1060. *The Reaction of Hydrogen Atoms with Nitrous Oxide*

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The reaction of hydrogen atoms with nitrous oxide has been studied in a slow-burning, laminar, premixed hydrogen–oxygen–nitrogen flame to which nitrous oxide was added as a trace. The reaction that occurs is the abstraction of the oxygen atom.

$$H + N_2O = OH + N_2$$

The rate of reaction was at a maximum in the region of maximum hydrogen atom concentration in the flame. It was found that log $k_1 = 7{\cdot}6 \pm 0{\cdot}3$ at 900°K and the results further indicate that probably $k_1 = 4{\cdot}3 \pm 1{\cdot}5$ l. mole^{-1} sec.$^{-1}$ at this temperature. Other literature values for k_1 are discussed, and it is suggested that the activation energy E_1 may be in the range $E_1 = 13 \pm 1{\cdot}5$ kcal. mole^{-1} rather than the normally quoted value of about 16 kcal. mole^{-1}. For $E_1 = 13 \pm 1{\cdot}5$ kcal. mole^{-1} the value of k_1 (l. mole^{-1} sec.$^{-1}$) is given by log $k_1 = 10{\cdot}7 \pm 0{\cdot}4 - (13{,}000 \pm 1500)/4{\cdot}606T$.

When a hydrogen atom collides with a molecule of nitrous oxide reactions (1) and (2) are possible.

$$H + N_2O \rightleftharpoons OH + N_2;\ \Delta H^\circ_{298} = -61{\cdot}6 \text{ kcal. mole}^{-1} \qquad (1)$$

$$H + N_2O \rightleftharpoons NH + NO;\ \Delta H^\circ_{298} \approx +30 \text{ kcal. mole}^{-1} \qquad (2)$$

In all such systems studied so far, the abstraction of the oxygen atom to give nitrogen and an hydroxyl radical predominated; though reaction (2) does occur to a minor extent in high-temperature nitrous oxide–hydrogen flames, resulting in the formation of NH radicals.

Reaction (1) plays an important chain-propagating role in the thermal oxidation of hydrogen by nitrous oxide, as was first shown by Melville,[1] from whose work the reaction was assigned [2] an activation energy of some 15—20 kcal. mole^{-1}. More recently, a detailed study of nitrous oxide–hydrogen flames by Fenimore and Jones [3,4] confirmed the importance of this reaction, and its rate was determined at various flame temperatures. In addition, the reaction has been investigated in systems in which hydrogen atoms have been produced by mercury photosensitisation,[5] electrical discharge,[6] or radiation.[7]

In this work a slow-burning, fuel-rich, hydrogen–oxygen–nitrogen flame was chosen as the source of hydrogen atoms. Under the conditions used, the concentration of hydrogen atoms (*ca.* 0·3 mole-%) is much greater than the concentrations of the other reactive species in the flame, *i.e.*, hydroxyl radicals and oxygen atoms. Thus, the reaction of hydrogen atoms with nitrous oxide cannot be seriously complicated by competitive reactions.

EXPERIMENTAL

The flame was burned adiabatically as a one-dimensional disc supported on an Egerton–Powling type of flat-flame burner as previously described.[8] High-purity hydrogen, oxygen-free nitrogen, and medical quality nitrous oxide (all from British Oxygen Gases) were used. They were dried, metered by calibrated capillary flowmeters, and well mixed before entering the burner. The composition (volume-%) of the unburnt gaseous mixture was 4·60% of oxygen, 18·83% of hydrogen, 76·26% of nitrogen, and 0·306% of nitrous oxide.

Gas samples could be abstracted from a number of positions through the flame by means of a quartz probe with an orifice about 25 μ in diameter. A continuous-flow sampling system was used and a small proportion of the sample was led through a capillary leak directly into an A.E.I. M.S. 10 mass spectrometer. Gases were measured as ratios of peak heights, and calibration factors were applied to allow for discrimination effects in the mass spectrometer. Temperatures were measured by means of a small quartz-coated platinum–platinum/13% rhodium thermocouple, and burning velocities were determined by the particle-track method. Both techniques have been previously described.[8] The final flame temperature was 1072° ± 30°K in the present case, and the burning velocity 9·2 ± 0·3 cm. sec.$^{-1}$ (gas flow converted into 18°/760 mm.).

RESULTS

Figure 1 shows the mole fractions X_{N_2O} at a number of distances y through the flame, together with the temperature profile. The distances were measured from the plane of the Schlieren maximum. The small increase in X_{N_2O} earlier in the flame results from diffusional processes and the stoicheiometry of the main flame oxidation reaction. The latter also produces a decrease in the molar burning velocity M, so that, in the absence of any chemical reaction, the overall flux of nitrous oxide remains constant. The overall reaction-rate term $\{\partial[N_2O]/\partial t\}_{\text{chem}}$ (in mole cm.$^{-3}$ sec.$^{-1}$) may be calculated [9] for any position on the measured profile by means of the equation.

$$\{\partial[N_2O]/\partial t\}_{\text{chem}} = \partial\{MG_{N_2O}\}/\partial y = \partial\{MX_{N_2O} + j_{N_2O}\}/\partial y$$

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[1] H. W. Melville, *Proc. Roy. Soc.*, 1933, *A* **142**, 524.

[2] H. W. Melville, *J.*, 1934, 1243.

[3] C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, 1959, **63**, 1154.

[4] C. P. Fenimore, " The Chemistry of Premixed Flames," Pergamon, Oxford, 1963.

[5] H. S. Taylor, *Trans. Faraday Soc.*, 1926, **21**, 560.

[6] M. Schiavello and G. G. Volpi, *J. Chem. Phys.*, 1962, **37**, 1510.

[7] G. Czapski and J. Jortner, *Nature*, 1960, **188**, 50.

[8] G. Dixon-Lewis and A. Williams, Ninth Symposium (International) on Combustion, Academic Press Inc., New York, 1963, p. 576.

[9] G. Dixon-Lewis and A. Williams, *Quart. Rev.*, 1963, **17**, 243.

Here y is the distance, and MG_{N_2O} represents the total molar flux of nitrous oxide, M being the molar burning velocity. X_{N_2O} represents the mole fraction of nitrous oxide, and j_{N_2O} represents its diffusional flux. Since there is also a temperature gradient in the region of nitrous oxide decay, the flux j_{N_2O} consists of two parts, one due to the concentration gradient and the other to thermal diffusion. In the hydrogen–oxygen–nitrogen flame without additive,[10] thermal diffusion of the oxygen was found to be unimportant, whilst a similar result has been found for the oxidant in a flame containing 21·46% of hydrogen, 66·44% of nitrogen, and 12·10% of nitrous oxide. Thermal diffusion of the nitrous oxide has therefore been assumed to be unimportant in the present flame, and the diffusional flux j_{N_2O} for the trace nitrous oxide has been computed according to the equation below, where ρ is the molar density,

$$j_{N_2O} = -\rho D_{N_2O}\, \partial X_{N_2O}/\partial y$$

$$1/D_{N_2O} = \sum_{i \neq N_2O} X_i/\mathscr{D}_{i-N_2O},$$

and D_{N_2O} is given by $\mathscr{D}_{i-N_2O}$ being the binary diffusion coefficient for mixtures of nitrous oxide with each other species i present in the flame. The profiles of the species i needed for the diffusional analysis have been reported elsewhere.[10] The diffusion values used were based on the slopes in the early part of the nitrous oxide profile, on the assumption that there is no decay by reaction in this region. The diffusion coefficients found were somewhat lower than would be expected from the molecular force constants quoted by Hirschfelder, Curtiss, and Bird.[11]

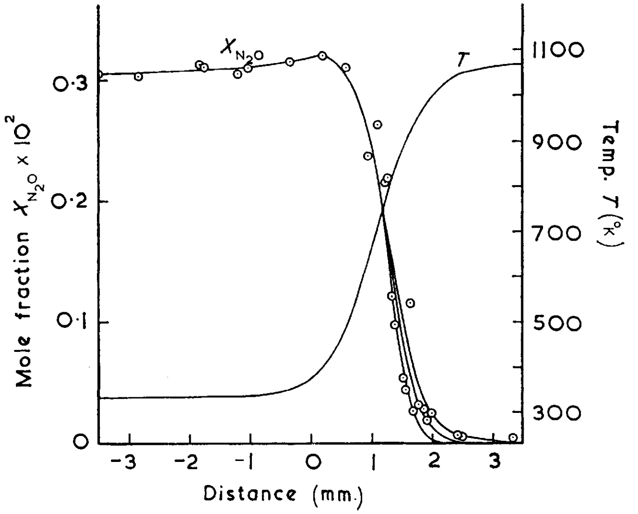

FIGURE 1. Profiles of mole fraction of nitrous oxide and temperature plotted against distance in the flame

In terms of reaction kinetics, the equilibrium conditions of reaction (1) are such that the back reaction (−1) is negligible for all measurable quantities of nitrous oxide. In the present flame, the other reactions of nitrous oxide are also unimportant, so that the rate constant k_1 is given by the equation below. Now the hydrogen-atom concentration profile in the flame had been measured previously,[12] and, for the present results to be meaningful, the decay of nitrous oxide must be consistent with the concentrations of hydrogen atoms encountered and with a reasonable sequence of values of k_1.

$$k_1[H][N_2O] = -\,[\partial[N_2O]/\partial t]_{chem}$$

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[10] G. Dixon-Lewis, M. M. Sutton, and A. Williams, Tenth Symposium (International) on Combustion, 1964.

[11] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, " Molecular Theory of Gases and Liquids," Wiley, New York, 1954.

[12] M. M. Sutton, M.Sc. Thesis, University of Leeds, 1963.

The three lines in Figure 1 show three series of values of X_{N_2O} that give meaningful results in this way. The corresponding fluxes MX_{N_2O}, j_{N_2O}, and MG_{N_2O} for the middle of these lines are shown in Figure 2. It should be noted that, since the rate of decay of the nitrous oxide is given by the first distance-derivative of the MG_{N_2O} curve, this rate depends on both the slope and the curvature of the original X_{N_2O} curve, the curvature being involved in the rate of change of diffusional flux. In the region of the maximum rate of decay of the nitrous oxide in Figure 2 (minimum gradient of the MG_{N_2O} curve) the relative rates of change of the convective (MX_{N_2O}) and diffusional fluxes are such that a 50% error in the diffusion coefficient would affect the final results by about 20%. For the shallowest of the curves in Figure 1, the effect on the final result of a similar error in the diffusion coefficient would be about 10 to 15%, whilst for the steepest it would be about 25%. The maximum reaction rates corresponding to the three curves shown in Figure 1 are given (from right to left) by $-100[\partial[N_2O]/\partial t]_{\text{chem}} = 1{\cdot}2_6$, $1{\cdot}5_5$, and $2{\cdot}2_6$ mole l.$^{-1}$ sec.$^{-1}$ at 900° ± 20°K, where the concentrations of nitrous oxide were $1{\cdot}3 \times 10^{-5}$, $1{\cdot}0(4) \times 10^{-5}$, and $7{\cdot}5 \times 10^{-6}$ mole l.$^{-1}$, respectively. The maximum hydrogen-atom concentration was $3{\cdot}5 \times 10^{-5}$ mole l.$^{-1}$ at about 900°K. This gives $k_1 = 2{\cdot}8 \times 10^7$, $4{\cdot}3 \times 10^7$, or $8{\cdot}6 \times 10^7$ l. mole^{-1} sec.$^{-1}$, at this temperature.

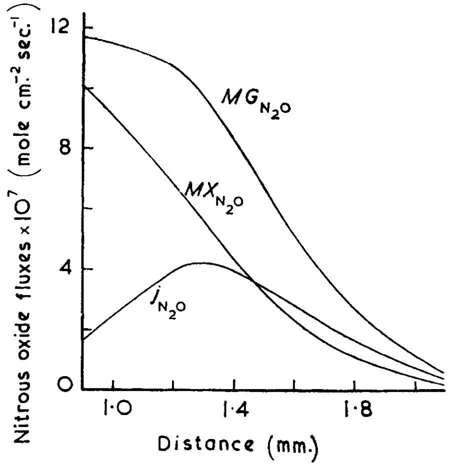

FIGURE 2. Molar fluxes of nitrous oxide through the flame in the intermediate case, plotted against distance. MX_{N_2O} is convective flux; j_{N_2O} is diffusional flux; MG_{N_2O} is overall flux

The above assessment indicates that at 900°K $\log_{10} k_1$ lies in the range $\log_{10} k_1 = 7{\cdot}6 \pm 0{\cdot}3$, with k_1 in l. mole^{-1} sec.$^{-1}$. The curves in Figure 1 from which this assessment was made also lead to a reasonable sequence of values of k_1 in the region between 1·5 mm. and 2·4, 2·2, and 2·0 mm. on the respective curves. The persistence of measurable nitrous oxide at 2·4 to 2·5 mm., and possibly even further into the hot gas supports a value at 900°K in the range $k_1 = 4{\cdot}3 \pm 1{\cdot}5 \times 10^7$ l. mole^{-1} sec.$^{-1}$.

DISCUSSION

Very few measurements of the rate of reaction (1) are reported in the literature, so that it is difficult to make comparisons with the value reported here. The previous values consist of

(*i*) A rate expression quoted by Fenimore and Jones[3] of $k_1 = 4 \times 10^{11} \exp(-16{,}300/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$ to represent six rate constants measured in flames in the temperature range 1100—1760°K. According to Fenimore and Jones the error in the expression should not exceed 2 kcal. mole^{-1} in the activation energy.

(*ii*) An approximate value obtained by Schiavello and Volpi[6] by following mass-spectrometrically the reaction of nitrous oxide with hydrogen atoms produced in a discharge tube. They obtained $k_1 \approx 10^4$ l. mole^{-1} sec.$^{-1}$ at 423°K.

(*iii*) A measurement in aqueous solution[7] giving $k_1 = 10^3$—10^4 l. mole^{-1} sec.$^{-1}$ at 298°K.

Of these, the results of Fenimore and Jones require further comment. At 900°K their expression above leads to $k_1 = 4{\cdot}9 \times 10^7$ l. mole^{-1} sec.$^{-1}$, or about 1·1 times our mean value. However, the calibration of the hydrogen-atom concentration used by Fenimore and Jones is different from ours. They measured the rate of formation of HD from heavy water, initiated by reaction (4). The only rate-constant

$$H + H_2O = OH + H_2 \qquad (3)$$

$$H + D_2O = OD + HD \qquad (4)$$

appearing in their final rate-expression[13] is k_4, for which they assumed $k_4 = 10^{12} \times \exp\,(-25500/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$. Dividing this into their mean expression for k_1 gives $k_1/k_4 = 0{\cdot}4 \times \exp(+9200/\boldsymbol{R}T)$, and, at 900°K, $k_1/k_4 = 66$.

From experiments where heavy water was added to our own hydrogen–oxygen–nitrogen flame it was found,[12] by using the same calibration of hydrogen-atom concentration as was used above to determine k_1, that $k_4 = 3{\cdot}6 \times 10^6$ l. mole^{-1} sec.$^{-1}$ at 1072°K.

If, as Fenimore and Jones have done, we assume $k_4 = k_3$ and follow Avramenko and Lorentso[14] by putting $E_3 = 25{\cdot}5$ kcal. mole^{-1}, we find $E_4 = 25{\cdot}5$ kcal. mole^{-1}, $k_4 = 3{\cdot}7 \times 10^5$ l. mole^{-1} sec.$^{-1}$ at 900°K, and our $k_1/k_4 = 116$. On the other hand, more recent work[15,16] than that of Avramenko and Lorentso would suggest a lower value of E_3, around 20 to 22 kcal. mole^{-1}, depending on the value assumed for the heat of formation of OH.[16]

There is a further problem: because of the difference in vibrational zero-point energy between D_2O and H_2O, it may be expected that E_4 will be greater than E_3. The magnitude of the difference is difficult to assess, because the total zero point energy difference between H_2O and D_2O (*ca.* 3·5 kcal. mole^{-1}) is made up of contributions from three different vibrational modes. If it is assumed that the only frequency that is altered in the transition state is the stretching frequency of the reacting O–H or O–D bond, and that this frequency approaches zero in the transition state, then[17] $E_4 - E_3 \approx 1{\cdot}4$ kcal. mole^{-1}. If, however, the other vibrational frequencies of H_2O and D_2O also decrease in the transition state, then $E_4 - E_3 > 1{\cdot}4$ kcal. mole^{-1}. As essentially a secondary isotope effect though, this excess over 1·4 kcal. mole^{-1} may be small; and, indeed, it may be opposed by a deficit due to the reactive stretching frequency not closely approaching zero in the transition state; the magnitudes of these interactions are not known.

Some information on the ratio k_3/k_4, and hence on the difference $E_4 - E_3$, has recently become available from a comparison of the ratio

$$H + CO_2 \rightleftharpoons OH + CO \qquad (5)$$

k_4/k_5 (= 4·3 ± 0·5 at 1072°K) measured by Dixon-Lewis, Sutton, and Williams[16] with the value of k_3/k_5 at the same temperature. The latter may be obtained in two ways: first, Ung and Back[18] find $k_{-5}/k_{-3} = 0{\cdot}032 \pm 0{\cdot}004 \times \exp\,(+4000 \pm 300/\boldsymbol{R}T)$ between 473 and 623°K. Direct extrapolation, inversion, and subsequent use of the appropriate water = gas equilibrium constant at 1072°K leads to $k_3/k_5 = 5{\cdot}1 \pm 0{\cdot}7$ at this temperature, and $k_3/k_4 = 1{\cdot}2 \pm 0{\cdot}3$. Alternatively, Baldwin and Cowe[19] quote $k_{-5}/k_{-3} = 0{\cdot}33$ at 773°K, compared with a mean 0·43 calculated from Ung and Back's expression. Extending the temperature range by combining Ung and Back's value at 550°K with Baldwin's figure at 773°K leads

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[13] C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, 1958, **62**, 693.
[14] L. Avramenko and R. Lorentso, *Zhur. fiz. Khim.*, 1950, **24**, 207.
[15] F. P. Del Greco and F. Kaufman, *Discuss. Faraday Soc.*, 1962, **33**, 128.
[16] G. Dixon-Lewis, M. M. Sutton, and A. Williams, *Trans. Faraday Soc.*, 1965, **61**, 255.
[17] K. B. Wiberg, *Chem. Rev.*, 1955, **55**, 713.
[18] A. Y. M. Ung and R. A. Back, *Canad. J. Chem.*, 1964, **42**, 753.
[19] R. R. Baldwin and D. W. Cowe, *Trans. Faraday Soc.*, 1962, **58**, 1768.

to $k_{-5}/k_{-3} = 0{\cdot}013 \times \exp(+5000/\boldsymbol{R}T)$, and at 1072°K $k_3/k_5 = 7{\cdot}9$. Wagner (private communication) obtains $k_{-5}/k_{-3} = 0{\cdot}05$ at 1773°K, compared with 0·05 (3) calculated from the second expression for k_{-5}/k_{-3}, and 0·1 direct from Ung and Back's figures. The evidence over the extended temperature range, although not absolutely conclusive since even at 1773°K only a factor of two is involved, thus favours the second of the above alternatives, leading to $k_3/k_5 \approx 7{\cdot}9$ at 1072°K, with $k_3/k_4 = 7{\cdot}9/4{\cdot}3 = 1{\cdot}8$.

To interpret the ratio k_3/k_4 in terms of an isotope effect causing the activation energy difference $E_4 - E_3$, it is noted that, at 1072°K, the population of all but the zero vibrational levels in both H_2O and D_2O is still virtually negligible. It is therefore assumed that the ratio k_3/k_4 is entirely fixed by $E_4 - E_3$, so that for $k_3/k_4 = 1{\cdot}8$ we find $E_4 - E_3 \approx 1{\cdot}3$ kcal. mole^{-1}. This will be used therefore as a reasonable estimate.

To be consistent with the new ratio k_3/k_4, the values of k_3 and k_{-3} at 1072°K previously quoted by Dixon-Lewis, Sutton, and Williams [16] should be increased to $k_3 = 6{\cdot}6 \pm 0{\cdot}9$ and $k_{-3} = 1{\cdot}6\ (2{\cdot}4) \pm 0{\cdot}3 \times 10^9$ l. mole^{-1} sec.$^{-1}$, respectively. The two values for k_{-3} depend on whether $\Delta H_f^\circ\ (\mathrm{OH})_{298} = 9{\cdot}33\ (10{\cdot}0)$ kcal. mole^{-1} is assumed for the heat of formation of OH, leading to $K_3 = 262\ (367)$. At 310°K Del Greco and Kaufman [15] find $k_{-3} = 4{\cdot}3 \times 10^6$ l. mole^{-1} sec.$^{-1}$, and in conjunction with the new k_{-3} at 1072°K this leads to $E_{-3} = 5{\cdot}3\ (5{\cdot}5) \pm 0{\cdot}6$ kcal. mole^{-1} with a mean log $A_{-3} = 10{\cdot}33\ (10{\cdot}49)$. Use of the appropriate enthalpy changes ΔH_3 to convert from E_{-3} into E_3 then gives $E_3 = 20{\cdot}5$ (21·4) kcal. mole^{-1}.

For $E_3 = 20{\cdot}5$ kcal. mole^{-1}, $E_4 = 21{\cdot}8$ kcal. mole^{-1}, $k_4 = 5{\cdot}2 \times 10^5$ l. mole^{-1} sec.$^{-1}$ at 900°K, and $k_1/k_4 = 83 \pm 30$. Both our values for k_1/k_4 and that of Fenimore and Jones are independent of the absolute calibration of the hydrogen-atom concentration, so that the level of agreement between our last ratio and that of Fenimore and Jones lends some further support to the values of E_3 around 20 to 22 kcal. mole^{-1}. Assuming $E_4 = 21{\cdot}8$ kcal. mole^{-1}, the value quoted above at 1072°K leads to $k_4 = 8{\cdot}5 \times 10^{10} \times \exp(-21{,}800/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$. Proceeding further and combining this with the mean expression of Fenimore and Jones for k_1/k_4 gives $k_1 = 3{\cdot}8 \times 10^{10} \times \exp(-12{,}600/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

At 423°K this revised value for k_1 becomes $1{\cdot}3 \times 10^4$ l. mole^{-1} sec.$^{-1}$, in good agreement with the single estimate of Schiavello and Volpi.[6] If the present assumed range of values for E_3 is correct, the overall evidence available suggests that $E_1 = 13 \pm 1{\cdot}5$ kcal. mole^{-1} (with $\log_{10} A_1 = 10{\cdot}7 \pm 0{\cdot}4$) as opposed to values nearer 16 kcal. mole^{-1}.

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