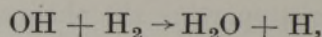


The Kinetics of the Reaction between Hydrogen and Nitrous Oxide
 III—*Effect of Oxygen*

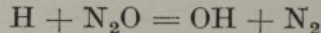
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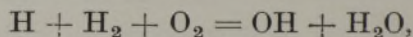
One of the most striking dissimilarities between the hydrogen-oxygen and hydrogen-nitrous oxide reactions is the absence in the latter of sharp explosion limits, a feature characteristic of the former. Another important difference is that propagation of chains in the $\text{H}_2\text{-N}_2\text{O}$ mixtures is rather less easy than in $\text{H}_2\text{-O}_2$, for the photochemical chain length is smaller for $\text{H}_2\text{-N}_2\text{O}$ than for $\text{H}_2\text{-O}_2$ at the same temperatures and pressures (see below). It has, however, been postulated that the carriers in the two reactions are identical and that at least one step, viz.,



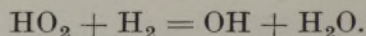
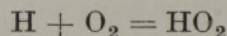
is common to both reactions. The differences in the propagation factors would therefore be due to these reactions



and



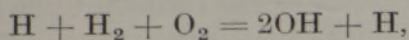
or



It may be anticipated that termination processes will be somewhat similar, and consequently the observed differences in the thermal reactions will also be partly due to initiation reactions.

In this paper, an attempt has been made to study the two reactions under similar conditions so that propagation and initiation reactions may be separated from each other. Experiments have therefore been made on the effect of small quantities of oxygen on the high and low pressure thermal reactions and on the high and low pressure photo reactions. As will be shown below, oxygen exerts a very marked effect in increasing the rate. Its addition has been controlled so that the increase is comparable with the rate of reaction of the oxygen-free mixtures, in order that the stationary concentration of the chain carriers and the nature of the termination reactions should be similar for the two reactions.

To account for the sharp explosion limits in $\text{H}_2\text{-O}_2$ mixtures, branching is supposed to occur in one of the reaction cycles, and the reaction presumed to be responsible for this is



or some slight modification of such a reaction. The nature of the process leading to branching need not be so particularly specified, the essential condition being that in a branching collision two carriers of one type (OH) are produced from one of the other type (H). If this happens once (on the average) before the chain is terminated, the chain length will increase indefinitely and explosion ensue. But with $\text{H}_2\text{-N}_2\text{O}$ there is no possibility of such an occurrence with H atoms or with OH radicals. In the $\text{H}_2\text{-O}_2$ reaction branching becomes possible because the oxygen molecule is diatomic; it is the splitting of this into two parts which ultimately yields the two carriers requisite for branching. Nitrous oxide, on the other hand, has only one atom available and cannot therefore give rise to two OH radicals even in a ternary collision such as $\text{H} + \text{N}_2\text{O} + \text{N}_2\text{O}$.

Although a very definite mechanism for the $\text{H}_2\text{-O}_2$ reaction has been adopted, which perhaps is not correct in detail, it will be of importance to find if homogeneous reactions between nitrous oxide and simple combustible molecules do exhibit well-defined lower and especially upper limits for explosion. If they do not then the following statement would appear to sum up the behaviour of the reactions: In combustion processes involving nitrous oxide, branching chains and therefore chain explosion limits do not occur. The lower limits observed are due to thermal explosions, initiated homogeneously or heterogeneously, of a type similar to those discussed by Semenov* some time ago. The reaction must, of course, take place under such conditions that these phenomena are usually observed. For instance, the mixture should be capable of propagating chains; the chain length should increase at low pressures and decrease at high pressures. These conditions can be realized with $\text{H}_2\text{-N}_2\text{O}$, but sharp limits are observed. The sharpness of a limit may be masked by the occurrence of a relatively fast reaction outside the explosion region, such as occurs with $\text{H}_2\text{-O}_2\text{-NO}_2$ mixtures.†

The Photochemical Low Pressure Reaction

To eliminate the possibility of thermal initiation, the experiments recorded in Table I were made at low temperatures, using the mercury lamp with mer-

* 'Z. Physik,' vol. 48, p. 571 (1928).

† Norrish and Griffiths, 'Proc. Roy. Soc.,' A, vol. 139, p. 147 (1933).

cury vapour present in the reaction tube. In Table II the oxygen content of the mixture was varied, maintaining the total pressure unaltered. It will be observed that oxygen accelerates the reaction from 340 to 600° C, but the increase does not change much with temperature, the ratio of the rates increasing 50% for a 20-fold increase in the rate. The energies of activation of the two reactions $\text{H} + \text{N}_2\text{O} = \text{OH} + \text{N}_2$ and $\text{H} + \text{O}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{OH}$ must therefore be nearly equal. If the values of R in Table II be plotted against the percentage of O_2 in the gas, a linear relation is obtained up to 33%.

Table I—5 cm tube. Composition of mixture 19.5 mm O_2 , 300 mm of H_2 and of N_2O

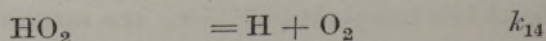
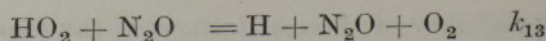
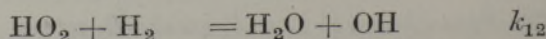
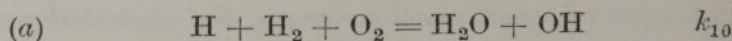
Temperature ° C	340	400	460	525	600
Initial pressure	15.95	16.00	17.67	18.24	19.68
Rate	0.26	0.52	0.92	2.50	7.0
Rate (O_2 -free)	0.115	0.23	0.41	0.92	2.20
RO_2/R	2.25	2.3	2.3	2.7	3.2

Table II—Temperature 390° C

Composition of mixture	O_2	—	10	20	40	100	100
	H_2	100	100	100	100	100	100
	N_2O	100	100	100	100	100	—
	$\text{O}_2\%$	0	4.8	9.1	16.6	33.3	50
Pressure		16.00	16.33	16.00	16.23	16.12	16.12
Rate		0.330	1.05	1.97	3.75	8.40	6.30

Small quantities of a foreign gas can exert a large influence on a chain reaction only by destroying the carriers before they would normally end, or by increasing the rate of initiation. It is improbable, in the present work, that O_2 molecules affect the rate of starting, for the quenching radius of O_2 is only twice as great as that of H_2 .* The acceleration will therefore be due to the participation of oxygen in the propagation reactions.

Two possibilities may be distinguished :



* Zemanski, 'Phy. Rev.', vol. 36, p. 919 (1930).

(a) will be considered first. The stationary concentrations of H and of OH will be given by the equations

$$\frac{d[H]}{dt} = I + k_5 [OH] [H_2] - k_4 [H] [N_2O] - k_{10} [H] [H_2] [O_2] - k_9 [H] = 0,$$

$$\frac{d[OH]}{dt} = k_4 [H] [N_2O] + k_{10} [H] [H_2] [O_2] - k_5 [OH] [H_2] - k'_9 [OH] = 0,$$

hence

$$\frac{d[H_2O]}{dt} = \{k_4 [N_2O] + k_{10} [H_2] [O_2]\} I / k_9.$$

There are difficulties in accepting this simple scheme, for it would be expected that a triple collision with an energy of activation similar to that of $H + N_2O$ would occur much less frequently than the latter reaction, whereas in fact, the rate of removal of H atoms by O_2 is faster than that by N_2O . By postulating the formation of the complex, HO_2 , this difficulty can, in part, be overcome. For (b) therefore,

$$\frac{d[HO_2]}{dt} = k_{11} [H] [O_2] - k_{12} [HO_2] [H_2] - k_{13} [HO_2] [N_2O] - k_{14} [HO_2] = 0,$$

$$[HO_2] = \frac{k_{11} [H] [O_2]}{k_{12} [H_2] + k_{13} [N_2O] + k_{14}}.$$

$$\frac{d[H]}{dt} = I + k_5 [OH] [H_2] - k_4 [H] [N_2O] - k_{11} [H] [O_2] - k_9 [H] = 0,$$

$$\frac{d[OH]}{dt} = k_4 [H] [N_2O] + k_{12} [HO_2] [H_2] - k_5 [OH] [H_2] - k'_9 [OH] = 0,$$

$$\frac{d[H_2O]}{dt} = \left\{ k_4 [N_2O] + \frac{k_{11} [O_2] \cdot k_{12} [H_2]}{k_{12} [H_2] + k_{13} [N_2O] + k_{14}} \right\} I / k_9.$$

If k_{13} and k_{14} are small compared with k_{12} then

$$\frac{d[H_2O]}{dt} = \{k_4 [N_2O] + k_{11} [O_2]\} I / k_9.$$

This equation is in agreement with experiment in that the rate should increase linearly with $[O_2]$. At 390° the ratio $k_{11}/k_4 = 13.3$. Oxygen molecules increase the rate of production of water by reaction with the atomic hydrogen of the H_2-N_2O chains. At higher temperatures, the combination of H_2 and O_2 may also increase the rate of initiation.

High Pressure Thermal Reaction

Having established that oxygen can affect the propagation, the next question is whether the homogeneous or heterogeneous combination of hydrogen and oxygen may give rise to molecules or atoms capable of initiating chains in hydrogen-nitrous oxide. First of all, experiments were made on the effect of O_2 on the thermal reaction; the results are given in Table III. The mixtures

Table III—1.7 cm tube. Temperature 585° C

% O_2	4.75	2.37	1.18	0.59	0.0
Total pressure	100.5	103.0	99.0	100.0	99.0
Rate	15.0	6.0	3.8	1.75	0.26

were made up separately in a gas holder before admission to the reaction bulb. As might be expected, oxygen considerably increases the rate, which may, of course, be due to the propagation. Examination of the values of Δp (not given) will not, however, sustain this explanation entirely. Comparison of the experimental with the calculated values of Δp indicated that hydrogen and oxygen do react to yield H or OH which then start off the chains. In order to find whether this additional source of carriers is due to a wall or to a homogeneous process, the kinetics of the reaction were further investigated with respect to $[N_2O]$, $[H_2]$ and packing. R is directly proportional to $[O_2]$, as may be seen if the results are plotted. Hydrogen and nitrous oxide are inhibitors, for the initial rate of reaction is very nearly independent of pressure, as is shown in fig. 1, where $\Delta p - t$ curves are plotted for a mixture containing 3.3% oxygen. One prominent point is that the curves bend round comparatively rapidly, especially at low pressures, long before the reaction has gone to completion. The oxygen must therefore be consumed in the initial stages. To investigate the individual effects of hydrogen and of nitrous oxide, the following procedure was adopted: p_{N_2O} was fixed at 50 mm, p_{O_2} at 2.4 mm, and p_{H_2} was varied within measurable limits. A similar set of experiments was made with $p_{N_2O} = 150$ mm. A third series was carried out in which p_{H_2} and p_{O_2} were respectively 50 and 2.6 mm, and p_{N_2O} was varied. The results are summarized in Table IV where it will be observed that hydrogen and nitrous oxide exert about the same inhibitory action. The approximate constancy of $R \cdot p_{H_2}^{\frac{1}{2}}$ and $R \cdot p_{N_2O}^{\frac{1}{2}}$ shows that the rate is inversely proportional to the square root of the pressure, but when the pressure of nitrous oxide is considerably greater than that of hydrogen, the latter ceases to have any effect.

Table IV—5 cm bulb. Temperature 568° C

P_{O_2}	P_{H_2}	R	$Rp_{H_2}^{\frac{1}{2}}$
4.2	2.4	15.0	7.5
4.2	2.4	11.4	8.1
4.2	2.4	7.2	7.3
4.4	2.4	4.6	6.5
4.0	2.4	4.0	6.9
14.0	7.0	5.6	6.9
13.6	7.0	5.6	5.6
14.2	7.0	6.6	4.6
14.1	7.1	6.0	3.0
$Rp_{N_2O}^{\frac{1}{2}}$			
19.5	2.6	2.1	3.0
14.7	2.7	2.8	3.4
9.1	2.7	3.6	3.6
4.4	2.7	5.2	3.6

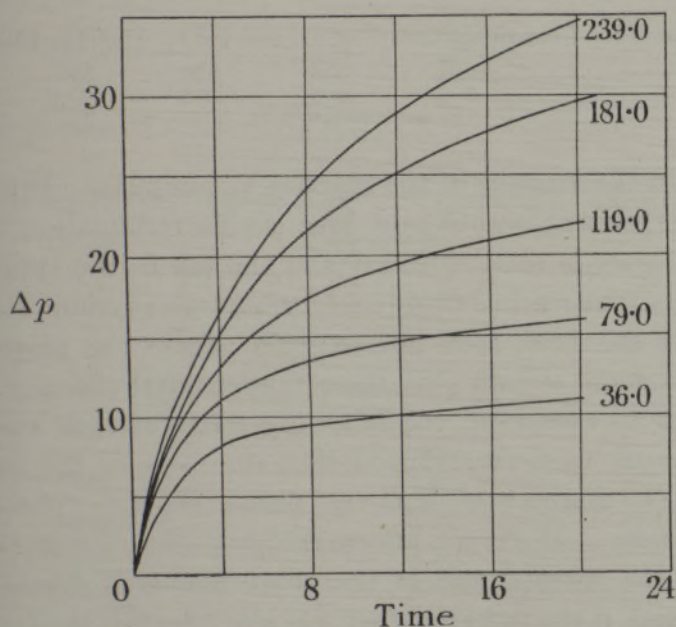


Fig. 1—Effect of total pressure, thermal high pressure reaction, 3.3% oxygen, temperature 532° C

Argon does not cause any inhibition when added to the extent of 200 mm to 400 mm of H_2 - O_2 - N_2O mixture. Packing experiments were also made to determine the nature of chain termination, using exactly the same tube and packing material as employed in the thermal high pressure experiments (Part I, p. 532). For comparison, the results are given in full in Table V. A decrease of 50% occurs in the rate, which is the same as that found for O_2 -free mixtures.

Table V—2.5 cm tube. Packing 0.7 cm tubes. Temperature 640° C
Composition of mixture, 10O₂, 250H₂, 250N₂O. Total pressure 100 mm

<i>t</i>	Packed		Empty	
	<i>Δp</i>	<i>Δp</i>	<i>Δp</i>	<i>Δp</i>
1	5.5	6.5	12.0	11.5
2	10.0	12.0	21.5	20.5
3	13.5	15.0	28.0	27.0
4	17.0	19.0	33.0	32.0
6	21.0	23.5	40.0	38.5
8	24.5	26.0	42.0	41.0
10	26.0	28.0	43.5	—

Since the discussion of the temperature coefficients of the different reactions has shown that there may be a possibility of assigning separate values to the various steps in the reaction, measurements were made of the apparent energy of activation of the present reaction, Table VI.

Table VI—Composition of mixture, 10O₂, 150H₂, 150N₂O

Temperature ° C	510	555	572	590	606	640
Rate	2.9	6.0	8.5	11.2	13.7	20.5

E = 17.4 k. cal.

The change in the kinetics of the reaction is complete. The effect of packing and of inert gases show, however, that similar termination reactions occur. The initiation factor is quite different and the fall in the apparent energy of activation shows that nitrous oxide no longer plays any important part in the first stages. It has been seen how oxygen affects the propagation factor, and in order to make certain that these fundamental changes in the kinetics were partly due to initiation, the following series of runs was made. Conditions for reaction were so arranged that the rates of the four reactions—thermal H₂-N₂O, thermal H₂-N₂O-O₂, photo H₂-N₂O, photo H₂-N₂O-O₂ were all comparable. If oxygen affects the propagation factor only, then the acceleration of the thermal and of the photo reactions should be the same. On the other hand, if the initiation factor is also affected, then the acceleration of the photo reaction will be somewhat smaller than that of the thermal. The reasons for these statements can be readily seen if the general velocity equations are set down for the four conditions:

$$R_T = P_T \cdot I_T^{\frac{1}{2}}, * \quad (1)$$

$$R_{T, O_2} = (P_T + P_{O_2}) (I_T + I_{O_2})^{\frac{1}{2}}, \quad (2)$$

$${}_P R_T = P_T \cdot (I_T + I_P)^{\frac{1}{2}}, \quad (3)$$

$${}_P R_{T, O_2} = (P_T + P_{O_2}) (I_T + I_{O_2} + I_P)^{\frac{1}{2}}. \quad (4)$$

* The termination factors are identical for all four reactions, and for simplicity are not inserted in the equations.

If $I_{O_2} = 0$,

$$R_{TO_2} - R_T = {}_P R_{T, O_2} - {}_P F_T.$$

If $I_{O_2} \neq 0$ and $I_T \doteq I_{O_2} \doteq I_P$,

$$R_{T, O_2} - R_T > {}_P R_T - {}_P R_{T, O_2}.$$

P and I are propagation and initiation factors. The suffixes T, O_2 , P refer respectively to the thermal, the O_2 , and the photo reactions. From these equations, the relative values of I_T , I_{O_2} , and I_P may be calculated. Let $P_{O_2} = P_T$, α can be computed from the oxygen content of the mixture and the results in Table VII. Equations (1) and (3) yield

$$I_T = I_P \{R_T^2 / ({}_P R_T^2 - R_T^2)\},$$

and (1), (2), (3), and (4) give

$$I_{O_2} = I_P \left(\frac{a + b}{a - b} \right),$$

where $a = {}_P R_{T, O_2}^2 - (1 + \alpha)^2 R_T^2$ and $b = R_{T, O_2}^2 - (1 + \alpha)^2 R_T^2$.

Table VII—5 cm tube. Composition of mixture, $5O_2$, $247H_2$, $247N_2O$.
 $\alpha = 0.30$

Temp °C	Pres- sure	R_T	R_{T, O_2}	${}_P R_T$	${}_P R_{T, O_2}$	$(R_{T, O_2} - R_T) ({}_P R_{T, O_2} - {}_P R_T)$
00550	100	0.60	2.75	1.95	3.45	2.15
00578	50	0.70	4.36	2.40	5.00	3.56
00572	100	1.05	4.20	3.3	5.9	3.15
00572	150	1.96	4.9	3.2	6.0	3.0
00618	100	3.4	8.7	5.9	10.5	5.3

I_T	:	I_P	:	I_{O_2}	I_T	:	I_P	:	I_{O_2}
1	:	9.6	:	11.7	0.14	:	1	:	1.22
1	:	10.6	:	21.9	0.095	:	1	:	2.07
1	:	8.9	:	8.9	0.112	:	1	:	1.00
1	:	1.66	:	2.60	0.60	:	1	:	1.57
1	:	2.01	:	2.87	0.50	:	1	:	1.43

Results for a few different pressures and temperatures are collected in Table VII. The acceleration of the two reactions is not equal, as will be observed from an examination of columns 7 and 8. This is more clearly shown by the calculations on the relative magnitudes of I . In the first set, $I_T = 1$ and in the second $I_P = 1$. I_P is nearly independent of temperature and pressure and hence the variation of the other quantities is given in better perspective. The second set of calculations demonstrates that the thermal reaction, compared with the photo, is greater as the temperature and pressure increase. The first shows that initiation by oxygen is of greatest importance

at low pressures and temperatures. This is in accordance with the value of E for the oxygen reaction being smaller than E for the normal reaction. Furthermore, since it has been found that the temperature coefficients of the propagation factors are nearly the same, the effect of packing is identical and there is initiation by O_2 , it must be concluded that, under these conditions, the initiation reaction involves both H_2 and O_2 and takes place in the gas phase with an energy of activation considerably less than that for the decomposition of nitrous oxide.

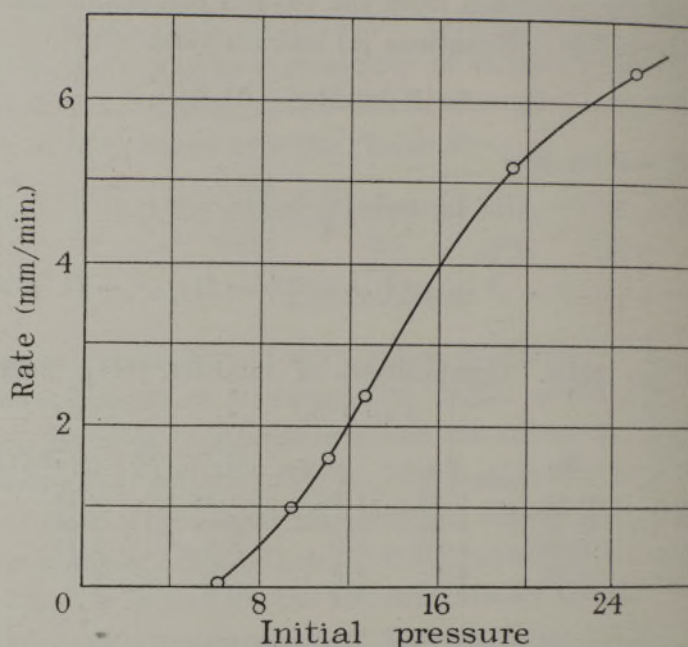


FIG. 2—Effect of total pressure, thermal low pressure reaction, temperature $602^{\circ}C$, 2.91% oxygen

The Low Pressure Reaction

It has been mentioned previously that, above 50 mm the pressure of a given $H_2-N_2O-O_2$ mixture does not affect the initial rate. As the pressure is reduced below this value, the rate diminishes linearly as is indicated by fig. 2. The curve does not pass through the origin, but makes an intercept on the pressure axis. The reaction velocity would thus appear to drop to a very small value when the pressure is below a certain critical point, in the present instance, 8 mm. If the individual runs are examined, it is found that Δp increases quite rapidly at first, but later changes only very slowly, although the reaction has not proceeded to completion. For example, with an initial pressure of 19.4 mm, Δp is almost steady after attaining 4 mm, which is equivalent to 40% of the

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possible increase. Had the observed value of Δp been due to the $\text{H}_2\text{-O}_2$ reaction alone, the pressure decrease would have been 0.6 mm. The comparatively abrupt bending over of the $\Delta p - t$ curves is due to the pressure of the mixture falling below the critical value. An essentially similar phenomenon is obtained when the oxygen content of a 1:1 $\text{H}_2\text{-N}_2\text{O}$ mixture at constant pressure is altered (Table VIII). Above 12.5% O_2 , the reaction is rapid and increases if the oxygen percentage is raised to 5. At 0.63%, however, the rate has dropped to a very small value. On raising the temperature to 650° , a conveniently measurable velocity is obtained, which does not greatly depend on the oxygen content and is, indeed, not much faster than that for the oxygen-free gas.

Table VIII

mp. °	570	570	570	560			
O ₂	5	1.25	0.63	0.63			
pressure	12.80	13.06	12.84	12.80			
	Δp	Δp	Δp	Δp			
0.25	2.25	0.25	0.46	0.5	0.00	0.5	0.38
0.50	3.46	0.50	0.76	2	0.04	1	0.62
0.75	4.16	0.75	0.88	4	0.06	2	1.00
1.0	4.44	1	1.02			3	1.30
1.25	4.54	1.5	1.36			4	1.56
1.75	4.82	2	1.54			6	1.88
		3	1.82			8	2.10
		6	2.06			10	2.30
Temp. ° C	650	650	650	650			
% O ₂	0.31	0.16	—	—			
Pressure	12.71	12.98	12.80	12.80			
	t	Δp	t	Δp	t	Δp	
	1	0.26	1.5	0.38	1	0.20	
	2	0.56	3	0.70	2	0.38	
	4	0.96	4	0.80	4	0.80	
	6	1.28	7	1.40	6	1.04	
	8	1.60	10	1.78	10	1.62	
	10	1.88	15	2.36	14	2.16	
	15	2.36	21	2.78			
	20	2.78					

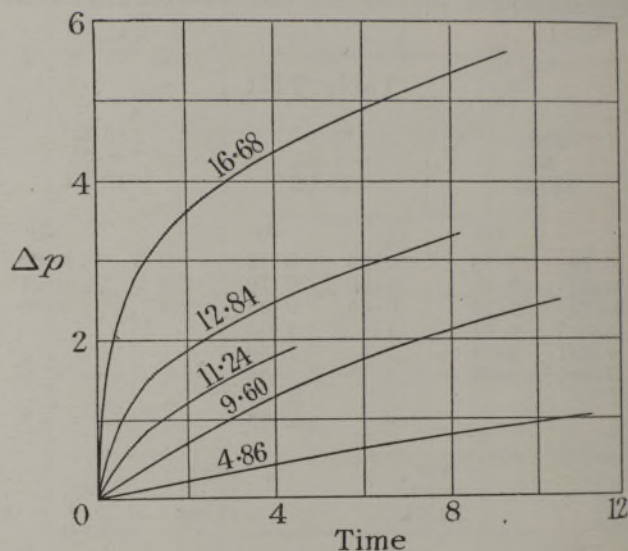
If the $\Delta p - t$ curves are plotted, the same tendency to bend over is not so marked at 650° . The oxygen pressure would thus seem to control the position of the critical point. If the reaction above the critical pressure is to be identified with that at high pressures, it would be expected that, as with O_2 -free gas, the apparent energy of activation would decrease with pressure. This is borne out by the data in Table IX, where it will also be noted that, for a given mixture at a constant pressure, there is a critical value for the temperature, below which the rate is slow.

Table IX—Composition 12O_2 , $200\text{N}_2\text{O}$, 200H_2 . Pressure 12.8 mm
5 cm tube

Temperature °C	510	519	525	540	580	625
Rate	0.01	0.95	1.25	2.05	3.3	8.2

$$E = 30.6 \text{ k. cal.}$$

Finally, packing experiments show clearly the importance of inhibition by walls. For example, in the 5-cm tube at 550° with a mixture containing 2.9% O_2 , the critical pressure was 6 mm, the rates at 7.67 and 20.10 mm being respectively 1.00 and 2.40 mm/min. On packing the tube completely with

FIG. 3—Effect of total pressure, packed reaction bulb. Temperature 710°C , 2.9% O_2 .

0.7 cm tubes, no measurable reaction occurred at all and the temperature had to be raised to 710° to get a conveniently observable rate, which for a pressure of 16 mm was 1.55 mm/min. The rate of the $\text{H}_2\text{-N}_2\text{O}$ reaction was now 0.50 mm/min. In the packed tube, however, there was still evidence of the existence of a critical pressure, for it will be seen from fig. 3, where $\Delta p - t$ curves are plotted for different total pressures, the form of the curves changes between 9.60 and 11.24 mm. This is brought out more clearly in Table X where a comparison is shown for an O_2 -free and an O_2 -containing mixture at 16.00 and at 8 mm, *i.e.*, above and below the critical pressure. The acceleration of the reaction is much greater at 16 than at 8 mm.

It should be mentioned that, in all these experiments, the mixtures were made up previously in a separate gas holder, for it was neither convenient nor

to add small amounts of oxygen to the $\text{H}_2\text{-N}_2\text{O}$ mixture. A considerable number of experiments was carried out in which the gases were added separately to the bulb and the important observation was made that, if only hydrogen and oxygen were admitted without nitrous oxide, there was immediate explosion and the pressure fell extremely rapidly. This occurred with pressures and temperatures above the critical values for the $\text{H}_2\text{-N}_2\text{O-O}_2$ reaction.

Table X—Composition of mixture as in Table IX

Above transition point				Below transition point			
O_2 free				O_2 free			
16.4				8.06			
16.24				8.00			
t	Δp	t	Δp	t	Δp	t	Δp
0.5	1.64	1	0.40	0.5	0.09	0.5	0.03
1.1	2.60	2	0.84	1	0.26	1	0.21
2.1	3.24	4	1.74	2	0.59	2	0.36
4	3.94	6	2.46	3	0.85	3	0.53
6	4.54	8	3.02	5	1.26	5	0.83
8	5.04	10	3.44	7.5	1.65	7.5	1.17
R_0 330				R_0 0.295			
$R_0/R = 7.9$				$R_0/R = 1.69$			

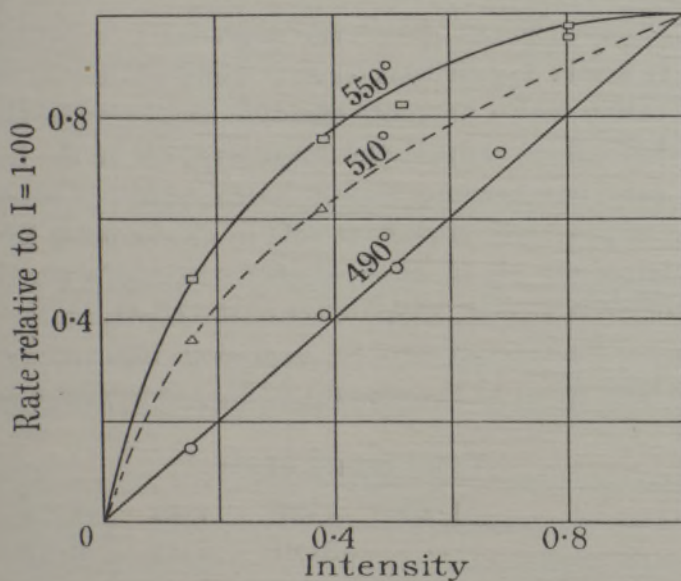


FIG. 4

unusual character of the reaction is further borne out by experiments on the effect of the intensity of the light in the photochemical reaction in the region of the transition point. The rate-intensity curves are given in fig. 4 for three temperatures. The dark reactions were not greater than 5% of the total. At 492°, a linear relation is obtained as might be expected, but at 510°

and still more so at 550° , curvature is marked in such a way as to indicate that the exponent of I at 510° is 0.5 and even less at 550° for the dotted curve refers to $R \sim I^{\frac{1}{2}}$. The interpretation of the results at 510° might simply be that the increase in rate has altered the termination process from a wall to a gas phase reaction. Although this may in part be true, the fact that at 550° , $R \sim I^{1/n}$ where $n > 2$ and that in the ordinary photo reaction, H_2-N_2O , at a rate of the order of 1 mm per minute surface termination is still pre-dominant, shows that this explanation is not sufficient.

Discussion of the Mechanism

The critical point observed in the low pressure O_2 -reaction bears a remarkable similarity to the lower limit in H_2-O_2 mixtures. The reaction above this point is not, however, an explosion, for it was quite easy to get spontaneous inflammation at low pressures if the temperature was raised sufficiently. Since the H_2-O_2 mixture itself is spontaneously explosive and, above the critical point initiation is largely due to the H_2-O_2 reaction, it may be that the stable reaction observed is not unlike the degraded ("entartete") explosions of Semenov.* It would appear that there is some additional inhibition factor coming into operation which prevents effective branching of the chains. The intensity-rate relationships support this argument, for at the highest temperature 550° , the rate has become almost independent of intensity; that is, initiation ceases to play any important role in determining the course of the reaction. This latter effect is one of the characteristics of a pure lower explosion limit. Nitrous oxide is, in fact, an inhibitor of the H_2-O_2 reaction for, although it reduces the lower limiting pressure for explosions like argon or helium,† the critical pressure rises again as the amount of N_2O increases, *e.g.*,

Temperature $515^\circ C$					
$p_{H_2+O_2}$	1.60	1.27	1.21	1.23	1.61
p_{N_2O}	—	3.20	4.81	6.57	9.61

The limit was determined by admitting a 2 : 1 H_2-O_2 mixture until inflammation was observed. A short time was allowed for the water formed in the explosion to be withdrawn by the P_2O_5 , when the residual pressure was noted. Nitrous oxide was then added and the foregoing procedure repeated.

* 'Z. phys. Chem.,' B, vol. 2, p. 464 (1931).

† Hinshelwood and Moelwyn-Hughes, 'Proc. Roy. Soc.,' A, vol. 138, p. 311 (1932).

Some curious observations were made during these experiments. If the $\text{H}_2\text{-O}$ mixture was quickly admitted to the tube and the lower limit passed, a much more violent explosion occurred at about 10 mm, which was accompanied by rapid vibration of the manometer pointer. If the flow of hydrogen and oxygen was arrested, the pressure fell very quickly as the water was removed. During this period, successive explosions were observed in the reaction tube, resembling those obtained with $\text{P}_4\text{-O}_2$ mixtures when the lower limit is passed. There may be some connection between these two types of explosion and the experiments of Ouellet* who used a quantum counter for investigating the lower limit of the $\text{P}_4\text{-O}_2$ reaction. In these, the lower limit was succeeded at a higher pressure by another explosion with a flash of a different colour, which alone affected the counter (it may be noted that the counter was only sensitive to radiation of $\lambda < 280 \text{ m}\mu$) and hence it was concluded that there were two kinds of explosion in so far as the nature of the chemiluminescence was concerned.

The modification of the previous theory of the effect of oxygen to allow for branching is simply made. It will be assumed that branching occurs in the step $\text{O}_2 + \text{H}_2$ and that as usual $(\alpha - 1)$ is the efficiency of branching, *i.e.*, the probability of two OH radicals being produced when one H atom disappears. The equations for the stationary concentrations of H and of OH are therefore

$$\frac{d[\text{H}]}{dt} = \text{I} + k_5[\text{OH}][\text{H}_2] - k_4[\text{H}][\text{N}_2\text{O}] - k_9[\text{H}] - k_{11}[\text{H}][\text{O}_2] = 0,$$

$$\frac{d[\text{OH}]}{dt} = \text{I} + k_4[\text{H}][\text{N}_2\text{O}] - k_5[\text{OH}][\text{H}_2] + \alpha k_{11}[\text{HO}_2][\text{H}_2] = 0,$$

when

$$\frac{d[\text{H}_2\text{O}]}{dt} = \{k_4[\text{N}_2\text{O}] + k_{11}[\text{O}_2]\} \frac{\text{I}}{k_9 + (1 - \alpha)k_{11}[\text{O}_2]}.$$

At low temperatures, α is very nearly unity and hence the second term in the denominator vanishes. The condition for explosion is $k_9 = (\alpha - 1)k_{11}[\text{O}_2]$ and therefore the limit should be sharp as in the thermal $\text{H}_2\text{-O}_2$ reaction. In the present reaction, however, a rather peculiar position arises. It has been seen that there is a little gas phase termination in the low pressure reaction. If the stationary concentration of H or of OH be raised much above that obtaining under the conditions employed in these experiments, for example, by a branching mechanism, gas phase termination will become of ever-increasing importance. The functioning of this additional inhibitory factor may, at any

* 'Trans. Faraday Soc.', vol. 29, p. 486 (1933).

rate in a small region, prevent effective branching and thus allow the stable reaction to be measured. The transition point is therefore reached when $[H]$ attains a certain value, which will naturally be affected by packing, temperature, and oxygen content of the mixture, in a somewhat similar manner to a lower limit. At high pressures gas termination is so important that a sharp transition is not obtained; likewise, when the chains are short, as in a packed tube, transitional characteristics are only slightly in evidence.

On p. 762 it was shown that although oxygen is more effective than N_2O in producing OH radicals from a hydrogen atom, yet the energies of activation of the two reactions are almost identical. First of all, this rules out the possibility of the simple reaction $H + H_2 + O_2 = H_2O + OH$ since, if such a ternary collision required the same energy of activation as $H + N_2O$, the probability of its happening would be extremely small. Recently, L. Farkas* has measured the rate at which H atoms are removed in a mixture of H_2 and O_2 at room temperature and found that the velocity was about $1/50$ of that calculated from the number of ternary collisions $H + H_2 + O_2$, and is not changed by temperature. This discrepancy can be explained by supposing that the removal of an H atom is not accompanied by the production of OH . This latter process requires as much activation as the reaction $H + N_2O$. But the oxygen molecule is more effective than the N_2O molecule in yielding OH , and therefore the rate of $HO_2 + H_2 = H_2O + OH$, although possessing the same energy of activation, is faster than $H + N_2O = OH + N_2$. The concentration of HO_2 must consequently be greater than that of H ; from the results in Table I, the order of magnitude is 10.

The author desires to thank Dr. E. B. Ludlam and Professor J. Kendall for their continued help and encouragement throughout the course of this work, which was carried out in the Chemistry Department of the University of Edinburgh and subsequently at the Department of Colloid Science of the University of Cambridge. He also thanks the Royal Commissioners of the Exhibition of 1851 for a Senior Studentship.

Summary

The effect of the addition of oxygen on the kinetics of the hydrogen-nitrous oxide reaction has been investigated in order to compare the H_2-N_2O and H_2-O_2 reactions under similar conditions.

* Private Communication.

Summary of Reactions

	Kinetic equation (observed) $R \sim$	Kinetic equation (calculated) $R \sim$	E (total)	E (initiation)
at high pressure	$[N_2O][H_2]^{0.5*}$	$[N_2O] \sqrt{\frac{[N_2O]([N_2O] + [H_2])}{([N_2O] + [H_2])}}$	36.5	57
at low pressure	$[N_2O]^2[H_2]^{0.5*}$	$[N_2O]^2([N_2O] + [H_2])$	49.5	50
at high pressure	$I^{\frac{1}{2}}$	$[N_2O] \sqrt{\frac{[H_2]}{([N_2O] + [H_2])^2}} I^{\frac{1}{2}}$	<36	0
at low pressure	$[N_2O][H_2]^0 I$	$[N_2O] \cdot \frac{[H_2]}{[N_2O] + [H_2]} \cdot I$	14	0
at high pressure + O_2	$[O_2] \cdot [N_2O]^{-0.5} \cdot [H_2]^{-0.5}$	$([N_2O] + \alpha[O_2]) \sqrt{\frac{?}{([N_2O] + [H_2])}}$	17	<57
at low pressure + O_2	$[O_2]$	$([N_2O] + \alpha[O_2]) \sqrt{?}$	31†	<50
at high pressure + O_2	—	$([N_2O] + \alpha[O_2]) \sqrt{\frac{[H_2]}{([N_2O] + [H_2])^2}}$	<17§	0
at low pressure + O_2	$[O_2] \cdot I^{(1 \rightarrow 0)†}$	$([N_2O] + \alpha[O_2]) \cdot \frac{[H_2]}{[N_2O] + [H_2]}$	14	0

* These exponents are to some extent a function of $[N_2O]$.

† Exponent depends on temperature.

‡ Measured above the transition point.

§ Estimated from the data in Table VII.

|| The coefficients for $[H]$ and $[N_2O]$ are not inserted.

The thermal and mercury photosensitized reactions have been studied in the pressure range 1–300 mm.

At high pressures, the addition of small quantities of oxygen increases the velocity, the kinetics change entirely and the energy of activation falls off. By using photochemical methods it is shown that oxygen participates in the initiation and in the propagation of the chains. From packing experiments it is also shown that initiation is homogeneous.

At low pressures in the thermal reaction, a transition point is observed above which the reaction is comparatively rapid and below which it is slow, provided wide bulbs are used. This point depends on the oxygen content and the temperature of the gases; it is displaced to higher temperatures on packing the reaction tube. The phenomenon has some definite connection with the low limit of the H_2-O_2 reaction. Photo experiments confirm these observations in that as the temperature is raised the value of the exponent n in the equation Rate = const. \times (intensity) n decreases from unity to almost zero.