113. *The Kinetics of the Thermal Decomposition of the Methylamines.*

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The kinetics of the decomposition of the three methylamines has been followed by analytical methods. The complexity of the decomposition processes increases very materially as we pass from the tertiary to the primary amine, but marked similarities are observed in the case of the secondary and the tertiary amine. The tertiary amine yields as main products methane and methylmethyleneimine, small quantities of hydrogen and of ethane being also formed. The rate of formation of methane is diminished by packing the reaction tube, and is increased by the addition of helium. The x–t graphs are of unimolecular form, the value of E being 59 kg.-cals. The process may be represented by the equations

$$\begin{aligned} N(CH_3)_3 &= CH_3\cdot + N(CH_3)_2\cdot \\ CH_3\cdot + N(CH_3)_3 &= CH_4 + N(CH_3)_2\cdot CH_2\cdot \\ N(CH_3)_2\cdot CH_2\cdot &= CH_3\cdot + CH_3\cdot N{:}CH_2 \end{aligned}$$

Dimethylamine yields methane, methylmethyleneimine, and methylamine, together with a little hydrogen, and at 420—440° the rate of formation of methane is very close to that in the case of the trimethylamine, the temperature coefficient of the reaction having nearly the same value. The rate of formation of methane is retarded by packing the reaction tube. The process is obviously more complex than in the case of the tertiary amine, and is probably initiated by the formation of methyl radicals, and carried on by a chain mechanism as in the case of the tertiary amine. The alternative explanation that it is initiated by a bimolecular process resulting in the formation of mono- and tri-methylamine, the latter undergoing changes as indicated above, does not seem likely.

The primary amine only decomposes at a rate comparable with that of the secondary and the tertiary amine when the temperature is 100° higher. The decomposition process is even more complex than that of the secondary amine, and seems to proceed in three successive stages. The first involves the liberation of hydrogen, with the formation of a product less volatile than methylamine, which decomposes in successive stages, yielding first methane, and afterwards hydrogen cyanide. There is little positive evidence that free radicals take part in the decomposition process. If they do so, the reactions originate in the dissociation of methylamine into $CH_3\cdot NH\cdot$ and $H\cdot$, and not into $CH_3\cdot$ and $NH_2\cdot$.

The amines and ammonia fall into two well-marked groups, di- and tri-methylamine belonging to one, and methylamine and ammonia to the other. Our knowledge of this type of molecule is too slight to allow of speculation as to the causes of the difference in the behaviour of the two groups.

General Experimental Methods.—The methods of investigation were the same as those employed in a number of similar researches, the chemical changes being followed by analytical methods. The amines were obtained from the purified hydrochlorides, the solutions of which were run into an evacuated flask containing a concentrated solution of potassium hydroxide, and the vapour being passed through a long tower containing the solid alkali. The amines were then stored in sealed glass bulbs containing freshly ignited lime, and samples of methylamine, from which it was suspected that there was a difficulty in removing water, were stored in this way for some months. This treatment had no influence on the results of experiments. Methylamine was stored as a gas in glass tubes over mercury, and quantities were measured in a gas burette. The liquid secondary and tertiary amines were stored in bulbs containing also a little lime. The quantities introduced into the reaction tubes were measured in the apparatus described by Seddon and Travers (*Proc. Roy. Soc.*, 1936, *A*, **156**, 239). The usual precautions were taken to remove and exclude the smallest traces of oxygen. Combustion of the gases over copper oxide, and measurement of the carbon/nitrogen ratio was the ultimate check on purity. However, different fractions of the gases gave identical results, so far as the results can be said to be reproducible.

Measured quantities of the gases, sealed in silica reaction tubes, were heated for known periods, after which the tubes were chilled, and their contents analysed. Recently, the method has been criticised on the ground that there must be a lag in the heating of the tube, with a consequent error in the results. It may be pointed out that this error is only material when we consider the overall changes between 0° and $t°$, and is eliminated when, as is often the case, the changes in consecutive intervals are considered independently (cf. *J. Soc. Chem. Ind.*, 1934, **53**, 323T). In any case it is easy to apply a correction if one knows the approximate value of the temperature coefficient of the process, and the rate of heating of the reaction tube. This can be determined by sealing a long stem to it, introducing a thin wire thermo-junction before placing the tube in the furnace, and observing the rate of rise of temperature. In experiments such as ours, in which the temperatures are low, and the rates of change slow, the corrections are small. The lag in the process of chilling a tube under a spray is of the order of 10 seconds which, again, can be allowed for.

The methods of removing the gases from the reaction tubes, etc., have been fully described elsewhere.

The Thermal Decomposition of Trimethylamine.

Romeny (*Ber.*, 1878, **11**, 835) found that when trimethylamine was passed through a tube heated to dull redness a liquid product having the formula $(C_2H_5N)_2$ was formed, together with hydrocarbons, hydrogen cyanide, and ammonia. He concluded that the main reaction could be represented by the equation

$$(CH_3)_3N = CH_4 + C_2H_5N \quad . \quad . \quad . \quad . \quad (1)$$

the methylmethyleneimine afterwards polymerising. This conclusion is substantially correct. Recently, Rice and Johnston (*J. Amer. Chem. Soc.*, 1934, **56**, 214) passed the vapours of di- and tri-ethylamine through tubes heated to 1000°, and measured the rate of removal of standard mirrors of antimony, obtaining a measure of the concentration of the methyl radicals in the emergent gas streams. From the results they estimate the energy of activation of the rupture of the CH_3–N bond at 51—52 kg.-cals., that for the C–C bond, determined by the same method for hydrocarbons and other simple straight-chain compounds, being between 81 and 71 kg.-cals.

Experiments with Trimethylamine.—The experiments were carried out at temperatures between 380° and 440°, and in this range the reaction proceeded mainly in accordance with equation (1), representing the initial and final conditions, but some hydrogen and ethane were also formed. At 480° hydrogen cyanide could be detected in the products, but not at lower temperatures; at this temperature methylamine, if it were formed, would begin to decompose.

After removal of hydrogen and methane at − 180°, the excess of trimethylamine and ethane could also be removed by maintaining the reaction tube at −80°, and connecting it with a bulb cooled to − 180°. There then remained in the reaction tube a residue, part of which was volatile at room temperature. Both this and the non-volatile fraction had a composition approximating to C_2H_5N. By means of a series of rather complex operations, the volatile part of the residue was transferred to a glass tube, in which its volume at 184° could be measured. It was afterwards transferred to a silica apparatus, in which it was burned in oxygen. The non-volatile residue in the reaction tube was also burned with oxygen. From the results of two experiments the formula of the volatile residue was found to be $(C_{1\cdot95}H_{4\cdot9}N)_{0\cdot99}$ and $(C_{1\cdot9}H_{4\cdot75}N)_{1\cdot01}$. In the early stages of the reaction the proportion of volatile constituent in the residue predominates; the ratio volatile/non-volatile in the set of experiments in Table I, in which the initial concentration was 2434 × 10^{-5} g.-mol./l., was 1·25 after 15 minutes, but only 0·4 after 30 minutes. It is evident that the monomer is the first product of the reaction. The units in all the tables are mins. and g.-mol./l. × 10^5 (or g.-atom/l. × 10^5).

To determine the effect of change of concentration on the rate of formation of methane, the experiments of which the results are recorded in Table I were carried out. In these, the quantities of ethane formed were not measured (see p. 498). The results can be represented by equations of unimolecular form, the values of the resulting constants diminishing linearly with fall in initial concentration.

To determine the effect of temperature on the rate of formation of methane, a series of experiments was carried out at an initial concentration 1217 × 10^{-5} g.-mol./l. The results (see Table II) are again, in each case, reproducible by formulæ of unimolecular type. The mean values of the constants plotted against $1/T$ (Table III) give a straight line from which the value of 59 kg.-cals. is calculated for the conventional constant E. The quantities of hydrogen collected vary irregularly with time; and although it is possible that a process of an intermittent character may be operating, the data are insufficient to settle the point.

TABLE I.

Thermal decomposition of trimethylamine at 440°.

t.	CH_4.	H_2.	$k \times 10^3$.	*t.*	CH_4.	H_2.	$k \times 10^3$.
		Initial concn., 1217.	Time of half-change, 64 mins.				
26·5	278	5	9·78	86·5	738	18	10·76
56·5	517	9	10·02	116·5	885	24	11·20
						Mean	10·77
		Initial concn., 1805.	Time of half-change, 59 mins.				
26·5	455	6	11·24	86·5	1166	28	11·54
56·5	859	21	11·06	116·5	1370	51	12·22
						Mean	11·52
		Initial concn., 2434.	Time of half-change, 60 mins.				
11·5	299	5	11·40	56·5	1204	23	12·11
26·5	695	15	13·59	86·5	1729	42	14·05
41·5	1045	14	13·76			Mean	12·97

TABLE II.

Thermal decomposition of trimethylamine: Influence of temperature at initial concentration 1217.

	440°.			420°.			400°.			380°.		
t.	CH_4.	H_2.	$k \times 10^3$.	CH_4.	H_2.	$k \times 10^3$.	CH_4.	H_2.	$k \times 10^3$.	CH_4.	H_2.	$k \times 10^3$.
26·5	278	5	9·78	100	3	3·24	43	4	1·26	—	—	—
56·5	517	9	10·02	218	—	3·47	71	8	1·14	—	—	—
86·5	738	18	10·76	321	—	3·54	124	5	1·10	—	—	—
116·5	887	24	11·20	415	1	3·57	150	16	1·13	—	—	—
146·5	—	—	—	509	17	—	182	7	1·11	—	—	—
176·8	—	—	—	560	24	3·49	201	7	1·10	49	5	0·233
,,	—	—	—	537	18	—	—	—	—	—	—	—
206·5	—	—	—	—	—	—	236	19	1·10	—	—	—
221·5	—	—	—	654	21	—	—	—	—	—	—	—
236·5	—	—	—	—	—	—	304	12	1·11	—	—	—
266·5	—	—	—	772	26	3·52	—	—	—	68	4	0·220
296·5	—	—	—	—	—	—	338	27	1·09	—	—	—
356·5	—	—	—	882	18	3·90	—	—	—	99	4	0·238
386·5	—	—	—	—	—	—	425	10	1·10	—	—	—
416·5	—	—	—	—	—	—	—	—	—	108	4	0·221
476·5	—	—	—	—	—	—	525	15	1·10	145	17	0·264

TABLE III.

Thermal decomposition of trimethylamine: Variation of velocity constant with temperature. (*Initial concn.*, 1217.)

Temp.	440°	420°	400°	380°
$k \times 10^3$	10·44	3·53	1·114	0·235

Two series of experiments were carried out to test the effect of packing a reaction tube with silica rods, so as to reduce the volume by one-third, and to increase the surface 6-fold. The results of the first series, at 400°, are given in Table IV, and those of the second series, at 440°, which were carried out while investigating the rate of formation of ethane, are given in Table VI. Packing the tube diminishes the rate of formation of methane to a marked extent, but less at the higher than at the lower temperature.

TABLE IV.

Thermal decomposition of trimethylamine: Effect of packing the reaction tube at 400° *and initial concentration* 1217.

	Packed tube.		Empty tube.	
t.	CH_4.	H_2.	CH_4.	H_2.
116·5	98	16	50	16
236·5	183	26	304	12
386·5	289	30	425	10

(See also Table VI.)

The results of experiments on the effect of addition of helium, which always increased the rate of formation of methane, are given in Table V.

TABLE V.

Thermal decomposition of trimethylamine: Influence of helium on the rates of change at 400° *and initial concentration* 1217.

	Empty tube.				Packed tube.		
t.	He.	CH_4, with He.	CH_4, no He.	*t*.	He.	CH_4, with He.	CH_4, no He.
116·5	1637	189	150	236·5	1950	263	183
236·5	2864	336	304	386·5	1789	334	289
386·5	1504	519	425				
386·8	3204	471	425				

The investigation of the formation of ethane was an afterthought, and was the subject of a separate set of experiments. After removal of hydrogen and methane from the reaction tubes, the contents, at room temperature, were allowed to distil into a tube, fitted with a stopcock, which was cooled to — 180° and contained a little oxalic acid and a few drops of water. The stopcock was then closed, and the receiving tube allowed to attain room temperature, after which it was again cooled to — 80°, and the ethane was pumped off. The results of the experiments are given in Table VI and in Fig. 1.

TABLE VI.

Thermal decomposition of trimethylamine: Rate of formation of ethane at 440°.

Tube.	Initial amine.	*t*.	CH_4.	H_2.	C_2H_6.	$d[C_2H_6]/d[CH_4]$.
Empty	2434	56·5	1334	43	57	—
,,	,,	86·5	1791	67	125	0·15
,,	,,	116·5	2129	86	180	0·16
,,	,,	146·5	2271	176	206	0·17
,,	,,	191·5	2288	102	220	0·13
,,	,,	236·5	2605	111	252	0·13
Packed	,,	56·5	1212	51	47	—
,,	,,	116·5	1894	102	123	0·09
,,	,,	236·5	2511	106	180	0·11
Empty	1217	116·5	850	34	48	—
,,	,,	176·5	1058	49	79	—
Packed	,,	116·5	545	28	26	—
,,	,,	176·8	703	46	48	—

Discussion of Results of Experiments with Trimethylamine.—The analytical data, and the results of the vapour density of the volatile product of the reaction, confirm the view that the thermochemical decomposition of the compound is represented stoicheiometrically by equation (1). The slowing down of the rate of reaction by packing the reaction tube, and the acceleration by addition of helium suggest a chain mechanism. The most obvious explanation complying with this condition may be represented by the equations,

$$(CH_3)_3N = CH_3\cdot + (CH_3)_2N\cdot \quad . \quad . \quad . \quad . \quad (2)$$

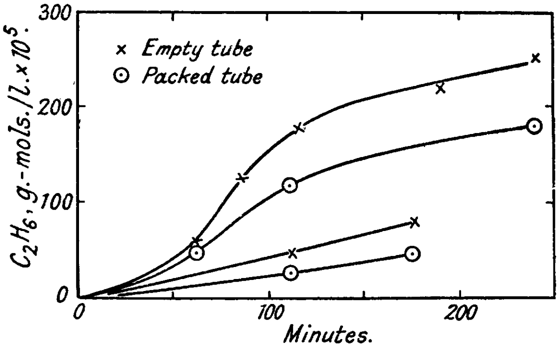
$$(CH_3)_3N + CH_3\cdot = CH_4 + \cdot CH_2\cdot N(CH_3)_2 \quad . \quad . \quad . \quad (3)$$

$$\cdot CH_2\cdot N(CH_3)_2 = CH_3\cdot + CH_3\cdot N{:}CH_2 \quad . \quad . \quad . \quad (4)$$

The methyl radicals are the chain carriers. The chains appear to originate in the gas phase, and to be broken at the surface. Changes involving the $(CH_3)_2N\cdot$ radicals, and the methyl radicals, which disappear when the chains are broken at the surface, would not be observable.

The reaction rates are very exactly represented by formulæ of unimolecular type, the constants in the series at 440° diminishing linearly with concentration. However, the rates of reaction were not studied at pressures low enough to indicate whether they showed a sudden drop at low pressures, such as a current theory of unimolecular processes suggests.

FIG. 1.



The unimolecular type of formula may indicate that the time-determining step in a process involves the decomposition of single molecules, or merely that the overall change is a very complex one, and we have at present no means of deciding whether processes, such as those under consideration, belong to one class or to the other.

The curious similarity in the behaviour of di- and tri-methylamines, and the dissimilarity between them and the monoamine will be referred to later (p. **501**).

It does not seem likely that the ethane is the product of union of pairs of methyl radicals. The form of the x–t graphs suggests that the production rate is initially zero, indicating that the process is, at least partially, a secondary one, involving some substance, such as methylmethyleneimine, of which the concentration is zero initially. The S-shape of the graphs suggests that the concentration of some reactant diminishes towards the end of the process. It is possible therefore that the ethane is formed by a reaction involving methyl radicals and methylmethyleneimine.

The only significant fact regarding the formation of hydrogen is that the non-volatile product contains less hydrogen than corresponds to the formula C_2H_5N. There is no indication of a mechanism.

The Thermal Decomposition of Dimethylamine.

Using the pressure-difference method of measuring the rate of chemical change, Taylor (*J. Physical Chem.*, 1932, **36**, 1960) investigated this process. His experimental results could be represented by a series of equations of unimolecular form over a temperature range 480—500°, and he obtained the value 44 kg.-cals. for E. He concluded " that the simplicity of the decomposition is illusory, due to the mutual compensation of several concurrent reactions," and suggested that methylhydrazine was formed at lower temperatures, and more complex compounds at higher temperatures, the gaseous products being hydrogen, methane, and ethane.

Our own experiments carried out at 420° and 440°, appeared to indicate that the decomposition process was represented by the equations

$$2NH(CH_3)_2 = N(CH_3)_3 + CH_3{\cdot}NH_2 \quad . \quad . \quad . \quad (5)$$
$$N(CH_3)_3 = CH_4 + CH_3{\cdot}N{:}CH_2 \quad . \quad . \quad . \quad (6)$$

a result which led us to investigate the thermal decomposition of the tertiary amine. The results suggest that these equations do not represent the changes taking place.

Experiments with Dimethylamine.—The procedure was exactly the same as in the case of trimethylamine. The contents of the reaction tube volatile at — 180° consisted of hydrogen and methane. After these had been pumped off, the tube was heated to — 80°, and connected to a tube cooled to — 180°. The residue then remaining was burned with oxygen to determine its composition, that of the volatile fraction being obtained by difference. The results of experiments with an empty tube and with a packed tube at 420°, and with an empty tube at 440°, are given in Table VII.

TABLE VII.

Thermal decomposition of dimethylamine at initial concentration 2283.

			Non-volatile residue remaining in reaction tube.				Volatile residue.
t.	CH_4.	H_2.	C.	H.	N.	Formula.	Formula.
			Empty tube, 420°.				
11·5	92	6	198	707	111	C_2H_7N	C_2H_7N
19	203	20	513	1726	276	C_2H_7N	C_2H_7N
22·75	247	18	755	2046	433	$C_2H_{5\cdot5}N$	C_2H_7N
26·5	217	16	782	2268	389	C_2H_6N	$C_{1\cdot9}H_7N$
41·5	359	37	848	2355	516	$C_2H_{5\cdot5}N$	$C_{1\cdot9}H_{5\cdot5}N$
49	423	57	1011	2748	528	$C_2H_{5\cdot5}N$	$C_{1\cdot9}H_{6\cdot7}N$
56·5	482	32	1149	3119	626	$C_2H_{5\cdot5}N$	$C_{1\cdot7}H_{6\cdot6}N$
86·5	516	109	1425	3864	793	C_2H_5N	$C_{1\cdot8}H_{6\cdot5}N$
116·5	753	58	1572	3784	869	C_2H_4N	$C_{1\cdot6}H_{6\cdot5}N$
296·5	1178	123	1974	4121	991	C_2H_4N	$C_{1\cdot25}H_6N$
			Packed tube, 420°.				
56·5	86	102	329	1044	187	$C_{1\cdot75}H_{5\cdot5}N$	—
86·5	134	101	470	1391	238	C_2H_6N	—
116·5	184	138	538	1414	257	$C_2H_{5\cdot5}N$	—
			Empty tube, 440°.				
26·5	573	39	—	—	—	—	—
56·5	949	102	1627	3483	722	C_2H_5N	$C_{1\cdot3}H_{5\cdot5}N$
86·5	1153	127	2058	4812	1014	C_2H_5N	$C_{1\cdot1}H_5N$
116·5	1308	149	1926	3954	1052	C_2H_4N	$C_{1\cdot1}H_{5\cdot5}N$
176·5	1547	190	2058	4261	1121	C_2H_4N	$C_{0\cdot9}H_{4\cdot5}N$

Discussion on the Results of the Experiments with Dimethylamine.—The composition of the non-volatile residue should correspond to that of methylmethyleneimine, C_2H_5N. It does so, except in the case of the first experiments in the first series, where the quantity is small, and in the last experiments of each series, where the hydrogen content is low. The latter result is probably due to the formation of hydrogen by the decomposition of the polymeric compound. It must be pointed out that the very prolonged experiments with the empty tube, particularly at 440°, indicate a side reaction giving more methane than corresponds to the stoicheiometric relationship represented by equations (5) and (6). Such complicating side-reactions become more and more obvious as we pass down the series from the tertiary to the primary amine. Since they apparently become more active, relatively to the main process, at the higher temperatures, any future experiments should be carried out at temperatures not higher than 420°.

The volatile residue approaches ultimately to the composition CH_5N, that of methylamine, but at intermediate stages it must contain excess of undecomposed secondary amine, with the primary amine, and possibly the tertiary amine, though there is actually no evidence that the last compound is formed. It is impossible to deal with it analytically.

Actually, it would not be worth while following the decomposition of the dimethylamine further, unless one could determine the rate of formation of monomethylamine, and so study the rate of the process by which it is formed.

For the purpose of determining the influence of packing the tube on the decomposition process, the data relating to the formation of methane can be plotted, and they are found to be nearly linear initially. The rate of formation of methane in the empty tube is between 5 and 6 times that in the packed tube. The effect is considerably greater than in the case of trimethylamine.

The experiments on dimethylamine bring out an interesting point, *viz.*, the similarity between the behaviour of the secondary and the tertiary amine on thermal decomposition, and their dissimilarity to the primary amine. The data are insufficient to give an accurate measure of the rates of formation of methane from dimethylamine, but by comparing the amounts of methane formed at 420° and 440°, in 26·5 minutes, and assuming that both processes are unimolecular in form (Tables II and VII), we obtain the following result. The rate for the secondary amine is 1·16 times faster at 420°, and 1·09 times faster at 440°, than that for the tertiary amine, and the temperature coefficient of the former reaction is 1·06 greater than that of the latter, giving 56 kg.-cals. as an approximate value for E for the formation of methane from dimethylamine.

As evidence that the decomposition of dimethylamine is initiated by the formation of free methyl radicals we have the identity of the rate of this process with that of the decomposition of trimethylamine, and of the values of E for the two processes. The results of the experiments of Rice and Johnson (see p. 496) on the formation of free methyl radicals from the two amines at higher temperatures support this conclusion. It must, however, be assumed that the compound $CH_2{:}NH$, which has not been detected in the products of reaction, is formed as an intermediate, so that it must react with the dimethylamine, yielding methylamine and methylmethyleneimine. It has been suggested that a similar change takes place as a second step in the decomposition of methylamine.

The Thermal Decomposition of Methylamine.

In 1886 Müller (*Bull. Soc. chim.*, **45**, 439) showed that the decomposition products at 1200° were ammonia, hydrogen cyanide, methane and hydrogen. In 1930 Hurd and Carnahan (*J. Amer. Chem. Soc.*, **52**, 4151) suggested that the primary amines were first dehydrogenated on heating, forming methyleneimines, and that these compounds then lost hydrogen, forming nitriles. Taylor and his co-workers (*J. Physical Chem.*, 1930, **34**, 2761; 1932, **36**, 670, 1960) attempted to follow the decomposition of the higher amines by the pressure-difference method. They concluded that the processes were unimolecular, the value for E being 40—45 kg.-cals. Sickman and Rice (*J. Amer. Chem. Soc.*, 1935, **57**, 22) measured the rates of change of pressure when propylamine was heated between 500° and 540°. They say that " no satisfactory explanation of the course of the reaction can be offered," but the process had some of the characteristics of a chain reaction, particularly with regard to the packing of the reaction tube, which retarded the reaction, and the presence of inert gases, which accelerated it. Jolley's experiments on methylamine (J., 1934, 1957) appeared to show that the decomposition process took place in two stages, represented by the equation

$$CH_3{\cdot}NH_2 = 2H_2 + HCN \quad . \quad . \quad . \quad . \quad . \quad (7)$$
$$CH_3{\cdot}NH_2 + H_2 = CH_4 + NH_3 \quad . \quad . \quad . \quad . \quad (8)$$

This investigation was followed up by Emeléus and Jolley (J., 1935, 929), who measured the rate of change of pressure in their apparatus, and analysed the end products. They experienced great difficulty in obtaining reproducible results, but suggested that there were actually two processes as above, the first being unimolecular and largely homogeneous, and the second heterogeneous. Both were initiated by the dissociation of the amine into free radicals.

Experiments with Methylamine.—Three separate investigations on methylamine were carried out. In the first two it was assumed that, since the facts discovered by Jolley and represented by equation (7) and (8) are correct for experiments in which a substantial proportion of the amine is decomposed, the course of the process could be followed by measuring the rates of formation of hydrogen and methane. The rate of process (7) is thus given by the quantities $\frac{1}{2}[H_2 + CH_4]$ for different time intervals, and that of process (8) by the quantities $[CH_4]$. It was found that the apparent rate of process (7) was always a little faster than that of process (8), but the two rates were generally so closely identical as to suggest some closer relationship than that indicated by Emeléus and Jolley. However, as we experienced great difficulty in obtaining reproducible results, a second investigation was undertaken to ascertain the cause of the difficulty, and to see whether it could be attributed to impurities in the amine. Finally, a few experiments were carried out on the changes taking place during the early stages of the decomposition process.

It must be pointed out that although the secondary and the tertiary amine decompose easily, and at about the same rate, at temperatures below 440°, the decomposition of the primary amine becomes just apparent at 440° and only reaches the rate corresponding to that of the two higher amines at about 540°. Also, surface effects, probably involving catalysis, seem to control the main changes in the case of the primary amine, but they are hardly material in those of di- and tri-methylamine.

A series of experiments from the second investigation will first be described. In these, two silica reaction tubes were used. Tube A_1 had a capacity of 58·7 c.c., but it was broken after the first set of experiments, and, after resealing, it became A_2 with a capacity of 41·5 c.c. Tube B had a capacity of 58·0 c.c. Different fractions from a large quantity of the amine were used. The results are set down in Table VIII.

TABLE VIII.

Thermal decomposition of methylamine in different reaction tubes at 530° and initial concentration 2000.

t.	Tube, etc.	H_2.	CH_4.	$\frac{1}{2}[CH_4+H_2]$.	*t*.	Tube, etc.	H_2.	CH_4.	$\frac{1}{2}[CH_4+H_2]$.
13	(1)	57	17	37	83	(1)	525	535	530
15	(2)	81	25	53	83	(2)	562	584	573
23	(2)	160	80	120	83	(3)	427	233	330
33	(1)	207	149	178	83	(4)	525	309	417
33	(3)	179	69	124	90·5	(2)	581	621	601
33	(4)	179	69	124	98	(2)	582	681	631
43	(2)	242	182	212	105·5	(2)	634	686	660
53	(1)	369	243	306	109	(2)	646	686	675
53	(2)	330	300	315	113	(3)	538	337	480
53	(3)	298	140	219	113	(4)	646	350	498
53	(4)	239	197	218	117	(2)	688	748	718
68	(1)	471	381	426	120·5	(2)	732	732	732
68	(2)	389	395	392	233	(3)	785	419	602
75·5	(2)	514	508	511	253	(3)	947	567	757

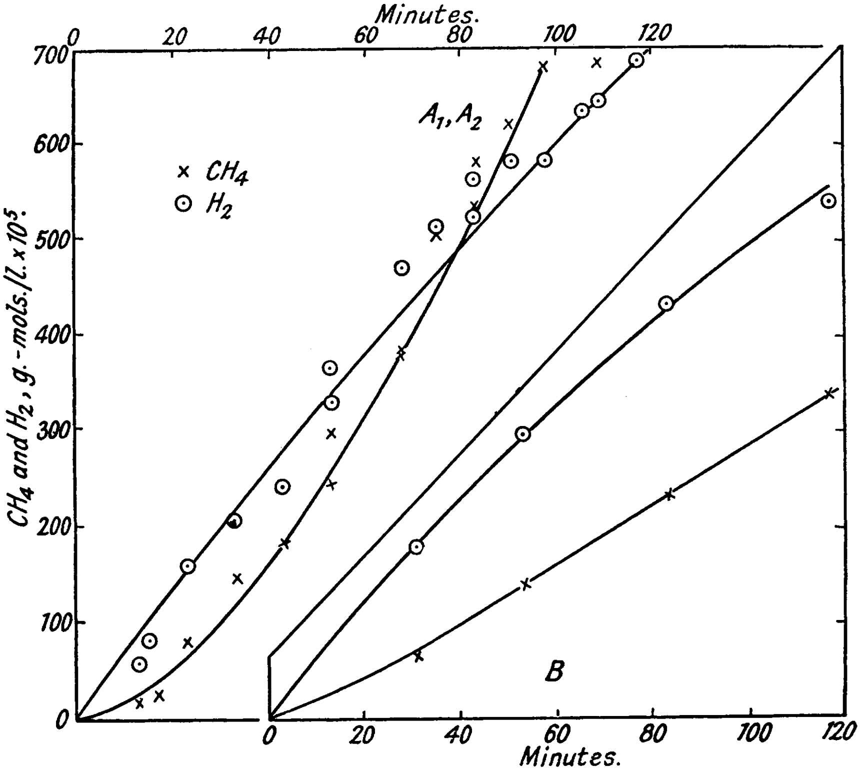
(1) Tube A_1. Gas fraction I.
(2) Tube A_2. Gas fraction VI.
(3) Tube B. Gas fraction VI.
(4) Tube B. Gas fraction VI.

An interesting fact is that, although the results obtained with tube A were sensibly identical before and after a repair involving melting and resealing the silica glass, yet those with tube B were quite different, and also this tube seemed to undergo some change in the course of the second set of experiments, the results obtained after the first experiment in the second series differing from those obtained in the first series. This was, unfortunately, a common experience.

The results show that the quantities represented by CH_4 and $\frac{1}{2}[CH_4 + H_2]$ for intervals 0 to *t* minutes seem to approach equality after a short time, and this may give the impression that, if these quantities represent the methylamine transformed according to equations (7) and (8), the processes which these equations represent are proceeding at the same rate. Alternatively, if we examine the rates of formation of hydrogen and of methane independently, it is clear that the former is rapid at first, and then tends to fall off, being approximately unimolecular in form, whereas the latter is slow at first and then shows acceleration over a considerable period, after which it slows down rather suddenly. This, again, might be taken as indicating that the reactions represented by equations (7) and (8) are consecutive processes, the reduction of methylamine by hydrogen increasing in rate with the hydrogen concentration, and later diminishing with the concentration of the methylamine. We return to this point on p. 504.

For the moment, it suffices to point out that both sets of graphs shown in Fig. 2 show similarity, which is also shown by the results of a set of experiments, taken from the first investigation, in which the rates of formation of hydrogen and methane were measured at 550° and at initial concentrations, *viz.*, 500, 1000, 2000, and 3000 g.-mols./l. × 10^5. The rates of formation of methane and of hydrogen are plotted in Fig. 3, A and B. No graph is drawn

FIG. 2.



through the points belonging to the series at the highest concentration, as they are insufficiently numerous for the shorter time intervals. However, the results show the common

TABLE IX.

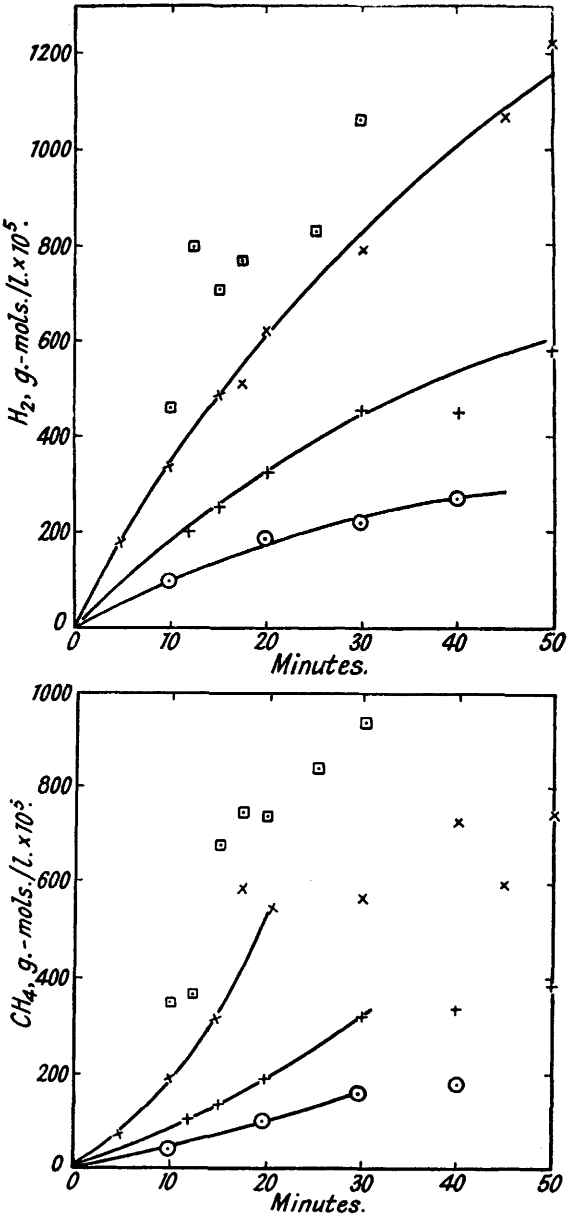
Thermal decomposition of methylamine: Influence of hydrogen at 550° *and initial concentration* 2000.

	Without hydrogen.			Initial hydrogen = 1900.		
t.	H_2.	CH_4.	½[$CH_4 + H_2$].	H_2.	CH_4.	½[$CH_4 + H_2$].
3	150	60	105	190	60	125
5·5	210	70	140	—	—	—
8	330	110	220	300	110	210
13	390	180	285	310	210	260
15·5	770	220	345	—	—	—
18	540	260	400	390	220	305
20·5	570	300	435	—	—	—
23	520	520	520	440	290	365
23·75	580	440	510	—	—	—
24·5	720	530	640	—	—	—
25·5	720	560	640	—	—	—
28	700	540	620	550	350	450
33	—	—	—	640	630	635
34	720	600	660	—	—	—
35·5	—	—	—	630	670	650
38·5	—	—	—	710	680	695
43	—	—	—	610	710	660

characteristics for the rates of formation of hydrogen and methane, which have already been referred to.

It was difficult to obtain reproducible results at any single temperature, but change of temperature of experiment was always followed by erratic behaviour of a reaction tube. Also, on returning to the original temperature, the results first obtained were generally not reproduced. We can, therefore, only give an estimate of the value of E, based upon the results of a large number of observations. It is not large, being probably about 45 kg.-cals.—it is certainly very much lower than the values obtained in the case of tri- and di-methylamine.

Figs. 3A and 3B.

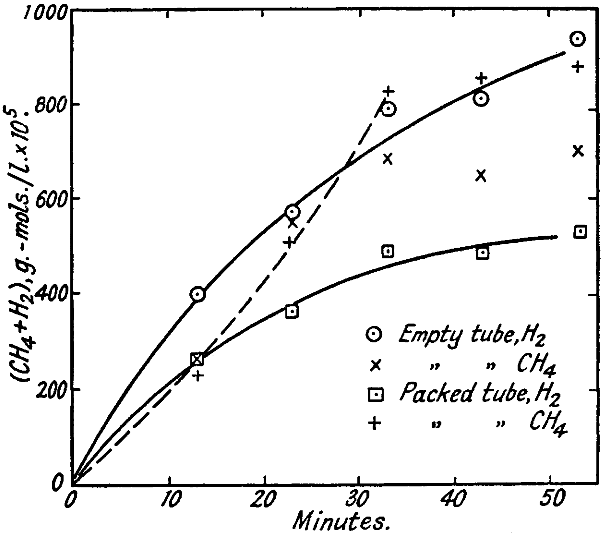


Experiments were carried out at 550° (Table IX) to determine the effect of hydrogen on the decomposition process, a mixture of approximately equal volumes of hydrogen and the amine being used. The results are somewhat irregular, but are sufficiently numerous to show quite clearly that the effect on the rate of formation of methane is almost negligible and the rate of formation of hydrogen is slightly reduced. If the methane were a product of the reduction of the amine by hydrogen, one would expect the effect on the rate of production to be considerable.

The effect of packing a reaction tube was also the subject of experiments at 550°. The results are plotted in Fig. 4. The effect is to lower the rate of formation of hydrogen; and though the results are not as regular as might be desired, the conclusion is obvious. The rate of formation of methane is practically unchanged for the shorter intervals, but the position of the break point is slightly different in the packed and in the empty tube.

The experiments carried to this point suggest that methane is not a product of the reaction of hydrogen with methylamine, but is a decomposition product of a compound formed simultaneously with hydrogen. To test this hypothesis the third investigation was undertaken, and a few experiments to which reference has been made elsewhere (*Trans. Faraday Soc.*, 1937, **33**, 1) were carried out at 520° and at an initial concentration of 2650 g.-mols./l. × 10^5. They showed that, although hydrogen and methane appear in the products of decomposition for the shortest time intervals, hydrogen cyanide does not, being formed at a much slower rate than the methane. It was also found that when methylamine was heated for a short time, after removal from the reaction tube of the contents volatile at and below − 80°, a non-volatile residue remained, which yielded methane, hydrogen cyanide and ammonia when reheated to 520°. The experiments were difficult, and it has not been possible to carry them beyond the preliminary stage.

FIG. 4.



Discussion on the Experiments with Methylamine, and General Conclusions.—The experimental results show that the thermal decomposition of methylamine is initiated by a surface reaction, the gaseous product of which is hydrogen. It probably takes place in three stages, which may possibly be represented by the equations

$$2CH_3{\cdot}NH_2 = H_2 + \text{Product 1} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\text{Product 1} = CH_4 + \text{Product 2} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\text{Product 2} = HCN + \ ? \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Ammonia is certainly a product of some stage. The evidence that the process is initiated by free radicals, or, indeed, that they play any part in it is slight, and consists in the fact that packing a reaction tube slightly reduces the rate of formation of hydrogen. The effect of addition of hydrogen is analogous to that observed in the experiments of

Hinshelwood and Burk (J., 1925, **127**, 1105, 2896), and may be due to the reduction of the active surface of the silica. If free radicals are formed it is probably by a process represented by

$$CH_3{\cdot}NH_2 = CH_3{\cdot}NH{\cdot} + H{\cdot} \qquad . \quad . \quad . \quad . \quad . \quad (12)$$

and not by the formation of free methyl and amino-radicals

$$CH_3{\cdot}NH_2 = CH_3{\cdot} + NH_2{\cdot} \qquad . \quad . \quad . \quad . \quad . \quad (13)$$

Though the former may account for the formation of hydrogen as a primary process, the apparent low value of E does not support the idea. The results summarised above suggest that, by a primary step in the reaction taking place at the surface, the compound $CH_2{:}NH$ is formed, and that at a later stage, a bimolecular reaction, possibly involving $CH_2{:}NH$ and $CH_3{\cdot}NH_2$, operates.

The great difficulty in following the changes is due to the fact that the primary step is strongly influenced by surface, which makes it difficult to obtain reproducible results.

One interesting outcome of this investigation is the discovery of the very marked difference in the behaviour of the primary amine, which is possibly related to that of ammonia on the one hand, and of the secondary and the tertiary amine on the other, which seems to suggest that the C–N bond energy has a much lower value for two or three C–N bonds than for one only. There seems to be very little doubt that the decomposition of the secondary and the tertiary amine is initiated by the formation of free methyl radicals, and that the process is carried on by a chain mechanism. A simple mechanism has been suggested to account for the decomposition of the tertiary amine, but in the case of the secondary amine, which is certainly more complex, for methylamine is a product of decomposition, as well as methane and methylmethyleneimine, no explanation can be offered.

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[*Received, January 11th*, 1939.]