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Chemical Kinetics of the Reaction of Oxygen with Hydrogen and with Deuterium[1]

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Introduction

Recently both Frost and Alyea[4] and Hinshelwood, Williamson and Wolfenden[5] have presented data on the reaction of oxygen with deuterium, and have concluded from comparison with the oxygen–hydrogen data that the substitution of deuterium for hydrogen does not affect the probability of chain branching. We felt that the oxygen–hydrogen reaction had not as yet been subjected to a sufficiently careful analysis to justify these authors' methods of comparison, and in attempting to supply this analysis we have found that the commonly accepted (or at least frequently published) theories of this reaction require considerable revision.

The Effect of Surface in Breaking Chains

Before considering any mechanism in detail, it is necessary to examine the mathematical theory of chain reactions with chains broken at the surface of the vessel. It has been customary to write the equivalent volume rate of surface destruction of chains as $(k/pd^2)n$, where n is the concentration of chains, d a linear dimension of the vessel, and p a linear function of the partial pressures of the various gases. Then, if the net branching rate in the gas phase is αn, the condition for the explosion limit is taken to be

$$\alpha = k/pd^2 \qquad (1)$$

This admittedly crude treatment is supposed to be justified by the more exact calculations of Bursian and Sorokin.[6] The diffusion equation for a spherical vessel is

$$\frac{\partial n}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n}{\partial r}\right) + \alpha n \qquad (2)$$

The condition for the explosion limit is that the number of chains in existence is not changing, that is

$$\partial n/\partial t = 0 \qquad (3)$$

The most general solution of (2) and (3) which remains finite at the origin is known to be

$$n = (A/r)\sin\sqrt{\alpha/D}\,r \qquad (4)$$

If every chain striking the surface is destroyed, the boundary condition for (4) is $n = 0$ at $r = r_0$, where r_0 is the radius of the vessel. This gives

$$\alpha = \pi^2 D/r_0^2 \qquad (5)$$

as the condition for the explosion limit; since D is inversely proportional to p, (5) is in fact equivalent to (1). This is essentially the treatment given by Bursian and Sorokin.

The assumption that no chains are reflected from the surface, however, is certainly incorrect. It has been supposed that the result of reflection would be to replace r_0 by some "effective radius" βr_0,[7] but it will now be shown that this is not the case. When ϵ is the fraction of chains destroyed on striking the surface we obtain the boundary condition for (4) by equating the total rate of branching throughout the volume to ϵ times the rate at which the chains strike the surface; the latter rate we take as $4\pi r_0(r_0 - \lambda) \times (\bar{v}/4)n_\lambda$, where n_λ is the concentration of chains one mean free path from the surface and $\bar{v}$ is the mean molecular velocity. This boundary condition reduces to

$$\epsilon\bar{v}r_0\sin\sqrt{\alpha/D}\,(r_0 - \lambda) = 4D\left[\sin\sqrt{\alpha/D}\,r_0 - \sqrt{\alpha/D}\,r_0\cos\sqrt{\alpha/D}\,r_0\right] \qquad (6)$$

Where $\lambda \ll r_0$, as is the case in all physically interesting conditions, (6) becomes

$$\frac{4D}{\epsilon\bar{v}r_0} = \frac{\sin\sqrt{\alpha/D}\,r_0 - \sqrt{\alpha/D}\,\lambda\cos\sqrt{\alpha/D}\,r_0}{\sin\sqrt{\alpha/D}\,r_0 - \sqrt{\alpha/D}\,r_0\cos\sqrt{\alpha/D}\,r_0} \qquad (7)$$

If $\sqrt{\alpha/D}\,r_0 = \pi$, (7) gives

$$D = \epsilon\bar{v}\lambda/4 \qquad (8)$$

The diffusion coefficient is usually taken as

$$D = \bar{v}\lambda/3 \qquad (9)$$

but the difference in the numerical coefficient is of the sort to be expected from taking all free paths equal to the mean free path, as we have done. This treatment thus gives essentially the same result for the case $\epsilon = 1$ as that found by Bursian and Sorokin.

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[4] Frost and Alyea, THIS JOURNAL, **56**, 1251 (1934).

[5] Hinshelwood, Williamson and Wolfenden, *Proc. Roy. Soc.* (London), **A147**, 48 (1934).

[6] Bursian and Sorokin, *Z. physik. Chem.*, **12B**, 247 (1931).

[7] Dalton and Hinshelwood, *Proc. Roy. Soc.* (London), **A125**, 294 (1929). Hinshelwood and Williamson, "The Reaction between Hydrogen and Oxygen," Oxford University Press, 1934, p. 59.

When ϵ is large enough, it is convenient to set

$$\sqrt{\alpha/D}\, r_0 = \pi - \delta \qquad (10)$$

If we then expand the trigonometric terms in series and use $D = \bar{v}\lambda/4$, (7) reduces to

$$1/\epsilon = 1 + (r_0\lambda - 1)(\delta/\pi)(1 - \delta^2/3 + \ldots)$$

We are interested in values of r_0/λ of the order of 10^3. Then when $\epsilon = 0.5$, $\delta/\pi = 10^{-3}$; when $\epsilon = 0.1$, $\delta/\pi = 9 \times 10^{-3}$; when $\epsilon = 0.01$, $\delta/\pi = 0.099$. That is, the critical value of $\sqrt{\alpha/D}\, r_0$ is only 10% less for a surface which destroys 1% of the chains striking it than for a surface which destroys all the chains. Surfaces of moderate efficiency are thus almost equivalent to surfaces of perfect efficiency, and the critical condition is approximately represented by (5).

For low efficiencies the relations are considerably different, as may be seen from Table I.

TABLE I

SOLUTIONS OF EQUATION (7)

$\sqrt{\alpha/D}\,(r_0/\pi)$	$(4r_0/\pi^2\epsilon\bar{v})\alpha$	$(4/\epsilon\bar{v}r_0)D$	$\dfrac{n_{\text{wall}}}{n_{\text{center}}}$	$(\lambda/\epsilon r_0)$
1.00	(λ/r_0)	(λ/r_0)	0.0	(λ/r_0)
0.99	0.009801	0.01000	0.01010	0.040
.97	.02831	.03009	.03088	.120
.95	.04548	.05039	.05241	.201
.90	.08349	.10307	.10930	.412
.85	.11577	.16023	.17001	.641
.80	.14352	.22425	.23387	.897
.70	.18863	.38495	.36789	1.14
.60	.22326	.62017	.50445	2.48
.50	.25000	1.0000	.63662	4.00
.40	.27042	1.6901	.75683	6.76
.30	.28549	3.1721	.85839	12.7
.20	.2958	7.396	.93549	29.6
.10	.3019	30.19	.98364	121
.05	.3034	121.38	.99586	485
.03	.3038	337.53	.99852	1330
.01	.3039	3039.4	.99984	12200

The first line of this table applies to the case $\epsilon = 1$; the rest of it is correct only when λ/r_0 and ϵ are sufficiently small. To determine how small these values need be, we note that each entry in column 3, say T, is an approximation to $T + (1 - T)(\lambda/r_0)$; then if the D value in line 2 is to be correct to 5% we must have $\lambda/r_0 < 5 \times 10^{-4}$; since for this line $\lambda/r_0 = 0.040\epsilon$, we must have $\epsilon < 0.0125$. For line 5, we need $\lambda/r_0 < 0.0055$, or $\epsilon < 0.013$, and for line 15, $\lambda/r_0 < 0.05$ or $\epsilon < 10^{-4}$. This table can now be used to deduce the relations between the different variables. Thus one sees that in the top few lines

$$(4r_0/\pi^2\epsilon\bar{v})\alpha \doteq (4/\epsilon\bar{v}r_0)D$$

which is again only the simple condition (5). Furthermore, the dependence upon ϵ in this region is slight. Thus, suppose that we have found some particular values ϵ_1 and D_1 such that $(4r_0/\pi^2\epsilon_1\bar{v})\alpha = 0.02831$ and $(4/\epsilon_1\bar{v}r_0)D_1 = 0.03009$; as may be seen from the third line of Table I, these values fall on the explosion limit. If now we change to a new value of ϵ, $\epsilon_2 = 2.888\epsilon_1$, we will have $(4r_0/\pi^2\epsilon_2\bar{v})\alpha = 0.009801$ and $(4/\epsilon_2\bar{v}r_0)D_1 = 0.01042$; it may be seen from the second line of the table, however, that the explosion limit is at $(4/\epsilon_2\bar{v}r_0)D_2 = 0.01000$. Evidently, then, if $D_2 = 0.960D_1$, we are again at the explosion limit. That is, a 4% decrease in diffusion coefficient compensates a three-fold increase in chain-breaking efficiency.

For the still lower efficiencies at the bottom of the table, the critical condition is approximately $(4r_0/\pi^2\epsilon\bar{v})\alpha = 3/\pi^2$ or

$$\alpha r_0/\epsilon\bar{v} = 3/4 \qquad (11)$$

independent of $(4/\epsilon\bar{v}r_0)D$ and hence of D. Here the surface destruction is so slow that there is no appreciable concentration gradient and hence no dependence on the diffusion coefficient. In fact, we can simply write

$$(4/3)\pi r_0^3\alpha n = (\epsilon\bar{v}/4)4\pi r_0^2 n$$

which reduces to (11).

Thus, on the basis of the more complete development of the diffusion theory which we have presented here, the critical condition changes gradually from $\alpha = \pi^2 D/r_0^2$ to $\alpha = (^3/_4)\epsilon\bar{v}/r_0$ as ϵ decreases. The fourth column of the table shows that the former relation applies only when the concentration gradient is large. Since when $\epsilon = 1$ the second condition yields a value of α some 10^3 times greater than the first, it is evident that a very slight amount of convective mixing would produce a considerable increase in the value of α at the limit. It is quite impossible to attempt any quantitative treatment of this extra mixing. In explosions at high temperatures, such as those of hydrogen and oxygen, the lower-limit measurements are made by admitting gas "slowly" to the reaction vessel until a flash or a pressure drop is observed. The gas being admitted enters a larger vessel through a narrow tube; it is probable that the entering gas is somewhat cooler than the main volume; in some work there is also a difference in composition. One must expect currents of appreciable velocity with such an arrangement. In the work of Dalton and Hinshelwood[8] on the oxidation of

(8) Dalton and Hinshelwood, *Proc. Roy. Soc.* (London), **A125**, 294 (1929).

phosphine a mixture of constant temperature and composition was compressed by the slow rise of mercury in a vertical tube of uniform cross section. Here the gas currents must have been comparatively small, and it is probably significant that this is one of the few reactions for which there is any real evidence that the critical α is inversely proportional to the square of the vessel diameter. The bromine-sensitized ozone explosions of Lewis and Feitknecht[9] are another case for which the square of the diameter may be applied with fair success. For both of these reactions, however, the limiting pressure is sufficiently sensitive to the condition of the surface to indicate disagreement with the simple Bursian–Sorokin theory.

We shall consider very briefly the problem of the steady state when α is too small to give explosions. We must now take explicit account of the rate of starting chains, say n_0 per unit of volume and time. Then our steady state condition is

$$\frac{\partial n}{\partial t} = D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n}{\partial r}\right) + \alpha n + n_0 = 0 \qquad (12)$$

which has the solution

$$n = (A/r)\sin(\alpha/D)^{1/2}r - n_0/\alpha \qquad (13)$$

The boundary condition is now used to determine A, with the result

$$A = \frac{n_0 r_0^2 \epsilon\bar{v}/\alpha}{r_0\epsilon\bar{v}\sin[(\alpha/D)^{1/2}(r_0 - \lambda)] - 4D\sin(\alpha/D)^{1/2}r_0 + 4(\alpha D)^{1/2}r_0\cos(\alpha/D)^{1/2}r_0} \qquad (14)$$

The denominator of (14) is negative within the explosion region, and zero at the limit. Any change in the experimental variables pressure, temperature, composition, etc., which takes the denominator from negative to zero values will, if continued, lead to larger and larger positive values, and hence to lower and lower rates. This can be shown directly by calculation in particular cases, but it is probably sufficiently obvious.

The problem of chains starting at the wall must be treated separately in obtaining the steady-state rates. We will again have the equation (2) and the solution (4); now, however, the boundary condition equates the net rate of branching throughout the volume to the rate of surface destruction of chains *minus* the rate of production of new chains by the surface. This equation may be solved for A to give

$$A = \frac{r_0^2 n_0}{(\epsilon\bar{v}r_0/4 - D)\sin(\alpha/D)^{1/2}r_0 + (\alpha D)^{1/2}r_0\cos(\alpha/D)^{1/2}r_0} \qquad (15)$$

where n_0 is the rate of production of new chains per unit of time and surface. The explosion condition, as given by the vanishing of the denominator, is the same as for volume starting, and the difference in the numerators is not likely to permit an experimental choice between the two equations. We do not know of any case in which a reaction above the upper limit with the characteristics predicted from (14) or (15) has been observed; the equations are presented here only to show that the reaction of hydrogen and oxygen above the upper limit is not of this type.

The Explosion Limits

When the two limits are far enough apart not to perturb each other seriously, the upper limit can be represented fairly well by a linear relation

$$f_H[H_2] + f_O[O_2] + f_X[X] = \text{const.} \qquad (16)$$

It is quite definitely established by the work of Grant and Hinshelwood[10] with quartz and alumina vessels and by that of Frost and Alyea[11] in Pyrex coated with potassium chloride that (16) is a good approximation except for high H_2/O_2 ratios;[12] one cannot be sure whether or not this latter deviation is due merely to closer approach of the two limits, but it is probable that a correct theory should be reducible to (16), even though this reduction involves assuming terms small which must be retained to fit the data more exactly. Our knowledge of the lower limit is extremely unsatisfactory. Hinshelwood and Moelwyn-Hughes[13] gave the condition

$$[H_2][O_2]\left(1 + \frac{\text{const. }[X]}{[H_2] + [O_2]}\right) = \text{const.} \qquad (17)$$

for the limit in quartz, while Frost and Alyea found

$$[O_2](g_H[H_2] + g_O[O_2] + g_X[X]) = \text{const.} \qquad (18)$$

for potassium chloride-on-Pyrex. The lower limit in quartz is extremely erratic, and although decrease in vessel size led to a very rapid increase in the pressure at the limit it is quite impossible to determine what power of the diameter is involved. Frost and Alyea did not investigate the effect of varying vessel size.

We shall now investigate the possibility of

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(9) Lewis and Feitknecht, THIS JOURNAL, **53**, 2910 (1931).

(10) Grant and Hinshelwood, *Proc. Roy. Soc.* (London), **141A**, 29 (1933).

(11) Frost and Alyea, THIS JOURNAL, **55**, 3227 (1933).

(12) *Cf.* Storch and Montgomery, *ibid.*, **56**, 2644 (1934).

(13) Hinshelwood and Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **138A**, 311 (1932).

fitting these results into the Semenoff–Hinshelwood isothermal branching chain theory. For this purpose we adopt the rather powerful method of writing down all possible reactions and then determining what choices of rate constants are needed to fit the experimental results. In determining what are "possible" reactions the general nature of the branching chain theory must be kept in mind. The critical condition is that the concentration of chain carriers shall remain constant at any given value if the chain starting reactions are suppressed and the reactant concentrations held constant. This evidently requires that all processes entering into the mechanism shall be of the same order with respect to the chain carriers. It is easy to write second order chain breaking processes: $H + H + M = H_2 + M$, $H + OH + M = H_2O + M$, etc., but it does not seem possible to devise any second order chain branching processes more plausible than $HO_2^* + HO_2^* = H + O + OH + O_2$. It therefore seems to be necessary either to reject the isothermal branching chain theory entirely or to assume that second order chain processes do not occur at an appreciable rate until the chain concentrations have become so high, and the reaction rate so great, that the temperature rises and a thermal explosion ensues. In the latter case the critical conditions will be given correctly by considering only reactions which are first order in the chain carriers, as we shall now do. The catalog of "possible" reactions for our present purposes then becomes

$$\begin{aligned}
H + O_2 &= HO_2^* && (1)\\
H + O_2 &= OH + O && (2)\\
HO_2^* + H_2 &= H_2O_2 + H && (3)\\
HO_2^* + H_2 &= H_2O_2^* + H && (4)\\
HO_2^* + H_2 &= H + 2OH && (5)\\
HO_2^* + H_2 &= OH + H_2O && (6)\\
HO_2^* + M &= HO_2 + M && (7)\\
H_2O_2^* &= 2OH && (8)\\
H_2O_2^* + M &= H_2O_2 + M && (9)\\
OH + H_2 &= H_2O + H && (10)\\
O + H_2 &= OH + H && (11)\\
O + O_2 + M &= O_3 + M && (12)\\
O + H_2 + M &= H_2O + M && (13)\\
H + O_2 + M &= HO_2 + M && (14)
\end{aligned}$$

The reaction

$$H_2O_2 = H_2O + O$$

might have been included but would make no essential change in the results. It would be necessary for a definite fraction of all the H_2O_2 to react in this way, independent of the concentrations of H_2, O_2 and X; in this case, however, the new process would be kinetically equivalent to others already written. The only other reactions intentionally omitted are "secondary activations" which we shall discuss subsequently.

Then, for the upper limit, where chain-breaking at the wall is negligible, a simple calculation shows that

$$k_1[H_2]\,\frac{k_3 + 3k_5 + k_6 + k_4(3k_8 + k_9[M])/(k_8 + k_9[M])}{(k_3 + k_4 + k_5 + k_6)[H_2] + k_7[M]} + k_2\,\frac{3k_{11}[H_2] + k_{12}[O_2][M] + k_{13}[H_2][M]}{k_{11}[H_2] + k_{12}[O_2][M] + k_{13}[H_2][M]} = k_1 + k_2 + k_{14}[M] \qquad (19)$$

where each term such as $k_{14}[M]$ represents $k_{14,\,H}[H_2] + k_{14,\,O}[O_2] + k_{14,\,X}[X]$. We must now find what conditions upon $k_1 \ldots k_{14}$ will reduce (19) to (16). The obvious way to obtain this reduction is to make the two fractions on the left side of (19) reduce to constants. For the first fraction this means $k_7 = 0$ and any one of k_4, k_8, $k_9 = 0$. For the second fraction it means $k_2 = 0$ or $k_{11} = 0$ or $k_{12} = k_{13} = 0$. Putting $k_7 = 0$ rules out all deactivations of HO_2^* and thus introduces a sharp distinction between HO_2^* formed in (1) and HO_2 formed in (14). Putting any one of k_4, k_8, $k_9 = 0$ effectively eliminates (4), since if $k_8 = 0$, (4) becomes equivalent to (3), and if $k_9 = 0$, to (5). The steps (4) and (8) were suggested by Hinshelwood and Williamson,[14] but this calculation shows that they cannot be of importance. For the second fraction the required conditions mean that either all or none of the oxygen atoms continue the chain, or that no oxygen atoms are formed.

There seems to be only one other way of obtaining (16). A formally correct result is obtained by making the first term a constant, and taking $k_{12} = k_{14} = 0$; if the first term becomes $k_1(1 - \beta)$, the result is

$$\beta k_1 k_{13}[M] = k_{11}(2k_2 - \beta k_1) \qquad (20)$$

Here β must be a small *positive* fraction if the limit is to occur at a positive pressure. If $k_7 = 0$, β is negative; but if $k_{7,\,H}$ is considerably larger than any other k_7, that is, if HO_2^* is selectively deactivated by H_2, a positive β is possible.

The first of these two mechanisms gives a rate of chain branching which may be written $k[H][O_2]$, since it is only for hydrogen atoms that there is any real competition; HO_2^* always

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(14) Hinshelwood and Williamson, "The Reaction between Hydrogen and Oxygen," Oxford University Press, 1934, p. 68.

reacts with H_2, and OH and O either always or never continue the chain by (10) and (11). The chain breaking is given by $k_{14}[H][O_2][M]$, and the mechanism is kinetically equivalent to

$$H + O_2 \longrightarrow \text{branching of chain}$$
$$H + O_2 + M \longrightarrow \text{destruction of chain}$$

Actually it is much more complex, since k depends upon the rates of (1), (2), (3), (5) and (6). Likewise the second mechanism may be written

$$O + H_2 \longrightarrow \text{branching of chain}$$
$$O + H_2 + X \longrightarrow \text{destruction of chain}$$

Here the first step depends upon (1), (2), (3), (5), (6), (7) and (11). These two formal kinetic equivalents both agree with the skeleton mechanism of Grant and Hinshelwood and Frost and Alyea, but it must not be forgotten that they represent schemes of far greater complexity.

We turn now to a consideration of the lower limit. Here all the gas-phase chain-breaking steps are to be replaced by destruction of chains at the wall. It is probably a good assumption that H and HO_2^* are the principal chain carriers and that only their destruction need be considered. Then the first of our two alternative mechanisms is effectively

$$H + O_2 = HO_2^* \qquad (1)$$
$$H + O_2 = 3H \qquad (2)$$
$$HO_2^* + H_2 = (1 + \beta)H \qquad (15)$$

The normal chain steps (1) and (3) are unquestionably fast enough to justify the assumption that H and HO_2^* occur in a constant ratio throughout the vessel, a chain spending the fraction $k_3[H_2]/(k_3[H_2] + k_1[O_2])$ of its life as H and $k_1[O_2]/(k_3[H_2] + k_1[O_2])$ as HO_2^*. The diffusion constants in these two forms are

$$D_{H} = (g_{H,O}[O_2] + g_{H,H}[H_2] + g_{H,X}[X])^{-1} \qquad (21)$$
$$D_{HO_2^*} = (g_{O,O}[O_2] + g_{O,H}[H_2] + g_{O,X}[X])^{-1} \qquad (22)$$

and hence the effective diffusion constant

$$D_{\text{eff.}} = (k_{15}[H_2]D_{H} + k_1[O_2]D_{HO_2^*})/(k_{15}[H_2] + k_1[O_2]) \qquad (23)$$

has a rather complex dependence on the concentrations of H_2, O_2 and X. The rate of branching based on the total number of chains H and HO_2^* is easily found to be

$$\alpha = (\beta k_1 + 2k_2)(k_{15}[H_2] + k_1[O_2])^{-1}k_{15}[H_2][O_2] \qquad (24)$$

Then, if we use (5), we obtain as a lower-limit condition

$$(\beta k_1 + 2k_2)k_{15}[H_2][O_2] = (\pi^2/r_0^2)(k_{15}[H_2]D_{H} + k_1[O_2]D_{HO_2^*}) \qquad (25)$$

which reduces to Frost and Alyea's experimental result if

$$k_{15}[H_2] \gg k_1[O_2]$$

and to that of Hinshelwood and Moelwyn-Hughes if $k_{15}[H_2]$ is comparable with $k_1[O_2]$ and certain plausible relations are satisfied by the coefficients in D_{H} and $D_{HO_2^*}$. We have seen, however, that (5) is a very dubious relation; in this case it is almost certainly incorrect, since the entire explosion is suppressed in a silver vessel,[15] and the value of ϵ in vessels which permit explosion must thus be quite small. The other extreme relation (11) which is to be used when ϵ is very small fails here, since it permits no inert gas effect. The experiments thus seem to fall in an intermediate range where the theory is almost unmanageable. It is clear, however, that as a first approximation we must introduce factors ϵ_{H} and $\epsilon_{HO_2^*}$ into (25). The Frost and Alyea condition is then

$$\epsilon_{H}k_{15}[H_2] \gg \epsilon_{HO_2^*}k_1[O_2],$$

and the Hinshelwood and Moelwyn-Hughes condition is that these quantities are comparable. Since Frost and Alyea's lower limits were roughly five-fold higher than those of Hinshelwood and Moelwyn-Hughes, the natural conclusion is that potassium chloride-on-Pyrex removes atomic hydrogen more efficiently than does quartz. This is of course an extremely crude treatment of the problem, but it does at least suggest a reconciliation of the two lower limits with a single value of k_{15}/k_1.

The idea of "secondary activations" is due to Semenoff,[16] who suggested in particular that hydrogen atoms produced in (3) frequently would have a large kinetic energy and might sometimes dissociate hydrogen molecules. The fraction of atoms which would do this can be written

$$[H_2]/(a[H_2] + b[O_2])$$

In order to fit the upper limit, this must reduce to a constant, which would occur if $a[H_2] \gg b[O_2]$. This new chain branching is kinetically equivalent to (5), since the OH produced there all forms H by (10). Other conceivable secondary activations would likewise have to be subjected to the condition of a concentration-independent efficiency, and would then become the kinetic equivalents of chain-branching reactions already considered. Thus we may conclude that secondary activation does not play an important role in fixing the explosion limits, though there is no reason for it to be entirely excluded.

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(15) Hinshelwood, Moelwyn-Hughes and Rolfe, *Proc. Roy. Soc.* (London), **A139**, 521 (1933).

(16) Semenoff, *Z. physik. Chem.*, **2B**, 169 (1929).

The Reaction above the Upper Limits

Above the upper explosion limit there is a reaction of high and variable order; the rate is proportional to something like the cube of the hydrogen pressure and is markedly accelerated by inert gases such as H_2O, N_2, A, and to a lesser extent He; the acceleration produced by O_2 is but little greater than that by N_2. The reaction is retarded by packing, and disappears completely in a silver vessel. This reaction is quite evidently a chain process, with the chains being destroyed at the wall more frequently than in triple collision. It was originally supposed by Thompson and Hinshelwood[17] that these chains were of a different type than those functioning between the explosion limits, and the correctness of this conclusion is supported by the discussion of a previous section. More recently, however, Grant and Hinshelwood wrote for the upper limit the equation

$$\nu k[\mathrm{X}][\mathrm{Y}] = Z_{\mathrm{H}_2}[\mathrm{X}][\mathrm{Y}][\mathrm{H}_2] + Z_{\mathrm{O}_2}[\mathrm{X}][\mathrm{Y}][\mathrm{O}_2] + Z_{\mathrm{M}}[\mathrm{X}][\mathrm{Y}][\mathrm{M}] \quad (26)$$

where X and Y are subsequently identified as H and O_2. This equation does represent the upper limit correctly, but the interpretation of it given by Grant and Hinshelwood and continued by Hinshelwood in subsequent publications is totally incorrect. This interpretation is that there is a probability ν that at a collision between X and Y the chain shall branch, but that if "any third molecule arrives while X and Y are associated in the 'collision complex' then the branching is prevented." This means that the original chain still survives the triple collision, and is thus available to account for the reaction above the upper explosion limit. This idea is stated later even more clearly. "The explosion ceases at the upper limit, because, as we have seen, *branching* of the chains is prevented by ternary collisions. But one particle may, and probably does emerge from the collision which is capable of continuing an unbranched chain." To derive (26), however, one must assume that the original chain is destroyed by the triple collision; the verbal assumption of Hinshelwood and Grant would lead to rather curious upper and lower limits. The net branching rate may be written as νk exp. $(-t_c/\tau)$ $[\mathrm{X}][\mathrm{Y}]$, where t_c is the time within which a third molecule can prevent branching and τ is the mean free time; this branching rate is balanced by wall destruction of the chain carrier X. Using (5), we would obtain

$$[\mathrm{Y}] \exp.\,(-t_0/\tau) = \text{const.} \times \tau \quad (27)$$

since D is proportional to τ. For very low pressures the right side of (27) is larger, which means that the chains are kept under control; and for very high pressures it is again larger, due to the overwhelming decrease in the exponential term. In between there may be two roots, giving lower and upper limits. The upper limit, however, is totally unlike that of (26) and cannot possibly account for the experimental results. In particular, (27) involves a dependence of the upper limit on the size and character of the vessel which is certainly incorrect. Above the upper limit, the chains of this mechanism would be shortened by adding inert gas, and the rate therefore reduced. The conclusions seem inescapable that a triple collision not only prevents branching, but breaks the original chain, and that the reaction above the upper limit is brought about by some quite new type of chain. We have no ideas concerning the nature of this chain other than the remark that the possibilities for a chemical chain seem to have been exhausted in accounting for the limits, and that an energy chain therefore suggests itself. Both mechanisms must, of course, operate under all conditions. The chemical chain probably requires a high energy to get started and is thus observable only when the chain length becomes infinite. The more abundantly produced energy chains may well be destroyed more efficiently by the wall and probably branch but rarely; they will then be too short to observe below the lower limit and of course could not be detected between the limits. Increase of pressure is likely to be helpful to these chains, since there is no reason for them to be destroyed at triple collisions more than at ordinary ones, and diffusion to the wall will be retarded. One can thus understand the main features of the reaction above the limit.

The Reaction with Deuterium

We now turn to the question whether the results obtained by substituting deuterium for hydrogen can be accounted for by the changed rate of collisions alone, or whether changes in the yield per collision must be assumed. We shall consider only the upper limit, since it is only here that a sufficiently developed theory is available.

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(17) Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A122**, 610 (1929).

We have already pointed out that the first of our two mechanisms is kinetically equivalent to

$$H + O_2 = \text{branching of chain}$$
$$H + O_2 + M = \text{destruction of chain}$$

Let γ_1 be the probability per collision of the former reaction, and γ_2, γ_3 that of the latter when M is H_2, O_2, respectively. Let $Z(A, B, C, \ldots)$ be the number of multiple collisions involving A, B, C, ... when each is present at unit concentration. The critical condition is then

$$\gamma_1 Z(H, O_2)[H][O_2] = \gamma_2 Z(H, O_2, H_2)[H][O_2][H_2] + \gamma_3 Z(H, O_2, O_2)[H][O_2]^2$$

or

$$\frac{\gamma_2}{\gamma_1}\frac{Z(H, O_2, H_2)}{Z(H, O_2)}[H_2] + \frac{\gamma_3}{\gamma_1}\frac{Z(H, O_2, O_2)}{Z(H, O_2)}[O_2] = 1$$

It is evident by comparison with (16) that

$$f_H = \frac{\gamma_2}{\gamma_1}\frac{Z(H, O_2, H_2)}{Z(H, O_2)} \qquad f_O = \frac{\gamma_3}{\gamma_1}\frac{Z(H, O_2, O_2)}{Z(H, O_2)}$$

Now we know that for an ordinary collision the masses enter Z only in the factor $[(m_1 + m_2)/m_1m_2]^{1/2} = \mu_{12}^{-1/2}$. Generalizing slightly a treatment given by Tolman,[18] we take the corresponding factor for a triple collision to be $F_1\mu_{23}^{-1/2} + F_2\mu_{13}^{-1/2} + F_3\mu_{12}^{-1/2}$, where the values of the F_i depend upon the exact, unknown specifications defining the particular kind of triple collision needed. The F_i will be the same for deuterium as for hydrogen. Putting in numerical values we find

$$Z(H, O_2, H_2)/Z(H, O_2) = F_1 + 0.718F_2 + 1.206F_3$$
$$Z(D, O_2, D_2)/Z(D, O_2) = F_1 + 0.728F_2 + 1.188F_3$$
$$Z(H, O_2, O_2)/Z(H, O_2) = 2G_1 + 0.246G_3$$
$$Z(D, O_2, O_2)/Z(D, O_2) = 2G_1 + 0.343G_3$$

It is then obvious that if the γ_i are the same for deuterium as for hydrogen, f_H and f_D cannot differ by more than 2% for any values of the F_i; f_O will be greater for deuterium than for hydrogen by from 0 to 40% depending upon the relative values of G_1 and G_3. For the other alternative mechanism similar calculations show that f_D is at least $0.95f_H$. The experimental result is that f_O is the same for both isotopes and $f_D = 0.7f_H$. These calculations have assumed that the reaction probabilities per collision are the same with deuterium as with hydrogen; the conclusion seems to be either that deuterium is less efficient as a third body than hydrogen, or that the branching probability γ_1 is greater for deuterium than for hydrogen. The experiments with deuterium therefore make no real contribution to our understanding of this reaction.

Summary

1. The mathematical theory of chain reactions for which the chains are broken at the wall at only a fraction of the total number of collisions has been developed and shown to differ in important respects from the case where every collision leads to destruction.

2. The possible chemical chain mechanisms for the explosion limits of hydrogen–oxygen mixtures have been exhaustively investigated; satisfactory mechanisms all involve

$$H + O_2 = HO_2^*$$
$$HO_2^* + H_2 = H_2O_2 + H$$

as the normal chain process, and either

$$H + O_2 + X = HO_2 + X$$

or

$$O + H_2 + X = H_2O + X$$

as the principal gas-phase chain-destroying process.

3. The slow reaction above the upper limit must be explained by a new chain, which is presumably an energy chain.

4. Analysis of experiments made with deuterium shows that these experiments do not indicate the same branching efficiency for hydrogen and for deuterium, as has been erroneously deduced by other authors.

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[18] Tolman, "Statistical Mechanics," Chemical Catalog Company, New York, 1927, p. 248.