinetics of the Thermal Decomposition of the Methylamines. Part II.*

By Morris W. Travers and John A. Hawkes.

The influence of nitric oxide on the rates of thermal decomposition of the three methylamines has been investigated, the results of the experiments confirming those obtained in the previous investigation and throwing some light on points of detail. The reactions between the amines and nitric oxide have also been studied qualitatively.

In Part I (Carter, Bosanquet, Silcocks, Travers, and Wilshire, this vol., p. 495) it was shown that in the neighbourhood of 400° the tertiary and the secondary amine decomposed to yield methane at practically identical rates, and that in both cases it was probable that the decomposition process was initiated by the dissociation of the amine, with formation of free methyl radicals. Hydrogen and ethane were also formed in small quantities. The primary amine did not decompose at a comparable rate till a temperature 100° higher was reached; the primary product was then hydrogen, the formation of which might be initiated by the formation of the free radicals $CH_3{\cdot}NH{\cdot}$ and $H{\cdot}$, methane being a secondary product.

The present paper describes experiments with the three amines, in which the influence of nitric oxide on the rate of reaction has been studied, and, in general, our results are in agreement with those of Hinshelwood and his collaborators. We have considered also the action of nitric oxide upon the amine and upon the individual radicals resulting from it, and the consequent differential inhibition of the processes initiated by these radicals. (i) In the case of the tertiary amine, the formation of methane and methylmethyleneimine, the main products of reaction, and also of the small quantity of hydrogen, is initiated by the radicals $CH_3{\cdot}$ and $(CH_3)_2N{\cdot}$ respectively, a mechanism for the former process being indicated in the last paper; the ethane probably results from the reaction of methyl radicals with methylmethyleneimine. (ii) With dimethylamine the main reaction results in the formation of methane, methylmethyleneimine, and methylamine; a minor reaction leads to formation of hydrogen in small quantity, and both reactions are initiated by the formation of free radicals. (iii) In the case of methylamine it is now shown that the greater part of the hydrogen is formed by a process initiated by the formation of radicals, $CH_3{\cdot}NH{\cdot}$ and $H{\cdot}$, but that the methane, and an equal quantity of hydrogen, are formed by a process which does not involve free radicals but, probably, the interaction of two molecules of methylamine.

## EXPERIMENTAL.

*Method.*—The method of investigation was that recently described (*Trans. Faraday Soc.*, 1939, **35**, 656). A measured quantity of the gaseous amine, with or without the addition of nitric oxide, was introduced into a heated silica bulb of 82 c.c. capacity, which, at the end of the reaction, was removed from the furnace, chilled under a spray, and its contents analysed. In all except the last series of experiments with methylamine, 25 c.c. of the amine, with successively increasing quantities of nitric oxide, were heated for a definite time to a definite temperature, and the inhibiting effect of the nitric oxide was observed. The gas which was pumped off when the reaction vessel was cooled to − 180° contained methane, hydrogen, and nitrogen, and in the case of the primary amine some nitric oxide. The behaviour of nitric oxide towards the amine is dealt with in a note at the end of the paper.

*Experiments with Trimethylamine.*—These experiments were carried out at 420°, and the results are shown by the graphs in Fig. 1. The main reaction is represented by the equation $(CH_3)_3N = CH_4 + CH_3{\cdot}N{:}CH_2$, the methylmethyleneimine rapidly polymerising. Small quantities of hydrogen and of ethane are also formed.

Reference to Fig. 1 shows that hydrogen formation is initially more inhibited relatively than that of methane. This may be due to the reversibility of the inhibition process $R{\cdot} + NO \rightleftharpoons R{\cdot}NO$, a suggestion which we owe to Dr. C. E. H. Bawn, the compound $R{\cdot}NO$ varying in stability with the radical R, so that the degree of inhibition of different reactions would vary according to the radical concerned. However, it seems clear that both the formation of hydrogen and that of methane are initiated by free radicals; in the latter case the process may be represented (*loc. cit.*, p. 499) by the equations

$$N(CH_3)_3 = CH_3\cdot + N(CH_3)_2\cdot \quad . \quad . \quad . \quad . \quad (1)$$

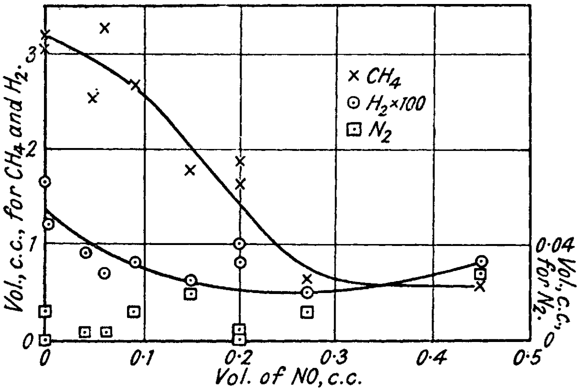
$$CH_3\cdot + N(CH_3)_3 = CH_4 + N(CH_3)_2\cdot CH_2\cdot \quad . \quad . \quad . \quad (2)$$

$$N(CH_3)_2\cdot CH_2\cdot = CH_3\cdot + CH_3\cdot N\colon CH_2 \quad . \quad . \quad . \quad . \quad (3)$$

There is no obvious mechanism for the formation of the hydrogen. In the former paper it was suggested that the formation of ethane was a secondary process, and it probably results from the reaction of the methyl radicals with the methylmethyleneimine.

FIG. 1.

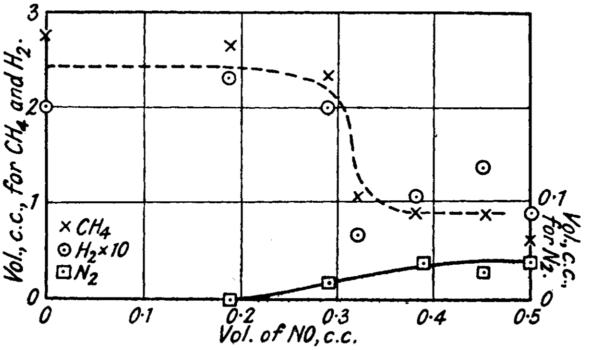
*Decomposition of trimethylamine* (25 *c.c. at* 420° *in* 30 *minutes*).



The nitrogen content of the reaction mixture is small, and the quantity of nitrogen is irregular. Nitrogen is not a product of the reaction of trimethylamine with nitric oxide (p. 1364), and is probably present in the amine as an impurity.

FIG. 2.

*Decomposition of dimethylamine* (25 *c.c. at* 420° *in* 30 *minutes*).



The experiments of Hinshelwood and his co-workers have indicated that the inhibition of chemical processes of a similar character is never complete, suggesting that all such reactions are initiated partly by free radicals, and partly by other means. The persistence of the value of the ratio of the rates of formation of methane and of hydrogen, which is even more marked in the case of the secondary amine, raises a doubt as to the validity of this explanation.

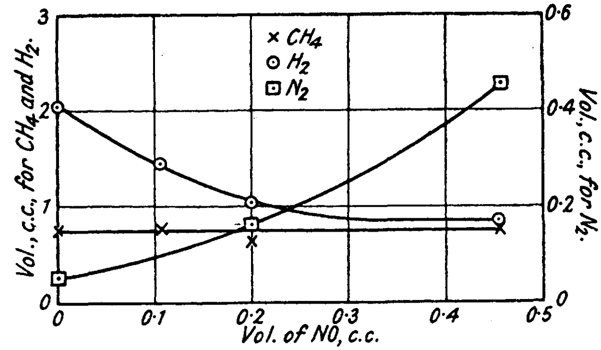
*Experiments with Dimethylamine.*—The main changes resulting when dimethylamine is heated to 420° are represented by the equation $2(CH_3)_2NH = CH_4 + CH_3\cdot N\colon CH_2 + CH_3\cdot NH_2$, the methylamine being stable at this temperature. The results of the experiments, shown by the graphs in Fig. 2, confirm the conclusion from the earlier experiments that the rates of formation of methane from the tertiary and the secondary amine, for identical conditions at 420°, are practically identical. Hydrogen, to the extent of about 10% of the methane formed, is also a product of the decomposition, and some ethane and ammonia are also formed.

Reference to the graph for hydrogen in Fig. 2 shows that little inhibition of the formation of either methane or hydrogen occurs till after a considerable quantity of nitric oxide has been added to the amine. We have no positive explanation of this fact, but it may be due to the formation of an addition compound which changes irreversibly into decomposition products (see note, p. 1363), and results in the removal of the nitric oxide. For small additions of nitric oxide only a trace of nitrogen appears in the gas. The inhibition of the formation of methane and hydrogen sets in after the same addition of nitric oxide, and proceeds in practically the same proportion, as is shown by the fact that the same graph represents the formation of both gases with different scales for the ordinates. This indicates either that the methane and the hydrogen are formed by processes initiated by the same free radical, or that the effect of the nitric oxide is exactly the same in both cases.

It is possible that the mechanism of the formation of the methane is similar to that suggested for the case of the tertiary amine, but that methyleneimine, $CH_2{:}NH$, is formed instead of $CH_3{\cdot}N{:}CH_2$. A second process then operates, *viz.*, $CH_2{:}NH + (CH_3)_2NH \rightarrow CH_3{\cdot}NH_2 + CH_3{\cdot}N{:}CH_2$. However, there is no proof that this happens. Also, we have no evidence as to the mechanism of the formation of hydrogen, except that the process appears to be initiated by the formation of a free radical.

FIG. 3.

*Decomposition of methylamine* (25 *c.c. at* 530° *in* 1 *hour*).



At 420° no hydrogen cyanide can be detected in the products of decomposition of dimethylamine. It is formed at higher temperatures, but the process is then too complicated to be followed.

*Experiments with Methylamine.*—In the first series of experiments, comparable with those carried out with tri- and di-methylamines, 25 c.c. of the amine, with increasing quantities of nitric oxide, were heated to 530° for one hour. The results are shown by the graphs in Fig. 3. Our earlier experiments had shown that the rate of formation of hydrogen was diminished by packing a reaction tube, which did not influence the rate of formation of methane. The present experiments show that increasing amounts of nitric oxide decrease the formation of hydrogen till it is equal to the quantity of methane formed, but have no effect on the latter.

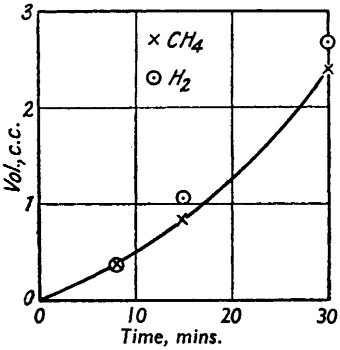
The facts that addition of nitric oxide does not produce a rapid drop in the quantity of hydrogen formed, and that relatively large quantities of nitrogen are formed, indicate that the nitric oxide reacts with the amine. However, it seems that we have here two reactions, one resulting in the formation of hydrogen, which is completely suppressed by addition of nitric oxide, and one resulting in equal quantities of methane and hydrogen, which is quite unaffected. We will consider the former first. It must be supposed to be initiated by the dissociation process $CH_3{\cdot}NH_2 = CH_3{\cdot}NH{\cdot} + H{\cdot}$, rather than $CH_3{\cdot}NH_2 = CH_3{\cdot} + {\cdot}NH_2$. In the latter case methane would be a primary product, its formation would be inhibited by nitric oxide, and nitrogen would probably be a product of the reaction.

What actually happens is obscure. The overall process of which hydrogen is a product is probably represented by the equation $CH_3{\cdot}NH_2 = HCN + 2H_2$. It was shown in Part I (*loc. cit.*) that there was some delay in the appearance of hydrogen cyanide, which suggests that the compound $CH_2{:}NH$ is formed as an intermediate, but we have been unable to detect it. If this is what happens, there is a similarity between the primary decomposition of methylamine and that of ethane, which still presents several obscurities. It may be noted that processes initiated by dissociation involving the formation of protons seem to be dependent in a marked degree, not only on the dimensions of the apparatus, regulated by packing the reaction vessel, but also on the state of the surface. In Part I attention was called to the great difficulty of obtaining reproducible results with methylamine, and one of us has reported a similar difficulty in experiments with ethane. We make no attempt to represent the mechanism of the primary decomposition of methylamine by equations.

We have carried out a few experiments on the thermal decomposition of a mixture of 25 c.c. of methylamine with 1 c.c. of nitric oxide, varying the time. The results are represented by the graphs in Fig. 4. It has already been noted that the nitric oxide tends to disappear from the system, so that the complete inhibition of the primary formation of hydrogen would only take place over a very short interval of time. It will be seen that for the 7½-minute interval the quantities of methane and hydrogen formed are equal, but that for longer periods the hydrogen is in excess, probably because, owing to the disappearance of the nitric oxide, the free radical process is no longer completely suppressed. The results confirm the previous result that the process is self-accelerated, indicating that the methane and hydrogen must both result from an intermediate.

FIG. 4.

*Decomposition of mixtures at* 530° *: methylamine,* 25 *c.c.; nitric oxide,* 1 *c.c.*



It was shown in the previous paper that methane does not result from a reaction represented by $CH_3{\cdot}NH_2 + H_2 = CH_4 + NH_3$, since the rate of the process is quite independent of the concentration of the hydrogen.

If the formation of dimethylamine is a step in the process, the formation of methane and hydrogen might be represented stoicheiometrically by $(CH_3)_2NH = CH_4 + H_2 + HCN$. Hydrogen cyanide is a product of the decomposition of dimethylamine at 530°, but even by itself at this temperature it yields much more methane than hydrogen; and, if the process were supposed to be initiated by free methyl radicals, in the presence of large excess of methylamine, it is unlikely that it would operate in so simple a manner.

Attention has been called to the similarity between the primary decomposition of ethane and that of methylamine, both of which are inhibited by the presence of nitric oxide. We have recently shown (*Trans. Faraday Soc.*, unpublished) that the secondary decomposition of ethane, resulting in the formation of methane and aromatic condensation products, appears to involve a bimolecular process, and is uninfluenced by nitric oxide. It may, therefore, have a mechanism similar to that which results in the formation of methane when methylamine is heated. It was with the view of ascertaining whether the study of the thermal decomposition of methylamine could throw any light on the mechanism of the thermal decomposition of ethane that this work was undertaken. However, beyond showing that there is a similarity between the two processes, it does not accomplish its object; but it does bring to light some interesting facts regarding the thermal decomposition of the methylamines.

*Note on the Reactions between Nitric Oxide and the Methylamines* (added by M. W. TRAVERS, *July* 30*th*, 1939).—No reaction between the dry gases occurs at room temperature. If, however, a mixture of dimethylamine and nitric oxide is liquefied by pressure at room temperature, or by condensation at a low temperature in a glass tube, which is sealed, and allowed to warm to room temperature, a white solid separates; *e.g.*, after 10 c.c. of dimethylamine and 15 c.c. of nitric oxide had been condensed at — 180° in a tube of 4 c.c. capacity, which was alternately warmed to room temperature and cooled to — 80° several times, 5 c.c. of practically pure nitric oxide could be pumped off at room temperature, the white solid of composition $(CH_3)_2NH,NO$ remaining practically undecomposed. It decomposes very slowly in the sealed tube at room temperature, and more rapidly on heating. Presumably a set of dissociation pressures for the system $(CH_3)_2NH,NO \rightleftharpoons (CH_3)_2NH + NO$ could easily be determind.

A mixture of trimethylamine with nitric oxide appears to liquefy easily, but under no conditions does any solid separate, and at — 80° a mixture of the two gases is given off.

Methylamine cooled to — 180° with nitric oxide yields a very yellow solid, melting to a liquid which, at — 80°, is still yellow, and gives off nitric oxide, appearing to boil. In these respects the behaviour of the primary amine is different from that of the tertiary and the secondary amine, and it is suggested that the nitric oxide only dissolves in the liquefied primary amine, but combines certainly with the secondary, and probably with the tertiary amine.

The action of heat on mixtures of equal volumes of nitric oxide and the secondary and the tertiary amine was also studied, the gases being heated together for 30 mins. to 420°. In each case 25—30% of the gases had undergone change. From the secondary amine the products were nitrogen, water, and a condensation product, and from the tertiary amine nitrous oxide, water, and a condensation product, with no more than a trace of nitrogen and methane. In neither case was there evidence of the formation of a compound by the addition of nitrogen or the elements of nitric oxide to the amine. However, the presence of a small quantity of such a compound would be almost impossible to detect, and it is yet possible that something of the kind may account for the fact that there is a lag in the inhibiting action of the nitric oxide, particularly in the case of the secondary amine.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF BRISTOL. [*Received, July 5th,* 1939.]