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Further Studies of the Rate Constant for Chemical Excitation of OH in Shock Waves

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Electronically excited $OH(^2\Sigma)$ is formed both by chemical and thermal excitations in the H_2-O_2 reaction. The $OH(^2\Sigma)$ emission in the partial equilibrium region of the reaction was measured in 1250—3450 K incident shock waves for a mixture, $H_2/O_2/Ar=2/2/96$, at starting pressures, 6—30 Torr. The correlation factor between the emission intensity and the concentration of $OH(^2\Sigma)$ was derived in the temperature region above 2800 K where the thermal excitation of $OH(^2\Sigma)$ is dominant. The factor was utilized to estimate the concentration of chemically excited $OH(^2\Sigma)$ and the rate constant of the reaction $O+H+M=OH(^2\Sigma)+M$ was determined as $10^{13.92\pm0.17}\exp[-(8.3\pm1.2)\ \mathrm{kcal}/RT)]$ $(\mathrm{cm^6\ mol^{-2}\ s^{-1}})$.

The UV emission of $OH(^2\Sigma)$, hereafter OH*, in the H_2-O_2 reaction has been studied in detail by many researchers in discharge flow systems,[1] in flames,[2] and in shock waves.[3-5] The origin of OH* in a relatively low temperature region is attributed to the chemical excitation of $O+H+M=OH^*+M$,[3,4] while, in a high temperature region, thermally excited OH* is more dominant than chemically excited.[4] The transition from chemical to thermal excitation has been observed to occur around 2300 K.[4]

The following reaction scheme represents the growth and decay of OH* in the low temperature region.[3-5]

$$O + H + M = OH^* + M \qquad \text{(a)}$$

$$OH^* + M' = OH + M' \qquad \text{(b)}$$

$$OH^* = OH + h\nu \qquad \text{(c)}$$

The reverse reaction (−b) is equivalent to the thermal excitation and it is left out in the low temperature region. The reverse reaction (−c) is self-absorption and it can be disregarded in the present experiment.[4] Since it is expected that $k_b > k_{-a}$ and $k_b[M'] > k_c$ under the present experimental conditions as discussed before,[4,5] the OH* formed is quenched mainly by reaction (b). Then, the steady state assumption for OH* leads to the following expression for OH* in the low temperature region.[4,5]

$$[OH^*]_{ch} = k_a[O][H][M]/k_b[M'] \qquad (1)$$

OH* is formed by the thermal excitation as well as by the chemical excitation as above, and the thermally excited [OH*] is expressed by the partition of OH and OH* as:

$$[OH^*]_{th} = [OH](f_{OH^*}/f_{OH})\exp(-93.4\ \mathrm{kcal}/RT), \qquad (2)$$

where the f's are partition functions of OH and OH*. The value of 93.4 kcal corresponds to the energy difference between the two states of $^2\Sigma(v=0)$ and $^2\Pi(v=0)$. Since the value of [OH] can be estimated by computer modeling with an appropriate reaction mechanism, the value of $[OH^*]_{th}$ is obtainable.

The UV emission intensity I due to the reaction (c) is related to [OH*] as:

$$I = C k_c[OH^*], \qquad (3)$$

where C is a correlation factor for the detecting system. In the preceding paper,[5] the dependence of $\log I$ on $10^4/T$ was analysed by computer modeling and a tentative value of k_a was reported. We mentioned in that paper that a more precise value of k_a could be obtained by absolute measurement of the emission intensity I in the low temperature region, though the method is not free from the correlation factor of a standard radiant bulb.

In the present paper, the value of $[OH^*]_{th}$ is correlated with the emission intensity I, and the constancy of $[OH^*]_{th}/I$ at high temperatures is demonstrated. The emission intensity I in the low temperature region, where the chemical excitation is predominant, is analysed to obtain more credible k_a values using the correlation factor so derived.

Experimental

The experiments were done in incident shock waves. The shock tube used in the previous work[5] was rebuilt and reinstrumented to improve the evacuation and the optics. The evacuation of the test section was less than 10^{-4} Torr (1 Torr≈133.322 Pa) before each run. A photomultiplier (Hamamatsu-TV, 7696) having S-11 response combined with a monochromator (Jarrell-Ash, JE-25, dispersion=3.3 nm/mm) was used to measure the OH* emission intensity. The wavelength of the monochromator was centered at 306.4 nm with entrance and exit slits having 1 and 2 mm width, respectively.

The gases used to prepare the test gas, $H_2/O_2/Ar=2/2/96$, were 99.99999% pure H_2, 99.999% pure O_2 and 99.999% pure Ar; all of them were from Nippon Sanso Co.

Results and Discussion

Even in the high temperature region, the oscillogram trace of the emission intensity resembles that shown in the previous paper[5] having a plateau height of I in the partial equilibrium.

The partial equilibrium $[OH^*]_{th}$ was evaluated by using a reliable partial equilibrium value of modeled [OH] and the ratio of the partition functions, f_{OH^*}/f_{OH}, in Eq. 2. The reaction mechanism adopted for the computer modeling is identical with that in the previous work.[5] The modeled [OH] along with the other species concentrations for the later discussion are shown in Fig. 1. The partition functions were evaluated using the molecular constants of OH and OH* reported.[6] If the thermal excitation is really predominant in the high temperature region, the above $[OH^*]_{th}$ divided by the emission intensity I should be constant. In Fig. 2, the values of $[OH^*]_{th}/I$ are plotted against T. Though the data are scattered,

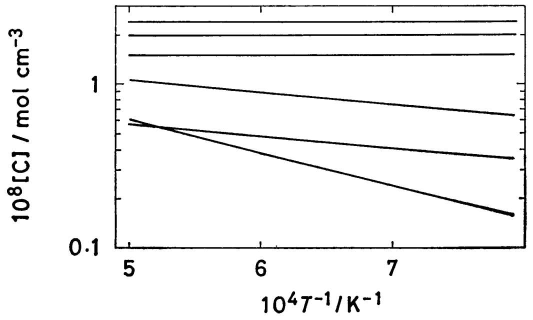

Fig. 1. Temperature variation of the modeled concentrations in the partial equilibrium ($P_1 = 10$ Torr). The species are, from top to bottom on the right hand side, H_2O, O_2, H, O, H_2, and OH.

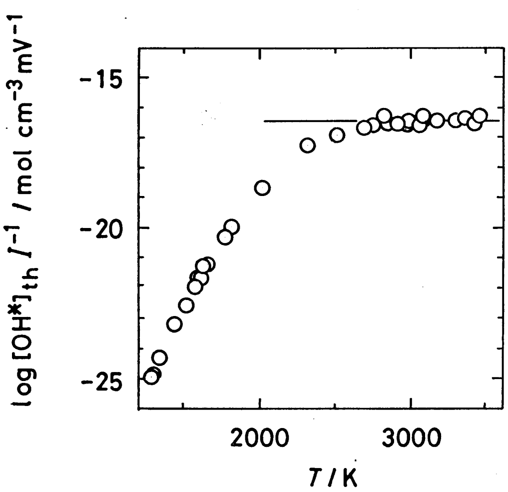

Fig. 2. Temperature variation of $[OH^*]_{th}/I$. The line shows an average value for $[OH^*]_{th}/I$ above 2800 K.

TABLE 1. QUENCHING CROSS SECTION, σ, BETWEEN OH* AND M′ AND CALCULATED k_b VALUE

M′	σ/Å^2	$(k_b/T^{0.5})$/cm^3 mol^{-1} s^{-1}
Ar	0.059[9)]	1.5×10^{10}
H_2	6.9[9)]	4.5×10^{12}
O_2	10[a)]	2.6×10^{12}
H_2O	57[b)]	1.7×10^{13}
H	22[9)]	2.0×10^{13}
O	5[c)]	1.5×10^{12}

a) H. P. Hooymayers and C. Th. Alkemade, *J. Quant. Spectrosc. Radiat. Transfer*, **7**, 495 (1967). b) M. Kaneko, Y. Mori, and I. Tanaka, *J. Chem. Phys.*, **48**, 4468 (1968). c) Assumed.

the constancy is adequate above 2800 K, and the value of $[OH^*]/I$ or C k_c in Eq. 3 was evaluated as:

$$[OH^*]/I = (3.0\pm1.0)\times10^{-17}\ (\text{mol cm}^{-3}\ \text{mV}^{-1}).$$

Because of the temperature variation of the rotational population in the $^2\Sigma(v=0)$ state, it is expected that each of the intensity maxima of six branches moves in or out of the wavelength range of 303.1—309.7 nm and, due to this effect, there might be a possibility not to hold the constancy of $[OH^*]/I$ in the temperature range. Such a temperature effect on the emission intensity could be seen by comparing following J_{max} values at different temperatures. In contrast with the vibrational and the electronic populations, the number of molecules does not simply decrease with increasing rotational quantum number. First it increases to a maximum and then decreases, and the rotational quantum number at which the number of molecules shows a maximum is given by:[6)]

$$J_{max} = 0.5896\times\sqrt{T/B}-1/2,$$

where B=rotational constant (17.355 cm^{-1} for OH*). Since the J_{max} values increase with temperature, only the J_{max} values at the lowest and the highest ends of the temperature range need be examined. The J_{max} values evaluated are 7.0 and 7.8 at 2800 K and 3450 K, respectively. According to the spectra reported for the $^2\Sigma^+—^2\Pi$ transition of OH,[7)] it is possible to assign each rotational transition to one of the emission lines as follows. $J=7$ and 8 of three branches, P_1, P_2, and Q_2 are out of the wavelength range. The J values in Q_1 branch are at the end of the wavelength range longer than 309.0 nm. As for R_1 and R_2 branches, the J values are almost at the center of the wavelength range. Thus, none of the intensity maxima of the six branches are expected to move in or out of the wavelength range in this temperature range of 2800—3450 K.

The rate constant k_c is the reciprocal of the radiative life time of OH*, which is reported to change slightly depending on the value of the rotational quantum number of the $^2\Sigma$ state.[8)] In this study, such dependence of the k_c value, as well as the temperature dependence, was assumed to be negligible. Therefore, the above value of $[OH^*]/I$ could be used in the lower temperature region to obtain the chemically excited [OH*] by observing I.

Once the chemically excited [OH*] is determined, unknown parameters to evaluate the k_a value from Eq. 1 are the concentrations of H, O, M, M′, and the k_b value. The partial equilibrium concentrations of H and O are shown in Fig. 1. The third body M of the reaction (a) was assumed to be all of the species in the reaction region having the same efficiency, *i.e.*, [M]=density. The quenching partner M′ considered are shown in Table 1 along with the k_b value. The k_b values were evaluated by collision theory using the collision cross sections of M′ reported elsewhere. OH was not considered as a collision partner, since it is reported that OH has negligible quenching effect on OH*.[9)]

Besides the above physical quenchings for OH*, the possibility of chemical quenchings such as $OH^*+H=H_2+O$ and $OH^*+H_2=H_2O+H$ are to be considered. The rate constant for the former reaction has been discussed in detail[9)] and is elucidated to be small compared with the physical quenching of H. The rate constant for the latter reaction can be assumed to be equal to the frequency factor of the ground state reaction of $OH+H_2=H_2O+H$. If the frequency factor of 5.25×10^{13} in the H_2-O_2 reaction mechanism in Ref. 5 is adopted, the chemical quenching of OH* by H_2 is about 1/3 of the physical quench-

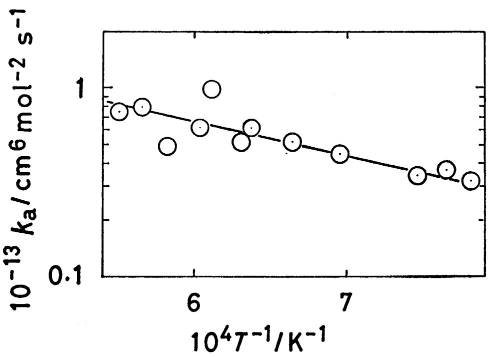

Fig. 3. Arrhenius plots for k_a.
The line shows the least squares fit for the data points.

ing by the same partner at 1500 K. Since the cross sections of the other species are larger than that of H_2, the physical quenchings are more effective than the chemical quenchings. Thus, no chemical quenchings were considered in this study.

The Arrhenius plot of k_a thus evaluated is shown in Fig. 3. The least squares fitting gave the following expression for the k_a value with one standard error.

$$k_a = 10^{13.92\pm0.17}\exp[-(8.3\pm1.2)\mathrm{kcal}/RT](\mathrm{cm^6\,mol^{-2}\,s^{-1}})$$
$$(1\ \mathrm{kcal}=4.184\ \mathrm{kJ})$$

Schiff *et al.*[1)] obtained the rate constant for the chemical excitation of OH* in the course of chemiluminescence studies in a discharge flow system at pressures of 0.4—4 Torr and 300 K. They assumed the bimolecular reaction of ground state O and H to form OH* and estimated the rate constant at $(3\pm1)\times10^{-21}$ cm^3 molecule^{-1} s^{-1}. If the figure is converted to the termolecular rate constant assuming $O+H+M=OH^*+M$, it is given as $(8.4\pm2.4)\times(10^{10}$—$10^{11})$ cm^6 mol^{-2} s^{-1}, which is 3 to 4 powers of 10 larger than our value extrapolated to 300 K. In a general discussion of Schiff's paper, Gardiner[10)] remarked that the absolute intensity measurement for the chemiluminescence of OH* in the shock heated H_2-O_2 reaction done in his laboratory gave the bimolecular rate constant of 1.0×10^{-18} cm^3 molecule^{-1} s^{-1} at 1500 K. If the termolecular reaction is assumed, the figure is 3.3×10^{11} cm^6 mol^{-2} s^{-1}, which is about 10 times less than the value determined in this study. His value was derived by assuming only H_2O and O_2 to be the physical quenchers of OH*. If all of the quenchers are taken into account as was done in this study, his value should be compatible to the present value.

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