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Lifetime Measurement of HO_2 Radical

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Synopsis. The formation and dissipation kinetics of HO_2 radical was investigated by means of UV absorption measurement in a gas mixture, H_2+*ca.* 1% O_2+a trace of Hg vapor which was irradiated by a 253.7 nm light pulse. The rate constant of the reaction $2HO_2 \rightarrow H_2O_2 + O_2$ was determined to be $(2.8 \pm 0.3) \times 10^{12}$ cm^3 mol^{-1} s^{-1}.

The reported values of the reaction rate constants of HO_2 which is relevant to photochemical pollution are not in very good agreement with each other.$^{1)}$ This may be attributed partly to lack of a reliable recombination rate constant of HO_2, since in most reactions the rate constants are determined relative to that of the recombination reaction. However, because of the difficulty in observing accurately the absolute concentration of HO_2, the recombination rate constants determined in different reaction systems show a relatively large scatter.$^{2-4)}$

In this note, the direct lifetime measurement as well as the determination of its absolute concentration are described. The method of HO_2 formation is based on the association reaction of H and O_2, the former of which is produced by the Hg photo-sensitized decomposition of H_2. The method is essentially similar to the one employed by Hunziker and Wendt who observed the near IR absorption spectrum of HO_2.$^{5)}$

The experimental apparatus is schematically shown in Fig. 1. The H_2 gas containing *ca.* 1% O_2 with a trace of Hg vapor is passed through a quartz cell, whose diameter and length are 3 and 30 cm, respectively, its flow rate being controlled to be several tens cm^3 s^{-1} at 1 atm and at room temperature. The cell was surrounded by six low pressure Hg lamps which were turned on periodically with a pulse width of *ca.* 20 ms and with a repetition frequency of several Hz. A d.c. source for the lamps was controlled by power transistors whose base current was supplied from a pulse generator. Thus, the Hg resonant light pulse with a rise time of 30 μs and variable pulse width was obtained. The UV light beam from a D_2 discharge lamp was passed through the cell, and fed into a monochromator. In order to measure a very weak absorption, the signal from the monochromator was digitized and accumulated to obtain the averaged signal of repeated light pulses. This made it possible to observe a change of transmittance as small as 5×10^{-5}. When a signal change Δ is obtained with the original light intensity of I_0, the optical density of the absorption is defined by

$$D \equiv \ln [I_0/(I_0-\Delta)] = \Delta/I_0$$
$$= \beta l[HO_2], \qquad (1)$$

where β is the absorption coefficient of HO_2 and l is an optical pathlength.

A transmittance change following the irradiation of the 253.7 nm light and its recovery after termination of the irradiation were found in the wavelength range of 200—250 nm as shown in Fig. 2. The absorption, which has a maximum intensity around 205 nm, is assigned to that of HO_2 since the absorption disappears with reduction of the O_2 content even if its fraction in H_2 is less than 10^{-2}. HO_2 must be formed by the reaction mechanism:

$$Hg + h\nu\,(253.7\,\text{nm}) \longrightarrow Hg^*, \qquad (R1)$$
$$Hg^* + H_2 \longrightarrow Hg + 2H, \qquad (R2)$$
$$H + O_2 + H_2 \longrightarrow HO_2 + H_2. \qquad (R3)$$

A large Hg* quenching cross section of H_2 leads to the instantaneous formation of H atoms by irradiation of the Hg resonant light pulse. In Fig. 2, the transmission of the 205 nm light begins to decrease at the onset of the 253.7 nm light pulse approaching gradually a stationary value. After termination of the light pulse, the transmission recovers to some extent, and for com-

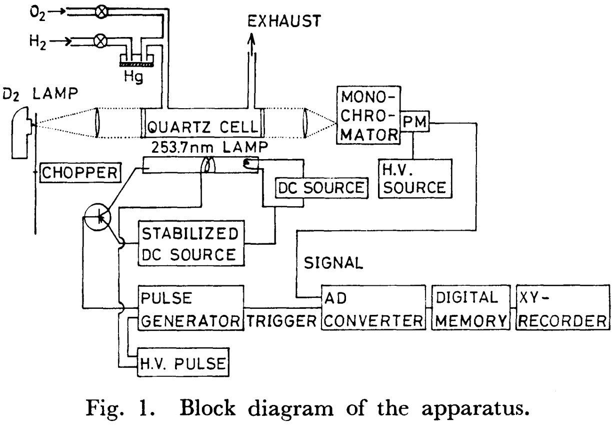

Fig. 1. Block diagram of the apparatus.

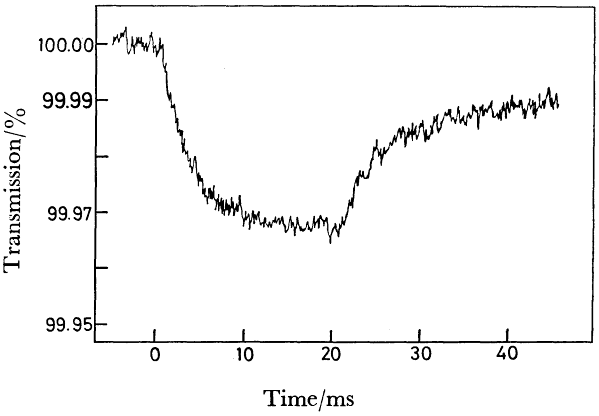

Fig. 2. An example of the observed transmittance change at 205 nm. The flow rates of H_2 and O_2 are 500 and 5 cm^3 min^{-1}, respectively, and the 253.7 nm light pulse width is 20 ms with its repetition frequency of 4 Hz. Number of data accumulated is 256.

plete recovery a fairly long time, during which the cell is refilled with fresh gas, is necessary.

Referring to the table of the reaction rate constants of HO_2,[1] the most probable reactions for the dissipation of HO_2 must be as follows:

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2, \qquad (R4)$$

$$HO_2 + H \longrightarrow H_2 + O_2. \qquad (R5)$$

Reaction R5 is excluded because $[HO_2]$ is at most on the order of 10^{-11} mol cm^{-3} in comparison with *ca.* 10^{-7} mol cm^{-3} of the O_2 concentration. Thus, H atoms react with O_2 rather than with HO_2. Hence, the following kinetic relation is derived;

$$d[HO_2]/dt = \alpha I - 2k_5[HO_2]^2, \qquad (2)$$

where I represents the 253.7 nm radiation intensity per unit volume and time and α is a constant to describe the conversion of the absorbed light quantum to moles of HO_2. After termination of the light pulse, Eq. 2 is integrated to give the relation

$$(1/[HO_2]_t) - (1/[HO_2]_{t=\tau}) = 2k_5(t-\tau), \qquad (3)$$

where τ is the duration of the light pulse. This equation is modified by substituting Eq. 1 as

$$(1/D_t) - (1/D_{t=\tau}) = 2(k_5/\beta l)(t-\tau). \qquad (4)$$

Thus, the absorption coefficient must be known in order to determine the relevant reaction rate.

Inspecting the data of Fig. 2, it is found that a stationary concentration of HO_2 is not realized strictly during the irradiation of 253.7 nm light, and that the UV light does not recover its original intensity long after the termination of the light pulse. These facts may be attributed to the formation of H_2O_2 which absorbs the UV light with an absorption coefficient smaller than that of HO_2. Hence, Eq. 1 should be corrected to

$$D = \beta l[HO_2] + \beta' l[H_2O_2], \qquad (5)$$

where β' is the absorption coefficient of H_2O_2. On the beginning of the irradiation, the increase of absorption intensity can be assumed to be solely due to the formation of HO_2, *i.e.*,

$$(dD/dt)_{t=0} = \beta l(d[HO_2]/dt)_{t=0}$$
$$= \beta l\alpha I. \qquad (6)$$

Since the absorption at the final stage should originate from H_2O_2, that is the end product, the stoichiometric relation

$$D_{t=\infty} = \beta' l[H_2O_2]_{t=\infty} = \beta' l\alpha I\tau/2_2 \qquad (7)$$

is satisfied. Substituting Eq. 7 into Eq. 6, the absorption coefficient β may be determined by the use of the equation

$$2D_{t=\infty}/(dD/dt)_{t=0}\tau = \beta'/\beta, \qquad (8)$$

where β' is known accurately.[6] The absorption coefficient thus determined is $(1.80\pm0.14)\times10^6$ cm^2 mol^{-1} at 205 nm in good agreement with the value reported.[4]

If we deal with the behavior of HO_2 after termination of the light pulse, the following stoichiometric relation is obtained:

$$[HO_2]_t + 2[H_2O_2]_t = 2[H_2O_2]_{t=\infty}, \qquad (9)$$

where $t \geq \tau$. Then, $[HO_2]_t$ may be determined by the equation

$$[HO_2]_t = [D(t) - D(t=\infty)]/l(\beta - 0.5\beta'). \qquad (10)$$

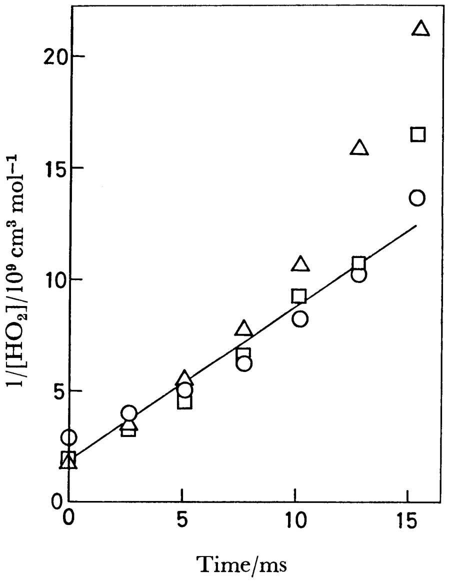

Fig. 3. Plots of $[HO_2]^{-1}$ *vs.* time after the termination of the light pulse. △: 1% O_2 in H_2, ○: 2%O_2, □: 0.5% O_2.

Table 1. Rate constant of $2HO_2 \rightarrow H_2O_2 + O_2$

Investigator	$k_5/10^{12}$ cm^3 mol^{-1} s^{-1}
Foner & Hudson[2]	*ca.* 1.8
Hochanadel *et al.*[4]	5.7±0.5
Paukert & Jonston[3]	2.2±0.3
This work	2.8±0.3

The reciprocals of the obtained values of $[HO_2]_t$ are plotted in Fig. 3 as a function of time lapse after termination of the light pulse, $(t-\tau)$. According to Eq. 3 the initial slope gives the relevant rate constant. A good linearity is found for the initial decay of $[HO_2]$ supporting the second order reaction of the HO_2 dissipation. However, in a later stage, the bimolecular process becomes a minor one since atomic hydrogen or impurity molecules may react with HO_2, so that the plots of $[HO_2]^{-1}$ *vs.* $(t-\tau)$ deviate significantly from the linear line, although the quantity of HO_2 which reacts in non-bimolecular processes is fairly small, probably less than 10% of the original $[HO_2]$. The rate constant obtained is given in Table 1 together with the literature values.

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