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## Kinetics of OH Radicals as Determined by Their Absorption Spectrum

VI. Attempt to Trace OH Radicals in the Thermal Hydrogen-Oxygen Reaction<sup>1</sup>O. OLDENBERG, J. E. MORRIS, C. T. MORROW, E. G. SCHNEIDER,\* AND H. S. SOMMERS, JR.\*  
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The steady thermal reaction of hydrogen and oxygen at a pressure of 60 cm and a temperature in the region of 550° C was searched by absorption spectrum technique for free OH radicals. None were detected, although the apparatus would have been sensitive to an OH radical pressure of  $4 \times 10^{-4}$  mm. This negative result indicates that the OH radicals have a very short lifetime in the reacting mixture.

## I. PROBLEM

THE existence and life history of free hydroxyl radicals has been investigated, as described in preceding papers,<sup>2</sup> by observing their absorption spectrum. In particular, this method was applied to free OH generated in low pressure water vapor by an electric discharge. The present paper describes an attempt to trace free OH in the thermal hydrogen-oxygen reaction. The various theories of this reaction agree in assuming the formation of free OH as an intermediary step. If we were able to test the concentration of free OH as a function of the time, interesting conclusions could be drawn regarding the mechanism of the reaction. The negative result reported below gives an upper limit for the free OH present under the most favorable conditions that can be prepared with a reasonable effort.

## II. EXPERIMENT

## (a) The Thermal Reaction

The *reaction vessel*, which was designed to have the greatest possible path length for the light used in the measurement of the absorption spectra, consisted of a Pyrex tube, of length 134 cm, and inner diameter 4.8 cm. Heavy windows of fused quartz were sealed with glyptal onto both ends. The two gases were admitted successively. If the gases were admitted through an

inlet attached to one end of the long cylindrical reaction vessel, the mixing would possibly not be quite thorough. In order to secure a uniform mixture the gases were admitted through two inlets properly located.

The reaction vessel was heated by an *electric oven* 11 cm shorter than the vessel. To protect the seals the protruding ends of the vessel were cooled with water running through lead pipes. The temperature was between 540 and 559°C. Great care was taken to keep the temperature uniform along the vessel. This was necessary since the rate of the reaction strongly depends on the temperature,<sup>3</sup> so that any local high temperature would cause an explosion. The temperature was kept uniform within  $\pm 2^\circ\text{C}$  from the average along a section of 80 cm length with the help of auxiliary heating coils wound on the same core with the main coil. The oven was thermostated by the arrangement described by Bancroft.<sup>4</sup> The temperature was measured with a platinum/platinum-rhodium thermocouple tested for homogeneity of the wires. To guard against danger from explosions the oven containing the reaction vessel was surrounded by copper gauze screens. *Electrolytic hydrogen and oxygen* were used, each being purified by passage through tubes containing  $\text{P}_2\text{O}_5$ , platinized asbestos, and again  $\text{P}_2\text{O}_5$ .

For most of the experiments, the surface of the reaction vessel was conditioned by successive reactions, separated by short periods of pumping. Previous work<sup>3</sup> had shown that this procedure leads to reproducible reaction rates.

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<sup>1</sup>The experiments reported were performed during the years 1938-41. The results obtained by the first group of experiments were reported in Phys. Rev. **58**, 1121 (1940).

<sup>2</sup>For references see O. Oldenberg and F. F. Rieke, J. Chem. Phys. **7**, 485 (1939).

<sup>3</sup>O. Oldenberg and H. S. Sommers, Jr., J. Chem. Phys. **9**, 432 (1941).

<sup>4</sup>D. Bancroft, Rev. Sci. Inst. **13**, 24, 114 (1942).

### (b) Optical Arrangement

The optical arrangement has been described in preceding papers.<sup>5</sup> In order to make the test by the absorption spectrum as sensitive as possible, a 21-foot concave grating was used in the second order. The length of the spectral lines was reduced and so the astigmatism, which is caused by the concave grating, was largely removed by a cylindrical quartz lens placed in front of the plate. For a continuous background the spectrum from the positive carbon of an arc burning in dry nitrogen was used. This seems to be the most intense background available around 3000Å. For some exposures the continuous spectrum from a discharge through dry hydrogen was applied. With the apparatus available, this was not quite as intense as the spectrum from the carbon, but it was more uniform with time.

In order to take advantage of the full resolving power of the grating, Eastman Process Plates or Spectroscopic Plates III-O were used. The times of exposure were between one and one-half and three minutes.

In order to increase the sensitivity of the test for OH and so give the negative result reported below greater significance, in the final group of experiments the light was twice reflected and so passed three times through the reaction vessel. This increased the effective length of the absorbing gas to 240 cm.

### (c) Procedure

The hydrogen was admitted to the reaction vessel first, and the oxygen second, to prevent a second-limit explosion during the mixing of the gases. This was particularly important in the experiments in which the hydrogen represented two thirds of the mixture. Immediately after the admission of both gases, the reaction had its maximum rate; that is, the induction period was negligible provided that the vessel had been prepared by preceding runs.<sup>3</sup> The rate was measured by the usual method of observing the pressure as a function of time. In most experiments the total initial pressure of the mixture was 60 cm. No pressures higher than 65.4 cm were used, because of the danger of a third-limit explosion.

<sup>5</sup> O. Oldenberg and F. F. Rieke, *J. Chem. Phys.* **6**, 442 (1938).

The absorption spectrum was photographed while the reaction progressed at a high rate. In some cases several exposures were made during one reaction, but in most cases only one exposure.

### III. RESULT

No trace of the absorption spectrum of OH could be observed. The conditions were so varied that in every attempt a high rate was obtained (see preceding section). The highest rate obtainable was 4.0 cm/min. In two cases it happened that the absorption spectra were taken at rates of the reaction so high that the steady reactions ended in violent explosions ("third" explosion) shattering the quartz windows. Even in these most favorable cases the photographic plates showed no trace of the absorption spectrum. (One of these plates was underexposed, but could be utilized when combined with another plate so that the two emulsions were in contact.)

In three experiments equal parts of hydrogen and oxygen were used, instead of the stoichiometric mixture, with the same negative result.

A quantitative statement can be made on the basis of the recent measurements of Dwyer and Oldenberg,<sup>6</sup> who observed absorption spectra of OH with the same spectrograph and with a known concentration of OH. In a mixture of  $\frac{2}{3}\text{H}_2\text{O} + \frac{1}{3}\text{O}_2$  at thermal equilibrium, the faintest observable trace of the absorption spectrum was found at a temperature of 768°C. From the equilibrium constants, the partial pressure of OH follows as  $4.2 \times 10^{-4}$  mm. (For our estimate we may disregard the fact that in our case the conditions are a little more favorable for the observation of the absorption spectrum, because, at our lower temperature [823 instead of 1041°K], the rotational energy is distributed over not quite so many levels and, furthermore, the lines are slightly narrower.) When we take into account the different lengths and temperatures of the absorbing layers, we find that in the rapid, steady thermal reaction the OH radicals, if present at all, are present in a mole fraction of less than  $2 \times 10^{-7}$ .

This negative result does not necessarily indicate that the free OH radical takes no part

<sup>6</sup> R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.* **12**, 351 (1944).

in the thermal reaction. More plausible is the alternative assumption, made by von Elbe and Lewis,<sup>7</sup> that, near 550°C, the rate of the reaction which consumes OH is so high that no appreciable accumulation of OH can occur.

At present, the theory of von Elbe and Lewis does not predict the concentration of OH, nor does any other theory, since the rates of the reactions *producing* and *consuming* OH are not sufficiently known. All schemes ever proposed agree in the assumption that the reaction *consuming* OH—except adsorption at the surface—is  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . This reaction is exothermic by 15.7 kcal. Its heat of activation is not known. On the other hand, many different reactions *producing* OH have been proposed, as is evident in the reaction scheme of von Elbe and Lewis. The principal result of the present experiment is that at 550°C the reaction just mentioned, consuming OH, is so rapid that no noticeable accumulation of OH occurs. This agrees with the result recently published by Avramenko,<sup>8</sup> who, on the basis of observations in dilute hydrogen flames, concluded that the reaction mentioned is very rapid.

#### IV. INCIDENTAL OBSERVATIONS

##### (a) Search for $\text{H}_2\text{O}_2$

Pease<sup>9</sup> discovered that a considerable percentage of  $\text{H}_2\text{O}_2$  was formed at 520–550°C in Pyrex vessels through which a 2:1 hydrogen-oxygen mixture was passing at atmospheric pressure. The yield of  $\text{H}_2\text{O}_2$  strongly depended on the treatment of the surface. Since this yield was as high as 1 mole  $\text{H}_2\text{O}_2$  to each 4 moles of  $\text{H}_2\text{O}$ , it seemed worth while to attempt to trace the concentration of  $\text{H}_2\text{O}_2$  by the intensity of its absorption spectrum.

It is known that the absorption spectrum of  $\text{H}_2\text{O}_2$  is continuous and has an intensity increasing toward short wave-lengths.<sup>10</sup> Therefore it is

<sup>7</sup> G. von Elbe and B. Lewis, *J. Chem. Phys.* **10**, 393 (1942).

<sup>8</sup> L. I. Avramenko, *Chem. Abs.* **39**, 3194 (1945); *J. Phys. Chem. (U.S.S.R.)* **18**, 197–206 (1944).

<sup>9</sup> R. N. Pease, *J. Am. Chem. Soc.* **52**, 5106 (1930) and **53**, 3188 (1931).

<sup>10</sup> H. C. Urey, L. H. Dawsey, and F. O. Rice, *J. Am. Chem. Soc.* **51**, 1371 (1929). In this paper the absorption coefficients  $a$  of  $\text{H}_2\text{O}_2$  are determined. However, the value of  $cd$  is given by a figure ten times too large. We assume that this is due to a misprint, so that the figures given for the absorption coefficients  $a$  are correct.

convenient to use as a background the continuous emission spectrum of the electric discharge through  $\text{H}_2$ . We observed the shortest wave-length easily photographed with a quartz spectrograph, that is, 2300Å. The reaction vessel was the same as in the experiments reported above, that is, Pyrex treated by preceding reactions, hence presumably covered with  $\text{H}_2\text{O}$ . The highest rate used was 2.6 cm/min.

The result was negative. Since consecutive exposures were compared, the accuracy of the photometric method was not higher than, say, 10 percent. This would indicate a partial pressure of  $\text{H}_2\text{O}_2$  of less than 0.6 mm. In view of the results of Pease, this low limiting value should be attributed to the surface conditions.

##### (b) Emission Spectra

Since in the experiments described an unusually deep layer of the reacting gases was available, it seemed worth while to investigate the *emission* spectra of the various types of the reaction.

Beginning with low pressure, at the *explosion of the second limit* ten successive explosions gave only the faintest trace of the OH bands photographed with a quartz spectrograph of high intensity.

The *steady reaction* between the second and third limits does not emit any light of appreciable intensity. This agrees with the result of W. Jono,<sup>11</sup> who needed (for photographing the OH bands) as many as 16,000 steady reactions at a rate only slightly below the first explosion limit.

These observations are in agreement with the proposed reaction schemes which entail free radicals and atoms, but not radicals or atoms or molecules in excited states.

When the first gas admitted has too low a pressure, *inflammation* (or explosion of the second limit) takes place at the admission of the other gas. When the admission is continued, burning takes place. The spectrum contains the OH bands with strongly abnormal rotation.<sup>12</sup> The rotational lines can be traced to about the same limit (quantum number 29) as in the hydrogen-oxygen flame.

<sup>11</sup> Reported by S. Horiba, *Rev. Phys. Chem. Japan*, **11**, 195 (1937).

<sup>12</sup> O. Oldenberg, *Phys. Rev.* **46**, 210 (1934).