RATE OF REACTION, O + H₂ → OH + H, IN FLAMES
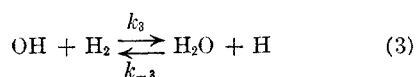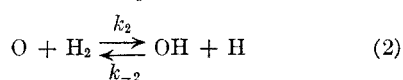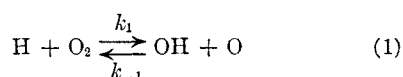
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By probing low pressure flames of H_2–O_2–N_2–N_2O, and using the ratios of rate constants previously determined in flames, we find that the rate constant for the reaction of oxygen atoms with hydrogen molecules is $2.5 \pm 0.4 \times 10^8$ l. mole^{-1} sec.$^{-1}$ at 1660°K. and $3.0 \pm 0.3 \times 10^8$ at 1815°. These values agree with a long extrapolation of Baldwin's results at about 800°K., and combine with them to give $k = 2.5 \times 10^9 e^{-7.7 \text{ kcal.}/RT}$ l. mole^{-1} sec.$^{-1}$.
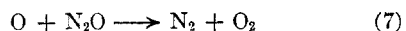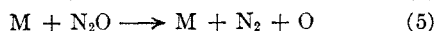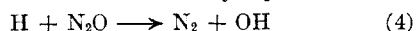
Introduction

Of the three important bimolecular reactions in H_2–O_2 mixtures

$$H + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} OH + O \tag{1}$$

$$O + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} OH + H \tag{2}$$

$$OH + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + H \tag{3}$$

$k_1{}^{1-4}$ and $k_3{}^{5,6}$ are moderately well known over a considerable range of temperature, but $k_2{}^2$ has not been measured above 820°K. and estimates of its value at high temperatures would be worthwhile. Measurement of k_2 in some H_2–O_2–N_2–N_2O flames are reported in this paper.

Nitrous oxide is included in the reactants because its irreversible decomposition in low pressure H_2–O_2 flames allows the measurement of radical concentrations. It reacts chiefly by

$$H + N_2O \longrightarrow N_2 + OH \tag{4}$$

$$M + N_2O \longrightarrow M + N_2 + O \tag{5}$$

$$O + N_2O \longrightarrow 2NO \tag{6}$$

$$O + N_2O \longrightarrow N_2 + O_2 \tag{7}$$

of which (4) is the fastest by far.

It is assumed that no important reaction of oxygen atoms has been omitted, so that we can write out the expression for $d[O]/dt$ due to the chemical reactions above and solve the resulting expression for k_2. Any consumption of oxygen atoms in the recombinations $2O + M \rightarrow O_2 + M$ or $O + H + M \rightarrow OH + M$ has been ignored, but these termolecular recombinations must be small compared to the reverse of reaction 1 which is included. Another simplification may as well be made from the start; it will always be possible to neglect the reverse of reaction 2 in the region where k_2 is evaluated, as will be shown, and to choose this region so that $d[O]/dt$ is approximately zero. Then

$$k_2 = \frac{-d[O]_2/dt + k_5[N_2O][M] - d[NO]/2dt}{[H_2][O]}$$

and everything on the right side of this expression can be measured.

The rates of change of $[O_2]$ and $[NO]$ can be obtained by probing flat, one dimensional flames and

(1) N. N. Semenov, *Acta Physicochim.*, **20**, 290 (1945).
(2) R. R. Baldwin, *Trans. Faraday Soc.*, **52**, 1344 (1956).
(3) G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, **29**, 1177 (1958).
(4) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **63**, 1154 (1959).
(5) L. Avramanko and R. Lorentso, *Zhur. Fiz. Khim.*, **24**, 207 (1950).
(6) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **62**, 693 (1958).

correcting the traverses for diffusion. The composition traverses also allow estimates of $k_5[N_2O]$-$[M]$ and $[H_2]$ at any point.

$[O]$ can be estimated in two independent ways. First, since the nitric oxide formed in reaction 6 does not undergo appreciable decomposition, $[O]$ can be obtained from

$$d[NO]/dt = 2k_6[O][N_2]$$

Second, it can also be estimated from the three reactions 4, 3 and 1 because

$$-d[N_2O]/dt = k_4[H][N_2O]$$

accounts for most of the decomposition of nitrous oxide and gives an estimate of $[H]$ which can be substituted into

$$d[H_2O]/dt = k_3[OH][H_2] - k_{-3}[H_2O][H]$$

to get $[OH]$. Both $[H]$ and $[OH]$ can then be substituted in

$$-d[O_2]/dt + k_7[O][N_2O] = k_1[H][O_2] - k_{-1}[OH][O]$$

to get $[O]$. In the last expression, the term in k_7 can be omitted whenever $d[NO]/dt$ is small compared to $-d[O_2]/dt$ because $k_7 < k_6/2$.

Although the determination of $[O]$ from reactions 4, 3 and 1 may seem involved, this method has two advantages over the simpler determination by reaction 6. It does not really depend on the separate values of k_4, k_3, k_1 but only on their ratios; and since these constants were measured relative to one another in the temperature range in which we use them, the ratios are probably more accurate than the separate values. $[O]$ from reaction 6 does of course depend on the separate value of k_6.

Also the reaction rates one uses in (4), (3) and (1) are fairly large and can be tested for internal consistency. In a region where $d[O]/dt$ and $d[OH]/dt$ are small, one should have $-d[N_2O]/dt - 2d[O_2]/dt = d[H_2O]/dt + d[NO]/dt$ since oxygen must be conserved. This relation holds experimentally within 10%, and $d[NO]/dt$ is always small compared to the three other terms in the equality. Therefore the three larger terms are at least consistent among themselves. The small $d[NO]/dt$ used in the determination of $[O]$ *via* reaction 6 cannot be tested in the same way because it does not make a very significant contribution to the conservation of oxygen or nitrogen.

The values adopted for the rate constants are quoted in Table I. k_1, k_3, k_4 and k_6 are correct relative to one another to perhaps 30%, and k_1 and k_3 also agree within a factor of two with independent estimates in the literature. k_5 is obtained from a correlation of much of the data on the pseudo-unimolecular, thermal decomposition of nitrous oxide.[7] The limiting low pressure con-
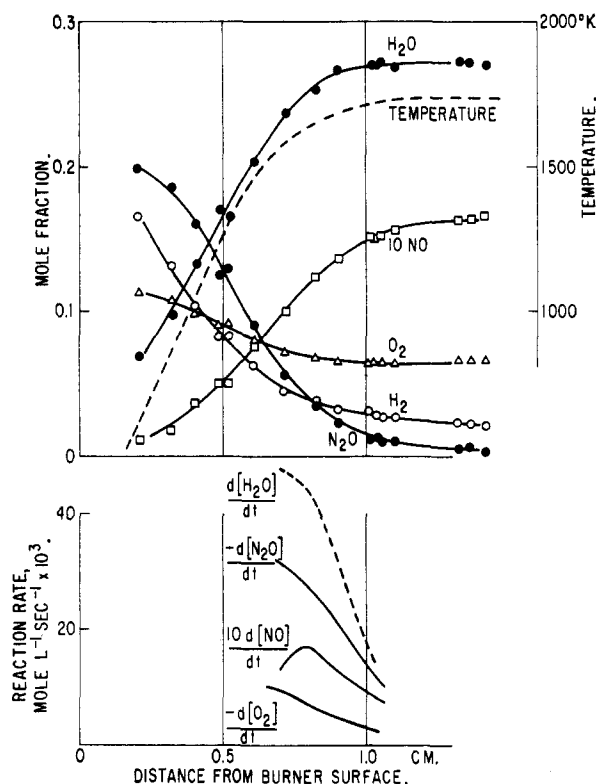
Fig. 1.—Traverses through a flame of reactant composition $H_2 + 0.66N_2O + 1.81$ air burnt at 2 cm. pressure of mercury with a mass flow of 2.32×10^{-3} g. cm.$^{-2}$ sec.$^{-1}$. Calculated reaction rates are plotted in the lower part of the graph.

stant listed is appropriate to initially pure nitrous oxide where [M] represents initial $[N_2O]$. If [M] represents the total concentration of a mixture of other gases, as it does in our flames, the

TABLE I

BIMOLECULAR RATE CONSTANTS[a]

Reaction	Rate constant, mole l.$^{-1}$ sec.$^{-1}$	Ref.
1	$6 \times 10^{11} e^{-18/RT}$	4
3	$2.5 \times 10^{11} e^{-10/RT}$	6
4	$4 \times 10^{11} e^{-16.3/RT}$	4
5	$4 \times 10^{12} e^{-59/RT}$	7
6	$1 \times 10^{11} e^{-28/RT}$	8
7	$k_7 < k_6/2$	9

[a] For reactions 1, 2 and 3, the rate constants for the reverse reactions can be obtained from the constants for the forward reactions and the equilibrium constants; $k_1/k_{-1} = 35e^{-16.6/RT}$, $k_2/k_{-2} = 2e^{-3.0/RT}$, $k_3/k_{-3} = 0.25e^{15.5/RT}$.

pre-exponential factor of k_5 could be wrong by a factor of about two, and we will discuss this possibility later. For any use we make of k_7, it will be enough to know that at the temperatures of interest k_7 is smaller than k_6.

The diffusion corrections to get $d[NO]/dt$, $-d[O_2]/dt$, $-d[N_2O]/dt$, $d[H_2O]/dt$ from experimental composition traverses caused us some trouble. With the diffusion coefficients D_{NO}, D_{O_2}, etc., assumed the chemical reaction rates were

(7) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1951).

(8) C. P. Fenimore and G. W. Jones, 8th Combustion Symposium at Pasadena, Calif., Sept. 1960.

(9) F. Kaufman, N. J. Gerri and R. E. Bowman, *J. Chem. Phys.*, **25**, 106 (1956).

calculated just as before.[4] The flames were 60 to 70% nitrogen, and we first tried approximate D_{NO} values appropriate to binary $NO–N_2$ mixtures.[10] These gave too great a correction however, and resulted in negative calculated values of $d[NO]/dt$ in the early parts of some flames. After several trials in different runs, we eventually used

$$D_{NO} = 2.3 \times 10^{-4} T^{1.67} \text{ cm.}^2 \text{ sec.}^{-1}$$

in all flames at 4 cm. pressure of mercury. For other species, the diffusion coefficient was taken from D_{NO} under the assumption that D was inversely proportional to the square root of the molecular weight. For other pressures, it was assumed that D varied inversely with pressure. The value chosen for D_{NO} is near the greatest value which did not overcorrect the nitric oxide traverse.

The calculation of [O] by means of reaction 6 is considerably more sensitive to changes in the diffusion coefficient than is the calculation via (4), (3) and (1). A smaller D_{NO} decreases the maximum [O] as calculated from (6).

Experimental

The arrangement was the same as used before. It included a water-cooled, porous, flat flame burner[11] of 31.1 cm.^{2} surface area mounted in a bell jar which was also equipped with a movable quartz probe (~ 0.1 mm. diam.), movable quartz coated thermocouple (made of butt-welded Pt–Pt, Rh wires 0.012 mm. diam.), pumps, and externally mounted cathetometer. The reactants were metered through critical flow orifices. Thermocouple readings were corrected for radiation[11] to get temperature traverses. Composition traverses of the stable components were obtained from mass spectrometric analyses of samples drawn through the quartz probe at critical flow rates.

Determination of k_2.—The upper half of Fig. 1 presents typical traverses through a flame burnt at 2 cm. pressure. The lower part of the figure shows reaction rates calculated from the traverses. [O] as calculated from

$$[O] = d[NO]/2k_6[N_2O]dt$$

attains a maximum value of 6.0×10^{-6} mole l.$^{-1}$ at 0.8 to 0.95 cm. from the burner surface.

Calculating [O] in the alternate way described above, we find that

$$[H] = -d[N_2O]/k_4[N_2O]dt$$

is relatively constant through most of the flame. At a position 0.8 to 0.95 cm. from the burner surface, $[H] = 1.4 \times 10^{-6}$ mole l.$^{-1}$; and then in turn, $[OH] = 0.83 \times 10^{-6}$ from reaction 3 and $[O] = 3.7 \times 10^{-6}$ from reaction 1.

The [O] obtained from reactions 4, 3 and 1 is smaller by a factor of 1.6 than [O] calculated from reaction 6. A similar discrepancy occurs in all the flames, by a factor of 3.6 in the worst case and 1.6 in the best, and always in the sense that [O] from reaction 6 is the larger.

Since [O] from reaction 6 is more sensitive to a change in the diffusion coefficient, we trust it less. Other reasons for preferring the smaller [O] from reactions 4, 3 and 1 have been given in the introduction; and we use the smaller [O] for estimating k_2.

For the flame described in Fig. 1, at 0.8 to 0.95

(10) A. A. Westenberg, *Combustion and Flame*, **1**, 346 (1957).

(11) W. E. Kaskan, "6th Symposium on Combustion," Reinhold Publ. Corp., New York, N. Y., 1957, p. 134.

cm. from the burner surface, the reverse of (2) is small compared to the forward reaction. This is apparent because the product of reaction partners for the forward process, $[O][H_2]$, is twenty times the product for the reverse, $[OH][H]$; but the equilibrium constant, k_2/k_{-2}, is of order unity.

$d[O]/dt$ is very small in the region 0.8 to 0.95 cm. from the burner surface, so we substitute into

$$k_2 = \frac{-d[O]_2/dt + k_5[N_2O][M] - d[NO]/2dt}{[O][H_2]}$$

to get $k_2 = 2.8 \times 10^8$ l. mole^{-1} sec.$^{-1}$ at 1675°K. The term, $k_5[N_2O][M]$, is small compared to $-d-[O_2]/dt$ and could have beem omitted in this example.

Estimates of k_2, obtained in a similar way in each flame, are listed in Table II. The first four runs are fuel rich flames, the last two are fuel lean. The last column of Table II gives the percentage contribution of the term $k_5[N_2O][M]$ to the value of k_2. If k_5 were wrong, only runs no. 2 and 3 would be affected.

Table II

Estimates of k^-_2

Run	P, cm.	T, °K.	[O] × 10^6, mole l.$^{-1}$	k_2 × 10^{-8}, l. mole^{-1} sec.$^{-1}$	k_5 term,[a] %
1	4	1825	1.2	3.0	∼0
2	6	1830	0.4	1.7	75
3	4	1790	.8	1.8	33
4	4	1640	.8	2.0	∼0
5	2	1675	3.7	2.8	∼0
6	4	1670	3.0	2.8	∼0

[a] Contribution of the term, $k_5[N_2O][M]$, to the value deduced for k_2 if k_5 is assumed to have the value in Table I. Actually k_5 is eventually assumed to be 2.25 times larger than this value, see text, and the eventual values of k_2 in runs 2 and 3 are 3.3 and 2.6 × 10^8, respectively.

As they stand, the first three runs in Table II average to $k_2 = 2.2 \times 10^8$ at about 1815°K. with a mean deviation of 26%. But k_5 is not known better than to a factor of about two, as was explained in the Introduction, and it is legitimate to vary the pre-exponential factor of k_5 in order to get the best agreement in k_2. If k_5 is multiplied by 2.25, the average deviation in k_2 decreases to only 8% and the average becomes identical with the only value of k_2 which is independent of k_5. Therefore we increase the k_5 given in Table I and accept $k_2 = 3.0 \pm 0.3 \times 10^8$ at 1815°.

The last three runs give an average at 1660°K. of $k_2 = 2.5 \pm 0.4 \times 10^8$, independent of k_5.

Comparison with Other Work.—Baldwin[2] deduced from the low pressure limit of explosions in H$_2$-O$_2$-N$_2$ mixtures that k_2 (or k_3) = 2.0×10^7 l. mole^{-1} sec.$^{-1}$ at 793°K. The ambiguity arose because reactions 2 and 3 have an identical dependence on [H$_2$]; but since 2×10^7 is only $^1/_{10}^5$ or $^1/_{20}^6$ of the value expected for k_3 from other work, it is probably k_2. He also reported an activation energy of 9.2 kcal., but disclaimed much accuracy; for k_2 was reproducible only within ±12% at constant temperature, and the variation over the whole temperature range was 44%. Perhaps it is not unfair to suggest that his error might have been ±3 kcal.

If his estimate at 793° is extrapolated to 1815°, using 9.2 kcal. activation energy, it gives $k_2 = 5.4 \times 10^8$ as compared to our observed 3×10^8. This is good agreement. His and our estimates combine to

$$k_2 = 2.5 \times 10^9 e^{-7.7/RT} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

and 7.7 is the same as 9.2 kcal. within the probable error of the latter. If the pre-exponential factor is taken proportional to $T^{1/2}$, part of the temperature dependence is absorbed by this factor, and E_2 becomes 6.4 rather than 7.7 kcal.

In much the same way as Baldwin, but with less complete data and interpretations, Azatian and co-workers[12] found $k_2 = 9 \times 10^{10} e^{-12.1/RT}$ at 840 to 930°K. from the lower explosion limits of CO-O$_2$ mixtures containing 0.76 to 8.0% added hydrogen. Their result extrapolates to twice Baldwin's estimate at 793° and to ten times our estimate at 1815°. It is not possible to reconcile our measurements with those of Azatian, et al., and still maintain an activation energy of 9 ± 3 kcal.

Note Added in Proof.—Clyne and Thrush[13] reported just recently an estimate of $k_2 = 1.2 \times 10^{10} e^{-9.2/RT}$ l. mole^{-1} sec.$^{-1}$ at 409 to 733°K. by a very different method; O atoms were generated in known concentration by titrating N atoms with nitric oxide, and the decay of the O atoms when mixed with hydrogen was followed by the radiation from the O + NO emission. Their estimate of k_2 is systematically larger than the expression deduced in this paper by a factor of 2 to 3; but a disagreement of this order is perhaps within the error of any of the data.

(12) V. V. Azatian, V. V. Voevodskii and A. B. Nalbandian, *Dokl. Akad. Nauk. SSSR*, **132**, 864 (1960).

(13) M. A. A. Clyne and B. A. Thrush, *Nature*, **189**, 135 (1961).