Supporting Online Material for

The Thermodynamics of the Elusive HO₃ Radical

Sébastien D. Le Picard,* Meryem Tizniti, André Canosa, Ian R. Sims,*
Ian W. M. Smith*

*To whom correspondence should be addressed. E-mail: sebastien.le-picard@univ-rennes1.fr (S.D.L.);
ian.sims@univ-rennes1.fr (I.R.S.); iwms2@cam.ac.uk (I.W.M.S.)

Published 4 June 2010, Science 328, 1258 (2010)
DOI: 10.1126/science.1184459

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The experiments were performed in a continuous flow CRESU apparatus to provide gas mixtures at low temperatures. In the CRESU technique, low temperatures are achieved through the isentropic expansion of a buffer gas through a convergent-divergent Laval nozzle. The method and its adaptation to the study of neutral-neutral reactions have been described in detail elsewhere (S1, S2). Each Laval nozzle provides an axially and radially uniform supersonic flow at a particular temperature, density and velocity for a given buffer gas. All these properties are conserved in the core of the flow over a distance of a few tens of centimeters. The relatively high density of the supersonic flow (typically, \(10^{16} - 10^{17}\) molecule cm\(^{-3}\), but higher in the present experiments) ensures that frequent collisions maintain thermal equilibrium.

In the present experiments, two Laval nozzles were employed. The first, used both in preliminary experiments to establish the temperature range in which OH concentrations would decay at long times to a non-zero value and in experiments on the kinetics of the association of OH radicals with O\(_2\), had been designed previously to provide a higher
than normal total density in the gas jet in order to examine the kinetics of the three-body association of CH(X^2\Pi) radicals with CO and N_2 (S3). When pure Ar was passed through this nozzle, the temperature in the gas jet was 52.7 K and the gas density was 8.2 \times 10^{17} \text{ molecule cm}^{-3}. By replacing a fraction of the argon flow with O_2 and adjusting the reservoir pressure and pumping speeds, uniform flows could be created in the supersonic jet with different combinations of temperature and density. Operated with pure O_2 (or pure N_2), the density in the uniform flow was 2.24 \times 10^{17} \text{ molecule cm}^{-3} and the temperature was 110.8 K. Kinetic traces obtained using this nozzle to give three different temperatures in the jet are shown in Fig. 1 of the main Report.

The second Laval nozzle was constructed specifically for use in the present experiments. It was designed to give a temperature in the uniform supersonic flow of 95 K, when operated with pure N_2 or pure O_2. The temperature could be ‘tuned’ within a fairly narrow range by adjusting the pressure in the chamber, and over a slightly wider range by replacing a fraction of the N_2 or O_2 by argon, along with a corresponding change of pressure in the reservoir and in the chamber. This ‘seeding’ changes the Mach number and \gamma, the ratio (C_p/C_v) of the specific heats at constant pressure (C_p) and constant volume (C_v), and hence the ratio of the temperatures in the jet and in the reservoir (S2).

OH radicals were generated by repetitively pulsed (10 Hz) laser photolysis of H_2O_2, which was included in the flowing gas mixtures at very low concentrations (ca. 10^{12} \text{ molecule cm}^{-3}), using the 248 nm output of an excimer laser (Lambda-Physics, LPX 210i). This laser produced pulse energies of ca. 70 mJ, corresponding to a fluence of ca.
60 mJ cm$^{-2}$ in the observation zone. OH radicals were observed using laser-induced fluorescence (LIF), which was excited in the $A^2Σ^+ − X^2Π$ (1,0) band using radiation at ca. 282 nm from a frequency-doubled dye laser (Continuum ND6000-UVX, using Exciton Pyromethene 580 dye), which was pumped by the frequency-doubled output from a Nd:YAG laser (Continuum Precision II). The probe laser fluence was in the range 0.1 – 0.5 mJ cm$^{-2}$ in the detection zone. Given that the absorption cross-section of H$_2$O$_2$ at 282 nm is only 20% of that at 248 nm, we estimate that the OH concentration formed by probe laser beam photolysis of H$_2$O$_2$ to be less than 0.2% of that produced by the photolysis laser. There is no information available about the ultraviolet absorption spectrum of HO$_3$. However, the fact that the LIF signals from OH in experiments at temperatures below 80 K (for example, those shown in Figs. 1A and S1) decay to effectively zero demonstrates that no signal arises from photolysis of HO$_3$ by the probe laser.

The fluorescence from OH was observed at the furthest distance downstream from the Laval nozzle consistent with the flow to that point being uniform, as tested by measurements using a Pitot tube (see below and ref. S2). The LIF was gathered with a UV-enhanced, optically fast telescope-mirror combination, passed through a narrowband interference filter (310 nm, bandpass 10 nm FWHM; Corion), and directed onto the photocathode of a UV-sensitive photomultiplier tube (EMI). Kinetic traces, like those shown in Figs. 1, S1 and S2, were obtained by recording the LIF intensity as the delay between the photolysis and probe pulses was systematically varied between zero and, typically, 250 μs.
In order to make the diffusive loss of OH radicals from the observation zone as slow as possible the cross-sectional area of the photolysis beam was kept as large as possible (\(ca. 1 \text{ cm}^2\)) and much greater than that of the probe laser (\(ca. 0.25 \text{ cm}^2\)). Diffusive loss was, at least partly, responsible for the decay in LIF signals in experiments when N\(_2\), rather than O\(_2\), was included in the gas mixture but was slower than in most previous CRESU experiments because of the relatively high total gas density in the jet.

The photolysis of H\(_2\)O\(_2\) at 248 nm is known to generate OH(\(v = 0\)) radicals over a wide range of rotational levels \((S4)\). However, in the present experiments, the high total pressure ensured that this non-Boltzmann distribution was relaxed on a time scale of \(ca. 5 \mu\text{s}\) to a Boltzmann distribution appropriate to the temperature in the gas jet \((S5)\). To ensure that relaxation was complete the fitting of the LIF signals was started at a time delay of 50 \(\mu\text{s}\).

The main gases were all taken directly from cylinders and regulated by means of separately calibrated mass flow controllers (MKS). The purities of the gases used are given by the manufacturer (Air Liquide) as follows: Ar \(\geq 99.997\%\); N\(_2\) \(\geq 99.995\%\); O\(_2\) \(\geq 99.995\%\).

**Analysis of Experimental Results**
Examples of the kinetic traces obtained in individual experiments are shown in Fig. 1 in the main Report, and in Figs. S1 and S2 in this Supporting Online Material. In all cases, when N₂ replaces O₂, the LIF signals from OH decrease at a slow but significant rate. For example, when the traces recorded at 95.4 K and shown in panel (a) of Fig. S2 are both fitted to exponential functions, the first-order constant for loss of OH in the absence of O₂ is $k_{\text{1st}}^o = 6.4 \times 10^2 \, \text{s}^{-1}$ compared with $k_{\text{1st}} = 8.0 \times 10^3 \, \text{s}^{-1}$ with O₂ present. The slow background loss in N₂ is, we believe, mainly due to diffusion of OH from the observation zone. There may be further small contributions to this apparent decay from reaction of OH with H₂O₂ – which is unlikely to yield a pseudo-first-order rate constant much greater than $10 \, \text{s}^{-1}$ – and possibly from other minor effects such as the divergence of the photolysis laser and any slight misalignment between the photolysis laser and the direction of the uniform supersonic flow.

If it is assumed that the slow background loss of OH and HO₃ can be represented by first-order terms, the rate equations for the concentrations of OH and HO₃ are:

\[
\frac{d[\text{OH}]}{dt} = -\{ k_{\text{ass}} [\text{O}_2][\text{M}] + k_{\text{1st,OH}}^o \} [\text{OH}] + k_{\text{diss}} [\text{M}][\text{HO}_3] \quad (S1)
\]

\[
\frac{d[\text{HO}_3]}{dt} = -\{ k_{\text{diss}} [\text{M}] + k_{\text{1st,HO}_3}^o \} [\text{HO}_3] + k_{\text{ass}} [\text{O}_2][\text{M}][\text{OH}] \quad (S2)
\]

Introducing $[\text{HO}_x] = [\text{HO}_3] + [\text{OH}]$, eq. (S1) can be written as:

\[
\frac{d[\text{OH}]}{dt} = -\{ k_{\text{ass}} [\text{O}_2][\text{M}] + k_{\text{diss}} [\text{M}] + k_{\text{1st,OH}}^o \} [\text{OH}] + k_{\text{diss}} [\text{M}][\text{HO}_x] \quad (S3)
\]
To proceed with the analysis, we made the further approximation that $k_{0,1st}^{\text{OH}} = k_{0,1st}^{\text{HO}_3} = k_{0,1st}^{\text{OH}}$. Then we can replace the term $k_{\text{diss}} [\text{M}] [\text{HO}_3]$ by $k_{\text{diss}} [\text{M}] [\text{OH}]_0 \exp(-k_{0,1st}^{\text{OH}} t)$, since at zero time $[\text{HO}_3] = [\text{OH}]_0$, that is the concentration of OH radicals created by pulsed laser photolysis of $\text{H}_2\text{O}_2$. Eq. (S3) then becomes:

$$d[\text{OH}] / dt = - \{ k_{\text{ass}} [\text{O}_2] [\text{M}] + k_{\text{diss}} [\text{M}] + k_{0,1st}^{\text{OH}} \} [\text{OH}] + k_{\text{diss}} [\text{M}] [\text{OH}]_0 \exp(-k_{0,1st}^{\text{OH}} t)$$  \hspace{1cm} (S4)

Although the rates of diffusion of OH and HO$_3$ presumably differ, the approximation is justified on the grounds that: (i) the dominant radical throughout the time period when LIF signals are recorded is OH, and (ii) the approximation introduces only a small change into what is already only a small correction (only about 10% or less).

Solution of eq. (S4) is standard yielding:

$$[\text{OH}]_t = [\text{OH}]_0 \{ A' \exp(-k_{0,1st} t) + B' \exp(-[k_{\text{ass}} [\text{O}_2] [\text{M}] + k_{\text{diss}} [\text{M}] + k_{0,1st}^{\text{OH}}])t \}$$  \hspace{1cm} (S5)

where $A' = \frac{k_{\text{diss}} [\text{M}]}{k_{\text{diss}} [\text{M}] + k_{\text{ass}} [\text{O}_2] [\text{M}]}$ and $B' = \frac{k_{\text{ass}} [\text{O}_2] [\text{M}]}{k_{\text{diss}} [\text{M}] + k_{\text{ass}} [\text{O}_2] [\text{M}]}$  \hspace{1cm} (S6)

Because $\exp(-k_{0,1st} t)$ is a common factor in both terms on the right-hand side of eq. (S5), the equation can be arranged to:

$$[\text{OH}]_t = [\text{OH}]_0 \exp(-k_{0,1st} t) \{ A' + B' \exp(-[k_{\text{ass}} [\text{O}_2] [\text{M}] + k_{\text{diss}} [\text{M}])]t \}$$  \hspace{1cm} (S7)
Eq. (S7) could be used to analyze our experiments, whether the temperature was above or below 80 K. Below 80 K, ten experiments have been performed at temperatures between 55.9 and 79.2 K. The variation in intensity of the LIF signals from OH, $I_{\text{LIF}}(t)$, with time in two of these experiments, those at 65.1 and 74.2 K, are shown in Figs. S1(a) and S1(b). The signals from all 10 of these experiments have been fitted to a function of the form:

$$I_{\text{LIF}}(t) = \exp(-k_{1st}^0 t) \{A + B \exp(-k_{1st} t)\} \quad (S7a)$$

(cf. eq. (S7)) in order to evaluate the ratio $A / (A + B)$. The values of this ratio are given in the fifth column of Table S1. It is clear that they are close to zero in all cases, which is entirely consistent with the forward association reaction being dominant and the backward dissociation reaction being negligible in this range of temperature; in other words, with $k_{\text{ass}}[O_2][M]$ being much greater than $k_{\text{dis}}[M]$. Consequently, eq. (S7) reduces to:

$$[\text{OH}]_t = [\text{OH}]_0 \{\exp(-[k_{1st}^0 + k_{\text{ass}} [O_2] [M]] t)\} \quad (S8)$$

and the concentrations of OH, and the LIF signals that reflect those concentrations, decay exponentially to a zero value at long times.

Therefore, in order to extract values of the rate constant, $k_{\text{ass}}$, the signals from each of these 10 experiments were subsequently fitted to a single exponential decay, of the form shown in eq. (S8). The pseudo-first-order rate constant ($k_{1st}$) that was obtained was then
‘corrected’ for other loss processes by subtracting the value of $k'_{1st}$, obtained from the 
traces obtained with N$_2$ rather than O$_2$ present, and then $(k_{1st} - k'_{1st})$ was divided by 
$[O_2][M]$ to determine a third-order rate constant for association of OH with O$_2$ at the 
temperature of that experiment. The conditions in these 10 experiments and the results 
from their analysis are shown in Table S1. The third-order rate constants, within this 
range of temperature, decrease with increasing temperature and can be fitted to the 
function:

$$k_{3rd}(T) = (4.2 \pm 1.9) \times 10^{-34} \left(\frac{T}{298 \text{ K}}\right)^{-\left(3.5 \pm 0.3\right)} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$$  \hspace{1cm} (S9)$$

a form which is frequently used to express the temperature-dependence of third-order rate 
constants for association reactions. We note that the strong negative temperature-
dependence of these rate constants appears to be in conflict with the theoretical finding of 
Varner et al. (S15) that there is a significant barrier on the minimum potential energy path 
between OH + O$_2$ and HO$_3$.

Fig. S2 shows the traces of LIF signals versus time recorded in the 7 experiments carried 
out at temperatures from 87.4 to 99.8 K, from which equilibrium constants ($K_e$) were 
derived for OH + O$_2$ = HO$_3$ (see Table 1 in the main Report). In these cases, the full form 
of eq. (S7a) was used to fit the signals. As explained in the main text, these traces were 
fitted to a function of the form $\exp(-k'_{1st}t) \{A + B \exp(-k_{1st}t)\}$ to find the value of $A / (A + B)$ which corresponds to $[\text{OH}]_\infty / [\text{OH}]_0$, where $[\text{OH}]_\infty$ is the concentration that the OH
radicals would reach at long times in the absence of background loss. Consequently, eq. (2) in the main text can be written as:

\[
K_c = \frac{[\text{HO}_2]_\infty}{[\text{O}_2][\text{OH}]_\infty} = \frac{1 - [A/(A + B)]}{[\text{O}_2][A/(A + B)]}
\]  

(S10)

The values of \(K_c[\text{O}_2]\) and \(\ln K_c\) given in Table 1 are derived from the fitted experimental traces through the use of this equation.

However, to obtain the fit shown in Fig. 2 of the main Report, the LIF signals from OH were first multiplied by \(\exp(+k_{1st} t)\) and these ‘corrected’ signals were then fitted to a function of the form \(\{A + B \exp (-k_{1st} t)\}\). This (equivalent) procedure makes it easier to visualize how the concentration of OH would vary – and reach a constant value at long times - if the background loss was negligible. Fig. S2(a) displays the same data as in Fig. 2. The remaining traces in Fig. S2 are arranged in order of increasing temperature.

Each pair of experiments, one with \(\text{O}_2\) present the other with \(\text{N}_2\), was accompanied by measurements, using a Pitot tube (S2), to determine the impact pressure \(p_i\) at the center of the gas flow, as a function of the distance \(z\) along the flow. Plots of \(p_i\) versus \(z\) revealed the small fluctuations in temperature and density from which the standard errors in the temperature, \(T\), and the concentration of oxygen, \([\text{O}_2]\), given in Table 1, could be estimated. The standard errors in the ratio \([\text{OH}]_\infty / [\text{OH}]_0\) were determined from the fits of the traces of LIF signals \(\text{versus}\) time. All other errors shown in the main body of Table 1 were obtained using standard error propagation analysis (S6) The results for both
weighted (S6) and unweighted means are essentially identical, and we have chosen to take the larger of the two 95% confidence limits. It is clear that the nature of the experimental determination of $D_0$ means that its value is very insensitive to errors in the experimental parameters, resulting in a very precise determination.

**Derivation of Thermodynamic Quantities**

Determination of $D_0$, the dissociation energy of the HO–O$_2$ bond from the values of $K_c$, required the use of eq. (3a) in the main Report, and hence evaluation of the partition functions for HO$_3$, O$_2$ and OH. For O$_2$, the standard expression (S7) for the rotational partition function (in which it assumed that the spacing between energy levels $\ll k_B T$) could be used. At all temperatures of interest in this work, $Q_{\text{elec}}(\text{O}_2) = 3$ and $Q_{\text{vib}}(\text{O}_2) = 1$.

For OH, it was necessary to evaluate $Q_{\text{int}}(\text{OH})$ by direct summation of $g_i \exp(-E_i/k_B T)$, where $g_i$ is the degeneracy of the $i$th rovibronic level, and we used the energies ($E_i$) of levels in OH(X$^2\Pi$) tabulated by Dieke and Crosswhite (S8). For HO$_3$, $Q_{\text{elec}}(\text{HO}_3) = 2$ and $Q_{\text{rot}}(\text{HO}_3)$ was evaluated using the rotational constants determined by Suma et al. (S9) for the trans-conformer of HO$_3$, $A = 2.361$ cm$^{-1}$, $B = 0.333$ cm$^{-1}$ and $C = 0.292$ cm$^{-1}$, and the standard equation for the rotational partition function of a near symmetric top molecule. $Q_{\text{vib}}(\text{HO}_3)$ was calculated using the frequencies for the four lowest frequency vibrations reported by Derro et al. (S10). Taking these to be harmonic oscillators introduces little error for the low temperatures of interest in this work.
Theoretical calculations \((S9, S13, S15)\) have shown that there are potential energy minima associated with both \textit{trans}- and \textit{cis}-conformers of HO\(_3\), with the \textit{trans}-conformer lying lower in energy and the barrier to isomerization lying below the dissociation energy. We can use the kinetic data from our experiments to estimate a lifetime with respect to dissociation of the HO\(_3\) radicals created in our experiments. At the highest temperature of our experiments (99.8 K), we estimate this lifetime to be \textit{ca}. 50 \(\mu\)s, compared with a time between collisions of \textit{ca}. 13 ns. It therefore seems reasonable to conclude that HO\(_3\) will be equilibrated both between the conformers and amongst their internal states. A small fraction will be present as the \textit{cis}-conformer but the partition function of this species will be very similar to that of the \textit{trans}-conformer since the translational contributions will be identical and the rotational contributions will be very similar. To illustrate this, we note that what is required to calculate \(D_0\) via eq. (3a) is \(\ln Q\) where \(Q = (1/q_{\text{rel\; trans}})^{3/2} \{q_{\text{int}\;(HO_3)} / q_{\text{int}(O_2)} q_{\text{int}(OH)}\}\) (see Table 1). At 95.4 K, \(\ln \{(1/q_{\text{rel\; trans}})^{3/2}\} = -57.130\) (and is, of course, independent of the ratio of \textit{trans}–HO\(_3\) to \textit{cis}–HO\(_3\)). The value of \(\ln \{q_{\text{int}(HO_3)} / q_{\text{int}(O_2)} q_{\text{int}(OH)}\}\) at this temperature is 1.507. Even a 50\% increase in our estimate of \(q_{\text{int}(HO_3)}\) would introduce less than 1\% error in \(\ln Q\).

In order to derive a value for \(\Delta_rH^\circ(298\; K)\), it was first necessary to use eq. (3a) to calculate \(K_c\) and then \(K^\circ\) (referenced to 1 bar as standard pressure) at 298 K, using the value obtained for \(D_0\) and calculating the partition functions as described in the previous paragraph. As stated in the main text, we find \(K^\circ(298\; K) = (8.9 \pm 0.12) \times 10^{-4},\)
corresponding to \( \Delta G^\circ (298 \text{ K}) = (17.3 \pm 0.3) \text{ kJ mol}^{-1}. \)

It was then necessary to calculate \( \Delta S^\circ (298 \text{ K}) \), the standard entropy change for reaction (4), and to use eq. (3b) to find \( \Delta H^\circ (298 \text{ K}) \), the corresponding enthalpy change. The standard entropies of HO\(_3\), O\(_2\) and OH were calculated using the spectroscopic properties for these species referred to in the previous paragraph and the formulas relating partition functions to standard entropies (S7). We found \( \Delta S^\circ (298 \text{ K}) = -118.6 \text{ J K}^{-1} \text{ mol}^{-1} \) and hence \( \Delta H^\circ (298 \text{ K}) = (-17.9 \pm 0.3) \text{ kJ mol}^{-1} \). Finally, combining this value of \( \Delta H^\circ (298 \text{ K}) \) with the literature value (S11) of \( \Delta f H^\circ (298 \text{ K}) \) for OH of \((37.2 \pm 0.2) \text{ kJ mol}^{-1} \), we find \( \Delta f H^\circ (298 \text{ K}) = (19.3 \pm 0.5) \text{ kJ mol}^{-1} \) for the standard enthalpy of formation HO\(_3\) at 298 K.

**Comparison of the present results with theoretical calculations on HO\(_3\)**

There have been numerous theoretical investigations of the HO\(_3\) radical – both to examine its structure and to find its binding energy \((D_e)\) and/or its enthalpy of formation \( (\Delta f H^\circ (298 \text{ K})) \). In 2002, Denis et al. (S12), besides performing detailed calculations employing density functional theory (DFT), coupled cluster (CC) and complete basis set (CBS) extrapolation methods on the isodesmic reaction HOOOH + OH \( \rightarrow \) HOH + HOOO to yield \( \Delta f H^\circ (298 \text{ K}) = (29.7 \pm 8.4) \text{ kJ mol}^{-1} \), surveyed earlier theoretical work that gave values of \( \Delta f H^\circ (298 \text{ K}) \). Similarly, in 2008, Braams and Yu (S13), as well as carrying out a series of calculations using different theoretical methods, listed earlier

*Errors cited in this paragraph correspond to 95% confidence limits.*
estimates of the HO–O₂ binding energy. Finally, both the theoretical papers on HO₃ (S14, S15) that have been published in 2009 provide extensive surveys of the theoretical work on HO₃. The data in Table S2 below are based on the results in these papers.

In comparing the values of \( D_e \) and \( D_0 \), it should be remembered that \( D_e \) should exceed \( D_0 \) by \( \Delta ZPE \), the difference in the zero-point energies in HO₃ and in OH + O₂. An accurate knowledge of \( \Delta ZPE \) depends on knowing the vibrational frequencies of HO₃. The most recent estimate of \( \Delta ZPE \) is given by Varner et al. (S15) as 10.3 kJ mol⁻¹. The difference between \( D_0 \) and \( \Delta f \text{H}^{\circ}(298 \text{ K}) \) does not depend on the individual values of these quantities and can therefore be assumed to be that given in the last row of the Table, in connection with the experimental results.

The results listed in Table S1 are in chronological order of the publication dates. Recent papers (S21, S12, S13, S14, S22, S24) give values of \( \Delta f \text{H}^{\circ}(298 \text{ K}) \) between 17.6 and 29.7 kJ mol⁻¹, in fair agreement with the value of (19.3 ± 0.5) kJ mol⁻¹, inferred from the present experiments.
**Table S1.** Third-order rate constants for OH + O₂ + M → HO₃ + M at temperatures below 80 K*

<table>
<thead>
<tr>
<th>% O₂</th>
<th>T / K</th>
<th>[M] / 10¹⁷ molecule cm⁻³</th>
<th>[O₂] / 10¹⁷ molecule cm⁻³</th>
<th>A / (A + B)</th>
<th>k₁ˢᵗ / 10³ s⁻¹</th>
<th>k°₁ˢᵗ / 10³ s⁻¹</th>
<th>k₃ʳᵈ / 10⁻³¹ cm⁶ molecule⁻² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>55.9 ± 0.2</td>
<td>7.70 ± 0.16</td>
<td>0.389 ± 0.008</td>
<td>-0.120 ± 0.16</td>
<td>4.939 ± 0.11</td>
<td>0.635 ± 0.11</td>
<td>1.44 ± 0.16</td>
</tr>
<tr>
<td>9.2</td>
<td>58.6 ± 0.3</td>
<td>7.28 ± 0.05</td>
<td>0.671 ± 0.005</td>
<td>0.050 ± 0.03</td>
<td>6.722 ± 0.088</td>
<td>0.456 ± 0.08</td>
<td>1.28 ± 0.13</td>
</tr>
<tr>
<td>12.9</td>
<td>60.7 ± 0.2</td>
<td>6.92 ± 0.03</td>
<td>0.893 ± 0.004</td>
<td>-0.017 ± 0.05</td>
<td>7.194 ± 0.134</td>
<td>0.359 ± 0.106</td>
<td>1.11 ± 0.11</td>
</tr>
<tr>
<td>18.2</td>
<td>63.7 ± 0.3</td>
<td>6.53 ± 0.05</td>
<td>1.186 ± 0.009</td>
<td>-0.060 ± 0.05</td>
<td>7.83 ± 0.132</td>
<td>0.796 ± 0.116</td>
<td>0.91 ± 0.09</td>
</tr>
<tr>
<td>19.9</td>
<td>65.1 ± 0.2</td>
<td>6.22 ± 0.04</td>
<td>1.240 ± 0.007</td>
<td>0.033 ± 0.05</td>
<td>7.166 ± 0.164</td>
<td>0.455 ± 0.118</td>
<td>0.87 ± 0.09</td>
</tr>
<tr>
<td>23.8</td>
<td>68.2 ± 0.4</td>
<td>5.72 ± 0.06</td>
<td>1.363 ± 0.015</td>
<td>-0.032 ± 0.11</td>
<td>6.238 ± 0.162</td>
<td>0.511 ± 0.108</td>
<td>0.73 ± 0.08</td>
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<tr>
<td>27.9</td>
<td>70.5 ± 0.4</td>
<td>5.27 ± 0.05</td>
<td>1.471 ± 0.015</td>
<td>-0.060 ± 0.08</td>
<td>5.493 ± 0.096</td>
<td>1.021 ± 0.102</td>
<td>0.58 ± 0.06</td>
</tr>
<tr>
<td>32.1</td>
<td>74.2 ± 0.5</td>
<td>4.86 ± 0.06</td>
<td>1.558 ± 0.020</td>
<td>-0.011 ± 0.16</td>
<td>4.835 ± 0.14</td>
<td>0.524 ± 0.098</td>
<td>0.57 ± 0.06</td>
</tr>
<tr>
<td>37.2</td>
<td>76.9 ± 0.3</td>
<td>4.36 ± 0.03</td>
<td>1.622 ± 0.013</td>
<td>-0.006 ± 0.18</td>
<td>4.495 ± 0.184</td>
<td>0.993 ± 0.088</td>
<td>0.50 ± 0.06</td>
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<td>41.5</td>
<td>79.2 ± 0.1</td>
<td>3.88 ± 0.01</td>
<td>1.610 ± 0.005</td>
<td>-0.001 ± 0.22</td>
<td>3.314 ± 0.11</td>
<td>0.554 ± 0.102</td>
<td>0.44 ± 0.05</td>
</tr>
</tbody>
</table>

*quoted uncertainties throughout the table are twice the standard error, corresponding to ca. 95% confidence limits.
**Table S2.** Comparison of theoretical values for the enthalpy of formation ($\Delta_f H^\circ(298 \text{ K})$) of HO\(_3\), of the HO–O\(_2\) binding energy ($D_e$), and HO–O\(_2\) bond dissociation energy ($D_0$) with the present experimental results.

<table>
<thead>
<tr>
<th>Method*</th>
<th>$D_e$, $D_0$ or $\Delta_f H^\circ(298 \text{ K})$/kJ mol(^{-1})</th>
<th>Ref. (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF/4-31G</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 96.2$</td>
<td>S16 (1973)</td>
</tr>
<tr>
<td>empirical</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 91.2$</td>
<td>S17 (1979)</td>
</tr>
<tr>
<td>MR/DZP</td>
<td>$D_e = 57.7$; $\Delta_f H^\circ(298 \text{ K}) = -13.0$</td>
<td>S18 (1983)</td>
</tr>
<tr>
<td>CASSCF</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 44.8$</td>
<td>S19 (1986)</td>
</tr>
<tr>
<td>CI</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 53.1$</td>
<td>S19 (1986)</td>
</tr>
<tr>
<td>BD(T)/6-31G(d,p)</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 47.7$</td>
<td>S20 (1995)</td>
</tr>
<tr>
<td>BLYP/6-31G(d,p)</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = -54.8$</td>
<td>S20 (1995)</td>
</tr>
<tr>
<td>CBS-QCI/APNO</td>
<td>$D_0 = 4.8$; $\Delta_f H^\circ(298 \text{ K}) = 25.5$</td>
<td>S21 (1996)</td>
</tr>
<tr>
<td>DFT, CC, CBS on isodesmic reaction</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 29.7 \pm 8.4$</td>
<td>S12 (2002)</td>
</tr>
<tr>
<td>MRCI</td>
<td>$D_e = 16.3$</td>
<td>S9 (2005)</td>
</tr>
<tr>
<td>MR-ACPF-CBS</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 21.2$</td>
<td>S22 (2005)</td>
</tr>
<tr>
<td>CASPT2//CAS(13,11)</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 25.5$</td>
<td>S23 (2007)</td>
</tr>
<tr>
<td>HCTH aug-cc-pVTZ</td>
<td>$D_e = 41.6$</td>
<td>S13 (2008)</td>
</tr>
<tr>
<td>CCSD(T)/aVnZ</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 17.6$</td>
<td>S24 (2009)</td>
</tr>
<tr>
<td>CCSD(T) on isodesmic reaction</td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 23.0 \pm 4.2$</td>
<td>S14 (2009)</td>
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<tr>
<td>CCSDT(Q)</td>
<td>$D_0 = 10.5$</td>
<td>S15 (2009)</td>
</tr>
<tr>
<td><strong>experiment</strong></td>
<td>$D_0 = 12.3 \pm 0.3$</td>
<td><strong>this work</strong></td>
</tr>
<tr>
<td></td>
<td>$\Delta_f H^\circ(298 \text{ K}) = 19.3 \pm 0.5$</td>
<td></td>
</tr>
</tbody>
</table>

*these acronyms are taken from refs. (S12) and (S13) and can be identified by reference to those papers.
Fig. S1(a) LIF signals from OH in an experiment in which \( T = 65.1 \) K, \([O_2] = 1.24 \times 10^{17}\) molecule cm\(^{-3}\) and \([M] = 6.22 \times 10^{17}\) molecule cm\(^{-3}\). The signals are fitted to a function of the form \( \exp(-k_{1st}^o t) \{ A + B \exp(-k_{1st}^o t) \} \) yielding the value of \( A / (A + B) \) given in Table S1. The inset shows the LIF signals from OH taken under identical conditions but with N\(_2\) in place of O\(_2\), from which the value of \( k_{1st}^o \) is derived.
**Fig. S1(b)** LIF signals from OH in the experiment in which $T = 74.2$ K, $[O_2] = 1.56 \times 10^{17}$ molecule cm$^{-3}$ and $[M] = 4.86 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(-k_{\text{1st}} t) \{A + B \exp(-k_{\text{1st}} t)\}$ yielding the value of $A / (A + B)$ given in Table S1. The inset shows the LIF signals from OH taken under identical conditions but with N$_2$ in place of O$_2$, from which the value of $k_{\text{1st}}$ is derived.
**Fig. S2(a):** LIF signals from OH in the experiment in which $T = 95.4 \text{ K}$, $[\text{O}_2] = 5.00 \times 10^{17} \text{ molecule cm}^{-3}$ and $[\text{M}] = 6.10 \times 10^{17} \text{ molecule cm}^{-3}$. The signals are fitted to a function of the form $\exp(-k^0_{1st} t) \{A + B \exp(-k_{1st} t)\}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with $\text{N}_2$ in place of $\text{O}_2$. 

\[ A + B = 5.46 \pm 0.30 \]

\[ A = 1.54 \pm 0.23 \]
Fig. S2(b): LIF signals from OH in the experiment in which $T = 87.4$ K, $[O_2] = 4.55 \times 10^{17}$ molecule cm$^{-3}$ and $[M] = 5.52 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(-k^0_{1st} t) \{A + B \exp(-k_{1st} t)\}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with N$_2$ in place of O$_2$. 
Fig. S2(c): LIF signals from OH in the experiment in which $T = 91.5$ K, $[\text{O}_2] = 4.52 \times 10^{17}$ molecule cm$^{-3}$ and $[\text{M}] = 5.52 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(-k_{\text{1st}} t) \{A + B \exp(-k_{\text{1st}} t)\}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with $\text{N}_2$ in place of $\text{O}_2$. 

$$A + B = 4.32 \pm 0.37$$

$$A = 0.64 \pm 0.33$$
Fig. S2(d): LIF signals from OH in the experiment in which $T = 94.9$ K, $[O_2] = 4.46 \times 10^{17}$ molecule cm$^{-3}$ and $[M] = 4.46 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(\frac{\sigma}{k_{1st}} t) \{A + B \exp(-k_{1st} t)\}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with N$_2$ in place of O$_2$. 

$A + B = 1.98 \pm 0.54$

$A = 0.63 \pm 0.05$
Fig. S2(e): LIF signals from OH in the experiment in which $T = 96.7$ K, $[O_2] = 4.63 \times 10^{17}$ molecule cm$^{-3}$ and $[M] = 4.63 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(-k_{1st} t) \{ A + B \exp(-k_{1st} t) \}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with N$_2$ in place of O$_2$. 

$A + B = 4.66 \pm 0.64$

$A = 2.23 \pm 0.13$
**Fig. S2(f):** LIF signals from OH in the experiment in which $T = 97.5$ K, $[O_2] = 4.75 \times 10^{17}$ molecule cm$^{-3}$ and $[M] = 4.75 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(-k_{1st}^0 t) \{A + B \exp(-k_{1st} t)\}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with N$\textsubscript{2}$ in place of O$_2$. 

\[ A + B = 2.79 \pm 0.26 \]

\[ A = 1.29 \pm 0.12 \]
Fig. S2(g): LIF signals from OH in the experiment in which $T = 99.8$ K, $[O_2] = 5.02 \times 10^{17}$ molecule cm$^{-3}$ and $[M] = 5.02 \times 10^{17}$ molecule cm$^{-3}$. The signals are fitted to a function of the form $\exp(-k^o_{1st} t) \{ A + B \exp(-k_{1st} t) \}$ yielding the value of $A / (A + B)$ given in Table 1. The inset shows the LIF signals from OH taken under identical conditions but with $N_2$ in place of $O_2$. 
References


