



Mechanisms of Complex Reactions and the Association of H and O2

Guenther von Elbe and Bernard Lewis

Citation: The Journal of Chemical Physics **7**, 710 (1939); doi: 10.1063/1.1750517 View online: http://dx.doi.org/10.1063/1.1750517 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/7/8?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Quantum mechanical calculation of the rate constant for the reaction $H+O2\rightarrow OH+O$ J. Chem. Phys. **100**, 733 (1994); 10.1063/1.466940

Accurate quantum mechanical reaction probabilities for the reaction $O+H2\rightarrow OH+H$ J. Chem. Phys. **87**, 1892 (1987); 10.1063/1.453205

Reaction path and variational transition state theory rate constant for Li++H2O \rightarrow Li+(H2O) association J. Chem. Phys. **84**, 3783 (1986); 10.1063/1.450088

Collision complex formation in the reaction of C+ with H2O J. Chem. Phys. **83**, 3958 (1985); 10.1063/1.449108

Unified statistical model for "complex" and "direct" reaction mechanisms: A test on the collinear H+H2 exchange reaction J. Chem. Phys. **70**, 325 (1979); 10.1063/1.437194



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.174.255.116 On: Fri, 19 Dec 2014 22:09:20

Mechanisms of Complex Reactions and the Association of H and O_2^*

GUENTHER VON ELBE, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

BERNARD LEWIS, Explosives Division, Central Experiment Station, Bureau of Mines, Pittsburgh, Pennsylvania (Received April 14, 1939)

The kinetics of the upper explosion limit and the nonexplosive thermal reaction of H2 and O2 uniquely demonstrates the formation of HO₂ in collisions $H+O_2+M$, its destruction on surfaces and its ability to propagate chains by gas phase reactions with H₂. Below 500° HO₂ gradually ceases to be a chain carrier in the gas phase; assuming its further reactions to be heterogeneous, involving selfneutralization and reaction with H₂, the kinetics of the mercury-photosensitized H2-O2 reaction are well interpreted. Bates' mechanism for this latter reaction, in which HO₂ is postulated to react in the gas phase, is shown to be inconsistent with the thermal reaction. Data on the oxygen-inhibited photosynthesis of HCl and on the H concentration in the mercury-photosensitized H₂-O₂ reaction indicate that a fraction of the associations of H and O₂ occurs in binary collisions. A quantum-mechanical treatment by Rosen shows that this process is possible. The par-

THE association of H and O₂ occurs in a number of complex reactions which have been extensively investigated experimentally. However, the available material has not yet been coordinated as a whole.

1. The Evidence for the Formation of HO_2 at the Upper Explosion Limit of H_2 and O_2

Measurements of the upper explosion limit of H_2 and O_2 have shown that at constant temperature the explosion condition is accurately expressed by the equation

$$k_{\rm H_2}({\rm H_2}) + k_{\rm O_2}({\rm O_2}) + k_X(X) = 1,$$
 (1)

where X denotes an inert gas, like nitrogen, and the constants $k_{\rm H_2}$, etc., are independent of vessel factors.¹ Since the phenomenon of the upper explosion limit is uniquely interpreted by the isothermal branched-chain theory, the kinetic tially binary character of the association is consistent with data on the photo-oxidation of HI. The reactions of HO2 in a mixture of H₂, Cl₂, O₂ and HCl are discussed. Recent confirmation of the reaction $HCO+O_2 = HO_2+CO$ greatly strengthens the proposed mechanism of the oxidation of aldehydes and hydrocarbons. The rate coefficient of the reaction $H+O_2+H_2=HO_2+H_2$ is found to be 0.81×10^{13} cm^6 mole⁻² sec.⁻¹ at room temperature. With O₂ as a third body the rate coefficient is about $\frac{1}{3}$, and with N₂ about $\frac{1}{2}$ of this value. The rate coefficient of the reaction $H+O_2=HO_2$ is found to be 0.74×10^8 cm³ mole⁻¹ sec.⁻¹ at room temperature. Comparison of the above value of the rate coefficient of $H+O_2+H_2$ with that estimated from data on the upper explosion limit shows that this reaction probably has no positive temperature coefficient, while a negative temperature coefficient is not ruled out.

explosion condition is $\beta/\alpha = 1$, where α and β are the coefficients of the net rates of chain-branching and -breaking, respectively. A relation of this form demands that all elementary reactions participating in the chain-branching and -breaking processes be of the same order with respect to the chain carriers. In the present case this can only be the first order, since no second-order branching reaction can be imagined, and higher orders are extremely improbable. If now a catalog of all imaginable first-order reactions of H, O, OH and HO_2 is written, it is possible to find eleven formal reaction schemes that lead to an explosion condition of the form of Eq. (1). However, the success of nine of these schemes rests on the assumptions that the reaction $OH+H_2+O_2$ $=H_2O+OH+O$ or H_2O+HO_2 be much faster than $OH+H_2=H_2O+H$, and that $O+H_2+O_2$ $=OH+HO_2$ be much faster than $O+H_2=OH$ +H. These assumptions are improbable, particularly in view of the concentration conditions at the upper limit and the fact that OH and O disrupt the hydrogen molecule even at room temperature.^{2, 3} These nine schemes may, there-

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded t IP: 132.174.255.116 On: Fri. 19 Dec 2014 22:09:20

^{*} Presented at the symposium on "Kinetics of Homogeneous Gas Reactions" (see page 633) and published by permission of the Director, Bureau of Mines, U. S. Department of the Interior, and the Director, Coal Research Laboratory, Carnegie Institute of Technology. (Not subject to copyright.)

¹A. A. Frost and H. N. Alyea, J. Am. Chem. Soc. 55, 3227 (1933); G. H. Grant and C. N. Hinshelwood, Proc. Roy. Soc. A141, 29 (1933).

² G. von Elbe, J. Am. Chem. Soc. 55, 62 (1933).

⁸ H. A. Smith and G. B. Kistiakowsky, J. Am. Chem. Soc. **57**, 835 (1935).

fore, be ruled out. A tenth scheme demands the impossible assumption that $O+H_2+H_2=H_2O$ + 2H be much faster than both $O+H_2+M$ = H₂O + M and O + H₂ = OH + H. This eliminates all but the scheme:

1.
$$OH+H_2=H_2O+H$$
,
2. $H+O_2=OH+O$,
3. $O+H_2=OH+H$,
4a. $H+O_2+H_2=HO_2+H_2$,
4b. $H+O_2+O_2=HO_2+O_2$,
4c. $H+O_2+X=HO_2+X$,
5. $HO_2 \rightarrow destruction$

The explosion condition becomes

$$k_{4a}(\mathbf{H}_2) + k_{4b}(\mathbf{O}_2) + k_{4c}(X) = k_2, \qquad (2)$$

whence $k_{4a}/k_2 = k_{H_2}$, etc. Experimentally it is found that $k_{O_2} \simeq \frac{1}{3} k_{H_2}$, and if the inert gas is nitrogen, $k_{N_2} \simeq \frac{1}{2} k_{H_2}$.

That the reactions 4, followed by 5, are the true chain-breaking reactions is shown further by the fact that there is only one alternative, namely, $O+H_2+M=H_2O+M$; this reaction, however, does not permit a solution of the problem unless it is assumed to be much faster than other reactions between O and H₂ in which the hydrogen molecule is disrupted; this is not the case even at room temperature³ and will, therefore, certainly not be true in the much higher temperature range of the upper explosion limit (ca. $450-580^{\circ}$). HO₂ is thus formed in ternary association reactions.

Further support for the scheme comes from other sources. If N₂O is substituted for O₂ in the reacting mixture, reaction 2 should be replaced by $H+N_2O=OH+N_2$, and the chain should be continued by reaction 1. The chain carriers H and OH should, at sufficiently low pressures, be destroyed principally at the wall, as is known from the kinetics of the lower explosion limit of hydrogen and oxygen.⁴ If chains are assumed to be initiated by the dissociation of N_2O into N_2 and O, which is followed by reaction 3, a scheme is obtained which is in complete agreement with the observations on the thermal reaction of N_2O and H₂ at low pressures.⁵

If traces of hydrogen are added to mixtures of

carbon monoxide and oxygen, upper explosion limits are obtained over the same temperature range as for mixtures of hydrogen and oxygen.⁶ According to Buckler and Norrish, the kinetics of these limits are completely described by adding the reactions $OH+CO=CO_2+H$ and O+CO $+M = CO_2 + M$ to the above mechanism.

In analogy to reaction 4, it may be expected that the ternary reaction $OH+CO+O_2$ leads to the products $CO_2 + HO_2$. Lewis and von Elbe⁷ have shown that this reaction uniquely explains the oxygen-inhibition of the water-catalyzed CO-O₂ reaction.⁸

2. REACTIONS OF HO₂ IN MIXTURES OF H₂ AND O₂

At the upper explosion limit the HO₂ radicals are mainly destroyed without generating other chain carriers, but as the hydrogen concentration is increased the chance for the reaction

6.
$$HO_2+H_2=H_2O_2+H$$
 (or H_2O+OH)

increases. Experimentally it is known that the chains in the slow reaction above the upper explosion limit are broken at the wall. If, now, reaction 5 is formulated as the destruction of HO₂ at the wall, reactions 1 to 6 form a scheme for this slow reaction that is in complete agreement with the extensive experimental facts.4, 9, 10 This is perhaps the most severe test for the whole mechanism because of all the possible chain carriers H, O, OH, and HO₂, only HO₂ is available to carry on chains at pressures above the upper explosion limit. There is, in fact, no other chain carrier at all imaginable unless one resorts

⁴L. S. Kassel, "Symposium on Gaseous Combustion," Chem. Rev. 21, 331 (1937). ⁵ H. W. Melville, Proc. Roy. Soc. A146, 737 (1934).

⁶ E. J. Buckler and R. G. W. Norrish, Proc. Roy. Soc. A167, 318 (1938).

⁷ B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Cambridge University Press, 1938), pp. 74–77; cf. G. von Elbe and B. Lewis, J. Am. Chem. Soc. **59**, 2025 (1937). ⁸ Hadman, Thompson and Hinshelwood, Proc. Roy. Soc

A137, 87 (1932).

⁹G. von Elbe and B. Lewis, J. Am. Chem. Soc. 59, 656 (1937); reference 7, pp. 37-52.

¹⁰ This mechanism demands (reference 9) that the inhibition of the reaction in a silver vessel should be due to gas phase rather than surface reactions of Ag. This apparent difficulty of the mechanism has been removed. It is known that in this temperature range silver is very volatile in oxygen (C. F. Plattner, 1856, cf. Mellor, Inorg. Chem., Vol. 3, p. 343) and experiments with a silver spiral in an atmosphere of hydrogen and oxygen have shown the formation and re-evaporation of silver deposits on the wall of the vessel (H. R. Heiple and B. Lewis, unpublished).

to energy chains, as has been done in the past.¹¹ Such schemes have proved to be unsuccessful kinetically and are inherently implausible.

Below 500°C HO₂ gradually ceases to be a chain carrier in the gas phase, as shown by the disappearance of the chain reaction.¹¹ Taylor and Salley¹² have studied the mercury-photosensitized reaction between hydrogen and oxygen for a 2 H₂+O₂ mixture at 600 mm Hg in a closed circulatory system from 534° down to 230°C. Excited Hg dissociates H₂ in collisions of the second kind. It is of interest to compare their data with the following simple scheme which is suggested by the foregoing discussion:

7 and 4.
$$Hg + h\nu = Hg^* \rightarrow 2H \xrightarrow{O_2 + M} 2HO_2,$$

6.
$$HO_2 + H_2 = H + [H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2],$$

5.
$$HO_2 + HO_2 \text{ adsorbed}$$

$$= O_2 + [H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2].$$

In each run, an induction period of one to two minutes preceded the establishment of a steady state at which there is a constant rate of pressure decrease. This may be understood to be the time required to build up the surface concentration of HO₂. This surface concentration should be independent of the gas phase concentration at high values of the latter, i.e., high light intensities, and proportional to it at low values; in general it should be proportional to $(HO_2)^{x/(1+x)}$, where x increases from zero to infinity as the intensity of the absorbed light is decreased. The equation for the quantum yield becomes

$$\frac{d(\mathrm{H}_{2}\mathrm{O})}{dt} \frac{1}{I_{\mathrm{abs}}} = \frac{k_{6}(\mathrm{H}_{2})}{k_{5}^{(1+x)/(1+2x)}I_{\mathrm{abs}}^{x/(1+2x)}} + 1, \quad (3)$$

where I_{abs} is the intensity of the absorbed light. At temperatures in the neighborhood of 500° the quantum yield should increase strongly with temperature and should be independent of light intensity if the latter is high. This is found experimentally. If I_{abs} is small, so that x is comparable with one, the quantum yield should increase with decreasing light intensity. Three runs at 534° (marked¹² I_6 , H_5 and D_5) show the existence of this effect. In agreement with Eq. (3), the effect disappears toward lower temperatures. However, in contradiction to Eq. (3), the quantum yield does not become entirely independent of temperature, but retains a slight positive temperature coefficient. This indicates that the reaction scheme is not quite complete. It may be suggested that HO₂ and H₂O₂ react at the surface with H₂, in analogy with the catalytic surface reaction of H₂ and O₂ in this temperature range.¹¹

The latter suggestion leads to an interpretation of certain data of other investigators on the mercury-photosensitized reaction at or not much above room temperature.¹³ These data have been interpreted previously by Bates¹³ by means of the mechanism consisting of reaction 7 followed by 6 and

8. $HO_2 + HO_2 = H_2O_2 + O_2$.

With this scheme and data on the relative quenching efficiencies of O₂ and H₂ for Hg*, Bates showed that, in agreement with observations, the reaction rate, in a certain series of experiments,¹³ should be proportional to the hydrogen pressure; that the quantum yield of H_2O_2 (this appears to be the sole product, H_2O) being formed by secondary decomposition) should vary between 1 and about 3; and that, in contrast to Taylor and Salley's results in the lower temperature range, increasing light intensity should decrease the quantum yield and also the temperature coefficient of the quantum yield, as was found for the range of 50° to 100°. However, it can be shown that a scheme comprising reactions 7 and 5 and

9. HO_{2 adsorbed} + H₂ = H₂O₂ +
$$\begin{bmatrix} O_2 \\ - \rightarrow HO_2 \\ H_{adsorbed} \\ HO_2 \\ - \rightarrow H_2O_2 \end{bmatrix}$$

is equally consistent with the above observations. This scheme avoids the difficulty of introducing reaction 6 in this low temperature range. There still remains the problem of accounting for Taylor and Salley's observations that between 230° and about 500°C both the quantum yield

¹¹ C. N. Hinshelwood and A. T. Williamson, *The Reaction between Hydrogen and Oxygen* (Oxford, 1934). ¹² H. S. Taylor and D. J. Salley, J. Am. Chem. Soc. 55, 96 (1933).

¹³ J. R. Bates, J. Chem. Phys. 1, 457 (1933). See this paper for earlier literature.

and its temperature coefficient are independent of the light intensity. It is conceivable that reaction 9 reverses its temperature coefficient and disappears and that a new reaction involving H_2O_2 and H_2 develops which would give the desired kinetic expression for Taylor and Salley's lower temperature experiments.

The idea expressed in the formulation of reactions 5 and 9 that toward lower temperatures reactions of radicals in H2-O2 mixtures are heterogeneous rather than homogeneous, receives further support from many experimental observations showing the activation of glass and silica surfaces by adsorption of atoms and radicals.¹⁴

Furthermore, it can be shown that Bates' mechanism is irreconcilable with the mechanism of the upper explosion limit. At this limit there exists the relation $k_5 \gg k_6(H_2)$. For a spherical reaction vessel $k_5 \leq \pi^2 D/r^2$, where D is the diffusion coefficient and r is the radius. The equality sign applies to the case of high surface chain breaking efficiency.15 The explosion limit of a stoichiometric mixture of H₂ and O₂ at 856°K is at a pressure of 160 mm Hg. Judging from data on the reaction above the limit, $k_6(H_2)$ should not be larger than 0.1 k_5 at this point. D is calculated to be approximately 10 cm² sec.⁻¹. Choosing r = 2.5 cm, which is smaller than the linear dimensions of Hinshelwood and co-workers' reaction vessels and which, therefore, increases the above inequality still further, one obtains $k_5 = 17 \text{ sec.}^{-1}$ and $k_6 \ll 0.5 \text{ mm}^{-1} \text{ sec.}^{-1}$ at 24°C. The latter inequality will now be used to determine a lower limiting value for the stationary HO₂ concentration required by Bates' mechanism for the mercury-photosensitized reaction at 24°C. For this purpose the data of Farkas and Sachsse¹⁶ are used. These investigators determined the stationary concentration of H atoms in the system by means of the para-orthohydrogen conversion in the absence of, and also in the presence of oxygen in small concentrations. In the oxygenfree system H is removed by

10. $H+H+H_2=2 H_2$.

Choosing from a set of their experiments at constant light intensity and constant hydrogen pressure (200 mm Hg) the value of $(H) = 2 \times 10^{-3}$ mm Hg for the oxygen-free system and $(H) \simeq 0$ for $(O_2)/(H_2) > 0.1$, one obtains from Bates' mechanism and reaction 10

$$(HO_2) = n(k_{10}/k_6) \times 4 \times 10^{-6}, \qquad (4)$$

where n+1 is the yield of H₂O₂ per quantum. Its value was estimated by Farkas and Sachsse to be about 4, in approximate agreement with earlier observations, ¹³ so that n becomes of the order of unity or larger. A rather reliable value of k_{10} is $1.1 \times 10^{16} \text{ cm}^{6} \text{ mole}^{-2} \text{ sec.}^{-1} = 32 \text{ mm}^{-2} \text{ sec.}^{-1}$ at 24°C.17 whence $(HO_2)\gg 3\times 10^{-4}$ mm Hg. Into this inequality there enters not only the abovementioned factor of at least 10, but a far more important factor due to the energy of activation of reaction 6. If this is chosen as low as 8000 calories, which is far too low, a factor of about 10⁴ results which brings the HO₂ pressure to the absurd value of >10 mm. This value would increase to the order of many atmospheres if a more correct value of the energy of activation were chosen.

3. FURTHER INFORMATION ON THE FORMATION AND DESTRUCTION OF HO₂ FROM OTHER KINETIC STUDIES

(a) Oxygen-inhibited photosynthesis of HCl

Another complex reaction in which reaction 4 participates is the oxygen inhibition of the photosynthesis of hydrogen chloride. Measurements by Norrish and Ritchie¹⁸ carried out at 25° over a wide range of concentrations of H2, Cl2, HCl and O2 in some 70 experiments show that the quantum yield, γ , of HCl is described with considerable precision by the equation

$$\gamma = \frac{(Cl_2)}{(O_2)} \frac{3.77 \times 10^{-4}}{(H_2) + 4(HCl) + 140},$$
 (5)

where the concentrations are expressed in mm Hg. This equation is valid for oxygen concentrations >10 mm except for high ratios of $(Cl_2)/(H_2)$. An equation of this form can be derived from the

¹⁴ Farkas, Haber and Harteck, Zeits. f. Elektrochem. **36**, 711 (1930); B. Lewis, J. Am. Chem. Soc. **55**, 4001 (1933); cf. reference 7, p. 66. ¹⁵ Reference 7, p. 41.

¹⁶ L. Farkas and H. Sachsse, Zeits. f. physik. Chemie B27, 111 (1934).

¹⁷ W. Steiner, Trans. Faraday Soc. **31**, 623 (1935); cf. I. Amdur, J. Am. Chem. Soc. **57**, 856 (1935). ¹⁸ R. G. W. Norrish and M. Ritchie, Proc. Roy. Soc.

A140, 713 (1933).

following scheme:

 $Cl_2 + h\nu = 2Cl_1$ 11. 12. $Cl+H_2=HCl+H$, $H+Cl_2=HCl+Cl$, 13. $H+O_2+H_2=$ chain breaking, 4a. 4d. $H+O_2+HCl=$ chain breaking, $H+O_2 = chain breaking,$ 4e.

which leads to

$$\gamma = \frac{(\text{Cl}_2)}{(\text{O}_2)} \frac{2k_{13}/k_{4a}}{(\text{H}_2) + (k_{4d}/k_{4a})(\text{HCl}) + k_{4e}/k_{4a}}.$$
 (6)

Experiments with high ratios of $(Cl_2)/(H_2)$ show that another term, $9(Cl_2)/(H_2)$, should be added to the denominator of Eq. (5), in substantial agreement with the earlier measurements of Thon.¹⁹ A corresponding term in Eq. (6) is obtained if the reaction

14.
$$Cl + O_2(+M) = ClO_2(+M)$$

is admitted to the scheme.20 This term is ordinarily small and the measurements do not allow one to distinguish between the binary or ternary character of reaction 14.

A point of disagreement between Norrish and Ritchie¹⁸ on the one side and Thon,¹⁹ Bodenstein and Schenk²¹ and Potts and Rollefson²² on the other is the introduction of the reaction

$$H+HCl=H_2+Cl$$

which Norrish and Ritchie consider necessary and which introduces a fifth term of the form $(HCl)/(H_2)$ in the denominator of Eq. (6). Since all authors agree that this term is in any case unimportant in the oxygen-inhibited reaction it can be dismissed here.

At small oxygen concentrations other chainbreaking reactions, such as the recombination of the Cl atoms and their destruction at the wall, come into prominence, and Eqs. (5) and (6) must be suitably modified.18

In the above scheme reactions 11, 12 and 13 have long been known to occur. Reaction 4a yields HO_2 ; while in reaction 4d, where HCl is the third body, products other than HO_2+HCl are not ruled out. This, however, is a minor question compared to the problem presented by the binary character of reaction 4e. This problem becomes apparent only from Norrish and Ritchie's work, since in the other investigations the pressure variations have not been carried far enough. Norrish and Ritchie's experimental quantum yields demand the retention of this reaction as written, or a series of kinetically equivalent reactions;²³ for, (1) if 4e is omitted, or (2) if it is written as a ternary reaction with O_2 or Cl_2 or both as third bodies (H₂ and HCl already appear as third bodies in 4a and 4d). the coefficients of the corresponding kinetic equation cannot be adapted to the experimental values of the quantum yield. The best average, as obtained by the method of least squares, leads to differences between calculated and experimental values of γ of over 50 percent in a large fraction of the experiments. Eq. (5), on the other hand, seldom leads to differences of more than a few percent, and in no case of more than 14 percent.

The hypothesis that the association of H and O₂ occurs partly in binary and partly in ternary collisions receives support from the quantum mechanical treatment of a simplified HO₂ model by Rosen.²⁴ He showed that if the total energy in the system HO₂ is but little more than that needed for dissociation, there exist discrete quantum states representing the distribution of the energy between the OH and OO bonds for which the average lifetime is very short (10^{-10} to) 10^{-14} sec.), and others, for which the lifetime is large enough (> 10^{-8} sec.) to permit stabilization in subsequent collisions. In view of the difficulties of kinetic alternatives, as described in reference

¹⁹ N. Thon, Zeits. f. physik. Chemie 124, 332 (1926).

²⁰ A kinetic alternative to reaction 14 is x. $H+O_2$ + $Cl_2 \rightarrow X$; y. $X+H_2 \rightarrow chain carrier$; and z. $X \rightarrow destruction$ (unimolecular) where X is an intermediate and $k_y(H_2) \gg k_s$. ²¹ M. Bodenstein and P. W. Schenk, Zeits. f. physik. Chemie B20, 420 (1933)

²² J. C. Potts and G. K. Rollefson, J. Am. Chem. Soc. **57**, 1027 (1935).

²³ Such a series of reactions can be formulated on the principle that an intermediate substance X is formed, without loss or gain of chain carriers, whose steady-state concentration is substantially proportional to the product $(H)(O_2)$, and which is destroyed at a unimolecular rate (either by decomposition in the gas phase or at the wall with a surface efficiency sufficiently small so that the influence of the total pressure is negligible; cf. reference 7, minute to the total pressure is hegigible; cf. reference 7, p. 25). An example is the following scheme: x. $Cl+O_2$ $+H_2 \rightarrow X$; y. $X+Cl_2 \rightarrow H$ or Cl; and z. $X \rightarrow destruction$ (unimolecular) where $k_y \gg k_z$. It is difficult to identify X with a plausible compound. Variations of the above principle present even greater difficulties. ²⁴ N. Rosen, J. Chem. Phys. 1, 319 (1933).

23, the above hypothesis becomes very plausible, and one may write

4e.
$$H + O_2 = HO_2$$
.

Since O_2 may act as a third body, it is necessary to admit the reaction

4b.
$$H+O_2+O_2=HO_2+O_2$$

to the scheme. The occurrence of reaction

4f.
$$H + O_2 + Cl_2 = HO_2 + Cl_2$$

is problematical, since the products may also consist, for example, of HCl+Cl+O₂, in which case the chain is not broken. An analysis of Norrish and Ritchie's data shows that both 4b and 4f may be admitted to the scheme without disturbing the agreement between the calculated and experimental quantum yields, if the values of the other coefficients are adjusted slightly. If only 4b is admitted, k_{4b} can be as large as ca. $0.2k_{4a}$ (see, however, below), while the coefficients k_{4d}/k_{4a} , k_{4e}/k_{4a} , $2k_{13}/k_{4a}$ in Eq. (6) may assume values within the ranges 4.24 to 4.67, 144 to 176 mm Hg, 3.79×10^{-4} to 4.17×10^{-4} mm Hg, respectively, at 25°C.

The further reactions of the radical HO₂ in a mixture of H₂, Cl₂, HCl and O₂ must be so postulated that they are consistent with previously discussed reactions and, (1) Eq. (6), modified to include reaction 4b, (2) the observation of Bodenstein and Schenk²¹ that in mixtures not over-rich in HCl the yield of H₂O per chain is approximately equal to the fraction

$$[(H_2)+0.2(HCl)]/[(H_2)+0.2(HCl)+3(Cl_2)],$$

and (3) the observation of Krauskopf and Rollefson²⁵ that on simultaneously decreasing the chlorine concentration and increasing the oxygen concentration the ratio of the yields of H_2O to HCl increases roughly to the limit 1, and can be raised above 1 by large increases in the HCl concentration. These requirements are met, for example, by the following reactions:

15.
$$HO_2 + Cl_2 = HCl + \begin{bmatrix} Cl \\ ClO_2 \rightarrow Cl_2 + O_2 \end{bmatrix}$$

16.
$$HO_{2 \text{ adsorbed}} + HCl = Cl_{adsorbed}$$

+
$$\begin{bmatrix} Cl \\ H_2O_2 \rightarrow H_2O + ClO \end{bmatrix}$$
,

²⁵ K. B. Krauskopf and G. K. Rollefson, J. Am. Chem. Soc. **56**, 327 (1934).

7. HO_{2 adsorbed}
$$+H_2 = H_{adsorbed}$$

+
$$\begin{bmatrix} Cl \\ H_2O_2 \rightarrow H_2O + ClO \end{bmatrix}$$
,

possibly followed by

17.
$$HO_2 + Cl_{adsorbed} = HO_2Cl \rightarrow ClO$$

+ $\left[HOCl \rightarrow H_2O + Cl_2\right]$,
5a. $HO_2 + H_{adsorbed} = H_2O_2 \rightarrow H_2O + ClO$,

18.
$$ClO \rightarrow \frac{1}{2}Cl_2 + \frac{1}{2}O_2$$

The reaction $H_2O_2 + Cl = H_2O + ClO$ is supported by Bodenstein and Schenk's observation that H_2O_2 is destroyed by chlorine atoms. H_2O_2 has been detected in the reacting mixture by Norrish,²⁶ using the sensitive titanic acid test. Assuming, therefore, that Cl is destroyed by H₂O₂, reactions 15 and 17 must also lead to the destruction of a chain carrier, as indicated, or else additional terms depending on the concentration of the reactants would be introduced in the denominator of Eq. (6) and it would be impossible to adapt the coefficients of this equation to the experimental quantum yields. The H₂O vields of Bodenstein and Schenk are correctly represented if $k_{15} \simeq 6k_7$, and $k_{16} \simeq 0.2k_7$. At very low Cl₂ and high O₂ concentrations, reactions 13 and 15 become negligible, which leads in the limit to a ratio (H_2O/HCl) formed of 1 or more. Bodenstein and Schenk have proposed a scheme of HO₂ reactions which conflicts with the latter requirement because they allow, for these conditions, the destruction of one or more HCl for every HO₂ formed.

The compound ClO₂, as prepared from chlorates, can be detected spectroscopically in extremely small concentrations, but it has not been found in the irradiated mixture of H₂, O₂ and Cl₂.²¹ Bodenstein and Schenk suggest that the compound formed in reaction 14 may be an isomer. This would also apply to the ClO₂ formed in reaction 15.

Although the above scheme of HO_2 reactions is speculative, it is experimentally certain that there exists one reaction path, 15, of HO_2 in which no H_2O is formed and which, therefore,

²⁶ R. G. W. Norrish, Trans. Faraday Soc. 27, 461 (1931).

very probably involves the destruction of Cl₂ and the formation of HCl. This increases the quantum yield by two for sufficiently large ratios $(Cl_2)/(H_2)$. Adding to it the hitherto neglected destruction of 1Cl₂ in the photodissociation, the total correction becomes three. This correction is not negligible in experiments where the chains are short, i.e., large ratios $(O_2)/(Cl_2)$, and it leads to an improved agreement between the calculated and experimental quantum yields in such experiments of Norrish and Ritchie. It also makes it possible to admit $k_{4b} \simeq 0.3 k_{4a}$, which is the same ratio found for these quantities at the upper explosion limit of H_2 and O_2 .¹

(b) H atom concentrations in mercury-photosensitized H_2-O_2 reaction

The occurrence of the binary reaction 4e is strikingly confirmed by Farkas and Sachsse's¹⁶ measurements of hydrogen atom concentrations in the mercury-photosensitized H₂-O₂ reaction at 200 and 500 mm total pressure and constant light intensity. The reactions to be considered are 7, 10, 4a and 4e. Reaction 4b can be neglected since the percentage of oxygen in the mixture is very small. The kinetic equations are: (a), in the absence of oxygen, since H is destroyed only by reaction 10,

$$2I_{abs} = k_{10}(H_0)^2(H_2), \tag{7}$$

where the subscript 0 refers to the oxygen-free mixture; and (b), in the presence of oxygen

$$2I_{abs} = k_{10}(H)^{2}(H_{2}) + k_{4a}(H)(O_{2})(H_{2}) + k_{4e}(H)(O_{2}), \quad (8)$$

whence

$$\frac{k_{10}}{k_{4a}} = \frac{(\mathrm{H})(\mathrm{O}_2)}{(\mathrm{H}_0)^2 - (\mathrm{H})^2} \left(1 + \frac{k_{4e}}{k_{4a}(\mathrm{H}_2)}\right).$$
(9)

By combining two Eqs. (9) for values of H and H_0 at 200 and 500 mm total pressure, k_{10}/k_{4a} can be eliminated and

$$\frac{k_{4e}}{k_{4a}} = \frac{\frac{(H)_{500}}{(H)_{200}} - \frac{(H_0)^2_{500} - (H)^2_{500}}{(H_0)^2_{200} - (H)^2_{200}}}{\frac{1}{200} \frac{(H_0)^2_{500} - (H)^2_{500}}{(H_0)^2_{200} - (H)^2_{200}} - \frac{1}{500} \frac{(H)_{500}}{(H)_{200}}},$$
 (10)

where all concentrations are expressed in mm Hg at 24°.

Table I contains data read from Farkas and Sachsse's Fig. 5, and the calculated values of k_{4e}/k_{4a} and k_{10}/k_{4a} . The values of k_{4e}/k_{4a} are in excellent agreement with the values of 144-176 found above from the oxygen inhibition of the photosynthesis of HCl.

From $k_{10}/k_{4a} = 1327$ and Steiner's¹⁷ value of $k_{10} = 1.1 \times 10^{16}$ cm⁶ mole⁻² sec.⁻¹ one obtains $k_{4a} = 0.83 \times 10^{13} \text{ cm}^{6} \text{ mole}^{-2} \text{ sec.}^{-1} \text{ It is of interest}$ to compare this value with a value of k_{4a} estimated from data at the upper explosion limit. Reaction 4e does not alter the form of the explosion condition at the upper explosion limit. k_2 in Eq. (2) now becomes $k_2 - k_{4e}$. It may be supposed, however, that 4e does not occur to any great extent at these high temperatures since the fraction of low energy collisions decreases with increasing temperature. For a stoichiometric mixture, using $k_{4b} = 0.3k_{4a}$ and neglecting k_{4e} , the explosion condition is

$$k_2 = 1.15k_{4a}(\mathbf{H}_2). \tag{11}$$

If reaction 4 is assumed to have no energy of activation, the energy of activation of reaction 2 is obtained from the observed pressure and temperature relations of the upper limit and equals about 26,000 cal.²⁷ If k_2 is set equal to $f \times Z \times \exp -(26,000/RT)$, where f is the "steric factor" and Z the collision frequency, then at 856°K where the explosion limit is 160 mm $k_{4a} \simeq f \times 7.5 \times 10^{13} \text{ cm}^6 \text{ mole}^{-2} \text{ sec.}^{-1}$. Since f < 1this suggests that reaction 4 has no positive temperature coefficient, while a negative temperature coefficient is not ruled out.

(c) Photo-oxidation of HI

The photodissociation of HI in the presence of O_2 leads to $\mathrm{H}_2,\,\mathrm{I}_2,\,\mathrm{and}\,\mathrm{H}_2\mathrm{O}_2.^{28}\,\mathrm{Since}$ the photo-act leads to H and I,29 the reaction scheme is uniquely given by

HI +
$$h\nu$$
 = H + I,
H + HI = H₂+I,
4. H+O₂(+M) = HO₂(+M),
HO₂+HI = H₂O₂+I.

Measurements by Cook and Bates²⁸ of the yields of H_2O_2 and H_2 showed that addition of

 ²⁷ G. H. Grant and C. N. Hinshelwood, reference 1.
 ²⁸ J. R. Bates and G. I. Lavin, J. Am. Chem. Soc. 55, 81 (1933); G. A. Cook and J. R. Bates, *ibid.* 57, 1775 (1935).
 ²⁹ B. Lewis, Nature 119, 493 (1927); J. Phys. Chem. 23, 270 (1928). K. F. Bonhoeffer and L. Farkas, Zeits. f. physik. Chemie 132, 235 (1928).

$(H_2) = 200 \text{ MM}$ $(H_0) = 2 \times 10^{-3} \text{ MM}$ $(H) \times 10^{-3}, \text{ MM}$	$(H_2) = 500 \text{ MM}$ $(H_0) = 1.264 \times 10^{-3} \text{ MM}$ $(H) \times 10^3, \text{ MM}$	(О2), ММ	k4e/k4a, MM	k10/k40
0.390 0.635 0.860 0.950 1.065	0.21 0.36 0.50 0.55 0.62	6.15 3.75 2.74 2.51 2.21	143 174 187 172 165	1069 1234 1400 1430 1500
		A	Average 168	

TABLE I. Calculation of k_{4e}/k_{4a} and k_{10}/k_{4a} from Farkas and Sachsse's measurements of the H concentration in the mercury-photosensitized H₂-O₂ reaction at 24°.

nitrogen increases the ratio H_2O_2/H_2 , thus confirming the partly ternary character of reaction 4. A comparison of the experimental and theoretical yields of these substances (including reaction 4e in the above scheme) shows that N_2 is about 1.5 to 2 times more effective as a third body than O₂. This is about the same relative effectiveness of these molecules that exists at the upper explosion limit of H_2 and O_2 .³⁰

(d) The oxidation of formaldehyde and methane

Experiments on the photolysis and the photooxidation of acetaldehyde make it practically certain that this molecule is oxidized to peracid by the following chain reaction:

$$CH_{3}CO \rightarrow CH_{3}CO(OO) \xrightarrow{CH_{3}CHO} CH_{3}CO(OOH) + CH_{3}CO.$$

The photo-oxidation of formaldehyde is also a chain reaction, but in contrast to the photooxidation of acetaldehyde, no peracid is formed. The main products are formic acid, CO and H₂O.³² Lewis and von Elbe³³ have interpreted this difference in the products by assuming that the radical HCO, which is the analog to CH₃CO in the acetaldehyde chain, is incapable of adding O_2 to form a peracid radical, but that it reacts according to

19.
$$HCO+O_2=HO_2+CO_1$$

followed by

20.
$$HO_2$$
+HCHO=HCOOH+OH,
OH+HCHO=H₂O+HCO.

Reaction 19 has since been confirmed by Harteck, Groth and Faltings³⁴ in experiments on the mercury-sensitized reaction between H₂ and CO in the presence of traces of oxygen: While in the oxygen-free mixture the only product is formaldehyde which involves the intermediate formation of HCO by the association of H and CO in a three-body reaction,¹⁶ a trace of O_2 (<0.1 percent) suppresses the formation of formaldehyde and yields, instead, H₂O₂. In the absence of CO, much higher percentages of O_2 are required in an H₂-O₂ mixture to yield detectable amounts of H₂O₂,^{16, 34} the H atoms being destroyed mainly by recombination. In explaining these facts no alternative to reaction 19 is apparent.

At high temperatures reaction 20 leads to CO and H₂O instead of formic acid. With the mechanism of the formaldehyde oxidation thus substantiated, the mechanism of the thermal oxidation of methane³⁵ is likewise confirmed since monovalent radicals are present and the main products are formaldehyde, CO and H₂O. The chain reactions are

> $OH+CH_4=H_2O+CH_3$, $CH_3+O_2=HCHO+OH$, $OH+HCHO=H_2O+HCO$, 19. $HCO+O_2=CO+HO_2$ 20a. $HO_2 + HCHO = CO + H_2O + OH$.

On the basis of this mechanism and other analytical and kinetic information, the proposed chain reactions in the oxidation of higher hydrocarbons³⁶ are well supported.

³⁰ A. A. Frost and H. N. Alyea, reference 1.

³¹ Reference 7, p. 84.

³² J. E. Carruthers and R. G. W. Norrish, J. Chem. Soc. 1036 (1936). 33 Reference 7, pp. 85-86.

³⁴ Harteck, Groth and Faltings, Zeits. f. Elektrochem. 44, 621 (1938).

³⁵ G. von Elbe and B. Lewis, J. Am. Chem. Soc. 59, 976 (1937); cf. reference 7, p. 89.

³⁶ Reference 7, Chapter 4.

DISCUSSION

J. A. Christiansen, Polytechnic Chemical Institule, Copenhagen: This reaction scheme seems to be consistent with all the facts. Such correlation of all the facts has been accomplished only for a few reactions. We should perhaps study fewer reactions but investigate them more thoroughly.

What we can do is to study the kinetics of the resultant reaction over a wide range of conditions and then find out which sequence (or sequences) of component reactions would lead to the kinetics actually found by experiment.

O. K. Rice, University of North Carolina: When HO_2 is formed, the energy can fluctuate from one degree of freedom to another and there is always sufficient energy to cause decomposition. It would seem that the fluctuation and the concentration of that energy in one bond would take place more quickly than the quantum transition considered by Rosen. I think that the suggested life period of 10^{-8} second is entirely too long from a theoretical point of view.

Guenther von Elbe, Coal Research Laboratory, Carnegie Institute of Technology: Might it not still be possible that a small fraction of the collision complexes have the required lifetime? The rate of binary association is supposed to be as fast as the rate of ternary association in collisions $H+O_2+H_2$ at 168 mm of hydrogen.