419. *The Kinetics of the Oxidation of Ethane by Nitrous Oxide. Part II.*[1]

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A closer examination of the early stages of the reaction between nitrous oxide and ethane within the range 553—588° has enabled the rate constant of the reaction $C_2H_5\cdot + N_2O \longrightarrow C_2H_5\cdot O\cdot + N_2$ to be calculated.

Initially hydrogen and ethylene are the major products of the reaction and both are produced at the same rate which, with equal amounts of nitrous oxide and ethane, is about twenty times faster than in the absence of nitrous oxide. The increase may be due to an additional chain-initiating step although " inert " gas effects can also contribute.

The preliminary results of another investigation show that ethylene reacts readily with nitrous oxide at 580°, whereat the separate gases are comparatively stable, the principal non-condensable products being nitrogen, carbon monoxide, and methane.

On the basis of kinetic measurements the following mechanism has been proposed[1] for the reaction between nitrous oxide and ethane,

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

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

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

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

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

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

$$C_2H_5\cdot O\cdot \longrightarrow CH_3\cdot + CH_2O \quad . \quad . \quad . \quad (7)$$

From the above it follows that $d[N_2]/d[C_2H_4] = (k_6/k_3)[N_2O]$, so that by comparing the rates of formation of nitrogen and ethylene at various nitrous oxide concentrations it should be possible to derive k_6/k_3. This has been done and in the process further observations have been made on the ethane–nitrous oxide reaction.

EXPERIMENTAL

The materials, apparatus, and procedure were as described before.[1] At first ethylene was determined by absorption in mercuric sulphate–sulphuric acid solution, but early results indicated that the initial rates of formation of hydrogen and ethylene were equal (see Fig. 1), so in subsequent experiments the procedure was simplified, and the non-condensable products only were measured and analysed mass-spectrometrically for hydrogen, carbon monoxide, methane, and nitrogen. The instrument used was a Metropolitan-Vickers, type M.S.2. The electron-accelerating voltage was maintained at 70 ev with a filament current of 100 μA; the ion-accelerating voltage was held constant at 2000 v and automatic magnetic scanning was employed with the recorder unit. An ion-repeller voltage (+12 v) was used in the comparatively stable " plateau " region of the ion-repeller curve; sample volumes were of the order of 0·5 to 1·5 ml. at N.T.P. Cracking patterns and sensitivities of pure components were measured in the usual way and checked at frequent intervals.

The contribution of methane to each spectrum was determined by use of $m/e = 15$ and those of carbon monoxide and nitrogen were estimated by solving two linear simultaneous equations involving $m/e = 28$ and $m/e = 14$. The alternative method for estimating carbon monoxide and nitrogen by using $m/e = 28$ and 29 was tried but proved unreliable.

The actual molar percentage compositions of the mixtures obtained from the pyrolysis of ethane + nitrous oxide varied very little and were of the order: H_2, 60%; N_2, 20%; CH_4, 10%; CO, 10%. Maximum possible errors estimated by analysis of mixtures similar to the above, of known composition, were ±3% of the molar percentage obtained.

RESULTS

Fig. 1 is a typical composition–time graph and represents the products formed from 100 mm. of ethane + 100 mm. of nitrous oxide at 580°. For comparison the hydrogen formed from 100 mm. of ethane alone at the same temperature is also shown.

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[1] Part I, Kenwright, Robinson, and Trenwith, *J.*, 1958, 660.

From the curves the following observations may be made: (*a*) There is a short induction period, not hitherto detected, varying from 16 sec. at 553° to 9 sec. at 588°, and independent of the nitrous oxide concentration; an induction period of the same order of time was observed in the methane–nitrous oxide reaction.[2] It seems likely that these represent the time necessary for chain-carrying radicals to attain steady-state concentrations. Howlett[3] has predicted the existence of induction periods of the same order of magnitude as the above in the pyrolysis of ethane alone. These have not been observed experimentally, probably because below 600° the rate of decomposition of ethane is extremely slow whilst above 600° the induction periods will be too short to be detected. That induction periods have been observed here seems good support of the view that they occur in the decomposition of ethane alone.

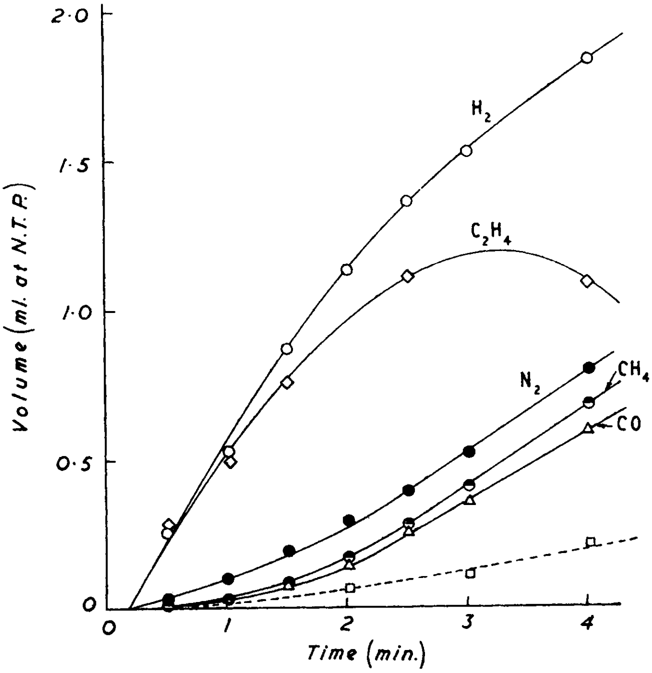

FIG. 1. *Products of pyrolysis of* 100 *mm. of* C_2H_6 + 100 *mm. of* N_2O *at* 580°.

The broken curve represents H_2 from 100 mm. of C_2H_6 alone.

(*b*) The rates of formation of carbon monoxide and methane are initially very low and increase steadily over the first 2½ min. This indicates that (7) is not a fast reaction since both methane and carbon monoxide result from subsequent reactions of the products of (7). The rate of formation of methane slightly exceeds that of carbon monoxide which is to be expected since the latter reacts slowly with nitrous oxide to form nitrogen and carbon dioxide[4] and methane is formed from the methyl radicals produced in both reactions (1) and (7).

(*c*) The initial rates of formation of hydrogen and ethylene are equal. The equality supports the mechanism already advanced since reaction (4) will be rapid and the hydrogen produced by (5) small compared with that formed by (4). The hydrogen formed from the formaldehyde of reaction (7) will be negligible in the early stages of the reaction.

A comparison of the two hydrogen curves, with and without nitrous oxide, shows that an equal volume of the latter increases the initial rate of hydrogen production about twenty-fold.

(*d*) The rate of formation of nitrogen increases with reaction time and this is held to be due to oxidation of primary products by nitrous oxide. Nitrogen is known to be produced by the reaction $CO + N_2O \longrightarrow CO_2 + N_2$, but the shapes of the methane and carbon monoxide curves indicate that only a small fraction of the nitrogen can come from the oxidation of the

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[2] Robinson and Smith, *J.*, 1952, **3895.**

[3] Howlett, *Trans. Faraday Soc.*, 1952, **48**, 35.

[4] Bawn, *ibid.*, 1935, **31**, 461.

latter. The other possibility is the ethylene and it is apparent that ethylene decomposes under the experimental conditions but in order to account for the increase in the rate of nitrogen formation with time it is necessary that the rate of formation of nitrogen from ethylene shall be greater than from ethane. From Fig. 2 which shows the reaction products from 100 mm. of ethylene + 100 mm. of nitrous oxide at 580° and, for comparison, the nitrogen from the ethane–nitrous oxide mixture, it may be seen that nitrogen is formed roughly 18 times faster in the ethylene–nitrous oxide system. Comparison of the pressure increase in the reaction vessel with the volumes of non-condensable products produced indicates that the reaction approximates to $N_2O + C_2H_4 \longrightarrow N_2 + CO + CH_4$ with little, if any, polymerization of the ethylene.

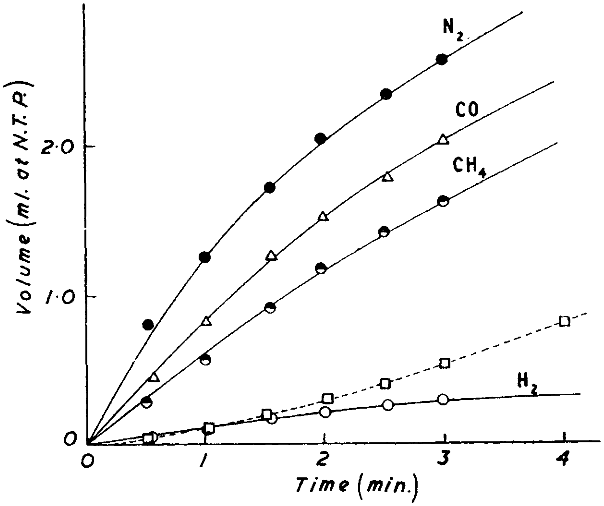

FIG. 2. *Products of pyrolysis of* 100 *mm. of* C_2H_4 + 100 *mm. of* N_2O *at* 580°.

The broken curve represents N_2 from 100 mm. of C_2H_6 + 100 mm. of N_2O.

From curves similar to those in Fig. 1 for different initial concentrations of nitrous oxide, values for $d[N_2]/d[C_2H_4]$ were deduced. A plot of these against nitrous oxide concentration was a straight line passing through the origin with a slope corresponding to k_6/k_3. Experiments at 553°, 568·5°, 575°, and 588° provided data for an Arrhenius plot of log k_6/k_3 which was a good straight line: $E_3 - E_6 = 8{\cdot}5$ kcal. mole^{-1} and $A_6/A_3 = 2{\cdot}0$ l. mole^{-1}. Taking E_3 and A_3 as 39·5 kcal. mole^{-1} and 3×10^{14} sec.$^{-1}$ respectively,[5] we have $k_6 = 6 \times 10^{14} \exp(-31{,}000/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

DISCUSSION

The energy of activation of reaction (3) is comparatively high for a radical–molecule reaction but this might be expected as neither methyl radicals nor hydrogen atoms react with nitrous oxide at the experimental temperature.[1]

The most striking observation made during the investigation is the marked increase in the rate of formation of hydrogen when nitrous oxide is present. According to the mechanism suggested $[H\cdot] = k_1k_3k_4/k_5$ so that the rate of formation of hydrogen from (4) should be independent of the nitrous oxide concentration.

One possible explanation of the increase is the occurrence of the additional chain-initiating step $C_2H_6 + N_2O \longrightarrow C_2H_5\cdot + OH\cdot + N_2$. The contribution of this reaction can only be significant, however, if the chains are long, since the formation of hydroxyl radicals must lead to the production of water and none could be detected among the products after prolonged heating of ethane–nitrous oxide mixtures.

A number of " inert " gases increase the rate of decomposition of ethane,[6,7] but with nitrous oxide the magnitude of the increase is such as to rule out the possibility that the

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[5] Bywater and Steacie, *J. Chem. Phys.*, 1951, **19**, 326.
[6] Küchler and Thiele, *Z. phys. Chem.*, 1939, *B*, **42**, 359.
[7] Parsons, Danby, and Hinshelwood, *Proc. Roy. Soc.*, 1957, *A*, **240**, 333.

" inert " gas effect is solely responsible, for if this were the case nitrous oxide would transfer energy much more efficiently than ethane itself. The increase in rate of decomposition of ethane may, however, be due partly to the activation of ethane molecules by collision with nitrous oxide.

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