

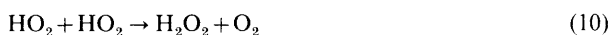
# The Mutual Reaction of HO<sub>2</sub> Radicals and the Rate Constants of the Hydrogen + Oxygen Reaction

BY ROY R. BALDWIN, CHRISTOPHER E. DEAN, THE LATE MALCOLM R. HONEYMAN  
AND RAYMOND W. WALKER\*

Chemistry Department, The University of Hull, Hull HU6 7RX

*Received 12th March, 1984*

The yields of *i*-butene and H<sub>2</sub> have been measured in the decomposition of tetramethylbutane (TMB) in the presence of O<sub>2</sub>. The relative yields are effectively independent of the concentration of TMB and O<sub>2</sub> and of temperature over the range 440–500 °C. If H<sub>2</sub> formation is due to reaction (10*a*):



the value of  $k_{10a}/k_{10}$  is obtained as  $0.065 \pm 0.005$  at 480 °C.

However, introduction of reaction (10*a*) into the mechanism of the H<sub>2</sub> + O<sub>2</sub> reaction at 500 °C has a marked effect on the calculated reaction rate, and a satisfactory interpretation of the variation of rate with mixture composition requires the ratio  $k_{15}/k_1$  to change from  $3.9 \pm 0.5$  to 1.07:



This latter value is totally inconsistent with values of  $3.2 \pm 0.5$  from studies of the decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of H<sub>2</sub>, and 2.7–3.6 from independent measurements of  $k_1$  and  $k_{15}$ . Further, studies in KCl-coated vessels do not significantly alter the  $[\text{i-C}_4\text{H}_8]/[\text{H}_2]$  ratios, in contrast to the large increase predicted by computer treatment, as a consequence of the much lower HO<sub>2</sub> concentration. It is concluded that reaction (10*a*) is not the source of H<sub>2</sub>.

Previous papers have shown that the second limit,<sup>1,2</sup> the induction period<sup>2,3</sup> and the maximum rate<sup>1,2</sup> of the H<sub>2</sub> + O<sub>2</sub> reaction can be interpreted with a high degree of precision for a wide range of mixture composition using the following reaction scheme.†



† The numbering system used in previous papers has been adopted to maintain continuity.



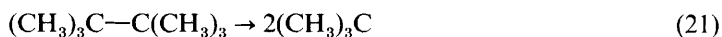
In this mechanism it is assumed that only the mutual reaction (10) occurs between HO<sub>2</sub> radicals. A number of studies around room temperature<sup>4-9</sup> have suggested that the apparent value of  $k_{10}$  is dependent on pressure and on the nature of other molecules present, indicating that at these temperatures the reaction process may be more complex, involving an intermediate H<sub>2</sub>O<sub>4</sub> species.

However, Sahetchian *et al.*<sup>10</sup> have detected traces of H<sub>2</sub> in the decomposition of di-n-heptyl peroxide at 220–238 °C in the presence of O<sub>2</sub>. They attribute this to the reaction (10a) of HO<sub>2</sub> radicals produced by the reaction of n-heptoxy radicals with O<sub>2</sub>:

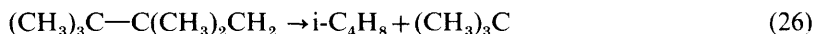
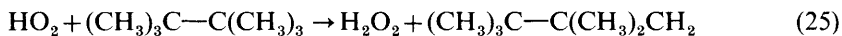
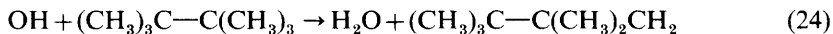


Although the very low yields of H<sub>2</sub> did not permit accurate analysis, a value of  $k_{10a}/k_{10} \approx 0.1$  was suggested. Since reaction (10a) is a termination reaction, its occurrence to this extent would have a marked effect on the kinetic features of the H<sub>2</sub> + O<sub>2</sub> reaction.

Recent studies<sup>11-13</sup> of the decomposition of 2,2,3,3-tetramethylbutane (TMB) in the presence of O<sub>2</sub> between 380 and 540 °C have shown that this system offers a simple and reproducible source of HO<sub>2</sub> radicals. In KCl-coated vessels the basic mechanism involved reactions (21)–(23), while in aged boric-acid-coated vessels the surface process (23) is replaced by reaction (10):

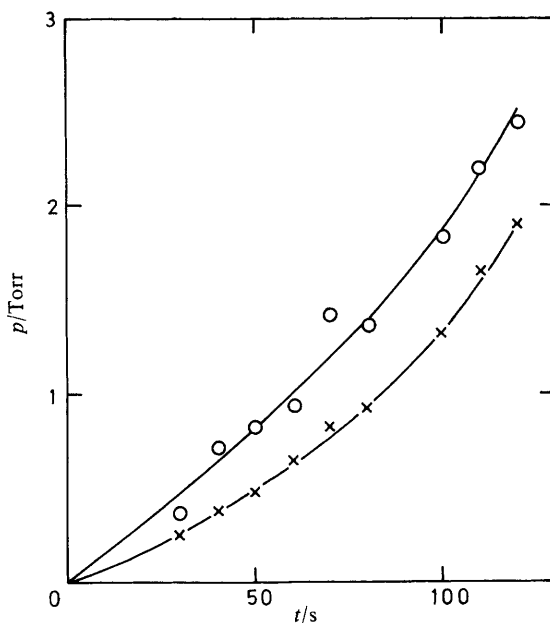


There is also a small-chain contribution from reactions (24) and (25), the OH radicals being produced by the dissociation reaction (7) of H<sub>2</sub>O<sub>2</sub>:



The minor reaction (27), with  $k_{27}/k_{22} \approx 0.01$ , plays little part but is incorporated in the computer treatment.

Studies both in KCl-coated and in aged boric-acid-coated vessels<sup>14</sup> provide consistent values of the two unknown parameters  $k_{21}$  and  $k_{25}/k_{10}^{\frac{1}{2}}$  over the temperature



**Fig. 1.** Yields of  $\text{H}_2$  and *i*-butene in an aged boric-acid-coated vessel at  $480^\circ\text{C}$ . (TMB = 5 Torr,  $\text{O}_2$  = 10 Torr): ○,  $\text{H}_2(\times 100)$ ; ×, *i*-butene.

range  $400\text{--}542^\circ\text{C}$ , and this confirms the validity of the proposed mechanism. The TMB +  $\text{O}_2$  system thus offers a convenient source of  $\text{HO}_2$  radicals, and this paper describes the use of the system to investigate the importance of the possible reaction (10a). At the same time the implications of the occurrence of this reaction for rate constants previously determined for the  $\text{H}_2 + \text{O}_2$  system are also examined.

## EXPERIMENTAL

The apparatus and procedures were as described in previous papers.<sup>11–13</sup> The boric-acid-coated vessel was aged by repeated reactions of  $\text{H}_2 + \text{O}_2$  mixtures until a standard rate was obtained. *i*-Butene was determined gas-chromatographically using a Perkin-Elmer Sigma 10 system involving microprocessor control and integration, and  $\text{H}_2$  was determined using an Erba-Science permanent gas analyser with helium as the carrier gas and a helium ionisation detector. The main study was made at  $480^\circ\text{C}$ , with more limited studies at  $440$  and  $500^\circ\text{C}$ . Analysis was restricted to the relatively early stages ( $> 20\%$ ) of reaction to avoid complications resulting from further reactions of the reactive intermediate *i*-butene. Since small amounts (*ca.* 1–2%) of  $\text{C}_3\text{H}_6$ , the main oxidation product from *i*-butene, were found, the yields of *i*-butene were corrected to allow for this loss.

## RESULTS

Fig. 1 shows yields of  $\text{H}_2$  and *i*-butene at various sample times for the mixture containing 5 Torr of TMB and 10 Torr of  $\text{O}_2$ . Fig. 2 shows that the ratio  $[\text{i-C}_4\text{H}_8]/[\text{H}_2]$  increases slightly as the sampling time is increased. The experimental scatter of  $\pm 4\%$  indicates the difficulty of measuring the extremely low  $\text{H}_2$  yields even with the sensitive Erba-Science equipment. No significant variation of the ratio was observed when the

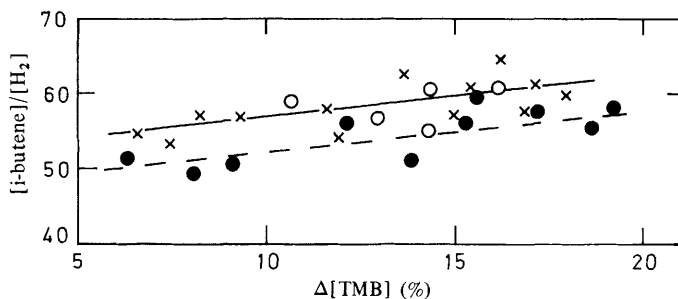


Fig. 2. Relative yields of i-butene and H<sub>2</sub> for different mixtures at 480 °C (aged boric-acid-coated vessel):

symbol	TMB/Torr	O <sub>2</sub> /Torr	N <sub>2</sub> /Torr
×	5	10	0
○	5	3	7
●	2.5	12.5	0

Table 1. Yields of H<sub>2</sub> in the TMB + O<sub>2</sub> reaction at 480 °C

time/s	[i-C <sub>4</sub> H <sub>8</sub> ]/[H <sub>2</sub> ]	
	obs.	calc.
TMB/Torr = 5.0, O <sub>2</sub> /Torr = 10.0, N <sub>2</sub> /Torr = 0		
90	55	53
110	56	54
130	57	54
150	59	55
170	61	56
TMB/Torr = 2.5, O <sub>2</sub> /Torr = 12.5, N <sub>2</sub> /Torr = 0		
110	51	48
130	52	49
150	53	50
170	54	50
190	55	51
TMB/Torr = 5.0, O <sub>2</sub> /Torr = 10, N <sub>2</sub> /Torr = 345		
40	54	60
45	54	61
50	54	61
55	54	62

concentrations of TMB and O<sub>2</sub> were varied and when the total pressure was increased from 15 to 360 Torr by addition of N<sub>2</sub>.

Table 1 shows the observed and calculated values of the ratio [i-C<sub>4</sub>H<sub>8</sub>]/[H<sub>2</sub>] at various times for the optimum value of  $k_{10a}/k_{10} = 0.065 \pm 0.005$  for the three mixtures studied in detail. A value of  $k_{10a}/k_{10} = 0.063$  is required to interpret the results at 15 Torr and a value of 0.074 for the mixture at 360 Torr total pressure.

**Table 2.** Variation of parameters<sup>a</sup> for H<sub>2</sub>+O<sub>2</sub> reaction with  $k_{10a}/k_{10}$  at 500 °C

parameter	$k_{10a}/k_{10}$			
	0	0.05	0.10	0.065
$k_{14}/k_2$	273	233	195	224
$k_{15}/k_1$	3.95	1.63	0.08	1.07
$k_{11}/k_{10}^{\frac{1}{2}}$	0.037	0.047	0.056	0.050
$k_8/k_2 k_{10}^{\frac{1}{2}}$	0.525	0.490	0.450	0.480
$k_{8a}/k_2 k_{10}^{\frac{1}{2}}$	0.081	0.074	0.067	0.071
r.m.s. deviation (%) (rate)	3.3	5.6	9.6	6.5
r.m.s. deviation (%) (induction period)	4.3	8.3	12.4	8.5

<sup>a</sup> Units: dm<sup>3</sup> mol s.

Previous papers have shown for a wide range of H<sub>2</sub>+O<sub>2</sub>+N<sub>2</sub> mixtures how measurements of the induction period<sup>2,3</sup> and maximum rate<sup>1,2</sup> of the slow reaction, and of the second limit,<sup>1,2</sup> can be used in conjunction with a computer treatment of the mechanism to obtain rate constants, or rate-constant ratios, for the reactions involved. Most rate constants appear as ratios in the computer treatment, which involves the following parameters:  $k_7$ ,  $k_2/k_4$ ,  $k_{14}/k_2$ ,  $k_{14a}/k_{14}$ ,  $k_{13}/k_3$ ,  $k_{13a}/k_3$ ,  $k_{15}/k_1$ ,  $k_{11}/k_{10}^{\frac{1}{2}}$ ,  $k_8/k_2 k_{10}^{\frac{1}{2}}$  and  $k_{8a}/k_2 k_{10}^{\frac{1}{2}}$ .

Of these parameters,  $k_7$  is known from direct studies<sup>15</sup> of the homogeneous decomposition of H<sub>2</sub>O<sub>2</sub>. In the absence of reaction (10a), the simple mechanism involving reactions (7), (15) and (10) gives a non-chain process with the rate equation

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

However, if reaction (10a) occurs, the rate equation is given by

$$-d[\text{H}_2\text{O}_2]/dt = (2 + \alpha)k_7[\text{H}_2\text{O}_2][\text{M}'] \quad (\text{ii})$$

where  $\alpha = k_{10a}/(k_{10} + k_{10a})$ . The previous expression,  $k_7 = 1.70 \times 10^{14} \exp(-23300/T)$ , is thus modified to  $k_7 = 1.65 \times 10^{14} \exp(-23300/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (M = H<sub>2</sub>).

The value of  $k_2/k_4$  can be obtained independently from the second limit in KCl-coated vessels,<sup>16</sup> where the quadratic branching reaction (8) plays a negligible role, and the value of  $k_{14a}/k_{14} = 0.143$  at 450 °C has been obtained<sup>17</sup> from studies of the decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of H<sub>2</sub>. The Arrhenius parameters for reactions (14) and (14a), obtained by combining this value with lower-temperature values as discussed in an earlier paper,<sup>2</sup> indicate that  $k_{14a}/k_{14} = 0.12$  at 500 °C.

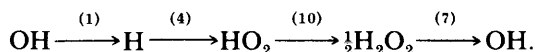
Reactions (13) and (13a) play only a minor role, as already indicated.<sup>2</sup> An estimate<sup>18</sup> of the rate constant for O+H<sub>2</sub>O<sub>2</sub> gives  $(k_{13} + k_{13a})/k_3 = 10.4$  at 500 °C but does not distinguish between reactions (13) and (13a). To minimise errors in the other parameters, therefore, it has been assumed that  $k_{13}/k_3 = k_{13a}/k_3 = 5.2$ .

The remaining parameters are obtained from experimental measurements on the H<sub>2</sub>+O<sub>2</sub> reaction. The induction periods are largely determined by  $k_{11}/k_{10}^{\frac{1}{2}}$ , which is adjusted to give minimum r.m.s. deviation between observed and computed induction periods. The maximum rate is then almost entirely determined by  $k_{14}/k_2$  and  $k_{15}/k_1$ ,

which are adjusted to give minimum r.m.s. deviation between observed and computed maximum rates. The rise in the second limit at very low O<sub>2</sub> concentrations, characteristic of the occurrence of quadratic branching, is determined by the parameters  $k_8/k_2k_{10}^{\frac{1}{2}}$  and  $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ , which are adjusted to give minimum r.m.s. deviation between observed and computed limits. The computer programs and the sensitivity of the experimental measurements to the parameters have been discussed elsewhere.<sup>1-3</sup>

The analysis was first made with  $k_{10a} = 0$ . The results, shown in table 2, differ very slightly from those previously published<sup>2</sup> because of slight adjustments of fixed parameters, particularly  $k_{14a}/k_{14}$ , which has been changed from 0.143 to 0.120 at 500 °C.

With  $k_{10a}/k_{10} = 0.05$ , there are significant changes in  $k_{14}/k_2$ ,  $k_{15}/k_1$  and  $k_{11}/k_{10}^{\frac{1}{2}}$ , but the alterations in  $k_{8a}/k_2k_{10}^{\frac{1}{2}}$  and  $k_8/k_2k_{10}^{\frac{1}{2}}$  are relatively small. With  $k_{10a}/k_{10} = 0.10$ , the value of  $k_{15}/k_1$  becomes unrealistically small, and it is clear that a value of  $k_{10a}/k_{10}$  as high as 0.10 cannot be tolerated. The reason for this marked effect of reaction (10a) is that in its absence the hydrogen + oxygen reaction proceeds essentially by a straight-chain process in which H<sub>2</sub>O<sub>2</sub> can be regarded as two chain centres, since it is formed from two chain centres by reaction (10) and decomposes to give two chain centres by reaction (7):



Superimposed on this straight chain is branching by reactions (2), (3) and (11), and it is balanced by the termination processes (13), (13a), (14), (14a) and (15). For a typical mixture (e.g. 140 Torr H<sub>2</sub>, 70 Torr O<sub>2</sub>, 290 Torr N<sub>2</sub>), the ratio of propagation rate to termination rate for the OH radical is *ca.* 100 if  $k_{15}/k_1 = 4$  (the value when  $k_{10a} = 0$ ), and for H atoms it is *ca.* 20. Reaction (10a) constitutes a powerful termination process and a value of  $k_{10a}/k_{10} = 0.1$  limits the chain length to 10, so that lower values of  $k_{14}/k_2$ , and particularly of  $k_{15}/k_1$ , are needed. The final column in table 2 shows the values of the parameters when  $k_{10a}/k_{10}$  is given the value of 0.065 suggested by the TMB + O<sub>2</sub> studies described earlier.

The values obtained for  $k_{15}/k_1$  in table 2 are dependent on the values taken for  $k_{13}/k_3$  and  $k_{13a}/k_3$ . If  $k_{13} = k_{13a} = 0$ ,  $k_{15}/k_1$  increases to 5.0 (with  $k_{10a}/k_{10} = 0$ ) and to 2.2 (with  $k_{10a}/k_{10} = 0.065$ ). Recent studies of the reaction of O atoms with H<sub>2</sub>O<sub>2</sub> over a relatively narrow temperature range by Davis *et al.*<sup>18</sup> (283–368 K) and by Wine *et al.*<sup>19</sup> (298–386 K) have given expressions which give extrapolated values of  $(k_{13} + k_{13a})/k_3$  of 2.6 and 1.1, respectively, compared with 10.4 calculated from results reported by Albers *et al.*<sup>20</sup> between 370 and 800 K and used in the calculations of table 2. However, these values would make O atoms less selective than OH, which is inconsistent with other evidence, and the ratio obtained from Albers *et al.* is considered more reliable. The discrepancy may arise from a non-linear  $\ln(k_{13} + k_{13a})$  against  $1/T$  dependence as suggested by Wine *et al.*

However, the value of  $k_{15}/k_1 = 1.07$ , required by  $k_{10a}/k_{10} = 0.065$ , in table 2 is totally inconsistent with studies<sup>17</sup> of the H<sub>2</sub>-sensitised decomposition of H<sub>2</sub>O<sub>2</sub>. In the absence of H<sub>2</sub>, the decomposition of H<sub>2</sub>O<sub>2</sub> is a non-chain process involving reactions (7), (15) and (10), and the rate is given by eqn (i), given earlier. In the presence of H<sub>2</sub>, reactions (1) and (14) create a chain decomposition of H<sub>2</sub>O<sub>2</sub>, and in the absence of other reactions the rate is given by

$$R_H = 2k_7[\text{H}_2\text{O}_2][\text{M}'] (1 + k_1[\text{H}_2]/k_{15}[\text{H}_2\text{O}_2]). \quad (\text{iii})$$

Eqn (iii) would imply a continuous increase in  $R_H$  with increasing  $[\text{H}_2]$ , and

**Table 3.** [i-C<sub>4</sub>H<sub>8</sub>]/[H<sub>2</sub>] ratios at 440 °C in KCl-coated vessels

TMB /Torr	O <sub>2</sub> /Torr	[i-C <sub>4</sub> H <sub>8</sub> ]/[H <sub>2</sub> ] <sup>a</sup>	
		Calc.	Obs.
5.0	10.0	1800	60 ± 20
2.5	12.5	5200	50 ± 20
5.0	55.0	350	—
2.5	57.5	640	—
5.0	495.0	84	50 ± 20
2.5	497.5	84	—

<sup>a</sup> The calculated values are for a reaction time of 4000 s, and varied only 5% between 2000 and 6000 s.

would give a chain length of almost 200 for [H<sub>2</sub>O<sub>2</sub>] = 1 Torr and atmospheric pressure of H<sub>2</sub> if  $k_{15}/k_1 \approx 4$ . However, the rate does not increase continuously as H<sub>2</sub> is increased because the chain length is then controlled by the effective termination reaction (14a), and with this reaction included the following rate equation is obtained:

$$R_H = 2k_7[H_2O_2][M'] \left( \frac{k_1[H_2] + k_{15}[H_2O_2]}{\beta k_1[H_2] + k_{15}[H_2O_2]} \right) \quad (\text{iv})$$

where  $\beta = k_{14a}/(k_{14} + k_{14a})$ .

From the initial increase in rate with H<sub>2</sub> concentration, the ratio  $k_{15}/k_1$  can be obtained. A computer treatment incorporating all the reactions mentioned, and including an allowance for the increase in [M'] as [H<sub>2</sub>] increases, gives  $k_{15}/k_1 = 3.9 \pm 0.6$  at 440 °C. From reasonable estimates of activation energy, this corresponds to  $3.2 \pm 0.6$  at 500 °C.

Confirmation of this value of  $k_{15}/k_1$  is obtained from recent studies of reaction (15) by Keyser,<sup>21</sup> who gives the expression  $k_{15} = 2.51 \times 10^9 \exp[(-126 \pm 76)/T]$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> over the range 245–423 K, and by Sridharan *et al.*,<sup>22</sup> who give  $k_1 = 1.78 \times 10^9 \exp[(-164 \pm 52)/T]$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> over the range 250–459 K. Extrapolation of these expressions to 773 K gives  $1.28 \times 10^9$  and  $1.44 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, respectively. A value of  $k_1 = (4.0 \pm 0.4) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 773 K has previously been obtained by drawing a smooth curve through the points in the range 300–900 K obtained by Greiner,<sup>23</sup> by Eberius *et al.*<sup>24</sup> and by Westenberg and de Haas.<sup>25</sup> A recent study by Tully and Ravishankara<sup>26</sup> over the range 298–992 K gives  $k_1 = 4.8 \times 10^8$  at 773 K. These individual rate constants give the ratio  $k_{15}/k_1$  as 2.7–3.6. The agreement is satisfactory, although the direct determination from the H<sub>2</sub> + O<sub>2</sub> and H<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> systems is probably more accurate than that obtained from the individual rate constants.

#### HYDROGEN YIELDS IN KCl-COATED VESSELS

The values for  $k_{10a}/k_{10}$  obtained from the hydrogen yields in the TMB + O<sub>2</sub> system, on the assumption that reaction (10a) is the source of H<sub>2</sub>, cannot be reconciled with studies of the H<sub>2</sub> + O<sub>2</sub> reaction. Yields of H<sub>2</sub> from the TMB + O<sub>2</sub> system in KCl-coated vessels at 713 K were therefore examined. Because HO<sub>2</sub> radicals are efficiently destroyed in KCl-coated vessels, particularly at low pressures, the yields of H<sub>2</sub> should be much lower than in aged B<sub>2</sub>O<sub>3</sub>-coated vessels. As the pressure is increased by increasing the O<sub>2</sub> pressure, HO<sub>2</sub> destruction at the surface becomes less marked and



the mutual homogeneous reaction (10) of HO<sub>2</sub> radicals, and reaction (10a), if it occurs, becomes increasingly important. This is shown in table 3, which gives the calculated yields of [i-C<sub>4</sub>H<sub>8</sub>]/[H<sub>2</sub>] when  $k_{10a}/k_{10} = 0.065$ . The calculated ratio [i-C<sub>4</sub>H<sub>8</sub>]/[H<sub>2</sub>] changes from *ca.* 2000 at 15 Torr total pressure to *ca.* 85 at 500 Torr total pressure. In contrast, the experimental ratios, although less accurate than in B<sub>2</sub>O<sub>3</sub>-coated vessels because of the slower rate, show little variation with pressure and are little different from the values obtained in B<sub>2</sub>O<sub>3</sub>-coated vessels.

This evidence, coupled with the conclusions from the H<sub>2</sub>+O<sub>2</sub> and H<sub>2</sub>+H<sub>2</sub>O<sub>2</sub> systems already discussed, suggests that reaction (10a) is not the source of H<sub>2</sub>. However, no financial support is available at the present time to enable this problem to be pursued.

S.E.R.C. grants to support M.R.H. and C.E.D. are gratefully acknowledged, as well as a grant for the purchase of the Erba-Science permanent gas analyser.

- <sup>1</sup> R. R. Baldwin, D. Jackson, R. W. Walker and S. J. Webster, *Trans. Faraday Soc.*, 1967, **63**, 1676.
- <sup>2</sup> R. R. Baldwin and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 140.
- <sup>3</sup> R. R. Baldwin, D. Jackson, R. W. Walker and S. J. Webster, *Trans. Faraday Soc.*, 1967, **63**, 1665.
- <sup>4</sup> S. P. Sander, M. Peterson, R. T. Watson and R. Patrick, *J. Phys. Chem.*, 1982, **86**, 1236.
- <sup>5</sup> B. A. Thrush and G. S. Tyndall, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 1469.
- <sup>6</sup> B. A. Thrush and G. S. Tyndall, *Chem. Phys. Lett.*, 1982, **92**, 232.
- <sup>7</sup> R. Patrick and M. J. Pilling, *Chem. Phys. Lett.*, 1982, **91**, 343.
- <sup>8</sup> M. Kaufmann and J. Sherwell, *Prog. React. Kinet.*, 1983, **12**, 1.
- <sup>9</sup> M. J. Howard and I. W. M. Smith, *Prog. React. Kinet.*, 1983, **12**, 55.
- <sup>10</sup> K. A. Sahetchian, A. Heiss and R. Rigny, *Can. J. Chem.*, 1982, **60**, 2896.
- <sup>11</sup> G. M. Atri, R. R. Baldwin, G. A. Evans and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 366.
- <sup>12</sup> G. A. Evans and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1458.
- <sup>13</sup> R. R. Baldwin, I. A. Pickering and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2374.
- <sup>14</sup> R. R. Baldwin, M. W. M. Hisham, A. Keen and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1165.
- <sup>15</sup> R. R. Baldwin and D. Brattan, *Proc. 8th Int. Combustion Symp.* (Williams and Wilkins, Baltimore, 1962), p. 110.
- <sup>16</sup> B. Lewis and G. von Elbe, *Combustion, Flame and Explosions in Gases* (Academic Press, London, 1961).
- <sup>17</sup> R. R. Baldwin, D. Brattan, B. Tunnicliffe, R. W. Walker and S. J. Webster, *Combust. Flame*, 1970, **15**, 133.
- <sup>18</sup> D. D. Davis, W. Wong and R. Schiff, *J. Phys. Chem.*, 1974, **78**, 463.
- <sup>19</sup> P. H. Wine, J. M. Nicovich, R. J. Thompson and A. R. Ravishankara, *J. Phys. Chem.*, 1983, **87**, 3948.
- <sup>20</sup> E. A. Albers, K. Hoyer mann, H. Gg. Wagner and J. Wolfrum, *Proc. 13th Int. Symp. Combustion* (The Combustion Institute, Pittsburgh, 1971), p. 81.
- <sup>21</sup> L. F. Keyser, *J. Phys. Chem.*, 1980, **84**, 1660.
- <sup>22</sup> U. C. Sridharan, B. Reimann and F. Kaufman, *J. Chem. Phys.*, 1980, **73**, 1286.
- <sup>23</sup> N. R. Greiner, *J. Chem. Phys.*, 1969, **51**, 5049.
- <sup>24</sup> K. H. Eberius, K. Hoyer mann and H. Gg. Wagner, *Proc. 13th Int. Symp. Combustion* (The Combustion Institute, Pittsburgh, 1971), p. 713.
- <sup>25</sup> A. Westenberg and N. de Haas, *J. Chem. Phys.*, 1973, **58**, 4061.
- <sup>26</sup> F. P. Tully and A. R. Ravishankara, *J. Phys. Chem.*, 1980, **84**, 3126.