129. *The Kinetics of the Oxidation of Ethane by Nitrous Oxide.*

By R. Kenwright, P. L. Robinson, and A. B. Trenwith.

The oxidation of ethane by nitrous oxide has been investigated between 530° and 670° and at pressures of 25—250 mm. The rate is measurable above 530°, at which temperature ethane decomposes and nitrous oxide is stable. The principal products are hydrogen, nitrogen, methane, carbon monoxide, and ethylene; small amounts of carbon dioxide and formaldehyde appear, but water, ethanol, and acetaldehyde were not detected. Initial-rate measurements indicate an empirical rate equation which is consistent with a mechanism involving the reactions generally accepted as occurring in the decomposition of ethane, together with certain others.

Formaldehyde, acetaldehyde, propionaldehyde, dimethyl ether, and diethyl ether have been separately pyrolysed in the presence of nitrous oxide. The reaction products indicate that of all the radicals produced under our experimental conditions, only ethyl reacts with nitrous oxide, so this, leading to the ethoxy-radical and nitrogen, is concluded to be the primary oxidation step in the ethane–nitrous oxide system.

The results throw light on the mode of decomposition of diethyl ether as they indicate that ethyl radicals are produced in the initial stages of its decomposition.

Hydrogen [1] and methane [2] are oxidised by nitrous oxide above 600° by chain processes. Each oxidation depends upon the thermal decomposition of nitrous oxide, the first step being the formation of atomic oxygen; this subsequently attacks the hydrogen or methane molecules. A qualitative examination showed that the normal paraffins from propane to nonane [3] reacted with nitrous oxide well below 600°, at which nitrous oxide is stable. It was suggested that all the reactions proceeded by chain processes resulting from a splitting of the hydrocarbon molecule into two alkyl radicals which then attack a nitrous oxide molecule: $R\cdot + N_2O \longrightarrow RO\cdot + N_2$. The alkoxy-radical subsequently breaks down into an aldehyde molecule and alkyl radical or hydrogen atom in the accepted manner.

There is thus a clear difference between the behaviour towards nitrous oxide of methane on the one hand, and of propane and higher hydrocarbons on the other. We now consider how ethane reacts with nitrous oxide, and show that its behaviour is similar to that of propane and higher hydrocarbons.

---

[1] Melville, *Proc. Roy. Soc.*, 1933, *A*, **142**, 524; 1934, *A*, **146**, 737.
[2] Robinson and Smith, *J.*, 1952, 3895.
[3] Smith, *J.*, 1953, 1271.

EXPERIMENTAL

Materials.—Nitrous oxide (anæsthesia grade) was dried (P_2O_5) and collected in a trap cooled in liquid nitrogen. Non-condensable gases were pumped off and the residue was purified by fractionation between −130° and −196° (head and tail fractions being rejected) and stored. Ethane, from a cylinder (Petrochemicals Ltd.), was frozen in a trap cooled in liquid nitrogen; after non-condensable gases had been pumped off, it was distilled in a low-temperature Podbielniak-type column. A middle cut of the fraction, b. p. −88°, was collected. Formaldehyde, prepared by Spence and Wild's method,[4] was kept at −196° until required. Acetaldehyde of reagent quality was purified by distillation from anhydrous sodium sulphate. A middle cut of the fraction, b. p. 21°, was vacuum-distilled into the apparatus and stored at −85°. Propionaldehyde, after the addition of 1 drop of concentrated sulphuric acid to 20 ml. of the liquid, was distilled. A middle cut of the fraction, b. p. 49°, was vacuum-distilled to a trap on the apparatus and stored at −85°. Diethyl ether (B.P.C.) was distilled, a middle cut of the fraction, b. p. 34·5°, being vacuum-distilled into the apparatus and stored at −85°.

Apparatus.—Two cylindrical silica reaction vessels were used, one empty, 15 × 4·5 cm., with a 1 : 1 surface : volume ratio, and the other, 11 × 4 cm., packed with silica tubing, with a 9 : 1 surface : volume ratio. Each had a thermocouple well and a capillary inlet and was connected to the rest of the system, which was of Pyrex glass, by a B7 cone and socket sealed with Picein wax. Evacuation was by a mercury-vapour pump backed by a rotary oil pump. The reaction vessel was embedded in a tubular electric furnace kept to within ±0·2° of the required temperature by a Sunvic resistance thermometer controller, type R.T.2. The temperture was measured by means of a chromel–alumel thermocouple and Doran potentiometer.

A constant-volume mercury manometer [5] was used to measure pressures except when these changed rapidly, when a simple U-manometer was more convenient. A two-way tap enabled the reaction vessel to be connected in turn to two sampling bulbs.

The reaction vessel was also connected through a capillary tap to a series of five traps. The first four were empty and the last contained activated charcoal. They were connected separately to a form of gas burette which might be used either as a Töpler pump or a McLeod gauge, so that volumes of 0·01 to 30 ml. could be measured with an accuracy of ±0·1%. The gas burette was connected to a pipette containing mercuric sulphate in sulphuric acid (57 g. of $HgSO_4$ in 100 g. of 22% H_2SO_4) for the absorption of ethylene, a small bulb packed with Carbosorb for the removal of carbon dioxide, and a take-off point fitted with a B14 socket.

Operation.—The reaction between ethane and nitrous oxide was followed by both change of pressure with time and analysis of the products after various periods of heating. To observe the pressures, nitrous oxide followed immediately by ethane was admitted to the reaction vessel from the apportioning bulbs, and readings were taken at approximately half-minute intervals during the first 10 to 15 min. In an attempt to secure uniform surface conditions, the reaction vessel was first conditioned by doing a few runs and subsequently kept under a vacuum for 15 min. before individual experiments.

For analysis, the reaction vessel was connected to the collecting traps, cooled in liquid nitrogen, to which the contents were transferred in approximately 10—15 sec. Condensable materials were frozen out in the first four traps and non-condensable gases were adsorbed on activated charcoal in the last. This trap was later heated to 300°; the released gas was withdrawn into a sampling bulb fitted with a B14 cone and a tap, and analysed mass-spectrometrically.

The condensable products were transferred to the gas burette and measured. Carbon dioxide was removed by passage over the Carbosorb and ethylene by absorption in the mercuric sulphate–sulphuric acid solution. Because of the solubility of nitrous oxide in this reagent a small correction to the volume reading was necessary. This correction was ascertained by following the rate of absorption of the mixture by the reagent. A rapid initial take-up was observed followed by a slow but regular one, the latter due to absorption of nitrous oxide; by allowing for it, a reliable determination of ethylene could be made.

Water, ethanol, acetaldehyde, and formaldehyde were also sought among the products. To detect water, a U-tube containing phosphoric oxide was introduced between the furnace and the collecting traps. This was evacuated and weighed before and after the passage of the

---

[4] Spence and Wild, *J.*, 1935, 338.

[5] Dodd and Robinson, " Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, p. 122.

products. To detect ethanol and acetaldehyde the condensable products were vacuum-fractionated between one trap at −135° and another at −196°. Ethanol and acetaldehyde, having negligible vapour pressures at −135°, tend to remain in the first trap.

To detect formaldehyde a separate apparatus was used in which a stream of purified ethane and nitrous oxide (approximately 1 : 1 at 1 atm.) was passed through a silica reaction vessel, heated to 580°, and fitted with a capillary inlet and outlet. The issuing gas was bubbled through a solution of chromotropic acid (50 mg. of sodium salt in 100 ml. of 75% H_2SO_4) at 60°.

Formaldehyde, acetaldehyde, propionaldehyde, and diethyl ether were separatedly pyrolysed both alone and in the presence of nitrous oxide. The initial rates of the reactions were measured and the products after various times of heating analysed.

RESULTS AND DISCUSSION

Ethane and nitrous oxide react measurably above 500°. A series of experiments, carried out between 530° and 670°, in which the pressure of either reactant was varied, gave pressure–time curves from which initial rates were derived. The effects on the rates of variation of the pressure of each reactant are shown in Figs. 1 and 2. The results conform to the empirical rate equation:

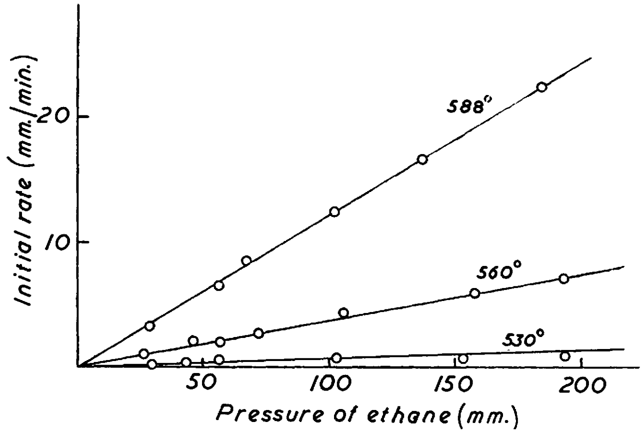

FIG. 1. *Variation of initial rate with pressure of ethane.* (*Pressure of* N_2O, 50 *mm.*)

$$\text{Rate} = k'[C_2H_6] + k''[C_2H_6][N_2O]$$

This relationship applied up to 670°, despite the appreciable rate of decomposition of nitrous oxide at this temperature—at 670° ethane decomposes so rapidly that any change in the rate of reaction caused by the decomposition of nitrous oxide is insignificant.

Fig. 3 shows the products from a mixture of ethane (100 mm.) and nitrous oxide (100 mm.) after various times of heating at 560°. In addition to the ethylene and hydrogen normally produced in the decomposition of ethane, appreciable quantities of nitrogen, carbon monoxide, methane, and carbon dioxide are present. The flow experiment indicated that formaldehyde is also formed, as a purple colour developed in the chromotropic acid solution after 2 min. which intensified with time. (Attempts to determine the formaldehyde were unsuccessful owing to its very small amount; ethane and nitrous oxide alone gave a blank.)

Repeated tests showed that water, ethanol, and acetaldehyde were always absent from the products.

These observations lead us to suggest the following mechanism for the reaction between ethane and nitrous oxide:

$$C_2H_6 \longrightarrow 2CH_3\cdot \quad . \quad . \quad . \quad (1)$$

$$CH_3\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + CH_4 \quad . \quad (2)$$

$$C_2H_5\cdot \longrightarrow C_2H_4 + H\cdot \quad . \quad . \quad (3)$$

$$H\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + H_2 \quad . \quad . \quad (4)$$

$$H\cdot + C_2H_5\cdot \longrightarrow C_2H_6 \text{ or } C_2H_4 + H_2 \quad (5)$$

$$C_2H_5\cdot + N_2O \longrightarrow C_2H_5O\cdot + N_2 \quad . \quad (6)$$

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O \quad . \quad (7)$$

It includes reactions (1)—(5) which are usually accepted as representing the decomposition of ethane, in addition to (6) and (7) which are discussed below. There is also the formation of carbon monoxide and hydrogen by the decomposition of the formaldehyde produced in (7), a reaction catalysed by nitrous oxide (p. 666). Subsequently carbon dioxide results from reaction (8) which, as Bawn [6] has shown, takes place under our experimental conditions. The maximum in the ethylene–time curve is in accord with Steacie and McDonald's observations [7] that ethylene polymerised and decomposed when heated with nitrous oxide above 530°.

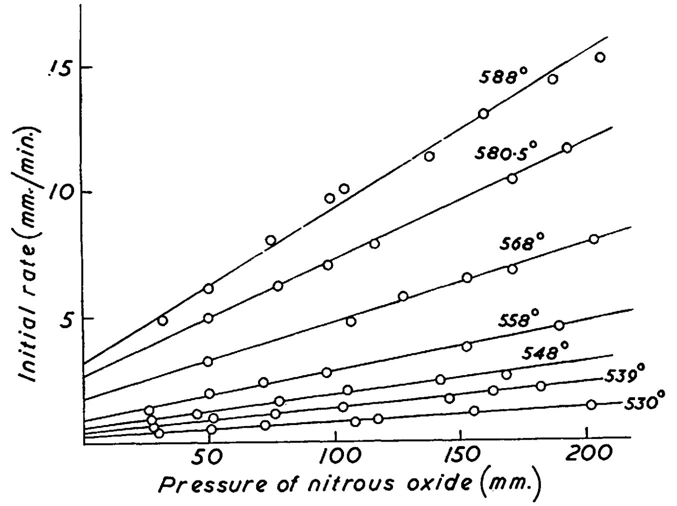

Fig. 2. *Variation of initial rate with pressure of nitrous oxide.* (*Pressure of* C_2H_6 = 50 *mm.*)

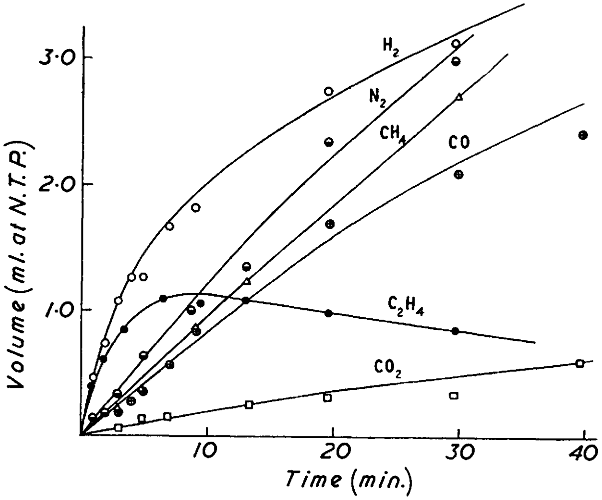

Fig. 3. *Products of pyrolysis of* 100 *mm. of ethane* +100 *mm. of* N_2O *at* 560°.

The mechanism suggested can be considered as including two simultaneous chain reactions. The chain-carrying steps of the first are (3) and (4) and lead to an equation (9) representing the decomposition of ethane. The chain-carrying steps of the second are

---

[6] Bawn, *Trans. Faraday Soc.*, 1935, **31**, 461.

[7] Steacie and McDonald, *Canad. J. Res.*, 1935, **12**, 711.

(6), (7), and (2) which, if the decomposition of the formaldehyde produced in (7) is rapid, yield eqn. (10). The inference that (8), (9), (10), and the polymerisation of ethylene are

$$CO + N_2O \longrightarrow CO_2 + N_2 \quad \ldots\ldots\ldots\ldots \quad (8)$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \quad \ldots\ldots\ldots\ldots \quad (9)$$

$$C_2H_6 + N_2O \longrightarrow CO + H_2 + N_2 + CH_4 \quad \ldots\ldots\ldots \quad (10)$$

the only reactions occurring is supported by the analytical data. For instance, hydrogen is the major product as would be expected since it is produced in both (9) and (10). Further, the concentration of carbon monoxide plus that of carbon dioxide after any time is approximately equal to that of methane, and the carbon dioxide concentration plus the methane concentration is approximately equal to that of nitrogen.

The reason for suggesting reaction (5) as the chain-ending process is that, of a number of possible terminators, it is the only one which yields a theoretical equation resembling that found empirically. Incidentally, similar considerations have had to be taken into account in arriving at a mechanism for the thermal decomposition of ethane.[8] Reaction (7) has been given as the most likely fate of the ethoxy-radical; [9] other possibilities are the abstraction of hydrogen from a donor molecule to form ethanol, and the loss of an atom of hydrogen to yield acetaldehyde. Failure to find either ethanol or acetaldehyde suggests that neither alternative reaction occurs appreciably under our experimental conditions, although they are important at lower temperatures.[9]

Although reactions (11) and (12), said to occur in other systems,[1, 2] also appear feasible, reaction (12) can be ruled out because the hydroxyl radicals should form water, and none was found. To decide on the validity of (11) a mixture of acetaldehyde (100 mm.) and

$$CH_3\cdot + N_2O \longrightarrow CH_3O\cdot + N_2 \quad \ldots\ldots\ldots \quad (11)$$

$$H\cdot + N_2O \longrightarrow HO\cdot + N_2 \quad \ldots\ldots\ldots\ldots \quad (12)$$

nitrous oxide (100 mm.) was heated at 560° for 10 min. Since acetaldehyde decomposes in part, at least, by a chain mechanism involving methyl radicals,[10] reaction (11) would be indicated by the presence of nitrogen in the products. As nitrogen is also formed by oxidation of the carbon monoxide, if (11) occurs the amount of nitrogen must exceed that of the carbon dioxide found. A trace of carbon dioxide appeared, but nitrogen was not detected by the mass spectrometer. From this it is concluded that reaction (11) does not occur under these conditions.

Temp.	Reactant	Reactant pressure (mm.)	N_2O pressure (mm.)	$(dp/dt)_{\text{init.}}$ (mm./sec.)
560°	$CH_3\cdot CHO$	100	0	0·32
,,	,,	100	100	0·85
,,	,,	190	0	0·86
,,	$C_2H_5\cdot CHO$	100	0	0·52
,,	,,	100	100	0·65
,,	$C_2H_5\cdot O\cdot C_2H_5$	95	0	0·42
,,	,,	95	100	0·94
587 *	C_2H_6	100	100	0·24
587 †	C_2H_6	100	100	0·21
531	H·CHO	50	0	0·03 [11]
,,	H·CHO	50	50	0·30

* Vessel not packed. † Vessel packed.

There is a marked increase in the rate of decomposition of acetaldehyde in the presence of nitrous oxide (see Table). This well-known accelerating effect is said [12] to be due to

---

[8] Trotman-Dickinson, " Gas Kinetics," Butterworths, 1955, p. 152.

[9] *Discuss. Faraday Soc.*, 1951, **10**, 242.

[10] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1956.

[11] Fletcher, *Proc. Roy. Soc.*, 1934, *A*, **146**, 357.

[12] Verhoek, *Trans. Faraday Soc.*, 1935, **31**, 1527.

reaction (13). That we were unable to detect nitrogen might be thought to preclude this mechanism, but under our experimental conditions the chain length of the aldehyde decomposition is very large (determinations of the hydrogen and methane produced by pyrolysis of acetaldehyde at 470° indicate a chain length [13] of approximately 1200), whence only a trace of nitrous oxide need react according to (13) markedly to increase the rate of acetaldehyde decomposition.

$$N_2O + CH_3{\cdot}CHO \longrightarrow N_2 + CH_3{\cdot} + OH{\cdot} + CO \quad . \; . \; . \; . \; . \; . \quad (13)$$

In search of confirmatory evidence for reaction (6) a mixture of propionaldehyde (100 mm.) and nitrous oxide (100 mm.) was pyrolysed at 560° for various times. Propionaldehyde yields methyl and ethyl radicals and atomic hydrogen on pyrolysis,[10] but since we can rule out the possibility of a reaction between methyl or atomic hydrogen and nitrous oxide, any nitrogen produced must result from (6) and (8). The composition of the products, shown graphically in Fig. 4, indicates the formation of nitrogen at a rate which increases slightly with time and is greater than the rate of formation of carbon dioxide. This evidence strongly supports the validity of reaction (6).

The results of a similar series of experiments with diethyl ether are shown in Fig. 5.

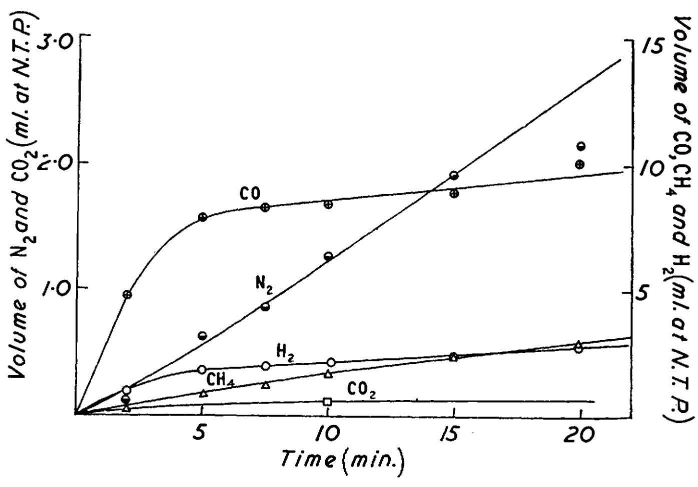

Fig. 4. *Products of pyrolysis of* 100 *mm. of propionaldehyde* +100 *mm. of nitrous oxide at* 560°.

Here also the nitrogen is produced in appreciable excess of the carbon dioxide, indicating again the probability of (6).

In connection with these observations, it has been borne in mind that ethane is produced by pyrolysis of both propionaldehyde and diethyl ether, so that nitrogen would be expected in the products. We consider, however, that the immediate appearance of nitrogen and the shape of the nitrogen-time curve suggest that the first-formed nitrogen is the result of a reaction between nitrous oxide and ethyl radicals from the parent organic molecule.

The theoretical rate equation derived from the mechanism given above is (14), which

$$-\frac{d[C_2H_6]}{dt} = \left(\frac{k_1k_3k_4}{k_5}\right)^{\frac{1}{2}}[C_2H_6] + \left\{k_6\left(\frac{k_1k_3k_4}{k_5}\right)^{\frac{1}{2}} \Big/ \left[k_3 - \left(\frac{k_1k_3k_5}{k_4}\right)^{\frac{1}{2}}\right]\right\}[C_2H_6][N_2O] \quad (14)$$

is identical in form with the empirical rate equation. The first term corresponds to the equation for the rate of decomposition of ethane alone so that k', in the empirical rate equation, should correspond to the rate constant for the decomposition of ethane. The intercepts on the ordinate of the graphs in Fig. 2 are equal to $k'p_{\text{ethane}}$ and values for k' can be derived from them. These yield the result $k' = 10^{13} \exp(-63{,}000/\boldsymbol{R}T)$ sec.$^{-1}$, which is close to the accepted value for the ethane rate constant.[10]

---

[13] Trenwith, unpublished work.

It is concluded that in the main the reaction between nitrous oxide and ethane can be satisfactorily accounted for by assuming it to proceed by the chain decomposition of ethane together with a chain reaction resulting from the attack of ethyl radicals upon nitrous oxide. The actual mechanism is a little more complex than this since, as indicated in the Table, when carried out in a packed vessel the reaction is slower at first. (The present work was carried out in a conditioned vessel.)

The experiments with diethyl ether and nitrous oxide are of interest since two possible modes of decomposition of diethyl ether have been postulated,[10] one involving both methyl and ethyl radicals and the other only methyl radicals. Although our results do not entirely rule out the second mechanism, since they indicate the formation of ethyl radicals during the pyrolysis of diethyl ether, they support the first.

The rate of decomposition of diethyl ether is increased by the presence of nitrous oxide (Table). Experiments at a slightly lower temperature throw light on the reason for this as nitrogen could not be detected when a mixture of diethyl ether (100 mm.) and nitrous oxide (100 mm.) had been heated at 500° for 15 min. The sigmoid pressure–time curve indicated (*a*) an initial rate equal to that expected for the decomposition of 100 mm. of diethyl ether alone, and (*b*) a subsequent increase in rate for about 10 min., followed by a steady decrease. This suggests that reaction (6) does not happen at this temperature, and that the action of nitrous oxide is restricted to catalysing the decomposition of acetaldehyde, the primary product.

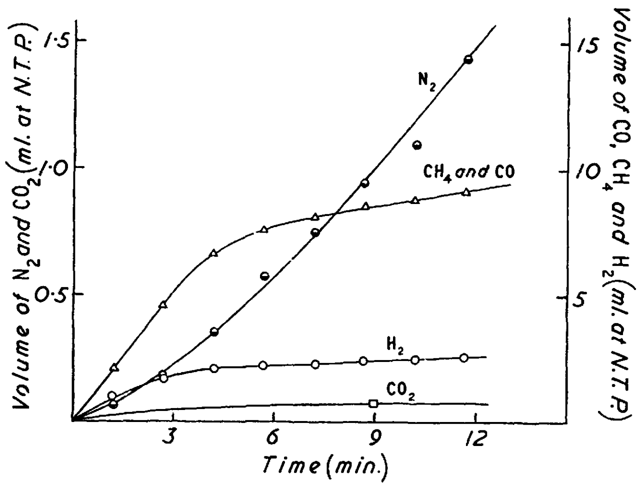

FIG. 5. *Products of pyrolysis of* 100 *mm. of diethyl ether* +100 *mm. of nitrous oxide at* 560°.

In the reaction of nitrous oxide with formaldehyde, it is difficult to obtain accurate results because of the condensation of the formaldehyde. Nevertheless it is clear that nitrous oxide markedly increases the rate of decomposition of the formaldehyde (Table); however, the nitrous oxide is not altered as nitrogen is absent from the products which consist of hydrogen and carbon monoxide in equal amounts. The way in which formaldehyde decomposes is not yet known with certainty, but if it be by a free-radical chain mechanism then a reaction similar to (13) would account for the acceleration by nitrous oxide.

Nitrous oxide has less effect on the decomposition of these aldehydes on passing up the series. Thus with equimolar mixtures under similar conditions, the initial rate of decomposition is increased about ten times for formaldehyde, three times for acetaldehyde, and one and a quarter times for propionaldehyde.

The authors thank Mr. P. Kelly, M.Sc., for the mass-spectrometric determinations.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1. [*Received, July* 29*th*, 1957.]