

748. *The Kinetics of the Oxidation of Methane by Nitrous Oxide.*

By P. L. ROBINSON and E. J. SMITH.

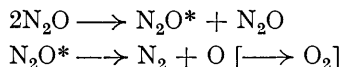
The slow non-inflammatory combustion of methane in nitrous oxide at about one atmosphere total pressure has been investigated. Carbon monoxide, carbon dioxide, and water vapour are the main products in a reaction which we find has two readily recognisable stages: (a) $\text{CH}_4 + 3\text{N}_2\text{O} \longrightarrow \text{CO} + 2\text{H}_2\text{O} + 3\text{N}_2$; (b) $\text{CO} + \text{N}_2\text{O} \longrightarrow \text{CO}_2 + \text{N}_2$. Each of these must be built up of a number of consecutive steps, involving free atoms and radicals, and the chain character of the process has been demonstrated.

Rate measurements support the idea that the reaction is initiated by oxygen atoms from the thermal decomposition of nitrous oxide, and the observed activation energies are in agreement with this. The kinetics are consistent with a chain termination which is of first order with respect to the carrier concentration: the terminating step is probably $\text{OH} + \text{N}_2\text{O} \longrightarrow \text{HO}_2 + \text{N}_2$.

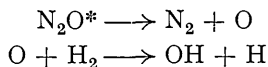
A reaction mechanism is advanced and discussed.

LITTLE attention has been paid to slow oxidation by nitrous oxide. Twenty years ago Melville (*Proc. Roy. Soc.*, 1933, *A*, **142**, 524; *ibid.*, 1934, *A*, **146**, 737) studied its reaction with hydrogen and, somewhat later, Bawn that with carbon monoxide (*Trans. Faraday Soc.*, 1935, **31**, 461); Steacie and MacDonald (*Canad. J. Res.*, 1935, **12**, 711) reported certain qualitative observations. So far as we know, the present work, begun four years ago, describes the first investigation of the slow oxidation of methane. Last year (Bridson-Jones, Buckley, Cross, and Driver, *J.*, 1951, 2999; Bridson-Jones and Buckley, *ibid.*, p. 3009; Buckley and Levey, *ibid.*, p. 3016) found no reaction between nitrous oxide and *n*-hexane or cycloparaffins at 200–400°/2000 atm., although controlled oxidation of olefins occurred readily under these conditions.

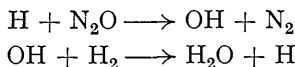
Oxidation by nitrous oxide is closely related to its thermal dissociation, which has been extensively studied (see Hinshelwood, "Kinetics of Chemical Change," Oxford Univ. Press, 1940). Decomposition is measurable above 600°, the reaction, with increase of pressure, changing from second to first order in accordance with Lindemann's collision theory of unimolecular processes. At our pressures, the apparent order is about 1.6; thus bimolecular activation, succeeded by unimolecular dissociation, is a significant feature of the decompositions:



Melville (*loc. cit.*) showed that hydrogen is not oxidised until thermal dissociation of the nitrous oxide is occurring, pointing to an initiating step involving oxygen atoms, and that, once started, the rate of oxygen consumption is far greater than that provided by dissociation, indicating a direct participation of the nitrous oxide molecules. Melville postulated the sequence

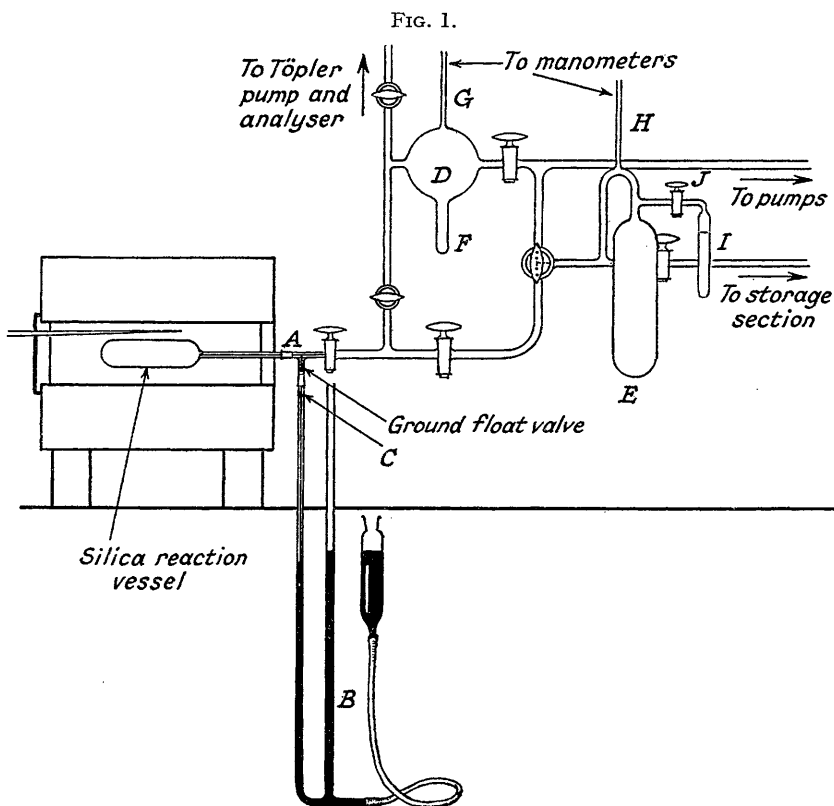


followed by the chain



to increase in the chain-breaking properties of the surface. The temperature of the tubular furnace was semi-automatically controlled by a Sunvic energy regulator and hot-wire switch, and measured by means of a Pt-Pt-Rh thermocouple and Cambridge auto-C.J. indicator. Temperatures varied by less than 2° over the operative length of the furnace and could be maintained within 1° for many hours.

The reaction vessel led through its ground joint *A* (Fig. 1), sealed with picein, to the constant-volume manometer *B*, in which the mercury was kept at a fixed point *C*; to the quenching vessel *D*, by which means a reaction could be rapidly stopped by expanding the reactants into a vacuum; and to the mixing chamber *E*. The "quencher," furnished with a prolongation *F*, in which material might be condensed, led to the analysis section. The "mixer" was in direct connection with the storage section. Two supplementary manometers, *G* and *H*, made for



convenience in manipulation. There was also a "doser" (not shown in Fig. 1) coupled to the "mixer" which allowed runs with a given mixture to be repeated several times. The tubing connecting the reaction vessel and manometer *B* was electrically heated to about 65° to prevent condensation of water vapour produced in the reaction. Evacuation was by a Kaye-type mercury-vapour pump, backed by a Speedivac rotary oil pump.

The analytical system consisted of a Töpler pump, to transfer the gas from the reaction and quenching vessels, after the carbon dioxide and the residual nitrous oxide had first been condensed by cooling the prolongation on the "quencher," and the spiral trap on the inlet side of the Töpler pump to -180° . This separation simplified the analysis and is necessary because of the appreciable solubility of nitrous oxide in the aqueous absorbents. The gases were passed to a calibrated gas burette (capacity 10 c.c.; graduations 0.01 c.c.), surrounded by a water-jacket and communicating, through a three-way capillary-bore tap, with absorption and combustion pipettes, and with sources of nitrogen and oxygen. A small dead space above the zero mark of the burette was filled with nitrogen before every analysis. The gases were kept saturated with water vapour during the estimations. Each 10-c.c., cylindrical, absorption pipette had an adjustable reservoir, so that, when absorption was complete, the liquid could be

restored to the fixed mark. The reagents used were 40% potassium hydroxide and alkaline pyrogallol solutions. The determination of carbon monoxide in the presence of methane was troublesome at first: combustion on a platinum spiral was not sufficiently specific in the presence of considerable amounts of methane. Methods involving the selective oxidation of carbon monoxide on metallic oxide catalysts were then tried. Of these, copper oxide gives a satisfactory response but requires a temperature of 300°. "Hopcalite" (a material containing oxides of copper, manganese, cobalt, and silver) was more attractive because of its higher specificity and lower operating temperature. It commences to oxidise carbon monoxide at room temperature but does not do this quantitatively, as others have observed (Thomas, Dunn, and Levin, *Analyt. Chem.*, 1949, 21, 1476). We found, however, that, when "Hopcalite" is maintained at 100°, rapid, quantitative oxidation even of high concentrations of carbon monoxide ensues and methane is unaffected; but, since the catalyst readily absorbs oxygen at 100°, this gas must be previously removed. A simple arrangement, consisting of a few pellets of "Hopcalite" located in a wider part of the (otherwise) capillary lead to the hydroxide

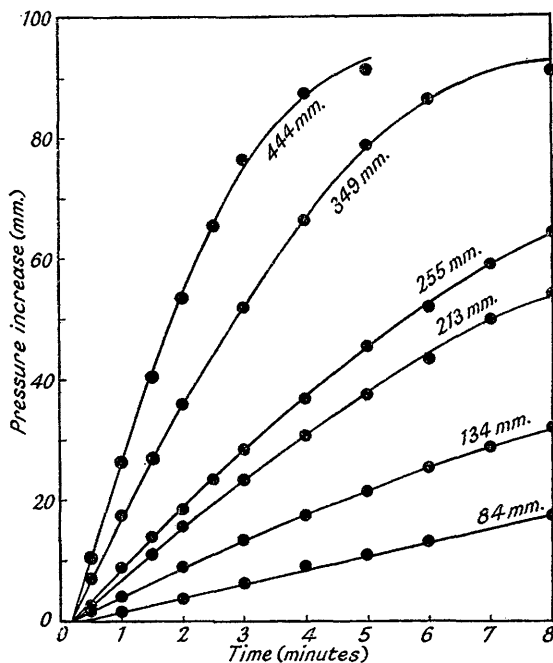


FIG. 2. Typical pressure-time records for 666°. Methane pressure 50 mm., nitrous oxide pressures indicated on curves.

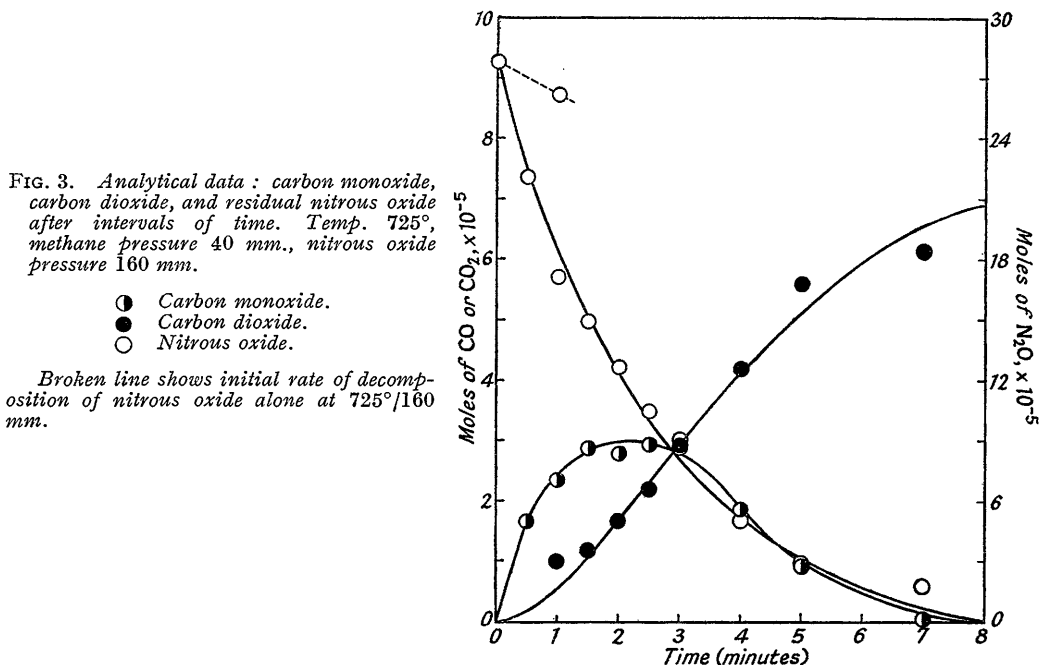
pipette and heated by a small, electrically wired, metal block, was easy and expeditious in operation and gave results with a tested accuracy of about 3%. Combined with the separation by freezing mentioned above, it was adequate for the mixtures under examination. The water vapour formed in the reaction was estimated by difference: from the total pressure of gases and water vapour, the partial pressure of the gases was deducted.

Operation.—The oxidation of methane by nitrous oxide gives a pressure increase, provided that the water vapour formed is allowed to contribute; but the changes in pressure resulting from a number of consecutive stages do not show a simple correspondence to changes in composition (Figs. 2 and 3). Hence, manometric observations were supplemented by chemical analysis. The proportionation of the reactants was done by admitting the nitrous oxide to *E*, measuring its pressure on manometer *H*, freezing it in *I*, and isolating the solid by closing tap *J*. The second compound was then admitted, and its pressure measured. Finally, tap *J* was opened and the gases were allowed to mix by diffusion for 5 hours or more. This procedure gave mixtures of precisely known composition, and avoided diffusion of the first component towards the storage vessel on admission of the second gas. Between runs, the reaction vessel, maintained at the working temperature, was evacuated for a standard period of 15 minutes.

As a test of apparatus and manipulation, certain of Melville's experiments on hydrogen were repeated with, incidentally, complete confirmation of his findings. The water vapour produced

was absorbed immediately outside the reaction vessel by phosphoric oxide, so that the combined pressures observed were due to hydrogen, nitrous oxide, and nitrogen: $\text{H}_2 + \text{N}_2\text{O} \longrightarrow \text{H}_2\text{O} + \text{N}_2$.

Measurements.—Analysis disclosed the two main stages (1) and (2) (p. 3896). Fig. 3 gives composition–time curves for mixtures having initial pressures of methane 40 mm., and nitrous oxide 160 mm., heated at 725°. It shows, initially, a close relation between the nitrous oxide used and the carbon monoxide produced. Precise measurement of the amounts of carbon dioxide produced in the early stages of the reaction is difficult, but it seems reasonable to extrapolate the curve showing its formation to zero time, asymptotically, since its rate of formation clearly depends on the concentration of carbon monoxide. Therefore the initial portions of the curves in Figs. 2 and 3 are taken as referring to stage (1) alone. A flattening of the pressure–time curves (Fig. 2), in a direction parallel to the time axis, occurs later and is ascribed in part to the intervention of stage (2) which does not itself involve an alteration in pressure, and in part to the consumption of the reactants. The slight induction periods evident when these curves are extrapolated to zero pressure, we believe to be mainly due to the interval



during which the reactants reach the starting temperature. From that point the reaction accelerates rapidly to its maximum rate; and the pressure–time curves have not the marked sigmoid form, so characteristic of the slow oxidation of hydrocarbons by molecular oxygen and ascribed to degenerate chain-branching.

Attempts at a quantitative determination of the more stable intermediate species were not made; but our qualitative observations, derived from a streaming system, are worth recording. Formaldehyde, indicated by Schiff's test, was obtained in sufficient amount to afford a crystalline derivative with dimedone, m. p. 187° (lit., 189°). Some cyanide and nitrite could be extracted from the effluent gases when these were bubbled through water, the nitrite being particularly prominent for mixtures rich in nitrous oxide and also for normal mixtures subjected to higher temperatures.

For comparison, Fig. 3 also shows the initial rate of the homogeneous decomposition of nitrous oxide alone, at the same temperature and pressure: the rate is about one-seventh of the rate of the reaction with methane measured in terms of consumption of nitrous oxide.

The effect, on the initial rate of the reaction, as expressed in pressure change in mm./min., of independently varying the nitrous oxide and methane partial pressures is shown in Fig. 4, wherein the starting pressure of methane is 50 mm. throughout and the temperatures 609—

685°; and in Fig. 5, wherein the starting pressure of nitrous oxide is 50 mm. and the temperature 665—725°. Evidently, the order with respect to nitrous oxide is greater than unity, and is proved, by reference to the parallel logarithmic plots obtained by using the data in Fig. 5, to be about 1.6. Independent experiments on the rates of decomposition of nitrous oxide alone, in the same pressure and temperature range, gave an identical value, 1.6.

FIG. 4. Influence of nitrous oxide pressure on initial rate, constant methane pressure = 50 mm.

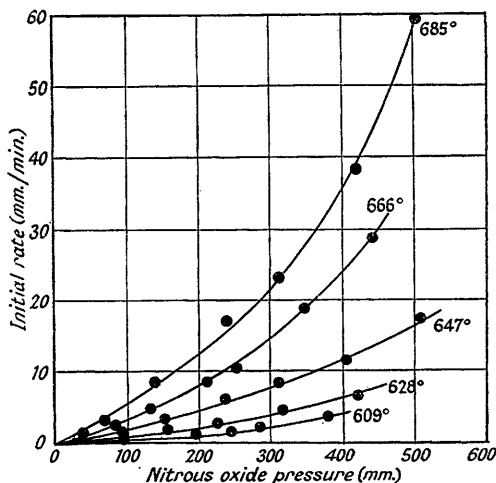
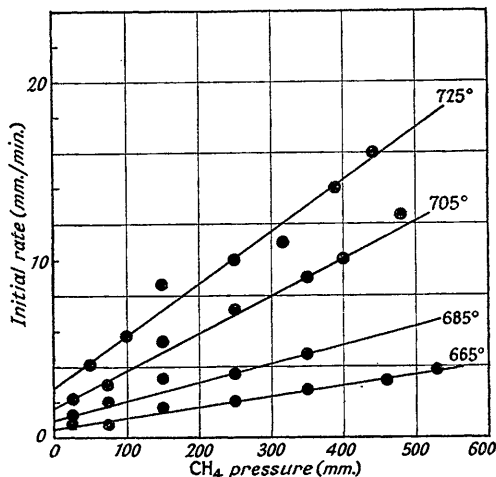


FIG. 5. Influence of methane pressure on initial rate, constant nitrous oxide pressure = 50 mm.



The curves in Fig. 4 pass through the origin: those in Fig. 5 make positive intercepts on the ordinate. If combined, these two sets of results suggest a rate equation of the form,

$$d\dot{p}/dt = k_1[N_2O]^x + k_2f([N_2O])[CH_4] \quad \dots \quad (3)$$

where $x \approx 1.6$, and where the function of the nitrous oxide concentration in the second term is such that the rate shall vanish at zero nitrous oxide pressure, as required by the experimental

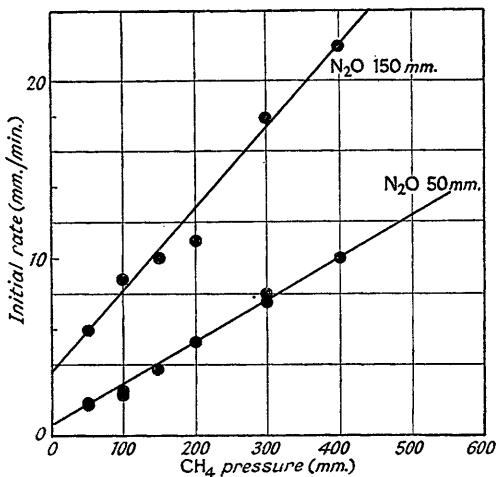


FIG. 6. Influence of methane pressure on initial rate at 665° at invariant nitrous oxide pressures of 50 mm. and 150 mm.

facts in Fig. 4. This function may be found, approximately, from the data in Fig. 6, viz., the plots of initial rates against methane pressure for invariant nitrous oxide pressure of 50 mm. and 150 mm., respectively, at 665°. Equation (3) requires the intercepts on the ordinate to equal $k_1[N_2O]^{1.6}$, and the slopes to vary as $f([N_2O])$. The intercepts show the required agreement. Comparison of the slopes shows $f([N_2O])$ to be representable by $[N_2O]$ to a power below

unity, since a three-fold increase in $[N_2O]$ increases the slope by a factor of 2, and $f([N_2O]) \simeq [N_2O]^{-1}$. Hence the empirical rate equation (3) becomes more precisely

$$dp/dt = k_1[N_2O]^x + k_2[N_2O]^y[CH_4] \quad (4)$$

where $x \simeq 1.6$ and $y \simeq 0.65$.

The constants k_1 and k_2 are both sensitive to temperature, since the intercepts and slopes in Fig. 5 which are proportional to k_1 and k_2 , respectively, increase with temperature. By plotting the natural logarithms of the slope against the reciprocal of the absolute temperature, as required by the Arrhenius equation, an activation energy of 50 kcal. was deduced from the temperature dependence of rate constant k_2 . Similar treatment of the intercepts gave an activation energy of about 53 kcal. from the temperature dependence of k_1 .

Since present knowledge of the oxidations of hydrocarbons and the temperatures at which they take place makes reaction chains probable, experiments were done in the presence of an inert gas and also in packed vessels. If deactivation of the chain-carriers at the surface occurred, an inert gas would, by impeding the diffusion of carriers to the walls, be expected to lead to an increase in the observed rate of reaction. Conversely, packing of the reaction vessel, by shortening the chains, would have the opposite effect. Tables 1 and 2 give the results obtained, and show a definite increase in the rate with large additions of nitrogen, and a noticeable decrease when the reaction vessel is packed with 5-mm. silica quill tubing. The influence of surface on reaction rates also reveals itself in the conditioning of the vessels by operation (see above) and is observable when measurements are repeated at long intervals. For this reason, particular sets of experiments were completed consecutively, with the minimum of interval of time and the employment of standard pumping times. The reproducibility of rates in a given series was better than 5%.

TABLE 1. *Initial rates in absence and in presence of nitrogen (685°; CH₄ = 25 mm., N₂O = 75 mm.).*

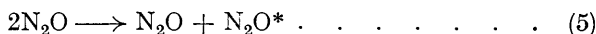
Nitrogen (mm.)	0	337	0	433
Initial rate (mm./min.)	5.2	7.4	4.8	7.0

TABLE 2. *Initial rates in unpacked and packed vessels (686°; CH₄ = 50 mm.).*

N ₂ O, mm.	400	350	270	200	100
Initial rate, mm./min. {					
unpacked	37.0	29.0	21.0	13.8	5.0
packed	26.5	21.0	13.3	9.8	3.3

DISCUSSION

Initiation of the oxidation by atomic oxygen from the fission $N_2^!O$ is suggested by the fact that it occurs only above a temperature high enough for this dissociation to take place, and is supported by the observed kinetics. Equation (4) reflects the finding that the rate depends mainly on the concentration of nitrous oxide and relatively slightly on that of methane. Its first term resembles the expression for the homogeneous decomposition of nitrous oxide, measurable just above 600° and varying in order between two, for very low, and one, for about 40 atm. pressure. The change in order indicates activation of the nitrous oxide molecules in binary collisions, followed either by deactivation in a subsequent collision or by unimolecular decomposition :



$$-d[N_2O]/dt = k_5[N_2O]^2/(1 + (k_6/k_7)[N_2O]) \quad (10)$$

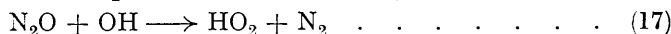
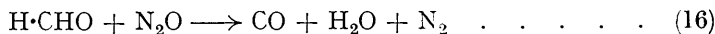
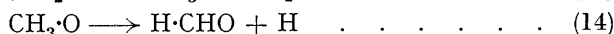
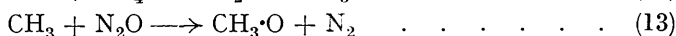
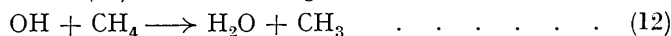
(A rate constant carries the serial number of the equation to which it refers.)

Reactions (8) and (9) are assumed to be very fast. Admittedly this is an over-simplification since it admits only one mode of excitation (Hinshelwood, *op. cit.*; Hinshelwood and Stubbs, *Discuss. Faraday Soc.*, Hydrocarbons, 1951) but it is in the main true. It predicts an apparent order which is a continuous function of pressure and lies between two and one,

in broad agreement with experiment. In the range 100—500 mm. we find an apparent order of about 1.6, making the first term in the oxidation equation (4) identical, apart from a numerical constant, with the sole term in the decomposition equation (10). The reactions have closely similar activation energies. These facts support the hypothesis that the oxidation is initiated by atomic oxygen and suggest that the term $k_1[\text{N}_2\text{O}]^{1.6}$ might be replaced by $k_1'k_5[\text{N}_2\text{O}]^2/(1 + (k_6/k_7)[\text{N}_2\text{O}])$, in which k_1' is a numerical constant. Direct evidence of oxygen atoms at the temperatures used is difficult to obtain, but Whittingham (*Nature*, 1947, **159**, 232) has identified the luminous decomposition of nitrous oxide at about 900° with the continuous emission produced during the combination of atomic oxygen and nitric oxide (Gaydon, *Trans. Faraday Soc.*, 1946, **42**, 293). Steacie and Parlee (*Canad. J. Res.*, 1938, **16**, B, 203) have shown that oxygen atoms react readily with methane and have estimated the activation energy to be *ca.* 8 kcal. per mole. No mechanism was given, but the most plausible initial step would appear to be



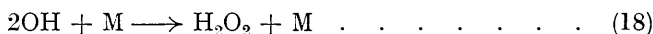
In the oxidation of methane by nitrous oxide, step (11) is consequential on the dissociation (7). An alternative initiation, involving molecular oxygen, $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CH}_3 + \text{HO}_2$, although not precluded by the kinetics, would require an activation energy much greater than 8 kcal. and is discounted. No evidence has been obtained, either phenomenal or analytical, of the presence of molecular oxygen at any stage. If present, it was certainly less than 0.25 mole % at 725°. From that point, the evidence suggests a chain mechanism; and a comparison of the rates of the oxidation and the dissociation reaction suggests a mean chain length, in terms of nitrous oxide molecules, of about 7. The kinetics may be explained, as far as the carbon monoxide stage, in terms of the chain mechanism continuing from reaction (11) in the following manner:



We recognise that this scheme is not free from ambiguity; the explicit study of some of the elementary steps may modify the postulated pattern.

The propagation step (12) appears indisputable and has been ascribed an activation energy of 8.5 kcal. (van Tiggelen, *Ann. Mines Belg.*, 1942, **43**, 117; quoted by Steacie, "Atomic and Free Radical Reactions," 1946). We have chosen to represent the formation of formaldehyde by the consecutive stages (13) and (14), rather than by the direct step, $\text{CH}_3 + \text{N}_2\text{O} \longrightarrow \text{H}\cdot\text{CHO} + \text{N}_2$, since the breakdown of alkoxy radicals to carbonyl compounds (14), is well established, as is also the relatively high stability of the methoxy radical (Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 205; George and Walsh, *Trans. Faraday Soc.*, 1946, **42**, 94; Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88, 95; Rust, Seubold, and Vaughan, *ibid.*, 1950, **72**, 338). The rôle of formaldehyde has not been ascertained, but it is probably always an intermediate of importance in the oxidative degradation of methane (Norrish, *Discuss. Faraday Soc.*, Hydrocarbons, 1951).

Some chain-terminating step keeps the hydroxyl-radical concentration finite, since a sudden approach to an explosion region is not observed. As the deactivation of hydroxyl radicals on a surface is not feasible at our pressures, there remain only two possible, homogeneous steps, *viz.*, (17) and the bimolecular recombination



M being a third body necessary to stabilise the H_2O_2 molecule on formation. Reaction (18) leads to a second term in the theoretical rate equation (22) at variance with experiment and is less likely because of the lower frequency of bimolecular collisions, whereas reaction (17) is in accordance with our kinetics. The latter accounts, by virtue of the surface destruction

of the HO₂ radicals, for the fall in rate observed when the surface/volume ratio is increased. This formation and surface destruction of the HO₂ radical has been frequently invoked as a chain-terminating step: typical examples are in the hydrogen-oxygen reaction, where its formation in ternary collisions accounts for the second explosion limit (Hinshelwood, *op. cit.*; Lewis and von Elbe, *J. Chem. Physics*, 1942, **10**, 366), the inhibition of the hydrogen-chlorine reaction by oxygen (Bodenstein and Schenk, *Z. physikal. Chem.*, 1933, *B*, **20**, 420; Norrish and Ritchie, *Proc. Roy. Soc.*, 1933, *A*, **140**, 713), and in the hydrogen-nitrous oxide reaction at high temperatures. In connection with the last, Fennimore and Kelso (*loc. cit.*) have shown that, above 850°, the explosion pressure for a mixture of nitrous oxide and hydrogen has a negative temperature coefficient, a peculiarity which they ascribe to the deactivation of hydrogen atom chain-carriers by oxygen molecules, formed through the rapid dissociation of nitrous oxide at this temperature. The reaction, $H + O_2 + M \rightarrow HO_2 + M$, produces this relatively stable radical which does not propagate chains with the facility of either the hydroxyl or the hydrogen atom.

The stability of the HO₂ radical has been considered by Minkoff (*Discuss. Faraday Soc.*, The Labile Molecule, 1947) and by Walsh (*J.*, 331, 1948) who says its heat of formation may be as high as 60 kcal. Electron-impact studies on hydrogen peroxide by Robertson (*Trans. Faraday Soc.*, 1952, **48**, 228) give the heat of the reaction, $H + O_2 \rightarrow HO_2$ as 46 ± 9 kcal. which is closer to the earlier estimates of 40 kcal. (Bodenstein and Schenk, *loc. cit.*) and 50 kcal. (Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 350).

If we take the value as 50 kcal., and the bond-dissociation energies of the oxygen molecule as 118 kcal. (Gaydon, "Dissociation Energies," Chapman and Hall), of the OH radical as 100 kcal. (Dwyer and Oldenberg, *J. Chem. Physics*, 1944, **12**, 351), and of the N-O bond in N₂O as 55 kcal., the heat of reaction (17) must be about 13 kcal. Therefore, at our temperature the reaction is thermodynamically acceptable; and, moreover, the simultaneous ejection of molecular nitrogen in the binary collisions predisposes towards stabilised HO₂ radicals. It is thus unnecessary to invoke a terminating step depending on triple collisions. The stabilised HO₂ radicals have a relatively high probability of surviving until they reach a surface.

The following rate equation may be deduced, if the usual simplifying assumption is made that the concentrations of the respective atoms, radicals, and formaldehyde become stationary once the reaction has been started. This we believe to be true of formaldehyde despite its being found in some quantity in the streaming experiments where the amounts of material involved are much larger.

$$\frac{d\rho}{dt} = \frac{3k_5[N_2O]^2}{1 + (k_6/k_7)[N_2O]} + \frac{4k_5k_{12}}{k_{17}} \times \frac{[N_2O][CH_4]}{1 + (k_6/k_7)[N_2O]} \quad (21)$$

or

$$d\rho/dt = 3k_5[N_2O]^{1.6} + 4(k_5k_{12}/k_{17})[N_2O]^{0.6}[CH_4] \quad (22)$$

This shows close similarity with the empirical rate equation. The empirical rate constant k_1 is identified with $3k_5$, and the activation energy, derived from temperature variation of k_1 , is confirmed as being the same as that for the decomposition of nitrous oxide alone; k_2 corresponds to the composite constant k_5k_{12}/k_{17} , and hence the activation energy deduced from the slopes in Fig. 6 must be $(E_5 + E_{12} - E_{17})$. Since $(E_5 + E_{12} - E_{17}) \simeq 50$ kcal., $E_5 \simeq 55$ kcal., and $E_{12} = 8.5$ kcal., E_{17} must be about 13.5 kcal. The fact that the second term makes a relatively small contribution to the total rate implies a difference between the frequency factors of reactions (12) and (17), that of (12) being lower by at least a power of 10.

If the bimolecular terminating reaction, $2OH + M \rightarrow H_2O_2 + M$ (18), were substituted for reaction (17) the predicted initial rate of pressure rise becomes

$$\frac{d\rho}{dt} = \frac{k_5[N_2O]^2}{1 + (k_6/k_7)[N_2O]} + 2k_{12} \left(\frac{k_5}{k_{18}} \times \frac{2[N_2O]^2}{\{1 + (k_6/k_7)[N_2O]\}[M]} \right)^{\frac{1}{2}} [CH_4]$$

where $M = N_2O + CH_4$.

If methane functioned effectively as a third body in (18), a progressive decrease in the order with respect to methane would follow a rise in its concentration, but the data expressed in Fig. 5 emphatically contradict this. Furthermore, in these circumstances the temperature dependence of k_2 would yield an activation energy equal to $(\frac{1}{2}E_5 + E_{12} - \frac{1}{2}E_{18})$, or about 33 kcal., in place of the 50 kcal. found. The available evidence is, in our opinion, definitely against a predominantly bimolecular termination.

The oxidation of carbon monoxide, stoichiometrically represented by equation (2), evidently proceeds at a similar rate to the oxidation of methane by which it is produced. It takes place under conditions approximating to those in which an explosive reaction was observed by Bawn (*loc. cit.*). But, in addition to the energy chain suggested by that author when only nitrous oxide and carbon monoxide were present, there are at least two other possible processes of oxidation: first, by atomic oxygen, $\text{CO} + \text{O} \longrightarrow \text{CO}_2$, and, secondly, by hydroxyl, $\text{OH} + \text{CO} \longrightarrow \text{CO}_2 + \text{H}$. In both, carbon monoxide would be competing for species necessary to the continuance of the chain reaction responsible for its own formation, a feature which would result in its concentration reaching a stationary value, as we have found.

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