The Kinetic Study of Surface-chemical Reactions at Extremely Low Pressures. V. The Thermal Reaction between Water Vapor and a Tungsten Filament. Part V

By Takuya HAMAMURA

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In previous papers$^{1-4)}$ of this series the reaction of water vapor with tungsten in the 1270 to 1950° K temperature range was presented. Here the data for this reaction from 1950 to 2460° K are given and discussed. The division into two temperature ranges is done for convenience in discussing the result. Below 1950° K a blue deposit having a mean apparent composition of $WO_{2.8}$ is produced on the wall of the vessel. Above 1950° K the ratio O/W of the deposit increases with the rise of the temperature and a colorless deposit is formed at higher temperatures.

Experimental

The apparatus was the same as that used in previous experiments. Tungsten filaments, 0.114mm. in diameter and 56mm. long, were used for determining the reaction rate and the composition of the reaction product. Procedures of measuring the reaction rate and determining the composition of the reaction products have been described previously. The two-filament method was not used to obtain the reaction probability owing to the too severe influence of hydrogen pressure on the reaction rate. The temperature of the reaction vessel remained at room temperature throughout the experiments.

Uptake of oxygen by the deposit was studied as follows. After the deposit had been produced, water vapor was removed from the vessel by cooling water reservior 1 in Fig. 1* with dry ice and a definite amount of oxygen was introduced into the vessel through cock 12 after the boiler of diffusion pump 7 was cooled. Then the vessel was heated in an electric furnace and the pressure decrease was measured by a McLeod manometer.

Desorption of a permanent gas from the deposit was studied as follows. After the deposit had been produced, water vapor was removed from the vessel in the manner mentioned above. The vessel was then heated in an electric furnace and the permanent gas given off was transferred into the glass balloon by diffusion pump 7. The pressure was measured by a McLeod manometer.

Results and Discussion

Reaction Rate.—Reaction rates were determined from 30×10^{-5} to 103×10^{-5} mmHg initial pressures of water vapor under various pressures of hydrogen in the vessel. It was found that the reaction rate decreased with the increase of hydrogen pressure more steeply as the temperature rose or the pressure of the water vapor decreased in a manner similar to that observed below 1950° K. The cause of decrease of the rate was studied by the following experiment. Two filaments of the same length** and diameter were heated in water vapor of the same initial pressure separately for the same interval of time with the same current under different pressures of hydrogen. The amount of hydrogen produced and the increment of resistance of the respective filaments were determined. Results for 1.5 amp. heating current (about 2350°K) are given in Table VI***. Increments of the resistance are almost the same for two filaments even though the amounts of hydrogen are considerably different. Therefore, it is apparent that the decrease is not caused by the retardation of the reaction of water vapor with tungsten by hydrogen.

The reaction probability at a definite temperature was evaluated from the reaction rate at zero pressure of hydrogen obtained by extrapolating back the rate vs. hydrogen pressure curve to zero pressure of hydrogen. Values of reaction probabilities at 60×10^{-5} mmHg of water vapor are given in Table VII. A probability at 1890°K is also given for comparison. These values are not free from the end effect of the filament.

Composition of Deposit.—Results obtained are given in Table VIII. It is obvious that the ratio O/W of the deposit increases with the rise of the temperature, whereas it decreases with the increase of the hydrogen pressure. Properties of deposits are as follows.

1) Deposits having ratio values O/W smaller than 3 appeared blue in transmitted light,

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1) N. Sasaki and T. Hamamura, This Bulletin, 29, 365 (1956).
2) T. Hamamura, ibid., 32, 845 (1959).
3) T. Hamamura, ibid., 32, 848 (1959).
4) T. Hamamura, ibid., 32, 1180 (1959).

[*] Fig. 1 is presented in the first paper of this series.

[**] Filaments, 12.8 cm. long, were used for this experiment.

[***] Tables in the present paper are numbered after those of previous papers.

TABLE VI

Expt. No.	Heating time min.	Initial press. of H_2O mmHg×10^5	Press. of H_2 in vessel mmHg×10^4	Amount of H_2 produced mol.×10^5	Initial resist. at 25°C ohm	Increment of resist. ohm
1	50	91.0	5.5	1.97	1.171	0.033
1′	50	91.0	62.5	1.40	1.164	0.032
2	120	56.5	2.4	2.02	1.194	0.052
2′	120	56.5	18.0	0.96	1.203	0.050

TABLE VII. REACTION PROBABILITIES

Temp. of filament (°K)	1890	2000	2100	2200	2300
k	7.7×10^{-3}	1.3×10^{-2}	1.7×10^{-2}	2.5×10^{-2}	3.0×10^{-2}

TABLE VIII

Filament temp. °K	Initial press. of H_2O mmHg×10^5	Press. of H_2 in vessel mmHg×10^5	Net weight loss of filament mol.×10^6	Amount of H_2 produced mol.×10^5	Composition in WO_x	Gas mass No., product %
2000	103	26	7.85	2.26	$WO_{2.88}$	
2000	103	108	8.26	2.35	$WO_{2.85}$	
2110	58	21	4.17	1.32	$WO_{3.16}$	
2110	58	82	4.44	1.34	$WO_{3.01}$	
2110	103	19	6.95	2.10	$WO_{3.02}$	
2210	60	22	3.93	1.37	$WO_{3.48}$	
2310	66	22	3.38	1.36	$WO_{4.03}$	28 1.2% 32 0.4%
2310	66	66	3.39	0.99	$WO_{2.93}$	28 0.6% 32 0.6%
2310	103	37	5.27	2.02	$WO_{3.82}$	
2310	103	91	6.47	2.04	$WO_{3.15}$	
2430	60	18	3.36	1.31	$WO_{3.90}$	28 2.3% 32 1.2%
2430	60	46	2.88	8.84	$WO_{3.07}$	
2460	104	32	5.16	2.05	$WO_{3.98}$	

whereas those having ratio values greater than 3 appeared colorless.

2) The deposition of a colorless product revealed a bleaching action upon the blue deposit, that is, when the colorless product was deposited on the blue deposit the blue color faded gradually with the accumulation of the colorless deposit.

3) When 100×10^{-5} mmHg of oxygen was admitted to the blue deposit, oxygen was hardly taken up at all at room temperature, but it was taken up swiftly at 200°C with fading of the blue color.

4) When the blue and the colorless deposits were heated separately in high vacuum at 300°C for two hours, the desorption of a permanent gas and the change of the color were not observed in either case.

The bleaching action of the colorless product upon the blue deposit may be explained by making an assumption that besides the reaction between water vapor and tungsten, the thermal decomposition of water vapor takes place with an increasing rate with the rise of the temperature and oxygen thus produced reacts with the blue deposit to make it colorless. Although the reduction of the deposit by hydrogen must take place at the same time, so long as the oxidation rate predominates over the reduction rate the colorless product is produced. It is shown experimentally that the blue deposit takes up oxygen to become colorless.

It has been stated⁴⁾ that the deposit produced below 1950°K has the ratio value O/W of 2.8. On the other hand, at temperatures above 1950 °K the ratio value was found to increase with the rise of the temperature to become greater than 4. The ratio value may increase owing to the formation of a higher oxide or may appear to increase by the production of hydrogen, not being accompanied by the weight loss of the filament, because the ratio value is determined by the amount of hydrogen produced and the weight loss of the filament. The presence of a higher oxide than tungsten trioxide has not been reported in literature. If the deposit was composed of a peroxide, oxygen or hydrogen peroxide would be generated when the deposit was dissolved in sulfuric acid or in aqueous solution of sodium hydroxide. However, the oxygen evolution was not observed at all and the hydrogen peroxide formation was not detected by luminol⁵⁾. Peroxytungstic acids⁶⁾ have been reported by some investigators, but these acids are described as being unstable and as decomposing with the evolution of oxygen by heating. Therefore, it is obvious that the colorless deposit is not composed of these acids. The colorless deposit is composed of tungsten trioxide.

Thermal decomposition of water vapor has been assumed to explain the bleaching action of the colorless product, but if all the oxygen produced reacts with the filament to form tungsten trioxide, the ratio value can not become greater than 3. It is necessary for the ratio value to become greater than 3 that oxygen be consumed by another process than the reaction with the filament. The following processes may be considered for such consumption.

1) Oxygen leaves the reaction vessel to be introduced into the glass balloon. 2) Oxygen produces hydrogen peroxide to be caught by the trap cooled with liquid nitrogen. 3) Oxygen is taken up by the wall of the apparatus or by the deposit on the wall of the vessel.

Results of the analysis by the mass spectrometer are given in Table VIII. It is evident that the amount of oxygen introduced into the balloon is too little to explain the observed ratio value. Hydrogen peroxide⁷˒⁸⁾ has been reported to be produced when the water vapor contacts with a Nernst tube at a high temperature or when atomic hydrogen combines with oxygen on a wall cooled with liquid oxygen. Therefore, hydrogen peroxide may be produced in the reaction of water vapor with the tungsten now being studied. The formation of hydrogen peroxide was studied by the following experiment; after a filament was heated at 2310°K in 60×10^{-5} mmHg of water vapor for two hours, the filament and the boiler of diffusion pump 7 were cooled and air was introduced into the apparatus to an atmospheric pressure. Trap 6 was then detached from the apparatus, warmed to room temperature and a luminol reagent was dropped in it within a dark room to detect hydrogen peroxide by its luminescence. As a result, hydrogen peroxide was not detected by this experiment although about 2×10^{-6} mol. of hydrogen peroxide must be produced if the observed ratio value is ascribed to the formation of hydrogen peroxide. A blank test revealed that about 2×10^{-7} mol. of hydrogen peroxide could be detected.

The fact that a permanent gas was not given off from the deposit at 300°C suggested that oxygen had not been physically adsorbed at all or that it had been chemisorbed by the wall of vessel and/or by the deposit. The uptake of oxygen by the wall of the apparatus was studied by carrying out an electrodeless discharge in oxygen within the vessel. The discharge vessel was 30 mm. in diameter and 130 mm. long. The vessel was connected with a trap cooled with liquid nitrogen and the pressure was measured with a McLeod manometer. The electrodeless discharge was carried out by placing the vessel in a coil through which a high frequency current flowed. After evacuating and degassing the apparatus, about 0.2 mmHg of oxygen was introduced into the apparatus. Then the discharge was carried out for two minutes, and the pressure was measured again. Thus, the oxygen pressure was measured every time after the two-minute discharge. The uptake of oxygen by the tungsten trioxide deposit was studied similarly by using a vessel whose wall had been covered with tungsten trioxide deposit formed by heating a tungsten filament mounted along the axis of a vessel in oxygen. As a result, it was found that the tungsten trioxide deposit hardly took up oxygen at all, whereas the wall of the apparatus took up some amount of oxygen. It is evident that excited molecules and atoms of oxygen were produced by the discharge and a part of them were taken up by the wall. In the reaction of water vapor with tungsten, too, excited molecules and atoms of oxygen would be produced and a part of them be taken up by the wall by chemisorption. Langmuir⁹⁾ has found that oxygen adsorbed on tungsten evaporates from the surface as atoms when the surface is nearly bare. Therefore, it is most reasonable to consider that the ratio value greater than 3 is caused by the fact that some amount of hydrogen is liberated, not being accompanied by the weight loss of filament, since oxygen is produced by the decomposition of water vapor and is taken up by the wall of the apparatus, and to consider that the reaction rate and the ratio value O/W of deposit decrease with the increase of hydrogen pressure, since oxygen thus taken up reacts with hydrogen to form water vapor.

Summary

1) Reaction probabilities above 1950°K are determined.

2) The ratio value O/W of the deposit increases with the rise of temperature.

3) The deposit having ratio value O/W greater than 3 appears colorless in transmitted light.

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5) W. Langenbeck and U. Ruge, *Ber.* 70, 367 (1937).

6) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XI, Longmans, Green Ltd., London (1954), p. 833.

7) W. Nernst, *Z. Elektrochem.*, 11, 710 (1905).

8) K. H. Geib and P. Harteck, *Ber.*, 65, 1551 (1932).

9) I. Langmuir and D. S. Villars, *J. Am. Chem. Soc.*, 53, 486 (1931).

4) The colorless deposit is composed of tungsten trioxide and the ratio value O/W greater than 3 is ascribed to the production of hydrogen, not being accompanied by the weight loss of filament, since the ratio value is determined from the amount of hydrogen produced and the amount of weight loss of filament.

5) Water vapor decomposes and a part of the oxygen thus produced is taken up by the wall of the apparatus, and hence hydrogen is produced, not being accompanied by the weight loss of filament.

6) The reaction rate and the ratio value O/W of the deposit decrease with the increase of hydrogen pressure, since the oxygen taken up by the wall recombines with hydrogen to form water vapor.

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Department of Chemistry
Faculty of Industrial Art
Kyoto Technical University
Sakyo-ku, Kyoto