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

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In continuation of the previous papers[1,2] in which the kinetics of the reaction of water vapor with tungsten was studied, this paper is concerned with the study of the effect of hydrogen pressure on the reaction rate, which seems to give some information about the adsorbed layer on the filaments surface.

Experimental

Apparatus. — The apparatus was essentially the same as that used in the previous experiments, except for an equipment for the control of hydrogen pressure. The pressure of hydrogen in the reaction vessel was changed by an adjustable needle valve placed in the path between trap 6 and diffusion pump 7 in Fig. 1*. If the flow of hydrogen in the path obeys Knudsen's law of molecular flow and the back diffusion through the pump is negligibly small, the quantity D in moles of hydrogen which flow into the balloons per second is given by the following equation similar to Eq. 1′

$$D=A'\overline{B}'P' \qquad (12)$$

where A' is the over-all conductance of the path from the reaction vessel to the pump, $\overline{B}'$ is a constant determined experimentally, and P' is the partial pressure of hydrogen in the vessel. Therefore, when A' was changed by varying the conductance of the needle valve, P' was changed correspondingly. The above procedure, however, did not change the pressure of water vapor in the vessel, since the conductance A of the path from the vessel to trap 6 was not changed even if A' was changed. The value of $A'\overline{B}'$ could be determined experimentally by measuring D and P' while hydrogen was flowing through the path. Thus after knowing $A'\overline{B}'$, P' could be calculated from the measured value of D.

The needle valve is shown schematically in Fig. 8. When the mercury was lowered, hydrogen flowed mainly through the wide tube, and when the mercury was raised to cut the wide tube off, it flowed through the capillary with a smaller conductance, then by moving a glass needle containing an iron rod by a solenoid into the capillary, the conductance could be decreased further. The over-all conductance of the path from the reaction vessel to the diffusion pump was $4.90\times10^{-3}\,\text{cm}^2$ when the mercury was lowered, $1.21\times10^{-3}\,\text{cm}^2$ when the mercury was raised and the needle was drawn out of the capillary, and $3.15\times10^{-4}\,\text{cm}^2$ when the whole length of the needle was in the capillary.

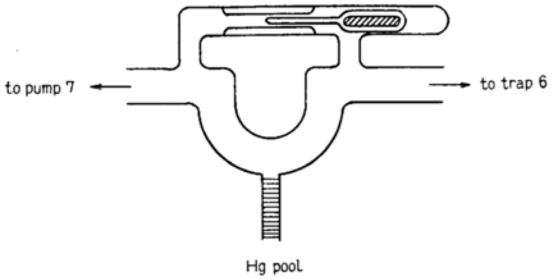

Fig. 8. The needle valve.

A tungsten filament 0.114 mm. in diameter and 81 mm. long was used. This was taken from the same spool as that used in the previous experiments and pretreated in a similar manner. A Pirani gauge of the same type as that attached to the glass balloons was attached to the reaction vessel.

Procedure.—The procedures of evacuating the apparatus, degassing the filament and introducing water vapor into the vessel were described previously. When the flow of water vapor became stationary, the pressure was measured with a quartz fiber manometer, and the filament was then heated to a desired temperature, the conductance of the needle valve being kept at a desired value. The pressure increase of the glass balloons was measured in a similar manner as mentioned previously. The pressure increase gave the reaction rate, and the hydrogen pressure in the vessel was calculated by Eq. 12. Thus, the effect of hydrogen pressure on the reaction rate was determined by the experiments carried out by heating the filament under various conductances of the valve at a fixed temperature and a constant initial pressure of water vapor. The temperature of the reaction vessel remained at room temperature throughout the experiments.

Results

The experiments were carried out at filament temperatures of 1850 and 1940°K

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[1] N. Sasaki and T. Hamamura, This Bulletin, **29**, 365 (1956).

[2] T. Hamamura, ibid., **32**, 845 (1959).

* Eqs. and Figs. are numbered after those of the previous papers.

under 12×10^{-5} and 32×10^{-5} mmHg initial pressures of water vapor and at 1510, 1615, 1850 and 1940°K under 62.5×10^{-5} mmHg.

The reaction rate was independent of the hydrogen pressure below 1850°K at all the initial pressures of water vapor studied. At 1940°K, however, the reaction rate was independent of the hydrogen pressure at 62.5×10^{-5} mmHg of water vapor, but decreased with the increase of hydrogen pressure gradually at 32×10^{-5} mmHg and steeply at 12×10^{-5} mmHg. These are shown in Fig. 9. It was apparent from these results that the reaction rate was independent of the hydrogen pressure at lower filament temperatures or higher pressures of water vapor but decreased with the increase of hydrogen pressure at higher filament temperatures and lower pressures of water vapor. Moreover, the reaction rate decreased more steeply as the temperature increased or the pressure of water vapor decreased.

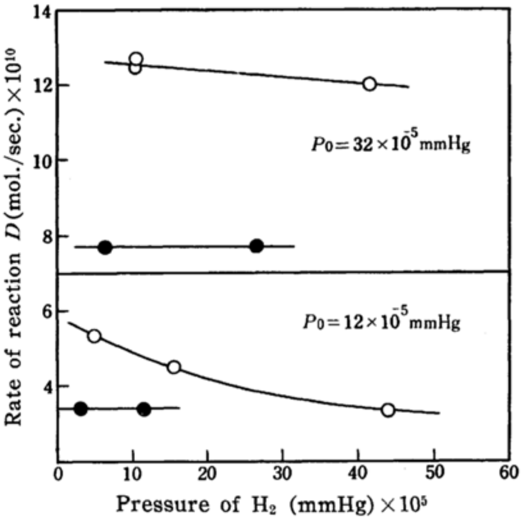

Fig. 9. Effect of hydrogen pressure on the reaction rate. ●-1850°K, ○-1940°K.

Discussion

The reaction rate might decrease owing to the retardation of the reaction by hydrogen or might decrease owing to the uptake of hydrogen by the wall, because the rate was calculated from the pressure increase of the glass balloons. The independency of reaction rates upon the hydrogen pressures at lower filament temperatures or higher pressures of water vapor might suggest that neither retardation nor uptake occurred under these conditions. As for the uptake, the following facts are known by the studies[3,4] of Langmuir: when a tungsten filament is heated above 1300°K in hydrogen at low pressure, the hydrogen gradually disappears. This action is caused by the hydrogen dissociated into atoms in contact with the filament, the atom then being driven on to the bulb and there held by adsorption. But the disappearance of hydrogen is suppressed almost completely by a trace of oxygen or water vapor at lower filament temperatures, presumably because of the formation of an adsorbed layer of oxygen acting as a catalytic poison against the dissociation of hydrogen. In the present work, too, the filament surface might be covered with oxygen at lower temperatures or higher pressures of water vapor, and in consequence neither retardation nor uptake occurred. However, the disappearance is known to take place again when the filament temperature rises or the pressure of oxygen or water vapor decreases, probably because of desorption of the adsorbed layer. In the present work, the reaction rate was found to decrease at higher temperatures and lower pressures of water vapor. This seemed to suggest that the decrease was caused by the uptake of hydrogen by the wall, the effect being known as "clean up".

Summary

Hydrogen hardly affected the reaction at lower filament temperatures or higher pressures of water vapor, but it decreased the rate of reaction at higher temperatures and lower pressures, as ascribed to the "clean up" of hydrogen by the filament.

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[3] I. Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912).

[4] I. Langmuir, ibid., **38**, 2221 (1916).