

# Interpretation of the Slow Reaction and Second Limit of Hydrogen Oxygen Mixtures by Computer Methods

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Computer programmes have been developed which calculate the reaction rate and second limit of  $\text{H}_2 + \text{O}_2 + \text{N}_2$  mixtures for a given set of velocity constant ratios. By coupling these to an optimization programme, a limited number of ratios can be adjusted to give minimum deviation between observed and calculated rates or limits. A more elaborate programme for reaction rate allows for consumption of reactants and permits the maximum reaction rate to be calculated. The use of these programmes both to establish a detailed mechanism and to obtain some velocity constant ratios over the temperature range 470–530°C is described. The best available values for the Arrhenius parameters of the reactions involved are summarized.

In boric-acid-coated vessels aged by repeated use, the slow reaction between  $\text{H}_2$  and  $\text{O}_2$  is highly reproducible.<sup>1</sup> A mechanism has been developed<sup>2</sup> for this reaction and, by making reasonable assumptions, analytical expressions have been obtained which provide a precise interpretation of the slow reaction and second limit<sup>3</sup> over a wide range of mixture composition. With the precision of interpretation that becomes possible, it is now feasible to use slowly reacting hydrogen+oxygen mixtures as a source of free radicals  $\text{H}$ ,  $\text{O}$ ,  $\text{OH}$  and  $\text{HO}_2$ , whose concentrations can be varied considerably by change in mixture composition and total pressure, and to study their reaction with added materials. Such studies have already been made with carbon monoxide,<sup>4</sup> methane<sup>5</sup> and neopentane.<sup>6</sup> Detailed interpretation of such studies requires a re-examination of the small approximations inherent in the analytical treatment of the slow reaction and limit.

With the availability of computer facilities, interpretation by computer programmes offers a way of analyzing the situation, and this paper discusses the interpretation of the slow reaction and second limit by such methods.

## EXPERIMENTAL

The second-limit measurements are those previously reported at 500°C by Baldwin, Mayor and Doran,<sup>3</sup> together with previously unpublished results at other temperatures, and the general experimental procedure has already been described. For these measurements, the thermocouple was placed at the point of maximum temperature in the furnace, since explosion will develop from this point.  $\text{H}_2\text{O}_2$  takes some time to reach its equilibrium concentration at temperatures below 500°C,<sup>7</sup> and the procedures adopted were those that gave the highest value for the second limit. Pressure changes in the slow reaction were followed by a pressure transducer. This facilitated the evaluation of the maximum rate.

Three independent measurements of rate were available. In the most recent (SJW), the thermocouple was placed at a point giving the average temperature along the reaction

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vessel. Earlier measurements, made by Doran (PD) and by Jackson (DJ) with the thermocouple at the point of maximum temperature, were corrected (*ca.* 5 %) for the fact that the mean temperature was 1.0°C below the maximum temperature. The corrections were obtained using the computer programme III to calculate the reaction rates of each mixture at two temperatures differing by 1°C, using reasonable temperature coefficients for the reactions involved. As Doran's results were the most extensive, these were used as one set involving twenty mixtures, while a second set was obtained using the mean values of the reaction rate for the thirteen mixtures common to all three studies.

## DISCUSSION

### COMPUTER TREATMENT

Using the reaction mechanism given in the preceding paper<sup>8</sup> together with the resultant equations (6)-(19), three main types of computer programme have been developed.

#### PROGRAMME III: SIMPLE SLOW REACTION

(i) Steps (i), (ii) and (iii)(a)-(e) of programme I<sup>8</sup> are used to obtain the equilibrium  $\text{H}_2\text{O}_2$  and radical concentrations for a given mixture with a given set of parameters  $R_1$ - $R_9$ . (ii) The reaction rate is obtained from eqn. (19), the processes then being repeated for all the mixtures under examination, and the r.m.s. deviation between observed and calculated rates obtained. (iii) If desired, the above programme III can be coupled to an optimization programme which adjusts a pre-selected number of the parameters  $R_1$ - $R_9$  until minimum r.m.s. deviation is obtained—programme III-M.

#### PROGRAMME IV: ALLOWANCE FOR CONSUMPTION OF REACTANTS

This programme follows exactly the procedure<sup>8</sup> of programme II and gives the maximum rate of each mixture for a given set of the parameters  $R_1$ - $R_9$ . This programme was considerably slower (7 min per mixture with an Elliott 803) than programme III (7 sec per mixture). Further, since the finite value of  $n$  limited accuracy to about 0.1 %, the rate was not a continuous function of the parameters, and this programme was unsuitable for coupling to an optimization programme.

#### PROGRAMME V: SECOND LIMIT

At the second limit, the cubic in  $G$  (eqn. (18))<sup>8</sup> has two equal positive roots. The basic programme III is used, with the following modifications. (i) A pressure  $P$  is estimated, and the reactant concentrations evaluated from the mole fractions. (ii) Using the successive approximation procedure (iii)(a)-(iii)(e) of programme I, the equilibrium peroxide concentration is obtained. (iii) By differentiation of the cubic equation in  $G$ , the value of  $G$  at the minimum of the cubic is obtained. (iv) If insertion of this value makes the cubic function positive,  $P$  is too low; if negative,  $P$  is too high. The cycle (i)-(iii) is repeated with different pressures until two pressures within a specified accuracy cause a change in sign of the cubic function. (v) By working out the r.m.s. deviation between observed and calculated limits, and coupling to an optimization programme, the optimum value of selected  $R$  parameters can be obtained.

### APPLICATION OF COMPUTER PROGRAMMES

#### SENSITIVITY TO PARAMETERS

Programmes III and V were first used to investigate the sensitivity of the slow reaction and limit to the various parameters. With the parameters  $R_2$ - $R_9$  set close

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to their final values, each in turn was varied 10 %. The results in table 1 show that the second limit is determined predominantly by the parameters  $k_7$ ,  $k_2/k_4$  and  $k_8/k_2k_{10}^{\frac{1}{2}}$ . The main parameters determining the induction period are  $k_7$ ,  $k_2/k_4$ , and  $k_{11}/k_{10}^{\frac{1}{2}}$ , while the slow reaction is largely determined by  $k_7$ ,  $k_2/k_4$ ,  $k_{14}/k_2$ ,  $k_{15}/k_1$ ,\* and  $k_{11}/k_{10}^{\frac{1}{2}}$ . These conclusions are effectively in agreement with the equations developed in an earlier analytical treatment. To develop this analytical treatment, it was necessary to neglect reaction (8) in the slow reaction, and to neglect (11) at the limit and to make further reasonable assumptions. Introduction of (8) and (11) simultaneously, and of other reactions such as (11a), (13) and (14a), and surface destruction of H, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, complicates the analytical treatment to a point where the validity of the approximations necessary is no longer clear. On the other hand, these additional reactions can easily be introduced into the computer treatment and operate mainly by altering the terms  $A_9$ - $A_{12}$ , and the equation for I.

TABLE 1.—EFFECT OF PARAMETERS ON SECOND LIMIT, INDUCTION PERIOD, AND REACTION RATE

effect of 10 % increase in	second limit		induction period C	D	reaction rate E	F
	A	B				
$R_2 = k_7$	+1.1	-4.1	-6.4	+8.2	+11.8	+10.0
$R_3 = k_2/k_4$	+10.0	-27.8	-5.3	0.0*	-2.6	+12.4
$R_4 = k_{14}/k_2$	-0.5	+2.3	-2.3	-5.7	—	—
$R_5 = k_{15}/k_1$	-0.1	+0.3	-0.3	-1.0	—	—
$R_7 = k_{11}/k_{10}^{\frac{1}{2}}$	+0.2	-1.1	-5.7	+3.7	+6.8	-1.1
$R_8 = k_8/k_2k_{10}^{\frac{1}{2}}$	+2.5	—	-0.1	+0.4	+0.2	+0.2
$R_9 = k_{14a}/k_2$	-0.5	+1.7	-0.3	-1.0	-2.0	0.0

\* There is no change in rate for the standard mixture, but for most mixtures there is a small increase in rate, usually 1-2 %. A, % increase in limit for standard mixture ( $x = 0.28$ ,  $y = 0.14$ ); B, % increase in optimum value of  $k_8/k_2k_{10}^{\frac{1}{2}}$ ; C, % increase in induction period for standard mixture; D, % increase in reaction rate for standard mixture; E, % increase in optimum value of  $k_{14}/k_2$ ; F, % increase in optimum value of  $k_{15}/k_1$ .

It is not realistic to use the computer programme for slow reaction, induction period, and second limit, to evaluate all the seven parameters  $R_2$ - $R_9$ , particularly as some of these can be obtained more accurately by independent methods.  $k_7$  is obtained most accurately by fitting statistically the equation  $k = A \exp(-E/RT)$  to the results of Baldwin and Brattan<sup>9</sup> for the homogeneous decomposition of H<sub>2</sub>O<sub>2</sub> over the temperature range 440-560°C, giving the values  $A = 3.19 \times 10^{14}$  l. mole<sup>-1</sup> sec<sup>-1</sup> ( $M = N_2$ ),  $E = 47.0$  kcal/mole. In these experiments the temperature quoted is the average over the reaction vessel, since allowance was made for the temperature distribution. Analytical treatments of the slow reaction and limit have suggested that reaction (14) is the predominant reaction of H atoms with H<sub>2</sub>O<sub>2</sub>. The sequence (7), (1) and (14) gives rise to a chain decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of H<sub>2</sub>, the chain length being determined at low H<sub>2</sub> concentrations by the competition between (14) and (14a), the latter reaction terminating the chain. From the chain length at high H<sub>2</sub> concentrations,<sup>4</sup>  $k_{14a}/k_{14} = 0.16 \pm 0.01$  at 440°C and is not expected to vary significantly with temperature over a 60°C range.  $k_2/k_4$  is obtained most accurately from the second limit in KCl-coated and other salt-coated vessels, allowance being made if necessary for the occurrence both of reaction (11) and of surface termination of H atoms.

$k_7$ ,  $k_{14a}/k_{14}$  and  $k_2/k_4$  have thus been taken as fixed points in the computer programme. Optimization of the second limit results gives  $k_8/k_2k_{10}^{\frac{1}{2}}$ , this parameter

\*  $k_{15}/k_1$  has most effect on the rate at low H<sub>2</sub>/O<sub>2</sub> ratios.

having almost negligible influence on the induction periods and slow reaction (table 1). Optimization of the induction period results gives  $k_{11}/k_{10}^{\frac{1}{2}}$ , and the slow reaction results are optimized to give  $k_{14}/k_2$ ,  $k_{15}/k_1$ . The programmes have also been used to examine the possible importance of reactions (11a) and (13).

#### EFFECT OF PRIMARY INITIATION RATE

The effect of the primary initiation rate  $R_1$  (assumed to produce  $\text{H}_2\text{O}_2$  and to be independent of mixture composition) is most marked with induction periods. As shown in the preceding paper, a value of  $R_1 = 0.01 \text{ mm Hg min}^{-1}$  is too high, the most probable value lying between 0.001 and 0.0001. The computer programme showed that at  $500^\circ\text{C}$ , increase in  $R_1$  from 0.0001 to 0.001 affected the rate by less than 0.01 mm Hg/min ( $>0.2\%$ ), and that further increase to 0.01 produced an increase in rate of about 0.05 mm Hg/min (0.3–2%, depending on mixture composition). Over the probable range of values, the effect of  $R_1$  on the rate of the slow reaction is thus negligible.

Since second limit pressures at  $500^\circ\text{C}$  are *ca.* 100 mm Hg, the value of  $R_1$  is almost certainly reduced. The figures below show the effect of  $R_1$  (assumed independent of pressure) on the second limit (mm Hg) for two mixtures, with  $\text{H}_2$  mole fraction 0.28 and  $\text{O}_2$  mole fractions of 0.14 and 0.0125 respectively for fixed parameters  $R_2$ – $R_9$ .

$R_1$	0.1	0.01	0.001	0.0001	0.00001
$P_2$ ( $y = 0.14$ )	93.12	92.62	92.56	92.55	92.55
$P_2$ ( $y = 0.0125$ )	156.02	146.77	145.13	144.94	144.93

Over the range of probable values,  $R_1$  has little effect on the limit.

#### REACTIONS (11) AND (11a)

Reactions (11) and (11a) have similar kinetic effects, increasing the rate as the  $\text{H}_2$  concentration is increased. The analytical treatment<sup>2</sup> gives the rate expression as:

$$d[\text{H}_2\text{O}]/dt = 2k_7[\text{H}_2\text{O}_2][\text{M}]^{\frac{1}{2}}G. \quad (\text{i})$$

The occurrence of reaction (11) increases the rate by increasing  $[\text{H}_2\text{O}_2]$ , the factor  $G$ , which is near unity, being only slightly modified by inclusion of (11). In contrast, reaction (11a) does not affect the value of  $[\text{H}_2\text{O}_2]$ , but increases the rate by increasing<sup>2</sup> the factor  $G$ . Moreover, the analytical treatment<sup>2</sup> shows that whereas the term  $(k_{11}/k_{10}^{\frac{1}{2}})$  is multiplied by the factor  $k_4[\text{M}]/k_2$ , the term involving  $k_{11a}/k_{10}^{\frac{1}{2}}$  is not, so that a much higher value is required. Using the analytical treatment,<sup>2</sup> reaction (11) was preferred to (11a) on the following grounds. (a) The variation of rate with total pressure and inert gas addition supports (11) rather than (11a). (b) Since the term  $(k_{11}/k_{10}^{\frac{1}{2}})$  is multiplied by the pressure-dependent factor  $k_4[\text{M}]/k_2$ , the contribution of (11) should be much less important at the limit than in the slow reaction, whereas with (11a), the reaction should be important in the slow reaction and at the limit, since the pressure-dependent multiplying factor is absent. The absence of any abnormal affects of high concentrations of  $\text{H}_2$  at the second limit thus provides support for (11). (c) Determination of the  $\text{H}_2\text{O}_2$  content of samples taken from the reaction vessel over a range of composition enables  $k_7$  to be determined from expression (i). The results were more consistent with the direct determination of  $k_7$  if (11) rather than (11a) was used.

In principle, the value of the parameter  $k_{11}/k_{10}^{\frac{1}{2}}$ , or the corresponding  $k_{11a}/k_{10}^{\frac{1}{2}}$ , can be determined solely from slow reaction studies by optimizing with respect to the

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three variables  $k_{11}/k_{10}^{\frac{1}{2}}$ ,  $k_{14}/k_2$  and  $k_{15}/k_1$ . This triple optimization proved extremely slow on the computer, however, and it was more convenient to select a series of values of  $k_{11}/k_{10}^{\frac{1}{2}}$  and carry out double optimizations with respect to  $k_{14}/k_2$  and  $k_{15}/k_1$ , locating by inspection the values which gave minimum r.m.s. deviation. However, the r.m.s. deviation changed rather slowly with  $k_{11}/k_{10}^{\frac{1}{2}}$ , as shown in table 2.

TABLE 2.

$k_{11}/k_{10}^{\frac{1}{2}}$	$k_{11a}/k_{10}^{\frac{1}{2}}$	$k_{14}/k_2$	optimum values for	
			$k_{15}/k_1$	% r.m.s. deviation
0.0010	0	247	4.70	4.68
0.0011		263	4.65	4.30
0.0012		279	4.60	4.06
0.0013		295	4.55	3.95
0.0014		312	4.49	3.95
0.0015		328	4.43	4.06
0.0016		345	4.39	4.24
0	0.008	235	4.78	7.42
	0.009	258	4.68	6.73
	0.010	282	4.58	6.24
	0.011	309	4.45	5.94
	0.012	336	4.33	5.86
	0.014	397	4.06	6.27
	0.015	430	3.91	6.69

A more satisfactory procedure is to use the induction period programme to obtain the optimum value of  $k_{11}/k_{10}^{\frac{1}{2}} = 0.00119$ , as described in the previous paper. The corresponding optimum values of  $k_{11a}/k_{10}^{\frac{1}{2}}$  are 0.0094 from Jackson's results and 0.0092 from Webster's results, the mean value being 0.0093. The minimum r.m.s. deviation is 4.0 % with reaction (11) and 3.0 % with reaction (11a), so that induction period measurements do not distinguish between these two reactions.

TABLE 3.

$k_{11}/k_{10}^{\frac{1}{2}}$	$k_{11a}/k_{10}^{\frac{1}{2}}$	$k_{14}/k_2$	optimum values of	
			$k_{15}/k_1$	r.m.s. deviation
0	0.0094	266	4.64	6.3
0.00119	0	277	4.40	3.9

TABLE 4.

	initial mixture mm Hg		ratio of rates		$R_{560}/R_{210}$	
	H <sub>2</sub>	O <sub>2</sub>	obs.	calc. (11), (15)	calc. (11a), (15)	calc. (11), (13)
increase in total pressure	140	70	6.10	6.5	4.8	7.3
addition of inert gas	140	70	1.55	1.63	1.31	1.75
addition of inert gas	59	151	1.39	1.45	1.24	1.85
addition of inert gas	181	29	1.52	1.63	1.23	1.67

The values of  $k_{14}/k_2$  and  $k_{15}/k_1$  which, combined with these values, give the minimum r.m.s. deviation for 20 mixtures (PD) are summarized in table 3. Although the smaller r.m.s. deviation provides some support for reaction (11) rather than (11a), this evidence is not decisive.

The effect of total pressure and inert gas addition depends on whether (11) or (11a) is used. Table 4 shows the experimental and calculated rates when the pressure

is changed from 210 to 560 mm Hg, either by increasing the total pressure of reactants, or by addition of 350 mm Hg of inert gas. Although these results again provide support for (11) rather than (11a), they are not conclusive in view of the possible errors ( $\pm 4\%$ ) in the measurement of the rate at low pressures.

It is not possible to distinguish effectively between (11) and (11a) from the variation of the second limit with oxygen mole fraction, the r.m.s. deviations being 1.5 and 3.8 % respectively, the corresponding values of  $k_8/k_2k_{10}^\ddagger$  being 10.4 and 6.7 (mm Hg min) $^\ddagger$  respectively. Some evidence against (11a) is provided by the systematic deviations obtained with this reaction, the calculated limits being some 4 mm Hg low at high O<sub>2</sub> mole fractions, and some 10 mm Hg high at low O<sub>2</sub> mole fractions. Reactions (11) and (11a) differ slightly in their effect on the second limit when the H<sub>2</sub> mole fraction is varied. This is shown in table 5.

TABLE 5.

mole fraction			second limit mm Hg		
H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	with (11)	with (11a)	obs.
0.86	0.14	0.00	64.6	67.6	65.5
0.56	0.14	0.30	76.3	77.7	78.5
0.28	0.14	0.58	92.5	90.6	94.0
0.14	0.14	0.72	103.3	98.5	102.5
0.07	0.14	0.79	108.3	101.6	105.5

The variation of limit between 0.14 and 0.86 mole fraction supports (11) rather than (11a), but at the lowest mole fraction of H<sub>2</sub>, the observed limit is below the calculated limit. This may be due to the occurrence of some additional reaction such as OH + HO<sub>2</sub>, since at even lower mole fractions of H<sub>2</sub>, the explosion disappears.

The above evidence, though supporting reaction (11), is not decisive. The most striking difference between the effects of (11) and (11a) is that (11) increases the rate by increasing the stationary concentration of H<sub>2</sub>O<sub>2</sub>, whereas (11a) increases the chain length. Table 6 shows the experimental and calculated values of the maximum H<sub>2</sub>O<sub>2</sub> concentrations for two mixtures of different H<sub>2</sub> content. The experimental values would be expected to be a little low due to loss of H<sub>2</sub>O<sub>2</sub> during sampling. The two results obtained support (11) decisively, but a more complete set of determinations is planned.

TABLE 6.

mixture composition (mm Hg)			partial pressure of H <sub>2</sub> O <sub>2</sub>		
H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	obs.	calc. (11)	calc. (11a)
140	70	290	0.22	0.288	0.185
430	70	0	0.49	0.532	0.195

#### RELATIVE IMPORTANCE OF REACTIONS (13) AND (15)

Reactions (13) and (15) have similar kinetic effects, particularly if the mixture composition is changed at constant pressure. This is shown in table 7 using the

TABLE 7.

optimum values of			r.m.s. deviation
$k_{13}/k_3$	$k_{15}/k_1$	$k_{14}/k_2$	
0	4.4	277	3.9
55	0	278	3.5

20 mixtures (PD). As shown in the last column of table 4, however, reaction (13) is much less effective in predicting the effect of inert gas and total pressure.



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Studies<sup>10</sup> of the sensitizing effect of  $H_2$  on the decomposition of  $H_2O_2$  indicate that the ratio  $k_{15}/k_1 = 3.9 \pm 0.2$  at  $440^\circ C$ , and little change with temperature would be expected. This is sufficiently close to the value of  $4.7 \pm 0.3$  (see later) as the best value from slow reaction studies with  $k_{13}/k_3 = 0$  as to suggest that reaction (13) is of little importance. An upper limit for  $k_{13}/k_3$  can be obtained by optimizing the slow reaction results with respect to  $k_{14}/k_2$  and  $k_{13}/k_3$ , using the value of 3.9 for  $k_{15}/k_1$ , when  $k_{13}/k_3 = 7.0$  is obtained.

## CONSUMPTION OF REACTANTS

Because of the autocatalytic nature of the reaction, significant consumption of reactants has occurred with most mixtures by the time maximum rate has been reached. Three methods of handling this situation were used. (i) The pressure change at the point of maximum rate was estimated experimentally, and allowance made in the computer programme III for the consequent changes in  $[H_2]$ ,  $[O_2]$ ,  $[M]$  and  $[M']$ . However, although the maximum rate could be measured to  $\pm 2.3\%$ , it was more difficult to decide the exact point at which maximum rate was reached. Three estimates have been made, one (A) by Doran using his results, and two by Webster, one (B) corresponding to the beginning of the straight line portion and one (C) corresponding to the middle. (ii) Using velocity constant parameters close to those finally selected, programme IV was modified to give estimates of the water formed at maximum rate. These were then used with the measured rates in programme III. (iii) Using parameters close to those finally selected, programme III was used to obtain the reaction rates that would have been obtained in the absence of reactant consumption, and programme IV was used to obtain the predicted rates allowing for reactant consumption. This gave a correction (varying between 35% at high  $O_2/H_2$  ratios to 2% at low ratios) which could be applied to the experimental rates to allow them to be used in the faster programme III-M with the consumption set at zero. The optimum values of  $k_{14}/k_2$ ,  $k_{15}/k_1$  obtained by each of these procedures is summarized below.

procedure	(i)A	(i)B	(i)C	(ii)	(iii)
$k_{14}/k_2$	286	281	266	282	272
$k_{15}/k_1$	4.9	5.5	4.6	4.6	4.8

SJW rates were used for these calculations. The changes in the parameters, particularly  $k_{15}/k_1$ , from (i)B to (i)C show that the procedure is sensitive to exact estimation of the pressure change at maximum rate. The agreement of procedures (ii) and (iii) suggest that the final values of  $k_{14}/k_2$ ,  $k_{15}/k_1$  should be accurate to about  $\pm 4\%$ .

## AGREEMENT OF DIFFERENT RESULTS

Two sets of results were used in the final evaluation of  $k_{14}/k_2$  and  $k_{15}/k_1$  at  $500^\circ C$ . The rates obtained for 20 mixtures by PD were used directly. For the 13 mixtures studied by SJW, the average value of the results of PD, DJ and SJW were taken. The agreement of the two sets of results is given below

rates	optimum values of		
	$k_{14}/k_2$	$k_{15}/k_1$	r.m.s. deviation
PD, 20 mixtures	279	4.6	4.3
average, 13 mixtures	262	4.9	4.6

The mean values of  $k_{14}/k_2 = 270$ ,  $k_{15}/k_1 = 4.7$  should be accurate within 4%. The agreement between the average observed rates and calculated rates for these values of the parameters is given in table 8.

TABLE 8.—OBSERVED AND CALCULATED RATES  
(rates as pressure change, mm Hg/min)

mole fraction		500°C		480°C		470°C	
H <sub>2</sub> mm Hg	O <sub>2</sub> mm Hg	R(obs.)	R(calc.)	R(obs.)	R(calc.)	R(obs.)	R(calc.)
140	360	17.0	15.8	5.35	4.88	3.26	2.96
	280	15.2	14.0	4.94	4.58	2.99	2.80
	140	9.72	9.44	3.62	3.52	2.29	2.21
	70	6.07	5.99	2.43	2.42	1.56	1.55
	35	3.77	3.70	1.57	1.54	1.00	1.00
430	70	15.7	16.3	7.01	7.51	4.77	5.09
280		10.3	10.5	4.53	4.64	3.06	3.08
70		3.90	3.97	1.41	1.42	0.84	0.87
35		2.74	2.81	0.83	0.87	0.48	0.51
35	140	3.82	4.07	1.06	1.09	0.59	0.63
35	280	5.13	5.35	1.24	1.25	0.68	0.71
70		8.86	8.64	2.26	2.35	1.43	1.38
220		21.9	20.0	7.80	7.44	5.14	4.69
r.m.s. deviation		4.8 %		4.7 %		5.3 %	

## OPTIMIZATION OF SECOND LIMIT RESULTS

As table 1 shows, the second limit is sensitive to  $k_7$ ,  $k_{14}/k_2$ ,  $k_2/k_4$  and  $k_8/k_2k_{10}^\ddagger$ .  $k_7$  has been independently determined, and in principle, both  $k_2/k_4$  and  $k_8/k_2k_{10}^\ddagger$  can be evaluated by optimization of the second-limit measurements in boric-acid-coated vessels over a wide range of O<sub>2</sub> mole fraction. The values obtained using 11 mixtures with O<sub>2</sub> mole fractions from 0.72 to 0.0125 are  $k_2/k_4 = 19.4$  mm Hg ( $M = H_2$ ),

TABLE 9.—OBSERVED AND CALCULATED SECOND LIMITS

mole fractions		500°C		480°C	
H <sub>2</sub>	O <sub>2</sub>	P(obs.) mm Hg	P(calc.) mm Hg	P(obs.) mm Hg	P(calc.) mm Hg
0.28	0.72	82.0	80.7	57.0	56.8
	0.56	83.0	81.4	57.0	57.4
	0.42	84.5	82.8	58.0	58.6
	0.28	86.5	85.7	59.5	60.8
	0.14	93.5	92.6	64.5	66.0
	0.10	97.5	97.0	71.5	69.2
	0.07	104.0	102.3	74.0	73.2
	0.035	116.5	115.6	84.0	82.9
	0.025	123.0	123.7	89.5	88.9
	0.0175	132.0	133.8	95.0	96.3
	0.0125	140.5	145.1	—	—
r.m.s. deviation		1.6 %		1.6 %	

$k_8/k_2k_{10}^\ddagger = 8.9$  (mm Hg min)<sup>1/2</sup> with a r.m.s. deviation of 0.8 %. This value for  $k_2/k_4$  is in close agreement with the value of 18.5 mm Hg obtained from second limit measurements in salt-coated vessels, allowance being made if necessary for the occurrence both of reaction (11) and of surface termination of H atoms. It is considered more realistic to use this latter value for  $k_2/k_4$ , and to optimize the second limit results in boric-acid-coated vessels with respect to  $k_8/k_2k_{10}^\ddagger$  only, when a value of



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10.4 is obtained with a r.m.s. deviation of 1.6 %. The agreement between observed and calculated second limits is summarized in table 9. The best presently available

TABLE 10—VELOCITY CONSTANT PARAMETERS USED IN CALCULATIONS

temp. °C	Units in mm Hg, min; M = H <sub>2</sub> in reactions (4), (7).					
	460	470	480	500	520	530
$R_1 = \theta$	$5 \times 10^{-5}$	$5 \times 10^{-5}$	$7 \times 10^{-5}$	$1 \times 10^{-4}$	$2 \times 10^{-4}$	$2 \times 10^{-4}$
$R_2 = k_7$	0.0095	0.0145	0.0219	0.0481	0.1013	0.1450
$R_3 = k_2/k_4$	9.0*	10.9	13.0	18.5	26.0	30.5
$R_4 = k_{14}/k_2$	330*	306	281	270	230	221
$R_5 = k_{15}/k_1$	6.2*	6.0	5.7	4.7	6.2	5.2
$R_6 = k_{13}/k_3$	0	0	0	0	0	0
$R_7 = k_{11}/k_{10}^{\frac{1}{2}}$	$5.0 \times 10^{-4}$	$6.4 \times 10^{-4}$	$7.6 \times 10^{-4}$	$11.9 \times 10^{-4}$	$17.5 \times 10^{-4}$	$21.1 \times 10^{-4}$
$R_8 = k_8/k_2 k^{\frac{1}{2}}$	22.0†	20.0†	16.6	10.4	8.0†	6.0†
$R_9 = k_{14a}/k_2$	52*	49	46	43	37	35

\* assessed from values at 470–500°C; † assessed from values at 480 and 500°C.

parameters for the H<sub>2</sub> + O<sub>2</sub> reaction at 500°C, which have been used in the calculations of tables 8 and 9, are summarized in table 10, together with the values at other temperatures.

## CALCULATIONS AT OTHER TEMPERATURES

Using the values of  $k_{11}/k_{10}^{\frac{1}{2}}$  obtained from induction period measurements, calculations were also carried out at 480 and 470°C. The values of  $k_7$ ,  $k_2/k_4$  are given in table 10 and values for  $k_{14a}/k_2$  of 46, 49 respectively were assumed using the value of  $k_{14}/k_2$  with  $k_{14a}/k_{14} = 0.16$ . Since the primary initiation rate  $R_1$  would be expected to decrease as the temperature is decreased, values of  $0.7 \times 10^{-4}$  and  $0.5 \times 10^{-4}$  were taken at 480 and 470°C, though the maximum rate and limit are not sensitive to small changes in  $R_1$ .  $R_8$  was obtained by optimizing the second-limit measurements in boric-acid-coated vessels at 480°C, but the value at 470°C was obtained by extrapolation as no experimental measurements were available at this temperature. The values of  $R_4$ ,  $R_5$  were obtained by optimizing the rate measurements (average rates for 13 mixtures on the assumption that  $R_6 = 0$ ). The results are summarized in table 11.

TABLE 11.

temp. °C	$R_4$	$R_5$	$R_7$	$R_8$	rate	r.m.s. deviation, limit	% i. period
500	270	4.7	0.00119	10.4	4.8	1.6	4.0
480	281	5.7	0.00076	16.6	4.6	1.6	4.7
470	306	6.0	0.00064	(20.0)	5.3	—	3.8

At 460°C, the induction periods were much less reproducible than at higher temperatures, and the calculated values, based on likely values of the relevant parameters (table 10), were about 30 % lower than the experimental values. The maximum rates were also 10–20 % lower than calculated. This can probably be attributed to the occurrence of significant surface destruction of H<sub>2</sub>O<sub>2</sub> at this temperature since the ratio  $k_8/k_7[M']$  may be as high as 0.1 even for an aged surface and the experimental results were thus not used to elucidate parameters.

At 520 and 530°C, respectively, the values of  $k_7$ ,  $k_2/k_4$  are 0.1013, 26.0 and 0.1450, 30.5 in mm Hg min (M = H<sub>2</sub>), and  $k_{14a}/k_2$  may be reasonably estimated at 37, 35. Using reasonable extrapolations (table 10) of the parameters  $k_{11}/k_{10}^{\frac{1}{2}}$ ,  $k_{14}/k_2$  and  $k_{15}/k_1$ , the calculated rates are significantly less than the observed rates for mixtures of high O<sub>2</sub> content. This is attributed to the occurrence of self-heating

due to the high rates with these mixtures; although mixtures of high  $H_2$  content also have high rates, the self-heating is presumably less because of the high thermal conductivity of these mixtures. Other indications of self-heating found by Doran were first the occurrence of explosion (presumably thermal in character) with mixtures of high  $O_2$  content at  $540^\circ C$ , and secondly the rise in temperature of a thermocouple placed outside the reaction vessel. Self-heating could also be detected as a curvature of the otherwise closely linear log rate against  $1/T$  plot for these mixtures. Optimization runs were made for  $k_{14}/k_2$ ,  $k_{15}/k_1$ , using reasonable extrapolations of  $k_{11}/k_{10}^\ddagger$ , since induction periods could not be used to obtain this parameter. Two runs were made (a) using all mixture compositions (b) ignoring mixtures for which the log rate,  $1/T$  plot indicated self-heating. The results are given below.

temp.	procedure	optimum values		% r.m.s. deviation
		$R_4$	$R_5$	
$520^\circ C$	(a)	229	5.7	7.8
	(b)	230	6.2	5.4
$530^\circ C$	(a)	226	4.6	8.8
	(b)	221	5.2	3.0

Although the values for  $k_{14}/k_2$ ,  $k_{15}/k_1$  are less accurate, they are consistent with those obtained at lower temperatures. Depending on the weight attached to these values at  $520$  and  $530^\circ C$ , the plot of  $\log R_4$  against  $1/T$  gives  $(E_2 - E_{14}) = 8.5$  to  $5.5$  kcal/mole, the corresponding values of  $A_{14}/A_2$  being  $1.1$  to  $17$ . Since there seems no reason for  $A_{14} \gg A_2$ , the combination  $(E_2 - E_{14}) = 7.5$  kcal/mole,  $A_{14}/A_2 = 2.2$  is considered better than the mean values. Using the values<sup>11</sup> of  $A_2$ ,  $E_2$ , the best values are  $A_{14} = 4.16 \times 10^{11}$ ,  $E_2 = 9.0$  kcal/mole.

Since hydrogen abstraction by H from hydrocarbons has  $A \approx 10^{11}$ , there seems no reason why  $A_{14a}$  should be less than  $A_{14}$ , and as  $A_{14}$  is close to the collision frequency, a higher value seems unlikely. Assuming  $A_{14} = A_{14a}$ , then  $E_{14a} = 11.8$  kcal/mole. Since (14a) is exothermic by 14 kcal/mole, this value is consistent with the estimate<sup>8</sup> of 25 kcal/mole for the reverse reaction.

### CONCLUSIONS

The best values available for the velocity constant ratios, absolute velocity constants at  $500^\circ C$ , and the Arrhenius parameters are summarized in table 12.

TABLE 12—VELOCITY CONSTANTS AND ARRHENIUS PARAMETERS

reaction	ratio used at $500^\circ C$	$k$ at $500^\circ C$ l. mole sec	$E$ kcal/mole	$A$ l. mole sec
1. $OH + H_2^a$	—	$7.8 \times 10^8$	$5.2 \pm 0.5$	$2.3 \times 10^{10}$
2. $H + O_2^b$	—	$4.5 \times 10^6$	$16.5 \pm 0.7$	$2.04 \times 10^{11}$
3. $O + H_2^c$	—	—	$10.2 \pm 0.5$	$4.0 \times 10^{10}$
4. $H + O_2 + M$	$k_2/k_4 = 18.5 \pm 0.5$ ( $M = H_2$ )	$1.17 \times 10^{10}$	$-1.3 \pm 0.5^d$	$5.0 \times 10^9$
7. $H_2O_2 + M'$	$k_7 = 0.0481 \pm 0.001$ ( $M' = H_2$ )	$3.86 \times 10^1$	$47.0 \pm 0.7$	$3.19 \times 10^{14}$
8. $H + HO_2^e$	$k_8/k_2 k_{10}^\ddagger = 10.4 \pm 1.0$	$7.0 \times 10^{10}$	—	—
10. $HO_2 + HO_2^f$	—	$1.8 \times 10^9$	—	—
11. $HO_2 + H_2$	$k_{11}/k_{10}^\ddagger = 0.00119 \pm 0.00004$	$1.43 \times 10^{10}$	$25.0 \pm 5$	$1.66 \times 10^{10}$
14. $H + H_2O_2$	$k_{14}/k_2 = 265^g \pm 10$	$1.19 \times 10^9$	$9.0 \pm 2$	$4.16 \times 10^{11}$
14a. $H + H_2O_2$	$k_{14a}/k_2 = 43 \pm 4$	$1.94 \times 10^8$	$11.8 \pm 2$	$4.16 \times 10^{11}$
15. $OH + H_2O_2$	$k_{15}/k_1 = 4.7 \pm 0.5$	$3.6 \times 10^9$	—	—

a ref. (12); b, ref. (11); c ref. (13); d calc. using  $k_4 = 4.43 \times 10^{10}$  at  $293^\circ K$  (ref. (14)); e calc. from  $k_{10}$  at  $293^\circ K$ , assumed independent of temperature; f ref. (15), the value quoted is at  $293^\circ K$ ; g from mean line through  $\log(k_{14}/k_2)$  against  $1/T$  over against range  $470$ – $530^\circ C$ .

Column 2 gives the value at  $500^\circ C$  of the ratio used to obtain the velocity constant given in column 3; the relevant velocity constants  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_{10}$  are obtained from the references given. Of these four velocity constants,  $k_{10}$  is least well

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established, only a single determination at room temperature having been made. Some support for the value quoted comes from the fact that an appreciably higher value would make the derived value of  $k_8$  unreasonably high. No Arrhenius parameters can be quoted for reactions (8) and (10), but since the value of  $k_{10}$  quoted at room temperature makes  $A_8$  close to a collision frequency, it seems unlikely that either reaction has a significant activation energy. There are no grounds for deciding whether the difference between  $k_{15}$  and  $k_1$  is due to an activation energy difference, or a difference in the  $A$  factor.

The interpretation of the slow reaction rate and second limit of  $\text{H}_2 + \text{O}_2$  using computer methods confirms the conclusions reached from earlier analytical interpretations, and indicates that the proposed mechanism is essentially correct over the temperature range 460–540°C, though there is some occurrence of surface reactions at the lowest temperature, and self-heating becomes important at the highest temperature. The choice between reactions (11) and (11a) is less decisive than indicated in the analytical treatment, but the computer treatment has shown that a clear choice is possible by determining the concentration of  $\text{H}_2\text{O}_2$  present in the reaction mixture.

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