THE MECHANISM OF THE COMBUSTION OF HYDROGEN

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INTRODUCTION

The combustion of hydrogen, in common with that of the other fuels dealt with in this symposium, may occur either as a slow reaction or as an explosion, depending upon the experimental conditions. This paper will treat these two main types of reaction separately. The reaction kinetic interpretation of the foregoing phenomena will constitute the third and final section. The space available does not permit anything like complete discussion of a reaction which even in 1934 could be the subject of a 100-page monograph (17), and many aspects of the reaction will be omitted entirely.

THE SLOW REACTION

The reaction between hydrogen and oxygen may be brought about catalytically by a variety of metallic surfaces. These catalytic reactions have been carefully studied in a number of cases, and have given interesting information concerning the relative adsorption of hydrogen, oxygen, and steam on the surfaces involved. The temperature of these reactions is so low, however, that they are almost totally unrelated to the phenomena of combustion as the term is usually understood, and they will therefore not be discussed in the present paper.

A catalytic reaction is found even with ordinary silica or porcelain reaction vessels. This catalysis, however, is far feebler than that by most metals, the rate being easily measured in a static system at 520°C. This reaction is approximately of the first order with respect to hydrogen, nearly of the zero order with respect to oxygen (except at quite low partial pressures), and retarded by steam. This catalysis can only be observed when the pressure is sufficiently high; at lower pressures there is a more or less instantaneous explosion, the nature of which is dealt with in the following section. When experimentation is confined to pressures above this explosion limit, very striking changes in the reaction kinetics are observed as the temperature is raised. Below about 540°C. the reaction is of low order, has a low temperature coefficient, is retarded by steam, and is accelerated in a packed vessel. At slightly higher temperatures the reaction is of high and variable order (about fourth), has a very high temperature coefficient, and is accelerated by steam or other inert gases and retarded in a packed vessel. There is no reason to doubt that the low-temperature surface reaction continues into this range with the characteristics that would be predicted for it by extrapolation. The changed kinetics are due to a quite new reaction, taking place predominantly in the gas phase, which becomes much faster than the surface reaction. This gas reaction can be studied only for a narrow range of conditions. The pressure must be above the previously mentioned explosion limit, and below a second (or, more precisely, as develops later, a third) limit. These limits come together as the temperature is raised and cut off the non-explosive reaction completely at about 580°C. Below about 550°C., on the other hand, the normal wall reaction is fast enough to obscure or even to obliterate the gas reaction.

The temperature coefficient of the homogeneous reaction increases with increase of both temperature and pressure. Values up to 4.3 for 10°C. at 560°C. are found, corresponding to an "activation energy" of 200 kg-cal. It will be seen in the third section, however, that there is no physical significance to the energy of activation for reactions of this type.

The gas reaction is of about the third order with respect to hydrogen and the 1.5 order with respect to oxygen (16, 12). The addition of nitrogen to a stoichiometric mixture increases the initial rate about linearly with the amount added, the increase being roughly the same as would be produced by an equal quantity of oxygen. Other inert gases behave similarly, the relative effectiveness of helium, nitrogen, argon, and water being in the ratio 1:3:4:5.

The rate is very markedly reduced by packing the reaction vessel. The effect of surface is best studied quantitatively, however, by working with cylindrical vessels of equal length but varying diameter. Initial rates for stoichiometric mixtures at 560°C. were found as follows (17):

BULB DIAMETER IN MM.	RATE AT 600 MM.	RATE AT 300 MM.
17	0.85	0.18
32	3.49	0.50
56	9.35	0.94
77	33.8	3.45

These values are roughly proportional to the square of the diameter; the rate at 600 mm. in the largest bulb is about double the expected value, presumably because this measurement was made on the borderline of the high-pressure explosion region.

When a silver reaction vessel is used, this homogeneous reaction is not found (15). There is a slow wall reaction with a rate nearly independent of the hydrogen pressure and unaffected by inert gases. Introduction of a silica rod is without effect. It therefore appears that the reaction chains which leave the silica surface are rapidly destroyed by some action of the silver.

The homogeneous reaction is sensitive to gaseous inhibitors. At 450 mm. and 550°C. the rate is markedly reduced by the addition of 0.01 mm. of chlorine, bromine, or iodine, falling to as little as one-tenth of its original value in the case of iodine (10). When the quantity of halogen is varied, the rate is found to pass through a minimum and then to increase slowly for larger additions, remaining for a long time less than if no halogen were present. There is good evidence that the increase is due to a wall reaction, one step of which is the known heterogeneous oxidation of the hydrogen halide. The actually observed minimum rate, therefore, does not represent the maximum inhibition of the homogeneous reaction. Since the gas reaction is slower in small reaction vessels, it is not surprising that it should be less susceptible to inhibitors; this is found to be the case.

THE EXPLOSION REGION

At pressures lower than those of the homogeneous reaction there is a region of more or less instantaneous reaction. This explosion normally takes place only between two well-defined pressure limits, which depend upon the temperature and composition.

Of the two limits, the upper is more easily studied, since the effect there is sufficiently vigorous to be easily noted, and still more since the position of the limit is quite stable. The upper limit is independent of the diameter of the vessel, and is nearly the same in porcelain, silica, and alumina. At constant temperature the limit can be fairly well represented by

$$f_{\mathrm{H}}(\mathrm{H_2}) + f_{\mathrm{O}}(\mathrm{O_2}) + f_{\mathrm{X}}(\mathrm{X}) = \text{const.}$$

where X represents any inert gas and the f_{H}, f_{O}, f_{X} are constants. The constant on the right of the equation increases with temperature at a rate corresponding to an activation energy of about 26 kg-cal. (25, 13, 9).

In quartz vessels of moderate size the lower limit is at pressures of the order of 1 mm. (25). In the region near the limit the explosions are feeble and correspondingly difficult to detect. The position of the limit is very susceptible to the pretreatment of the surface, and it is for that reason practically impossible to make really comparable experiments in different vessels. It is at least approximately true, however, that the limit is represented by

$$(\mathrm{H_2})(\mathrm{O_2})d^2 = \text{const.}$$

in the absence of inert gases. In the presence of inert gases the lower limit is lowered, that is, explosion occurs for partial pressures of hydrogen and oxygen which by themselves would be unreactive. The effect of helium is greater than that of argon. It appears to be an unwarranted exaggeration of the experimental accuracy in this difficult region to deduce the functional form of the lower limit taking account of the inert gas effect. The effect of temperature also is rather uncertain. It seems that when the upper and lower limits are far apart, the lower limit decreases only slightly as the temperature is increased, but that for low temperatures, where the two limits come together, the effect is considerably greater.

Within the explosion region ignition is by no means instantaneous. Kowalsky (20) used a photographically recorded membrane manometer to follow the course of the reaction at pressures only moderately above the lower limit. The initial parts of his curves show an exponential increase in rate with time, the acceleration being greater the higher the temperature and the greater the pressure excess over the lower limit. The maximum rates were reached at times of the order of 0.1 sec. This "induction period" is thus quite distinct from the very much longer induction periods characteristic of hydrocarbon–oxygen explosions near the lower limit.

The boundaries of the ignition region are profoundly altered by various departures from the "normal" conditions prevailing in quartz vessels. It has already been suggested that the position of the lower limit is sensitive to the condition of the surface. It is not surprising, therefore, that marked changes are produced when totally different surfaces are used. Thus Frost and Alyea (9), using potassium chloride-coated Pyrex vessels, found the lower limit at pressures some tenfold higher than other workers report in quartz; the dependence of the limit on concentration is also changed, being given by

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

The complete absence of surface produces an equally striking effect. Alyea and Haber (1) found by experiments with crossed streams of separately preheated gases that ignition did not occur at 520°C. at pressures of 20–100 mm., well within the ignition region in quartz. The non-igniting gases could be lit by a rod of quartz, glass, porcelain, copper, or iron, but not by one of aluminum. It had previously been shown (12a) that ignition took place with crossed streams at 560°C. and atmospheric pressure.

When an aluminum vessel is used, the ignition is apparently suppressed, but the presence of a quartz rod restores the normal ignition region. With a silver vessel no ignition could be obtained even at 700°C., and in this case the presence of quartz had no effect (15). In fact, it was found that even with a quartz vessel ignition was frequently prevented by the presence of silver wires; this result was considered ambiguous, however, since the silver wires used, which were apparently more active catalytically than the surface of the silver reaction vessel, produced sufficient steam to quench the explosion.

The addition of a few hundredths of a per cent of nitrogen dioxide produces a very great broadening of the ignition region, the upper limit being raised and the lower limit lowered, and the minimum ignition temperature reduced to about 350°C. (25). For larger additions the limits are narrowed again; as a result, for any fixed mixture and temperature, there are two limiting concentrations of nitrogen dioxide, between which ignition occurs, but beyond which it does not. For constant temperature and composition these limits approach each other as the pressure is raised. For constant pressure and composition they approach as the temperature is lowered. At constant pressure and temperature the upper limit is lowered when the proportion of oxygen is increased, or when nitrogen is added.

Small quantities of halogens affect the ignition in the opposite way, and one part of iodine or bromine in 10,000 suppresses it completely, at least in the normal temperature range. The effect of chlorine is similar but much feebler, 0.25 per cent being required for suppression (10).

Steam has a similar effect, but of quite a different magnitude, 36 per cent being required to suppress explosion as compared with 0.002 per cent of iodine in a similar experiment (10).

A vast number of experiments have been carried out in which reaction in oxygen–hydrogen mixtures is initiated by atoms, by ions, or by molecules in higher quantum states. Tremendous broadening of the ignition region is produced by these additions. The production of active centers by electric discharges passed through the mixture, by means of which explosions can be obtained at room temperature, which is the best-known example of this effect, has been treated in detail in a preceding paper by Bradford and Finch (see page 221). We shall consider here experiments in which atoms are generated by a discharge through one of the gases before mixing. When hydrogen atoms are produced in this way, at a partial pressure of about 0.05 mm., the explosion limits are considerably widened (7), the effect increasing somewhat with the concentration of atomic hydrogen. Atomic oxygen gives a far more striking change, however. With it, ignition of a sort is produced even at room temperature. The upper limit, moreover, either completely disappears or at least recedes beyond the experimental range (22). The different nature of the changes in the limits for the two cases suggests that the addition of atomic hydrogen merely starts more of the normal chains, but that atomic oxygen leads to chains of a new and more fecund kind (17). There are several difficulties in such a view, however, which will be considered later.

Many other experiments deal with ignition or slow reaction due to atoms of hydrogen, oxygen, or chlorine produced photochemically, either directly or by means of photosensitizers such as mercury vapor (23, 19, 21, 3). The most important result of such work is the evidence that slow reaction initiated by either atomic hydrogen or atomic oxygen involves chains which are very short at room temperature, but increase rapidly in length as the temperature nears the ignition region, and that the chief primary product is hydrogen peroxide rather than water.

THE REACTION MECHANISM

The general features of the interpretation of these results are the same as have been discussed in the preceding paper on the mechanism of combustion of hydrocarbons. The greater chemical simplicity of the present reaction, however, makes it reasonable to expect the details of the mechanism to be established more completely and more definitely. As yet, unfortunately, this represents more a hope for the future than an accomplishment of the past.

The ignition region is unquestionably due to a chain reaction. The chains ordinarily start on the walls, but a few originate in the gas (1, 12a). Branching occurs in the gas. The chains may be broken either by a triple collision in the gas, or by diffusion to the wall. Ignition takes place, according to the simple theory, when the rate of branching is greater than the rate of breaking. This mechanism gives upper and lower limits to the ignition region. At the upper limit chain breaking is predominantly due to triple collisions. Hence the limit is nearly independent of factors which influence the rate of chain breaking at the walls, that is, of the vessel diameter and of the material and pretreatment of the reaction vessel. Inert gases break chains at triple collisions and hence reduce the upper limit. The lower limit, on the other hand, is determined predominantly by the rate of chain breaking at the walls. It is therefore sensitive to the nature of the walls and to the size of the vessel. Inert gases retard diffusion, and thus lower the lower limit. If no chains start, there can be no ignition, but according to the simple theory any finite rate of starting, however small, is sufficient to give ignition if the net branching rate is greater than zero. In the Alyea–Haber experiment with crossed streams, however, ignition will not be observed unless it develops to a sufficient extent before the crossed streams have been too much weakened by diffusion; in the absence of suitable surface the rate at which chains start in the gas alone does not seem to fulfill this condition below 560°C. Likewise in an aluminum vessel, so few chains start that they do not have time to develop sufficiently before the catalytically formed steam has wiped out the ignition region. When a silica surface also is present, chains start more rapidly, and ignition occurs. The results in a silver vessel seem to require a different explanation, which will be discussed later.

The effects of sensitizers and inhibitors can be understood in principle as due to their creation of new possibilities for chain branching and chain breaking. A single substance may participate in both processes and thus function in both rôles, as nitrogen dioxide appears to do.

The broadening of the ignition region by artificial creation of chain carriers does not fit easily into the framework of the classical theory. The results with atomic oxygen might be interpreted as representing an entirely new chain, with new limits; the effect of atomic hydrogen, however, is quite obviously a mere broadening of the already existent limits. A possible interpretation is that in addition to the set of branching and breaking reactions involving a single carrier and fixing the normal limits, there are additional branching and breaking reactions involving two carriers in each step, which would, if left to themselves, determine wider limits. For mixtures beyond the normal ignition limits, the first set of reactions alone would determine a steady concentration of chain carriers dependent on the rate of starting chains. If this steady concentration is small enough, it is not appreciably altered by the existence of the second-order reactions. But if the first-order reactions permit the number of chain carriers to increase sufficiently, the second-order set will take command and lead to ignition.

This interpretation may be illustrated by the following very formal example, where normal chain-carrying reactions are omitted, only starting, branching, and breaking steps being shown.

$$\mathrm{A} \rightarrow \mathrm{X} \tag{1}$$

$$\mathrm{A} + \mathrm{X} \rightarrow \mathrm{B} + \mathrm{X} + \mathrm{X} \tag{2}$$

$$\mathrm{A} + \mathrm{A} + \mathrm{X} \rightarrow \text{no chain} \tag{3}$$

$$\mathrm{X} + \mathrm{X} \rightarrow \mathrm{X} + \mathrm{X} + \mathrm{X} \tag{4}$$

$$\mathrm{A} + \mathrm{X} + \mathrm{X} \rightarrow \text{no chain} \tag{5}$$

Then

$$\mathrm{dX}/\mathrm{d}t = k_1\mathrm{A} + (k_2\mathrm{A} - k_3\mathrm{A}^2)\mathrm{X} + (k_4 - k_5\mathrm{A})\mathrm{X}^2$$

The condition for ignition is that $\mathrm{dX}/\mathrm{d}t > 0$ for all values of X. This condition cannot be fulfilled unless

$$k_4 - k_5\mathrm{A} > 0 \tag{I}$$

and also either

$$k_2\mathrm{A} - k_3\mathrm{A}^2 > 0 \tag{II}$$

or

$$k_1\mathrm{A} > (k_2\mathrm{A} - k_3\mathrm{A}^2)^2/4(k_4 - k_5\mathrm{A}) \tag{III}$$

Values of A for which expression II is not satisfied, but both I and III are, represent broadening of the ignition region. It is evident that the amount of this broadening is greater the greater k_1A is, that is, the faster chains are being started.

In many experiments, the conditions are better described as a high initial value of X than by a large value of k_1A. The condition for ignition in such cases is that $dX/dt > 0$ for all $X > X_0$. If k_1A can be neglected, which is probably a reasonable approximation under these conditions, ignition will occur if

$$X_0 > (k_3A^2 - k_2A)/(k_4 - k_5A) \qquad \text{(IV)}$$

Here also, as the initial concentration of chains is increased, the normal limits are progressively widened.

It is obvious that any dependable theory of the lower limit and of the high-pressure gas reaction as well must be based on a sound treatment of the rate of breaking chains at the surface. In many cases it has been thought sufficient to take the surface breaking as equivalent to a volume rate of breaking kn/pd^2, where n is the average concentration of chains, p is a linear function of the various partial pressures, and d is a linear dimension of the vessel. This treatment can in fact be justified by a consideration of the diffusion equation (5), subject to three conditions: (*a*) every chain reaching the wall is destroyed; (*b*) the net rate of branching is proportional to the number of chains in existence; and (*c*) branching occurs at only a small fraction of all chain-continuing reactions. When the fraction of chains destroyed by a single collision with the walls is a fraction $\epsilon < 1$, and conditions *b* and *c* are fulfilled, rather different results are obtained (18, 27). In the range $1 > \epsilon > 0.01$, the rate of breaking at the wall is scarcely dependent on the value of ϵ and the preceding simple rate law is nearly obeyed. As ϵ decreases below 0.01, the rate law changes gradually from kn/pd^2 to $3\epsilon\bar{v}n/2d$, where $\bar{v}$ is the mean molecular velocity. In the upper range the rate of breaking is nearly independent of the condition of the surface, and nearly inversely proportional to the diffusion coefficient and to the square of the diameter. In the lower range it is nearly proportional to the chain-breaking efficiency of the surface, nearly independent of the diffusion coefficient, and nearly inversely proportional to the first power of the diameter. When either *b* or *c* is not satisfied, special investigation is required. Such an investigation with regard to *c* appears farther on in this paper.

One of the most puzzling features of this reaction has been the relation between the chain in the ignition region and that in the high-pressure gas reaction. Thompson and Hinshelwood (25) had originally postulated totally different chains in the two regions. This unsatisfying view was rejected by Grant and Hinshelwood (13), who proposed the following formal theory. Normally the upper limit might be described by

$$X + Y = \text{branching}$$

$$X + Y + M = \text{breaking}$$

They suggested that if the rôle of M at a triple collision was not to break the original chain but merely to prevent branching, sufficient chains would survive to provide the gas reaction above the upper limit. Kinetic analysis of this theory, however, showed (18) that it predicted totally wrong characteristics both for the gas reaction and for the upper limit, and it seemed necessary to return to the idea of unrelated chains. Very recently, von Elbe and Lewis have found a more plausible interpretation (26). The upper limit is caused by triple collisions

$$X + Y + M \rightarrow Z + M$$

Z is neither a perfectly stable molecule nor a real chain carrier. At the upper limit it is destroyed by diffusion to the walls, but above the limit this diffusion becomes increasingly slow and there is time for Z to regenerate chains by some reaction such as

$$Z + U \rightarrow X + ..$$

This theory can even account formally for a third isothermal explosion limit, although, as von Elbe and Lewis point out, the actually observed third limit is probably a thermal explosion.

SPECIFIC MECHANISMS

The foregoing analysis has provided only skeleton mechanisms. We shall now consider the problem of replacing non-committal X's and Y's with specific intermediates. A systematic treatment of this problem, for the normal ignition limits, was attempted by Kassel and Storch (18), who constructed a catalog of all imaginable reactions involving only a single chain carrier, and investigated the conditions under which the resulting complicated equation for the upper limit would reduce to the correct experimental form. They found two solutions. In one, branching took place at collisions $H + O_2$, breaking by

$$H + O_2 + M \rightarrow HO_2 + M$$

HO_2 was not a chain carrier. The second, less plausible, solution involved branching at collisions $O + H_2$, and breaking by

$$O + H_2 + M \rightarrow H_2O + M$$

The first solution envisaged the normal chain as (the numbering follows that of Kassel and Storch, with additions as necessary)

$$H + O_2 \rightarrow HO_2^* \tag{1}$$

$$HO_2^* + H_2 \rightarrow H_2O_2 + H \tag{3}$$

The chains were broken by

$$H + O_2 + M \rightarrow HO_2 + M \tag{14}$$

The distinction between HO_2 and HO_2^* was that the latter possessed its heat of formation and was an active chain carrier, while the former did not continue the chain. It was necessary for this distinction to be a sharp one, that is, the rate of reaction of HO_2^* with H_2 had to be large compared to its rate of deactivation to HO_2 by collision with other molecules; if this was not the case, the resulting expression for the upper limit was incorrect. Branching could occur by one or both of

$$H + O_2 \rightarrow OH + O \tag{2}$$

$$HO_2^* + H_2 \rightarrow H + 2OH \tag{5}$$

Since all HO_2^* reacted with H_2, the second of these branching reactions was kinetically equivalent to the first. Branching was completed by

$$OH + H_2 \rightarrow H_2O + H \tag{10}$$

which had to be the only important reaction of OH. If reaction 2 was a branching reaction it was necessary to have also

$$O + H_2 \rightarrow OH + H \tag{11}$$

which had to be the only important reaction of O.

The occurrence of

$$H + O_2 \rightarrow HO_2^* \tag{1}$$

in this mechanism was based on the authors' reluctant acceptance of the Bates and Lavin (2) view that HO_2 could be formed in a bimolecular association reaction. It is now firmly established by the work of Cook and Bates (6), Farkas and Sachsse (8), and Bodenstein and Schenk (4) that this reaction occurs only at triple collisions. It has been pointed out by von Elbe and Lewis (26) that the mechanism remains unharmed when steps 1, 3, and 5 are deleted. The effectively slow chain step is now

$$H + O_2 \rightarrow OH + O \tag{2}$$

All O and OH formed in reaction 2 react by equations 10 and 11, so that the stoichiometric result of reaction 2 is

$$\mathrm{H + O_2 + 3H_2 \rightarrow 3H + 2H_2O} \tag{2a}$$

The complete mechanism to account for the ignition region and the high-pressure gas reaction should then be

$$\mathrm{H + O_2 \rightarrow OH + O} \tag{2}$$

$$\mathrm{OH + H_2 \rightarrow H_2O + H} \tag{10}$$

$$\mathrm{O + H_2 \rightarrow OH + H} \tag{11}$$

$$\mathrm{H + O_2 + M \rightarrow HO_2 + M} \tag{14}$$

$$\mathrm{HO_2 + H_2 \rightarrow H_2O_2 + H} \tag{15}$$

$$\mathrm{H \rightarrow wall}$$

$$\mathrm{O \rightarrow wall}$$

$$\mathrm{OH \rightarrow wall}$$

$$\mathrm{HO_2 \rightarrow wall}$$

We shall proceed to a systematic development of the consequences of this mechanism. Since the chain branches at every link, the earlier treatment of the diffusion equation given by Kassel and Storch (18) is not applicable. For an exact treatment it would be necessary to solve four simultaneous diffusion equations. This will not be attempted; instead, various plausible approximations will be investigated separately.

One such approximation which might be applicable at the lower limit is to neglect reactions 14 and 15, and to assume that reaction 10 is very rapid. The kinetic equations for the lower limit are then

$$\mathrm{H + O_2\ (+\ H_2) \rightarrow H + O + H_2O} \qquad \text{rate} = \alpha$$

$$\mathrm{O + H_2\ (+\ H_2) \rightarrow 2H + H_2O} \qquad \text{rate} = \beta$$

The diffusion equations for plane parallel plates are

$$\partial \mathrm{H}/\partial t = D_{\mathrm{H}}(\partial^2 \mathrm{H}/\partial r^2) + 2\beta \mathrm{O} = 0$$

$$\partial \mathrm{O}/\partial t = D_{\mathrm{O}}(\partial^2 \mathrm{O}/\partial r^2) + \alpha \mathrm{H} - \beta \mathrm{O} = 0$$

The most general solution which is permitted by the physical requirements is

$$\mathrm{O} = A \cos (\beta/2D_{\mathrm{O}})^{\frac{1}{2}} R_{+} r + B \cos (\beta/2D_{\mathrm{O}})^{\frac{1}{2}} R_{-} r$$

$$\mathrm{H} = A(\beta/2\alpha)\ (R_{+}^{2} + 2) \cos (\beta/2D_{\mathrm{O}})^{\frac{1}{2}} R_{+} r + B(\beta/2\alpha)(R_{-}^{2} + 2) \cos (\beta/2D_{\mathrm{O}})^{\frac{1}{2}} R_{-} r$$

where

$$R_{\pm} = [-\ 1 \pm (1 + 8\alpha D_{\mathrm{O}}/\beta D_{\mathrm{H}})^{\frac{1}{2}}]^{\frac{1}{2}}$$

Equating the net branching rate in the gas to the rate of destruction by the walls gives

$$\begin{gathered}(\epsilon_O\bar{v}_O/4)[A\cos(\beta/2D_O)^{1/2}R_+r_0 + A(\beta/2D_O)^{1/2}R_+\lambda\sin(\beta/2D_O)^{1/2}R_+r_0 \\ + B\cos(\beta/2D_O)^{1/2}R_-r_0 + B(\beta/2D_O)^{1/2}R_-\lambda\sin(\beta/2D_O)^{1/2}R_-r_0] \\ = AR_+(\beta D_O/2)^{1/2}\sin(\beta/2D_O)^{1/2}R_+r_0 + BR_-(\beta D_O/2)^{1/2}\sin(\beta/2D_O)^{1/2}R_-r_0\end{gathered}$$

and

$$\begin{gathered}(\epsilon_H\bar{v}_H/4)[-A(\beta/2\alpha)R_-^2\cos(\beta/2D_O)^{1/2}R_+r_0 \\ - A(\beta/\alpha)(-\alpha/D_H)^{1/2}R_-\lambda\sin(\beta/2D_O)^{1/2}R_+r_0 - B(\beta/2\alpha)R_+^2\cos(\beta/2D_O)^{1/2}R_-r_0 \\ - B(\beta/\alpha)(-\alpha/D_H)^{1/2}R_+\lambda\sin(\beta/2D_O)^{1/2}R_-r_0] \\ = (A/R_+)(8\beta D_O)^{1/2}\sin(\beta/2D_O)^{1/2}R_+r_0 + (B/R_-)(8\beta D_O)^{1/2}\sin(\beta/2D_O)^{1/2}R_-r_0\end{gathered}$$

These two equations determine A/B and r_0. Since no simple explicit solution for r_0 can be found, it is hard to visualize the results. We may, however, investigate a few extreme assumptions.

Case I.

$$\epsilon_H = \epsilon_O = 1$$

Here the solution is simply

$$B = 0$$

$$(\beta/2D_O)R_+^2r_0^2 = \pi^2/4$$

Since

$$D_O^{-1} = g_H(H_2) + g_O(O_2) + g_X(X)$$

and β is proportional to (H_2), this becomes

$$(H_2)[g_H(H_2) + g_O(O_2) + g_X(X)]R_+^2r_0^2 = \text{const.}$$

The two possible extreme cases are

$$\alpha D_O >> \beta D_H \qquad R_+^2 = (8\alpha D_O/\beta D_H)^{1/2}$$

and

$$\alpha D_O << \beta D_H \qquad R_+^2 = 4\alpha D_O/\beta D_H$$

The corresponding conditions for the lower limit are

$$(H_2)^{1/2}(O_2)^{1/2}[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

and

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

The latter of these corresponds in form with the Frost and Alyea expression for the lower limit in potassium chloride on Pyrex.

Case II.

$$\epsilon_H = 0 \qquad \epsilon_O = 1$$

It is easily seen that for this case the chains branch faster than they can be broken, and there can be no lower limit. This same conclusion can be reached from the general equations, but only after considerable algebra.

Case III.

$$\epsilon_H = 1 \qquad \epsilon_O = 0$$

For this case also the lower limit is given by

$$(O_2)[g_H(H_2) + g_O(O_2) + g_X(X)]r_0^2 = \text{const.}$$

A far more thorough investigation should be made, but it seems likely that the lower limit data of Frost and Alyea as well as those of Hinshelwood (15) are reconcilable with this mechanism.

The upper limit is treated by neglecting reaction 15 and all wall reactions except the destruction of HO_2, which is supposed to be fast. The limit is then given by

$$k_{14,H}(H_2) + k_{14,O}(O_2) + k_{14,X}(X) = 2k_2$$

Since there is no reason to expect that the various k_{14} values have appreciable temperature coefficients, comparison with experimental results requires an activation energy of 24 to 26 kg-cal. for reaction 2. This reaction could then take place at only 1 collision in 10^7 at 550°C. Such a value seems rather small in comparison with the probable rate of triple collision.

For the reaction above the upper limit we restore reaction 15 and take the rate of destruction of HO_2 on the wall as $k_w(HO_2)/Xd^2$, a form which is approximately correct when the chains start in the gas and are destroyed at nearly every collision of HO_2 on the wall (27). The rate of starting chains is represented formally by S. Then

$$\frac{d(H_2O)}{dt} = \frac{2k_2S[k_{15}(H_2)(X)d^2 + k_w] + k_{14}k_{15}(H_2)(X)^2d^2}{k_{14}k_w(X) - 2k_2[k_{15}(H_2)(X)d^2 + k_w]}$$

It is possible to show that this equation reproduces at least all the striking qualitative characteristics of the reaction above the limit.

This mechanism thus seems to account for everything to which it is reasonably applicable, *except for the results in silver vessels.* This problem has been discussed fully by von Elbe and Lewis (26). Undoubtedly chains are broken faster in silver vessels than in glass, quartz, or alumina; this cannot be because walls of the latter substances break chains very inefficiently, since in that case the observed lower limit must be inversely proportional to the first power of the diameter and independent of inert gas. These authors have suggested breaking in the gas phase by silver sputtered from the surface by the exothermic reactions occurring there.

Space does not permit any elaborate discussion of the rôle of inhibitors and sensitizers. The mechanism of inhibition by halogens has always been rather clear.

The reactions

$$H + X_2 \rightarrow HX + X$$

are rapid in all cases, and serve to remove chain carriers. The reaction

$$Cl + H_2 \rightarrow HCl + H$$

is also rapid, while the corresponding reactions with bromine and iodine are slow; the relatively weak inhibition by chlorine is thus easily understandable.

The more interesting effects due to addition of nitrogen dioxide have received considerable attention. A mechanism for it has recently been found by von Elbe and Lewis (28) which is consistent with that given above for the non-sensitized reaction, and which will probably stand or fall with the latter.

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