

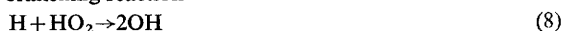
Second Limit of Hydrogen+Oxygen Mixtures: the Reaction $\text{H} + \text{HO}_2$

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Measurements of the second limit of $\text{H}_2 + \text{O}_2$ mixtures at very low O_2 concentrations have shown that the results at 500°C cannot be interpreted on the assumption that the only reaction between H atoms and HO_2 radicals is the quadratic branching reaction



whereas a precise interpretation is possible by introducing the additional reaction



with the ratio $k_{8a}/k_8 = 0.17$. An alternative explanation in terms of destruction of H atoms at the surface has been eliminated by measurement of the first limit. Comparison of the above estimate at 500°C with the mean of $k_{8a}/(k_8 + k_{8b}) \approx 1$ obtained at 20°C suggests that $E_8 - E_{8a} \approx 1725 \text{ cal mol}^{-1}$; if $E_{8a} = 0$, $(k_8 + k_{8b}) = 3.1 \times 10^{11} \exp(-1725 \text{ cal mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The present work does not distinguish between (8) and the kinetically equivalent reaction



but other workers have suggested that $k_{8b}/k_8 \approx 0.1$. A higher activation energy and higher pre-exponential factor for the equivalent reaction, involving O—O bond fission rather than H abstraction, has also been found in the reaction $\text{H} + \text{H}_2\text{O}_2$.

The remarkable rise in the second limit of $\text{H}_2 + \text{O}_2$ mixtures at low mole fractions of O_2 was first observed by Egerton and Warren,¹ who attributed it to the occurrence of quadratic branching through reaction (8). A detailed examination of the second limit,² and the maximum rate² and induction period³ of the slow reaction in aged boric-acid-coated vessels, has enabled the basic mechanism given below to be established.



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To calculate the second limit resulting from such a mechanism, and its variation with mixture composition, a computer programme is used² which involves the parameters k_7 , k_2/k_4 , k_{14}/k_2 , k_{14a}/k_2 , k_{15}/k_1 , $k_{11}/k_{10}^{\frac{1}{2}}$ and $k_8/k_2k_{10}^{\frac{1}{2}}$. Only k_7 enters directly, the remaining velocity constants appearing as ratios. Reaction (13) has a similar kinetic effect to reaction (15), and has been considered negligible in previous interpretations.² As already shown, the second limit is determined predominantly by the values of three parameters only, k_2/k_4 , k_7 and $k_8/k_2k_{10}^{\frac{1}{2}}$, and is insensitive to the remaining parameters, which can be evaluated with sufficient accuracy as discussed elsewhere.² The value of k_2/k_4 can be determined from measurements of the second limit in CsCl-coated vessels, where the basic mechanism is essentially reactions (1)-(4), the HO_2 radical being destroyed at the surface, so that the limit is given by $M = 2k_2/k_4$. k_7 can be obtained by direct studies^{2, 4, 5} of the homogeneous decomposition of H_2O_2 ; moreover, the parameters k_7 and $k_8/k_2k_{10}^{\frac{1}{2}}$ are interlocked, and any small error in k_7 merely alters the value of $k_8/k_2k_{10}^{\frac{1}{2}}$. This single parameter $k_8/k_2k_{10}^{\frac{1}{2}}$ thus determines the variation of the second limit with mixture composition, and since a hundred-fold range of O_2 mole fraction can be used, the mechanism can be subjected to critical testing.

Over the range of O_2 mole fraction from 0.0125 to 0.72, the second limits of $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixtures containing 0.28 mole fraction of H_2 can be predicted with considerable precision,² the root mean square (r.m.s.) deviation between observed and calculated limits being only 2.1 %. However, the deviations are systematic in character, the calculated limit being about 2-3 Torr low at high O_2 concentrations, and about 2-4 Torr high at low O_2 concentrations. To examine these small discrepancies further, limits were determined for even lower concentrations of O_2 . At the same time, the computer programme was modified to include two reactions which might account for these discrepancies, first the surface destruction of H atoms, and secondly the reaction (8a), which has been suggested by other workers.⁶⁻¹¹



EXPERIMENTAL

The apparatus and procedure for determination of the second limit has already been described.¹² $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixtures were used, with a constant mole fraction of H_2 equal to 0.28. With mixtures of low O_2 content, care was taken to ensure that the N_2 used was free from O_2 by frequent reduction of the copper used in the N_2 purification train. At the lowest concentrations of O_2 , the limit could only be detected by observation of the small pressure pulse on the Bourdon gauge used to measure the pressure. Measurements reported² in 1967 agreed with recent measurements (JSH) to within 1 Torr. For measurements of the first limit, an SE 180 Southern Electronics pressure transducer was used, with a sensitivity of 0.5 Torr for full scale deflection on a 1 mV chart recorder. No limit could be observed if the mole fraction of O_2 was reduced below 0.0044.

DISCUSSION

The computer programme,² which calculates the limits for a given set of parameters, was combined with an optimisation programme¹³ which adjusts the value of $k_8/k_2k_{10}^{\frac{1}{2}}$ until minimum r.m.s. deviation between observed and calculated limits is obtained. The two extra reactions introduced are represented by the parameters k_{H}/k_2 and $k_{8a}/k_2k_{10}^{\frac{1}{2}}$, respectively. The parameters k_7 and k_2/k_4 , and the ratio k_{14a}/k_{14} , used previously, were adopted. An improved interpretation of the maximum rate and induction period was made using an improved treatment of the induction period

and a preliminary allowance for the occurrence of self-heating.¹⁴ With $k_{13}/k_3 = 0$, the optimum values obtained at 500°C, using the procedure already discussed, were $k_{11}/k_{10}^{\frac{1}{2}} = 0.001\ 07\ (\text{Torr min})^{-\frac{1}{2}}$, $k_{14}/k_2 = 235$, and $k_{15}/k_1 = 5.2$. While these parameters may be modified (a few per cent) by further treatment, the limit, as already noted, is insensitive to small changes in these parameters. With these values, and the extra parameters k_H/k_2 and $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ set at zero, a minimum r.m.s. deviation of 4.0 % is obtained with $k_8/k_2k_{10}^{\frac{1}{2}} = 9.22\ (\text{Torr min})^{\frac{1}{2}}$; the corresponding optimum value when the three mixtures of lowest O₂ content are omitted is 10.05 with a r.m.s. deviation of 2.08 %. However, examination of the results which are given in column A of table 1 shows that there is a systematic change in the deviation from +4½ % to -9½ % as the mole fraction of O₂ is decreased.

TABLE 1.—OBSERVED AND CALCULATED LIMITS FOR DIFFERENT COMBINATIONS OF PARAMETERS

		A			B		C	
		0			0		0.4	
		0			2.0		0.0	
		9.22			14.15		11.47	
H ₂	O ₂	obs. limit*	calc. limit	% deviation	calc. limit	% deviation	calc. limit	% deviation
0.28	0.72	82.0	78.6	+4.2	81.8	+0.3	81.1	+1.1
	0.56	83.0	79.5	+4.3	82.8	+0.3	82.2	+1.0
	0.42	84.5	81.0	+4.2	84.5	+0.1	83.9	+0.1
	0.28	86.5	83.8	+3.1	87.6	-1.3	87.2	-0.8
	0.14	93.5	90.6	+3.1	94.8	-1.4	94.6	-1.2
	0.07	104.0	99.9	+3.9	104.2	-0.2	104.4	-0.4
	0.035	116.5	112.5	+3.4	116.2	+0.3	116.8	-0.3
	0.025	123.0	120.1	+2.4	123.1	-0.1	124.0	-0.8
	0.0175	132.0	129.5	+1.9	131.2	+0.6	132.3	-0.2
	0.0125	140.5	139.9	+0.4	139.8	+0.5	141.0	-0.3
	0.0088	151.0	152.7	-1.2	149.8	+0.8	150.6	+0.3
	0.0066	160.5	165.0	-2.8	158.7	+1.1	158.7	+1.1
	0.0044	169.5	185.6	-9.5	172.3	-1.7	169.5	0.0
r.m.s. deviation		4.00 %			0.84 %		0.73 %	

* The limits are given in Torr.

EFFECT OF REACTION (8a)

Values of $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ from 1 to 5 were then taken, and the corresponding optimum values of $k_8/k_2k_{10}^{\frac{1}{2}}$ determined, with the results shown in table 2.

TABLE 2.—EFFECT OF REACTION (8a) ON SECOND LIMIT

$(k_{8a}/k_2k_{10}^{\frac{1}{2}})/(\text{Torr min})^{\frac{1}{2}}$	0	1	2	3	4	5
optimum value of $(k_8/k_2k_{10}^{\frac{1}{2}})/(\text{Torr min})^{\frac{1}{2}}$	9.22	11.65	14.15	16.65	19.20	22.80
% r.m.s. deviation	4.00	2.05	0.84	2.01	3.59	5.70

The values for the limits with the optimum pair of parameters are shown in column B of table 1. With values of $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ above 2, not only does the r.m.s. deviation increase, but also the deviation becomes increasingly skew, the calculated limits being high at high O₂ and low at low concentrations of O₂. This form of skew

distribution is unsatisfactory, since the experimental limits of the lowest O_2 concentrations might possibly be low because of some occurrence of surface termination. A value of $k_{8a}/k_2k_{10}^{\frac{1}{2}} > 2$ thus appears unlikely.

EFFECT OF SURFACE DESTRUCTION OF H ATOMS

With $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 0$, optimum values of $k_8/k_2k_{10}^{\frac{1}{2}}$ for values of k_H/k_2 from 0.1 to 0.5 are shown in table 3. Column C of table 1 shows the calculated limits for the optimum parameters and no systematic deviation is apparent.

TABLE 3.—EFFECT OF k_H/k_2 ON SECOND LIMIT

$(k_H/k_2)/\text{Torr}$	0	0.1	0.2	0.3	0.4	0.5
optimum value of $(k_8/k_2k_{10}^{\frac{1}{2}})/(\text{Torr min})^{\frac{1}{2}}$	9.22	9.71	10.24	10.82	11.47	12.21
% r.m.s. deviation	4.00	3.17	2.26	1.28	0.73	1.82

The low r.m.s. deviations do not permit distinction between the combinations $k_H/k_2 = 0$, $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 2$, and $k_H/k_2 = 0.4$, $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 0$, or any intermediate combinations. The value of $k_H/k_2 = 0.4$ Torr implies a partial pressure of 0.2 Torr of O_2 at the first limit, equivalent to a limit of 1.5 Torr for the standard mixture (0.28, 0.14, 0.58 mole fractions of H_2 , O_2 , N_2 , respectively). Limits of this magnitude are not easy to determine, since the visible glow gradually becomes weaker as the pressure is decreased, and it is not easy to decide whether the disappearance of the glow corresponds to the true limit, or merely the limit of detection.

However, experiments with several observers showed that visible luminosity could be detected down to pressures of 0.4 Torr with the standard mixture at 500°C . This observation alone indicates that $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ must be at least 75 % of the value of $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 2 (\text{Torr min})^{\frac{1}{2}}$ obtained when $k_H = 0$. Moreover, by the use of the pressure transducer in its more sensitive range, pressure decreases on admission of the reaction mixture to the reaction vessel could be detected down to pressures of about 0.1 Torr, indicating that the first limit of the standard mixture is below this value. It may thus be concluded that surface termination of H atoms is negligible even at the lowest mole fraction of O_2 .

EFFECT OF REACTION (8b)



Since the O atom formed in this reaction eventually produces two H atoms by reactions (3) and (1), this reaction is kinetically extremely similar to (8), the only difference arising because the probabilities of the occurrence of reactions (3) and (1) are not unity. With reaction (8b) replacing (8) in the computer programme, minimum r.m.s. deviation of 1.84 % was obtained between observed and calculated limits for the ten original mixtures with $k_{8b}/k_2k_{10}^{\frac{1}{2}} = 9.99 (\text{Torr min})^{\frac{1}{2}}$, compared with the corresponding values of 2.08 % and 10.05 when reaction (8) is used; for all ten mixtures, the difference between the calculated limits in the two cases is less than 0.4 Torr. With all thirteen mixtures, use of reaction (8) gave a minimum r.m.s. deviation of 3.83 % with $k_8/k_2k_{10}^{\frac{1}{2}} = 9.18$, the corresponding values with (8b) being 4.00 % and 9.22, respectively.

The effect of reaction (8a), with (8b) as the quadratic branching, was similar to that found with (8); minimum r.m.s. deviation of 0.90 % was found with $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 1.8$. Similarly, when surface destruction of H atoms was introduced with (8b) as the

quadratic branching reaction, minimum r.m.s. deviation of 0.70 % was obtained with $k_H/k_2 = 0.4$ Torr. Thus, the conclusions reached are not dependent on the choice between (8) and (8b) as the quadratic branching reaction.

EFFECT OF REACTION $O + H_2O_2$

Two possible reactions may be written for the reaction of O atoms with H_2O_2 :



Both these reactions have similar kinetic effects to reaction (15) as all three are termination processes which compete with a reaction of the chain centre with H_2 . The effect of reaction (13) on the slow reaction at pressures of 500 Torr has already been considered, and a much higher value of $k_{13}/k_3 = 55$ has been found necessary if $k_{15} = 0$, compared to the value of $k_{15}/k_1 = 4.4$ if $k_{13} = 0$. Since this high value is unlikely, reaction (13) was ignored in the initial interpretation.² However, since the ratio $[O]/[OH]$ increases as the pressure is decreased, reaction (13) will become relatively more important at the limit. Reactions (13), (13a), and (15) only affect the limit at high O_2/H_2 , where they increase the destruction of H_2O_2 (normally destroyed by reactions (14) and (14a)) and thus reduce the limit slightly by decreasing the contribution from quadratic branching. Reactions (13) and (13a) thus modify slightly the skew feature, already referred to, which has been used to assess the role of reaction (8a).

No estimates of k_{13} or k_{13a} were available when the original interpretation of the $H_2 + O_2$ reaction was made,^{2, 3} but a value of $(k_{13} + k_{13a}) = 2.8 \times 10^{10} \exp(-3220 \text{ K}/T)$ has recently been given¹⁵ which, combined with $k_3 = 1.74 \times 10^{10} \exp(-4755 \text{ K}/T)$,¹⁶ gives $(k_{13} + k_{13a})/k_3 = 11.7$ at 500°C. Albers *et al.*¹⁵ use measurements of $[OH]$ and $[H_2O]$ to assess the relative importance of (13) and (13a), and suggest $k_{13} \approx k_{13a}$; however, the reaction $OH + HO_2 \rightarrow H_2O + O_2$, which converts OH to H_2O , is fast, so that k_{13a} may be significantly greater than k_{13} . Since (13) is a more efficient termination process than (13a), the maximum effect of the reaction $O + H_2O_2$ can be obtained by assuming that $k_{13}/k_3 = 11.7$, $k_{13a}/k_3 = 0$.

The introduction of reaction (13) has negligible effect on the optimum values of $k_{11}/k_{10}^{\frac{1}{2}}$ and k_{14}/k_2 , which become 0.001 07 (Torr min)^{- $\frac{1}{2}$} and 236, respectively, but the optimum value of k_{15}/k_1 is now 3.70. With these values, the r.m.s. deviation of the second limit for the thirteen mixtures is 5.58 % when $k_{8a} = 0$, the optimum value of $k_8/k_2k_{10}^{\frac{1}{2}}$ being 9.41. Introduction of reaction (8a) reduced the r.m.s. deviation in a similar way to that found when reaction (13) was absent, and minimum r.m.s. deviation of 1.65 % was obtained with $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 2.7$ (Torr min) ^{$\frac{1}{2}$} , the corresponding value of $k_8/k_2k_{10}^{\frac{1}{2}}$ being 16.2 (Torr min) ^{$\frac{1}{2}$} .

The optimum values of $k_{8a}/k_2k_{10}^{\frac{1}{2}} = 2.7$ and $k_8/k_2k_{10}^{\frac{1}{2}} = 16.2$ (Torr min) ^{$\frac{1}{2}$} , obtained when $O + H_2O_2$ is included with $k_{13}/k_3 = 11.7$, give $k_{8a}/k_8 = 0.17$ at 500°C. Since, as already shown, reactions (8) and (8b) have almost identical kinetic effects at the second limit, this ratio is really $k_{8a}/(k_8 + k_{8b})$. A similar value of 0.15 at 900 K has been given by Dixon-Lewis, Day and Thomson,¹⁰ who also obtained the ratio $k_{8b}/k_8 = 0.1$ which they consider consistent with the bent transition state involved in (8b) compared with the linear transition state in (8). These values were required to interpret the burning velocity of $H_2 + O_2 + N_2$ flames over a range of composition near the H_2 -rich limit. Four values of $k_{8a}/(k_8 + k_{8b})$ have been reported at room temperature by the use of flow-discharge methods. Clyne and Thrush⁶ used

pressures of 2 Torr, and obtained the ratio $k_{8a}/(k_8 + k_{8b}) = 0.51 \pm 0.2$ from measurement of the H_2O production and the H atom consumption. Dodonov ⁷ *et al.* used pressures of *ca.* 20 Torr and from mass spectrometric analysis for OH and H_2O obtained $k_{8a}/(k_8 + k_{8b}) = 0.76$, though their ratio $k_8/k_{8b} \approx 0.1$ is excessively low, perhaps due to unsatisfactory sampling for OH. Bennett and Blackmore ⁸ obtained the ratio $k_{8a}/(k_8 + k_{8b}) = 0.75 \pm 0.25$ using e.s.r. to measure the H atom concentration; their total pressure was 50–250 Torr. A recent determination by Westenberg and de Haas ¹² has given the somewhat higher value of $k_{8a}/(k_8 + k_{8b}) = 1.6$ by the use of e.s.r. to measure H_2O and OH.

Combination of the mean value of $k_{8a}/(k_8 + k_{8b}) = 1.0 \pm 0.5$ at room temperature with the value of 0.17 at 500°C gives $(E_8 - E_{8a}) = 1725 \text{ cal mol}^{-1}$, and $A_{8a}/(A_8 + A_{8b}) = 0.056$, if it is assumed that $k_{8b}/k_8 = 0.1$, independent of temperature. Similar values for these parameters have been given by Dixon-Lewis *et al.*¹⁰ From the best value ¹⁷ for $k_2 = 4.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and a mean value ^{18, 19} of $k_{10} = 2 \times 10^9$, the limit studies give $(k_8 + k_{8b}) = 1.02 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{8a} = 0.17 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 500°C.

Albers ²⁰ gives $(k_8 + k_{8a}) \leq 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K. Combining the upper limit with the mean ratio $k_{8a}/(k_8 + k_{8b}) = 1$ at 300 K, $k_{8a} = 1.0 \times 10^{10}$ at 300 K and combination with $k_{8a} = 1.7 \times 10^{10}$ at 773 K gives $k_{8a} = 2.4 \times 10^{10} \exp(-520 \text{ cal mol}^{-1}/RT)$, so that $(k_8 + k_{8b}) = 4.4 \times 10^{11} \exp(-2245 \text{ cal mol}^{-1}/RT)$. However, it is doubtful whether the accuracy of Albers' determination ²⁰ is sufficient to permit distinction between the above parameters and those obtained by assuming $E_{8a} = 0$, in which case $A_{8a} = 1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $(k_8 + k_{8b}) = 3.1 \times 10^{11} \exp(-1725 \text{ cal mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. A value of E_{8a} greater than 520 cal mol^{-1} seems unlikely, since it would increase A_{8a} , and A_8 would then rise to an unrealistic value. On the assumption that $k_{8b}/k_8 = 0.1$, independent of temperature, the separate values of k_8 and k_{8b} can be obtained in each case.

The greater activation energy required for the O—O bond fission in reaction (8) is consistent with values of k_{14} , k_{14a} , for the corresponding reaction of H atoms with H_2O_2 . Studies ²¹ of the $\text{H}_2\text{O}_2 + \text{H}_2$ reaction at 440–480°C give $k_{14a}/k_{14} \approx 0.16$, whereas Albers *et al.*¹⁵ obtain a ratio of 10 for the corresponding reactions (14aD) and (14D) of H_2O_2 with D atoms. Since isotopic effects will be small, it will be assumed that $k_{14a}/k_{14} = 10.0$ at 294 K, the lowest temperature used by Albers *et al.* Combination of the two values then gives the minimum value of $(E_{14} - E_{14a}) = 4035 \text{ cal mol}^{-1}$ and $A_{14}/A_{14a} = 100$.

Albers *et al.* give $k_{14aD} = 7 \times 10^9 \exp(-4200 \pm 400)$. Reaction (14a) is expected to have a slightly higher activation energy than (14aD) because of the extra zero-point energy in the transition state. The zero-point energy difference between H_2 and HD is 1140 cal mol^{-1} , so that $(E_{14a} - E_{14aD}) = 600 \text{ cal mol}^{-1}$ would be reasonable. With this difference, and if $A_{14a}/A_{14aD} = 1.4$, the ratio of the collision frequencies, $k_{14a}/k_{14aD} = 0.62$ at 375 K, in reasonable agreement with the experimental value of 0.43 obtained by Albers *et al.* The value of E_{14a} becomes 4800 cal mol^{-1} , so that $E_{14} = 8835 \text{ cal mol}^{-1}$. From the ratio $k_{14}/k_2 = 235$, $k_{14} = 9.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, so that with $E_{14} = 8835$, $A_{14} = 3.0 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The corresponding values of E_{14a} and A_{14a} are 4800 cal mol^{-1} , $3.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The value for A_{14} is reasonable, and consistent with the value for the pre-exponential factor of $(k_8 + k_{8b})$ given above. The value of A_{14a} is somewhat less than would be expected from the value of $A_{14aD} = 6.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ given by Albers *et al.*¹⁵ The parameters obtained by the above calculations become much less reasonable if the value given by Albers *et al.*¹⁵ of $k_{14aD}/k_{14D} = 10$ is considered to be at the mean temperature of *ca.* 420 K in which case $(E_{14} - E_{14a})$ becomes *ca.* 8500 cal mol^{-1} and

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$A_{14}/A_{14a} = 2.4 \times 10^3$, so that A_{14} rises above 10^{12} . It is possible that the difficulty of measuring small amounts of HDO may cause error in the ratio $k_{14aD}/k_{14D} = 10$, given by Albers *et al.*

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- ¹ A. C. Egerton and D. R. Warren, *Proc. Roy. Soc. A*, 1951, **204**, 465.
- ² R. R. Baldwin, D. Jackson, R. W. Walker and S. J. Webster, *Trans. Faraday Soc.*, 1967, **63**, 1676.
- ³ R. R. Baldwin, D. Jackson, R. W. Walker and S. J. Webster, *Trans. Faraday Soc.*, 1967, **63**, 1665.
- ⁴ D. E. Hoare, J. B. Prothero and A. D. Walsh, *Trans. Faraday Soc.*, 1959, **55**, 548.
- ⁵ R. R. Baldwin and D. Brattan, *8th Int. Symp. Combustion* (The Combustion Institute, 1962), p. 110.
- ⁶ M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc. A*, 1963, **275**, 559.
- ⁷ A. F. Dodonov, G. K. Lavrovskaya and V. L. Talrose, *Kinetika i Katalyz*, 1969, **10**, 701.
- ⁸ J. E. Bennett and D. R. Blackmore, *13th Int. Symp. Combustion* (The Combustion Institute, 1971), p. 51.
- ⁹ G. Dixon-Lewis, *Proc. Roy. Soc. A*, 1970, **317**, 235.
- ¹⁰ M. J. Day, K. Thompson and G. Dixon-Lewis, *14th Int. Symp. Combustion* (The Combustion Institute, 1973), p. 47.
- ¹¹ A. A. Westenberg and N. deHaas, *J. Phys. Chem.*, 1972, **76**, 1586.
- ¹² R. R. Baldwin, P. Doran and L. Mayor, *Trans. Faraday Soc.*, 1962, **58**, 2410.
- ¹³ G. Peckham, *Computer J.*, 1970, **13**.
- ¹⁴ R. R. Baldwin, M. E. Fuller and R. W. Walker, unpublished work.
- ¹⁵ E. A. Albers, K. Hoyemann, H. Gg. Wagner and J. Wolfrum, *13th Int. Symp. Combustion* (The Combustion Institute, 1971), p. 81.
- ¹⁶ D. L. Baulch, D. D. Drysdale and A. C. Lloyd, *High Temperature Reaction Data*, Report no. 2 (University of Leeds, 1969).
- ¹⁷ D. L. Baulch, D. D. Drysdale and A. C. Lloyd, *High Temperature Reaction Data*, Report no. 3 (University of Leeds, 1969).
- ¹⁸ S. N. Foner and R. L. Hudson, *Adv. Chem. Ser.*, 1962, **36**, 3.
- ¹⁹ T. T. Paukert and H. S. Johnston, *J. Chem. Phys.*, 1972, **56**, 2824.
- ²⁰ E. A. Albers, *Dissertation* (University of Göttingen, 1969).
- ²¹ R. R. Baldwin, D. Brattan, B. Tunnicliffe, R. W. Walker and S. J. Webster, *Combustion and Flame*, 1970, **15**, 133.