431. *The Thermal Oxidation of Methylamine.*

By Leslie J. Jolley.

THE vapour-phase oxidation of aliphatic amines has hitherto received little attention. The subject is of interest because, in the case of a primary amine, either the alkyl or the amino-group could conceivably be attacked by oxygen. In the former case one would expect to observe the general characteristics of hydrocarbon combustion, which appears to proceed by a chain mechanism in the typical cases of methane, ethylene, and benzene (Hinshelwood *et al.*, *Proc. Roy. Soc.*, 1929, *A*, **125**, 276 ; 1930, **127**, 218 ; 1930, **129**, 284), whereas in the latter case the oxidation should resemble that of ammonia, which is a heterogeneous process.

Trillat (*Compt. rend.*, 1903, **136**, 53) found that the main products of the oxidation of aliphatic amines on a platinum spiral at a high temperature, in presence of steam, were aldehydes and nitrous acid; he supposed the initial stage of the reaction in such conditions to be hydrolysis of the amine to alcohol and ammonia. Trümpler (Swiss Patent 111,120, 1924) found that a mixture of methylamine, steam, and air passed over granular diatomite at 300° gave almost quantitative yields of formaldehyde and ammonia. The reactions studied by both authors were presumably heterogeneous. Emeléus and Taylor (*J. Amer. Chem. Soc.*, 1931, **53**, 3370) observed that methylamine and oxygen react photochemically, and supposed that scission of the C–N link took place. Further work is in progress on this aspect of the problem.

Preliminary observations on the thermal oxidation of methylamine showed that a homogeneous reaction takes place at temperatures above 250°, and can be conveniently studied at 300°. The main products are formaldehyde, carbon monoxide and dioxide, ammonia, and water. Some hydrogen cyanide is also formed. In the experiments described below, the nature of the reaction products has been studied at temperatures between 270° and 410°. The effect on the velocity of the surface/volume ratio of the reaction vessel, the concentrations of methylamine and oxygen, and the admixture of foreign gases has also been studied, and some account of the ignition of methylamine–oxygen mixtures is given. In addition, a series of experiments on the thermal decomposition of methylamine is described. Data on this reaction have not been recorded, and it is necessary to know whether the oxidation can be preceded by a thermal dissociation of the amine molecule.

EXPERIMENTAL.

Methylamine was prepared by warming its hydrochloride with quicklime in an evacuated glass apparatus and condensing the vapour in a U-tube cooled in liquid air. This product was

6 M

dried by distillation through a tube packed with freshly ignited quicklime, and then fractionally distilled in a vacuum. The middle fraction (v. p. at $-52° = 57—60$ mm.) was separated, and stored in a 3-litre glass globe. Oxygen from a cylinder was used; it contained $0·5—1·0\%$ of nitrogen (for which a correction was in all cases made in the analyses) and was dried by passage through a tube 1 m. long packed with phosphoric oxide, and stored in a previously evacuated glass globe.

The reaction vessel was either a cylindrical or a spherical bulb, attached to a constant-volume capillary manometer, and having taps connecting it to (1) reservoirs of methylamine and oxygen, (2) a Töpler pump delivering into a Bone and Wheeler gas-analysis apparatus, (3) a reservoir in which gases could be mixed, (4) a pumping line fitted with a liquid-air trap and a McLeod gauge, connected to a mercury-vapour pump backed by a Cenco pump. Methylamine was found to have no appreciable effect on the tap grease, and a vacuum of $0·001$ mm. could be maintained in the system for several days.

The dead space in the reaction system (*ca.* 1% of the total volume) was minimised by the use of capillary connexions wherever possible. The reaction vessels were of soft glass, pyrex, or silica in various runs, and were in each case cleaned with chromic–nitric acid, washed with water, and baked out in a vacuum at $300°$.

A large, well-lagged, cylindrical furnace with side and end windings was used throughout, and gave a temperature uniform to $1°$ over an axial distance of 15 cm. Temperatures were measured with a calibrated platinum–rhodium thermocouple, or with a calibrated mercury thermometer.

In analysing the reaction products, direct-pressure measurements in the reaction vessel were used as far as possible. After a run, the reaction vessel was cooled in liquid air, and carbon monoxide, hydrogen, methane, and nitrogen were pumped into the Bone and Wheeler apparatus and analysed. Any condensable gas in the dead space of the reaction system was frozen out in a small liquid-air trap and returned to the reaction vessel before the residual pressure was measured. The reaction vessel was then cooled to $-115°$, and any ethylene and ethane present pumped off. At this temperature, ammonia, the most volatile of the residual gases other than ethane and ethylene, has a vapour pressure of less than 1 mm. Carbon dioxide was always present in the residue as carbonates of ammonia and methylamine. The latter is the more stable, but has a dissociation pressure of 7 mm. at $20°$. It was therefore possible to distil the mixture of carbonates in a vacuum into a bulb containing dilute sulphuric acid, which absorbed the bases, and then to return the carbon dioxide to the reaction vessel and measure its pressure (moist). In the experiments in which a complete analysis of the reaction products was made, the reaction vessel was detached after removal and estimation of non-condensable gases, and dilute sulphuric acid introduced. Carbon dioxide was then pumped into a gas burette and measured. The acid solution was cautiously distilled, and cyanide determined in the distillate by Volhard's method. The bases in the residue were estimated by adding an excess of alkali and distilling into standard acid. It was necessary to calculate formaldehyde indirectly, as indicated below, since its determination by either the cyanide or Romijn's iodometric method in the distillate from acid solution was found to be inapplicable in presence of cyanide.

Decomposition of Methylamine.—Müller (*Bull. Soc. chim.*, 1887, **45**, 439) found that the products of decomposition at $1200°$ were ammonia, hydrogen cyanide, methane, hydrogen, and nitrogen; and Upson and Sands (*J. Amer. Chem. Soc.*, 1922, **44**, 2036) found that ethylamine at $500°$ gave ammonia, acetonitrile, hydrogen, and ethylene as main products. The experiments recorded below were made to determine whether methylamine can undergo appreciable decomposition at $300—350°$, *i.e.*, in the range of temperature in which it oxidises rapidly.

Methylamine was admitted at a series of temperatures to a pyrex bulb of 150 c.c. capacity, and pressure measurements were taken in each case over a period of some hours. The bulb was then cooled, and the contents analysed. Decomposition was barely perceptible at $430—440°$, the pressure rising in 5 hours from $571·5$ to $573·0$ mm. (measured at $428°$). On cooling the bulb in liquid air, the residual pressure was $0·1$ mm., showing that only a trace of non-condensable gas had been formed. The residual pressure after the condensable portion had been treated with dilute sulphuric acid was less than 1 mm. (measured at $20°$). At $0°$ there was no trace of condensate in the bulb.

A similar experiment showed that at $536°$ appreciable decomposition took place, with formation of hydrogen, hydrogen cyanide, and methane. In 1 hour the pressure had risen from $532·5$ to $610·5$ mm., and after 3 hours it was $753·0$ mm. At this point the bulb was cooled and the contents analysed. The pressures of the products (measured at $536°$) were 208 mm. hydrogen, $64·5$ mm. methane, and $1·3$ mm. nitrogen. Qualitative examination of the condensable

product showed that much hydrogen cyanide was present. On cooling the reaction bulb to 0°, a colourless crystalline solid, methylamine hydrocyanide, was deposited.

In the next experiment the bases and hydrogen cyanide present in the product were estimated volumetrically.

Initial pressure of methylamine at 500°   =   535·5 mm.
After 3 hours at 540—560°, total pressure (measured at 500°) = 1042·2 mm.
Analysis of products (partial pressures, mm., measured at 500°) : Total bases = 249·0; H_2 = 536·0; HCN = 243·0; CH_4 = 56·1. Ethane and ethylene, traces only.

If it is assumed that the only bases present are ammonia and methylamine, an estimate of the ammonia formed can be made from a consideration of the hydrogen balance on the analysis. It appears that the ammonia present cannot be less than 54·5 mm., and the partial pressure of undecomposed methylamine must be less than 194·5 mm.

Hence, in mm., 341·0 of methylamine give 54·5 of ammonia, 243·0 of hydrogen cyanide, 56·1 of methane, and 536·0 of hydrogen. It follows that at 540—560° about 80% of the methylamine decomposes according to the reaction $CH_3 \cdot NH_2 = HCN + 2H_2$, and about 20% according to $CH_3 \cdot NH_2 + H_2 = CH_4 + NH_3$.

A rough extrapolation from the above results indicates that at 300° the decomposition of methylamine would produce a pressure change of the order of 0·0005 mm./hr., and such a reaction may therefore be neglected as a direct factor in the thermal oxidation.

Thermal Oxidation of Methylamine at 300°.—Reaction products. At this temperature the reaction period is of the order of one hour, and further heating causes no appreciable change of pressure or disappearance of oxygen. When the reaction vessel is cooled, a dew is deposited, and some ammonium carbonate crystallises out on standing. At 300° no carbon is liberated, and the condensed liquid is almost colourless.

The analysis of the condensable product is complicated by the fact that formaldehyde reacts with hydrogen cyanide in the conditions prevailing at the end of a run to give glycollonitrile, $CH_2(OH) \cdot CN$, and products so combining cannot be directly determined. A further portion of the formaldehyde formed condenses with ammonia, giving hexamethylenetetramine. This can be hydrolysed to ammonia and formaldehyde with dilute acid, and the formaldehyde detected by Schryver's test. Estimation of ammonia and free hydrogen cyanide in the condensable product enabled some 90% of the nitrogen initially present to be accounted for.

Detailed analyses were made in two similar experiments in spherical soft-glass bulbs of 400 c.c. capacity. An excess of oxygen was present, and heating was continued until no further pressure change occurred; it was assumed that no unchanged methylamine remained. The method of analysis was that already outlined. In one case an attempt was made to estimate formaldehyde by Romijn's iodometric method. The result is, of course, low, but affords additional evidence of the formation of formaldehyde.

Results are expressed as pressures (mm.) in the reaction vessel at the reaction temperature.

	Run A.	Run B.		Run A.	Run B.
Temp.	281°	276°	N_2 formed	10·5	14·1
Init. press. of $CH_3 \cdot NH_2$.......	311·7	304·1	H_2 formed	1·5	—
,, ,, O_2...............	394·7	381·5	CH_4 formed	—	—
Final press.	869·3	854·5	$C_2H_6 + C_2H_4$..................	—	—
Pressure rise	161·3	162·7	CO_2 formed	66·0	66·0
Residual O_2.....................	74·4	54·5	NH_3 formed	226·0	199·0
O_2 consumed	320·3	327·0	HCN formed	24·8	37·0
CO formed	61·6	64·7	CH_2O formed.................	18·0	—

The formation of the above products may be represented by the equations : (1) $2CH_3 \cdot NH_2 + O_2 = 2CH_2O + 2NH_3$; (2) $CH_3 \cdot NH_2 + O_2 = CO + H_2O + NH_3$; (3) $CH_3 \cdot NH_2 + O_2 = HCN + 2H_2O$; (4) $2CH_3 \cdot NH_2 + 3O_2 = 2CO_2 + 2H_2O + 2NH_3$; (5) $4NH_3 + 3O_2 = 6H_2O + 2N_2$. By using these equations, the amount of water formed can be calculated from the analyses, and balances drawn up for the carbon, hydrogen, nitrogen, and oxygen. The percentages of the initial elements thus accounted for are : Run A, C, 54·8; H, 74·4; N, 87·3; O, 72·2. Run B, C, 55·2; H, 74·3; N, 87·0; O, 72·6.

The nitrogen deficit (which is small) has been taken to represent hydrogen cyanide lost as glycollonitrile. If the deficit on the balances quoted above be expressed as partial pressures in the reaction system, the percentage composition and pressure of the product still unidentified may be calculated. In both runs, the molecular formula of this residue is to a close approximation CH_2O_n, where n is between 1 and 2. Since no formic acid was found, this may represent

a polymerised oxidation product of formaldehyde. It has been included in the values for formaldehyde given below :

Percentage of methylamine oxidised to :

	Run A.	Run B.		Run A.	Run B.
CH_2O (reaction 1)	37·9	31·6	CO (reaction 2)	19·8	21·3
HCN (reaction 3)	20·8	25·3	CO_2 (reaction 4)...............	21·2	21·7

Effect of Reaction Temperature on the Nature of the Products.—The products were analysed in a series of runs at temperatures from 300° to 410°. The initial concentrations of methylamine and oxygen were kept constant ($4MeNH_2 : 3O_2$). In cases where the rapidity of the reaction prevented direct measurement of the initial pressure, the mixture was admitted to the evacuated reaction vessel from a second bulb at a known temperature and pressure, and the change of pressure in the latter measured. The volume ratio of the two bulbs being known, the initial pressure in the reaction bulb could be calculated. Analyses were made of the carbon monoxide, nitrogen, hydrogen, methane, and carbon dioxide formed.

For the purpose of comparison, the amounts of the products formed are expressed in arbitrary units such that the oxygen consumed is equal to 100.

Temp.	CO.	N_2.	H_2.	CH_4.	CO_2.	Temp.	CO.	N_2.	H_2.	CH_4.	CO_2.
305°	11·6	6·9	0·0	0·0	11·6	385°	16·9	15·5	—	—	8·3
305	14·6	7·2	0·0	0·0	8·1	409	20·4	16·8	3·9	2·4	6·2
353	14·9	13·2	1·7	0·0	8·0						

The discrepancy between the two experiments at 305° is outside the errors of gas analysis, and was probably due to different surface conditions in the two cases. Apart from this discrepancy, it appears that at higher temperatures there is increased formation of carbon monoxide and nitrogen, and a slight diminution in the formation of carbon dioxide. The general character of the reaction, however, suffers no marked change.

The Induction Period in the Thermal Oxidation of Methylamine.—In the slow combustion of methylamine, the pressure of the reaction mixture increases. The rate of increase, which is at first very small, rises continuously to a maximum, and then falls off again. Such an induction period is typical of the slow combustion of many hydrocarbons and related compounds. Hinshelwood (*loc. cit.*) assumes that the similar lag in the oxidation of, *e.g.*, methyl alcohol does not indicate that the initial reaction velocity is very small, but merely that the initial stage of the reaction, which preponderates at the outset, takes place without change of pressure.

Experiments recorded below show that this cannot be the explanation in the case of methylamine oxidation. The mean rates of disappearance of oxygen in the induction period and in the total reaction were compared in precisely similar experiments in which samples of the reacting mixture were withdrawn into a cold bulb at a suitable stage of the reaction, and analysed. For this purpose a methylamine–oxygen mixture containing a known proportion of nitrogen was used, and the oxygen consumed was estimated from the change in the oxygen/nitrogen ratio. A correction was made for the small amount of nitrogen formed in the reaction.

In one experiment at 300°, during the first 13 mins. the oxygen consumed was 22 mm., while in the succeeding 32 mins. it was 152 mm. In a second experiment at the same temperature, 5 mm. of oxygen disappeared during the first 5 mins., and 137 mm. during the next 6·5 mins. In the two experiments, the pressure changes in the first periods were respectively 9 and 6% of the final value. These results indicate that the reaction velocity during the induction period is actually very much less than during the later stages of the reaction, and that the peculiar form of the pressure–time curve is not due to distortion by an initial oxidation process involving no change in the total number of molecules present.
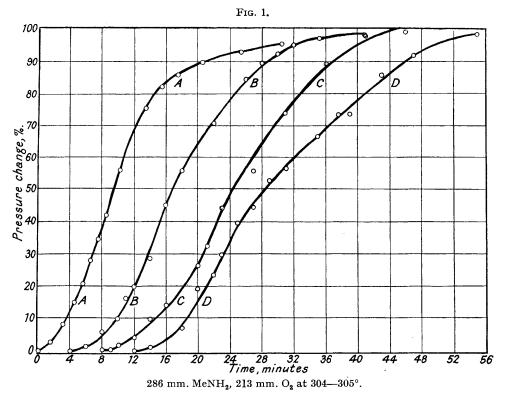
Kinetic Aspects of Methylamine Oxidation.—The effects of vessel dimensions, concentration of reactants, reaction temperature, and presence of foreign gases on the reaction velocity were studied, the course of the reaction being followed by pressure measurements. This procedure is only valid if the pressure change can be shown in all cases to be proportional to the oxygen consumed. It has already been shown that its validity is not affected by the existence of the induction period. In a series of runs in vessels of silica, pyrex, and soft glass, of diameters ranging from 3 to 9 cm., and at temperatures between 272° and 408°, the ratio of total pressure increase to pressure of oxygen consumed (measured in the reaction bulb at the reaction temperature) varied between 0·40 and 0·50 for initial methylamine : oxygen ratios ranging from 4 : 3 to 1 : 3·2. An exact proportionality is not to be expected from a reaction of such complexity, but the agreement is sufficiently close to admit of a semi-quantitative study of the effect of the

above controlling factors by the manometric method. Hinshelwood's method (*Proc. Roy. Soc.*, 1930, *A*, **129**, 284) of plotting pressure change as a percentage of its final value has been adopted.

Effect of surface/volume ratio of the reaction vessel. The curves in Fig. 1 show the pressure–time records of four runs in soda-glass bulbs of different diameters, in which all other controlling factors were as far as possible kept constant. The maximum velocity attained is seen to increase with the vessel diameter, and the times taken by corresponding fractions of the total pressure change show a parallel systematic decrease as the vessel diameter increases.

The effect of packing the vessel with fragments of soft-glass tubing 3 mm. in diameter was studied by comparing the reaction in a packed bulb with that in a similar empty bulb at the same temperature and initial pressure. The pressure–time curves show that the reaction is almost

FIG. 1.

286 mm. MeNH$_2$, 213 mm. O$_2$ at 304—305°.

Time (minutes) for fraction of pressure change : Bulb diam., A 53 mm., B 30 mm., C 20 mm., D 16 mm.

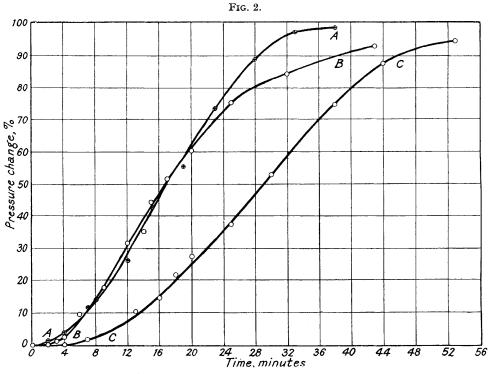|	A.	B.	C.	D.
20—60%	5·2	6·5	10·1	11·2
20—80%	9·4	12·3	15·4	19·8

completely inhibited in the packed bulb. Hence it appears that the effect of the vessel diameter becomes more marked as the diameter decreases. In another experiment, packed and unpacked bulbs were filled with a mixture containing a known proportion of nitrogen, and the rates of consumption of oxygen compared in identical conditions of temperature, initial pressure, and pre-treatment by determinations of the oxygen/nitrogen ratio. It was found that in a 150 c.c. pyrex bulb at 300°, the effect of packing was to reduce the rate of consumption of oxygen from 12 mm./min. to 0·24 mm./min.

Effect of concentration of reactants. In a series of runs the initial concentrations of the reactants were varied, the other conditions being kept constant. Fig. 2 shows pressure–time curves for three typical experiments in a bulb of 20·4 mm. diameter at 300°. Further typical results are given below, the time (*t*, in mins.) for the fraction 20—60% of the reaction being used as a measure of the reaction rate. Temp. 304—305°. Pressures in mm. (measured at the reaction temperature).

Bulb, 30 mm. diam.			Bulb, 20·4 mm. diam.			Bulb, 20·4 mm. diam.			Bulb, 53·0 mm. diam.		
$MeNH_2$.	O_2.	t.	$MeNH_2$.	O_2.	t.	$MeNH_2$.	O_2.	t.	$MeNH_2$.	O_2.	t.
290·0	217·0	7·0	285·0	213·0	9·4	285·0	213·0	9·4	286·0	213·0	5·2
145·0	217·0	10·3	145·0	217·0	15·4	286·0	107·0	10·6	286·0	107·0	4·0

From these results it appears that the effect of variation of methylamine concentration is more pronounced than that of oxygen concentration. The reaction velocity appears to be proportional to a power of the methylamine concentration lying between 1 and 2, and approximately to the first power of the oxygen concentration.

The Temperature Coefficient of the Reaction Velocity.—The effect of temperature was examined in a series of five runs at three different temperatures in a silica bulb 3 cm. in diameter, the same initial concentrations of the reactants being used in each case (172 mm. methylamine and 128 mm.

FIG. 2.

A. 213 mm. O_2, 285 mm. $MeNH_2$.   B. 107 mm. O_2, 286 mm. $MeNH_2$.   C. 217 mm. O_2, 145 mm. $MeNH_2$.

oxygen at 305°). The following figures are taken from the pressure–time curves obtained, and show the time in minutes taken by the given specific fractions of the total pressure change in each case.

Fraction, %.	Temp. 304—305°.			Temp. 343·5°.	Temp. 375·5°.
	Run A.	Run B.	Run C.	Run D.	Run E.
20—40	2·84	3·00	3·67	0·467	0·166
40—60	2·70	2·60	3·27	0·467	0·176
60—80	2·67	2·73	2·87	0·467	0·216

When the logarithm of the time for a given fraction is plotted against the reciprocal of the absolute temperature, the points obtained for each of the above fractions lie approximately on a straight line whose gradient corresponds to a heat of activation of about 30,000 cals.

Explosion Limits.—Many attempts were made to detect upper and lower explosion limits of the type characteristic of those reactions which involve a branching-chain mechanism, but no such limits were found. If the mechanism of the oxidation of methylamine be such as to render these phenomena possible, it may be that they only come into play in a region of temperature and pressure in which the normal slow reaction is too rapid to permit their detection.

The Ignition of Methylamine–Oxygen Mixtures.—If a mixture of a given composition is admitted into a bulb at a given temperature, the reaction follows the uniform course hitherto discussed provided that the initial pressure be less than a certain well-defined critical value. If this pressure is exceeded, ignition takes place after the normal slow oxidation has proceeded to a certain point. The character of the resulting explosion depends on the composition of the mixture; those containing more than 50% of methylamine give a faint, barely luminous flash accompanied by a large increase of pressure, while those containing less methylamine give a brilliant flash accompanied by a decrease of pressure. The transition between the two types of explosion occurs abruptly at an exactly equimolecular methylamine/oxygen ratio at all temperatures between 400° and 600°; no explosions of intermediate character have been observed.

It was at first supposed that the feeble flames of mixtures rich in methylamine might be analogous to the phosphorescent flames of ether, acetaldehyde, and some hydrocarbons. Unlike these, the temperature range in which methylamine–oxygen mixtures ignite is the same for both types of flame. If the feeble flames are due to a pure chain explosion (as distinct from a thermal explosion), the products may be expected to be of the same type alike in the slow reaction and in the explosion, since the slow reaction itself appears to have a chain mechanism. A series of analyses of the products of the explosion of methylamine-rich mixtures was therefore made.

Four experiments were carried out in a 150 c.c. pyrex bulb at 412°; in these conditions, the minimum initial pressure for ignition of the particular mixture used ($1\cdot14MeNH_2 : 1O_2$) is 190 mm. For comparison, the result of an initial experiment in which the pressure was less than 190 mm., so that only the slow reaction was involved, is placed first, the runs in which ignition took place following in order of increasing initial pressure.

Amounts of products are again referred to oxygen consumed as 100.

No.	Initial press., mm.	Press. rise before expn.	Press. rise in expn.	Products.				
				CO.	N_2.	H_2.	CH_4.	CO_2.
1	146·0 (no explosion)	38·0	—	13·4	17·4	4·4	1·4	10·1
2	206·0	50·0	53·0	41·8	19·6	74·8	1·6	—
3	260·0	38·5	147·5	84·6	50·8	163·7	3·6	—
4	288·5	37·5	187·5	90·0	56·6	183·5	3·4	15·7
5	296·7	39·8	197·5	92·5	54·1	195·0	2·7	15·6

A number of interesting facts emerge from these figures. First, it is evident that the incidence of ignition is accompanied by a marked change in the proportions of the products : notably a large quantity of hydrogen and greatly increased amounts of carbon monoxide and nitrogen. Also, as the initial pressure increases beyond the minimum value of 190 mm., ignition supervenes at a progressively earlier stage of the reaction, as may be seen from the variation of the pre-ignition rise of pressure. At the same time, there is a progressive increase in the fraction of the total combustion taking place *via* the reactions involved in the flame, as shown by the magnitude of the pressure rise in the explosion, which runs parallel with the increased formation of hydrogen, carbon monoxide, and nitrogen.

Hence it may be inferred that the explosion is a thermal one, and that its incidence depends on the attainment by the slow reaction of a critical speed at which heat is evolved by the system more rapidly than it can be lost to the walls, so that the temperature rises indefinitely. Presumably, at the elevated temperature of the flame there occurs a decomposition of some intermediate product which in the slow reaction disappears by oxidation. The fact that in runs 4 and 5 as much as 90% of the initial carbon and nitrogen present are accounted for in the products, enables certain conclusions to be drawn. The formation of hydrogen cannot be due to decomposition of methylamine, since this is known to occur mainly by the reaction $CH_3 \cdot NH_2 = HCN + 2H_2$, whereas very little hydrogen cyanide can actually be formed.

The total reaction involved in the explosion agrees well with the equation $2CH_3 \cdot NH_2 + O_2 = 2CO + N_2 + 5H_2 + 38$ Cals.; the assumption that all the hydrogen found is formed in this way is very well borne out by the figures quoted above if it is taken into account that the explosion is invariably preceded by a period of slow reaction.

Any further conclusions as to the mechanism of the ignition process do not appear to be justified by the data at present available, but a detailed study of the temperature coefficient of the limiting explosion pressure of amine–oxygen mixtures by Sagulin's method (*Z. physikal. Chem.*, 1928, *B*, **1**, 275) is now in progress.

The violent explosions of oxygen-rich mixtures are no doubt due to secondary ignition of the hydrogen formed in the reaction dealt with above.

Effect of Foreign Gases on Reaction Rate.—Many reactions for which chain mechanisms have been postulated are markedly accelerated by the admixture of inert gases, and in some cases are inhibited by small amounts of readily oxidisable substances. The effect of some foreign gases on the slow reaction was examined by comparing pressure–time curves in presence and in absence of inert gas. In one experiment, 2% of ethylene was added to the reaction mixture at 300°, and in another experiment at 300° the reaction mixture was saturated at 20° with the vapour of tetraethyl-lead. In neither case was the effect of addition of the foreign gas outside the normal limits of experimental error.

By using Sagulin's method (*loc. cit.*), the effect of addition of nitrogen on the minimum pressures at which methylamine–oxygen mixtures exploded at a series of temperatures was studied. The figures given below are taken from curves showing the relation between minimum explosion pressure (in mm.) and temperature.

	400°.	420°.	440°.	460°.	480°.
Press. for 4MeNH$_2$: 3O$_2$ mixture	548	318	202	131	87
„ „ „ „ in presence of 3N$_2$	547	316	200	130	86
Press. for 1MeNH$_2$: 1·82O$_2$ mixture	870	527	342	219	147
„ „ „ „ in presence of 2·82N$_2$	600	377	262	176	122

A lowering of the ignition pressure must be taken to indicate an acceleration of the slow reaction.

The same technique was used to study the effect of carbon dioxide, ethylene, and benzene vapour. In all these cases a small increase in the ignition pressure was produced by the foreign gas; this was probably a dilution effect. In the typical case of carbon dioxide, an increase of only 15% in the ignition pressure was produced by a partial pressure of carbon dioxide equal to six times the pressure of methylamine or of oxygen, which in this case were equal. These three added gases, therefore, do not produce either acceleration or inhibition.

DISCUSSION.

The thermal decomposition of methylamine proves to be a relatively simple process. At 550° two reactions are involved, the predominant one a dehydrogenation to hydrogen cyanide : $CH_3 \cdot NH_2 = HCN + 2H_2 - 37 \cdot 6$ Cals. The hydrogen formed is involved in a subsidiary reaction, whereby the amine is reduced : $CH_3 \cdot NH_2 + H_2 = CH_4 + NH_3 + 22 \cdot 6$ Cals. The latter reaction may occur in two stages, the methylamine decomposing either to methylene and ammonia or to free methyl and amino-radicals, with subsequent hydrogenation of the free radicals; the first alternative would be a parallel process to the thermal decomposition of methane (Belchetz, Faraday Society Discussion on " Free Radicals," 1933, p. 170) and of aldehydes (Bone and Smith, J., 1905, **87**, 910) :

$$\frac{H}{H}{>}CH_2 = CH_2 + H_2 ; \qquad \frac{R}{H}{>}CO = RH + CO ; \qquad \frac{H_2N}{H}{>}CH_2 = CH_2 + NH_3.$$

The speed of decomposition is, however, inappreciable at 300°, at which temperature the oxidation is rapid. Hence the initial stage of the oxidation cannot be a dissociation of the methylamine molecule. It must be a collision between integral molecules of methylamine and oxygen, and the question arises whether the collisions which initiate oxidation are bimolecular or termolecular. This can be decided from the connexion between the heat of activation and the reaction velocity at a given temperature, provided long chains be not involved. The rough value of the heat of activation deduced above from the temperature coefficient of the reaction velocity (30,000 cals.) indicates that the reaction should go at a measurable speed at about 250° if it is bimolecular; if it is termolecular it should not go at a measurable speed below about 520°. Actually the reaction rate becomes conveniently measurable at about 250°, justifying the assumption of a bimolecular initial process followed by a series of comparatively rapid reactions.

Further information about the nature of the initial process is given by the products of the reaction. These are (in the slow reaction) formaldehyde, carbon monoxide, hydrogen cyanide, carbon dioxide, and ammonia, and can be satisfactorily explained by assuming a

series of successive hydroxylations of the methyl group, similar to those postulated by Bone in hydrocarbon oxidation.

$$CH_3 \cdot NH_2 \longrightarrow CH_2(OH) \cdot NH_2 \longrightarrow CH(OH)_2 \cdot NH_2$$

$$CH_2O + NH_3 \qquad\qquad H_2O + CH{<}^{O}_{NH_2} \longrightarrow$$

$$\nearrow HCN + H_2O$$
$$\longrightarrow CO + NH_3$$
$$\searrow NH_2 \cdot CO_2H \longrightarrow CO_2 + NH_3$$

The intermediate products are assumed to be capable of undergoing either further oxidation or decomposition. The two alternative modes of decomposition assumed for formamide are both known to take place readily below 300° (Freer and Sherman, *Amer. Chem. J.*, 1898, **20**, 226). The amino-group appears to remain intact throughout the process. The observed formation of formaldehyde cannot arise directly from the interaction of a molecule of methylamine with both atoms of a molecule of oxygen in a binary collision, since this would give a product corresponding to the second hydroxylation stage (carbon monoxide or hydrogen cyanide). Hence the formation of formaldehyde must take place in more than one stage. A probable explanation appears to be that the initial binary process results in a complex $(CH_3 \cdot NH_2),O_2$, of unknown structure. This complex preserves its integrity until it suffers a collision with a second methylamine molecule, whereupon a binary process of low activation energy gives $2CH_2(OH) \cdot NH_2$, which can either lose ammonia to give formaldehyde, or be further oxidised. This is substantially the mechanism proposed by Hinshelwood for hydrocarbon oxidation.

It is significant that the single equation deduced for the explosive reaction, *viz.*, $2CH_3 \cdot NH_2 + O_2 = 2CO + 5H_2 + N_2$, also involves two molecules of methylamine per molecule of oxygen used.

The reaction has been shown to exhibit the essential characteristics of a chain reaction, *viz.*, retardation by an increase in the surface/volume ratio of the containing vessel, and a high apparent order of reaction. In particular, in every aspect of the reaction which has here been studied, the similarity to hydrocarbon oxidation is striking. It appears that methylamine oxidises as a derivative, not of ammonia, but of methane. If it be taken as established that a chain mechanism is involved, the question of the origin, nature, length, and termination of the reaction chains arises. Their origin is indicated above. The precise nature of the active substances which propagate them, and the process which leads to the regeneration of these substances at the completion of each cycle of the chain, cannot be decided from the available evidence. If the chains are broken exclusively at the walls of the vessel (which is approximately true if they are long), then according to Semenoff (*Z. physikal. Chem.*, 1929, **2**, B, 161) the reaction velocity should be proportional to the square of the vessel diameter. Actually the influence of the walls is much less than this, and inhibition does not become very marked until the effective vessel diameter is made less than 1 cm. It must be concluded that the chains are short, and terminate largely in the gas phase.

SUMMARY.

(1) The slow combustion of methylamine in oxygen is a homogeneous reaction between 250° and 600°, and gives a complex series of products, consisting mainly of formaldehyde, carbon monoxide, carbon dioxide, hydrogen cyanide, ammonia, and water.

(2) The reaction appears to proceed by a chain mechanism. It is retarded by an increase in the surface/volume ratio of the containing vessel. The reaction velocity is proportional to a power of the methylamine concentration between 1 and 2, and approximately to the first power of the oxygen concentration.

(3) Ignition takes place if the initial pressure of the reaction mixture exceeds a critical value which is determined mainly by the temperature of the system. The ignition is a thermal process, and gives rise to a set of products which differ markedly from those of the slow reaction.

(4) The reaction between methylamine and oxygen is invariably preceded by an induction period, during which oxidation proceeds at an abnormally slow rate.

(5) Thermal decomposition of methylamine becomes appreciable at 500°, and goes mainly by the reactions $CH_3 \cdot NH_2 = HCN + 2H_2$ and $CH_3 \cdot NH_2 + H_2 = CH_4 + NH_3$. These reactions do not take part in the oxidation process.