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# Vibrational relaxation of OH by oxygen atoms

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## Abstract

The collisional removal of OH(v = 1) by  $O(^{3}P)$  atoms is investigated. OH is generated by 193 nm photolysis of  $H_2O_2$ , and  $O(^{3}P)$  atoms are generated by a microwave discharge in  $O_2$  diluted in Ar. OH(v = 0 and 1) concentrations are monitored by laser-induced fluorescence vs. the time after the photolysis laser pulse. From comparison of these concentrations with kinetic simulations, the room-temperature total removal rate constant for OH(v = 1) in collisions with  $O(^{3}P)$  is determined to be  $(3.9 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This value is slightly larger than the OH(v = 0)- $O(^{3}P)$  reaction rate constant, but the difference is within the experimental uncertainty. © 2005 Elsevier B.V. All rights reserved.

## 1. Introduction

The OH radical is an important species in the earth's atmosphere and other environments. An understanding of its collisional vibrational relaxation rates is important in modeling OH chemistry in the upper atmosphere [1,2]. Collisional vibrational relaxation of OH in a wide range of vibrational levels by stable collision partners has been investigated [3–10]. Investigation of collisional relaxation of vibrationally excited OH by oxygen atoms, present at significant concentration in the upper atmosphere, is also relevant. This energy transfer process is interesting from a fundamental point of view [11] since it involves two open-shell species and occurs through formation and decay of a transient HO<sub>2</sub> complex (see Fig. 1).

OH(v = 0) can be removed in collisions with oxygen atoms through the reaction

$$\begin{aligned} & OH(X^2\Pi) + O(^{3}P) \to H + O_2 \\ & \Delta H^{\circ}(0 \text{ K}) = -16.29 \pm 0.09 \text{ kcal/mol.} \end{aligned} \tag{1}$$

Because of its importance in atmospheric and combustion chemistry, the rate of reaction 1 has been extensively

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studied; the IUPAC subcommittee for gas phase data evaluation [12] and the NASA panel [13] recommend  $k_{v=0}$ -(OH–O) = (3.5 ± 0.4) and (3.3 ± 0.7) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K, respectively.

Collisional removal of  $OH(v \ge 1)$  by  $O({}^{3}P)$  can occur by both chemical reaction and vibrational relaxation. In EPR studies, Spenser and Glass [14] report values of  $(1.45 \pm 0.25)$  and  $(1.05 \pm 0.53) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $OH(v = 1) - O(^{3}P)$  vibrational relaxation and chemical reaction rate constants, respectively. Marschall et al. [15] have investigated collisional removal of OH(v) by  $O({}^{3}P)$ through laser-induced fluorescence measurements of timedependent OH(v) concentrations after 248 nm photolysis of ozone and subsequent reaction of  $O(^{1}D)$  with water to form vibrationally excited OH. They reported a preliminary value  $k_{v=2}(OH-O) = 4.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (quoted in [16]) for the room-temperature OH(v = 2)-O(<sup>3</sup>P) total removal rate constant. Varandas [17] has computed rate constants for reactive and non-reactive  $OH(v) - O(^{3}P)$  collisions at several temperatures through trajectory calculations on the lowest HO<sub>2</sub> potential energy surface (PES).

We present here an investigation of the collisional removal of OH(v = 1) by  $O({}^{3}P)$ . Oxygen atoms are prepared in a flow system by a microwave discharge in O<sub>2</sub> diluted in argon. Hydroxyl is generated by 193 nm photolysis of

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Fig. 1. Schematic energy diagram of the  $OH(X^2\Pi) + \ O(^3P) \to H + O_2$  reaction.

 $H_2O_2$  added to the flow, and OH(v = 0 and 1) concentrations are followed by laser-induced fluorescence. The measured time-dependent OH(v) concentrations are compared with full kinetic modeling of species concentrations in order to extract the  $OH(v = 1)-O({}^{3}P)$  total removal rate constant  $k_{v=1}(OH-O)$ . This method of studying vibrational relaxation of OH is challenging because of the very small (~1%) v = 1 to v = 0 population ratio of OH formed in the photolysis of  $H_2O_2$  [18,19] but avoids problems in modeling the population of OH(v = 1) from collisional cascade from higher OH vibrational levels.

# 2. Experimental

These experiments were performed in a modified apparatus previously employed for collisional energy transfer studies [20,21]. Oxygen atoms were generated by passing a 5% mixture of  $O_2$  in Ar at a total pressure of 2.2 Torr through a 2450 MHz microwave discharge (80 W). The gas mixture flowed (120 sccm total, measured with calibrated flow meters) at an estimated velocity of 150 cm/s through a 3.1 × 6.3 cm rectangular section mounted on a 1 m spectrometer, employed with wide slits (4 nm spectral resolution) to isolate fluorescence in a given vibrational band. Surfaces downstream of the discharge were coated with fluorocarbon wax to inhibit wall recombination. Pressures were measured with a capacitance monometer (MKS).

The photolytic OH precursor  $H_2O_2$  was added  $(2.5 \pm 1 \text{ mTorr})$  neat through a teflon needle valve 10 cm upstream of the fluorescence detection zone, and OH was generated by 193 nm photolysis using radiation from an excimer laser (Lambda Physik COMPex 102). The  $H_2O_2$  partial pressure was determined by monitoring the needle valve opening with the pressure rise into the  $O_2/Ar$  flow. Typical laser energies were 10 mJ in a 1.2 cm diameter beam in the apparatus. Concentrated liquid  $H_2O_2$  ( $\geq 95\%$ ) was prepared by pumping on 30% reagent. The

vapor above a 95% solution is ~90% H<sub>2</sub>O<sub>2</sub>, with the remainder H<sub>2</sub>O [22]. Based on the 193 nm H<sub>2</sub>O<sub>2</sub> absorption cross section and quantum yields for the OH + OH and H + HO<sub>2</sub> dissociation channels [12], we estimate 0.8% dissociation of H<sub>2</sub>O<sub>2</sub> and an initial OH concentration of  $7 \times 10^{11}$  molecules cm<sup>-3</sup>. H<sub>2</sub>O<sub>2</sub> was deemed to be a more suitable precursor than the commonly employed HNO<sub>3</sub> precursor since the latter also yields at 193 nm O(<sup>1</sup>D) [23,24], which reacts with hydrogen-containing compounds to form OH(*v*), causing a cascade contribution to [OH(*v* = 1)]. Photolysis at 248 nm would provide a cleaner source of OH, but the absorption cross sections are too low [13] to allow detectable photolytic production of OH(*v* = 1) at the required low partial pressures of the precursor.

OH(v = 0 and 1) were detected vs. time after photolysis by pulsed laser fluorescence excitation on the A-X (1,0)  $Q_1(1)$  and (2,1)  $Q_1(2)$  lines and detection in the (1,1) and (2,2) bands, respectively. The frequency-doubled output of an optical parametric oscillator (Continuum Sunlite EX) was employed for excitation. The probe beam counterpropagated along the photolysis laser beam and was introduced through the opposite sidearm of the apparatus. The delay between the photolysis and probe lasers was set by a digital delay generator which was controlled by the data acquisition computer. A run consisted of recording the fluorescence intensity (10-shot average) while cycling through a grid of delays 10 times [20 times for OH(v = 1)with the microwave discharge on].

# 3. Results

The total removal rate constant  $k_{v=1}$  (OH–O) was determined by comparison of the temporal decays of OH(v = 0)and 1) concentrations with the results of kinetic modeling, as described below. Figs. 2 and 3 present measured OH(v = 0 and 1) concentration profiles, as detected by laser-induced fluorescence on given rotational transitions, with the microwave discharge off and on, respectively. The OH(v = 0) concentration with the discharge off is seen to decay very slowly, mainly from diffusion out of the laser excitation/detection zone. By contrast, [OH(v=0)] decays more rapidly with the discharge on, due to reaction with  $O(^{3}P)$  atoms. This decay rate was used with a literature value [12] of  $k_{v=0}$ (OH–O) to estimate the O(<sup>3</sup>P) concentration, as described below. The decay of [OH(v = 1)] with the discharge off results mainly from vibrational relaxation by  $H_2O_2$  and is used to estimate the  $k_{v=1}(OH-H_2O_2)$  total removal rate constant. Finally,  $k_{v=1}$ (OH–O) was determined by analysis of [OH(v = 1)] decay with the discharge on, taking into account removal by  $H_2O_2$  and other species.

The OH(v = 0 and 1) profiles displayed in Figs. 2 and 3 were taken at the same photolysis laser energy ( $\pm 1$  mJ), and Ar, O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> partial pressures (constant to  $\pm 0.001$  Torr). The stability of [O(<sup>3</sup>P)] was monitored by the OH(v = 0) decay rate with the microwave discharge on; this decay rate was constant to <0.5% on a given day



Fig. 2. Time-dependent concentrations of (a) OH(v = 0) and (b) OH(v = 1) vs. the time between the photolysis and probe laser pulses, with the microwave discharge off. The partial pressures of the added reagents were: Ar, 2.1; O<sub>2</sub>, 0.1; H<sub>2</sub>O<sub>2</sub> 0.0025 ± 0.001 Torr. The plots in (a) and (b) represent sums over 16 and 13 runs, respectively. The solid lines show least squares fits of the decay profiles to exponential functions.



Fig. 3. Time-dependent concentrations of (a) OH(v = 0) and (b) OH(v = 1) vs. the time between the photolysis laser and probe laser pulses, with the microwave discharge on. The partial pressures of the added reagents were: Ar, 2.1; O<sub>2</sub>, 0.1; H<sub>2</sub>O<sub>2</sub> 0.0025 ± 0.001 Torr. The plots in (a) and (b) represent sums over 22 and 37 runs, respectively. The solid lines show least squares fits of the decay profiles to exponential functions.

and varied by  $\leq 5\%$  between days. The baseline was determined by runs with the excimer laser blocked. The spike at t = 0 in Figs. 2b and 3b is due to scattered light from the excimer laser. After an initial buildup due to rotational thermalization, the concentrations are seen to decay exponentially.

Comparison of the fluorescence intensities plotted in Figs. 2 and 3 shows that the OH concentration drops by a factor of ~3 when the microwave discharge is turned on. This is due to loss of H<sub>2</sub>O<sub>2</sub> from a slow chain reaction involving O(<sup>3</sup>P) atoms, HO<sub>2</sub>, OH, and H atoms. With the photolysis laser off and the discharge on, no OH laser fluorescence was observed, and [OH(v = 0)] is <1% of the concentration with the laser on.

We have simulated this decomposition by kinetic modeling in order to estimate species concentrations in the flow with the microwave discharge on and  $O(^{3}P)$  atoms present. Table 1 presents the processes included the model (10 species and 29 processes). Rate constants were taken from the IUPAC compilation [12] and other sources [4,5,7,25,26]. OH vibrational levels were considered separate species in order to model the vibrational relaxation, discussed below. This modeling qualitatively, but not quantitatively, reproduces the observed decomposition of H<sub>2</sub>O<sub>2</sub>. For Ar, O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> partial pressures 2.1, 0.1, and 0.0025 Torr and an assumed 8% O<sub>2</sub> dissociation fraction, we compute the following concentrations (in molecule  $cm^{-3}$ ) after 0.2 s reaction time:  $[O_2] = 3.1 \times 10^{15}$ ,  $[O(^3P)] = 4.1 \times 10^{14}$ ,  $[H_2O_2] = 5.6 \times 10^{13}$ ;  $[H_2O] = 7.0 \times 10^{12}$ ;  $[HO_2] = 1.2 \times 10^{10}$ ;  $[OH] = 2.8 \times 10^{10}$ ;  $[H] = 2.2 \times 10^{13}$ ;  $[H_2] = 9.4 \times 10^{11}$ . It can be seen that, aside from  $O({}^{3}P)$ , the free radical predicted to have the highest concentration is the H atom. This model predicts 29% H<sub>2</sub>O<sub>2</sub> decomposition, significantly less than observed, and a higher OH concentration than inferred ( $<7 \times 10^9$  molecules cm<sup>-3</sup>) from our observations. Nevertheless, these results are useful in taking account of the decomposition of H<sub>2</sub>O<sub>2</sub> in computing  $k_{v=1}$ (OH–O) and were employed to estimate species concentrations just before the photolysis laser pulse. Inclusion of the possible effects of  $O(^{1}D)$ ,  $O_{2}(a)$ , or  $O_{3}$  in the flow did not significantly affect the H<sub>2</sub>O<sub>2</sub> decomposition computed by our kinetic model.

The OH(v = 0 and 1) decays were fitted (solid lines through measured concentrations in Figs. 2 and 3) to exponential functions in a nonlinear least squares procedure over  $18 \le t \le 200 \ \mu$ s to determine decay rates. The decay of [OH(v = 0)] with the discharge off (Fig. 2a) was fitted to a first-order diffusion loss rate of  $250 \pm 60 \ s^{-1}$ . This loss was included for all the free radicals in kinetic modeling to fit OH(v) decays after the photolysis laser pulse. A decay rate of  $(1.13 \pm 0.01) \times 10^4 \ s^{-1}$  was determined for the time-dependent OH(v = 0) concentration with the discharge on (Fig. 3a). The assumed O<sub>2</sub> dissociation fraction was varied in the kinetic model to match this decay rate, and we estimate  $[O(^{3}P)] = (4.1 \pm 0.2) \times 10^{14} \ atom \ cm^{-3} \ at$ the laser excitation/detection zone, with the dissociation fraction given above; the quoted error includes fitting

Table 1

Kinetic model for simulating concentrations [species included: Ar,  $O_2$ ,  $O(^{3}P)$ , OH(v = 0), OH(v = 1),  $H_2O_2$ ,  $H_2O$ , H,  $HO_2$ ,  $H_2$ ]

Reaction	$k_{298} \ (\text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1})$	Reference
$\overline{O(^{3}P) + OH(v=0)} \rightarrow H + O_{2}$	$3.5 \times 10^{-11}$	[12]
$O(^{3}P) + OH(v = 1) \rightarrow \text{products}^{a}$	$3.9 \times 10^{-11}$	This work
$O(^{3}P) + H_{2}O_{2} \rightarrow OH(v = 0) + HO_{2}$	$1.7 \times 10^{-15}$	[12]
$O(^{3}P) + HO_{2} \rightarrow OH(v = 0) + O_{2}$	$5.8 \times 10^{-11}$	[12]
$OH(v) + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 \times 10^{-12}$	[12]
$OH(v) + H_2 \rightarrow H_2O + H$	$6.7 \times 10^{-15}$	[12]
$OH(v) + HO_2 \rightarrow H_2O + O_2$	$1.1 \times 10^{-10}$	[12]
$OH(v) + OH(v) \rightarrow H_2O + O$	$1.5 \times 10^{-12}$	[12]
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.6 \times 10^{-12}$	[12]
$H + H_2O_2 \rightarrow OH(v = 0) + H_2O$	$4.2 \times 10^{-14}$	[25]
$\rightarrow$ H <sub>2</sub> + HO <sub>2</sub>	$5.2 \times 10^{-15}$	
$H + HO_2 \rightarrow H_2 + O_2$	$5.6 \times 10^{-12}$	[12]
$\rightarrow$ OH( $v = 0$ ) + OH( $v = 0$ )	$7.2 \times 10^{-11}$	
$\rightarrow$ H <sub>2</sub> O + O	$2.4 \times 10^{-12}$	
$H + OH(v) \rightarrow H_2 + O$	$1.1 \times 10^{-16}$	[26]
$O + O + M \rightarrow O_2 + M$	$1.0 \times 10^{-33}$	[26]
$H + H + M \rightarrow H_2 + M$	$6.0 \times 10^{-33}$	[25]
$H + O_2 + M \rightarrow HO_2 + M$	$5.4 \times 10^{-32}$	[12]
$H + OH(v) + M \rightarrow H_2O + M$	$4.3 \times 10^{-30}$	[12]
$OH(v) + OH(v) + M \rightarrow H_2O_2 + M$	$6.9 \times 10^{-31}$	[12]
$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	$4.0 \times 10^{-32}$	[12]
$OH(v = 1) + O_2 \rightarrow OH(v = 0) + O_2$	$1.3 \times 10^{-13}$	[5]
$OH(v=1) + H_2O \rightarrow OH(v=0) + H_2O$	$1.9 \times 10^{-11}$	[7]
$OH(v=1) + H_2O_2 \rightarrow OH(v=0) + H_2O_2$	$4.0 \times 10^{-11}$	This work
$OH(v = 1) + H \rightarrow OH(v = 0) + H$	$1.5  imes 10^{-10}$	[29]
$OH(v=1) + H_2 \rightarrow OH(v=0) + H_2$	$1 \times 10^{-15}$	[4]
$OH(v = 1) + Ar \rightarrow OH(v = 0) + Ar$	$1 \times 10^{-15}$	[4]
$OH(v = 1) + OH \rightarrow OH(v = 0) + OH$	$5 \times 10^{-11}$	Assumed
$OH(v = 1) + HO_2 \rightarrow OH(v = 0) + HO_2$	$3.5 \times 10^{-11}$	Assumed

<sup>a</sup> The branching between reaction and vibrational relaxation was assumed to follow the prior distribution (see text).

uncertainties, but not the uncertainty in  $k_{v=0}$ (OH–O) employed [12] in the model.

The  $[O({}^{3}P)]$  determined from the OH(v = 0) decay rate is slightly different from a value computed by just considering the diffusion loss and reaction 1, because of the effect of several OH-producing reactions in our kinetic model. It is well known [27] that a microwave discharge in O<sub>2</sub> also creates some metastable O<sub>2</sub>(a). This species would be expected to de-activate OH(v = 1) at a rate comparable to that for O<sub>2</sub>(X), which is much slower than for O( ${}^{3}P$ ) atoms.

The vibrational relaxation of OH by  $H_2O_2$  has not been previously reported. The decay of [OH(v = 1)] with the discharge off was employed to estimate the rate constant. A decay rate of  $(4.45 \pm 0.13) \times 10^3 \text{ s}^{-1}$  was determined for [OH(v = 1)] with the discharge off (Fig. 2b). By comparison of this decay rate with kinetic modeling results, the  $OH(v = 1)-H_2O_2$  vibrational relaxation rate constant  $k_{v=1}(OH-H_2O_2)$  was estimated to equal  $(4.0 \pm 1.0) \times$  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, or approximately twice that for relaxation by  $H_2O$  [7]. The quoted uncertainty includes the uncertainty in  $[H_2O_2]$ . This  $OH(v = 1)-H_2O_2$  relaxation rate was used in our kinetic modeling.

The observed decay of the OH(v = 1) concentration with the microwave discharge on (Fig. 3b) is primarily determined by collisional removal by O(<sup>3</sup>P) atoms, with a significant contribution due to H<sub>2</sub>O<sub>2</sub> and H atoms. A decay rate of  $(2.19 \pm 0.16) \times 10^4$  s<sup>-1</sup> was determined for [OH(v = 1)] with the discharge on (Fig. 3b). Through comparison of this decay rate with variation of  $k_{v=1}$ (OH–O) in our kinetic model with concentrations of H2O2 decomposition products taken from above, we derive a value  $k_{v=1}$ (OH–O) = (3.9 ± 0.6) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [1 $\sigma$ uncertainty, including the uncertainty in the literature value [12] for  $k_{v=0}$ (OH–O)]. The major contributions to [OH(v=1)] decay can be estimated by multiplying OH(v = 1) removal rate constants (Table 1) by concentrations to yield first-order decay rates (in  $10^4 \text{ s}^{-1}$ ): O(<sup>3</sup>P), 1.59; H, 0.32; H<sub>2</sub>O<sub>2</sub>, 0.23; O<sub>2</sub>, 0.04; H<sub>2</sub>O, 0.01. It can be seen that the determined rate of removal of OH(v = 1) by  $O(^{3}P)$  is somewhat dependent upon the assumed value for [H]. Since  $[O(^{3}P)]$  and  $k_{v=1}(OH-O)$  are determined by the OH(v = 0 and 1) decay rates, respectively, the ratio of  $k_{v=1}$ (OH–O) to  $k_{v=0}$ (OH–O) is better determined than  $k_{v=1}$ (OH–O) itself; we have determined the ratio  $k_{v=1}(\text{OH-O})$  to  $k_{v=0}(\text{OH-O})$  to equal  $1.1 \pm 0.1$  Hence,  $k_{v=1}$ (OH–O) is found to be slightly larger than  $k_{v=0}$ (OH–O), but the difference is within the experimental uncertainty.

#### 4. Discussion

The present study provides slight support to the previous experimental studies [14,15] and a single-surface classical trajectory study [17] that the removal of OH(v = 1) by  $O({}^{3}P)$  atoms is enhanced by vibrational excitation. Our total collisional removal rate constant is significantly lower than that determined in an EPR study [14] and somewhat lower than the value reported for the collisional removal of OH(v = 2) [15]. The single-surface classical trajectory study of Varandas [17] predicts a similar small enhancement of the total removal rate constant in  $OH(v)-O({}^{3}P)$  collisions vs. the OH vibrational quantum number.

Since the collisional removal of OH with O(<sup>3</sup>P) atoms is mediated by the initial formation of an HO<sub>2</sub> complex, it would be expected that enhancement in  $k_v$ (OH–O) by OH vibrational excitation would result from an enhanced formation rate of the complex. The rate of formation of the complex is determined by the strongly attractive  $\tilde{X}^2 A''$  and  $\tilde{A}^2 A' HO_2$  PESs. Hence, the enhancement in  $k_v$ (OH–O) with an increasing v should reflect the dependence of the PESs on the OH internuclear separation in the entrance channel.

Collisional removal of  $OH(v \ge 1)$  by  $O({}^{3}P)$  atoms occurs by both chemical reaction and vibrational relaxation. Since this process proceeds through formation and decay of a transient HO<sub>2</sub> complex (see Fig. 1), we can make an estimate of the branching ratio for chemical reaction vs. vibrational relaxation through a statistical theory, namely the prior distribution [28]. Summing over the accessible rovibrational molecular levels (in both the  $X^{3}\Sigma_{g}^{-}$  and  $a^{1}\Delta$  electronic states of O<sub>2</sub>), the prior statistical model predicts branching ratios of 85 and 15% for chemical reaction and collisional vibrational relaxation, respectively, in OH- $(v = 1) + O({}^{3}P)$  collisions. It would be interesting to compare the rate constants  $k_{v}(OH-O)$  and predicted branching ratios with the results of multi-surface theoretical treatments of the collision dynamics.

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