The Review of Physical Chemistry of Japan Vol. 13f No. 2 (1939)

EMISSION SPECTRUM OF THE OXY-HYDROGEN FLAME AND ITS REACTION MECHANISM.*

(I) Formation of the Activated Water Molecule in Higher Vibrational States.

By TETSUZÔ KITAGAWA.

I. Introduction.

That the flame of hydrogen burning in the air has some remarkable radiation of band spectra in the ultra-violet region was discovered in 1880 by Liveing and Dewar[1] and also by Huggins[2]. These emission bands were called "Ultra-violet water vapour bands". Watson[3], however, elucidated that the emission bands belonged to the free OH radical, being not caused by the molecule of water. Bonhoeffer and Haber[4], introducing for the first time the OH radical into a chemical reaction mechanism as the intermediate product, proposed what was called Haber's chain reaction mechanism in the combination reaction between hydrogen and oxygen. The free OH radical has been accepted as the intermediate product in various chemical reactions since then. Accordingly, the determination of the intermediate product of a reaction from the emission spectrum of the flame is an important part in the study of the chemical reaction mechanism. If the presence of any other intermediate product than the OH radical should be noticed by photographing the emission spectrum of the oxy-hydrogen flame, a new interpretation would have to be given to the mechanism of the combustion reaction between oxygen and hydrogen.

The present author found many complex band spectra in the region between 7000 Å and 5500 Å by photographing the emission spectrum of the oxy-hydrogen flame[5]. There will be discussed in the present paper to what molecules the band spectra belong and what part they play in the reaction mechanism as intermediate products.

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* This paper is the English translation of the same article published in *Rev. Phys. Chem. Japan*, **10**, 317 (1936).

[1] G. D. Liveing and J. Dewar, *Proc. Roy. Soc.*, **30**, 494, 580 (1880); **33**, 274 (1882).

[2] W. Huggins, *Proc. Roy. Soc.*, **30**, 576 (1880); *Compt. rend.*, **90**, 1455 (1880).

[3] W. W. Watson, *Astrophys. J.*, **60**, 145 (1924).

[4] K. F. Bonhoeffer u. F. Haber, *Z. physik. Chem.*, **137**, 263 (1928).

[5] T. Kitagawa, *Proc. Imp. Acad. Tôkyô*, **12**, 281 (1936).

II. "Red Emission Bands" of the Oxy-Hydrogen Flame.

(1) Apparatus.

The apparatus used is shown in Fig. 1. Q is a tube made of transparent quartz about 3 cm. in diameter and about 10 cm. in length. Through the side tubes G_1 and G_2 oxygen (or hydrogen) and hydrogen (or oxygen) were introduced respectively. The oxy-hydrogen flame was made at the quartz jet J in the same way as mentioned in another report[6]. The image of the flame was focussed on the slit S of the spectrograph by means of condenser lens L. The window W was cooled with a constant flow of air from a tube A.

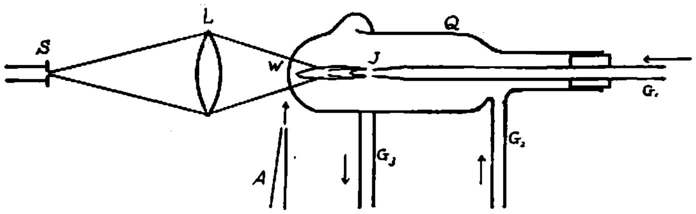

Fig. 1. The main part of the apparatus.

For the ultra-violet region a small Zeiss quartz spectrograph was used and for the visible region a glass spectrograph (three prisms) made by the author[6]. The plates used were the Ilford Hypersensitive Panchromatic Plates. *Fe*- or *Ne*- spectrum was adopted for comparison.

(2) "Red emission bands".

There are two ways of making the oxy-hydrogen flame, namely (i) the flame of hydrogen in oxygen and (ii) the flame of oxygen in hydrogen. In the present experiment the latter flame was used, because the flame is more slender in shape and does not heat the jet so much. The inner flame of it is very radiant, being bluish white; the outer flame, on the contrary, is remarkably reddish and has a long red-coloured after-glow up to the end of the flame. The emission spectrum covering the wave-length range $\lambda\lambda$ 7000～2000 Å was photographed.

(I) $\lambda\lambda$ 3500～2000 Å. There are some intense OH bands[7] in this range.

(II) $\lambda\lambda$ 5000～3600 Å. There are several emission bands which are relatively weak.

(III) $\lambda\lambda$ 7000～5500 Å. There are a large number of very complex emission bands which are mainly in the red region of the spectrum and they will be hereafter called the "red emission bands" for simplicity.

(3) Measurement of the wave length of the red emission bands.

The radiation of the oxy-hydrogen flame in the range of $\lambda\lambda$ 7000—5500 Å was photographed by means of the glass spectrograph, whose dispersion was 64

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6) T. Kitagawa, *Rev. Phys. Chem. Japan*, 11, 61 (1937); 12, 135 (1938).

7) T. Tanaka and Z. Koana, *Proc. Phys.-Math. Soc. Japan*, (III) 15, 272 (1933); 16, 365 (1934).

Å/mm. and 33 Å/mm. at 6500 Å and 5500 Å respectively. The spectrum taken is shown in Plate 1. In the plate numerous complex emission bands are seen, whose band heads are not so distinct, but all the bands shade to the red. The wave-length of the maximum intensity of the emission bands was measured in comparison with the *Ne*-spectrum. In Table 1 the wave-length, the intensity and the wave-number in vacuo of these bands are given.

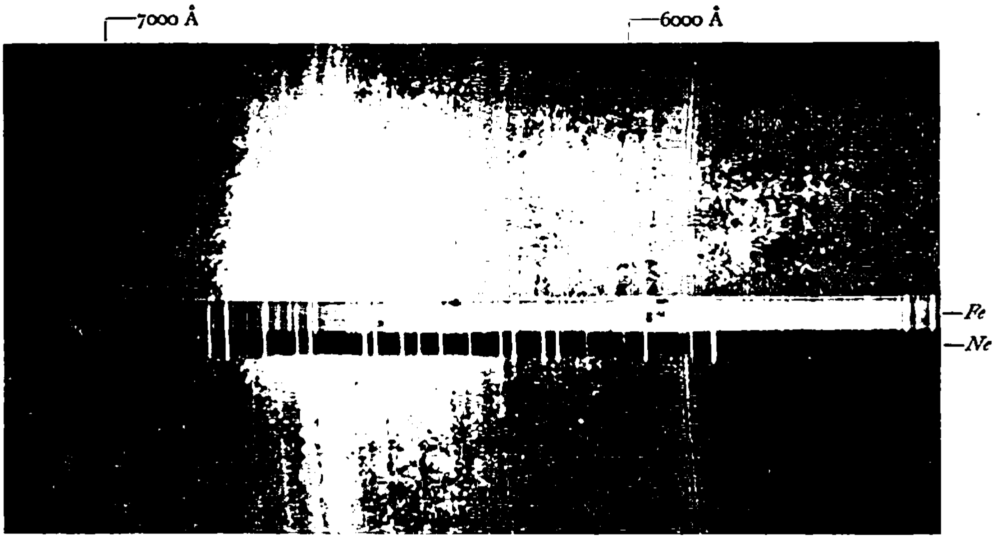

Plate 1.
The red emission bands of the oxy-hydrogen flame. [Ref., *Fe* and *Ne* spectra] (×ca. 4)

Table 1.
The wave-length and the wave-number of the 'red emission bands' of the oxy-hydrogen flame.

No.	λ, Å	Int.	ν, cm⁻¹	No.	λ, Å	Int.	ν, cm⁻¹
1	5683.3	2	17590	13	6220.0	5	16072
2	5715.3	1	17492	14	6255.1	7	15982
3	5806.9	3	17215	15	6321.6	7	15815
4	5861.6	3	17056	16	6377.1	7	15676
5	5880.2	6	17001	17	6457.5	8	15482
6	5900.2	6	16943	18	6468.0	9	15456
7	5923.8	4	16878	19	6490.4	9	15404
8	5948.8	6	16807	20	6516.8	10	15340
9	5988.8	6	16692	21	6574.5	8	15207
10	6165.7	7	16215	22	6628.6	7	15083
11	6181.5	4	16173	23	6922.0	2	14443
12	6202.6	7	16119	24			

(4) On the emitter of the red emission bands.

From the complex appearance of the red emission bands, it is supposed that the emitter of the bands is not a diatomic molecule, but a polyatomic one. The polyatomic molecules present in the flame may be H_2O, H_2O_2, HO_2, O_3, etc. Of these molecules, the latter three are very unstable because of their small heats of decomposition. On the other hand, the water molecule (H_2O) is very stable and may be assumed to be formed as the end product of the reaction possessing excessive energy. It seems, therefore, most probable that the water molecule is the emitter of the red emission bands.

In the wave-length region of $\lambda\lambda$ 7000—5500 Å no emission bands belonging to the H_2O molecule have ever been found.[8] [9] As to the absorption spectrum of the molecule, Leifson,[10] Henning[11] and Rathenau[12] found many broad absorption bands and continuous spectra in the range of $\lambda\lambda$ 1780—500 Å. But no absorption bands caused by electron transition is observed in longer wave-length region.

The rotation bands of the H_2O molecule are found in the far infra-red region above about 8 μ, and the vibration-rotation bands begin to appear in the neighbourhood of 6 μ and are found in shorter wave-length region. Mecke, Baumann and Freudenberg[13] have lately investigated the vibration-rotation bands of water vapour in the Fraunhofer lines[14] and found 17 vibration-rotation bands in the range of $\lambda\lambda$ 6.27—5600 Å. The wave-length of the origin of the vibration-rotation bands of water vapour is shown in Table 2.

The H_2O molecule has the shape of an isosceles triangle, which has the O atom at its vertex and the H atom at each end of its base (In the normal state, the vertical angle, 105°6′; the distance between O and H, 0.970×10^{-8} cm.) The model of the molecule, therefore, belongs to an asymmetrical top molecule[15]. The molecule possesses three freedoms of vibration. According to Mecke, if three fundamental vibrations be represented by $\nu(\sigma)$, $\nu(\pi)$ and $\delta(\pi)$, and their vibrational quantum numbers v_σ, v_π, and v_δ respectively, then a vibrational state will

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[8] F. Paschen, *Ann. d. Phys.*, **50**, 409 (1893); **51**, 1 (1894); **52**, 209 (1894); **53**, 334 (1894).

[9] M. Neunhoeffer, *Ann. d. Phys.*, (V) **2**, 334 (1924); **4**, 352 (1930).

[10] S. Leifson, *Astrophys. J.*, **63**, 73 (1926).

[11] H. J. Henning, *Ann. d. Phys.*, **13**, 599 (1932).

[12] G. Rathenau, *Z. Physik*, **87**, 32 (1934).

[13] R. Mecke, *Z. Physik*, **81**, 313 (1933); W. Baumann u. R. Mecke, *ibid.*, **81**, 445 (1933); K. Freudenberg u. R. Mecke, *ibid.*, **81**, 465 (1933).

[14] C. St. John, C. E. Moore, L. M. Ware, E. F. Adams and H. D. Babcock, "*Revision of Rowlands Preliminary Table of Solar Spectrum Wavelengths*", Carnegie Institution of Washington, Publication No. 396, 1928.

[15] D. M. Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931); and G. B. B. M. Sutherland, "*Infra-Red and Raman Spectra*", 1935.

be expressed by $(v_\sigma, v_\pi, v_\delta)$. All the bands shown in Table 2 are the absorption bands having the normal state (0, 0, 0) as the first term, i.e. the bands caused by such quantum transitions as $(v_\sigma, v_\pi, v_\delta) \leftarrow (0, 0, 0)$.

Table 2.
Vibration-rotation bands of water vapour (by R. Mecke).

No.	$(\nu(\sigma), \nu(\pi), \delta(\pi))$	λ, μ	ν_0, cm^{-1}	Vibrational energy, kcal.
1	(3, 2, 0)	.5714	17495.44	49.7
2	(1, 4, 0)	.5916	16898.81	48.0
3	(1, 3, 2)	.5943	16821.62	47.8
4	(3, 1, 1)	.6314	15832.47	45.0
5	(1, 3, 1)	.6514	15347.90	43.6
6	(3, 1, 0)	.6982	14318.73	40.7
7	(1, 3, 0)	.7228	13830.91	39.3
8	(3, 0, 1)	.7956	12565.01	35.7
9	(1, 2, 1)	.8228	12151.23	34.5
10	(3, 0, 0)	.9062	11032.33	31.4
11	(1, 2, 0)	.9420	10613.25	30.2
12	(1, 1, 1)	1.135	8807.0	25.0
13	(1, 1, 0)	1.379	7253	20.6
14	(1, 0, 1)	1.875	5332.3	15.2
15	(1, 0, 0)	2.663	3756.35	10.7
16	(0, 1, 0)	2.8	(3600)	10.2
17	(0, 0, 2)	3.168	3152	9.0
18	(0, 0, 1)	6.269	1595.4	4.5

Does the emission bands of the oxy-hydrogen flame, as is expected, belong to the H_2O molecule? To solve this question the author has photographed the absorption spectrum of water vapour and drawn comparison between the absorption bands and the red emission bands.

III. Absorption Spectrum of Water Vapour.

(1) Photographing vibration-rotation bands of the water molecule.

In 1932, Lueg and Hedfeld[16] measured for the first time the vibration-rotation bands of the H_2O molecule in the photographic region and photographed the absorption bands in λλ 9062 (3, 0, 0), 9420 (1, 2, 0) and 11350 Å (1, 1, 1) on infrared plates, using the water vapour present in the air as the absorption layer. Baumann and Mecke[13] in 1933 photographed the absorption band of water vapour

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16) P. Lueg u. K. Hedfeld, *Z. Physik*, 75, 512 (1932).

at 8228 Å (1, 2, 1) on infrared plates, through the layer of the water vapour 1.5 m. thick.

The intensity of the absorption hand diminishes rapidly as the vibrational state is raised.15) In the present experiment, therefore, the absorption layer of the water vapour should be thicker than in the experiments made by the above-mentioned investigators, because it is necessary to photograph the absorption bands in the shorter wave-length region than 7000 Å.

(2) Apparatus.

In Fig. 2 the absorption tube T is 3 cm. in diameter and 4 m. in length. It is evacuated, and about 10 c.c. of distilled water is present in the reservoir R. R and T can be heated up to 144°C electrically. The light from the tungsten lamp (6 V—8 V), which is reflected on the mirror M, passes through T twice and is focussed on the slit S of the spectrograph. The spectrograph and the photographic plates used are the same as in the preceding experiment.

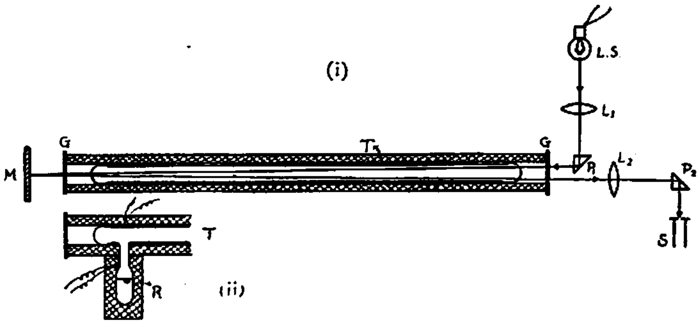

Fig. 2. Experimental apparatus for photographing the absorption spectrum of the vibration-rotation bands of water vapour.

The relation between the temperature and the vapour pressure of water is as follows: about 1 atm. at 100°C., 2 atm. at 120°C., 3 atm. at 134°C. and 4 atm. at 144°C. The effective path-lengths of light are, then, 8 m., 16 m., 24 m. and 32 m. under 1 atm., 2 atm., 3 atm. and 4 atm. of the vapour pressure respectively.

(3) Experimental results.

The absorption spectrum of the water vapour was photographed by about 10 minutes' exposure. Under $1 \sim 2$ atm. of the vapour pressure no absorption band was observed. At 3 atm. an absorption band slightly appears, and some bands clearly at 4 atm. The wave-length of the absorption bands was measured in comparison with the *Ne*-spectrum. As seen in Table 3, 1, four absorption bands were observed in the region of 6517—5881 Å. The effective path-length was about 32 m. as calculated under 1 atm. of vapour pressure.

Table 3.

Absorption spectrum of the vibration-rotation bands of water vapour in the region of $<\lambda$ 7000 Å and its comparison with the emission bands of the flame.

I					II			
Absorption bands of water vapour.					Emission bands of the oxy-hydrogen flame			
No.	λ, Å	Int.	ν, cm^{-1}	Remarks	No.	λ, Å	Int.	ν, cm^{-1}
1	5880.6	6	17001	broad	5	5880.2	6	17001
2	5914.2	4	16903	diffuse	7	5923.8	4	16878
3	5943.0	6	16821	broad	8	5948.8	6	16807
4	6517.4	10	15340	relatively sharp	20	6516.8	10	15340

(4) Comparison of the red emission bands of the oxy-hydrogen flame with the absorption bands of water vapour.

The most intense band in the red emission bands of the flame lies at λ 6516.8 Å (Table 1, No. 20). In the absorption bands of water vapour the most intense and sharp one is at λ 6517.4 Å (Table 3, I, No. 4). These two bands, thus, agree markedly with each other. The other three absorption bands (No. 1, 2 and 3) correspond to the emission bands of the flame in wave-length and intensity. (Table 3, II.) Accordingly, it becomes clear that the red emission bands of the oxy-hydrogen flame contain the vibration-rotation bands of the water molecule.

Table 4.

Comparison of the emission bands of the oxy-hydrogen flame with the band-origin of the water vapour band.

I			II			III	
Band-origin (by R. Mecke)		Quantum numbers	Emission band of the flame		Diff.	Absorption band of the water vapour.	
No.	ν_0, cm^{-1}	V_σ, V_π, V_δ	No.	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	No.	ν, cm^{-1}
1	17495.44	3, 2, 0	2	17492	+ 3		—
2	16898.81	1, 4, 0	7	16878	+21	2	16903
3	16821.62	1, 3, 2	8	16807	+15	3	16821
4	15832.47	3, 1, 1	15	15815	+17		—
5	15347.90	1, 3, 1	20	15340	+ 8	4	15340

In Table 4, column I denotes the wave-number of the band-origin of the vibration-rotation bands, column II the emission bands of the oxy-hydrogen flame and column III the absorption bands of water vapour measured by the author. The wave-numbers coincide with each other within the error of about 20 cm^{-1}.

As to the vibration of the plane asymmetrical top molecule, such as H_2O, Dennison[15] has theoretically deduced that when the change of electric moment is along the least axis of inertia, the rotation lines forming the vibration band tend to gather round the centre of the band and that a very sharp and intense maximum belonging to the *Q*-branch appears near the band origin. The vibration-rotation bands in Table 4 are all of this vibrational type (v_σ=odd number), and it is inferred that the absorption bands and emission bands in Table 4 (columns II and III) are all attributable to the sharp maxima caused by the *Q*-branches of the vibration-rotation bands near the band origins. It is considered, therefore, that the emission bands caused by the *R*- and *P*-branches are also included in the red emission bands (Table 1) of the oxy-hydrogen flame.

It is made clear, then, that in the red emission bands of the flame exist the vibration-rotation bands of the water molecule whose vibrational quantum numbers are (3, 2, 0), (1, 4, 0), (1, 3, 2), (3, 1, 1) and (1, 3, 1). The bands in Table 2, as above mentioned, are caused by the transition between a normal state (0, 0, 0) and higher vibrational states. It is possible, therefore, that in the red emission bands another band due to the transition among various vibrational states is present. To which transition it belongs would be determined by the fine structure analysis, but its determination requires higher resolving power, and so this question is left untouched.[17]

(5) Emission of the vibration-rotation bands of the H_2O molecule.

A few studies have been done concerning the emission spectrum of the hydrogen flame in the infrared region. Paschen[8] has found that the radiation of the hydrogen flame has its maxima at 1.34 μ, 1.8 μ, 2.8 μ and 5.6—6.56 μ. Garner and Tawada[18] have found the maximum of the infrared radiation of the oxy-hydrogen flame in the neighbourhood of 2.8 μ. Neunhoeffer[9] has measured two emission bands of the hydrogen flame at 2.7 μ and 1.8 μ.

On comparing with the results analysed by Mecke (See Table 2), it is found that the infrared emission band at 2.8 μ observed by Paschen and others corres-

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[17] If the oxygen atom in the ^1D state is present in the oxy-hydrogen flame, the line spectrum caused by $^1D \rightarrow {}^3P$ would be found in the flame. The transition between the ^1D state and the ^3P state is prohibited spectroscopically, but, according to Paschen and others [F. Paschen, *Naturwiss.*, 18, 752 (1930); J. J. Hopfield, *Phys. Rev.*, 37, 160 (1931).], the lines at λ 6300.23 Å [$^1D_2 \rightarrow {}^3P_2$] and λ 6363.88 Å [$^1D_2 \rightarrow {}^3P_1$] were found at the intensity ratio of about 4 : 1 in the discharge tube under a suitable condition. In Plate 1, however, two emission lines are seen just at the above-mentioned wave lengths in the red emission bands of water vapour. Further research will ascertain the results.

[18] W. E. Garner and K. Tawada, *Trans. Farad. Soc.*, 26, 36 (1930).

ponds to the (1, 0, 0) band of the H_2O molecule, and the other emission bands at 1.34 μ, 1.8 μ and 5.6—6.56 μ to the (1, 1, 0), (1, 0, 1) and (0, 0, 1) bands respectively. It has not yet been reported, however, that the vibration-rotation bands of the H_2O molecule make their appearance as emission within the visible region below 7000 Å as in this report.

It is evident, therefore, that in the oxy-hydrogen flame the water molecules which have been excited to higher vibrational states, such as (3, 2, 0), (1, 4, 0), (1, 3, 2), and (1, 3, 1), are formed. For simplicity, the H_2O molecule in such higher vibrational states will be indicated by $\widetilde{H_2O}$ hereafter. The highest vibrational energy possessed by the $\widetilde{H_2O}$ molecule is about 50 kcal [(3, 2, 0) state].

IV. Discussion on the Chemical Reaction Mechanism.

The thermal energy of the oxy-hydrogen flame originates from an exothermic chemical reaction. In the process of the formation of a H_2O molecule in an elementary reaction it happens that the molecule formed immediately after the reaction reserves so much reaction energy directly generated in the reaction as to cause the formation of a $\widetilde{H_2O}$ molecule possessing high vibrational energy. In other words, it is appropriate to consider that the $\widetilde{H_2O}$ molecule is directly formed as the primary product of a chemical reaction.

Gibson and Hinshelwood[19] derived the following reaction mechanism in their study of the homogeneous reaction between oxygen and hydrogen :

$$
\begin{array}{ll}
(1) & 2H_2+O_2=H_2O+H_2O^*, \\
(2) & H_2O^*+O_2=H_2O+O_2^*, \\
(3) & 2H_2+O_2^*=H_2O+H_2O^*, \\
(4) & 2H_2+O_2^*=2H_2O \quad \text{(on the wall)}, \\
(5) & H_2O^*\rightarrow H_2O,
\end{array}
$$

where the molecules denoted by * have been supposed to be what are called activated molecules possessing much energy. In the case of a burning flame, a reaction on the wall, such as (4), may be excluded. In what quantum state the activated molecule H_2O^* is has not been elucidated there.

Let us suppose now the H_2O^* molecule to be in a higher vibrational state, then it can be writen as $\widetilde{H_2O}$ as mentioned above. It is appropriate to consider that the reaction energy generated in reaction (1), i.e. 114 kcal., is transmitted equally to two H_2O molecules simultaneously formed,[20] not to one H_2O molecule

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19) C. H. Gibson and C. N. Hinshelwood, *Proc. Roy. Soc.*, A 119, 591 (1928).

20) L. S. Kassel, "*The Kinetics of Homogeneous Gas Reactions*", 1932.

as in the above mechanism. Then, reaction (1) becomes

$$(1a) \qquad 2H_2+O_2=\widetilde{H_2O}+\widetilde{H_2O},$$

where each $\widetilde{H_2O}$ molecule has $\frac{114}{2}=57$ kcal., which is enough to activate the molecule to the highest vibrational state observed in the emission spectrum of the flame. Moreover, if we suppose that two $\widetilde{H_2O}$ molecules are formed simultaneously as in (1a) and that the succeeding chain reaction proceeds by the secondary activation, the mechanism of branching of the chain reaction will be also explainable.

Semenoff[21] proposed the following reaction mechanism:

$$(6) \qquad O+H_2=H_2O^*$$

$$(7) \qquad H_2O^*+O_2=H_2O+O+O.$$

It has been supposed that in reaction (6) H_2O^*, which possesses the whole reaction energy generated, i.e. 116 kcal., is brought forth and by the collision between H_2O^* and O_2 the latter decomposes into two O atoms (the decomposition heat of $O_2=117$ kcal.). According to Bear and Eyring's[22] theoretical study of the reaction between the H_2 molecule and the O atom, when the H_2 molecule approaches to the O atom which is in a normal state (^{3}P), the O atom lies on the repulsing curve of the H_2O molecule and the quasi-molecule H_2O^* is temporarily brought forth. If another H_2O molecule collides with this quasi-molecule, it may be considered that the former deprives the latter of its partial energy, and it gives birth to two stable water molecules, thus:

$$(8) \qquad H_2O^*+H_2O=\widetilde{H_2O}+\widetilde{H_2O}.$$

In this case, too, if the excessive energy of the H_2O^* molecule is supposed to be transmitted equally to two molecules as vibrational energies, each molecule will have $\frac{116}{2}=58$ kcal. Thus, the formation of the $\widetilde{H_2O}$ molecule is explained.

When the chain reaction is broken by the recombination between the intermediate products H and OH as in Haber's reaction mechanism,[23] i.e.

$$(9) \qquad H+OH=H_2O+112 \text{ kcal.},$$

it requires a part of the formation heat to be dissipated by a triple collision. Let us assume the water molecule of high concentration as the third molecule of the

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[21] D. Kopp, A. Kowalsky, A. Sagulin u. N. Semenoff, *Z. physik. Chem.*, B 6, 307 (1929).

[22] R. S. Bear and H. Eyring, *J. Amer. Chem. Soc.*, 56, 2020 (1934).

[23] L. Farkas, F. Haber u. P. Harteck, *Naturwiss.*, 18, 266 (1930).

triple collision, then we have

$$\text{(9a)} \qquad H+OH+H_2O=\widetilde{H_2O}+\widetilde{H_2O}.$$

In this reaction, if it is considered that the formation heat is transmitted equally to two water molecules, each molecule will have the excessive energy of $\frac{112}{2}=56$ kcal., which would be sufficient to bring forth the activated $\widetilde{H_2O}$ molecule.

From these several examples, it may be apparent that what is called the activated water molecule ($\widetilde{H_2O}$) of high vibrational energy is directly formed as the primary product of the chemical reaction.

The chief action of $\widetilde{H_2O}$ as the intermediate product is to transmit its abundant vibrational energy to other reacting molecules and to let them accelerate the reaction according to the secondary activation phenomenon. On the other hand, as seen in (1a), (8) and (9a), two $\widetilde{H_2O}$ molecules simultaneously formed in the reaction urge the branching of the chain reaction so much. In other words, $\widetilde{H_2O}$ seems to play a part of what is called homogeneous catalysis, which is to accelerate the reaction in combustion or explosion. From this point of view, the autocatalytic effect of water vapour on the homogeneous combination reaction between oxygen and hydrogen found by Hinshelwood and Thompson[24] may have some relationship to the above-mentioned facts.

Summary.

1) The emission spectrum of the flame of oxygen burning in the atmosphere of hydrogen (the oxy-hydrogen flame) has been studied in the visible region and a number of complex emission bands found in the wave-length region of λλ 7000—5500 Å (the 'red emission bands').

2) Assuming that the red emission bands of the oxy-hydrogen flame belong to the H_2O molecule, the absorption spectrum has been photographed directly through the layer of water vapour (4 atm.; 8 metres). In the range of λλ 5800—6500 Å several absorption bands (vibration-rotation bands) have been found, which agree well with the emission bands of the oxy-hydrogen flame.

3) From the results obtained it has been ascertained that the red emission bands of the oxy-hydrogen flame include the emission spectra of the vibration-rotation bands of the H_2O molecule. The vibrational states of the H_2O molecules ($\widetilde{H_2O}$) in the oxy-hydrogen flame have been made clear to be the (3, 2, 0),

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[24] C. N. Hinshelwood and H. W. Thompson, *Proc. Roy. Soc.*, A 118, 170 (1928).

(1, 4, 0), (1, 3, 2), (3, 1, 1), (1, 3, 1) states etc., whose maximum vibrational energy is about 50 kcal.

4) Assuming that the activated water molecule ($\widetilde{H_2O}$) is formed directly as the primary product of the chemical reaction between oxygen and hydrogen, the formation mechanism has been elucidated on the basis of the chain reaction mechanisms proposed by Gibson, Hinshelwood, Haber, Semenoff and others. The important action of the activated molecule as the transmitter of energy has been also discussed.

The author wishes to express his appreciation to Professor S. Horiba for his guidance and to Professor S. Kimura for his advice. He acknowledges his indebtedness to the Japan Society for the Promotion of Scientific Research for a grant-in-aid and also to the Iwadare Syogakukai for scholarship.

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