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OH yields from the CH₃CO + O₂ reaction using an internal standard

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Abstract

Laser flash photolysis of $\text{CH}_3\text{C}(\text{O})\text{OH}$ at 248 nm was used to create equal zero time yields of CH_3CO and OH . The absolute OH yield from the $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$ reaction was determined by following the OH temporal profile using the zero time OH concentration as an internal standard. The OH yield from $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$ was observed to decrease with increasing pressure with an extrapolated zero pressure yield close to unity (1.1 ± 0.2 , quoted uncertainties correspond to 95% confidence limits). The results are in quantitative agreement with those obtained from 248 nm acetone photolysis in the presence of O_2 .

1. Introduction

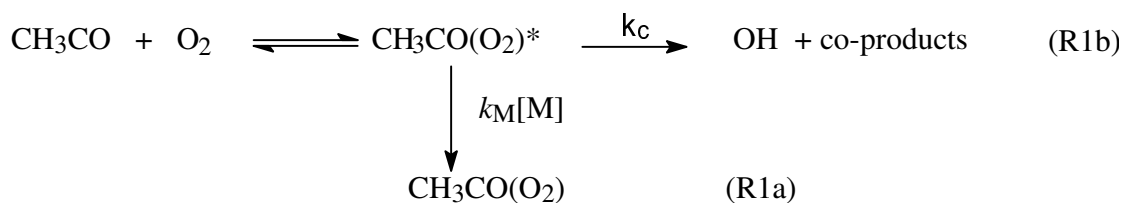
The acetyl radical plays an important role in both atmospheric and combustion processes [1,2]. In the atmosphere, it can be formed by the reactions of radicals/atoms (OH, NO₃, Cl, Br) with acetaldehyde [3] or by the photolysis of some ketones [4,5]. Under tropospheric conditions, the acetyl radical reacts with oxygen to produce acetylperoxy radicals:



which can further react with NO₂ to form peroxyacetyl nitrate (PAN):



PAN is a component of polluted environments and an important NO_x reservoir species [6]. However, experimental [3,7-9] and theoretical [10,11] studies have shown that reaction (R1) has a dissociation channel that forms OH, especially at low pressure. The suggested mechanism is shown in Scheme 1 [7]:



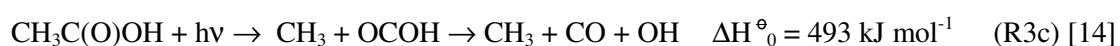
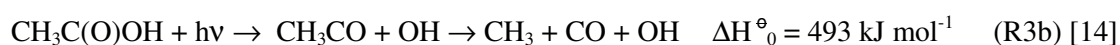
Scheme 1

Although of insignificant atmospheric importance in its own right, R1b has been used as a convenient experimental marker for the acetyl radical (in the presence of O₂) in a study of the atmospherically important photolysis of acetone and of other methylketones [4,5,12].

There is good agreement between kinetic studies of reaction R1 [7,8,13], but the pressure dependence of the OH yield is not well established. There is only one

previous experimental study where OH yields were measured directly at different pressures of He; absolute, pressure dependent OH yields were assigned assuming unity OH yield at zero pressure [7] on the basis of the reaction mechanism and a strong collision model. However, the pressure dependence obtained does not agree with indirect measurements of channel R1b obtained by Tyndall *et al.* [8] or with OH yields obtained by theoretical methods [10].

The method presented here for assigning absolute OH yields from reaction R1 is based on acetic acid photolysis. Hunnicutt *et al.* [14] showed that at 218 nm acetic acid photolysis (R3) produces $\text{CH}_3\text{CO} + \text{OH}(v''=0)$ (R3a) in a 1:1 ratio with little or no subsequent decomposition of the acetyl fragment (R3b). Dissociation to three fragments via (R3c) could not be ruled out at 218 nm on energetic grounds, but at 248 nm (equivalent to 481 kJ mol^{-1}) it is an endothermic process even when allowance is made for the thermal energy of the photolyte:



In this study, acetic acid was photolysed at 248 nm in the presence of O_2 in order to assign absolute OH yields from R1 as a function of total pressure. At zero time, the photolysis generates equal amounts of OH and CH_3CO radicals and this instant, photolytic OH signal provides a convenient internal standard for the subsequent reactive formation of OH.

Experimental

The apparatus, which uses slow flow laser flash photolysis combined with LIF (Laser Induced Fluorescence), has been described previously [5]. The pressure in the cell was measured using capacitance manometers and adjusted by throttling the exit valves on the cell. Acetic acid was photolysed using an excimer laser operating at 248 nm (Lambda Physik, Compex, KrF-Ne) with a photon density between $1-5 \times 10^{16}$ photon cm^{-2} . OH was probed by LIF at ~ 282 nm (detection limit was $\sim 10^9$ molecule cm^{-3}) using the doubled output of a dye laser (PDL3, Rhodamine 6G) pumped at 532 nm from a Nd:YAG laser (Spectra Physics). The fluorescence at ~ 308 nm was passed through an interference filter (Barr Associates Inc., 308.5 ± 5 nm) and was detected using a photomultiplier (EMI 9813). The signal from the photomultiplier was integrated with a boxcar averager, whose output was digitised and passed to a personal computer for subsequent data analysis. The delay time between the photolysis laser and probe laser was scanned using a delay generator such that the recorded OH temporal profile consisted of 1000 time points, each averaged over 2-3 laser shots. The pulse repetition frequency of the lasers was varied between 10 and 5 Hz, and the total flow rate of gas ensured there was a fresh sample for each laser shot. The typical initial concentration of radicals in the system was estimated to be about 2×10^{10} molecule cm^{-3} .

The experimental concentrations of acetic acid were in the range 10^{13} - 10^{14} molecule cm^{-3} to ensure that the dimer contributed less than 0.5% of the total concentration [15]. Furthermore, the absorption cross section of the dimer at 248 nm is expected to be small in comparison to that of the monomer [16] and it will not interfere in the measurements.

Acetic acid (99.8%), supplied by Aldrich, was degassed and diluted in He. Helium, nitrogen (BOC, CP grade, 99.999%) and O₂ (Air Products, high purity, 99.999%) were used straight from the cylinder.

Results

Acetic acid (0.25-3 mTorr) was photolysed in the presence of O₂ (<1 Torr) and either He (5-100 Torr) or N₂ (5-25 Torr) as the buffer gas. A typical OH temporal profile is shown in Figure 1. From this trace the two OH contributions are readily identified: the instant, photolytic signal at time zero (S₀) and the relatively slow growth signal from reaction R1b (S₁). The equation that describes the OH temporal profile is obtained from the solution of the rate equations for Scheme 1 [7] and the inclusion of an instant OH signal (S₀):

$$S_{\text{OH}} = S_0 [\exp(-k_4 t)] + \frac{S_1 k_1'}{k_1' - k_4} [\exp(-k_4 t) - \exp(-k_1' t)] \quad (\text{E1})$$

where k_1' is the pseudo-first-order rate constant for reaction R1 and k_4 represents the slow loss of OH from the system due to reaction with acetic acid ($k_{298\text{K}} = 7.4 \times 10^{-13}$ molecule⁻¹ cm³ s⁻¹ [17]) and diffusion:



Absolute OH yields for reaction R1, Φ_{OH} , were obtained by fitting equation E1 to the data, varying S₀, S₁, k_1' and k_4 , and then simply dividing S₁ by the photolytic signal S₀:

$$\Phi_{\text{OH}}([\text{M}]) = \frac{S_1}{S_0} \quad (\text{E2})$$

At low total pressures (< 10 Torr) O₂ can comprise a significant fraction (≤10%) of the total composition. Small corrections (<2%) were made in the He experiments to allow for the greater collisional stabilization efficiency of O₂ relative to He, by assuming that the efficiency of O₂ in stabilising the CH₃C(O)O₂* intermediate is the same as that of N₂. The results are summarized in Tables 1 and 2 for helium and nitrogen bath gases, respectively.

Experiments were performed for [O₂] = 5×10¹⁴- 2×10¹⁶ molecule cm⁻³, and from fitting equation E1 to the data the rate coefficient of R1 could be obtained as well as the OH yield. The rate coefficients obtained for R1 when He was the buffer gas are shown in Table 1. The present experiments are not ideally suited to accurate determinations of *k*₁, especially at higher pressures, because of the zero time signal and because of the fact only 2 or 3 different O₂ concentrations were used in some cases. As a result the uncertainties in *k*₁ are large. Except for the measurements at [He] = 5.51 × 10¹⁷ and 1.68 × 10¹⁸ molecule cm⁻³, the uncertainties in the fitted *k*₁ for these experiments and the more accurately measured values obtained by Blitz *et al.* [7] overlap. In order to test the validity of the approach, an alternative method was used for one of the cases with poor agreement: the *k*₁ (*k* = 2.87 × 10⁻¹² molecule⁻¹ cm³ s⁻¹) value obtained by Blitz *et al.* [7] was used in the fitting process. This gave an averaged value $\phi_{\text{OH}} = (0.30 \pm 0.09)$ in agreement with the averaged value obtained without fixing *k*'₁ rate coefficient ($\phi_{\text{OH}} = 0.32 \pm 0.08$).

At higher concentrations of acetic acid (>3 × 10¹³ molecule cm⁻³), *k*'₁ was observed to increase and the OH yield to decrease, possibly because of a reaction between acetyl radical and acetic acid that competes with CH₃CO+O₂ (+M) reaction.

Consequently, only data obtained in conditions where this effect was negligible were used ($[\text{O}_2]/[\text{CH}_3\text{C}(\text{O})\text{OH}] > 300$).

Discussion

A steady-state solution of the coupled rate equations generated from Scheme 1, using the strong collision assumption gives an equation for the OH yield that can be expressed in a linearized form (Stern Volmer plot):

$$\frac{1}{\Phi_{\text{OH}}(\text{M})} = 1 + \frac{k_{\text{M}}}{k_{\text{C}}}[\text{M}] \quad (\text{E3})$$

where $k_{\text{M}}/k_{\text{C}}$ is the Stern Volmer constant. Fitting equation (E3) to the weighted data a straight-line with a slope equal to $k_{\text{M}}/k_{\text{C}}$ was obtained. Plots for the He and N₂ data are shown in Figures 2 and 3, respectively. For He as bath gas $k_{\text{M}}/k_{\text{C}} = (1.31 \pm 0.51) \times 10^{-18}$ molecule⁻¹ cm³ was obtained (the uncertainties correspond to 95% confidence limits).

Figure 2 shows Stern Volmer plots from the current work and also from previous studies on acetone photolysis [7,18] together with new data obtained in this laboratory also using acetone photolysis:



The OH yields obtained with acetone photolysis are relative and were converted to absolute yields by assuming that the zero pressure OH yield from R1 is unity and that a strong collision model is valid. A value of $k_{\text{M}}/k_{\text{C}}$ equal to $(1.07 \pm 0.06) \times 10^{-18}$ molecule⁻¹ cm³ was obtained [7], in good agreement, within error bars, with the present study $((1.31 \pm 0.51) \times 10^{-18}$ molecule⁻¹ cm³). The CH₃C(O)OH data confirm that at zero pressure the OH yield is approximately unity, as evidenced by the intercept in Figure 2 which is (1.07 ± 0.24) . This result is supported by the theoretical

calculations of Lee *et al.* [11] and Hou *et al.*[10] where at room temperature, OH is almost exclusively the bimolecular product; the yield of HO₂+CH₂CO, the next most facile bimolecular channel, was calculated by Hou *et al.*[10] to be $\leq 1\%$.

An advantage of the present study over our previous relative OH study is that this internal OH standard method is independent of any other collisional stabilization in the photolytic source. For example, there is good evidence from fluorescence studies that the excited state in acetic acid is long-lived [19]. If it is collisionally stabilised, then the yield of products is reduced but there is still a 1:1 relationship between OH and CH₃CO. In our previous relative OH study [7,18], it was assumed that the yield of CH₃CO following 248 nm acetone photolysis is independent of total pressure. However, subsequent studies on acetone photolysis by Somnitz *et al.* [20] and Khamaganov *et al.* [21] have observed a weak pressure dependence of the quantum yield for acetyl formation which decreases slightly with increasing N₂ bath gas pressures. Applying a correction factor to the OH yields in Figures 2 for acetone photolysis for this effect increase k_M/k_C by 16%. Nevertheless, in view of the good agreement between the present results and our previous work, the assumption that the acetyl formation from acetone photolysis is pressure independent seems to be reasonable in He and in the range of pressures under which these experiments were carried out (10-200 Torr). The present method has large error bars at higher pressures. The OH yield from R1 decreases with increasing pressure and the experimental data trace shows only a small growth on a large photolytic OH background. Analysing such traces using equation E1 results in large errors in S_1 , which in turn propagate to large errors in $\Phi_{OH}(M)$. Moreover, any errors in the determination of either S_0 or S_1 will be magnified in $\Phi_{OH}(M)$ due to the correlation of these parameters. These errors

and their effects on the comparison in Figure 2 may mask any weak pressure dependence in the acetyl yields from acetone photolysis.

Figure 3 shows a Stern-Volmer plot of $1/\Phi_{\text{OH}}(M)$ vs. $[M]$ for nitrogen as the buffer gas, yielding k_M/k_C equal to $(3.59 \pm 0.60) \times 10^{-18}$ molecule⁻¹ cm³; about three times higher than for helium, consistent with N₂ being a more efficient quencher than He. Consequently, at a given total pressure a smaller OH yield is obtained in N₂ than in He. This is the reason, together with a larger quenching of the LIF OH signal by N₂, why measurements were made over a smaller total pressure range. The results of this study together with those of Tyndall *et al.* [8,22] and Hou *et al.* [10] are plotted in Figure 3. The OH yields shown in Figure 3 for the work from Tyndall *et al.*[8] have been recalculated from the original data using $F_c = 1$. Note that in the original reference [8], incorrect values of the rate coefficients are given, as a result of an incorrect fitting routine. The new fit gives k_M/k_C to be equal to 5.9×10^{-18} molecule⁻¹ cm³ [22]. Our results show a factor of ca. one and a half less quenching of CH₃CO(O₂)* than the work from Tyndall *et al.* [8,22] and ca. two and a half less quenching than the work from Hou *et al.* [10]. The reasons for this discrepancy are not clear. The present study is absolute and directly measures the OH, in contrast with the study of Tyndall *et al.* [8] in which OH yields were indirectly obtained by FTIR monitoring of the stable products coupled with the fitting of kinetic data. The theoretical study by Hou *et al.*, that obtained smaller OH yields, using multichannel RRKM theory, appears to be in better agreement with the Tyndall *et al.* data. However, in the master equation calculations the quenching parameter is highly sensitive to the energy of the exit barrier to OH. If this barrier were decreased by a few kJ mol⁻¹, still within the accuracy of the *ab initio* calculation used to calculate the

potential energy surface, the calculation would better fit our data. These calculations have been performed and will be described in detail in a forthcoming paper.

Conclusions

A novel method of studying the absolute OH yield from the $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$ reaction is presented based on acetic acid photolysis at 248 nm which produces equal concentrations of CH_3CO and OH. By adding O_2 to the system, the absolute OH yield from $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$ is assigned by comparison of the ensuing growth of OH with the instant, photolytic OH signal, which acts as internal standard. The OH yield from $\text{CH}_3\text{CO} + \text{O}_2$ was observed to depend on the pressure and is close to unity at zero pressure. This result is in agreement with previous measurements of relative OH yields in helium made in this laboratory; both studies gave a similar OH Stern Volmer constant. Measurements of the OH yield from $\text{CH}_3\text{CO} + \text{O}_2$ in N_2 buffer gas show less quenching than found in measurements in another laboratory.

Acknowledgments

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FIGURES

Figure 1. Temporal evolution of OH following the 248 nm photolysis of acetic acid and the reaction $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$. The solid line represents a fit to the data using equation (E1). $T = 298 \text{ K}$, $[\text{N}_2] = 3.24 \times 10^{17} \text{ molecule cm}^{-3}$, $[\text{O}_2] = 5.58 \times 10^{15} \text{ molecule cm}^{-3}$, $[\text{acetic acid}] = 5 \times 10^{12} \text{ molecule cm}^{-3}$, $[\text{OH}] \sim 2 \times 10^{10} \text{ molecule cm}^{-3}$. The residuals are shown as the lower trace.

Figure 2. Plot of $1/\phi_{\text{OH}}$ versus $[\text{He}]$ for $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$ at room temperature using two different acetyl radical sources. Open circles (acetic acid), squares (acetone from [7,18] and new data obtained in this laboratory). The solid line represents a fit to the data obtained in this work using equation (E3).

Figure 3. Comparison of OH yields using N_2 as bath gas for $\text{CH}_3\text{CO} + \text{O}_2 (+\text{M})$ obtained in this work (squares), by Tyndall *et al.*[8] (circles, data calculated using equation E3 and a value of $k_{\text{M}}/k_{\text{c}} = 8.9 \times 10^{-18} \text{ molecule}^{-1} \text{ cm}^3$) and by Hou *et al.*[10] (triangles), respectively. The solid and dashed lines represents a fit to the data obtained in this work and the work from Tyndall *et al.* [8,22] (scaled values, see comments in the text) using equation (E3), respectively.

Figure 1.

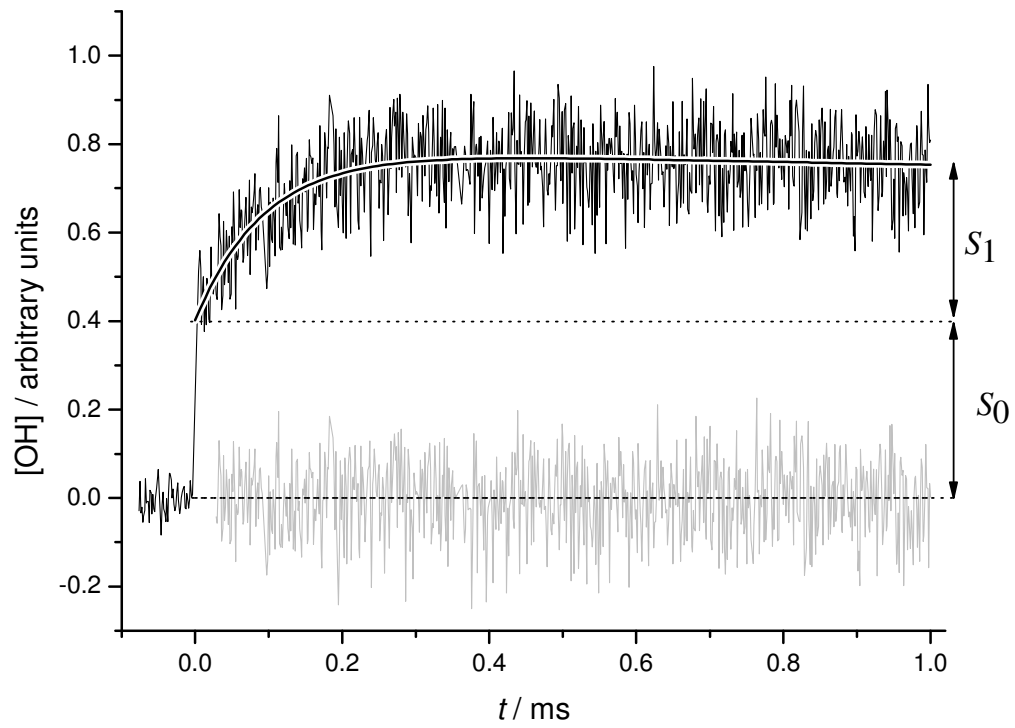


Figure 2

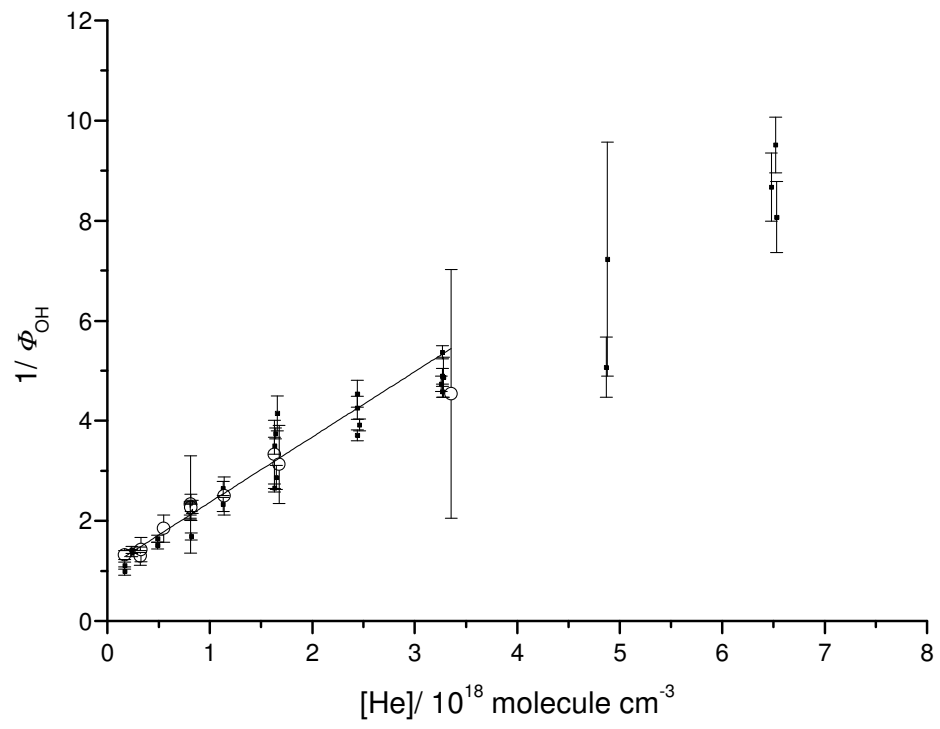


Figure 3.

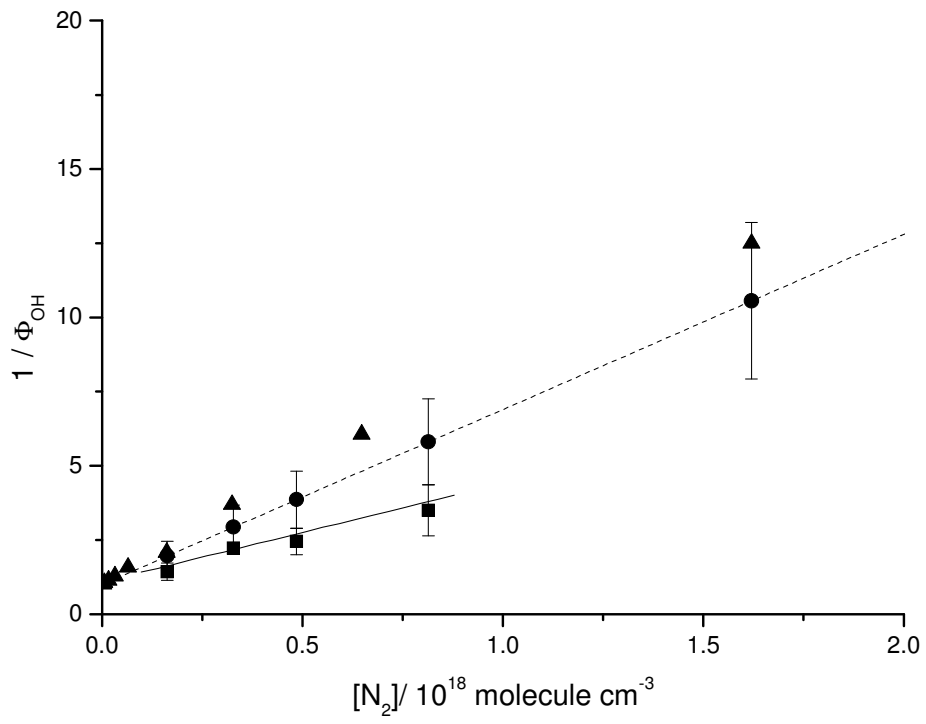


Table 1. Absolute OH yields for CH₃CO+O₂ (+M) reaction as function of [He] at room temperature. The quoted uncertainties correspond to 95% confidence limits.

No of expt.	[M] / 10 ¹⁸ molecule cm ⁻³	1 / Φ_{OH}	1 / $\Phi_{\text{OH}}^{\text{b}}$	$k_1^{\text{a}} / 10^{-12}$	$k_1^{\text{a,b}} / 10^{-12}$
23	0.17	1.32 ± 0.09	1.18 ± 0.15	1.39 ± 0.37	1.80 ± 0.23
13	0.32	1.30 ± 0.18	1.35 ± 0.16	1.94 ± 0.94	1.95 ± 0.23
18	0.33	1.43 ± 0.24	1.35 ± 0.16	1.38 ± 0.60	1.96 ± 0.23
11	0.55	1.85 ± 0.27	1.59 ± 0.18	3.21 ± 0.60	2.16 ± 0.24
12	0.81	2.33 ± 0.97	1.87 ± 0.21	2.6 ± 1.0	2.36 ± 0.27
29	0.82	2.27 ± 0.26	1.88 ± 0.21	2.29 ± 0.31	2.36 ± 0.27
22	1.14	2.50 ± 0.38	2.23 ± 0.26	1.97 ± 0.85	2.58 ± 0.30
9	1.63	3.33 ± 0.67	2.75 ± 0.34	2.16 ± 0.67	2.84 ± 0.36
12	1.67	3.13 ± 0.78	2.80 ± 0.35	4.6 ± 1.2	2.87 ± 0.36
6	3.35	4.55 ± 2.48	4.60 ± 0.70	---	3.54 ± 0.53

^a In molecule⁻¹ cm³ s⁻¹

^b Generated using the data given in [7] together with new data obtained in this laboratory using 248 nm acetone photolysis as CH₃CO source and assuming a unit yield of OH at zero pressure and a strong collision model.

Table 2. Absolute OH yields for the CH₃CO+O₂ (+M) reaction as a function of [N₂] at room temperature. The quoted uncertainties correspond to 95% confidence limits.

No of expt.	10 ⁻¹⁸ [N ₂] / molecule cm ⁻³	1 / Φ_{OH}
39	0.16	1.43 ± 0.29
27	0.33	2.22 ± 0.10
18	0.48	2.45 ± 0.45
21	0.81	3.50 ± 0.86

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