ENERGY PARTITIONING IN THE REACTION $O(^1D) + H_2O \rightarrow OH + OH$. THE INFLUENCE OF $O(^1D)$ TRANSLATIONAL ENERGY ON THE REACTION RATE CONSTANT

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For the exothermic reaction $O(^1D) + H_2O \rightarrow OH + OH$ the rate constant and its energy dependence were determined by monitoring the concentration of the OH product. This was done by integrating the distribution of product molecules over all accessible states. The rate constant, determined at different velocity distributions of the reacting metastable over a wide range, is energy independent.

Oxygen atoms in their first excited state — that is, the $O(^1D)$ state — are of considerable significance for atmospheric chemistry. They have an excitation energy of ≈ 45 kcal/mol and are chemically very reactive. In particular they react with water vapor in the atmosphere, forming OH radicals in the exothermic reaction

$$O(^1D) + H_2O \rightarrow OH + OH + \Delta H ,$$

$$\Delta H = -28.4 \text{ kcal/mol} .$$

(1)
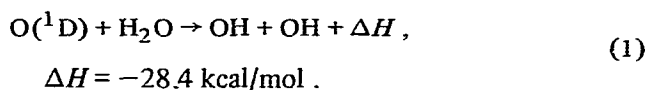
Excited $O(^1D)$ atoms are formed in the atmosphere by photodissociation of various oxygen-containing molecules, the principal source being the photodissociation of ozone below 310 nm:

$$O_3 + h\nu \, (<310 \text{ nm}) \rightarrow O(^1D) + O_2(^1\Delta_g) .$$

(2)
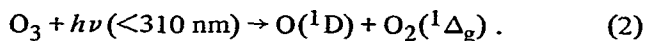
The quantum yield for this process is ≈ 0.9 [1—3]. Since the OH radicals that are formed react with many important trace constituents of the atmosphere, they play a key role in atmospheric chemistry. For this reason, investigations of reaction (1) are always of special interest to those studying the chemistry of the atmosphere.

The rate constant k_1 of reaction (1) has been determined in a number of studies [4—16]. In these measurements the rate constant of the reaction was obtained from the rate of consumption of $O(^1D)$ atoms. While the chemical methods were frequently used for the determination of relative rate constants,

a few absolute determinations have also been performed, especially in recent times. However, these methods yield an upper limit for the rate constant, since the measured values may reflect other mechanisms consuming $O(^1D)$ atoms besides the process of interest.

The present experiment exploits for the first time the possibility of directly measuring the rate constant by determination of the concentration of the OH molecules which are produced. A laser system consisting of a Nd : YAG laser and a dye laser was employed for this purpose [17]. The Q-switched Nd : YAG laser is frequency doubled (532 nm) and quadrupled (266 nm); the pulse length $\Delta t = 6$ ns. The UV flash is used for the photolysis of ozone, which flows through the reaction chamber with water vapor. The partial pressure of ozone is held constant at 1.5 Torr, while the partial pressure of water vapor is varied between 2.5 and 19 Torr. The $O(^1D)$ atoms produced by the 266 nm radiation react with water as in eq. (1), producing OH molecules. The range of pressures employed in the present study leads to reaction times between 8 and 40 ns.

The product OH molecules are observed through their absorption around 308 nm. By utilizing the known transition probabilities, the absolute quantity of OH molecules can be determined from the strength of their absorption [18]. For this purpose the frequency-doubled light (532 nm) of the Nd : YAG laser

is used to pump a narrow-band dye laser whose emission is frequency doubled in a KDP crystal. This narrow-band UV laser ($\Delta\nu \approx 1.5$ GHz) is selectively tuned to the desired molecular transitions of OH by pressure tuning. In order to allow the $O(^1D)$ atoms an opportunity to form OH molecules by reaction with H_2O while keeping the product OH molecules as collision-free as possible, the UV impulse of the dye laser ($\Delta t \approx 5$ ns) is delayed by 10 ns relative to the photolysis flash.

For OH molecules at room temperature, the Doppler width of the resonance transition is ≈ 3 GHz. Therefore the small bandwidth of the laser permits the linewidth of the absorption to be determined. Thus, not only the rotational and vibrational state of OH — its internal energy — but also its external energy, the energy of translation, can be determined [19].

To obtain the rate constant of reaction (1), the distribution of the product OH molecules over the various rotational and vibrational states of the electronic ground state was measured at four different partial pressures of water vapor. By summing the populations of the individual states, the total amount of OH is obtained, and the rate constant of the reaction determined.

The number of OH molecules at time t in a particular state i is given by the equation

$$N_i = A\,\frac{k_{1,i}[H_2O]}{k_1[H_2O] + k_2[O_3]}$$

$$\times\,[1 - \exp\{-(k_1[H_2O] + k_2[O_3])t\}]\,. \qquad (3)$$

The proportionality constant A incorporates all necessary information about the intensity of the photolyzing radiation, the photodissociation cross section of ozone at 266 nm wavelength, and the quantum yield $\phi(O(^1D))$. Here k_{1i} are the individual rate constants and k_2 is the rate constant for the reaction of $O(^1D)$ with O_3. If the effect of ozone on the $O(^1D)$ atoms is small compared with that of water, eq. (3) reduces to

$$N_i \approx (k_{1i}/k_1)\,\{1 - \exp(-k_1[H_2O]\,t)\}. \qquad (4)$$

The rate constant k_1 then follows from the summation

$$k_1 = \sum_i k_{1i}\,.$$

By measuring the N_i at various partial pressures of H_2O, k_1 as well as k_2 can be determined. In the practical implementation of the present work, however, the determination of k_2 was dispensed with.

Experimental results for four different partial pressures of H_2O are shown in fig. 1. Calculations based on these results lead to a value

$$k_1 = (1.90 \pm 0.48) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\,\text{s}^{-1}$$

for the rate constant of reaction (1).

This procedure for determination of rate constants has advantages. In the first place the rate constant for the production of OH molecules in reaction (1) is based on direct observation of product molecules. Secondly, all product molecules are detected. This latter point is of special importance if, for instance, the molecular product is determined by resonance fluorescence; the population numbers of the molecular states change by relaxation as a function of the changing total pressure during a series of measurements.

The translational energy distribution of excited oxygen atoms formed in the photolysis of ozone depends upon the quantum energy of the radiation employed for photolysis. This energy distribution was determined by Sparks et al. [1] for the case of photolysis by the 266 nm radiation of the Nd:YAG laser. They found a mean energy of 4.6 kcal/mol for the oxygen atoms, so that the present experiment deals with the reaction of energy-rich $O(^1D)$ atoms.
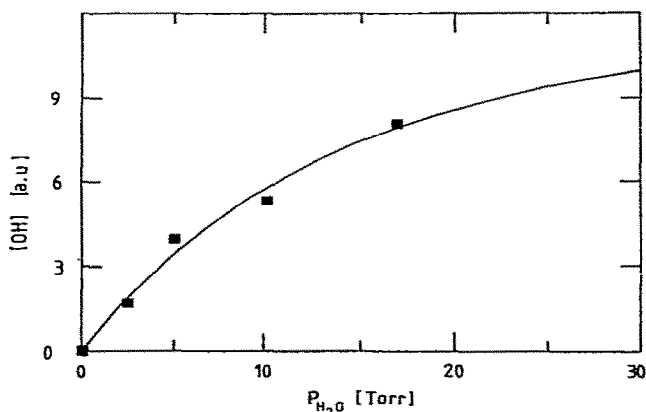

Fig. 1. Experimentally observed number of OH product molecules at 10 ns delay time for a laser pulse width of 5 ns as function of water vapor pressure.

It has previously been established that reactions involving $O(^1D)$ atoms occur without activation energy, so that the rate constant of reaction (1) should be energy independent [12]. However, the experiment here described in principle allows this question to be investigated over a very wide range of energies $O(^1D)$ is demonstrably only weakly quenched by addition of inert collision partners such as helium or argon. Thus the effect of collisions with helium or argon is primarily a relaxation of the translational energy [11,14,20]. For this reason a further experiment was performed in which the O_3/H_2O mixture was augmented with 40 Torr of argon. The relaxing effect of the argon can be distinctly observed by the diminution of the linewidth of the OH absorption (fig. 2). Since argon reacts neither with $O(^1D)$ nor with OH, the observed total number of OH molecules produced is a direct measure of the rate constant of the reaction of the now slow $O(^1D)$ atoms with water vapor.

The observations lead to the following value for the rate constant k_1:

$$k_1 = (2.2 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The velocity distribution of $O(^1D)$ upon addition of 40 Torr of argon can be estimated from the distribution for OH. If the absorption line of OH is interpreted as a Doppler profile, an equivalent translational temperature can be calculated from the linewidth.
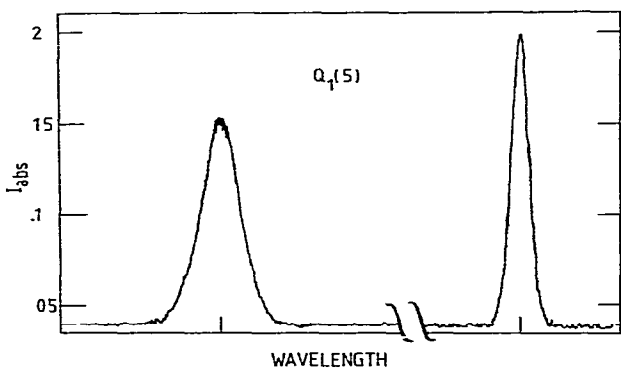

Fig. 2. Absorption line shapes of $Q_1(5)$ at 32403.47 cm^{-1} [18] as measured with a laser of linewidth $\Delta\nu_L = 0.05$ cm^{-1} showing translational cooling by added argon. (a) 1 5 Torr O_3, 5 Torr H_2O: $\Delta\nu_D^{-1} = 0.23$ cm^{-1}. (b) 1 5 Torr O_3, 5 Torr H_2O, 40 Torr Ar: $\Delta\nu_D^{-1} = 0.13$ cm^{-1}. $\Delta\nu_D$ is corrected for the laser linewidth $\Delta\nu_L$.

For OH this temperature is 1750 K when the partial pressure of H_2O is 5 Torr. An extrapolation of observed values to $p_{H_2O} = 0$ results in a translational temperature of ≈ 3500 K for nascent OH. The addition of 40 Torr of argon reduces the translational temperature of OH to 450 K, as can be seen by comparison of the linewidths in fig. 2. For the absorption line $Q_1(5)$ in fig. 2, 1.5 Torr O_3 and 5 Torr H_2O must be taken into account in addition to the 40 Torr of argon. OH molecules and $O(^1D)$ atoms are nearly equal in mass. Collisions with ozone and with water are effective for relaxation of OH molecules, while such collisions with $O(^1D)$ result in reaction, and thus in the removal of $O(^1D)$. Therefore only collisions with argon are effective in the translational relaxation of $O(^1D)$. The mean translational energy of OH (without argon) and that of $O(^1D)$ in this experiment differ by less than 20%. In the case of added argon, to be sure, a somewhat higher translational energy must be assigned to $O(^1D)$ than to OH in view of the ineffectiveness of collisions with water molecules. It can be assumed that, in the case of 40 Torr of argon, $O(^1D)$ still retains roughly 1/3 of its original energy (that is, ≈ 1.5 kcal/mol). This agrees well with Luntz's discussion [20] of the translational relaxation of $O(^1D)$ in collisions with argon.

An accurate determination of the distribution of product OH molecules over the energetically possible rotational and vibrational states, with and without addition of argon, permits calculation of the effect of the translational energy of $O(^1D)$ on the distribution of internal energy in the reaction as well as the extent of relaxation of these molecular states by added gas. Results will be published elsewhere [21].

The translational energies of the $O(^1D)$ atoms reacting in (1) correspond roughly to 2 to 5 times the energy at room temperature. However, the velocity distribution of the oxygen atoms cannot be exactly described by a thermal distribution. The experimental results show that the rate constant of reaction (1) remains independent of energy within 15%. This result is in excellent agreement with earlier determinations of the temperature dependence of the reaction [12]. However, such a comparison is of limited validity because only relative velocities have been changed, not the internal energy content of the water molecule. The two series of measurements yield a weighted average for the energy-independent value of k_1:

Table 1
Absolute rate constant of the reaction of $O(^1D)$ with H_2O[a]

Authors	Year	Ref.	$10^{10} k_1$ (cm^3 molecule^{-1} s^{-1})	Remarks
Paraskopoulos and Cvetanović	1971	[4]	4.75	b)
Scott and Cvetanović	1971	[5]	4.95	b)
Fortin et al	1972	[6]	1.93	b)
Simonaitis and Heicklen	1972	[7]	4.95	b)
Gauthier and Suelling	1973	[8]	3.33	b)
Cvetanović	1974	[9]	3.5	c)
Hampson and Garvin	1975	[10]	3 5	c)
Davidson et al.	1976	[11]	2.1	
Davidson et al.	1977	[12]	2.3	
Amimoto et al.	1979	[13]	1 95	
Lee and Slanger	1979	[14]	2.6	
Baulch et al	1980	[15]	2.8	c)
Wine and Rivishankaras	1980	[16]	1.95	
this work	1981		2.02±0 41	

a) All literature values are for 298 K The new value given in this work was taken as a mean from two velocity distributions.
b) From relative values [9] based upon CO_2.
c) Referred to as "preferred value".

$$k_1 = (2.02 \pm 0.41) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Table 1 presents a summary of determinations of the rate constant for the reaction of $O(^1D)$ atoms with H_2O carried out during the last 10 years [4–10,13, 15,16]. For this context, the relative values of the rate constant taken from the survey by Cvetanović have been converted to absolute values by appropriate multiplication. It will be noted that these rate constants exhibit a consistent trend with time. The latest results approach a value around 2.0×10^{-10} cm^3 molecule^{-1} s^{-1}. Although the values for k_1 found in the present work cannot be referred to definite temperatures, they nevertheless strongly support the assumption that k_1 can be viewed as energy independent over a very wide range.

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