[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reaction between Hydrogen and Oxygen above the Upper Explosion Limit[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

The application of the isothermal chain-branching theory to the explosion limits of hydrogen and oxygen makes it necessary to ascribe to the reaction above the upper limit a different mechanism than that which governs the limits themselves.[4] Moreover, since the theory demands that the chain-breaking reactions be of the same order, with respect to the chain carriers, as the chain-branching reactions, and since plausible branching reactions are all of the first order with respect to the carriers, the most plausible reaction for breaking chains in the gas phase becomes

$$\mathrm{H + O_2 + M = HO_2 + M} \qquad (1)$$

M being any third molecule. This demands that the reaction between HO_2 and H_2 to form another chain carrier shall be a rare event in comparison with such reactions of HO_2 from which no chain carrier emerges.

It may now be assumed that in the low-pressure region where the limits occur, HO_2 is removed efficiently by diffusion to the wall but that at higher pressures there is an increasing probability for either or both of the chain continuing reactions

$$\mathrm{HO_2 + H_2 = H_2O_2 + H} \qquad (2)$$
$$\mathrm{HO_2 + H_2 = H_2O + OH} \qquad (3)$$

This conception makes it unnecessary to resort to the hypothesis of energy chains, the difficulties of which have been amply dealt with elsewhere.[5]

The necessity to introduce reaction (1) as a chain-breaking mechanism was originally demonstrated in a study of the inhibition of the photochemical reaction of hydrogen and chlorine by oxygen,[6] although it is to be remembered that the temperature in these experiments was low. More recently it has been shown that the formation of HO_2 in a ternary collision adequately accounts for the photochemical oxidation of HI[7] and that the earlier concept of a long-lived excited HO_2 molecule formed in a binary collision[8] should be abandoned. This latter fact uniquely determines from the "catalog" of possible reactions[4] the chain mechanism responsible for the explosion limits. The reactions are

$$\mathrm{H + O_2 = OH + O} \qquad (4)$$
$$\mathrm{O + H_2 = OH + H} \qquad (5)$$
$$\mathrm{OH + H_2 = H_2O + H} \qquad (6)$$

to which must be added the ternary reactions

$$\mathrm{H + O_2 + H_2 = H_2O_2 + H} \qquad (7)$$

and

$$\mathrm{H + O_2 + H_2 = HO_2 + H_2} \qquad (1a)$$

which are contained in the "catalog" in their kinetic equivalents. Therefore, H_2 is able either to react or to stabilize the HO_2 molecule. The selection of reaction (7) instead of the alternative $\mathrm{H + O_2 + H_2 = H_2O + OH}$ must be made on the basis of the results of the mercury-sensitized hydrogen–oxygen reaction.[9] Reaction (7) also harmonizes the results of the photochemical hydrogen–chlorine–oxygen reaction.[10] As far as can be seen, there is no contradictory evidence in the literature to any of the proposed reactions.[11]

---

(1) Published by permission of the Director, U. S. Bureau of Mines, and the Director, Coal Research Laboratory, Carnegie Institute of Technology. Read at the meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1936. (Not subject to copyright.)

(2) Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(3) Physical chemist, Explosives Division, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

(4) L. S. Kassel and H. H. Storch, THIS JOURNAL, **57**, 672 (1935); G. H. Grant and C. N. Hinshelwood's, *Proc. Roy. Soc.* (London), **141A**, 29 (1933) attempt to describe the limits and the reaction above the upper limit was shown by Kassel and Storch to be incorrect.

(5) C. N. Hinshelwood and A. T. Williamson, "The Reaction Between Hydrogen and Oxygen," Oxford Univ. Press, Oxford, England, 1934.

(6) *Cf.* M. Bodenstein and P. W. Schenck, *Z. physik. Chem.*, **B20**, 420 (1933).

(7) G. A. Cook and J. R. Bates, THIS JOURNAL, **57**, 1775 (1935).

(8) J. R. Bates and G. I. Lavin, *ibid.*, **55**, 81 (1933).

(9) J. R. Bates, *J. Chem. Phys.*, **1**, 457 (1933). This author's successful description of the mercury-sensitized reaction by assuming the consecutive steps

$$\mathrm{H + O_2 = HO_2}$$
$$\mathrm{HO_2 + H_2 = H_2O_2 + H}$$
$$\mathrm{HO_2 + HO_2 = H_2O_2 + O_2}$$

may be duplicated by substituting the above ternary collision reactions (1a) and (7) for the first two steps.

(10) M. Bodenstein and P. W. Schenck's[6] mechanism requires that as a consequence of a successful collision between $\mathrm{H + O_2 + H_2}$ two chains must be broken and two molecules of H_2O must be formed. For this reason they originally objected to the reaction products being $\mathrm{H_2O_2 + H}$ as in Bates' scheme[9] since the H is capable of continuing the chain, and adopted instead the products $\mathrm{H_2O + OH}$. Later, however, they postulate (p. 439) that for every H_2O_2 molecule formed, two chains are broken and two molecules of H_2O are formed by a series of reactions involving two chlorine atoms and two HCl molecules. Indeed, they prove that H_2O_2 readily reacts with chlorine atoms (p. 440). Thus their claim to be able to distinguish between the two mechanisms ($\mathrm{H_2O_2 + H}$ or $\mathrm{H_2O + OH}$) and their objection to Bates' scheme may be considered withdrawn.

(11) Reaction (4) has an energy of activation of at least 13 kcal., since it is endothermic to this extent. Reaction (5) also possesses a considerable energy of activation [Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931)]. Experiments of Kistiakowsky [THIS

The description of the explosion limits follows the treatment of Kassel and Storch.[4] For a given temperature the upper limit is reached when

$$2k_4 = k_1(\mathrm{M}) \qquad (8)$$ [12]

Frost and Alyea's[13] lower limit equation determined in a potassium chloride-coated vessel is obtained and Hinshelwood and Moelwyn-Hughes,[14] lower limit equation determined in a silica vessel can be approximated if it is assumed that on a silica surface H, O and OH are destroyed at the same rate, whereas on a potassium chloride surface H is destroyed[15] preferentially.

For the reaction rate above the upper explosion limit it is necessary to introduce the chain-initiating reaction. A decision must first be made whether chains are initiated at the surface or in the volume of the vessel. It has been demonstrated[16] that up to 540° at pressures below the upper explosion limit (20 to 100 mm.) two streams of hydrogen and oxygen may be crossed at some distance from the nozzles without inflaming, and that inflammation will occur if a silica rod is inserted at the junction of the streams; an aluminum rod was ineffective. These experiments were not extended to temperatures at which the gas would inflame in the absence of a surface. It has been demonstrated,[17] however, that streams of hydrogen and oxygen will inflame without the aid of a surface when crossed at atmospheric pressure and 560°. Of the different initial conditions in these two sets of experiments, namely, temperature and pressure, the former must be assigned a greater role. Thus, it appears that between 540 and 560° chain initiation becomes appreciable in the gas phase.

The reaction rate above the upper explosion limit has been studied largely with quiescent gas mixtures in vessels of silica and porcelain. If it is tentatively assumed that in the usual sized vessels volume initiation becomes predominant over surface initiation from 540 to 560° upward, then the observations made in such vessels on the effect on inert gases, the influence of diameter, the order of reaction, and the absence of any effect of poisoning the surface may be explained. There are, however, other experimental facts not easily explained on the basis of this assumption. These will be discussed more advantageously after the silica and porcelain vessel experiments have been treated in the light of the above hypothesis.

Chain Initiation in the Gas Phase

For reasons given below only the spontaneous formation of hydrogen atoms need be considered as a chain-initiating reaction. Their rate of formation per unit volume is denoted by I_{H}. Chains are broken by diffusion of HO_2 to, and their destruction at, the wall.

$$\mathrm{HO_2} \xrightarrow{\text{surface}} \text{destruction} \qquad (9)$$

For the kinetic treatment the same formal result will be obtained by the use of either reaction (2) or (3), provided hydrogen peroxide decomposes to form water. It is thus sufficient to consider only one of them, say reaction (3).

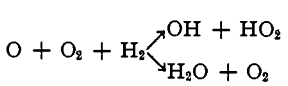
From reactions (1), (3), (4), (5), (6) and (9) the expression for the reaction rate above the upper explosion limit is easily shown to be

$$\frac{\mathrm{d}(\mathrm{H_2O})}{\mathrm{d}t} = I_{\mathrm{H}} \frac{2k_3(\mathrm{H_2})(\mathrm{M})d^2 + \dfrac{2k_4}{k_1(\mathrm{M})}\left(k_3(\mathrm{H_2})(\mathrm{M})d^2 + k_9\right)}{k_9\left(1 - \dfrac{2k_4}{k_1(\mathrm{M})}\right) - \dfrac{2k_4}{k_1}k_3(\mathrm{H_2})d^2} \qquad (10)$$

k_1, k_3, etc., being the velocity coefficients of reactions (1), (3), etc., and d the diameter of the vessel. It is assumed here that the gas is quiescent and that the rate of diffusion is inversely proportional to the total pressure and inversely as the square of the vessel diameter, an assumption that is ideally true only if the chain carriers are not reflected from the walls,[4] but which holds with suffi-

---

JOURNAL, **52**, 1868 (1930)] and Smith and Kistiakowsky [*ibid.*, **57**, 835 (1935)] with photochemically generated oxygen atoms in hydrogen–oxygen mixtures at room temperatures and pressures of the order of one atmosphere can be interpreted according to these authors, by



$$\mathrm{O + O_2 + H_2} \begin{array}{l} \nearrow \mathrm{OH + HO_2} \\ \searrow \mathrm{H_2O + O_2} \end{array}$$

the competing reaction (5) being too slow under these conditions. These facts, however, do not make it improbable that reactions (4) and (5) should become sufficiently fast at the high temperatures in question in the present paper. For the same reason, it may be proposed that reaction (6) is so fast here that the recombination $OH + OH + M = H_2O_2 + M$ is slow in comparison. (For the requirement of a third body in the recombination of two OH, see Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).) The inclusion of reaction (6) in Smith and Kistiakowsky's reaction scheme appears to furnish a suitable representation of the water yields obtained by these authors. These yields increase with lower total pressure, but not at the expense of either the ozone or hydrogen peroxide yields. Reaction (6) predicts this effect, short chains being formed, whose length increases toward lower pressures because of the decreased probability of the OH recombination reaction.

(12) This follows from Kassel and Storch's equation 19 if the constants k_1, k_{12} and k_{13} equal zero.

(13) A. A. Frost and H. N. Alyea, THIS JOURNAL, **55**, 3227 (1933).

(14) C. N. Hinshelwood and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **138A**, 311 (1932).

(15) The unsatisfactory state of our knowledge of the lower limit makes further elaboration inadvisable.

(16) H. N. Alyea and F. Haber, *Z. physik. Chem.*, **B10**, 193 (1930).

(17) F. Goldman, *ibid.*, **B5**, 316 (1929).

cient accuracy provided $\lambda/\epsilon r$ is small compared with 1.[18] λ is the mean free path, r the radius of the vessel, and ϵ the fraction of collisions of chain carriers with the wall that lead to destruction.

From equation (10) the condition for explosion is given by

$$k_9\left(1 - \frac{2k_4}{k_1(\mathrm{M})}\right) - \frac{2k_4}{k_1}k_3(\mathrm{H_2})d^2 = 0 \qquad (11)$$

which may be written in the form

$$k_1(\mathrm{M}) = 2k_4\left(1 + \frac{k_3(\mathrm{H_2})}{k_9/(\mathrm{M})d^2}\right) \qquad (12)$$

This agrees with the relationship (8) for the upper explosion limit if $k_9/(\mathrm{M})d^2 \gg k_3(\mathrm{H_2})$; that is, if at the upper limit the assumption made earlier holds, namely, that reaction (3) is a rare event compared with the destruction of HO_2 at the wall.

As the pressure is raised somewhat above the upper limit, the reaction rate drops sharply to small values as equation (11) increases rapidly from zero to finite positive values. On increasing the pressure still further, $2k_4/k_1(\mathrm{M})$ becomes small compared with 1, and $(2k_4/k_1)k_3(\mathrm{H_2})d^2$ increases until eventually a third explosion limit is reached at approximately

$$k_9 = (2k_3k_4/k_1)(\mathrm{H_2})d^2 \qquad (13)$$

It is doubtful that the observed third explosion limit is governed exactly by this condition. It is more likely that explosion occurs already at some lower pressure due to the very rapid increase of the reaction rate with pressure, which destroys the isothermal condition (see also reference 5).

For the further comparison of the theoretical expression for the reaction rate above the upper limit with experiment, it is necessary to introduce specific assumptions concerning the chain-initiating reaction. Experiments show that an increase in the oxygen concentration has no more effect than the addition of an equal amount of nitrogen,[5] that is, the oxygen concentration as such does not enter into the expression for the reaction rate. There remain, therefore, as initiating reactions only the formation of hydrogen atoms by dissociation of hydrogen and the formation of hydroxyl and hydrogen atoms or of oxygen atoms by dissociation of water. In initially dry mixtures the second reaction can be appreciable only after the reaction has progressed for some time. An accelerating influence of water actually has been observed.[5] It is to be noted, however, that part of the accelerating effect of water, as that of other inert gases, is caused by the change in diffusion characteristics due to different molecular weights and diameters; that is, k_9 is decreased. It is easily shown that the radical HO_2 should diffuse through oxygen about as readily as through water. However, the accelerating influence of water has been found to be considerably in excess of that of oxygen. Thus, the possibility that part of the accelerating effect of water is due to the above initiating reaction may remain open to consideration.

Assuming that a fraction of collisions of H_2 with other molecules leads to dissociation, the rate of chain initiation is given by

$$I_\mathrm{H} = k_{14}(\mathrm{H_2})(\mathrm{M}) \qquad (14)$$

A corresponding expression would apply for the water dissociation.

Equations (10) and (14) determine the change in reaction rate with the total pressure, the partial pressure of hydrogen and the vessel diameter at constant temperature. Whereas, at the upper limit itself the order of the reaction is minus infinity, the order increases continuously with rising pressure depending on the values of $2k_4/k_1(\mathrm{M})$ and $2k_4/k_1k_3(\mathrm{H_2})d^2$, until at the third explosion limit it becomes plus infinity.

The variable order is fully supported by experiment. For example, for a stoichiometric hydrogen–oxygen mixture at 569° the upper explosion limit was found to be at about 120 mm., almost unaffected by the size or material of the vessel,[19] as demanded by equation (12). In a porcelain bulb having a capacity of 200 cc. the order of the reaction rose from 2.6 at 225 mm. to over 6 at 600 mm.[20] The third explosion limit (not determined) was at a pressure above 600 mm.[20] Similar results were found in a silica vessel at 567°.[21]

Since k_3 and k_4/k_1 increase markedly with temperature the order of the reaction changes more rapidly with pressure at higher temperatures in agreement with experiment.[20,21] At a given pressure an increase in temperature may result in an increase or a decrease in the order depending upon the relative importance of k_3 and k_4/k_1, that is, upon the location of the pressure and temperature of the mixture with respect to the upper limit.

Reaction rates have been determined in silica vessels of different sizes from 1.7 to 7.7 cm. in diameter using stoichiometric mixtures at 300

---

(18) G. von Elbe and Bernard Lewis, "The Steady State Rate of a Chain Reaction for the Case of Chain Destruction at Walls of Varying Efficiencies" submitted.

(19) H. W. Thompson and C. N. Hinshelwood, *Proc. Roy. Soc.* (London), **122**, 610 (1929).

(20) C. H. Gibson and C. N. Hinshelwood, *ibid.*, **119**, 591 (1928).

(21) C. N. Hinshelwood and H. W. Thompson, *ibid.*, **118**, 170 (1928).

and 600 mm. pressure at 560°.[5] The rate was found to increase approximately with the square of the diameter, a relation that may be obtained from equation (10) if $2k_4/k_1(\mathrm{M}) \ll 1$ and $\frac{2k_4}{k_1} k_3(\mathrm{H_2})d^2 \ll k_5$ and $k_3(\mathrm{H_2})(\mathrm{M})d^2 \gg \frac{k_4k_5}{k_1(\mathrm{M})}$. These experiments are in an intermediate pressure range between the upper and third explosion limits characterized by an order of about four.[21] The fact that the proportionality of the rate with d^2 has been observed over a considerable range of pressure and vessel diameter can be considered to justify the assumption that the chain-breaking efficiency of the wall is not very small, thus allowing neglect of $\lambda/\epsilon r$ compared with 1, as has been done in deriving equation (10). It may be pointed out that for chain-breaking efficiencies less than 100%, the theory[18] predicts that the ratio, reaction rate/d^2, shall be constant only over a limited range of diameters, increasing toward small as well as large diameters. The minimum becomes more pronounced toward larger values of $\lambda/\epsilon r$, that is, lower pressures. Therefore, it is of interest to reproduce the experimental results of Williamson, Pickles and Hinshelwood,[5] in the following table.

TABLE I

REACTION RATE IN SILICA BULBS OF STOICHIOMETRIC MIXTURES OF HYDROGEN AND OXYGEN AT 560°

	d, mm.	17	32	56	77
Initial pressure 600 mm.	Rate/d^2	0.0030	0.0034	0.0030	0.0057
Initial pressure 300 mm.	Rate/d^2	.00062	.0005	.0003	.00058

Furthermore, reaction rates have been determined[20] in the intermediate pressure range by adding increasing amounts of hydrogen to a constant amount of oxygen, or *vice versa*, or by adding an inert gas like nitrogen to a mixture of hydrogen and oxygen. In order to compare these results with those derived from equation (10) it is necessary to consider, in addition to the inert gas effect expressed by the variable (M) in equation (10), the change in the diffusion characteristics of the mixtures due to differences in molecular weights and molecular diameters. An exact expression for the diffusion of $\mathrm{HO_2}$ through a mixture of hydrogen and oxygen and sometimes a third gas cannot be given. However, one may determine the diffusion coefficient of a hypothetical gas having an average molecular weight and diameter depending on the mole fraction, f, of hydrogen. The average molecular weight $\bar{m}$ of a mixture of hydrogen and oxygen may be given by $2f + 32(1 - f)$ and the average molecular diameter $\sigma_{\mathrm{av.}}$ by $f\sigma_{\mathrm{H_2}} + (1 - f\sigma_{\mathrm{O_2}})$. $\sigma_{\mathrm{HO_2}}$ may be identified with $\sigma_{\mathrm{O_2}}$. If a third inert gas is present the average molecular weight and diameter are calculated in a corresponding way. The substitution of this hypothetical gas should not be seriously in error, especially when relative rates are compared. Equation (10) reduces to

$$\frac{\mathrm{d(H_2O)}}{\mathrm{d}t} = \text{const.}\ \frac{(\mathrm{H_2})^4}{f^2} \frac{\bar{\sigma}^2}{\sqrt{\frac{1}{m_{\mathrm{HO_2}}} + \frac{1}{m}}} \left[f\sigma^2_{\mathrm{H_2}} \sqrt{\frac{1}{m_{\mathrm{H_2}}}} + (1 - f)\sigma^2_{\mathrm{H_2O_2}} \sqrt{\frac{m_{\mathrm{H_2}} + m_{\mathrm{O_2}}}{m_{\mathrm{H_2}}m_{\mathrm{O_2}}}}\right] \quad (15)$$

where $\bar{\sigma} = {}^1/_2(\sigma_{\mathrm{HO_2}} + \sigma_{\mathrm{av.}})$.

The following table contains the observed and calculated ratios of the reaction rates at the pressures indicated in the first two columns for different mixtures.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED RATIOS OF REACTION RATES

Oxygen pressure = 100 mm. 569°. $\sigma_{\mathrm{O_2}} = \sigma_{\mathrm{HO_2}} = 2.93 \times 10^{-8}$ cm.; $\sigma_{\mathrm{H_2}} = 2.36 \times 10^{-8}$ cm.[22]

Increase in $\mathrm{H_2}$ pressure, mm.		Ratio of reaction rates	
From	To	Obsd.	Calcd.
200	300	3.0	3.3
300	400	2.8	2.5

Hydrogen pressure = 300 mm. 569°.

Increase in $\mathrm{O_2}$ pressure, mm.		Ratio of reaction rates	
From	To	Obsd.	Calcd.
100	200	2.4	2.0
200	250	1.5	1.3

Hydrogen pressure = 300 mm. Oxygen pressure = 100 mm. 569°. $\sigma_{\mathrm{N_2}} = 3.10 \times 10^{-8}$ cm.[22]

Increase in $\mathrm{N_2}$ pressure, mm.		Ratio of reaction rates	
From	To	Obsd.	Calcd.
0	100	2.3	2.0
100	150	1.4	1.3

Hydrogen pressure = 300 mm. Oxygen pressure = 150 mm. 569°. $\sigma_{\mathrm{He}} = 1.89 \times 10^{-8}$ cm.[22]

Increase in He pressure, mm.		Ratio of reaction rates	
From	To	Obsd.	Calcd.
0	300	2.45	2.51
300	500	1.59	1.55

Hydrogen pressure = 200 mm. Oxygen pressure = 100 mm. 559°. $\sigma_{\mathrm{A}} = 2.84 \times 10^{-8}$ cm.[22]

Increase in A pressure, mm.		Ratio of reaction rates	
From	To	Obsd.	Calcd.
0	200	5.24	2.78
200	500	2.71	2.78
500	700	1.35	1.64

The agreement is good, on the whole, considering the uncertainties in the underlying assumptions.

---

[22] R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, Appendix 3.

In the range of gas-phase chain initiation a change in the character of the surface should have little or no effect on the reaction rate under the conditions of the foregoing experiments, since $\lambda/\epsilon r \ll 1$. Whereas coating a surface with potassium chloride strongly inhibits the reaction under conditions of predominance of surface initiation (Pease[23]), such coating, according to unpublished experiments referred to by Hinshelwood and Williamson,[5] has "failed to reveal any effect on the reaction in a silica vessel under conditions corresponding to most of the experiments" described in this section of gas-phase initiation.

Chain Initiation at the Wall

A plausible assumption concerning the surface initiating reaction is that H_2O_2 formed catalytically at the wall dissociates sometimes into 2OH.[23] Thus

$$H_2 + O_2 \xrightarrow{\text{Surface}} (H_2O_2) \longrightarrow 2OH \qquad (16)$$

If I_{OH} denotes the rate of chain initiation per unit area and γ is the ratio of surface to volume of the vessel, then $\gamma\ I_{OH}$ is the rate of chain initiation per unit volume.

If $K(HO_2)$ denotes the rate per unit volume of destruction of HO_2 at the surface, then reactions (1), (3), (4), (5), (6), (9) and (16) lead to the following relation between initiation, branching and breaking of chains

$$\frac{k_1(M)}{k_1(M) - 2k_4}\gamma I_{OH} + \frac{2k_4}{k_1(M) - 2k_4}k_3(H_2)(HO_2) = K(HO_2) \qquad (17)$$

The first term in equation 17 is the equivalent of the rate of release of HO_2 from the surface.

In a spherical vessel

$$K = \frac{\epsilon r}{2\lambda}\left(\frac{\pi^2 D}{r^2} - \frac{2k_4}{k_1(M) - 2k_4}k_3(H_2)\right) \qquad (18)$$

where D is the diffusion coefficient.[24]

For π^2D/r^2 one may substitute $k_9/(M)d^2$, k_9 being the same as in equation (10). For $\epsilon r/2\lambda$ one may substitute $k\epsilon(M)d$. Therefore

$$K = k\epsilon(M)d\left(\frac{k_9}{(M)d^2} - \frac{2k_4}{k_1(M) - 2k_4}k_3(H_2)\right) \qquad (19)$$

The rate of formation of H_2O then becomes, for $\lambda/\epsilon r \ll 1$

$$\frac{d(H_2O)}{dt} = \frac{\gamma I_{OH}}{1 - \frac{2k_4}{k_1(M)}}\left[\frac{\left(1 - \frac{2k_4}{k_1(M)}\right)2k_3(H_2)d}{\epsilon k\left(k_9\left(1 - \frac{2k_4}{k_1(M)}\right) - \frac{2k_4}{k_1}k_3(H_2)d^2\right)} + 1\right] \qquad (20)$$

It is seen that the conditions for explosion remain the same as before.

According to equation (20), the reaction rate between the upper and third explosion limits again has a variable order, which increases with pressure, and for $2k_4/k_1(M) \ll 1$, that is, at pressures sufficiently above the upper limit, increases with temperature. This is in agreement with experiment.[19,20]

If the temperature is not much above 500°, the rate of the chain reaction given by equation (20) is unimportant compared with a catalytic water-forming surface reaction.[20,21] This catalytic surface reaction possibly involves the primary formation of hydrogen peroxide[23] and predominates up to much higher temperatures if the vessel is packed. It is of zero order in a Worcester porcelain vessel and of first order with respect to hydrogen in a silica vessel. In an unpacked Worcester porcelain vessel the order of the total reaction was found to be 0.6 at 506° and more than 2 at 529° at intermediate pressures[19] due to the increased part played by the chain reaction.

Over a temperature range 520 to about 560° at intermediate pressures a gradual increase in the temperature coefficient of the reaction rate was found.[20,21] This may be understood to reflect essentially the transition from surface initiation with low temperature coefficient to gas-phase initiation with high temperature coefficient, as is indicated by equations (20) and (10) for intermediate pressures.

Equation (20) indicates that the reaction rate should be independent of the diameter of the vessel at intermediate pressures. No experiments in this temperature–pressure range are available.

Further Discussion of Volume Initiation Versus Surface Initiation

Experiments on quiescent gas mixtures in a silver vessel up to 700°, that is, in a temperature

---

[23] This would account for the observation of Pease [THIS JOURNAL, **52**, 5106 (1930)] that coating of the wall with potassium chloride slows down the reaction rate very markedly. Potassium chloride destroys peroxidic substances efficiently, as is borne out by Pease's and other authors' experiments on the oxidation of hydrogen, aldehydes and hydrocarbons (see von Elbe and Lewis, *ibid.* (in print), thus preventing the release of chain carriers from the wall. However, Pease's results may also be interpreted as being due to an increase in the efficiency of destruction of HO_2 on a potassium chloride surface. Some of Pease's experiments were conducted in a temperature range in which gas phase initiation would be expected to predominate. However, his experiments were made by a flow method, and the gases were far from quiescent. This has a dual effect. In the first place, it enhances the release of chains from the surface and, second, it increases the dependence of the rate of chain breaking on the efficiency of the wall beyond that obtaining were the transport of chain carriers to the wall governed solely by diffusion.

[24] See ref. 18. ϵ is assumed to be small compared with 1.

range where volume initiation was assumed to occur, show that the chain reaction is practically suppressed.[25] Even at temperatures at which the reaction has become very fast or even explosive in a silica vessel, only a slow catalytic surface reaction occurs in a silver vessel. If the initiation is occurring in the gas phase, these facts cannot be explained by the presumably very high efficiency of chain breaking at a silver surface, because an increase in the chain-breaking efficiency from a moderate value, such as is found in silica vessels, to perfect efficiency, should have, according to the theory, no pronounced effect on the reaction rate; this is different for surface initiation (compare equations 10 and 20 and also reference 18). If one attempts to attribute the above effects to high chain-breaking efficiency of a silver surface, one must reconsider the results obtained at high temperatures in silica and porcelain vessels on the basis of surface initiation. This leads to difficulties. In the first place, it is evident that surface initiation is inconsistent with the observation that coating of a silica vessel with potassium chloride does not affect the reaction in the high-temperature range. In the second place, equation (20) does not describe the facts concerning vessel diameter and inert gases.

A possible answer to this latter objection is that OH radicals that are formed by reaction (16) and for which a silica or porcelain but not a silver surface is highly reflective, may diffuse for a considerable distance, on the average, into the gas phase before they react to form HO_2. This would be equivalent to gas-phase initiation as far as inert-gas effect is concerned, but it would demand a dependence of the rate on d instead of d^2. It would also conflict with the fact that the introduction of a silica rod into a silver vessel failed to initiate reaction even at pressures and temperatures within the explosive region below the upper limit.[25] It will be recalled that a silica rod caused ignition in crossed stream experiments under similar conditions. Thus, one is faced with several new difficulties not accounted for by high chain-breaking efficiency of a silver surface.

This leads to an alternative hypothesis, namely, that in a silver vessel chain carriers are destroyed in the gas phase by the action of silver or some compound of silver in the vapor form. The presence of silver in the gas phase need not necessarily arise from the thermal evaporation of silver at the temperature of the experiments. It is well known that atomic hydrogen, for example, on recombining in contact with metals causes sputtering of the metal. This sputtering phenomenon has been observed especially well on silver.[26] In addition to the possible sputtering effect of atoms and radicals in a hydrogen–oxygen mixture, it is entirely possible energetically for the catalytic formation of water on the surface of silver to give rise to the same phenomenon. It may also be mentioned that in an atmosphere of pure hydrogen the volatility of silver is increased somewhat.[27]

Once this hypothesis is conceded,[28] then the assumptions made earlier in this paper regarding gas phase and surface initiation remain plausible. Should it fail and if all experimental observations mentioned in this paper are correct, then the treatment of the reaction between hydrogen and oxygen would require a radically new approach.

Summary

The only mechanism for the interaction of hydrogen and oxygen consistent with photochemical experiments (mercury-sensitized reaction, photoöxidation of hydrogen iodide, inhibition by O_2 of the photochemical reaction between hydrogen and chlorine) and experiments on the lower and upper explosion limits is

$$\begin{aligned} \mathrm{H + O_2 + M} &= \mathrm{HO_2 + M} \\ \mathrm{H + O_2 + H_2} &= \mathrm{H_2O_2 + H} \\ \mathrm{HO_2 + HO_2} &= \mathrm{H_2O_2 + O_2} \\ \mathrm{H + O_2} &= \mathrm{OH + O} \\ \mathrm{O + H_2} &= \mathrm{OH + H} \\ \mathrm{OH + H_2} &= \mathrm{H_2O + H} \\ \mathrm{H, O, OH} + \text{surface} &\longrightarrow \text{destruction} \end{aligned}$$

to which is to be added the chain-initiating reaction at the surface or in the gas phase.

If it is now assumed that in the thermal reaction HO_2 is normally destroyed at the surface but at high temperatures and pressures is capable of undergoing reaction with H_2 to an appreciable extent either by

$$\mathrm{HO_2 + H_2 = H_2O_2 + H}$$

or

$$\mathrm{HO_2 + H_2 = H_2O + O\dot{H}}$$

the reaction above the upper limit can be described adequately, provided chains are initiated

---

[25] C. N. Hinshelwood, E. A. Moelwyn-Hughes and A. C. Rolfe, *Proc. Roy. Soc.* (London), **139**, 521 (1933).

[26] K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

[27] A. Farkas, *ibid.*, **5B**, 467 (1929).

[28] A number of experiments suggest themselves among which is the passage of cold streams of hydrogen, oxygen, and mixtures of these past a heated silver screen and noting the formation of a silver deposit.

predominantly in the gas phase above about 540–560°. The latter assumption makes it necessary to ascribe the suppression of the reaction in a silver vessel to gas-phase deactivation due to silver. This is discussed in some detail.

PITTSBURGH, PENNA. RECEIVED JANUARY 21, 1937

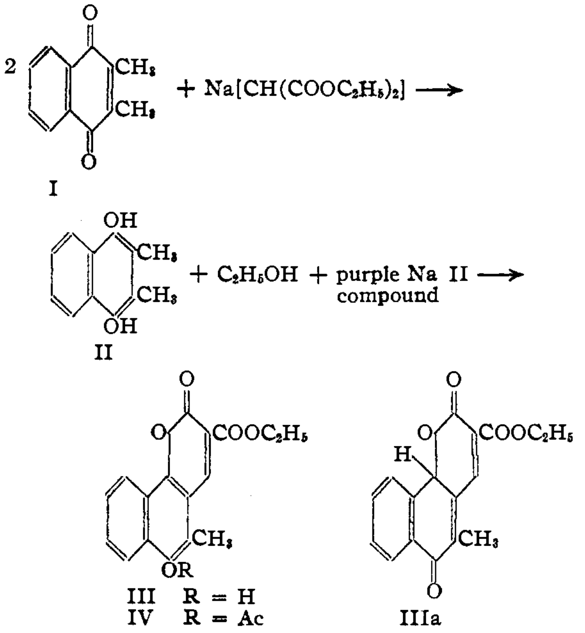
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Quinones and Sodium Enolates. V. 2,3-Dimethylnaphthoquinone and Sodium Malonic Ester[1]

BY LEE IRVIN SMITH AND ISABELLA M. WEBSTER[2]

Previous papers in this series have dealt with the reaction between sodium enolates and two types of quinones: (1) duroquinone, a fully methylated para benzoquinone, and (2) trimethylquinone, a para benzoquinone with one unsubstituted position in the ring. In case 1, the reaction involved one of the methyl groups attached to the nucleus, and led ultimately to a coumarin derivative. In case 2 the reaction was most simply interpreted as involving an initial 1,4-addition of the reagent to the conjugated system which terminated in the unsubstituted position of the ring. In the latter case, the final products were benzofuran derivatives. In both cases only one molecule of reagent (sodium malonic ester) could be made to react.

In order to explore somewhat further the limits of the coumarin formation shown by duroquinone (case 1) the work described in this paper was undertaken and a benzolog of duroquinone, 2,3-dimethylnaphthoquinone (I), was selected for study. This quinone, like duroquinone, has two methyl groups attached to the quinone nucleus in positions 2 and 3, but positions 5 and 6, instead of holding methyl groups, are fused to a benzene ring. This quinone, if it were to react with sodium malonic ester in the same manner as duroquinone, should give rise to an intermediate sodium compound (II), which on hydrolysis would produce an α-naphthocoumarin derivative (III)[3] together with an equivalent amount of the hydroquinone.



I

II

III R = H
IV R = Ac

IIIa

This quinone, however, proved to be far more difficult to handle than duroquinone, and it was only after the original procedure used by Smith and Dobrovolny[4] had been modified considerably that a crystalline product could be obtained in good yield by decomposition of the sodium derivative II. In several experiments, the black quinhydrone derived from I was produced as a by-product. As this quinhydrone was apparently fairly stable in ether (the solvent used) it was necessary to allow time for the air to oxidize it back to the quinone in order to obtain the maximum yield of III from I, otherwise 3 moles of I were required to produce 1 mole of III.

The product III formed fine yellow needles melting at 212–213° with decomposition, and it had the composition and molecular weight corresponding to the formula $C_{17}H_{14}O_5$. No carbonyl derivatives could be formed using hydroxylamine or 2,4-dinitrophenylhydrazine, but the presence of one hydroxyl group was shown by the formation

---

[1] Paper IV, THIS JOURNAL, 58, 629 (1936).

[2] Abstracted from a thesis by Isabella M. Webster, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1936.

[3] These compounds are more correctly termed 7,8-benzocoumarins. However, in the literature the term α-naphthocoumarin is used to designate them; therefore this term will be used throughout this discussion.

[4] Smith and Dobrovolny, THIS JOURNAL, 48, 1701 (1926).