743. *The Kinetics of the Oxidation of Ethylene by Nitrous Oxide.*

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The oxidation of ethylene by nitrous oxide has been investigated at temperatures between 555° and 602° and at pressures from 20 to 100 mm. The reaction is homogeneous and the principal products are nitrogen, carbon monoxide, methane, and ethane; small amounts of acetaldehyde, hydrogen, and hydrocarbons of high molecular weight are also formed. The overall reaction is complex, consisting of both the oxidation of ethylene and its free-radical induced polymerization. In the initial step, acetaldehyde is formed; this is followed by the reaction of ethylene with free radicals derived from the decomposition of acetaldehyde.

A MAJOR product of the reaction of ethane with nitrous oxide is ethylene. Ethylene itself, however, reacts readily with nitrous oxide at 580°.[1,2] A more detailed investigation of the ethylene reaction has shown that it involves both the oxidation and the polymerization of ethylene. The initial step is a bimolecular reaction between ethylene and nitrous oxide. This system therefore differs from others in which molecules are oxidised by nitrous oxide, since these former depend upon an initial splitting either of the nitrous oxide into nitrogen and atomic oxygen,[3] or of the other reactant into two free radicals.[1,2,4]

EXPERIMENTAL

Materials.—Pure nitrous oxide was obtained as before.[1] Ethylene, from a cylinder, was frozen in a liquid-nitrogen trap and, after the non-condensable gases had been removed by pumping, was distilled in a low-temperature, Podbielniak-type column. A middle cut of the fraction of b. p. −104° was collected.

Apparatus and Procedure.—These were as described previously,[1,2] except that the condensable products were analysed with a Perkin–Elmer gas chromatography apparatus. Nitrous oxide, ethylene, and ethane were determined by use of a column of active carbon (40—70 B.S.S.) at 72°, and a didecyl phthalate column at room temperature was used to estimate acetaldehyde. For each hydrogen was the carrier. Chromatogram peaks were identified both by the mass-spectrometric analysis of gas leaving the columns, and by a comparison of the peaks obtained with those produced by pure compounds.

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

[2] Kenwright and Trenwith, *J.*, 1959, 2079.

[3] Melville, *Proc. Roy. Soc.*, 1933, *A*, **142**, 524; 1934, *A*, **146**, 737; Robinson and Smith, *J.*, 1952, 3895; Bell, Robinson, and Trenwith, *J.*, 1955, 1440.

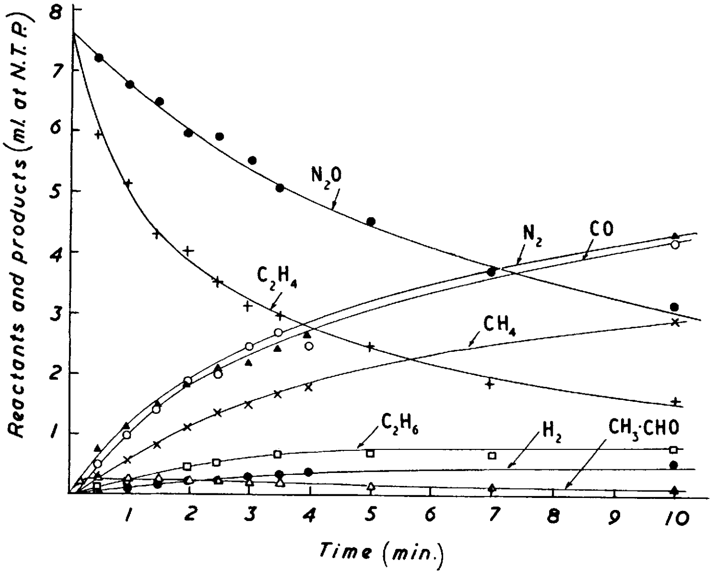
[4] Smith, *J.*, 1953, 1271.

To obtain a complete analysis of the products, mixtures of 100 mm. of nitrous oxide + 100 mm. of ethylene were heated at 580° for periods up to 10 min. Measured amounts of the condensable products were taken from duplicate runs and separately analysed for acetaldehyde, and for nitrous oxide, ethylene, and ethane. This led to some inconsistency in the results, as appears from the deviation of the points from the nitrous oxide curve in Fig. 1, since the more volatile condensable products, when transferred to the gas burette, would tend to concentrate at the top and it was from there that samples were subsequently withdrawn. To obtain kinetic data on the reaction, only the nitrous oxide in the products was determined and, to avoid errors arising from inadequate mixing, much smaller quantities of the reactants were employed (15—25 mm. of nitrous oxide and 20—40 mm. of ethylene) and all the condensable products were passed through the gas-chromatography apparatus.

RESULTS

1. *The Products of the Reaction.*—The plot of products formed against heating time for 100 mm. of nitrous oxide plus 100 mm. of ethylene at 580° is shown in Fig. 1. Of the ethylene which reacted during 5 min., 70% can be accounted for; the missing material had the empirical formula CH_2 and is believed to be polymeric. Thus a mass-spectrometric analysis of a sample of the condensable material showed the presence of small amounts of hydrocarbons with three, four, and five carbon atoms in the molecule. There were three small chromatogram peaks of samples passed through the didecyl phthalate column which followed the acetaldehyde peak. Attempts to identify the compounds causing these peaks were unsuccessful because of the very small amounts involved. In time a tar slowly appeared in the capillary leading to the reaction vessel, but the total amount collected was insufficient to permit its identification.

FIG. 1. *Products of the pyrolysis of* 100 *mm. of nitrous oxide* + 100 *mm. of ethylene at* 580°.



The strong evidence that the amount of ethylene polymerizing is comparatively small, differs from the findings of Steacie and MacDonald [5] who, from a qualitative examination of the ethylene–nitrous oxide system at the slightly lower temperature of 530°, concluded that large amounts of tar and other condensable materials were formed. (Presumably the lower temperature favours the formation of high molecular weight products.)

An examination of the curves for carbon monoxide, methane, hydrogen, and ethane shows that the rates of formation of these products must increase during the early stages of the

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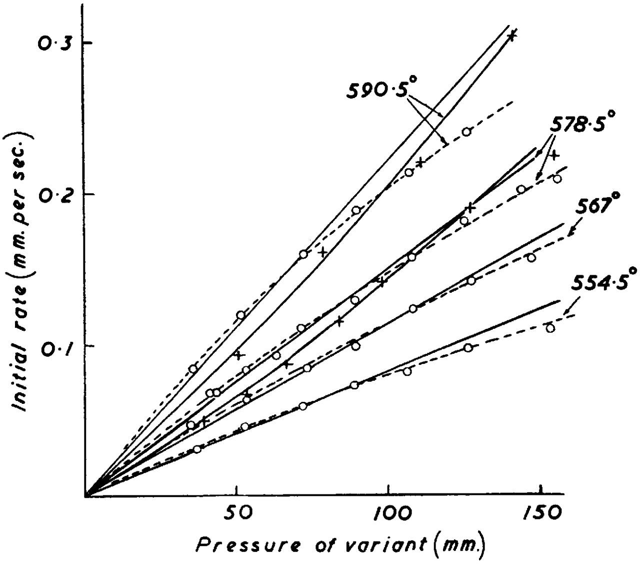
[5] Steacie and MacDonald, *Canad. J. Chem.*, 1935, **12**, 711.

reaction, as a smooth curve drawn through the experimental points cuts the time axis at approximately 5 sec. The rate of formation of acetaldehyde is almost constant during the first 15 sec. and is approximately equal to the rate at which nitrous oxide disappears; thereafter the former falls rapidly to zero and the amount of acetaldehyde present subsequently decreases very slowly. Thus it is concluded that acetaldehyde is a primary product and that carbon monoxide, methane, hydrogen, and ethane are secondary products.

2. *Kinetic Measurements.*—Mixtures of ethylene and nitrous oxide were heated at 555°, 567°, 580°, and 590° and the course of the reaction was followed from the increase in pressure with time. Runs were performed with constant initial pressures of nitrous oxide and varying initial pressures of ethylene and *vice versa.* The graphs of the initial rate of change of pressure against pressure of the variable reactant are shown in Fig. 2. The logarithmic plots of these points yielded the rate equation: $\mathrm{d}p_0/\mathrm{d}t = k[N_2O]^{1\cdot2}[C_2H_4]^{0\cdot9}$.

FIG. 2. *Variation of initial reaction rate with the pressure of each reactant* (o, 100 *mm. of nitrous acid*; +, 100 *mm. of ethylene*).



The graphs for constant pressures of nitrous oxide are very nearly straight lines when pressures of ethylene are less than 100 mm. If we make the approximation that in this region the reaction is of first order with respect to each reactant, the slopes of these lines give: $k = 10^{9\cdot9} \exp(-38{,}000/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

Runs performed in a packed vessel showed that a ninefold increase in the surface area had no measurable effect upon the rate.

Other experiments were performed at 580°, 590°, and 602° in which the initial pressure of each reactant was varied as before, and in which the reaction was followed by removing condensable products and determining their content of nitrous oxide. The initial slopes of the curves of $[N_2O]$ *versus* time were determined, and from these, graphs of $-\mathrm{d}[N_2O]/\mathrm{d}t$ *versus* the concentration of ethylene and of nitrous oxide were plotted. The points lay close to straight lines passing through the origin, which suggested a first-order dependence of each reactant, but the results were too scattered to permit an exact estimate of the orders. If we assume a first-order dependence, the rate constant from the analytical results is given by: $k = 10^{10.1} \exp(-39{,}000/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

The two expressions for k are in good agreement and a close correspondence is to be expected, since total pressure change is simply related to the corresponding change in pressure of nitrous oxide during the reaction. Thus for 100 mm. of nitrous oxide + 100 mm. of ethylene at 580°: $-\Delta p_{N_2O} = 1{\cdot}4\Delta p_{\text{total}}$.

DISCUSSION

The following scheme is suggested to account for the experimental results:

$$C_2H_4 + N_2O \longrightarrow CH_3\cdot CHO + N_2 \quad \dots\dots \quad (1)$$
$$CH_3\cdot CHO \longrightarrow CH_3\cdot + CO + H\cdot \quad \dots\dots \quad (2)$$
$$H\cdot + C_2H_4 \longrightarrow C_2H_5\cdot \quad \dots\dots \quad (3)$$
$$\text{or} \quad \longrightarrow H_2 + C_2H_3\cdot \quad \dots\dots \quad (4)$$
$$CH_3\cdot + C_2H_4 \longrightarrow C_3H_7\cdot \quad \dots\dots \quad (5)$$
$$\text{or} \quad \longrightarrow CH_4 + C_2H_3\cdot \quad \dots\dots \quad (6)$$
$$C_2H_5\cdot + C_2H_4 \longrightarrow C_4H_9\cdot \quad \dots\dots \quad (7)$$
$$\text{or} \quad \longrightarrow C_2H_6 + C_2H_3\cdot \quad \dots\dots \quad (8)$$
$$C_2H_3\cdot + C_3H_7\cdot \text{ (or } C_4H_9\cdot) \longrightarrow \text{products} \quad \dots\dots \quad (9)$$

The rate equation derived from pressure–time measurements indicates that the actual mechanism is more complex, but the above reactions are evidently the important ones since they account satisfactorily for all the analytical results. There is no obvious reason for the small divergences from unity of the experimentally determined orders. The decomposition of nitrous oxide itself, although very slow at the temperatures used, may play a significant part at higher pressures, and this reaction has an order of roughly 1·5 with respect to nitrous oxide at the pressures used. The derived rate constant must approximate to that for reaction (1), which therefore has an activation energy of about 38 kcal.

There cannot fail to be other radical recombinations besides reaction (9) but these have been neglected since, under the experimental conditions, reactions (3)—(8) must be fast, and hence radical concentrations will be very small. Previous work[1] has shown that neither hydrogen atoms nor methyl radicals react measurably with nitrous oxide under the experimental conditions and, further, the reaction between ethyl radicals and nitrous oxide, which has an activation energy of 31 kcal.,[2] will be slow compared with reaction (7), for example, for which an activation energy of 5·5 kcal. has been reported.[6]

Reaction (1) might be expected to yield ethylene oxide rather than acetaldehyde, but a comparison of the chromatograms obtained from the condensable products with those produced by pure acetaldehyde and ethylene oxide proved that none of the last was formed.

The shape of the acetaldehyde curve indicates that reaction (2) must be rapid. It has been found[2] that the addition of nitrous oxide markedly increases the rate of decomposition of acetaldehyde, and this would therefore seem to be due to the effect of nitrous oxide on the initial step in the acetaldehyde decomposition. As the concentration of acetaldehyde is always very small, possible metathetical reactions between it and free radicals have been disregarded.

As will be shown later, $k_3/k_4 \sim 10$. If we assume that $d[CH_3\cdot CHO]/dt = 0$, which is almost true after a reaction time of $\frac{1}{2}$ minute, then from the proposed mechanism: $d[C_2H_4]/d[N_2O] = 3{\cdot}9$. The experimental value corresponds closely to this; during the first $\frac{1}{2}$ minute the ratio is approximately 3·5, indicating the essential validity of the suggested mechanism.

If we adopt the notation that R_X represents the initial rate of formation of the substance X, according to the reaction scheme, $R_{CO} = R_{H\cdot}$ and hence assuming reactions (3) and (4) are fast, $R_{CO} - R_{H_2} = R_{C_2H_5\cdot}$. Then $k_3/k_4 = (R_{CO} - R_{H_2})/R_{H_2}$, which from the experimental results, equals 9·8. A value of 4·1 kcal. has been reported for the activation energy of reaction (3)[7] (although this value is probably low; see ref. 8, page 284), so that, provided the A factors for the two reactions are the same, reaction (4) should have an activation energy of 8·0 kcal.

In a similar manner $k_5/k_6 = (R_{CO} - R_{CH_4})/R_{CH_4} = 1{\cdot}2$.

[6] Pinder and LeRoy, *Canad. J. Chem.*, 1957, **35**, 588; Lampe and Field, *ibid.*, 1959, **37**, 995.
[7] Darwent and Roberts, *Discuss. Faraday Soc.*, 1953, No. 14, 55.
[8] Trotman-Dickenson, " Gas Kinetics," Butterworths Scientific Publications, London, 1955.

According to the results of Mandelcorn and Steacie[9] $E_5 = 7{\cdot}0 \pm 1{\cdot}5$ kcal. and $A_5 = 10^{11\cdot4}$ ml. mole^{-1} sec.$^{-1}$ and Steacie and Trotman-Dickenson[10] give $E_6 = 10{\cdot}0 \pm 0{\cdot}4$ kcal. and $A_6 = 10^{11\cdot3}$ ml. mole^{-1} sec.$^{-1}$. From these k_5/k_6 at the experimental temperature is 5·8. Although this figure is appreciably different from the experimental value it is noted that, if we take values of 8·5 and 9·6 kcal. for E_5 and E_6 which are within the stipulated limits of experimental error, k_5/k_6 becomes 1·9, in much better agreement with the experimental result. Using the value $E_5 = 8{\cdot}9$ kcal.[11] and taking $E_6 = 10{\cdot}0$ kcal., we again arrive at a value of 1·9 for k_5/k_6.

The above procedure can also be applied to the two possible reactions of ethyl radicals: $R_{C_2H_5\cdot} = 1{\cdot}18$ and $R_{C_2H_6} = 0{\cdot}28$, hence $k_7/k_8 = 3{\cdot}2$. E_7 has been found to be 5·5 kcal.[6] so that, with the same proviso as before, $E_8 = 7{\cdot}5$ kcal.*

Values for E_4 and E_8 have not been found in the literature, but the figures reported here are of the order of those obtained for the activation energies of related reactions.[8,12]

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* James and Steacie[12] reported the activation energy for the addition of ethyl radicals to alk-1-enes to be 7·0 kcal. This slightly higher value for E_7 yields $E_8 = 9{\cdot}0$ kcal.

[9] Mandelcorn and Steacie, *Canad. J. Chem.*, 1954, **32**, 79.

[10] Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1951, **19**, 169.

[11] Brinton, *J. Chem. Phys.*, 1958, **29**, 781.

[12] James and Steacie, *Proc. Roy. Soc.*, 1958, *A*, **244**, 289.