Time-resolved Study of Hydrogen Atoms in the H_2-O_2 System under Conditions close to Criticality

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A time-resolved study has been performed at conditions close to criticality in the H₂–O₂ system. Reaction was initiated by the exciplex laser flash photolysis of O₂ at 193.3 nm. H was monitored using time-resolved resonance fluorescence and showed an approximately biexponential time dependence. Near the explosion limit, the long-time behaviour is dominated by the competition between the branching and terminating H + O₂ channels. Rate coefficients for these channels were inferred from this time dependence over the ranges $800 \le T/K \le 850$ and $100 \le P/Torr \le 243$.

The reaction of H atoms with O_2 has long been recognized as important in the combustion of hydrogen and hydrocarbons.¹ Various workers have simulated the dynamics of the $H + O_2$ interaction, often on the well defined Melius-Blint potential-energy surface.² The entrance barrier is negligible and, at thermal collision energies, H inserts into the O-O bond.³ Miller¹ rejected any direct O-abstraction component to the reaction and asserted that reaction only proceeds via a long-lived complex. Following formation, this HO₂ complex can dissociate to O + OH,⁴ or it can be stabilized by collisions to the HO₂ radical. The branching ratio between these channels, which depends sensitively on temperature and pressure, is responsible for the second explosion limit in the H₂-O₂ system.⁵.

The channel $H + O_2 \rightarrow O + OH$ causes chain branching, whereas $H + O_2 + M \rightarrow HO_2 + M$ converts reactive H into HO_2 which is relatively unreactive at these temperatures, and thus corresponds to chain termination. At high temperature and low pressure, the branching channel dominates: the chain carriers H, O and OH accumulate and the overall reaction rate increases. At low temperature and high pressure, chain-carriers are converted into unreactive HO_2 , and the reaction is slow.

Previous work measured $k(H + O_2 + M)$ at low temperatures,⁴ or $k(H + O_2)$ at very high temperatures.⁶ The position of the explosion limits has also been determined. There have been few direct measurements of either channel in the temperature range 700–900 K, where the balance between the channels is important. Table 1 demonstrates the significant discrepancies found between several extrapolations of $k(H + O_2 + M)$ to 800 K.

Table 1 Literature values of $k(H + O_2 + M)/10^{-33}$ cm⁶ molecule⁻² s⁻¹ at 800 K (some measurements have been extrapolated)

ref.	M, <i>k</i>	T/\mathbf{K}	technique(s)
4	N ₂ , 2.2	200-400	review (1986)
6	Ar, 7.1	746–987	flash photolysis-shock tube, atomic resonance absorption spectroscopy (1989)
7	He, 8.0, N ₂ , 15.2, H ₂ O, 71	298–639	discharge flow, titration (1989)
8	$Ar, 2.1, N_2, 6.3, H_3O, 53$	231-512	flow, gas chromatography and mass-spectrometry (1983)
9	Ar, 6.1, Na. 9.1	964–1176	induction time (1977)
10	Ar, 9.0	300-2000	review (1990)

The work described here is a study of the H_2-O_2 system close to the second explosion limit using time-resolved, laserinitiated techniques. This approach was chosen to examine a potentially sensitive direct method of investigating the interaction of the branching and terminating channels in the reaction of H with O_2 .

Experimental

The apparatus and methods of data collection and analysis have previously been described in detail.¹¹ H₂, O₂ and He or N₂ were allowed to flow through the heated stainless-steel reaction cell. The conditions covered the ranges: pressure = 100-243 Torr, temperature = 800-850 K, [H₂] = $(0.9-1.6) \times 10^{16}$ molecule cm⁻³, [O₂] = $(3.5-11) \times 10^{15}$ molecule cm⁻³.

At high temperature, vibrationally excited $O_2(X \ ^3\Sigma_g^-)$ is photolysed at 193 nm to yield $O(^3P)$. At 800 K, Keiffer¹² found that the oxygen atom yield $[O]_0 = 10^{-4}[O_2]$ for a laser energy of 110 mJ. In this experiment, the laser energy was 80 mJ, incident on the same area, so $[O]_0$ may be estimated at *ca*. 5×10^{11} cm⁻³. Production of $O(^1D)$ is not energetically feasible in a single-photon process.¹³

H was detected by resonance fluorescence at 121.6 nm. Experimental molecular oxygen concentrations severely reduced the oxygen atom fluorescence signal, since the thermally populated v = 1 level of O₂ absorbs 130 nm radiation strongly.¹⁴ To ensure a good signal-to-noise ratio, all experiments were performed by detecting H. Fig. 1(*a*) shows a typical decay.

The balance between branching and termination is very sensitive to temperature, so temperature fluctuations were reduced to $ca. \pm 0.3$ K. Pressure and temperature rises due to reaction were not observed.

Gas purities are given below, with typical levels of the main contaminants taken from the manufacturer's analysis. O_2 (BOC zero grade, 0.3% N_2 , Ar) and N_2 (BOC CP grade, 1 ppm each of O_2 , CO_2 , CO, H_2 , H_2O and hydrocarbons) were used as received. H_2 (BOC CP grade, 5 ppm N_2) and He (BOC CP grade, 2 ppm each Ne, N_2) were passed through Oxisorb filters (Messer-Griesheim) to reduce O_2 to 0.2 ppm.

Results and Discussion

Simple Kinetic Scheme

The general features of the time dependence of [H], generated following the laser photolysis of O_2 in H_2-O_2 -N₂-He



Fig. 1 (a) Typical experimental decay trace. Conditions: 825 K, 125 Torr He, $[O_2] = 4.0 \times 10^{15}$ molecule cm⁻³, $[H_2] = 1.1 \times 10^{16}$ molecule cm⁻³. (b) Residuals from FACSIMILE fit to the decay shown in (a). Best-fit parameters: $[O]_0 = 7.2 \times 10^{11}$ cm⁻³; $k'_2 = 510$ s⁻¹; $k'_3 = 226$ s⁻¹

mixtures, may be appreciated from an analysis of the following simple reaction scheme:

$$O_2 \xrightarrow{n\nu} O + O (t = 0)$$
$$O + H_2 \longrightarrow OH + H; \quad k_1$$
(1)

$$H + O_2 \longrightarrow OH + O; k_2$$
 (2)

$$H + O_2 + N_2 \longrightarrow HO_2 + N_2; \quad k_3 \tag{3}$$

H
$$\longrightarrow$$
 escape; k_4 (4)

$$OH + H_2 \longrightarrow H + H_2O; \quad k_5 \tag{5}$$

$$O \longrightarrow escape; k_6 \qquad (6$$

H and O were lost from the viewing zone by reactions (4) and (6) which include diffusion and pump-out. Since $k_5 > 10k_1$ and $k_5[H_2] \approx 120k_2[O_2]$ (Table 2), OH was rapidly converted to H. Omitting H₂O, reactions (1, 5) and (2, 5) merge to:

$$O + 2H_2 \rightarrow 2H$$

 $H + O_2 + H_2 \rightarrow H + O$

Using k'_1 , k'_2 , k'_3 to denote the pseudo-first-order rate coefficients $k_1[H_2]$, $k_2[O_2]$, $k_3[O_2][N_2]$, the differential equa-

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tions describing the time dependence of [H] and [O] are:

$$\frac{\mathrm{d}}{\mathrm{d}t} [\mathrm{H}] = -k'_{\mathrm{H}} [\mathrm{H}] + 2k'_{1} [\mathrm{O}]$$
$$\frac{\mathrm{d}}{\mathrm{d}t} [\mathrm{O}] = k'_{2} [\mathrm{H}] - k'_{\mathrm{O}} [\mathrm{O}]$$

where k'_0 is the rate coefficient for O-atom loss $(=k_6 + k'_1)$, and k'_H is the rate coefficient for H-atom loss $(=k_4 + k'_3)$. These equations imply that

$$[H]_{t} = A_{-} \exp(\lambda_{-} t) + A_{+} \exp(\lambda_{+} t)$$
 (I)

where A_+ and A_- are functions of $[O]_0$, $[H]_0$, k'_1 , k'_2 , k'_H and k'_0 . [O] decays with the same time coefficients but different pre-exponential factors. The time coefficients are:

$$2\lambda_{\pm} = -k'_{\rm loss} \pm \sqrt{[(k'_{\rm loss})^2 + 4(2k'_1k'_2 - k'_0k'_{\rm H})]}$$
(II)

where $k'_{\rm loss} = k'_{\rm O} + k'_{\rm H}$. Typical values of k'_1 , k'_2 , k'_3 , k_4 and k_6 are given in Table 2. If

$$4(2k'_{1}k'_{2}-k'_{0}k'_{H}) \ll (k'_{loss})^{2}$$

then λ_+ may be approximated:

$$\lambda_{+} = \frac{k'_{1}(2k'_{2} - k'_{H})}{k'_{loss}}$$
(III)

giving

or

$$\lambda_+ \approx 2k_2[O_2] - k_3[O_2][M] - k_4$$

 $\lambda_+ \approx 2k_2' - k_3' - k_4$

In these experiments, $|\lambda_{-}| \ge |\lambda_{+}|$: the photolysis product O is converted to H on a short timescale determined by λ_{-} , which is dominated by k'_{loss} , and hence by k'_{1} . On the much longer timescale described by λ_{+} , the chain-carriers (O and H) are then lost by conversion into less reactive HO₂ and by physical escape from the viewing zone, whilst their total concentration is increased by the branching reaction (2). Typically, $|\lambda_{-}|$ was >1000 s⁻¹; in a typical experiment, $|\lambda_{+}|$ ranged from 1–10 s⁻¹.

The long-time behaviour of the system is completely described in this model by λ_+ , in which large pseudo-firstorder chemical rate coefficients $(k'_2, k'_3 \text{ and } k_4)$ cancel to within 1%. Simulations (Fig. 2) demonstrate that the longtime behaviour is very sensitive to small changes in k'_2 and k'_3 , and hence can potentially provide precise values for k_2 and k_3 . If $\lambda_+ < 0$, [H] decays exponentially, following a rapid rise described by λ_- . If $\lambda_+ > 0$, [H] increases without limit and the system explodes. $\lambda_+ = 0$ represents the explosion limit. λ_+ is very sensitive to small changes in experimental [O₂], pressure, and temperature.

Data Fitting to the Simple Scheme

 k_4 and k_6 , the rate coefficients for atom escape from the viewing zone, were determined in separate experiments. N₂O was used as the precursor since 193 nm photolysis produces O(¹D) cleanly.¹³ In N₂O-nitrogen mixtures, O(¹D) was quenched within a few μ s to O(³P), whose decay was fitted to a single exponential (rate coefficient k_6) using the Marquardt algorithm for non-linear least-squares fitting.¹⁵ k_4 was determined by adding enough H₂ to a N₂O-He mixture to convert O(¹D) rapidly to OH + H: at these temperatures, the conversion of OH to H by reaction (5) was complete on a much faster timescale than that for H escape. H decays were fitted to a single exponential of rate coefficient k_4 .

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Table 2 Rate coefficients at 825 K and with $[N_2] = 2.3 \times 10^{18}$ molecule cm⁻³

no	reaction	k	k'/s^{-1}	S _i	ref.				
1	$O + H_2 \rightarrow OH + H$	1.13×10^{-13} a	1469	0.160	10				
2	$H + O_2 \rightarrow OH + O$	1.16×10^{-14} a	116	3.10	10				
$3N_2$	$H + O_2 \rightarrow HO_2; M = N_2$	2.15×10^{-32} b	495	-4.30	4				
$3H_2$	$H + O_2 \rightarrow HO_2; M = H_2$	2.30×10^{-32} b	3.0	-0.0273	4, A				
30 ₂	$H + O_2 \rightarrow HO_2; M = O_2$	2.15×10^{-32} b	2.2	-0.0187	4				
3H ₂ O	$H + O_2 \rightarrow HO_2; M = H_2O$	8.42×10^{-32} b	2.7×10^{-3}	-1.34×10^{-5}	4, B				
4	$H \rightarrow escape$	38.5°	38.5	-0.533	Ť				
5	$OH + H_2 \rightarrow H + H_2O$	1.05×10^{-12} a	13650	0.0454	10				
6	O → escape	25 ^c	25	-0.084	Т				
7 A	$H + HO_2 \rightarrow H_2 + O_2$	3.01×10^{-11} a	39	-0.458	4				
7 B	$H + HO_2 \rightarrow 2OH$	1.64×10^{-10} a	213	1.26	4				
7C	$H + HO_2 \rightarrow O + H_2O$	3.00×10^{-12} a	3.9	0.0204	4				
9	$O + OH \rightarrow H + O_2$	2.80×10^{-11} a	2.0×10^{-3}	-1.06×10^{-3}	L				
11	$OH + HO_2 \rightarrow H_2O + O_2$	6.50×10^{-11} a	85	-0.0441	10				
12	$O + HO_2 \rightarrow OH + O_2$	5.30×10^{-11} a	67	-0.0691	10				
13	$2HO_2 \rightarrow O_2 + H_2O_2$	8.85×10^{-13} a	0.62	0.0616	10				
16	$H + H_2O \rightarrow OH + H_2$	4.59×10^{-16} a	1.5×10^{-3}	-5.56×10^{-8}	10				
17 A	$H + H_2O_2 \rightarrow HO_2 + H_2$	2.83×10^{-13} a	0.048	-2.76×10^{-4}	10				
17 B	$H + H_2O_2 + OH + H_2O$	1.87×10^{-12} a	0.32	-2.09×10^{-4}	10				
18	$O + H_2O_2 \rightarrow OH + HO_2$	1.00×10^{-13} a	0.017	-7.13×10^{-6}	10				
19	$OH + H_2O_2 \rightarrow H_2O + HO_2$	3.36×10^{-12}	0.57	-1.55×10^{-4}	10				
20N ₂	$H_2O_2 \rightarrow 2OH; M = N_2$	$1.12 \times 10^{-19} a$	0.26	0.437	4				
$20H_2$	$H_2O_2 \rightarrow 2OH; M = H_2$	1.12×10^{-19} a	1.5×10^{-3}	2.48×10^{-3}	4. C				
$26N_2$	$HO_2 \rightarrow H + O_2; M = N_2$	1.08×10^{-21} a	2.5×10^{-3}	0.0139	4				
$27N_2$	$O + O_2 \rightarrow O_3; M = N_2$	4.07×10^{-35} b	0.94	đ	D				
$27H_{2}^{-}$	$O + O_2 \rightarrow O_3; M = H_2$	1.22×10^{-34} b	0.016	đ	D				
270,	$O + O_2 \rightarrow O_3; M = O_2$	4.59×10^{-35} b	4.6×10^{-3}	đ	D				
$28N_2$	$O_3 \rightarrow O + O_2; M = N_2$	6.19×10^{-16}	1424	-9.11×10^{-7}	4				
28H ₂	$O_3 + O + O_2; M = H_2$	6.19×10^{-16}	8.0	-5.67×10^{-9}	4. C				
280_{2}	$O_3 \rightarrow O + O_2; M = O_2$	6.99×10^{-16}	7.0	-4.44×10^{-9}	4				
28H2Õ	$O_3 \rightarrow O + O_2; M = H_2O$	3.10×10^{-15} a	9.9×10^{-3}	3.82×10^{-13}	4				
29	$O + H_2O \rightarrow 2OH$	1.39×10^{-15} a	4.4×10^{-3}	1.70×10^{-7}	4				
30	$HO_2 + H_2 \rightarrow H + H_2O_2$	6.35×10^{-18} a	0.083	0.501	4				

Units of k: ^a cm³ molecule⁻¹ s⁻¹; ^b cm⁶ molecule⁻² s⁻¹, ^c s⁻¹. Eqn. (4) defines S_i , the log-normalized sensitivity of [H] at 0.16 s to the *i*th rate coefficient. ^d S_i was not calculated for this reaction. L denotes a fit to literature values. T, this work. A, Relative efficiencies of H₂ and N₂ taken from the reverse reaction. B, Relative efficiencies of N₂ and H₂O taken as the mean of ref. 7 and 8. C, Relative efficiences of H₂ and N₂ assumed to be the same on the basis of the HO₂ decomposition data. D, The rate coefficient was calculated from k_{28} .

Fig. 1(a) shows a typical experimental decay profile for H, at long times, under conditions where $\lambda_+ < 0$. Conditions with $\lambda_+ > 0$ were also established, leading to increases in [H] on a similar timescale. Under these conditions, [H] remained high for several seconds and it proved impossible to determine satisfactory H-atom profiles. All the data were, therefore, generated with $\lambda_+ < 0$.

Attempts were made to fit the experimental data to the biexponential model [eqn. (1)]. Trials on simulated data showed that, for good recovery of parameters, adequate data should be available both for short timescales (dominated by λ_{-}) and for long timescales (dominated by λ_{+}). Experimental conditions were usually adjusted such that the long-time decay was in the range 0.1–1 s, *i.e.* such that the atom removal and branching rates were closely balanced. Thus, the time coefficients differed by such a large factor (at least 100) that a sample interval appropriate to the long-time behaviour generated very little short-time information. Convergence from only a small range of starting values, and visual examination of residuals, confirmed that good biexponential fits could not be made to single traces.

An attempt was made to combine the limited information available in different traces to obtain more chemical information. Knutson *et al.*¹⁶ have shown such procedures to be useful in analysing multi-exponential decays. Some parameters were floated locally (over just one trace) and others globally (constrained to be the same over all traces). However, fits only converged slowly, and this approach was abandoned.

The main aim of the analysis is to study the interaction

between reactions (2) and (3), which is apparent at long times, where the behaviour is determined by the balance between k_2 , k_3 and k_4 . Long-time decay profiles [cf. Fig. 1(a)] could be treated as single-exponential decays because $|\lambda_+| \ll |\lambda_-|$. Tests on simulated data with added noise showed that parameter recovery was optimized by collecting data over 2-3 decay times.

2.0 1.6 1.6 1.2 1.2 1.2 1.2 1.2 1.2 0.8 0.4 0.4 0.0 0.00 0.00 0.16 0.32 0.48 0.64 0.80 1/8

Fig. 2 The sensitivity of $[H]_t$ to small changes in k'_3 for the simple kinetic scheme at fixed $[O]_0$. $k'_1 = 1468$, $k'_2 = 116$, $k_4 = 39$, $k_6 = 25$ s⁻¹. From top to bottom, $k'_3 \{=k(H + O_2 + M)[O_2][M]\}$ has the values of 188.99, 189.12 and 189.25 s⁻¹

Data were gathered near the explosion limit, where the long-time decay constant was $1-10 \text{ s}^{-1}$, for 0.16, 0.32 or 0.8 s after the laser fired: the longest timescale used was 3.2 s. For each trace, the decay time constant $-\lambda_+$ was obtained, and was then processed to yield the rate coefficients k_2 and k_3 , by using eqn. (3). The effective third-body concentration [M] was taken as [He] or [N2], since all other species were present in small amounts, and H₂ is a poor third body for stabilizing HO₂ complexes.

Attempts to derive both k_2 and k_3 from experimental decay time constants $(-\lambda_+)$ via eqn. (3) were unsuccessful. The reaction scheme also predicted decay rate constants very different from those found experimentally. Typical concentrations and literature rate coefficients (Table 2) predict a decay constant of ca. 260 s⁻¹, significantly greater than the observed values of $1-10 \text{ s}^{-1}$, clearly demonstrating inadequacies in the simple mechanism.

Whilst the atom concentrations are comparatively small (ca. 5×10^{11} cm⁻³), the competition between reactions (2) and (3, 4) results in very long lifetimes for H, permitting radical-radical reactions to become significant. In particular, HO₂ accumulates and its reactions should be considered explicitly.

Full Kinetic Scheme

All reactions among the set of species {H, O, H₂, OH, O₂, H_2O , HO_2 , O_3 and H_2O_2 , with third bodies $M = N_2$, H_2 , O_2 , H_2O were considered. Rate coefficients at 825 K, drawn from the most recent evaluations, or sometimes estimated using thermodynamics and the literature value for the forward rate coefficient, are shown in Table 2.

Pseudo-first-order rate coefficients are also shown for typical experimental conditions: T = 825 K, $[N_2] = 2.3$ × 10¹⁸ molecule cm⁻³, $[H_2] = 1.3 \times 10^{16}$ molecule cm⁻³, $[O_2] = 10^{16}$ molecule cm⁻³ and $[H] = 1.3 \times 10^9$ cm⁻³, $\begin{bmatrix} O_2 \end{bmatrix} = 10^{\times} \text{ molecule cm}^3 \text{ [OH]} = 7.0 \times 10^7 \text{ molecule cm}^3, \\ \begin{bmatrix} H_2 O \end{bmatrix} = 3.2 \times 10^{12} \text{ molecule cm}^{-3}, \\ \begin{bmatrix} HO_2 \end{bmatrix} = 1.3 \times 10^{12} \text{ molecule cm}^{-3}, \\ \end{bmatrix}$ concentrations are taken from simulations at 0.1 s with $[O]_0 = 5 \times 10^{11}$ cm⁻³. Pseudo-first-order rate coefficients refer to the removal of the first-named species by all others: thus in reaction (11), OH is removed by the calculated $[HO_2]$ with a time constant of 85 s^{-1} .

A fuller reaction scheme was used in the numerical analysis, and in the data fitting described below, than is shown in Table 2 (see supplementary material, SUP 56846, 10 pp[†]). Reactions with pseudo-first-order rate coefficients less than 10^{-3} s⁻¹ have been omitted to simplify the table. The detailed sensitivity analysis (see below) demonstrated that the reactions not included in Table 2 are of no significance.

† Details available from the Editorial Office.

The experimental data were fitted to the detailed model, using the numerical integration program FACSIMILE,¹⁷ by varying four parameters, $[O]_0$, k_2 , k_{3N_2} , and Q, where Q is the ratio of calculated [H] to the fluorescence intensity from H. Minimum χ^2 was used as a fitting criterion. Estimated uncertainties in fitted values were given by the sensitivity of χ^2 to small changes in the parameter values. Fig. 1(b) shows that the residuals were randomly scattered around zero, indicating a good fit to the experimental data. All starting values were changed by a factor of 10, and the fitted values did not change.

Fitting was tested for correct parameter recovery. Several different starting values were used to ensure that the fits represented a true minimum on the χ^2 hypersurface. Local minima were rare. For each data file, the detailed results of all converged fits were treated as independent estimates of the best-fit parameter values. They usually agreed well, and were combined to yield the best estimate of the fitted values for that file. Four data files were gathered under each set of conditions: the detailed results are available as supplementary material. The final averaged results at the three experimental temperaures are shown in Table 3.

The full mechanism was also used to create concentration vs. time curves for species other than H. Fig. 3 shows concentration-time information for the typical conditions described above. H, O and OH decay together as HO₂ and H_2O are formed; $[H_2O_2]$ and $[O_3]$ are always small. H decays (Fig. 4) were simulated with $[O]_0 = 10^9$ to 10^{12} cm⁻³. If little molecular oxygen is photolysed, radical-radical reactions are unimportant and H decays at a rate independent of $[O]_0$. As the laser energy is increased, more O_2 is photolysed, and radical-radical reactions replenish H at long times: H decays more slowly as reactions such as H



Fig. 3 Concentrations of transient species and H₂O calculated by FACSIMILE. From top to bottom, the five species are H_2O , HO_2 , H, O and OH. Conditions: 825 K, $[N_2] = 2.3 \times 10^{18}$ molecule cm⁻³, $[O_2] = 1.0 \times 10^{16}$ molecule cm⁻³, $[O]_0 = 5 \times 10^{11}$ cm³

Fable 3	Experimental v	values for $k_2 =$	$k(H + O_2)$	\rightarrow OH +	O) and k_{3N} ,	$= k (\mathbf{H} + 0)$	$D_2 + N_2 -$	$\rightarrow HO_2 + N_2$)
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		$k_2/10^{-14} \text{ cm}^3$	molecule ⁻¹ s ⁻¹	$k_3/10^{-32} \text{ cm}^6 \text{ m}$	nolecule ⁻² s ⁻¹		
Т	N	this work	ref. 10	this work	ref. 10		
800 825 850	299 423 397	$\begin{array}{c} 0.66 \pm 0.40 \\ 1.43 \pm 0.40 \\ 1.38 \pm 0.40 \end{array}$	$\begin{array}{c} 0.84 \pm 0.25 \\ 1.16 \pm 0.35 \\ 1.57 \pm 0.50 \end{array}$	$\begin{array}{c} 0.99 \pm 0.60 \\ 2.95 \pm 0.60 \\ 3.45 \pm 0.60 \end{array}$	$1.8^{+4.0}_{-1.3}$		

Literature values are presented for comparison. The errors are 1σ and include contributions from the overall uncertainties of each fit, and an assumed 10% uncertainty in each significant reaction of the full mechanism (but 35% for $k_{\gamma c}$). N is the total number of converged fits.



Fig. 4 Effect of initial oxygen-atom concentration on the hydrogenatom profile. From top to bottom, $[O]_0 = 10^{12}$, 10^{11} , 10^9 cm⁻³. Each decay is normalized at the maximum value of [H]. Conditions: 825 K, $[N_2] = 2.3 \times 10^{18}$ molecule cm⁻³, $[O_2] = 3.52 \times 10^{15}$ molecule cm⁻³, $[H_2] = 1.01 \times 10^{16}$ molecule cm⁻³

+ HO₂ \rightarrow 2OH turn the unreactive HO₂ radicals into OH, which is rapidly converted to H by reaction (5). Values of [O]₀ in accordance with estimates of O₂ photolysis (Keiffer¹²) are required in order to generate the enhancement in the H-atom lifetime which is observed experimentally.

Although there was some covariance between Q and $[O]_0$, and between k_2 and k_3 , there was no systematic correlation between $[O]_0$ and fitted rate coefficients. The value of $[O]_0$ affects the timescale of the decay, but there is enough information in the experimental decay profiles to determine the rate coefficients largely independently of $[O]_0$. The best-fit values of $[O]_0$, which were in the range (4-11) × 10¹¹ cm⁻³ depending on conditions, are in excellent agreement with the values measured by Keiffer.¹²

Sensitivity coefficients, S_i , were then calculated using the Green's function method with the computer code CHEMSEN.¹⁸ The log-normalized sensitivity coefficient for H with respect to a rate coefficient k_i is defined as

$$S_i = \frac{\partial \ln[\mathbf{H}]}{\partial \ln k_i} \tag{4}$$

with all other parameters held constant.

The kinetic scheme of Table 2 was used for typical experimental conditions. The species concentrations agree well with those generated via FACSIMILE. Values of S_i are presented in Table 2 at a time (0.16 s) corresponding to the middle of a typical experimental decay trace.

Sensitivities are plotted for important reactions at all times in Fig. 5. [H] is mainly influenced by the target reactions (2) and (3), because these control the branching or terminating character of the system. The decay profiles are less sensitive to H escape which was carefully measured in separate experi-



Fig. 5 Normalized sensitivity coefficients for the five most significant reactions (from top to bottom: k_{3N_2} ; k_2 ; k_{7b} ; k_4 ; k_6). Conditions: 825 K, $[N_2] = 2.32 \times 10^{18}$ molecule cm⁻³, $[O_2] = 1.0 \times 10^{16}$ molecule cm⁻³, $[H_2] = 1.3 \times 10^{16}$ molecule cm⁻³

ments. The analysis demonstrates the importance of the reactions

$$H + HO_2 \rightarrow 2OH$$
$$HO_2 + H_2 \rightarrow H_2O_2 + H$$

which, as discussed above, are responsible for the enhanced lifetime of H. The only other reactions showing significant sensitivity coefficients are the other $H + HO_2$ channels (7*a*, 7*c*), reaction (1), and reaction (20), the decomposition of H_2O_2 .

The sensitivity analysis permits a more detailed investigation of the uncertainties in the measured values of k_2 and k_3 deriving from uncertainties in the rate coefficients of sensitive reactions (Table 4). Table 5 examines the effects of a 25% increase in the rate coefficients; it shows that fitted values of k_2 and k_{3N_2} are moderately sensitive to the values used for these rate coefficients, but insensitive to errors in temperature measurement. Following the error estimates given in ref. 4, k_{7c} was assumed to be uncertain by a factor of two, and all other rate coefficients by $\pm 10\%$. The uncertainty in all input rate coefficients was estimated to cause total uncertainties in k_2 of $\pm 0.40 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, and in k_{3N_2} of $\pm 0.60 \times 10^{-32}$ cm⁶ molecule⁻² s⁻¹.

A source of uncertainty which is more difficult to quantify derives from the behaviour of the diffusive loss processes at long times. On the timescales over which diffusive loss of H and O could be studied directly, the decays were sensibly exponential, but theoretical considerations¹⁹ suggest that this first-order behaviour may be lost on the long timescales on which the H_2-O_2 experiments were conducted. A further complication is the contribution from diffusive loss of HO_2 which would be slower than that of H or O but which would be significant on the experimental timescales. The difficulties

Table 4 Uncertainty in input rate coefficients. The rate coefficients refer to 825 K

no.	reaction	A	B/K	k	uncertainty
4	H escape			63.8	10%
6	O escape			31	10%
7a	$H + HO_2 \rightarrow H_2 + O_2$	1.1×10^{-10}	1070	3.0×10^{-11}	10%
7b	H + HO ₂ → 2ÔH	2.8×10^{-10}	440	1.6×10^{-10}	10%
7c	$H + HO_{2} \rightarrow O + H_{2}O$	3.0×10^{-12}	0	3.0×10^{-12}	factor of 2
30	$\mathrm{HO}_2 + \mathrm{H}_2 \rightarrow \mathrm{H} + \mathrm{H}_2 \mathrm{O}_2$	5×10^{-11}	13100	6.4×10^{-18}	10%

 $k = A \exp(-B/T)$, where A and k have cm, molecule, s units. Uncertainties are 2σ . The total pressure for this experiment was 125 Torr.

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 Table 5
 Dependence of fitted parameters on input parameters

quantity	4	6	7a	76	7c	20N ₂	30	Т
$ \begin{array}{c} Q\\ [O]_0\\ k_2\\ k_{3N_2} \end{array} $	1.0	-2.7	-9.2	14	-9.0	-1.9	-6.3	0.0
	2.1	-2.8	-8.2	14	-9.3	-1.7	-7.6	0.4
	1.1	-0.8	2.2	16	-3.1	0.8	-3.9	0.8
	2.1	1.0	10	6.0	-7.0	1.0	-7.0	1.0

Percentage changes in the fitted parameters were generated by a 25% increase in each input rate coefficient and by a 4 K reduction in the temperature (T). This data file could not be fitted if FACSIMILE assumed the simple scheme.

of modelling long-time diffusion²⁰ and of measuring diffusive loss of HO₂ directly make a quantitative correction for this process impossible. All of these problems further compromise the accuracy of k_2 and k_{3N_2} .

 k_2 has a positive temperature dependence as expected. k_{3N_2} has a strong positive temperature dependence. As an association reaction, it would be expected to have a weak negative temperature dependence. Since k_2 and k_{3N_2} have a covariance of +0.3 to +0.8, the less well determined k_{3N_2} may have been forced to follow the temperature dependence of k_2 .

Conclusions

The use of a laser method to probe the interaction between branching and termination in the O-H-H₂-O₂ system has been demonstrated. The long-time H decay could not be represented by a simple mechanism which excluded HO₂ reactions. Inclusion of HO₂ provides the necessary extension of the timescale to reproduce the experimental data. In particular, the reactions H + HO₂ \rightarrow 2OH and HO₂ + H₂ \rightarrow OH + H₂O are significant. The importance of the former, which is a radical-radical reaction, and is therefore sensitive to the overall radical concentrations, appreciably limits the use of this expimental technique to generate reliable rate coefficients for the H + O₂ branching and termination reactions. Further complications arise from the difficulty of incorporating diffusive loss processes on the long timescales studied. Best-fit values are given in Table 3.

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