334. *Kinetics of the Thermal Oxidation of Methylamine.*

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The oxidation of methylamine at 250—600° is a homogeneous reaction which yields a complex series of products consisting mainly of formaldehyde, carbon monoxide and dioxide, hydrogen cyanide, ammonia, and water (Jolley, J., 1934, 1957). The reaction is retarded by increase in the surface : volume ratio of the reaction vessel, and proceeds by a chain mechanism. The pressure increase accompanying it has been shown to give a measure of the reaction rate, and the **S**-shaped pressure–time curve obtained is similar to that characterising the oxidation of hydrocarbons.

We were led to extend these observations by the discovery that reproducible reaction rates could be obtained by washing the reaction vessel with dilute hydrofluoric acid between each series of experiments (Kowalsky, Sadovnikov, and Tschirkov, *Physikal. Z. Sovietunion*, 1932, **1**, 451). This made it possible to obtain comparable kinetic data for the slow oxidation with varying mixture composition, pressure, and temperature, and to correlate these with the results of experiments on the explosive oxidation of methylamine. A basis for such a correlation is furnished by Semenoff's theory of degenerate chain branching ("Chemical Kinetics and Chain Reactions," 1935, p. 68), according to which the rate of a reaction in which degenerate branching occurs should be given by the expression

$$v = n_0 e^{(\delta - \beta)t/\Delta\tau}/(\delta - \beta) = Ae^{\phi t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this equation v is the reaction velocity at time t, n_0 is the rate of formation of initial active centres, δ and β are the respective probabilities of chain branching and chain breaking, and $\Delta\tau$ is the time required for the development of one link in the chain. The variation of ϕ [$= (\delta - \beta)/\Delta\tau$] with pressure, temperature, and composition of the reaction mixture should be given by

$$\phi = Bp^n\gamma^a e^{-C/T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where γ is the mol.-fraction of combustible gas in the mixture, and B, n, a, and C are constants. The transition from the slow to the explosive reaction should occur when the pressure exceeds a limiting value p_c (Semenoff, *op. cit.*, p. 86), the temperature dependence of which is given by

$$\log_e p_c/T = A'/T + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Finally, the constants n, C, and A' in equations (2) and (3) should be connected by the expression

$$A'(n + 1) = C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It was with the object of testing the validity of the above theoretical relationships that the experiments described below were carried out.

EXPERIMENTAL.

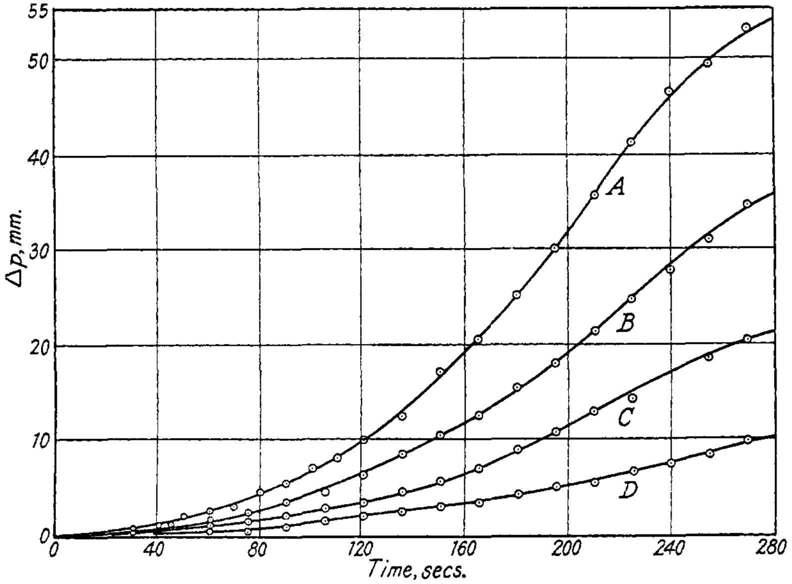
Methylamine was prepared from the hydrochloride (Jolley, *loc. cit.*). Oxygen was taken from a commercial cylinder and contained 0·5—1·0% of nitrogen, for which a correction was applied.

The slow oxidation was studied at 330—390° in a 200-c.c. cylindrical silica bulb connected through 1-mm. capillary tubing with a capillary mercury manometer. We have already described the electrically heated furnace and thermometer used (J., 1935, 929). The reactants were admitted to the evacuated silica bulb in the furnace from a 2-litre globe, which was kept in a thermostat and in which mixtures of known composition were made up manometrically. In earlier experiments (Jolley, *loc. cit.*) the reaction vessel was cleaned with chromic–nitric acid before each series of runs. The lack of reproducibility in the oxidation rates after such treatment was entirely avoided by using a 5% solution of hydrofluoric acid instead. Kowalsky, Sadovnikov, and Tschirkov (*loc. cit.*) obtained increased rates of oxidation of ethane when this method of cleaning was employed. We found no marked change in the rate, though the subsequent measurements of reaction rate were remarkably reproducible (to ± 5% over the whole series of measurements). After the acid treatment, the reaction vessel was used for a series of experiments without further cleaning, apart from evacuation for at least 1 hour at 300—400° between successive runs.

The pressure–time curve was studied for two sets of mixtures containing severally 30·8 and 50·0% of methylamine, and for various temperatures and initial pressures. A typical series of curves for four different initial pressures at 344° and 30·8% of amine in the mixture is shown in Fig. 1.

The total pressure of the reaction mixture increased continuously with time until the completion of the reaction, whereas the rate of pressure change increased with time up to the moment of half-change and then diminished. The initial increase in rate follows an approximately exponential law, as may be shown by plotting log Δp against time over the range 10—45% of the total reaction, an approximately straight line being obtained; in Fig. 2 the data of Fig. 1 are so plotted. The reaction rate over this range is therefore represented by an expression of the form $v = Ae^{\phi t}$, in agreement with the theoretical equation (1). The curves in Fig. 1 for initial pressures of 252, 180, and 120·5 mm. can be superposed on that for an initial pressure of 328 mm. (Fig. 1) merely by altering their time scales in the ratios 0·804 : 1, 0·635 : 1, and 0·435 : 1 respectively (cf. Semenoff, *op. cit.*, Chap. XII). This superposition on to the 328 mm. curve can also be extended to other pressure–time curves obtained at different temperatures and mixture compositions. Values of the ratio ϕ/ϕ_0 by which the time scales must be changed are given in Table I : γ is the mol.-fraction of methylamine in the gas mixture. The significance of this superposition is that to a first approximation the variation with reaction conditions of the factor A in the expression $v = Ae^{\phi t}$ may be neglected in comparison with that of ϕ. This appears to be fairly generally true in cases of hydrocarbon combustion so far examined from this standpoint.

FIG. 1.



A, p_i = 328·0 mm.; B, p_i = 252·0 mm.; C, p_i = 180·0 mm.; D, p_i = 120·5 mm.

TABLE I.

Temp.	Initial press., mm.	γ.	ϕ/ϕ_0.	Temp.	Initial press., mm.	γ.	ϕ/ϕ_0.
335°	141·2	0·308	0·340	344°	96·0	0·50	0·437
	215·2	0·308	0·503		152·0	0·50	0·696
	284·0	0·308	0·682		184·0	0·50	0·764
344	120·5	0·308	0·435		213·0	0·50	0·988
	180·0	0·308	0·635		237·0	0·50	1·044
	252·0	0·308	0·804		278·0	0·50	1·180
	328·0	0·308	1·000		293·0	0·50	1·210
357	142·2	0·308	0·825		321·0	0·50	1·302
	241·5	0·308	1·430	358	112·5	0·50	0·780
367·5	178·5	0·308	1·625		182·5	0·50	1·370
	207·0	0·308	1·800		260·5	0·50	1·980
	281·0	0·308	2·290	377	104·0	0·50	1·670
					180·3	0·50	2·620
					279·0	0·50	3·720
				386	167·0	0·50	3·400
					221·0	0·50	4·450

The values for ϕ/ϕ_0 in Table I are based on Δp–time curves similar to those in Fig. 1, but obtained at the temperatures and pressures shown. From these results the variation of ϕ with pressure and temperature may be deduced. When log ϕ/ϕ_0 is plotted against log p for each of the temperatures and mixture compositions examined (Table I), a series of approximately parallel straight lines is obtained which is shown in Fig. 3. The gradient (0·83) is the same for $\gamma = 0{\cdot}50$ and for $\gamma = 0{\cdot}308$, and the variation of ϕ with pressure is therefore given by the expression $\phi = kp^{0\cdot83}$. The index 0·83 corresponds to the index n in equation (2).

The variation of ϕ with temperature may be obtained from Fig. 3 by taking a line parallel to the log ϕ/ϕ_0 axis and reading off the values of ϕ/ϕ_0 for the various temperatures. Data for p = 224 mm. are given below :

$\log_{10}\phi/\phi_0$	$\bar{1}$·718	$\bar{1}$·870	0·105	0·281	$\bar{1}$·988	0·220	0·491	0·644
γ	0·308	0·308	0·308	0·308	0·500	0·500	0·500	0·500
Temp. (° C.)	335°	344°	357°	367·5°	344°	358°	377°	386°

On plotting these values of ϕ/ϕ_0 against the reciprocals of the absolute temperatures, a good straight line is obtained for each value of γ. The lines for the two values of mixture composition are almost parallel, and their mean gradient may be used to calculate C in equation (**2**); a value of 15,000 is thereby obtained. The variation of ϕ with temperature and pressure may therefore be expressed by the equation $\phi = Bp^{0\cdot83}e^{-15{,}000/T}$. The value of C = 15,000 can now be used in testing equation (4) by studying the temperature dependence of the critical explosion pressure of methylamine–oxygen mixtures. This should give a relationship of the same type as equation (3), yielding a value of the constant A' from which C can be calculated by applying equation (4).

FIG. 2.

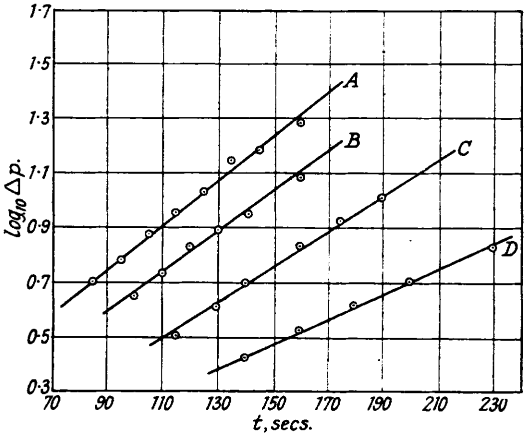


FIG. 3.

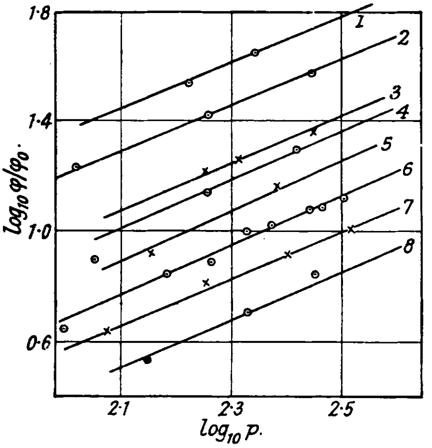


FIG. 2.—A, p_i = 328·0 mm.; B, p_i = 252·0 mm.; C, p_i = 180·0 mm.; D, p_i = 120·5 mm.
FIG. 3.—1. 386°, B; 2. 377°, B; 3. 367°, A; 4. 358°, B; 5. 357°, A; 6. 344°, B; 7. 344°, A; 8. 335°, A. A = 30·8% $CH_3{\cdot}NH_2$; B = 50% $CH_3{\cdot}NH_2$.

The Explosive Reaction.—The apparatus used in measuring the critical explosion pressures of methylamine–oxygen mixtures is similar to that described by Sagulin (*Z. physikal. Chem.*, 1928, *B*, **1**, 275). It consisted of a spherical 100-c.c. Pyrex bulb A, connected with a mercury manometer. The bulb was heated in an electrical furnace, the temperature of which was constant to within ± 1° over the space occupied by the bulb. A mixture of methylamine and oxygen of known composition was prepared manometrically and admitted into a second bulb B of approximately 100 c.c. capacity up to a measured pressure, the ratio of the volumes of A and B having been previously determined accurately. A wide-bore tap between A and B was then momentarily opened, and the subsequent changes in pressure of the gas mixture in A were recorded until reaction was complete. Ignition was shown by a kick of the mercury meniscus.

A series of experiments was made at temperatures between 400° and 600°. At each temperature there was found to be a limiting pressure (p_c) below which ignition did not occur; this was determined in each case by trial. At pressures below p_c the normal slow reaction with increase of pressure was observed. When the initial pressure exceeded p_c the slow reaction started normally, but before it was completed the mixture exploded. Ignition occurred at an earlier stage the more the initial pressure was in excess of p_c, and at about the instant of half-change (*i.e.*, of maximum velocity) when the initial pressure was just greater than the limiting value.

Typical data for the determination of p_c are given in Table II.

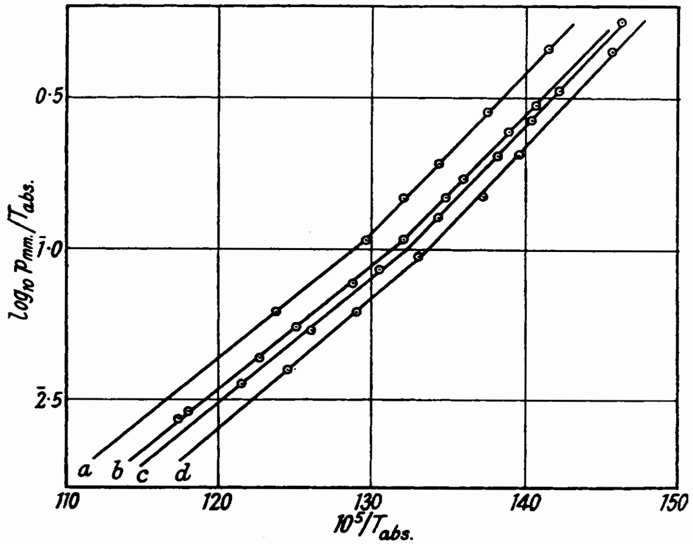
TABLE II.

Mixture, $CH_3{\cdot}NH_2 : O_2 = 1 : 1$. Temperature = 500° ± 1°.

$p_{\text{initl.}}$, mm.	50	52	53·5	55	57	57
Explosion	No	No	No	No	Yes	Yes
p_{final}, mm.	56	60	58	64	69	71
Δp in explosion, mm.	—	—	—	—	12	14

The value of p_c in this particular experiment lies between 55 and 57 mm., and in other experiments it was determined with a similar degree of accuracy. The less the initial pressure exceeded p_c the greater was the pressure change preceding the explosion, and the less the pressure change in the explosion. This is because a correspondingly lower proportion of the reactants is used up in the slow reaction, a conclusion supported by analytical data already published (Jolley, *loc. cit.*). Explosions in mixtures containing more than 50% of oxygen were very much more violent than those in more dilute mixtures, and differed in appearance. An experiment in which an explosion had occurred tended to be followed by an explosion in the next experiment, made at a different pressure. Similarly, absence of an explosion tended to suppress the explosion in subsequent experiments, even though the pressure exceeded p_c. The consequent lack of reproducibility was minimised by increasing the efficiency of pumping between successive experiments, and experiments at pressures which produced an explosion and did not do so were alternated as far as possible.

FIG. 4.



a, $1CH_3{\cdot}NH_2 : 0{\cdot}5O_2$; *b*, $1CH_3{\cdot}NH_2 : 0{\cdot}75O_2$; *c*, $1CH_3{\cdot}NH_2 : 1{\cdot}00O_2$; *d*, $1CH_3{\cdot}NH_2 : 1{\cdot}82O_2$.

Values of p_c were determined at a series of temperatures with five different ratios of amine to oxygen. The results for four mixtures are shown in Fig. 4. Those with an amine ratio of 1 : 2·52 were similar, but are omitted for the sake of clarity. In this figure, the values of $\log_{10} p_c/T$ are plotted against $1/T$. For each mixture two straight lines are obtained intersecting at a point corresponding to temperatures of 470—500°. The lines for different mixtures are very approximately parallel, and resemble results obtained by Sagulin (*loc. cit.*) for the explosions of mixtures of carbon disulphide, methane, ethane, propane, or pentane with oxygen, and for mixtures of chlorine or bromine with hydrogen. The results for ethane, propane, and pentane showed a discontinuity at 680° similar to that now observed with methylamine–oxygen mixtures. The linear relationship is in agreement with equation (3). The values of the constant A' calculated on the natural logarithmic basis from the gradients of the curves above and below 490° are given below for different values of γ.

γ	0·667	0·571	0·500	0·355	0·284
A' (below 490°)	12,200	12,200	12,400	12,800	13,100
A' (above 490°)	9,320	9,320	9,420	9,780	9,320

In the low-temperature region there was a tendency for the value of A' to vary with the concentration of methylamine, but the effect was not marked. It is noteworthy that the values of A' for amine-rich are the same as those for oxygen-rich mixtures, although the explosions were completely different in appearance in the two cases. No entirely satisfactory explanation has yet been given of the break in the log p_c/T–$1/T$ graphs (cf. Sagulin, *loc. cit.*).

DISCUSSION.

The value of A' obtained from explosion data is 12,500 for temperatures between 400° and 490°, and 9400 for temperatures between 490° and 600°. Since the value of n, the index of p in the expression for the variation of ϕ with reaction conditions, has been found to be 0·83, the values of C obtained by applying equation (4) are 23,000 and 17,200 for the corresponding temperature ranges. The experimental value of 15,000, obtained from the variation of ϕ with temperature, is completely different from the first of these values and in rough agreement with the second.

Other workers on hydrocarbon combustions have attempted the correlation of data for the slow and the explosive reaction on the basis of the Semenoff theory. In, *e.g.*, the oxidation of methane, the value $C = 46{,}000$ was obtained for the slow reaction (Semenoff, *op. cit.*, p. 299), whereas from direct explosion experiments, in the course of which the induction period was measured, the value $C = 41{,}000$ was obtained (Neumann and Egorov, *Physikal. Z. Sovietunion*, 1932, **1**, 700). Here the agreement between data from the slow and the explosive reactions is good. For ethane, on the other hand, the slow reaction gave $C = 19{,}000$ (from data of Bone and Hill, *Proc. Roy. Soc.*, 1930, *A*, **129**, 434) and $C = 21{,}000$ (Kowalsky, Sadovnikov, and Tschirkov, *loc. cit.*). From the explosive reaction the values of C were approximately 34,000 (Sagulin, *loc. cit.*) and 26,000 (Taylor and Riblett, *J. Physical Chem.*, 1931, **35**, 2667). Here the discrepancy is as pronounced as in the oxidation of methylamine. There are still other instances of a similar lack of agreement (cf. Semenoff, *op. cit.*).

The basic assumption upon which equation (4) rests is that the incidence of explosion depends simply on the attainment by the slow reaction of a critical velocity. In complex reactions, such as those taking place in the oxidation of methylamine or ethane, complicating factors may well arise. In the case of, *e.g.*, ethane, published curves (Semenoff, *op. cit.*, p. 323) show that the explosion did not take place until the slow reaction was practically completed. It may, indeed, have been a subsequent reaction of one of the products without any direct connection with the slow oxidation of ethane. Again, the reaction products may catalyse or retard the main reaction, in which case a modification of the simple theory would be necessary because the value of A in equation (1) would not be constant. The explosions of methylamine took place in a complex mixture of amine, carbon monoxide, and other intermediate oxidation products. In these circumstances it is not surprising that a theory developed for an idealised case is apparently not strictly valid when applied to a complex reaction. The best agreement between theory and our experiments was obtained at temperatures above 490°, a region in which complications due to incomplete oxidation and surface effects would be reduced.

SUMMARY.

(1) The rate of the slow thermal oxidation of methylamine at 330—390° is given by an expression of the form $v = Ae^{\phi t}$.

(2) The variation of ϕ with pressure and temperature is given by $\phi = B'p^{0\cdot83}e^{-15{,}000/T}$.

(3) The critical explosion pressure, p_c, of methylamine–oxygen mixtures is related to the absolute temperature by the expression $\log_e p_c/T = A'/T + B$. The value of A' is 12,500 below 490° and 9300 above 490°.

(4) Data for the slow and the explosive oxidation of methylamine are correlated by means of the theory of degenerate chain reactions.

The authors are indebted to Imperial Chemical Industries Ltd. for a grant.

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, August 25th*, 1936.]