VI coming into prominence at higher temperatures because of its larger energy of activation. Therefore, at low temperatures the L. C. C. is independent of pressure and depends on vessel conditions. Unfortunately, no experiments are available in this range on the effect of inert gases or change of mixture composition. With increasing temperatures both mechanisms overlap. The full expression for the composite mechanism is complicated but it suffices to state that the consequence would be a gradual increase in the pressure dependence of the L. C. C. with increasing temperature. One would expect the approximate linear dependence at 410° to be replaced by a dependence of even higher order at still higher temperatures. However, the phenomena become more involved at higher temperatures as the reactions that determine the normal explosion limits of hydrogen and oxygen come into play. The almost negligible effect of nitrogen on the L. C. C. at an intermediate temperature, 395°, found in an isolated experiment,[5] might be taken to indicate the overlapping of the two mechanisms. The second of the above assumptions makes the U. C. C. inversely proportional to the pressure and independent of surface conditions as demanded by the experimental data for the ranges of temperature and pressure investigated. Remembering that (M) in the positive terms of (8) and (10) represents only concentrations of oxygen and inert gases, it is evident that an increase of the percentage of oxygen or addition of inert gas should decrease the U. C. C. The effect of temperature is given correctly by the equations for both the U. C. C. and L. C. C. The energies of activation of VII and XI far exceed those of VIII and IX; therefore, the U. C. C. will increase with increasing temperature. Since both IV and XII have little or no energy of activation, then by the same token the L. C. C. will decrease with increasing temperature.

Summary

The nitrogen peroxide-sensitized explosion of hydrogen and oxygen has been subjected to kinetic analysis. The evidence rules out a mechanism based on oxygen atoms and points to a mechanism in which NO_3, H, OH and HO_2 take part. Equations are developed for the lower and upper critical concentrations of nitrogen peroxide which satisfactorily account for the known experimental facts.

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Kinetics of the Dry and Water-Catalyzed Reaction between Carbon Monoxide and Oxygen at and above the Upper Explosion Limit[1]

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

Like mixtures of hydrogen and oxygen, mixtures of carbon monoxide and oxygen exhibit the phenomenon of the low pressure explosion peninsula.[4,5] The tip of the peninsula is at about 600° and the upper explosion limit extends upward from about 70 mm.; evidently the peninsula is in a considerably higher temperature and pressure region than the hydrogen–oxygen explosion peninsula. The position of the upper limit is practically uninfluenced by water vapor; it is independent of vessel size; it is shifted toward higher pressures on replacing carbon monoxide by oxygen and *vice versa*, but the effect is not marked; inert gases lower the upper limit in that they can replace to some extent either of the reactants—nitrogen is particularly striking, the $CO + O_2$ mixture being replaceable fairly exactly by equal amounts of nitrogen. On the other hand, the reaction above the upper limit is strongly accelerated by traces of water vapor and hydrogen, in the absence of which only a slow and predominantly heterogeneous reaction takes place.

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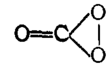
[4] Kopp, Kowalsky, Sagulin and Semenoff, *Z. physik. Chem.*, **B6**, 307 (1930).

[5] Hadman, Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A137**, 87 (1932); **A138**, 297 (1932).

The reactions that govern the upper limit are homogeneous and, since water vapor is without effect, they must involve only carbon monoxide and oxygen and such intermediates as can be formed from these compounds. It would seem to be a somewhat simpler task to develop a catalog of possible reactions than it was for the hydrogen–oxygen reaction.[6] One may exclude with considerable assurance dissociation of CO into C and O since the energy of dissociation is very large; therefore, reactions of free C are also excluded. Oxygen may be present in the form of atoms or ozone. Besides carbon dioxide it is possible that higher oxides can be formed. These are probably limited to the hypothetical but not implausible oxide CO_3, whose structure presumably could be , a type of compound known in organic peroxide chemistry. Such compounds are formed by the action of ozone on aldehydes.[7]

The Upper Explosion Limit.—The phenomena associated with the upper limit require both chain breaking and branching reactions, the former to increase faster with pressure than the latter. If these reactions are first order with respect to the chain carriers and if ozone and oxygen atoms are considered to be chain carriers, then reactions between them are excluded. It will now be investigated whether a satisfactory mechanism can be derived which is based exclusively on material chain carriers or whether it is necessary to consider energy chains.

As usual, the treatment of the limits does not require knowledge of the exact nature of the chain initiating reaction. Analysis of the system leads to the following catalog of reactions where M is any third molecule

$$\begin{array}{rcll}
O + O_2 + M &=& O_3 + M & \text{I} \\
O + CO + M &=& CO_2 + M & \text{II} \\
O_3 + CO &=& CO_2 + 2O - 15\text{ kcal.} & \text{III} \\
O_3 + CO &=& CO_3 + O & \text{IV} \\
CO_3 + CO &=& 2CO_2 & \text{V} \\
O_3 + CO + M &=& CO_2 + O_2 + M & \text{VI} \\
O_3 + CO + CO &=& CO_3 + CO_2 & \text{VIa} \\
O + O_2 + CO &=& CO_2 + 2O & \text{a} \\
O_3 + CO &=& CO_2 + O_2 & \text{b} \\
O_3 + CO_3 &=& CO_2 + 2O_2 & \text{c} \\
O + CO_3 &=& CO_2 + O_2 & \text{d}
\end{array}$$

Reactions a and b cannot be important because they constitute branching and breaking reactions, respectively, of the wrong reaction order. If reactions c and d are assumed to be important, reaction V cannot be admitted because it would result in a dependence of the CO_3 concentration on the chain carrier concentration and this would violate the rule that all reactions must be of the same order with respect to the carriers. If V is omitted, then IV, being necessarily followed by c or d, becomes a chain breaking process; but, like b, it would be of the wrong reaction order. Therefore, c and d must be omitted.

The expression for the upper limit, which is determined from reactions I to VI, is

$$k_6(\text{M}) = \frac{k_3 - (k_3 + k_4)k_2(\text{CO})/k_1(\text{O}_2)}{1 + k_2(\text{CO})/k_1(\text{O}_2)} \qquad (1)$$

This equation adequately accounts for the effect of CO, O_2 and inert gases on the upper limit. $k_6(\text{M})$ is composed of three terms, $k_{6\text{CO}}(\text{CO})$, $k_{6\text{O}_2}(\text{O}_2)$ and $k_{6\text{X}}(\text{X})$, X being an inert gas. Since the molecular weights and diameters of N_2, CO and O_2 are almost the same, it is understandable that N_2 can replace an equal amount of CO and O_2. The specific influence of CO and O_2 on the limit is not large and, therefore, the ratio $k_2(\text{CO})/k_1(\text{O}_2)$ must be rather small compared to 1. This conclusion is in harmony with experiments[8] on the reaction of O atoms in mixtures of CO and O_2 at room temperature where it was found that reaction I is at least 150 times faster than reaction II. The temperature dependence of the upper limit is well represented by the equation[4,5]

$$p = \text{const.}\ e^{-E/RT} \qquad (2)$$

E being 35 kcal. This equation follows from equation 1 if $k_2(\text{CO})/k_1(\text{O}_2)$ is small.

The above demonstrates that a material chain mechanism gives a satisfactory description of the available experimental facts on the upper limit.

Neglecting the ratio $k_2(\text{CO})/k_1(\text{O}_2)$ in equation 1, it is of interest to test the ternary reaction VI for the distance δ that two of the colliding molecules approach the third molecule in order for reaction to take place, using the method of Tolman.[9] A three body mechanism can be considered justifiable if δ is small compared with the molecular diameter. The upper limiting explosion pressure at 650° is at about 265 mm. δ is calculated to be 10^{-13} cm. which is the same value calculated by Tolman for the ternary reaction $2NO + O_2$.[9] It is interesting that for the ternary

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[6] Von Elbe and Lewis, THIS JOURNAL, **59**, 656 (1937).

[7] Rieche, "Alkylperoxyde und Ozonide," T. Steinkopff, Dresden, 1931, p. 77.

[8] Jackson and Kistiakowsky, THIS JOURNAL, **52**, 3471 (1930); Jackson, *ibid.*, **56**, 2631 (1934).

[9] Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, pp. 245–50.

reaction $H + O_2 + M = HO_2 + M$ which is the chain breaking reaction in the hydrogen–oxygen reaction,[6] δ is found to be 100 times larger.

It seems rather certain that ozone must play a role in the mechanism since it is formed in large quantities if O atoms are liberated in the presence of oxygen and carbon monoxide. If the mixed material-energy chain

$$\begin{aligned} O + O_3 &= 2O_2^* \\ O_2^* + O_3 &= 2O_2 + O \end{aligned}$$

which has been proposed[10] for the decomposition of ozone, were important under conditions of the upper limit, ozone could no longer act as a chain carrier unless the mechanism of the upper limit was based entirely on reactions that are second order with respect to the chain carriers, which is out of the question since it is quite impossible to devise a plausible scheme based on second order chain carrier reactions. However, the energy-rich O_2^* could be conceived of as a chain carrier inasmuch as it could react with CO to form CO_2 and O. But even though branching and breaking reactions of the proper reaction order could be postulated, it easily can be shown that such a mechanism is entirely unsuitable.

It appears to be difficult to find plausible alternatives to the proposed mechanism of the upper limit.

The Water-Catalyzed Reaction Outside the Explosion Region.—Since water does not affect the position of the limits to an appreciable extent, its influence on the reaction above the limit can only be in the chain-initiating reaction. The water-catalyzed reaction is very different from the reaction of the dry gases. Not only is the reaction strongly accelerated by water, but the rate increases with vessel size, being approximately proportional to the square of the diameter.[5] This fact suggests a chain reaction with chain initiation in the gas phase.[11] No experiments are available on the effect of inert gases. The reaction rate is proportional to the concentration of water as far as this has been measured and approximately proportional to the concentration of carbon monoxide. It is approximately inversely proportional to the oxygen concentration.

It is immediately clear that the chain carriers O and O_3 cannot themselves take part in the reactions of the catalytic process, otherwise the upper limit would be influenced strongly by water and the limit would depend on the dimensions of the vessel. It follows that hydrogen cannot be formed in appreciable amounts because the reaction

$$O + H_2 = OH + H$$

would have to play a role at the limit.[12] The number of additional reactions that can be postulated are limited. These are:

$$\begin{aligned}
H_2O + M &= H + OH + M && \text{VII} \\
H_2O &= H + OH && \text{VIIa} \\
H + O_2 &= OH + O && \text{VIII} \\
H + O_2 + O_2 &= O_2 + HO_2 && \text{IX} \\
H + O_2 + CO &= CO_2 + OH && \text{X} \\
OH + CO &= CO_2 + H && \text{XI} \\
OH + CO + O_2 &= CO_2 + HO_2 && \text{XII} \\
HO_2 + CO &= CO_2 + OH && \text{XIII} \\
HO_2 &\xrightarrow{\text{surface}} \text{destruction} && \text{XIV}
\end{aligned}$$

Chains are assumed to be initiated by the thermal dissociation of water. Whether this is a bimolecular process (VII) as in the thermal dissociation of hydrogen[6] or a unimolecular process (VIIa) appears uncertain, although the latter might be favored because the water molecule, possessing more degrees of freedom, would presumably have a longer lifetime as an activated molecule. As in the hydrogen–oxygen reaction,[6] reactions VIII and IX are operative. If no inert gases are present reaction IX is assumed to take place only if O_2 is the third body. It is thus sharply distinguished from reaction X, this being necessary to account for the specific retarding effect of O_2. Reaction XI is similar to the reaction

$$OH + H_2 = H_2O + H$$

which is operative in the hydrogen–oxygen reaction, and reaction XII is most probable in view of the free H atom liberated in XI. In order to obtain a dependence of the rate on the square of the diameter it is necessary to have a chain-continuing reaction compete with XIV. For this there is hardly any other choice than reaction XIII. The reaction

$$H + CO + M = HCO + M$$

might have been included in the scheme but it would be followed by[13]

$$HCO + O_2 = CO + HO_2$$

and therefore could lead to chain breaking in competition with IX. This would result in an inhibiting effect of large concentrations of CO

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(10) Schumacher and Beretta, *Z. physik. Chem.*, **B17**, 405, 417 (1932).

(11) Von Elbe and Lewis, THIS JOURNAL, **59**, 970 (1937).

(12) This reaction is important already at much lower temperatures.[6]

(13) Von Elbe and Lewis, THIS JOURNAL, **59**, 976 (1937).

which is contrary to the facts. Other association reactions may be possible theoretically but they are not required to explain the experimental facts.

The kinetic expression for the rate of formation of carbon dioxide will now be developed from the above two reaction schemes. The rate of formation of O atoms due to water catalysis is given by $k_{12}(O_2)(H)$. The exact expression for the H atom concentration is cumbersome. Two justifiable approximations greatly simplify it. One is that reaction XIII must proceed much faster than XIV in order to account for the diameter dependence of the reaction rate. The other is that reaction XI is much faster than XII. Then

$$(H) = \frac{2k_7k_{11}k_{13}}{k_{14}k_{12}}\,d^2\,\frac{(H_2O)(CO)(M)^2}{(O_2)^2[k_8 + k_{10}(CO) + k_9(O_2)]} \quad (3)$$

O atoms are destroyed essentially in reaction I. From the equations equating the rates of formation and destruction of O atoms and ozone, one obtains for the ozone concentration

$$(O_3) = \frac{k_8(O_2)}{[k_6(M) - k_3](CO)}\,(H) \quad (4)$$

By far the predominant CO_2-forming reaction is IV, there being only a few CO_2 molecules formed incidental to the formation of an O atom in the second of the above reaction schemes. Therefore

$$\frac{d(CO_2)}{dt} = k_4(CO)(O_3) =$$

$$\frac{2k_4k_7k_8k_{11}k_{13}}{k_{12}k_{14}[k_6(M) - k_3]}\,d^2\,\frac{(H_2O)(CO)(M)^2}{(O_2)[k_8 + k_{10}(CO) + k_9(O_2)]} \quad (5)$$

Equation 5 explains rather well the experimental facts. Independent of the water concentration, the reaction becomes explosive if $k_6(M)$ equals k_3 which is identical with equation 1 for the upper limit if one neglects reaction II as has been done for simplification in deriving equation 5. In a temperature and pressure range sufficiently removed from the upper limit, *i. e.*, where $k_6(M) \gg k_3$, the rate is seen to be approximately proportional to (H_2O), (CO) and (M) and inversely as (O_2). The proportionality with (M) arises from the use of equation VII instead of VIIa. Specifically, the influence of water was determined up to only 25 mm. pressure of H_2O, at a total pressure of about 300 mm.[5] Thus, (M) was hardly affected and the rather accurate linear relation found for H_2O is described by the equation. The CO and O_2 concentrations were varied over a much greater range. The (CO) contained in the (M) and in the denominator partially cancel each other. Actually, the rate increases slightly more than with the first power of (CO). In a packed vessel the coefficient of the chain breaking reaction XIV is no longer inversely proportional to (M) but is independent of it.[14] The factor (M) left in the numerator of equation 5 now disappears and the accelerating effect of carbon monoxide in a packed vessel should become smaller toward higher carbon monoxide pressures. This has been found experimentally.[5] In a packed vessel it has also been found that a large excess of carbon monoxide retards the rate,[5] a fact that is not described by equation 5. In an unpacked vessel the experimental data suggest that the inhibition by O_2 is somewhat stronger than appears from equation 5.

If reaction VIIa is used instead of VII the factor $(M)^2$ in equation 5 becomes (M) and the influence of CO and O_2 on the rate receives a much better description while the description of the influence of H_2O remains unchanged. For instance, in a packed vessel (M) would enter into the denominator of the equation and it is understandable that a large excess of CO should eventually retard the rate. In an unpacked vessel (M) would disappear from the equation altogether and the inhibition by O_2 would then be given practically as found experimentally. Therefore, the facts favor the choice of reaction VIIa as the initiating reaction.

The Lower Explosion Limit.—The lower limit should be due to the destruction of O and O_3 at the wall. Experimentally, it has been almost impossible to study the influence of diameter because the position of the limit was found to be influenced in an uncontrollable way by the condition of the vessel wall.[5] The inert gas effect is in the expected direction, *i. e.*, the limit is lowered by adding inert gases.[5] Judging from the simultaneous influence of wall conditions and inert gases it may be concluded that the experiments fall in an intermediate range where $\lambda/\epsilon r$ is comparable with 1. (λ is the mean free path, ϵ the efficiency of chain destruction at the wall and r the radius.) In such cases the theory of the limit becomes very complicated. A similar situation was met with in the treatment of the hydrogen–oxygen lower explosion limit.[15]

Summary

A chain mechanism based on material chain carriers has been proposed which explains the experimental facts of the dry and water-catalyzed

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(14) See reference 11, equation 13.

(15) Kassel and Storch, THIS JOURNAL, **57**, 672 (1935).

reaction between carbon monoxide and oxygen at and above the upper explosion limit. The mechanism of the upper limit involves oxygen atoms and ozone as chain carriers. The mechanism of the reaction above the upper limit includes the mechanism of the upper limit and in addition a chain initiating mechanism that involves water.

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

Studies on Aging of Precipitates. XV. The Mechanism of the Interaction between Dissolved Bromide and Solid Silver Chloride

BY I. M. KOLTHOFF AND H. C. YUTZY[1]

When silver chloride is shaken with a solution containing chloride and bromide of such a composition that no mass-action precipitation of pure silver bromide occurs, mixed crystals of silver chloride and bromide will be formed. In a previous study[2] indication has been obtained that the penetration of the bromide into the solid is not solely a result of recrystallization of the precipitate but that other factors mainly account for the relatively large speed of penetration of bromide into well aged silver chloride. The mechanism of the distribution of the bromide is further investigated in the present study.

Experimental

The materials and methods of analysis used were the same as described in previous papers.[2]

In the first place experiments were carried out with a silver chloride precipitate which had been aged drastically for thirty-five days in a 2 *M* sodium chloride solution at room temperature. After aging, the silver chloride was filtered on a sintered glass crucible, washed and made air dry. Weighed portions were shaken for various periods of time with 225 ml. of an aqueous solution being 0.0888 *M* in sodium chloride and 2.2×10^{-4} *M* in potassium bromide. The supernatant liquids obtained after centrifuging were analyzed for bromide and the final bromide concentrations plotted against the time of shaking. If it were assumed that the value obtained after extrapolation of the curve to a time of shaking of zero corresponded to the bromide concentration in the solution after exchange equilibrium in the surface had been attained, the amount of surface could be calculated from the known distribution coefficient of bromide between solution and silver chloride.[3] A detailed account of the experiments and the calculations is given in the thesis of the junior author.[1] The results indicated that 6.3% of the silver chloride used consisted of surface. Microscopically, the size-distribution curve of the same product was determined; from the average particle diameter it was calculated that 0.017% of the silver chloride consisted of surface. The value calculated from the exchange experiments is about 400 times greater than the microscopic one. It is hardly possible to attribute this large difference to a large internal surface as the silver chloride was very well aged. For the same reason the great speed of penetration of the bromide into the silver chloride hardly can be attributed to a rapid recrystallization of the solid. That this rapid disappearance of anomalously large amounts of bromide from the solution is not due to mass precipitation of silver bromide as a separate phase is easily shown. If such a precipitation occurs the ratio of the concentration of chloride ions to that of bromide ions in the solution must be equal to the ratio of the solubility products—about 300. In the case cited, the bromide concentration was found by analysis, after a week's shaking, to be 6×10^{-5}; the chloride concentration was 8.90×10^{-2}, corresponding to a ratio of chloride to bromide of 1450.

That the rapid penetration of bromide is not to be attributed to a large internal surface or a rapid recrystallization of the silver chloride was also shown by working with extremely coarse silver chloride which had been recrystallized from ammonia and with products which had been aged for a year at 27° as an equivalent body in water. Both were made air-dry before use. A systematic study was made with the year old precipitate varying widely experimental conditions, such as concentrations, volume of solutions, amount of precipitate, etc., in order to discover factors which determine the speed of penetration of the bromide into the solid. The results are given in a condensed form in Table I. As an indication of the speed of penetration of the bromide into the silver chloride the values of *K'* after eighty hours of shaking are given in the last

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[1] From a thesis submitted by H. C. Yutzy to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the Degree of Doctor of Philosophy (June, 1936).

[2] I. M. Kolthoff and H. C. Yutzy, THIS JOURNAL, **59**, 1634 (1937).

[3] H. C. Yutzy and I. M. Kolthoff, *ibid.*, **59**, 916 (1937).