DYNAMIC ASPECTS OF THE REACTION O(^{1}D) + H$_2$S → OH + SH

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The energy distribution of nascent OH($^2\Pi$, v, J) produced in the reaction of O(^{1}D) with H$_2$S has been measured by laser-induced fluorescence. The rotational distributions in $v'' = 0$ and $v'' = 1$ are Boltzmannian with temperature parameters $T_{v'' = 0} = 2300 \pm 100$ K and $T_{v'' = 1} = 2650 \pm 150$ K A population ratio $N(v'' = 1)/N(v'' = 0) = 0.17$ is observed The product-state distribution over the different spin and Λ components is statistically within the experimental uncertainty of 20%. A comparison of the OH product populations from the title reaction with the well known OH yield from the O(^{1}D)+H$_2$O reaction shows that 25% of the reactive encounters follow the reaction channel which produces OH in $v'' = 0$ and $v'' = 1$.
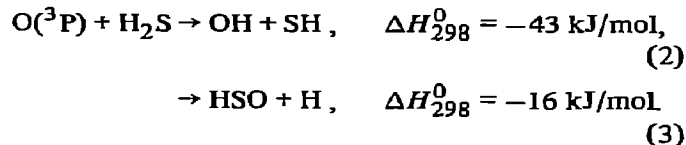
1. Introduction

Detailed studies concerning the reaction of electronically excited oxygen atoms, O(^{1}D), have been carried out, not only because of their importance to the chemistry of the atmosphere [1], but also to understand the dynamics of reactive collisions [2]. The dynamics of such reactive collisions have been discussed from observations of energy distributions of the product molecules [3—11]. The reaction of ^{16}O(^{1}D) with isotopically labeled water, H$_2^{18}$O and D$_2^{18}$O, provides one of the most complete analyses of the product states of O(^{1}D) reactions [5—7]. With the use of information theory it was possible to determine, for the first time, microscopic reaction probabilities for two coincident product molecules emerging from a chemical reaction [6].

We have now extended this study of the dynamics of four-center systems to the homologous reaction

$$O(^1D) + H_2S \rightarrow OH + SH, \qquad \Delta H^0_{298} = -233 \text{ kJ/mol.} \tag{1}$$
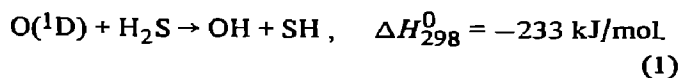
Some indirect information for this reaction was obtained from the observation of HSO radicals originating from the interaction of SH and O$_3$ in a system where SH was claimed to be the product of reaction (1) [12]. Very recently OH product molecules were detected in an IR chemiluminescence study [13].

Much better known is the reaction of an oxygen atom in its ground state, O(^{3}P), with H$_2$S [‡]:

$$O(^3P) + H_2S \rightarrow OH + SH, \qquad \Delta H^0_{298} = -43 \text{ kJ/mol,} \tag{2}$$

$$\rightarrow HSO + H, \qquad \Delta H^0_{298} = -16 \text{ kJ/mol.} \tag{3}$$

In this reaction more than 50% of the total products are formed via the reaction channel OH + SH, whereas about 10—20% lead to HSO + H [16]

2 Experimental

The study of the dynamics of reaction (1) was performed using a laser optical system with fast photochemical production and detection which utilizes the laser-induced fluorescence technique (LIF) to probe the unrelaxed distribution of OH product molecules. O(^{1}D) was produced by photodissociating O$_3$ with a 5 ns UV pulse of the fourth harmonic of a Nd . YAG laser (Quanta Ray, DCR 1) at 266 nm. The OH product radical was detected after a delay of 17 ns by a pulsed and frequency-doubled dye laser (Quantel,

‡ Data for heats of formation were taken from ref. [14] except for HSO, which was taken from ref. [15]

TDL III) pumped by the second-harmonic of the same Nd · YAG laser. Detection of nascent OH is accomplished by resonant excitation of the $X^2\Pi(v'', J'')$ → $A^2\Sigma^+(v', J')$ transition and observation of the total fluorescence. The positions of the absorption lines, the transition probabilities as well as the energy levels of OH product molecules were taken from the literature [17—19].

Typical pressures employed were P_{H_2S} = 0.25 mbar, P_{O_3} = 0.09 mbar, and P_{He} = 0 18 mbar which were sufficiently low to observe the OH in its nascent state distribution. H_2S and the O_3 + He mixture were introduced into the reaction cell through different inlets. To obtain "clean" conditions before each laser shot, the gases were continuously pumped through the chamber. Thus the observed OH radicals are result of reaction (1) and are not produced by chemical reactions which may be initiated by preceding photolysis pulses

3. Results and discussion

The applied pump-and-probe technique has the advantage, if one compares it with the molecular-beam technique, that, besides the simpler experimental arrangement, the observed number density is directly proportional to the production probability $P(f)$. In a molecular-beam experiment the probability $P(f)$ depends additionally on the translational energy $E_{trans}(f)$ of the product molecules, where f describes the quantum state of the product. Thus, using the given experimental method, it is not necessary to know the translational energy of each individual elementary collision

The observed rotational state distributions of OH in the different vibrational manifolds, $v'' = 0$ and $v'' = 1$, are shown in fig. 1. The horizontal axis represents the OH internal energy, $E_I = E_{vib} + E_{rot}$, given in wavenumbers and the vertical axis represents the natural logarithm of the ratio of the observed population and

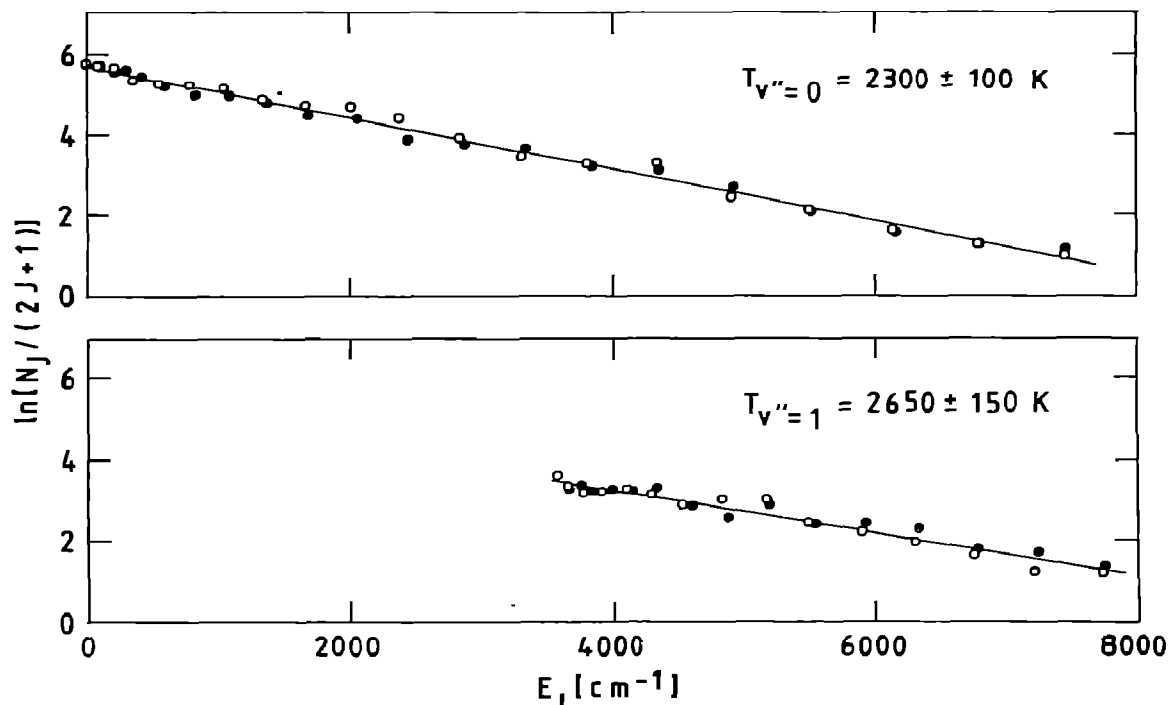Fig. 1. Boltzmann plot of the distributions of OH products emerging from the reaction $O(^1D) + H_2S \rightarrow OH + SH$ in the rotational states of $^2\Pi_{3/2, 1/2}(v'' = 0)$ (upper part in the figure) and of $^2\Pi_{3/2, 1/2}(v'' = 1)$ (lower part of the figure) for both Λ levels. Open circles represent the $^2\Pi_{3/2}$ spin system while filled circles stand for the $^2\Pi_{1/2}$ spin system. Values for the temperature parameters T_v for both observed vibrational levels are given. Experimental conditions were. P_{H_2S} = 0.25 mbar, P_{He} = 0.18 mbar, P_{O_3} = 0.09 mbar, delay time 17 ns.

of the degeneracy of the respective state.

The population of the Λ components was found to be distributed statistically within the experimental uncertainty of 20% and the measured experimental points in the figure represent the average of these populations. As can be seen, the plotted distributions of product molecules in different rotational levels are Boltzmann-like, yielding temperature parameters $T_{v''=0} = 2300 \pm 100$ K for the lowest vibrational state $v'' = 0$ and $T_{v''=1} = 2650 \pm 150$ K for the vibrational state $v'' = 1$, respectively. Both spin systems lead to the same distribution, as is indicated by open circles for the $^2\Pi_{3/2}$ system and by filled circles for the $^2\Pi_{1/2}$ system.

Although the rotational distribution of OH product molecules is roughly the same in the two vibrational states there is a remarkable difference in the vibrational population $P(v'')$. To demonstate the difference in the vibrational population numbers, one can compare single transitions which originate from the same rotational level, but from different vibrational levels. This is possible in the case of the title reaction because the rotational distributions in $v'' = 0$ and $v'' = 1$ are roughly the same. Fig. 2 shows a small section of a scan where the $P_1^0(8)$ or $O_{12}^0(5)$ line of the (0—0) transition can be compared directly with the R_1^1 lines of the band head of the $v'' = 1 \rightarrow v' = 1$ transition (superscripts in the line assignment are the values of v'')

An accurate value for the ratio of number densities in $v'' = 1$ to $v'' = 0$ is obtained by summation over the population of all quantum states in one vibrational manifold:

$$P_1/P_0 = P(v=1)/P(v=0)$$

$$= \left(\sum_J^{J_{max}} P(v=1, J) \right) \left(\sum_J^{J_{max}} P(v=0, J) \right)^{-1}. \quad (4)$$

This ratio P_1/P_0 was found to be 0.17 ± 0.03. If the observed trend in the vibrational state distribution would further continue, then 85% of all OH product molecules would be generated in $v'' = 0$. There is, however, some indication from an independent measurement using IR chemiluminescence which claims that the vibrational population increases when going from $v'' = 1$ to higher states with a maximum around $v'' = 3$ [13] This measurement and our experimental result resemble very much observations found for the reaction of $O(^1D)$ with H_2 showing two different microscopic reaction channels which lead to a bimodal vibrational distribution inverted above $v'' = 1$ [4,20].

From the study of the OH production in the reaction of $O(^1D)$ with H_2O, absolute yields were determined [5]. In this case an absorption method was applied to obtain the rovibrational distribution of the OH product. Now it was verified that the same distribution was also receivable with the fluorescence technique. A comparison of this reaction with the title reaction allows us to determine the absolute yield of OH formation for reaction (1). It showed that 21% of all reactive encounters lead to an OH formation in $v'' = 0$ and only to 4% in $v'' = 1$. If we simply add the populations from the IR chemiluminescence measurements, then 40—50% of all $O(^1D)$ encounters with H_2S lead to OH products according to reaction (1). Another reaction channel may result in the formation of HSO radicals [14,15]:

$$O(^1D) + H_2S \rightarrow HSO + H, \quad \Delta H_{298}^0 = -206 \text{ kJ/mol}. \quad (5)$$
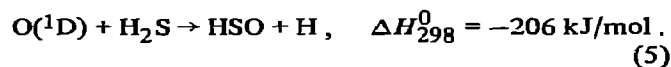
It may be possible that, similar to the reaction $O(^1D)$ + H_2, microscopic branching occurs between a simple hydrogen abstraction channel and insertion into the H—S bond to form a short-lived vibrationally excited complex, with the insertion channel dominating the formation of OH in $v'' = 0$ and $v'' = 1$. The macroscopic branching leads to OH + SH molecules and probably to HSO and H radicals where 50% of the reactive en-
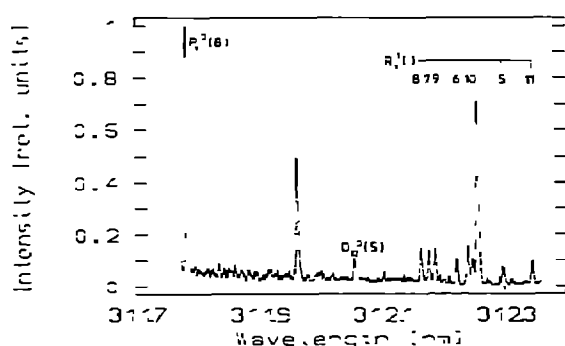

Fig. 2. A portion of the laser-induced fluorescence spectrum of the A $^2\Sigma$—X $^2\Pi$ (1—1) R_1 branch band head of the OH product of the $O(^1D) + H_2S$ reaction. $P_1(8)$ and $O_{12}(5)$ lines of the (0—0) transition are also assigned.

counters of $O(^1D)$ with H_2S result in OH + SH formation. To clarify this possibility, experiments are in progress concerning the distribution of energy on the partner molecule, SH, the rotational distribution of OH in $v'' = 2$, and the translational energy of both product radicals. The results of these measurements will be published in a forthcoming paper.

Acknowledgement

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