sence of such resonance. This accounts for the fact that the value of 2.63 Å. for the length of these hydrogen bonds is much smaller than the corresponding value of 2.76 Å. in ice.[21] On the other hand, each oxygen atom of a hydrogen peroxide molecule serves as an acceptor of two hydrogen bonds O· · ·H–N of lengths 2.94 Å. and 3.04 Å. These are comparable in length to the hydrogen bonds N–H· · ·O of lengths 2.93 and 3.05 Å. connecting neighboring layers of glycine molecules in the crystal of glycine.[22] They are, however, distinctly longer than the hydrogen bonds N–H· · ·O of lengths 2.76 and 2.88 Å. in the same layer, since, in the case of glycine, resonance in the molecule leads to formal charges on both nitrogen and oxygen atoms, which then tend to make much stronger hydrogen bonds.

Our structure satisfactorily accounts for the cleavages. The crystal may be cleaved parallel to (100) or (110) by breaking only four hydrogen bonds of the type N–H· · ·O per unit cell. The strong hydrogen bonds O–H· · ·O and the close double-layer structure are mainly responsible to the poor cleavage parallel to (001). Cleavages along other planes would break more bonds.

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Summary

The crystal structure of the addition compound between urea and hydrogen peroxide, "hyperol," $CO(NH_2)_2 \cdot H_2O_2$, has been investigated. Its space group is D_{2h}^{14}—*Pnca*; and there are four molecules in a unit cell of the following dimensions: a_0 = 6.86 Å., b_0 = 4.83 Å., c_0 = 12.92 Å. The eight atomic parameters have been evaluated (Table I). The urea molecules have the same configuration, to within experimental error, as in the urea crystal. The configuration of the hydrogen peroxide molecules is that proposed by Penney and Sutherland, the two OH bonds lying in planes making a dihedral angle of about 106°. The O–O distance is 1.46 ± 0.03 Å. The packing of the molecules is essentially effected through hydrogen bonds.

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[21] W. H. Barnes, *Proc. Roy. Soc.* (London), **A125**, 670 (1929).

[22] G. Albrecht and R. B. Corey, THIS JOURNAL, **61**, 1087 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARIZONA]

The Reaction between Hydrogen and Pyrex Glass

BY LATHROP E. ROBERTS AND CLARENCE BITTNER[1]

In a recent investigation of the thermal decomposition of dimethyl carbonate in this Laboratory,[2] hydrogen was identified as one of the principal products. Analysis showed, however, that a considerable portion of the hydrogen originally present remained unaccounted for. It seemed possible that this hydrogen had either diffused through the Pyrex glass wall of the reaction vessel, had been adsorbed by the glass, or had reacted with it. An extensive darkening of the glass indicated that reaction had occurred to some extent. Since hydrogen is frequently a product of thermal decompositions, and since a reaction of the hydrogen with the glass, or its adsorption, might affect the course of the decomposition, further investigation of the phenomenon was desirable.

Williams and Ferguson[3] found that, at 1 atmosphere and 640°, quartz glass was permeable to helium and hydrogen, the rate of diffusion for helium being 22 times that for hydrogen. They found that hydrogen did not diffuse through Pyrex under the same conditions. They attributed an observed darkening of the Pyrex to its reaction with hydrogen, and stated that this was not a surface reaction; but did not further investigate the phenomenon. Alyea,[4] working with bulbs packed with Pyrex powder, found that Pyrex adsorbed no hydrogen at 25°, but adsorbed it rapidly at 480°. He found the adsorption to be reversible, and recovered the greater part of the adsorbed gas, but did not attempt to measure accurately

[1] Taken in part from a thesis submitted by Clarence Bittner to the Graduate College, University of Arizona, in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry, in May, 1939.

[2] D. Olson, "The Pyrolysis of Dimethyl Carbonate," Thesis, University of Arizona, 1938.

[3] Williams and Ferguson, THIS JOURNAL, **44**, 2160 (1922).

[4] Alyea, *ibid.*, **53**, 1324 (1931).

the amount of hydrogen recovered. He noted that a small amount was consumed in reducing the Pyrex. Williamson,[5] also working with powdered Pyrex, found that adsorption of hydrogen occurred at temperatures between 400 and 542°, the rate of adsorption increasing rapidly with the temperature. He found that equilibrium was established after sixty-two hours of contact at 542°, and that 95% of the hydrogen was recoverable. He determined three points on an adsorption isotherm at that temperature. Working with soft glass, Langmuir[6] found that there was no adsorption of hydrogen at room temperature, and that at the temperature of liquid air, which is especially favorable for physical adsorption, and a pressure of 200 barytes, the maximum adsorption was less than that corresponding to a unimolecular layer.

The investigation reported in this paper was undertaken to account for the "disappearance" of the hydrogen in the work with dimethyl carbonate[2]; to determine whether the loss of hydrogen was due primarily to diffusion, adsorption, or reaction; and to determine whether this loss of hydrogen might, in general, be great enough to necessitate its being taken into account in the study of thermal decompositions producing hydrogen in Pyrex vessels.

Experimental

A 150-cc. cylindrical Pyrex bulb, walls 2 mm. thick, was filled in run 1 with chips of from 4 to 10 mesh prepared by breaking up a new Pyrex beaker and washing with dilute hydrochloric acid, and in all other runs with 1 cm. lengths of fresh 4 mm. outside diameter Pyrex tubing. The geometrical surface of bulb plus tubing was 1440 sq. cm. Capillary tubing was used throughout the rest of the apparatus, except for a closed-end manometer, and a small tube for freezing out water and vapors in dry-ice–alcohol. The bulb was heated in an oven controlled manually by a rheostat to ±2° during the day, and ±5° during the night. Preceding each run, the system was pumped out with a Hyvac pump for four hours a day over a three-day period. A measured volume of hydrogen, prepared by electrolysis of potassium hydroxide, was then admitted to bring the pressure to 700 mm., and readings of time and pressure taken throughout the day. The initial pressure was at no time greater than barometric. The next morning, hydrogen was admitted to restore the pressure of 700 mm., and readings repeated. This procedure was followed for nine days in run 1, and for two or three days in other runs. The glass tube immersed in freezing mixture was sealed off, and residual hydrogen withdrawn with the Töpler pump. In all runs except no. 1 the evacuated system was kept at the same temperature for forty-eight hours, and any additional hydrogen which accumulated was pumped off at the end of each twenty-four hour period.

Discussion

The process occurring in the reaction bulb will be referred to as the "reaction" without excluding the possibility that adsorption may play a part.

A determination of the free space in the packed bulb was made at room temperature, and at 540°, with air, nitrogen, helium, and hydrogen. The same value was found, regardless of the gas. When hydrogen or helium was used at the higher temperature, the reading was taken within one minute after their introduction, as a slow decrease in pressure set in. Any adsorption of hydrogen at this temperature within one minute was therefore within the error of reading the gas buret. With helium, the observed drop of pressure was believed due to the well-known diffusibility of helium through hot Pyrex.[3,7] Before making run 1, the packed flask was filled with helium at 700 mm. and kept at 540° for three and one-half days. The pressure decrease was 182 mm. During the first twenty hours it was 56 mm. In run 1, using hydrogen under the same conditions, the pressure decrease in twenty hours was 337 mm. While Williams and Ferguson[3] found Pyrex impermeable to hydrogen, Urry found that hydrogen diffused through a number of glasses of high silica content at a rate about one-twentieth that of helium at 283°. Williams and Ferguson found the rate of diffusion of hydrogen through quartz glass at 500° was about one-twenty-second that of helium. Assuming that the hydrogen may have diffused through the Pyrex at a rate one-twentieth that of helium, the pressure decrease due to diffusion during the first twenty hours would have been 2.8 mm., as compared to the observed decrease of 337 mm. Any pressure decrease in the runs with hydrogen due to diffusion must therefore have been small, and probably negligible.

In Fig. 1 is shown the decrease in pressure of hydrogen with time following successive additions of hydrogen for run 5, at 580°. If diffusion alone were the cause of the pressure decrease, the curves should coincide. For the runs at lower temperatures, curves similar to those of Fig. 1 were obtained, the slope of the curves being less, the lower the temperature.

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[5] Williamson, This Journal, **55**, 1437 (1933).

[6] Langmuir, *ibid.*, **40**, 1361 (1918).

[7] Urry, *ibid.*, **54**, 3887 (1932).

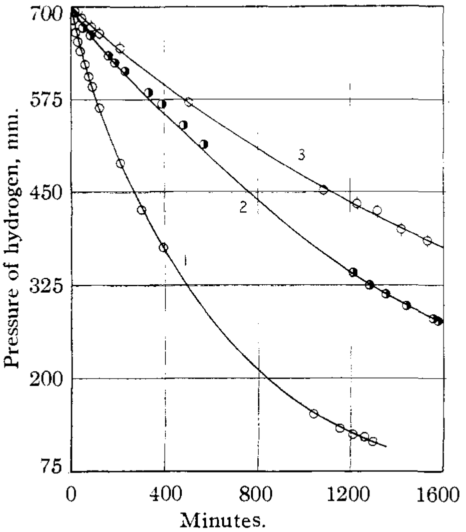

Fig. 1.—Change in pressure of hydrogen with time when heated with Pyrex at 580°. Curves (1), (2) and (3) are for first, second and third addition of hydrogen, respectively.

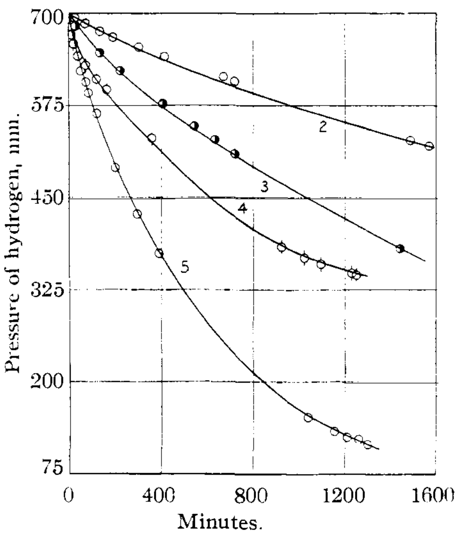

Fig. 2.—Decreases in pressure of hydrogen with time, for initial addition of hydrogen at different temperatures: Curve (2), 500°; (3), 540°, (4) 560°, (5) 580°.

Figure 2 shows the effect of temperature upon the rate of pressure decrease for the first addition of hydrogen as observed in runs 2 to 5. Results for run 1 are not plotted, as in this run glass chips were used and a different surface exposed.

The decrease in the slope of the curves with time as shown in Figs. 1 and 2, and with successive additions of hydrogen as shown by Fig. 1, might be explained as due to an approach to equilibrium characteristic of adsorption. In no case, however, was equilibrium established. In run 1, the Pyrex chips were in contact with hydrogen at 540° for two hundred and thirteen hours, yet at the termination of the run the reaction was proceeding at a diminished but easily measurable rate, the decrease in pressure during the last twenty-three hours being 53 mm. Since equilibrium was not established, it was not possible to determine an adsorption isotherm.

In view of the failure to attain equilibrium, and of other facts to be presented, it is logical to assume that the chief process occurring is an actual reduction of substances present in the glass. The decrease in rate of reaction with time may be due to the decrease in pressure of hydrogen, and to the fact that as the reaction proceeds, the hydrogen must penetrate the glass more deeply in order to come in contact with reducible material.

In Table I are shown the volumes of hydrogen, at standard conditions, needed at different elapsed times to restore the initial pressure. These volumes therefore represent the amounts of hydrogen that had reacted at the times indicated. It is seen that relatively large amounts of hydrogen reacted, as had been previously indicated in the work on dimethyl carbonate.

Table II shows the efficiency of recovery of the hydrogen. The volume of hydrogen obtained at each exhaustion is shown. The efficiency of recovery varied from 55% in run 2 to 23.5% in no. 5, and was less, the higher the temperature.

The hypothesis that an extensive reaction had taken place is supported by the appearance of the glass. In every case it was blackened, the intensity of discoloration being greater the higher the temperature, and the longer the time of contact with hydrogen. The effect is not a surface effect, as the glass tubes showed a definite zone of penetration, while the glass of the reaction bulb was blackened to about one-half of its thickness, the line of demarcation from the uncolored glass being quite sharp.

In every run, a small amount of water was collected in the side tube. These weights of water are given in Table II. On the average, they do not account for more than about 10% of the hydrogen which disappeared. The method used was intended chiefly as a qualitative test for water.

The exact nature of the reduction taking place is uncertain. The darkening might be due to free silicon, arsenic, or iron. Since 50 cc. of hydrogen would produce only 0.03 g. of silicon, distributed through 100 g. of glass, any quantitative determination would be difficult.

TABLE I

VOLUMES OF HYDROGEN REQUIRED TO RESTORE INITIAL PRESSURE

Time (t) in minutes; temperature in °C.; volume (v) in cc. at standard conditions

(1) 540°		(2) 500°		(3) 540°		(4) 560°		(5) 580°	
t	v	t	v	t	v	t	v	t	v
0	39.5	0	53.7	0	53.5	0	51.6	0	49.0
1186	30.9	1565	16.1	1440	26.0	1215	28.2	1296	42.3
2771	14.5	3400	....	2805	19.3	2425	31.3	2870	31.4
4251	10.7			4505	....	4440	....	4395	....
5664	9.1								
6914	7.8								
8554	10.8								
9979	5.5								
11219	5.8								
12814	....								

TABLE II

EFFICIENCY OF RECOVERY OF HYDROGEN AFTER HEATING IN CONTACT WITH PYREX

Time (t) in minutes; temperature in °C.; volume (v) in cc. at standard conditions

Temp., °C.	t	Total v H_2 added	v H_2 recovered (a)	(b)	(c)	Wt. of water found, g.	v H_2 accounted for as water
540°[a]	12814	124.6	37.6			0.0074	9.2
500°	3400	69.8	36.8	0.6	1.4	.0022	2.7
540°	4505	98.8	31.9	1.7	1.0	.0047	5.9
560°	4440	101.1	22.7	2.4	3.1	.0112	13.9
580°	4395	122.7	23.3	2.1	3.3	.0135	16.8

[a] Run using glass chips.

Assuming that the geometric surface is the true surface, the hydrogen which disappeared in run 6 would, if adsorbed, have formed a layer 3472 molecules thick. The ratio of true to geometric surface is uncertain, but it seems improbable that it could be as great as 3472, which would be required to explain the phenomenon as adsorption in a unimolecular layer.

The behavior of the Pyrex used in this work was quite different from that used by Alyea[4] and by Williamson.[5] Both of these workers used powdered Pyrex, with undoubtedly a much greater surface–volume ratio. In the present work, some of the water formed may, by its adsorption on the glass surface, have prevented the activated adsorption of hydrogen reported in Williamson's isotherms. The results described are best interpreted as indicating that at temperatures between 500° and 580° an extensive reaction takes place between hydrogen and Pyrex.

Summary

1. When hydrogen is heated with Pyrex glass at an initial pressure of 700 mm., and at temperatures of 500 to 580°, a steady drop in pressure is observed. This was shown not to be due to diffusion.

2. The rate of pressure drop increases rapidly with temperature; and at a given temperature, when hydrogen is added to restore the initial pressure, proceeds with diminishing rate with successive additions.

3. No equilibrium was reached. Hydrogen recovery varied from 23.5 to 55%, being less, the higher the temperature. About 10% of the hydrogen which disappeared was accounted for as water.

4. The glass is greatly darkened, the effect extending far below the surface.

5. The process is interpreted as being due chiefly to an irreversible reaction, rather than as adsorption.

6. The amount of hydrogen removed is sufficient to be of importance in pyrolyses in Pyrex in which hydrogen is a product.

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