211. *Kinetics of the Thermal Decomposition of Methylamine.*

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METHYLAMINE decomposes at 500—550° into a relatively simple series of products (Jolley, J., 1934, 1957). The main process is a dehydrogenation, $CH_3 \cdot NH_2 = HCN + 2H_2$, but a secondary hydrogenation takes place to a much smaller extent, yielding methane and ammonia : $CH_3 \cdot NH_2 + H_2 = CH_4 + NH_3$. The object of the present investigation was to examine the kinetics of these two reactions and to compare the pyrolysis of methylamine with that of other aliphatic amines.

Müller (*Bull. Soc. chim.*, 1886, **45**, 439) found that the products of decomposition of methylamine at 1200° were ammonia, hydrogen cyanide, methane, hydrogen, and nitrogen. Other previous work on the decomposition of aliphatic amines has been restricted to ethyl-, *n*- and *iso*-propyl-, dimethyl-, and benzyl-amine, and has resulted in contradictory conclusions. For instance, Upson and Sands (*J. Amer. Chem. Soc.*, 1922, **44**, 2306) found that ethylamine and *n*-propylamine when passed over kaolin at 500—1000° gave nitriles, saturated and unsaturated hydrocarbons, ammonia, and hydrogen; they considered that, in addition to dehydrogenation of the amine to the nitrile, a dissociation into an alkylidene radical and ammonia occurred ($R \cdot CH_2 \cdot NH_2 \longrightarrow R \cdot CH \colon + NH_3$). This conclusion was criticised by Hurd and Carnahan (*ibid.*, 1930, **52**, 4151), who worked with ethylamine and benzylamine, and regarded the first step as the formation of an aldimide ($R \cdot CH_2 \cdot NH_2 \longrightarrow R \cdot CH \colon NH + H_2$), which underwent further dehydrogenation to nitrile; they found that olefin formation took place to only a small extent, and that there was some evidence of hydrogenation ($R \cdot NH_2 + H_2 = RH + NH_3$). The decomposition of ethyl-,

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dimethyl-, and *n*- and *iso*-propylamine was followed manometrically by H. A. Taylor and his co-workers (*J. Physical Chem.*, 1930, **34**, 2761; 1931, **35**, 2568; 1932, **36**, 670, 1960), who assumed from the observed doubling of the initial pressure, except in the case of dimethylamine, that an olefin and ammonia were formed (*e.g.*, $C_2H_5 \cdot NH_2 = C_2H_4 + NH_3$). These reactions were believed to be homogeneous and unimolecular, with energies of activation in each case between 40,000 and 45,000 g.-cals. The unimolecular constant fell off at lower pressures, as predicted by the theory of collisional activation in unimolecular reactions. In his work on dimethylamine, Taylor showed the reaction to be more complex than had been supposed. Schumacher and Wiig (*Z. physikal. Chem.*, 1932, *A*, **162**, 419) were unable to confirm his conclusions on the decomposition of ethylamine, or, indeed, to detect the formation of ethylene in this reaction. These authors, and also Rice and Sickman working on propylamine (*J. Amer. Chem. Soc.*, 1935, **57**, 22), showed that at lower pressures the decomposition of these amines has some of the characteristics of a chain reaction, notably an influence of the extent of surface of the reaction vessel, and of the presence of inert gases, on the reaction rate.

The observations on methylamine described below began with a series of experiments to verify the reaction mechanism. The effect of surface was next studied by using a packed reaction vessel, and it was found that the hydrogenation reaction was heterogeneous and the dehydrogenation was mainly homogeneous. Finally, the dependence of the reaction rate on the concentration of reactants, on the temperature, and on the presence of the products of the reaction and of added hydrogen was studied.

<div align="center">Experimental.</div>

Methylamine, prepared by dropping a saturated solution of its hydrochloride on solid potash, was dried with quicklime and fractionated in a vacuum by distillation at 3—5 mm. and rejection of large head and tail fractions. The purity of the middle fraction was checked by vapour-pressure measurements, which agreed closely with the standard values (Landolt–Börnstein, " Tabellen "). The middle fraction was stored in a 3-litre globe. Hydrogen was taken from a cylinder and purified by passage over 10% palladised asbestos at 250°. It was dried with phosphoric oxide and stored in a globe. The reaction system consisted of a bulb, connected by 40 cm. of 1-mm. capillary tubing to a constant-volume mercury manometer, the storage vessels for reactants, a mercury diffusion pump, and a Töpler pump for delivering gases into a Bone and Wheeler gas analysis apparatus. Four reaction bulbs were used : (*a*) a 200-c.c. Pyrex bulb; (*b*) a similar bulb uniformly packed with Pyrex tubing to give an 8-fold increase in surface; (*c*) a 200-c.c. quartz bulb; (*d*) a quartz bulb of the same dimensions, uniformly packed throughout its volume with irregular pieces of quartz. Corrections were applied throughout the investigation for the dead space in the reaction system, which amounted to 1·5% of the total volume.

The furnace was the same as that used by Jolley (*loc. cit.*), but two additional coaxial iron pots were introduced into it to increase the uniformity of temperature. Temperatures were measured with a calibrated platinum resistance thermometer and a calibrated Callendar and Griffiths bridge, which gave readings to 0·1°. The furnace temperature was constant during a run to ± 0·5°. The pre-treatment of the reaction vessels consisted in 1—2 hours' heating at 100° with concentrated nitric acid, washing with water, drying and baking in a high vacuum, which was tested with a McLeod gauge permanently connected in the set-up.

General Course of the Reaction.—Preliminary analyses of the decomposition products of methylamine have already been recorded (Jolley, *loc. cit.*). It was necessary, however, to establish that the two reactions (*a*) $CH_3 \cdot NH_2 = HCN + 2H_2$ and (*b*) $CH_3 \cdot NH_2 + H_2 = CH_4 + NH_3$ will account for the products under the more varied conditions used in the present investigation. Since reaction (*b*) occurs without pressure change, the pressure of hydrogen cyanide present at any instant should equal half the pressure increase in the decomposition up to that point. The following confirmatory data were obtained by stopping four experiments in Pyrex bulbs at 543° at different stages. The initial methylamine pressure in each case was 350 mm. The cyanide present was determined by Volhard's method with 0·1*N*-silver and thiocyanate solutions.

Δp in reaction (mm.)	168	287	365	451
$2 \times p_{HCN}$ (mm.)	136	278	350	458

A further criterion for the correctness of the above reaction scheme is that at the completion of the reaction the sum of the pressure of methane formed (p_{CH_4}) and half the observed pressure increase in the reaction (Δp) should equal the initial methylamine pressure. In an experiment at 620° in the unpacked quartz bulb, Δp was 180% of the initial pressure (p_i) and p_{CH_4} was 9% of p_i; in another experiment in a packed quartz bulb at 593°, Δp and p_{CH_4} were 80% and 50% respectively of p_i. Agreement in a large number of other experiments under widely varied conditions was of the same order, *viz.*, within 10%.

A third criterion which should be satisfied is that in the completed reaction the gas formed which is condensable in liquid air should have a pressure equal to that of the methylamine taken. This was tested in four experiments in the packed bulb, and the condensable gas pressure had a mean value of 93% of the methylamine pressure. The agreement found in these three tests was considered to justify the use of equations (*a*) and (*b*) as representing the two main reactions. The fact that the analytical data do not give an exact check must mean that other reactions took place to a small extent. The deviation is in the direction which would result from a slight polymerisation of the products.

Considerable difficulty was experienced in obtaining reproducible reaction rates. For instance, in a series of experiments carried out in the Pyrex bulb (*a*) at constant temperature, without chemical cleansing of the bulb, the reaction velocity decreased progressively, although the bulb was evacuated for several hours between successive experiments. Such an effect must be attributed to the poisoning effect of some reaction product deposited on the walls. The reaction velocity, however, was reproducible to within $\pm$ 10% over a long series of experiments if the reaction bulb was filled with oxygen, heated for an hour at 800°, and then evacuated before each experiment was started. This pre-treatment was given in all the work with quartz bulbs.

In the experiments in which a bulb packed with silica was used there was a pronounced adsorption of hydrogen on the surface; *e.g.*, when hydrogen was admitted to a pressure of 300 mm. into the previously evacuated bulb at 600°, the pressure decreased by 40 mm. in 1 hour. This was not due to reaction with adsorbed oxygen, since adsorption and desorption of hydrogen could be repeated many times with successive quantities. This adsorption renders pressure measurements and gas analyses in packed-bulb experiments subject to larger errors than in the case of the empty bulb, where adsorption effects were negligible. Such errors do not, however, affect the main conclusions drawn from packed-bulb experiments.

Effect of Surface on the Reaction Rate.—The relative amounts of dehydrogenation and hydrogenation taking place in the decomposition of methylamine may be determined from the methane content of the non-condensable gaseous reaction products. The effect of packing the quartz bulb on the relative proportion of these two reactions was deduced from these data. In preliminary work in Pyrex bulbs packed with Pyrex tubing, the reaction rate was greater in the packed bulb, the reaction (*b*) being accelerated to a greater extent than (*a*). Typical results are in Table I; p_i is the initial methylamine pressure; *t* is the time for the pressure to increase by 25% of its initial value, and its reciprocal is an approximate measure of the rate of dehydrogenation; Δp is the total pressure change expressed as a percentage of p_i; p_{CH_4} is the percentage of the methylamine hydrogenated; and r_1 and r_2 are ratios expressing the increase in the rates of dehydrogenation and of hydrogenation respectively due to packing the bulb. The results at 592·6° and 617·5° are mean values for a number of different initial pressures.

TABLE I.

| Temp.	Bulb.	p_i (mm.).	*t*, sec.	Δp.	p_{CH_4}.	r_1.	r_2.
568·4°	Empty	164	360	154	9·35 }	2·1	10
	Packed	160	173	65	44·6 }		
592·6	Empty	38—207	164	173	8·2 }	3·4	15
	Packed	139—231	48	75	36·0 }		
617·5	Empty	33—200	65	178	6·3 }	3·5	18
	Packed	176—297	19	78	33·0 }		

The table shows that the rate of formation of methane was increased 10—18 fold by packing, according to the temperature. The increase in the surface in the packed bulb could not be measured directly, but could be estimated from measurements of the rate of thermal decomposition of methyl formate. This reaction is known to be heterogeneous (Steacie, *Proc. Roy. Soc.*, 1930, *A*, **127**, 314), and the time for 15% decomposition was used to compare the rates in the empty and in the packed bulb at 413—537°; the decomposition was thus found to be 105 times faster in the packed bulb.

There is no *a priori* reason why the surface should be the same for these two reactions, and the observed increase in rate in the case of methylamine may be interpreted as showing that the hydrogenation reaction is predominantly heterogeneous. This conclusion is supported by the effect of addition of hydrogen on the formation of methane, data for which are recorded later (Table IV). The reaction is shown to be of zero order with respect to hydrogen.

A similar argument applies to the effect of packing on the reaction (*a*). If the increase in surface due to packing is taken as 18-fold, the dehydrogenation reaction will be over 80% homogeneous. The fact that packing the bulb does affect this reaction is, however, very significant. It must mean that the reaction is partly heterogeneous or that it is homogeneous but is initiated by a heterogeneous process. This point is discussed later.

Effect of Methylamine Pressure on the Reaction Rate.—The decomposition of methylamine into hydrogen cyanide and hydrogen was strictly of the first order when the reaction was carried out in an unpacked bulb, for when the pressure change expressed as a fraction of p_i is plotted against time, the curves obtained for different initial pressures are superposable. In Fig. 1 a

FIG. 1.
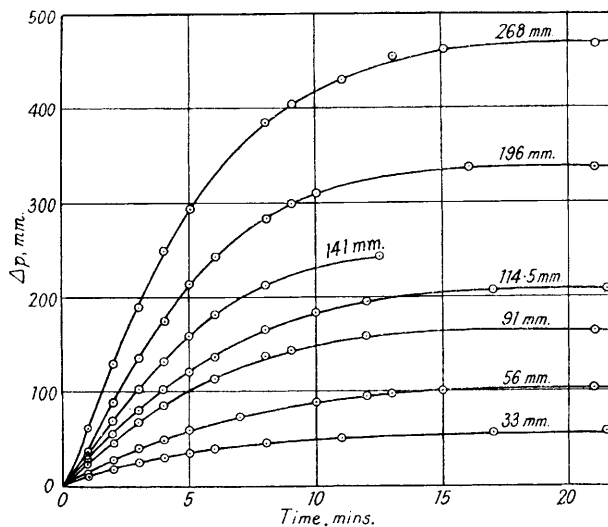
series of experiments at 617—618° is recorded, the pressure increase being plotted as a function of time; when the fractional pressure increments corresponding to these data are plotted against time, all the points from the seven curves fall closely on one smooth curve. A similarly close agreement was obtained in series of experiments at 593°, 640°, and 667°. Further, when log $(a - x)$ is plotted against t, a straight line is obtained over the range 20—70% of the total reaction, so that for each experiment the unimolecular velocity constant $k = 1/t \cdot \log_e a/(a - x)$ can be calculated (Table II). The value of a used is that corresponding to the theoretical end-point of the reaction, *i.e.*, twice the initial pressure. This procedure is justifiable on the grounds that the value of the constant is deduced from a stage of the reaction at which the effect of the secondary hydrogenation (which is mainly responsible for the deviation from the theoretical end-point) can be neglected. During the first 20% of the reaction there is a deviation from the unimolecular law, due to an ill-defined induction period.

TABLE II.

Temp.	p_i (mm.).	k, min.$^{-1}$.	Temp.	p_i (mm.).	k, min.$^{-1}$.
592·6°	38·5	0·0590	617·6°	141	0·153
	123	0·0630		196	0·152
	207	0·0572	639·6	46	0·305
617·6	33	0·127		113	0·300
	56	0·131		237	0·308
	91	0·145	667·0	43	0·900
	114·5	0·136		97·5	0·888

In experiments with the packed silica bulb the time for a given fractional change was still independent of the initial pressure down to 100 mm., as shown in Table III. Experiments at still lower pressures would have a special theoretical significance, referred to later, and are in progress. They were not possible with the experimental arrangement described here.

TABLE III.

Temp. 568·4°.		Temp. 592·6°.		Temp. 617·5°.	
p_i, mm.	t (0—50%), secs.	p_i, mm.	t (0—50%), secs.	p_i, mm.	t (0—50%), secs.
375	290	231	95	297	39
157	300	139	100	176	46

Effect of Reaction Products and Hydrogen on the Reaction Rate.—In an experiment at 593°, 150 mm. of methylamine were allowed to decompose completely in the packed quartz bulb. A further 150 mm. of methylamine were then admitted, and its decomposition followed at the same temperature. The reaction rate was slightly greater in the second case, and the corresponding pressure increase was about 15% greater than that in the first half of the experiment. This discrepancy is of the same order as that which could arise from adsorption of hydrogen in the first half of the experiment, and was not considered to be evidence that the reaction products influenced the rate. In the same connexion, experiments were carried out to determine if the addition of hydrogen increased the proportion of methane in the final product, since in the normal decomposition the hydrogen for the hydrogenation is supplied by the decomposition of methylamine itself into hydrogen cyanide and hydrogen. The data in Table IV show no systematic variation in the proportion of methane due to the addition of hydrogen, the variation in the results being within the limits of error arising from adsorption of hydrogen.

TABLE IV.

Packed quartz bulb, at 568—569°.

p_i, mm.	157·5	158	170	157	163·5
p_{H_2} added, mm.	0	0	3·5	90·2	212
Δp	60	74	82	69·5	64
p_{CH_4} found, mm.	61·5	61·2	62·5	80·0	64·5

Effect of Temperature on Products : Temperature Coefficient.—Measurements were made at a series of temperatures of the percentage of methane in the non-condensable reaction product, in order to determine the effect of temperature on the proportion of methylamine reacting according to the equation (*b*). In Table V the majority of the data are the mean of several determinations at the temperature in question, with different initial pressures of methylamine. At each temperature the proportion of methane found was shown to be independent of the initial pressure (down to 50 mm.).

TABLE V.

Bulb.		Temp.	CH_4, %.	Bulb.		Temp.	CH_4, %.
Pyrex (empty)	....	543°	12·3	Quartz (empty)	....	640°	3·1
,, (packed)	....	543	33·3	,, ,,	....	653	3·0
Quartz (empty)	....	558	13·9	,, ,,	....	667	2·8
,, ,,	....	568	6·4	,, (packed)	....	568	56·0
,, ,,	....	593	5·1	,, ,,	....	593	51·6
,, ,,	....	618	3·9	,, ,,	....	618	47·9
,, ,,	....	624	3·6				

These data show the marked effect of packing the reaction vessel in increasing the relative extent of the hydrogenation reaction. They also show that the proportion of methane found rises as the temperature is decreased, the maximum value observed in the unpacked bulb being 13·9% at 558°. Experiments at still lower temperatures were not made owing to the slowness of the reaction. This general behaviour shows that the hydrogenation reaction has a smaller temperature coefficient than the dehydrogenation reaction.

The temperature coefficient of the homogeneous reaction was calculated from values of the unimolecular velocity constant (k) at temperatures between 590° and 670°. A straight line was obtained when log k was plotted against $1/T$ (Fig. 2), giving an activation energy of 58,000 g.-cals. The variation of k with temperature is expressed by the equation $\log_e k = 30\cdot65 - 58,000/RT$. Since the homogeneous decomposition of methylamine is formally unimolecular

down to a pressure of 30 mm., it is possible to calculate a minimum value for the number of degrees of freedom in the methylamine molecule required to account for the observed reaction rates. The number is found to be 13. The values found for the other amines by Taylor (*locc. cit.*) were only 1 or 2.

FIG. 2.
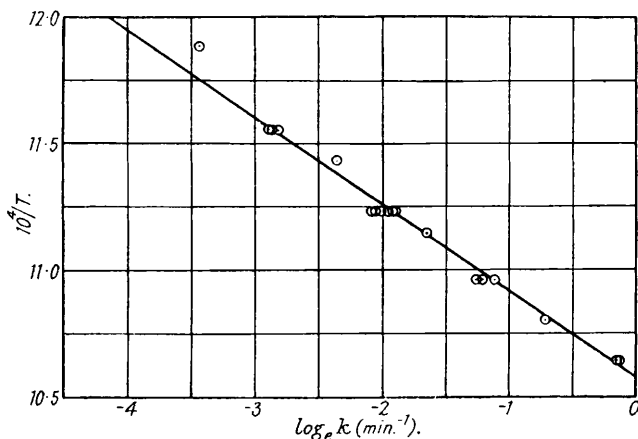
DISCUSSION.

The decomposition of methylamine into hydrogen cyanide and hydrogen is a reaction which shows the general characteristics observed in the case of other amines. The formation of hydrogen cyanide as a main product corresponds to that of nitriles observed by Upson and Sands and by Hurd and Carnahan (*locc. cit.*) in the decomposition of ethyl-, propyl-, and benzyl-amine. Dehydrogenation appears to be a general feature of amine pyrolysis, and side reactions become increasingly prominent as the complexity of the amine increases. In the case of methylamine the only side reaction of any importance is a hydrogenation to methane and ammonia, for which the requisite hydrogen is supplied by the primary dehydrogenation.
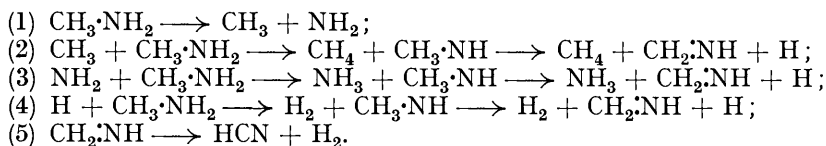
It is usual to treat kinetic data obtained from a complex reaction as the sum of the effects of a small number of concurrent simple reactions, among which one will often predominate. In the present case the data can be interpreted as arising from a dehydrogenation reaction which takes place mainly in the gas phase and to a smaller extent on the surface, accompanied by a smaller proportion of heterogeneous hydrogenation. As a first approximation, these three concurrent reactions may be considered separately.

Regarded in this light, the homogeneous dehydrogenation, which is strictly of the first order, agrees in a general way with Taylor's observations on the other amines (*locc. cit.*). There are, however, some striking differences. The energy of activation (58,000 cals.) is much greater than the values found in the decomposition of the other amines (40,000—45,000 cals.), and the number of degrees of freedom required to account for the observed rate of methylamine decomposition on the basis of the classical theory of unimolecular reactions is much higher than that for the other amines. Some such discrepancy as this would be intelligible if the higher amines decomposed into olefin and ammonia, as assumed by Taylor, since no corresponding reaction could occur with methylamine. The work of Hurd and Carnahan and of Schumacher and Wiig, however, has shown that the other amines, far from following the scheme assumed by Taylor, decompose mainly by a dehydrogenation which is analogous to the main reaction in the case of methylamine. The explanation of the apparent anomalies in the present case must therefore be sought elsewhere.

The marked sensitivity of the reaction velocity to the state of the vessel walls cannot be adequately explained if the reaction is almost entirely homogeneous. A similar anomaly was found by Schumacher and Wiig (*loc. cit.*) in the case of ethylamine. It may be that the homogeneous and the heterogeneous reaction are not in reality mutually independent.

If this is so, it may indicate that reaction chains play a part in the mechanism. Such a view must be regarded with considerable reserve in the case of methylamine, where no direct evidence of chain mechanism has been observed; but the possibility cannot be ignored in view of the definite chain characteristics which appear in the low-pressure decomposition of ethyl- and propyl-amine. The authors hope to settle the point in the near future by an investigation of the decomposition of methylamine at lower pressures.

Rice and Herzfeld (*J. Amer. Chem. Soc.*, 1934, **56**, 284) have recently shown that a number of supposedly simple unimolecular organic pyrolyses can be explained by a chain mechanism involving free radicals. The same considerations can be applied to the present case, and the entire series of products in methylamine decomposition can be predicted in this way. The following steps may be tentatively suggested :

(1) $CH_3 \cdot NH_2 \longrightarrow CH_3 + NH_2$;

(2) $CH_3 + CH_3 \cdot NH_2 \longrightarrow CH_4 + CH_3 \cdot NH \longrightarrow CH_4 + CH_2 \colon NH + H$;

(3) $NH_2 + CH_3 \cdot NH_2 \longrightarrow NH_3 + CH_3 \cdot NH \longrightarrow NH_3 + CH_2 \colon NH + H$;

(4) $H + CH_3 \cdot NH_2 \longrightarrow H_2 + CH_3 \cdot NH \longrightarrow H_2 + CH_2 \colon NH + H$;

(5) $CH_2 \colon NH \longrightarrow HCN + H_2$.

Thus the chain theory predicts that the decomposition will proceed via an aldimide $CH_2 \colon NH$, as already postulated by Hurd and Carnahan. We hope to deal with this matter more fully later.

In conclusion, reference may be made to the photodecomposition of methylamine (Eméleus and H. S. Taylor, *J. Amer. Chem. Soc.*, 1931, **53**, 3370). Further work in progress has shown that ammonia and hydrogen are the only significant gaseous products of this reaction. No hydrogen cyanide has been detected, but there are indications that close analogy is to be expected between the mechanisms of the thermal and the photochemical decomposition reaction.

SUMMARY.

(1) Methylamine decomposes at 550—670° according to the reactions : (*a*) $CH_3 \cdot NH_2 = HCN + 2H_2$; (*b*) $CH_3 \cdot NH_2 + H_2 = CH_4 + NH_3$.

(2) Reaction (*a*) is unimolecular and is largely homogeneous, with an energy of activation of 58,000 cals.

(3) Reaction (*b*) is heterogeneous, the amount of methane formed increasing when the vessel is packed or the reaction temperature lowered.

(4) The reactions (*a*) and (*b*) may be accounted for by a chain reaction initiated by the decomposition of methylamine into methyl and amino-radicals.