REACTION OF OH RADICALS WITH CS_2

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The title reaction was studied by the direct time-resolved laser-induced fluorescence method at room temperature. The rate constants for the forward and reverse reactions were measured to be $(1.9\pm0.5)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and $(7.4\pm2.5)\times10^4$ s^{-1}, respectively. The rate constant for the reaction of CS_2OH adduct with ozone was found to be $(0.9\pm0.3)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.

1. Introduction

Oxidation of the reduced compounds of sulfur (CS_2 being one of them) is probably the most important source of SO_2 and H_2SO_4 in the earth's atmosphere. The most probable oxidation reaction for CS_2 in the atmosphere is

$$OH+CS_2\rightarrow\text{products}\,. \qquad (1)$$

Measurements of the rate constant for reaction (1) have been performed by two different methods [1–5]: (1) time-resolved flash photolysis with direct detection of OH radicals, and (2) competitive methods under continuous photolysis conditions with slow monitoring of temporal profiles of reagent (CS_2) decay or product (COS, SO_2) accumulation.

The data obtained by both methods show very strong scatter – from 3×10^{-12} to 10^{-14} cm^3 molecule^{-1} s^{-1}, and are strongly dependent on the partial pressure of oxygen in the system.

The following mechanism was suggested for reaction (1):

$$OH+CS_2+M \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CS_2OH+M\,, \qquad (2)$$

$$CS_2OH+O_2\rightarrow\text{products}\,. \qquad (3)$$

A recent report from the Bordeaux conference [6] presented the observation by LIF of the equilibrium in reaction (2) and some results on the dependence of the equilibrium constant $K_{eq}=k_f/k_r$ on temperature.

In this paper we present our results on the title reaction obtained by laser photolysis/laser-induced fluorescence. The laser photolysis of ozone in the presence of water vapour was used as a source of OH radicals:

$$O_3+h\nu\rightarrow O(^1D)+O_2(^1\Delta)\,, \qquad (4)$$

$$O(^1D)+H_2O\rightarrow 2OH\,. \qquad (5)$$

By using direct monitoring of the OH concentration in the presence of CS_2 we have measured the rate constants k_f and k_r for reaction (2), and have also studied the reaction of CS_2OH with ozone (at room temperature).

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2. Experimental

2.1. Procedure

The reagents – ozone, water and CS_2, diluted with argon – were flowed through separate needle valves and mixed in a slow flow before entering the fluorescence cell. The concentrations were calculated by using the total pressure in the cell during the experiment, and the flow times of different components to the known volume.

Two laser beams, flash and probe, were crossed in the cell center at right angles and were triggered with repetition rate of 2 Hz. The probe beam was tuned to the strong OH absorption feature at 308.3 nm. The OH concentration in relative units was measured by total fluorescence radiation. The time delay between the flash and the probe pulses was changed during the experiment to obtain the temporal profiles of the OH concentration.

Depending on the experimental conditions, we accumulated from 10 to 100 kinetic curves in one experiment. The ratio of useful signal to base level (scattering, CS_2 luminescence) varied from 1 to 10. After accumulation the data were send to an on-line minicomputer (DVK-2M) for storage and processing.

2.2. Chemicals

Ozone was prepared by passing dried (Molecular sieve 5 Å + liquid nitrogen) oxygen through an ozonator, which was a home-made, water-cooled, low-frequency electric discharge device. Ozone was trapped in a double U tube at 77 K, which was pumped slowly and continuously to remove any oxygen present. After collecting ozone for several hours it was allowed to expand to room temperature and was stored in a 40 ℓ stainless-steel tank, diluted by dried argon (1:20).

CS_2 was of commercial origin and was stored under water before the experiments. The purity of CS_2 was checked before use with an IR spectrometer (IKS-29). No extra lines were detected. Air was removed by three freeze–pump–thaw cycles. Purified CS_2 was stored in a bulb on the vacuum line.

The H_2O used was doubly distilled. It was admitted to the reaction mixture by bubbling argon through a 10 cm water layer at ambient temperature.

Ar and O_2 were of commercial origin with purities

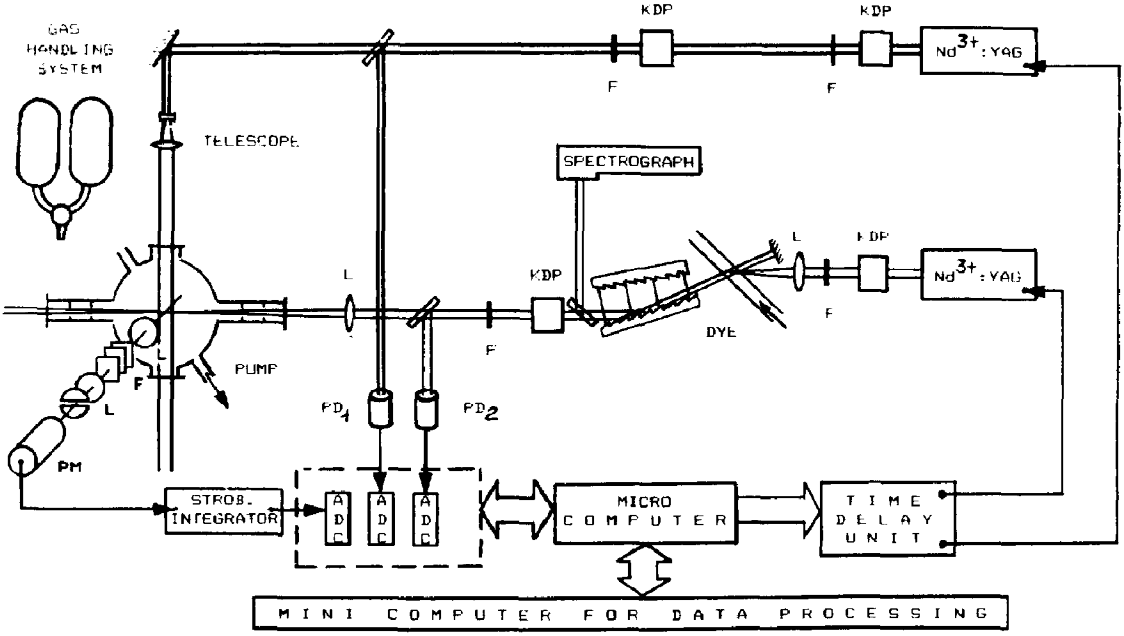

Fig. 1. Schematic of experimental apparatus.

of at least 99.992%. They were used without further purification.

2.3. *Equipment*

The photolysis laser (IZ-25) was a multimode FQ Nd:YAG which provided 1 mJ, 10 ns pulses at 266 nm. A quartz telescope (×4) was used to expand the beam to 12 mm in order to decrease the diffusion effect during measurements.

The probing source was a frequency-doubled tunable dye laser with two gratings: one was set to the position of grazing incidence, the other was used in a Littrow's mounting. The dye laser was pumped by a FD Nd:YAG laser similar to that used in the flash system. The output parameters of the probe laser were as follows: spectral tuning range (with 6-aminophenolenon) from 295 to 330 nm, bandwidth of 0.01 nm (in the UV region), pulse energy 0.2 mJ, pulse duration 10 ns. The probing wavelength could be checked by a grating spectrograph with an accuracy of 0.2 Å in the red. Fine tuning was always done via the signal itself. The probing beam was focused to the cell center with an $f=30$ cm quartz lens.

The main body of the reaction vessel was a stainless-steel cylinder with internal diameter 80 mm and volume 0.7 ℓ. Two 20 cm long sidearms with sets of light baffles were fitted to the cell in the probe direction to decrease the laser beam scattering.

The fluorescence was collected by a 4 cm diameter quartz lens held as the cell window at its focal length of 5 cm away from the cell center. A second identical lens focused this light onto a 1 mm entrance pinhole in front of a UV-sensitive photomultiplier (PM FEU-106). Coloured glass filters (Soviet Standard, UFS-2 and BS-4) were used for PM tube protection against strongly scattered photolysis radiation.

The PM output was sampled by a stroboscopic integrator (V9-5, 4 ns gatewidth), amplified (10–100 times) and digitized in 8 ms by standard ADC of F7077.1 type. The energies of both laser pulses were measured by vacuum photoelements, 10 MOm loaded, and the same ADC. All three figures were stored in a D3-28 microcomputer after each laser shot. This microcomputer was also employed for variation of the time delay between the two lasers (with 50 ns accuracy) after each pulse.

3. Results and discussion

Under the conditions of our experiments ($[H_2O]=10^{17}\,cm^{-3}$, $[O_3]=2\times10^{14}$–$10^{15}\,cm^{-3}$) the formation of OH radicals takes place over an approximately 100 ns time scale due to reactions (4), (5). The OH vibrational relaxation in collisions with H_2O molecules is also very fast: the lifetime of excited radicals is less than 1 μs [7]. The lifetime of ground-state OH radicals in our system with no CS_2 added is determined by reaction with ozone,

$$OH+O_3\rightarrow HO_2+O_2\,, \tag{6}$$

and diffusion, and is of the order of several milliseconds. The role of any second-order processes is negligible: the initial radical concentrations are less than $3\times10^{12}\,cm^{-3}$.

After addition of CS_2 to the system OH radicals begin to react due to reaction (1). A typical kinetic curve of OH concentration with CS_2 added is presented in fig. 2.

As can be seen from fig. 2, the OH concentration decay profile in the presence of CS_2 strongly deviates from an exponential shape. It consists of two parts: an initial fast fall to some fixed level, and a further more slower decay. The characteristic lifetime of the second portion is approximately 100 times longer than that of the first.

This overall kinetic behaviour of OH radicals is in accordance with a mechanism similar to (2), (3). Here, the first part of the curve involves the OH con-

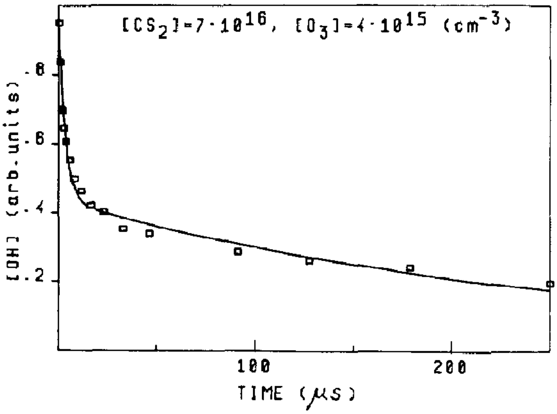

Fig. 2. Temporal profiles of OH concentrations in arbitrary units. The solid line is the best fit to the experimental data made in accordance with the three-step mechanism (2), (7).

centrations reaching its equilibrium level, defined by

$$[OH]_{eq} = [OH]_0 k_r / (k_r + k_f[CS_2]) . \qquad (i)$$

The second portion is connected with the slow decay of the CS_2OH adduct in the reaction with ozone,

$$CS_2OH + O_3 \rightarrow \text{products} . \qquad (7)$$

The main observed features of the OH kinetic behaviour are in agreement with mechanisms (2), (7): the higher the CS_2 concentration, the faster is the initial decay and the lower the equilibrium concentration level $[OH]_{eq}$.

It is difficult to suggest any alternative explanation for the observed OH kinetic curve. Actually, the equilibrium point is reached in a very short time (10–20 μs), and the rate of any process returning OH to the system would be unreasonably high. No other reactions involving ozone and ozone photolysis products can be fast enough to interfere with first portion of the curve as the ozone concentration is too small.

We have performed a set of experiments under a total pressure of 150 Torr with CS_2 concentration varied in the range $(1.5\text{–}8.2) \times 10^{16}$ cm^{-3}. This range was limited due to the following reasons. When the CS_2 concentration was low the difference between the initial radical concentration $[OH]_0$ and its equilibrium level $[OH]_{eq}$ was too small for reliable processing of the first portion of the curve. The experiments with high CS_2 concentration were difficult because of (a) the high level of luminescence from CS_2 itself at the probing wavelength, and (b) some extra radiation of chemiluminescent origin just after the photolytic flash. This chemiluminescent radiation is probably due to the reaction

$$O(^1D) + CS_2 \rightarrow \text{products} \qquad (8)$$

and its role increases for higher CS_2 concentrations.

The data processing was carried out in a simple but most reliable way. The first portion of the kinetic curve was treated as monoexponential with a "zero level" equal to the equilibrium value $[OH]_{eq}$. The effective quasi-first-order rate constant for such a decay is the sum of that for the forward and reverse processes in reaction (2):

$$K_{eff} = k_f[CS_2] + k_r .$$

Fig. 3 shows the dependence of K_{eff} versus CS_2 concentration obtained from our data. The values of $k_f = (1.9 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_r = (7.4 \pm 2.5) \times 10^4$ s^{-1} were determined from the least-squares linear fit to the data as the slope and intersect, respectively. The equilibrium constant obtained was

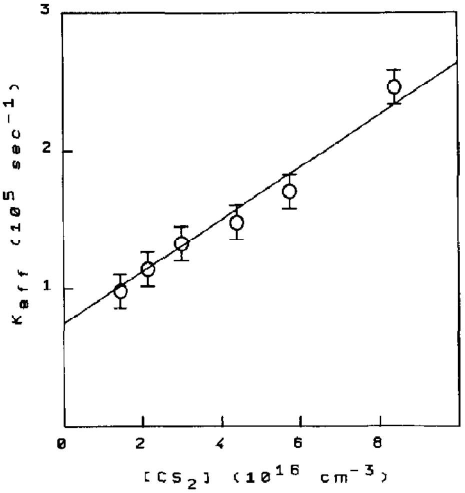

Fig. 3. Dependence of $K_{eff} = k_f[CS_2] + k_r$ versus CS_2 concentration.

$$K_{eq} = k_f / k_r = 1.54 \times 10^4 \ \ell/\text{mole} .$$

The value of k_f is in good agreement with reported data [3–5] measured under high oxygen pressure. This provides additional confirmation of the validity of the reaction scheme.

A recent paper of interest on this topic is by Hynes et al. [8]. They used a laser photolysis/laser-induced fluorescence technique similar to that employed by us. Their results are in good agreement with ours: they find the same kinetic behaviour of OH radicals and an identical k_f value within error limits.

At long time delays the kinetic curve is determined by the slow decay of CS_2OH due to the reaction with ozone.

The steady-state approximation in the framework of mechanisms (2), (7) gives for the second portion of the curve a monoexponential decay with an effective rate constant of

$$K_{eff}(2) = K_{eq}[CS_2]k_7[O_3] .$$

Processing our data in this manner yields the value of k_7 to be $(0.9 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} which is independent of CS_2 concentration.

The k_7 value is 30 times higher than the rate constant for adduct reaction with oxygen (3) [8]. This suggests that environmental ozone does not affect the subsequent fate of the CS_2OH adduct in the atmosphere.

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