

The Mechanism of the Reaction of Hydrogen Atoms with Oxygen

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Citation: *The Journal of Chemical Physics* **1**, 457 (1933); doi: 10.1063/1.1749318

View online: <http://dx.doi.org/10.1063/1.1749318>

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The Mechanism of the Reaction of Hydrogen Atoms with Oxygen

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(Received April 15, 1933)

(1) A mechanism has been suggested for the reaction of hydrogen atoms with oxygen. This mechanism unifies a considerable number of hitherto conflicting data which have been assembled in connection with studies of the reaction. (2) The rate variation with the concentration of hydrogen and oxygen has been explained. (3) The quantum yield has been predicted, using the same constants as

those necessary to reproduce the rate variation. Also the variation of quantum yield with light intensity is found to be as predicted. (4) The temperature coefficient is also as predicted by the mechanism, but agreement is only semi-quantitative. (5) The bearing of this mechanism on a series of reactions which have been and are still under investigation has been indicated.

IN a number of recent investigations¹ it has been shown that many of the current ideas of the mechanism of the reaction of hydrogen atoms with oxygen must be revised. In particular it was demonstrated that experimental results did not at all agree with the mechanism suggested by Haber and Bonhoeffer² and revised by Frankenburg and Klinkhardt.³ Several mechanisms were suggested which, it was thought, agreed better with the sum total of the available experimental data. At that time, however, no attempt was made to obtain a quantitative proof of the exactness of any of the reactions schemes postulated. It is the purpose of this work to propose a mechanism which agrees with a remarkable degree of exactitude with all the measurements which have been carried out on the reaction.

EXPERIMENTAL DATA

Products of the reaction

It has been quite conclusively demonstrated by Salley and Bates that hydrogen peroxide constitutes at least 85–90 percent of the primary products of the reaction of dry gases. This has been indicated also in the work of Marshall⁴ and

of Bonhoeffer⁵ and Boehm for moist gases. Salley and Bates were of the opinion that hydrogen peroxide was the sole product, the 10–15 percent water being the result of decomposition of the peroxide.

Yield of peroxide per hydrogen atom (quantum yield)

Measurements of Marshall⁶ show 2.5 molecules of hydrogen peroxide per absorbed quantum for electrolytic gas. Later measurements of Frankenburg and Klinkhardt³ gave a mean value of 1.2 for a gas containing but 2–3 percent oxygen.

Effect of concentration on the mercury sensitized reaction

Measurements of Marshall indicate that at 60°C the rate of this reaction is proportional to the mole fraction of hydrogen present:

$$d[\text{H}_2\text{O}_2]/dt = K [\text{H}_2]/[\text{H}_2] + [\text{O}_2].$$

This would seem to show that hydrogen and oxygen are equally efficient in receiving the energy of an excited mercury atom on collision. However, the measurements of Zemansky⁷ on relative quenching efficiencies give values of $tk/p = 1.10$ for hydrogen and 0.68 for oxygen, where t is the lifetime of the mercury atom

¹ Salley and Taylor, *J. Am. Chem. Soc.* **55**, 96 (1933). Salley and Bates, *ibid.* **55**, 110 (1933). Lavin and Bates, *ibid.* **55**, 81 (1933). Bates, *Proc. Nat. Acad. Sci.* **19**, 81 (1933).

² Haber and Bonhoeffer, *Zeits. f. physik. Chemie* **A137**, 263 (1928).

³ Frankenburg and Klinkhardt, *Zeits. f. physik. Chemie* **B15**, 421 (1932).

⁴ Marshall, *J. Am. Chem. Soc.* **49**, 2763 (1927).

⁵ Bonhoeffer and Boehm, *Zeits. f. physik. Chemie* **119**, 385 (1926).

⁶ Marshall, *J. Phys. Chem.* **30**, 1078 (1926); *J. Am. Chem. Soc.* **54**, 4460 (1932).

⁷ Zemansky, *Phys. Rev.* **36**, 919 (1930).

(1×10^{-7} sec.), p is the pressure of hydrogen or oxygen in mm of mercury, and k is the number of effective collisions for mercury atom per second. It can readily be seen that these give the bimolecular reaction constants for excited mercury and hydrogen and oxygen, k_{O_2} , k_{H_2} , = 1.1 and 0.68×10^7 , respectively.⁸

Temperature coefficient of the reaction

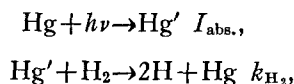
Marshall's measurements of the temperature coefficient between 50 and 100°C give apparently discordant results. For example, he finds that with an arc current of 3 amperes he obtained 1.13 per 10°C, at 5 amp., 1.04, at 3 amp., 1.03. The more recent work of Salley and Taylor over a larger temperature range indicates that the temperature coefficient has a value of 1.07 between 400 and 490°C and a value of 1.39 between 510 and 530°C.

Light intensity. (Rate of formation of hydrogen atoms)

Marshall has shown that the rate of the reaction falls off from linearity at high arc currents, indicating that the rate is proportional to either the light intensity or to some fractional power of it, depending upon how this varies with the arc current.

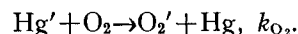
THEORETICAL CONSIDERATIONS

Since most of the quantitative data available are connected with the mercury sensitized process, it is quite obvious that we must first concern ourselves with this reaction. It is generally conceded that this result of the collision of an excited mercury atom with a hydrogen molecule is two hydrogen atoms. Thus we may write:



where $I_{\text{abs.}}$ represents the rate of absorption of light of wave-length 2537 by the mercury present in the system, or the rate of formation of excited mercury atoms. However, not all excited mercury atoms produce hydrogen atoms. Some are re-

moved by collision with an oxygen molecule,



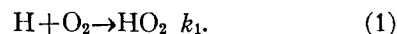
This excited oxygen molecule is undoubtedly incapable of reacting with hydrogen molecules⁹ and so any mercury atoms which transfer their energy to oxygen are "lost." Since, at the stationary state $d[\text{Hg}']/dt = -d[\text{Hg}']/dt$, it is evident that the rate of formation of hydrogen atoms will be given by the expression:

$$\frac{d[\text{H}]}{dt} = \frac{2[\text{H}_2]k_{\text{H}_2}I_{\text{abs.}}}{[\text{H}_2]k_{\text{H}_2} + [\text{O}_2]k_{\text{O}_2}}.$$

As has been stated, the values of k_{H_2} and k_{O_2} are known from quenching data, and this expression then reduces to

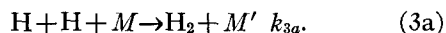
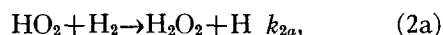
$$\frac{d[\text{H}]}{dt} = \frac{2.20[\text{H}_2]I_{\text{abs.}}}{1.10[\text{H}_2] + 0.68[\text{O}_2]}.$$

The reaction of the hydrogen atoms with oxygen molecules, is generally conceded to be



Previous to the work of Lavin and Bates¹ it was considered necessary that the molecule HO_2 so formed could only exist for an extremely short time without decomposing again to hydrogen atom and oxygen molecule, unless before this occurred the molecule suffered a collision in which it could give up its energy of formation. However, from the evidence offered by those authors it is quite plausible to write this expression in the form of a straight bimolecular reaction, at least at ordinary pressures.

The fate of the HO_2 molecule, however, has been the subject of considerable dispute. Taylor and Marshall have suggested



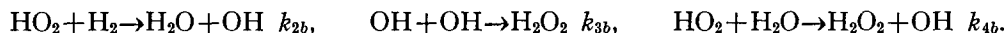
As the concluding steps of the reaction, M represents the third body in the association of two hydrogen atoms. The rate of formation of hydrogen peroxide from these reactions can be shown to be

⁸ These constants are expressed in mm reacting per mm of reactants.

⁹ Kistiakowsky, J. Am. Chem. Soc. **52**, 1868 (1930).

$$d[\text{H}_2\text{O}_2]/dt = [\text{O}_2](k_1/k_{3a})^{1/2}([\text{H}_2]k_{\text{H}_2}I_{\text{abs.}}/([\text{H}_2]k_{\text{H}_2} + [\text{O}_2]k_{\text{O}_2})M)^{1/2}. \quad \text{I}$$

The mechanism suggested by Haber, and modified by Frankenburger and Klinkhardt, may be represented as substituting for reactions (2a) and (3a) the three alternative steps:



These lead to an expression for the rate of peroxide formation:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = \left[\frac{2k_{4b}[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]k_{4b} + [\text{H}_2]k_{2b}} + 1 \right] \frac{k_{\text{H}_2}[\text{H}_2]I_{\text{abs.}}}{[\text{H}_2]k_{\text{H}_2} + [\text{O}_2]k_{\text{O}_2}}. \quad \text{II}$$

The reaction scheme which has been proposed by the present author¹⁰ in a short note is



These two concluding steps lead to a rate expression:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{k_2}{k_3^{1/2}}[\text{H}_2] \left(\frac{[\text{H}_2]k_{\text{H}_2}I_{\text{abs.}}}{[\text{H}_2]k_{\text{H}_2} + [\text{O}_2]k_{\text{O}_2}} \right)^{1/2} + \frac{[\text{H}_2]k_{\text{H}_2}I_{\text{abs.}}}{[\text{H}_2]k_{\text{H}_2} + [\text{O}_2]k_{\text{O}_2}}. \quad \text{III}$$

In order to demonstrate the unique correctness of reaction III as compared with I and II, it is necessary to show that the former can be made to explain all the observed data, and at the same time to indicate that I, and II, will fall down in its relation to one or more of the parameters of the system.

REACTION I

Reaction I gives as the primary product of the reaction 100 percent hydrogen peroxide, in agreement with the experimental results. The quantum yield can vary between zero and infinity, depending upon the magnitudes of k_1 and k_{3a} , and thus, if a completely free adjustment of these can be made, the correct quantum yield can be obtained. The variation of rate with the square root of the light intensity might possibly also be in agreement with Marshall's results, since they did not exclude a square root relationship. The variation of the rate with $[\text{H}_2]$, $[\text{O}_2]$ is shown in column 6 of Table I, by giving the constancy of $k_1(I_{\text{abs.}}/k_{3a})^{1/2}$, which should remain constant over all variations of H_2 and O_2 , if this be the correct mechanism. The value of M chosen is that of the total pressure ($[\text{H}_2] + [\text{O}_2]$). The experimental data are taken from Marshall. The value of R/N_{H_2} indicates the agreement of the empirical rate expression of Marshall, and is obtained by

¹⁰ Bates, J. Am. Chem. Soc. 55, 426 (1933). Reaction (3) was also suggested by Salley and Bates.¹

dividing the rate by the mole fraction of hydrogen. It can be readily seen that there exists no constancy in the value of $k_1(I_{\text{abs.}}/k_{3a})^{1/2}$ over the range of concentrations studied.

There might be some objection to the use of values of the total pressure for M in the rate expression I, since a collision of an O_2 molecule with two hydrogen atoms might result in the formation of a hydrogen peroxide molecule. However, it is quite easy to show that a substitution of the partial pressure of oxygen or of hydrogen for M , instead of the total pressure, does not make Eq. I fit the experimental results.

There is still another consideration which militates against the acceptance of I as the true mechanism. This is connected with the possible values of k_1 and k_{3a} . As we have already said, provided these may be chosen at liberty we can make this expression fit the quantum yield. However, we can show, from other considerations, that these constants must have values which would be in disagreement with the observed facts. Lavin and Bates have shown that k_1 must have such a value that only 1 in every thousand collisions is effective.

From this value and an approximate knowledge of the volumes of the apparatus used by Marshall, it is possible to obtain a value of the absolute magnitude of k_1 and k_{3a} . The total volume of Marshall's reaction system he estimates at 1500 cc (an explosion which destroyed his original

TABLE I.

Run No.	H ₂ mm	O ₂ mm	Rate (-Δ <i>p</i>) mm/min.	<i>R/N</i> _{H₂}	I		II				III		
					$\frac{k_1(I_{\text{abs.}})^{\frac{1}{2}}}{(k_{3a})^{\frac{1}{2}}}$	<i>I</i> _{abs.}	<i>3I</i> _{abs.}	$\left(\frac{k_2/k_3^{\frac{1}{2}}}{=1 \times 10^{-4}}\right)$	1×10^{-3}	$\frac{I_{\text{abs.}}}{1.5 \times 10^{-3}}$	2×10^{-3}	10^{-2}	Mol/h <i>v</i>
1	364	475	0.92	2.14	0.075	5×10^{-13}	1.66	1.59	1.15	0.926	0.790	0.093	1.00
2	581	239	1.52	2.14	0.238	6×10^{-10}	1.91	1.83	1.19	0.953	.772	.083	1.60
3	775	58	2.00	2.15	0.878	9×10^{-9}	2.09	1.98	1.22	0.960	.736	.071	2.08
4	781	10	2.10	2.12	5.92	3×10^{-9}	2.11	2.00	1.22	0.962	.750	.066	2.18
5	146	699	3.0 ^a	19.9	0.250		11.8		11.0	10.2			
6	425	368	12.3	21.2	1.16		20.4		16.8	15.8			0.78
7	740	20	20.	21.7	4.76		22.2		18.7	17.3			1.15
8	581	237	17-22 ^b	24.7	2.48		24.4		21.2	19.9			

Runs 1-4, arc current 1 ampere; runs 5-8, 15 amperes.

^a Value very uncertain. See Marshall, reference 4.

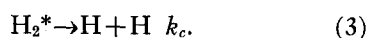
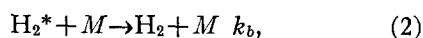
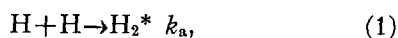
^b Also apparently uncertain. Calculations based on average value (19.5).

The rates are all expressed in Marshall's unit, mm decrease in pressure per minute. Since he was removing his hydrogen peroxide as it was formed, these are in 0.5 mm of hydrogen peroxide per minute. It is especially to be observed that *I*_{abs.} is expressed in the same units, which is equivalent to 0.5 mm of Hg' being formed per minute. Since this is so, the quantum yield is obviously given by the ratio of -Δ*p* and *I*_{abs.}. The reaction constants are expressed then, in 0.5 mm reacting per mm of reactants, since they are all bimolecular.

set-up prevented an accurate volume measurement). The total volume illuminated he estimates at 220 cc. When 1500 cc of hydrogen peroxide at 0.5 mm and 20°C have been formed, $1500 \times 1.66 \times 10^{16}$ collisions have occurred, since there are 3.32×10^{16} atoms per cc at 1 mm and 20°C. The portion of the reaction system illuminated was maintained at 60°C in these experiments. The total number of collisions per minute in this volume at this temperature, and at a pressure of 1 mm can be calculated for any given molecular species by means of the kinetic theory. (See page 463.)

The value of a bimolecular constant expressed in the units of Marshall can be seen to be equal to the ratio of these two, provided every collision is effective. This comes out to be $\approx 10^8$. Since only 0.001 of the total collisions are effective $k_1 = 10^5$.

An evaluation of k_{3a} is a bit more involved. A three-body reaction can, in general, be divided into three distinct processes: the formation of the bimolecular association product, an energy rich quasi molecule, which then may either dissociate spontaneously, or be stabilized by collision with a third body. Formulating these three for the case in hand:



Here k_a and k_b are bimolecular reaction constants, and k_c is a unimolecular reaction constant and is equal to the reciprocal of the lifetime of the energy rich molecule. The two bimolecular constants will again be of the order of 10^8 or less, as already discussed in the case of k_1 ($k_a \approx 10^8$, $k_b \approx 10^8$). They will probably not differ from 10^8 by a very large amount. k_c we can show is of the order of magnitude of 10^{14} .¹¹ The rate of formation of hydrogen molecules will be governed by reaction (2), whence

$$\frac{d[\text{H}_2]}{dt} = [\text{H}_2^*][\text{M}]k_b$$

$$= \frac{[\text{H}]^2[\text{M}]k_b k_a}{(Mk_b + k_c)} = [\text{H}]^2 M k_{3a}.$$

For ordinary pressures $M = 10^2 - 10^3$, and Mk_b is equal to $10^{10} - 10^{11}$ and may be neglected as compared with $k_c = 10^{14}$. It therefore follows immediately that

$$k_{3a} = k_b k_a / k_c = (10^8 \times 10^8) / 10^{14} = 100.$$

Substituting these values of k_1 and k_{3a} in $k_1(I_{\text{abs.}})^{\frac{1}{2}}/k_{3a}^{\frac{1}{2}}$ and solving for *I*_{abs.} we obtain the values listed under column 6 of Table I. Since the quantum yield is given by the ratio of the rate divided by *I*_{abs.}, we can quite readily see that

¹¹ Steiner, Zeits. f. physik. Chemie **B15**, 249 (1932).

the mechanism of Taylor and Marshall would call for quantum yields which are many orders of magnitude greater than those experimentally determined. For these reasons, then, this mechanism cannot be accepted at the concentrations and light intensities employed. It is quite possible that at extremely low oxygen concentrations this mechanism might be involved, but not under those conditions under which our experimental data were obtained.

REACTION II

This reaction gives the quantum yield approximately as determined, and can be made to yield high concentrations of peroxide, provided k_{4b} is much greater than k_{2b} . In fact, Salley and Bates showed that, if this be the correct mechanism, $k_{4b} = 5000 k_{2b}$. (But these authors also failed to find the dependence on water concentration which this relationship would demand.)

In attempting to discover what agreement can be obtained for this rate expression, we must make use of the necessary assumption that $k_{4b} = 5000 k_{2b}$. Marshall's gases were always saturated with water vapor at room temperature, $H_2O = 20$ mm. If we apply this fact to I it can be easily seen that $[H_2]k_{2b}/[H_2O]k_{4b} = 700/100,000 = 0.007$ whence the expression $H_2 k_{2b}$ may be neglected entirely and I simplifies to

$$\frac{d[H_2O_2]}{dt} = \frac{3k_{H_2}[H_2]I_{abs.}}{k_{H_2}[H_2] + k_{O_2}[O_2]}.$$

The constancy of $3 I_{abs.}$ is shown by the values in column 7 of Table I. Again, there is not very good agreement. This fact, coupled with the reasons contained in the discussion of Salley and Bates, makes it appear necessary to discard this reaction scheme.

REACTION III

In fitting the experimental data to Reaction III it appears immediately that $k_2/k_3^{1/2}$ is an undetermined constant, whose value must be discovered in order to evaluate the constant, $I_{abs.}$, which is used to test the validity of the mechanism. The values of $I_{abs.}$ obtained from Marshall's data for values of $k_2/k_3^{1/2}$ from 10^{-2} to 10^{-4} are given in Table I, columns 9-13. In solving for $I_{abs.}$ two positive roots are obtained. One of these can be

discarded, however, since to make this root fit Eq. III it would be necessary to take the negative value of the square root in III, which would have no physical significance under the postulates of the mechanism. If the various values of $I_{abs.}$ are plotted for each value of $k_2/k_3^{1/2}$ it can be seen that the four curves obtained for the cases where the arc current was one ampere, come very close to intersecting at a point where $k_2/k_3^{1/2} = 1.5 \times 10^{-3}$. At points above and below this they become divergent. We shall accept then this value as the correct one for the reaction system of Marshall. This constant is thus chosen arbitrarily to give the best agreement among these four $I_{abs.}$ values in runs 1-4. Once chosen, however, it must remain constant for all data (within the experimental error) and must give good agreement with the other experimental facts connected with the reaction. It can be shown that the quantum yield, the effect on the reaction of a change in light intensity and temperature are all dependent upon the magnitude of this constant, $k_2/k_3^{1/2}$. Hence, if in choosing the value for it which fits the rate expression it appears that we have been given a freely adjustable constant, this is not so, since its value must also be governed by these other parameters. It will be shown that the value which gives a constancy for $I_{abs.}$ is also in agreement with the other facts connected with the reaction, and that furthermore, there is no known reason for ascribing to $k_2/k_3^{1/2}$ any other value.

When the values of $I_{abs.}$ for the reactions which were carried out at a higher light intensity are calculated the agreement is not as good as was the case in runs 1-4. However, runs 5 and 8 are distinctly uncertain and runs 6 and 7 differ by less than 10 percent. There is nothing in these data to indicate a lack of agreement with the theory.

The quantum yields for the various runs have been calculated for $k_2/k_3^{1/2} = 1.5 \times 10^{-3}$ and are given in the last column of Table I.

As can be seen, these vary from unity to 2.18, depending upon the oxygen concentration employed. Such results are in complete agreement with the experimental determinations of this magnitude, which give values from unity to 2.5. The quantum yields will be dependent upon the light intensity, as well as the concentrations of H_2 and O_2 , and the temperature, according to III. Thus, for example, in Fig. 1 is plotted the varia-

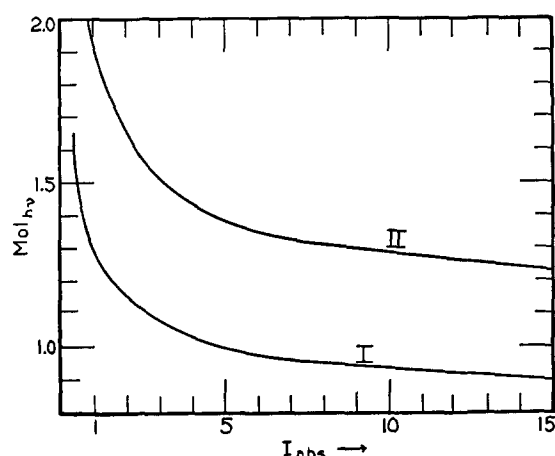


FIG. 1. Curve I: H_2 , 400 mm; O_2 , 200 mm; $k_2/(k_3)^{1/2} = 1.5 \times 10^{-3}$. Curve II: H_2 , 600 mm; O_2 , 10 mm; $k_2/(k_3)^{1/2} = 1.5 \times 10^{-3}$.

tion of quantum yield with light intensity. High light intensities should give lower quantum yields than low intensities. In seeking to find experimental verification of this prediction of III it was found that Frankenburger and Klinkhardt used intensities a hundred-fold greater than did Marshall in his quantum yield determinations. Thus Frankenburger and Klinkhardt obtained rates of formation of hydrogen peroxide of 6 grams per hour, which is equivalent to $6.06 \times (6/34) \times 10^{23} = 1.1 \times 10^{23}$ quanta per hour. Marshall employed 2.16×10^{21} quanta per minute, or 1.3×10^{21} quanta per hour. It can be seen at a glance that the data are qualitatively in agreement with the predictions, since Marshall reports a yield of 2.5 and the other authors a mean value of 1.2. The values of Frankenburger and Klinkhardt should be revised upward, since they found water in their products, which, according to the work of Bates and Salley, could only have come from a secondary peroxide decomposition. Assuming that $k_2/k_3^{1/2} = 10^{-3}$ in both cases we may calculate approximate quantum yields as called for by III. By using the values $[O_2] = 250$, $[H_2] = 510$ for Marshall, and $[O_2] = 20$, $[H_2] = 740$ for the others. The light intensities must also be correlated as to order of magnitude with the $I_{abs.}$ of Table I if we are to use this value of $k_2/k_3^{1/2}$. The number of quanta per hour represented by $I_{abs.} = 1$ is

$$\frac{6.06 \times 10^{23} \times 1500 \times 60}{22400 \times 760 \times 2} = 1.6 \times 10^{21}$$

quanta per hour, close to the intensity used by Marshall in his quantum yield measurements. Hence we shall take as the two light intensities $1.3/1.6 = 0.81$ and $110/1.6 = 69$. The quantum yields which result are 1.1 and 1.5 as compared with 1.2 and 2.5 reported. If the discrepancy were due entirely to water formed from secondary peroxide decomposition it would mean that 40 percent decomposition had occurred, close to the molecule for molecule appearance of peroxide and water suggested as possible by these authors. Mechanism I would call for an eight-fold increase of quantum yield for a decrease in light intensity of a hundred fold while II would call for a decrease under these conditions, of 20 percent. Obviously neither of these predict the experiments with the nicety of III, which calls for an increase of about 35 percent.

Temperature coefficient

The temperature coefficient predicted for the reaction by III is a function of the magnitude of $k_2/k_3^{1/2}$, and its rate of change with temperature. It will also vary with the light intensity, at least over some range of intensities, at a given tem-

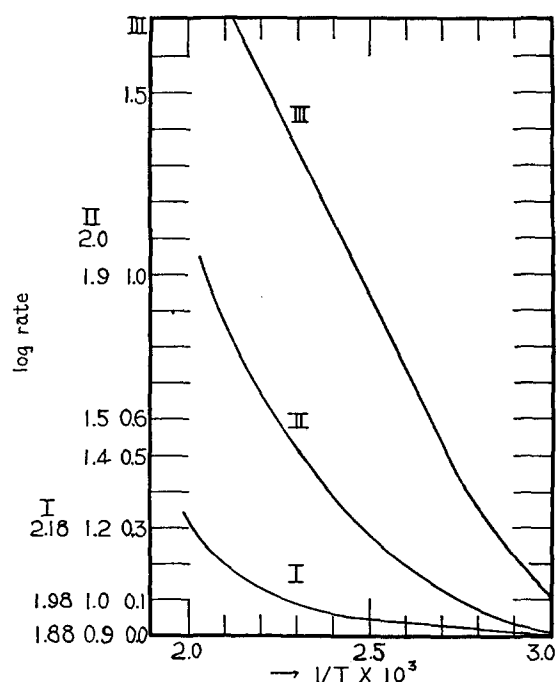


FIG. 2. Curve I, $I_{abs.} = 100$; curve II, $I_{abs.} = 10^8$; curve III, $I_{abs.} = 1$. $Q_{III} = 11.0$ cal.; $H_2 = 400$ mm; $O_2 = 200$ mm; $k_2/(k_3)^{1/2} = 1.5 \times 10^{-3}$.

perature interval. Thus, if we neglect any temperature dependence of $I_{\text{abs.}}$, which would in general be smaller than usual temperature coefficients of chemical processes, the temperature sensitive term, involving $k_2/k_3^{1/2}$, if it is of the same order of magnitude or greater than the second term which we have assumed independent of temperature, may give rise to a high temperature coefficient. If, however, this term is small with respect to the second term, which would be true for small values of $k_2/k_3^{1/2}$ and high $I_{\text{abs.}}$, the temperature coefficient may be nearly unity. Any or all conditions in between these two should be possible. (Fig. 2.)

This immediately explains some of the difficulties which Marshall mentions in his paper. In studying the kinetics of the reaction he experienced little difficulty in obtaining reproducible results. When, however, he came to measurements of temperature coefficients he found that he could not obtain as good an agreement. For example with 3 amperes current through his arc he obtains a temperature coefficient of 1.13, with 5, 1.044, with 15, 1.038. These are obviously qualitatively what might be expected from Eq. III.

It becomes of interest to calculate the temperature coefficient if $k_2/k_3^{1/2} = 1.5 \times 10^{-3}$. Reaction constants may be expressed

$$k = Z\gamma e^{-Q/RT},$$

where Z is a collision factor, γ a factor depending upon "steric" effects, and Q is the energy of activation of the process. Obviously, then

$$\frac{k_2}{k_3^{1/2}} = \frac{Z_2\gamma_2 e^{-Q_2/RT}}{(Z_3\gamma_3 e^{-Q_3/RT})^{1/2}} = 1.5 \times 10^{-3}, \quad (a)$$

$$e^{-Q_{\text{III}}/RT} = e^{(Q_{3/2} - Q_2)/RT} = \frac{(Z_3\gamma_3)^{1/2} 1.5 \times 10^{-3}}{Z_2\gamma_2}, \quad (b)$$

where $Q_{\text{III}} = Q_2 - Q_{3/2}$. Z_2 and Z_3 will be equal to the total number of collisions in the illuminated or reaction volume per minute divided by the number of collisions it takes to bring about the formation of 0.5 mm of peroxide. These can thus be calculated from the ordinary kinetic theory by using the equation for the number of collisions

per second per cc.

$$Z = 2(2\pi)^{1/2} N_1 N_2 \sigma_{12}^2 \left(\frac{m_1 + m_2}{m_1 m_2} kT \right)^{1/2} \frac{v_{60}}{VN_{20.5}},$$

where

v = Volume illuminated (= 220 cc (Marshall)),
 V = Total volume (= 1520 cc (Marshall)),
 N = No. molecules per cc at 1 mm and 20°C,
 N_1 and N_2 are the number of molecules in 1 cc at 1 mm pressure at temperature T .

The other symbols have their usual significance, and the Z 's are expressed in mm colliding per mm pressure per sec.

If we use the value for σ of the oxygen molecule as that of HO_2 , we obtain values for $Z_2 = 2.70 \times 10^8$ and $Z_3 = 5.9 \times 10^7$ at 60°C. And for any temperature,

$$Z_2 = (16.0 \times 10^{11})/T^{3/2}, \quad Z_3 = (36 \times 10^{10})/T^{3/2},$$

since N_1 and N_2 will vary inversely as the temperature of the reaction vessel.

If we knew the values of γ_2 and γ_3 it would be possible to obtain from Eq. (b) Q_{III} exactly and thus express the variation of $k_2/k_3^{1/2}$ as a function of the temperature. These values, however, would be extremely uncertain since the fact that γ_3 appears to the half power would make the absolute magnitude of the γ 's as well as the ratio of considerable importance in estimating the value of Q_{III} . For example if $\gamma_2/\gamma_3^{1/2} = 1$ ($\gamma_2 = \gamma_3 = 1$) then Q_{III} would be 11.6 cal.; if $\gamma_2/\gamma_3^{1/2} = 3$ ($\gamma_2 = \gamma_3 = 9$), $Q_{\text{III}} = 10.6$ cal. Unfortunately, the one significant value in Marshall's data (that at 3 amp.) is the result of but a single experiment which, considering alterations in arc characteristics is not sufficient data upon which to base a value of $\gamma_2/\gamma_3^{1/2}$.

It becomes of interest to go briefly through the results of Salley and Taylor and see whether their anti-Arrhenius temperature coefficient agreed with a mechanism here postulated. At high temperatures there might, however, be other factors such as branching chains bringing about the large changes in temperature coefficient in short temperature intervals. A simple calculation, however (with $Q_{\text{III}} = 11$ cal., $\text{H}_2 = 400$, $\text{O}_2 = 200$ $I_{\text{abs.}} = 4$), will show that this would require that $(KT + 10)/KT = 1.12$ at 60°C, and = 1.26 at 200° in disagreement with their observed values. It is

useless to speculate on this discrepancy with the present data on the temperature coefficient, which will be much more sensitive to changes in $k_2/k_3^{1/2}$ than is I_{abs} , in Table I. A study of the change in temperature coefficient with concentration, light intensity and temperature, would give a definite answer.

It is well to note, however, that there are several facts arising from the data of Salley and Taylor, which are in semi-quantitative agreement with the theory. In the first place, the definite, but small increase in temperature coefficient with decreased mercury pressure is understood in light of a decrease in I_{abs} . Also a marked increase in temperature coefficient with a decrease in light intensity, which only appears in the anti-Arrhenius region. Thus a comparison of the ratios of runs D_3 and D_4 , H_4 and H_5 , I_5 and I_6 , all at different light intensities shows that the increase in rate for the same temperature interval goes up four to five-fold for a six-fold decrease in light intensity.

Objections to the theory

Aside from the lack of exact agreement with the temperature coefficients of Salley and Taylor noted in the last section the theory fits the results with considerable success. Objections may be raised that most of the measurements were conducted in flowing or circulating systems and hence that the assumptions of stationary states used in deriving the kinetics may not be valid. Marshall,¹² however, has been able to get similar, but not such exact results from a static system at 50°C. The low temperature, static experiments of Barak and Taylor,¹³ are entirely unexplained. The author is inclined to the belief that in this case we are dealing with complex diffusion phenomena involving the alternate oxidation and reduction of mercury and mercuric oxide. An objection based on the fact that oxygen does not enter into the reaction kinetics equation (except in quenching) is certainly valid for some low pressure of oxygen. This can be allowed for by considering in the kinetics the possibility of hydrogen atom recombination. This leads to a complicated fourth degree equation in HO_2 with which it is not practical to deal. The lack of agree-

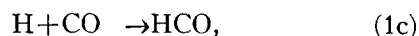
ment of I with the results indicates that this does not concern us at higher oxygen pressures. The fact that Reaction II might be too strongly endothermic (32 cal.) to be worth considering would give some difficulty were the two hydrogen atoms adding to an oxygen molecule to give off an equal amount of energy (69 cal.). However, Professor Bodenstein has, in a private communication informed the author that according to some unpublished data the first goes on with the liberation of 40 cal., the second with 98 cal., which removes this objection.

APPLICATIONS TO OTHER REACTIONS

The theory of the reaction of hydrogen atoms and oxygen given here will have a bearing on the kinetics of many reactions. A mention should be made of the possibly necessary alteration of some of our ideas of the mechanisms of certain more important examples of these.

Hydrogen—carbon monoxide

A close parallel exists between the mechanism suggested and that advanced by Frankenburger¹⁴ for the mercury sensitized formation of formaldehyde and glyoxal from hydrogen and carbon monoxide. The analogous reactions as given by our mechanism would be



Reaction II, it is claimed by him, does not take place, and, indeed, the fact is substantiated by a quantum yield less than 2 aldehyde groups per quantum. He suggests (1c), (3c) and (4c) as the mechanism.

Hydrogen chlorine reaction

The author has already given the bearing on this reaction of the necessity of allowing HO_2 formation to take place in a bimolecular reaction between a hydrogen atom and an oxygen molecule. The success of the same assumption in the present work only serves to emphasize the importance of taking this into account in the

¹² Marshall, J. Phys. Chem. **30**, 34 (1926).

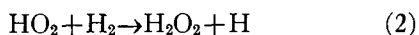
¹³ Barak and Taylor, Trans. Faraday Soc. **28**, 569 (1932).

¹⁴ Frankenburger, Zeits. f. Electrochemie **36**, 757 (1930).

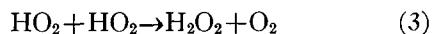
theoretical treatments of the effect of oxygen on the hydrogen chlorine reaction. In the earlier discussion it was shown that the reaction



did not necessarily end a $\text{H}_2 - \text{Cl}_2$ chain, since for example, the reaction



propagated the chain. The chain can, however, now, quite definitely be broken by reaction (3)



but only some fraction of the atoms removed by (1) really result in broken chains.

Photodissociation of hydrogen peroxide

This reaction has been treated in papers by von Elbe and Lewis¹⁵ and von Elbe.¹⁶ Their theoretical discussion is based entirely upon the mechanism of Haber and Bonhoeffer which, as we can see, is wrong. The author offered cogent reasons why this mechanism should not be so completely accepted when von Elbe presented his work at the Buffalo meeting in 1931. My objection was based upon the earlier work of Bates and Taylor,¹⁷ and of Marshall. The fact that the mechanism of Haber and Bonhoeffer is not definitely proven is also mentioned by Frankenburg and Klinkhardt in their final paper on this subject. It is quite obvious that in the light of the present work this subject is opened for a complete reconsideration.

The "anti-Arrhenius" temperature coefficient

The appearance of an "anti-Arrhenius" temperature coefficient in a reaction has been used as a criterion for the existence of a long chain. It would appear that this should be used with

¹⁵ von Elbe and Lewis, *J. Am. Chem. Soc.* **54**, 552 (1932).

¹⁶ von Elbe, *J. Am. Chem. Soc.* **55**, 62 (1933).

¹⁷ Bates and Taylor, *J. Am. Chem. Soc.* **49**, 2438 (1927).

caution, since the mechanism suggested here gives one when the "chain" part of the reaction rises from an extremely small value to unity.

Oxidation processes in general

It is quite well to note that in suggesting that the oxidation of hydrogen atoms,—the simplest process of oxidation,—goes through the intermediate peroxide, HO_2 , we are bringing this oxidation in agreement with numerous others¹⁸ in which the peroxide intermediate has been detected. Of more specific interest is the bearing this bimolecular peroxide formation has on the oxidation of methyl groups studied by Bates and Spence.¹⁹ They attempt to disprove the possibility of intermediate peroxide formation by showing the lack of effect of excess nitrogen on their reaction, assuming that the nitrogen would tend to stabilize the bimolecularly associated peroxide (CH_3O_2). This study, of course, proves nothing inasmuch as the methyl peroxide will probably need no such third body, if HO_2 needs none. Thus, it must be remembered that either of the two mechanisms, involving peroxide or hydroxyl, are equally well substantiated by their experimental results.

The evidence which has been offered that the mechanism suggested by Haber and Bonhoeffer cannot be the true one at low temperatures does not of necessity rule out the possibility of the more important postulates of these authors being involved in the high temperature or explosive reaction of hydrogen and oxygen. For example, although the intermediate hydroxyl group which is characteristic of their mechanism and which is spectroscopically found in hydrogen oxygen flames, is ruled out in the mechanism suggested, there is always the possibility of these being formed at the higher temperatures.

¹⁸ Callendar, *Engineering* **123**, 147, 182, 210 (1927). Bone and Hill, *Proc. Roy. Soc.* **A129**, 434 (1930), etc.

¹⁹ Bates and Spence, *J. Am. Chem. Soc.* **53**, 1689 (1931); *Trans. Faraday Soc.* **123**, 468 (1931).