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Kinetic Studies of Ammonia Oxidation in Shock Waves. III. The Radiation of Excited OH Radicals

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Mixtures of ammonia and oxygen in argon were heated by reflected shock waves to temperatures between 1600 and 2100°K, and the ultraviolet radiation from OH($^2\Sigma^+$) was observed by means of monochromator and a photomultiplier. The radiation profiles showed two types of radiation: a strong spike which appeared after an induction period, and a weak and constant-level emission, which followed the spike and persisted for up to 500 μsec. The former emission was observed also in the oxidation of hydrogen, methane, and acetylene, but the latter emission was observed only in the oxidation of methane and acetylene. The temperature coefficients of the intensities of the latter emission divided by the sum of spectral emissivities were found, for the oxidation of ammonia, not large enough to be explained by the thermal excitation of the ground-state OH($^2\pi$) to the $^2\Sigma^+$ state. Possible reaction processes for this chemiluminescence were proposed to explain the experimental results.

OH radicals in the ground state, $^2\pi$, have been found, by absorption spectrophotometry, to persist more than one millisecond in oxidation reactions of hydrogen,[1] methane,[2] acetylene,[3] and ammonia[4] in shock waves. On the contrary, excited OH radicals, $^2\Sigma^+$, were observed in the detonation of hydrocarbons to last for a very short period, showing spike in their time history of radiation.[5] Also, the chemiluminescence of excited OH in hydrogen-oxygen reactions was studied in detail recently.[6]

In the course of the study of the ammonia oxidation, we have measured the change with time in concentrations of excited OH radicals and other intermediate species simultaneously.[4] We have thereby found the interesting fact that the spike of OH radiation is followed by a weak radiation which persists at an essentially constant level from 100 to 500 μsec. This prompted us to clarify whether the radiation is chemiluminescent or thermal in nature, and to see whether or not the same type of radiation is observed in the oxidation of other fuels.

Experimental

The experimental apparatus and procedure have been described in detail previously.[3,4,7] In brief, the ultraviolet radiation of OH has been observed through a quartz window, mounted 5.5 mm. from the end wall of the shock tube, by a Shimadzu QR-500 monochromator and a Hamamatsu-TV R106 photomultiplier. The monochromator has been set at 3067 Å, and its slit width, at 0.15 mm., allowing a band pass of 6 Å. The incident shock speed has been measured by two platinum-thin-film thermometers, stationed 139.0 mm. apart, and an electronic counter. After each run, the debris of the Lumirror (polyester film) diaphragm was taken out of the shock tube, and the quartz window was cleaned. Gas mixtures were prepared manometrically in an all-glass apparatus, and stirred magnetically for at least an hour before being used in the experiment.

Calculation

That the radiation of OH observed in the oxidation of ammonia is chemiluminescent in nature has been determined in the following manner.

The basic phenomenological law for the emission of radiation at wave-number ω from uniformly-distributed radiators is[8]:

$$R_\omega = R_\omega^0[1-\exp(-P_\omega X)], \tag{1}$$

where R_ω is the total spectral radiancy; R_ω^0, the black body radiancy; P_ω, the spectral absorption coefficient, and X, the optical density. The term in brackets is referred to as the spectral emissivity, α_ω. Thus, the spectral intensity, I_ω, measured in the experiment by a monochromator and a photo-

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[1] H. Miyama and T. Takeyama, *J. Chem. Phys.*, **41**, 2287 (1964).

[2] H. Miyama and T. Takeyama, This Bulletin, **38**, 37 (1965).

[3] T. Takeyama and H. Miyama, ibid., **38**, 936 (1965).

[4] T. Takeyama and H. Miyama, *J. Chem. Phys.*, **42**, 3737 (1965); This Bulletin, **38**, 1670 (1965).

[5] G. J. Minkoff, A. J. Everett and H. P. Broida, Fifth Symposium (International) on Combustion, Reinhold Publishing Corporation, New York (1955), p. 799.

[6] E. F. Belles and M. R. Lauver, *J. Chem. Phys.*, **40**, 415 (1964).

[7] T. Takeyama and H. Miyama, This Bulletin, in press.

[8] S. S. Penner, "Quantitative Molecular Spectroscopy and Gas Emissivities," Addison-Wesley Publishing Company, Inc., Mass. (1959).

multiplier may be represented by:

$$I_\omega = AR^0_\omega \alpha_\omega, \tag{2}$$

where A is a constant determined by the selected conditions of the optical system and the measuring instruments. By applying Wien's radiation law, $R^0_\omega = B\exp(-\boldsymbol{h}c\omega/\boldsymbol{k}T)$, to Eq. 2, the following relation can be obtained:

$$I_\omega/\alpha_\omega = C(\omega)\exp\left(-\frac{\boldsymbol{h}c\omega}{\boldsymbol{k}T}\right), \tag{3}$$

where C is a coefficient which is variable with the wave number but which is independent of the temperature, and where $\boldsymbol{h}$, c, and $\boldsymbol{k}$ are Planck's constant, the light velocity, and Boltzmann's constant respectively. Therefore, for the thermal radiation, a plot of $\log(I_\omega/\alpha_\omega)$ vs. $1/T$ would give a straight line, the slope of which corresponds to $-\boldsymbol{h}c\omega/\boldsymbol{k}$.

In the actual measurement, the monochromator allows a band pass of several angstrom, and, hence, a certain number of spectral lines reach the photomultiplier. Accordingly, the observed intensity, I, is a sum of the intensity of each line; namely:

$$I = \sum_i I_i \tag{4}$$

On the assumption that, for a narrow range of wave numbers, the right hand side of Eq. 3 may be represented approximately by the value for the average wave number, ω_{av}, the following relation can be obtained from Eqs. 3 and 4:

$$\frac{I}{\sum_i \alpha_i} = C(\omega_{\mathrm{av}})\exp\left(-\frac{\boldsymbol{h}c\omega_{\mathrm{av}}}{\boldsymbol{k}T}\right) \tag{5}$$

Thus, the plot of $\log(I/\sum_i \alpha_i)$ vs. $1/T$ gives a check on whether the radiation is thermal or chemiluminesent.

As we measure the spectral-line emission, the radiancy for the isolated spectral line, R_{L}, must be used rather than R_ω, which refers to the radiancy at wave number ω, in the calculation of emissivitives by means of Eq. 5. Taking into account the natural-line-, the collision-, and the Doppler-broadening effects, the following relation is valid[8]:

$$\frac{R_{\mathrm{L}}(\ln 2)^{1/2}}{2R^0{}_\omega b_{\mathrm{D}}} = \frac{1}{2}\int_{-\infty}^{\infty}[1-\exp(-P_{|\xi|}X)]\,\mathrm{d}\xi,$$

where;

$$P_{|\xi|} = P'\left(\frac{a}{\pi}\right)\int_{-\infty}^{\infty}\frac{\exp(-y^2)}{a^2+(\xi-y)^2}\,\mathrm{d}y, \tag{7}$$

$$P' = \frac{S}{\omega_0}\left(\frac{mc^2}{2\pi\boldsymbol{k}T}\right)^{1/2} = \frac{S}{b_{\mathrm{D}}}\left(\frac{\ln 2}{\pi}\right)^{1/2}, \tag{8}$$

$$a = \frac{(b_{\mathrm{N}}+b_{\mathrm{C}})}{b_{\mathrm{D}}}(\ln 2)^{1/2}, \tag{9}$$

$$\xi = \frac{\omega-\omega_0}{\omega_0}\left(\frac{mc^2}{2\boldsymbol{k}T}\right)^{1/2} = \frac{\omega-\omega_0}{b_{\mathrm{D}}}(\ln 2)^{1/2} \tag{10}$$

and where b_{N}, b_{C}, and b_{D} refer to the natural line-, the collision-, and the Doppler-broadening respectively; where S refers to the integrated absorption, a, to the line-shape parameter, and ω_0, to the wave number at the line center and where m is the mass of electrons. All these quantities can be estimated from the experimental conditions; accordingly, P can be numerically calculated by using one of several approximate expressions of Eq. 7.[7,8]

However, the results of the computations of these approximate formulae have been conveniently summarized[9] in the "curves of growth," where the dimensionless parameter, $R_{\mathrm{L}}(\ln 2)^{1/2}/2b_{\mathrm{D}}R^0_\omega$, is plotted against $\log(10.6P'X)$ for various values of the line-shape parameter, a. Therefore, the emissivity for each spectral line, $R_{\mathrm{L}}/R^0_\omega$, can be estimated from the curves of growth.

Results and Discussion

Figure 1 shows profiles of the ultraviolet radiation of OH radicals due to the $^2\Sigma^+\rightarrow{}^2\Pi$ transition, and of the ultraviolet absorption of ammonia at 2245 Å,[7] which have been obtained by shock-heating mixtures of ammonia and oxygen diluted in argon to 1930°K. These profiles are essentially the same for all the experiments: the intensity of OH emission rises steeply, after an induction period, to a sharp maximum; there follows an approximately exponential decay to 1/4—1/8 the level of the maximum, and then the intensity remains at this level for a period varying from 100 μsec. for the strong shock ($T_5 = 1980$°K) to 500 μsec. for the weak ($T_5 = 1650$°K), until finally it falls to zero emission.

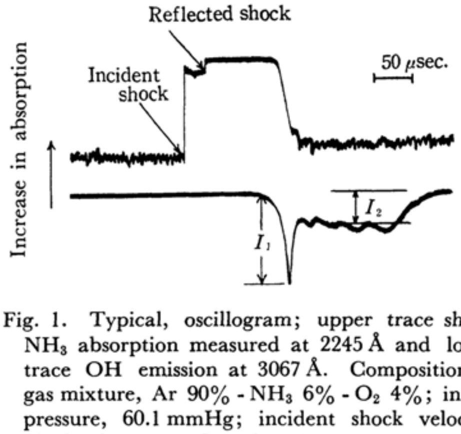

Fig. 1. Typical, oscillogram; upper trace shows NH_3 absorption measured at 2245 Å and lower trace OH emission at 3067 Å. Composition of gas mixture, Ar 90% - NH_3 6% - O_2 4%; initial pressure, 60.1 mmHg; incident shock velocity, 985.8 m/sec.; reflected shock temperature, 1930°K; equilibrium pressure, 4.74 atm.

We were more interested in the weak emission, I_2, than in the strong emission, I_1, because, so far as we know, no paper has yet been published on

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9) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge at University Press, Cambridge (1961), p. 132.

TABLE I. VALUES OF SPECTRAL EMISSIVITIES ESTIMATED FROM CURVES OF GROWTH
(Mixture, Ar 90% - NH_3 6% - O_2 4%; initial pressure, 55.0 mmHg; incident shock speed, 999.6 m./sec.; equilibrium temperature, 2785°K; equilibrium pressure, 4.550 atm.; a,$^{a)}$ 0.735; b_D,$^{b)}$ 0.1494 cm^{-1})

Line	ω, cm^{-1}	J'' c)	S_J d)	$\log(10.6P'X)$ e)	$\frac{R_L(\ln 2)^{1/2}}{2b_D R_\omega^0}$	α_i f)
R_1^7	32626	$7^1/_2$	26.9	1.59	1.97	0.707
R_1^{11}	625	$11^1/_2$	43.7	1.62	2.07	0.743
R_1^6	618	$6^1/_2$	22.7	1.57	1.93	0.693
R_1^{12}	616	$12^1/_2$	47.8	1.63	2.09	0.750
R_1^5	607	$5^1/_2$	18.4	1.55	1.86	0.668
R_1^{13}	603	$13^1/_2$	51.9	1.63	2.09	0.750
R_1^4	593	$4^1/_2$	14.2	1.52	1.80	0.646
R_2^{10}	589	$9^1/_2$	37.0	1.63	2.09	0.750
R_2^9	587	$8^1/_2$	32.9	1.63	2.09	0.750
R_1^{14}	586	$14^1/_2$	56.0	1.63	2.09	0.750
R_2^{11}	586	$10^1/_2$	41.0	1.63	2.09	0.750
R_2^8	582	$7^1/_2$	28.8	1.62	2.07	0.743
R_2^{12}	579	$11^1/_2$	45.1	1.64	2.14	0.768
R_1^3	578	$3^1/_2$	10.1	1.46	1.64	0.589
R_2^7	573	$6^1/_2$	24.8	1.61	2.07	0.743
R_2^{13}	567	$12^1/_2$	49.1	1.64	2.14	0.768
R_1^{15}	565	$15^1/_2$	57.2	1.62	2.07	0.743
R_1^2	560	$2^1/_2$	6.1	1.37	1.40	0.502
R_2^6	559	$5^1/_2$	20.7	1.60	2.00	0.718

a) Calculated from the empirical formula[10]: $a=450p/T$, where p is in atm., and T in degrees Kelvin.

b) Calculated from the equation[8]: $b_D=(2\boldsymbol{k}T\boldsymbol{N}\ln 2/Mc^2)^{1/2}\omega_0$, where $\boldsymbol{k}$, $\boldsymbol{N}$, M and c refer to Boltzmann's constant, Avogadro's number, molecular weight of OH, and velocity of light respectively; the averaged value of 32590 cm^{-1} was used as ω_0.

c) Total angular momentum of lower state.

d) Line strength of Ref. 11, Table IV.

e) Calculated from the relation[12]: $10.6P'X=23.1S_J/(2J''+1)$.

f) Calculated from the relation $\alpha_i=\frac{R_L}{R_\omega^0}$.

this emission. Thus, we tried to identify the nature of I_2 by the method described above; measurements were mainly made of two mixture (Ar 90% - NH_3 6% - O_2 4% and Ar 90% - NH_3 4% - O_2 6%) which had been investigated previously.[4]

Since the slit width of the monochromator allowed a band pass from 3064 to 3070 Å, nineteen spectral lines of R_1 and R_2 branches of (0, 0) band in the $^2\Sigma^+ \rightarrow {}^2\Pi$ transition were regarded as contributing to the intensity of emission; the satellite branches, R_{21} and S_{21}, were neglected because of their weakness compared with R_1 and R_2. The values of emissivities calculated for one set of experimental condition are presented in Table I. The equilibrium temperature and pressure[13] have been used in the calculation, since the majority of the ammonia (more than 95%) has reacted before I_2 appears, as is shown in Fig. 1; accordingly, the reaction system can be considered to be close to the equilibrium condition.

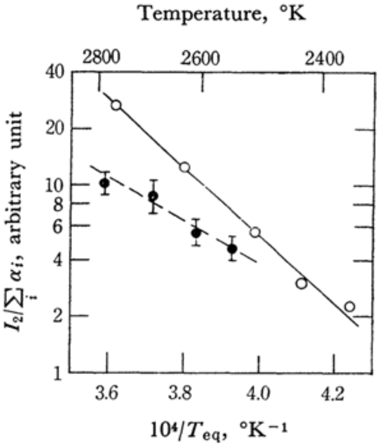

Fig. 2. Plot of $\log(I_2/\alpha_i)$ against reciprocal temperature. Open circles represent data obtained for mixture of 90%Ar, 4%NH_3, and 6%O_2, and solid circles for mixture of 90%Ar, 6%NH_3, and 4%O_2.

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[10] W. E. Kaskan, *J. Chem. Phys.*, **31**, 944 (1959).

[11] G. H. Dieke and H. M. Crosswhite, "The Ultraviolet Bands of OH," Bumblebee Rept. No. 86, The Johns Hopkins University, 1948.

[12] T. Carrington, *J. Chem. Phys.*, **31**, 1243 (1959).

[13] We are greatly indebted to Prof. W. C. Gardiner, Jr. of University of Texas for the equilibrium-state calculation.

The temperature dependence of the intensity of emission is shown in Fig. 2 as a plot of $\log(I_2/\sum_i \alpha_i)$ vs. $1/T$; the temperature coefficients are 56 and 82 kcal./mol., less than the quantity needed for the thermal excitation of OH ($^2\Pi$).

The dependence of the intensity of I_2 upon the equilibrium concentration of OH, H, O_2 and H_2 was studied by using several mixtures presented in Table I of the previous paper⁷⁾ (Part II of this series). It was found that the intensity of I_2 is independent of the equilibrium OH concentration $[OH]_{eq}$ over the concentration range from 3.2×10^{-5} to 3.2×10^{-6} mol./l., but that it is approximately proportional to $[H]_{eq}[H_2]_{eq}[O_2]_{eq}$ when $[OH]_{eq}$ is kept almost constant, as is shown in Fig. 3.

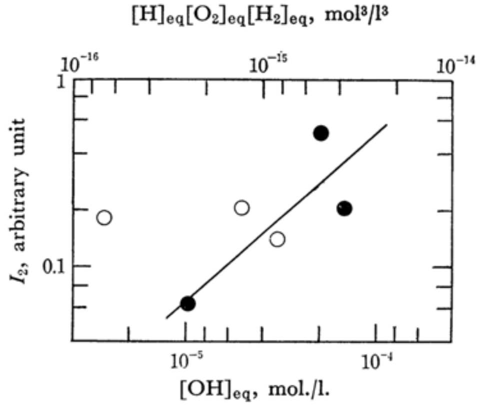

Fig. 3. Intensity of OH emission against equilibrium concentration of OH (open circles) and against the products of equilibrium concentration of H, O_2 and H_2 (solid circles). Slope of the solid line is about 0.9 by inspection.

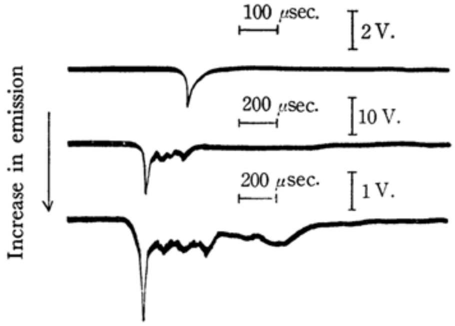

Fig. 4. Profiles of OH emission observed in oxidations of other fuels.

Top trace: Ar 90% - H_2 6.67% - O_2 3.33%; initial pressure, p_1, 100.3 mmHg; incident shock velocity, w_1, 722.3 m./sec.; reflected shock temperature, T_5, 1150°K; reflected shock pressure, p_5, 2.60 atm.

Middle trace: Ar 90% - C_2H_2 4% - O_2 6%; p_1, 100.3 mmHg; w_1, 716.0 m./sec.; T_5, 1135°K; p_5, 2.82 atm.

Bottom trace: Ar 90% - CH_4 3% - O_2 7%; p_1, 79.9 mmHg; w_1, 903.6 m./sec.; T_5, 1690°K; p_5, 4.30 atm.

For purposes of comparison, measurements were made of the OH emission in reactions of hydrogen, methane, and acetylene with oxygen. The profiles obtained are shown in Fig. 4. Although the profiles for the oxidation of methane and acetylene are similar to those for ammonia oxidation, that for the oxidation of hydrogen is very different from the others; no weak emission following a spike can be observed.

The temperature coefficients of the intensity of OH emission, I_2, obtained in Fig. 2 for both mixtures are definitely less than that required for the termal excitation:

$$OH(^2\Pi) + M \rightarrow OH(^2\Sigma^+) + M \quad -93.5\,\text{kcal./mol.} \qquad (I)$$

indicating that the excited OH radicals are produced by chemical reaction processes. This is supported also by the fact that the intensity of I_2 is independent of the ground-state OH concentration.

The proportionality of I_2 to $[H]_{eq}[H_2]_{eq}[O_2]_{eq}$ seems to suggest that the following excitation mechanism is valied:

$$H + O_2 + H_2 \rightarrow OH^* + H_2O \qquad (II)$$

This mechanism has been proposed by Belles and Lauver⁶⁾ for the OH* chemiluminescence observed during the induction period of the hydrogen-oxygen reaction. The absence of I_2 in the hydrogen-oxygen reaction, as is shown in Fig. 4, suggests that most of the hydrogen has been used up before the appearance of I_2 emission. On the contrary, considerable amounts of hydrogen are produced near the end of the ammonia oxygen reaction (order of 10^{-4} mol./l., according to equilibrium calculation); therefore, Reaction II can be considered to be operating during the period when I_2 is observed. A similar explanation may serve for the acetylene-oxygen and methane-oxygen reactions. However, Reaction II is not the only possibility. Further studies will be required to elucidate a detailed mechanism for this chemiluminescence.

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