The Sorption of Gases on Reduced Nickel. II. Sorption of Gaseous Hydrogen Bromide and Hydrogen Chloride and Sorption of Hydrogen Bromide through a Liquid Medium.

By Matsuji TAKEBAYASHI.

(Received June 23, 1939.)

Reduced nickel reverses the direction of addition of hydrogen bromide to ethenoid compounds, and activates hydrogen bromide in the isomerization of a certain cis compound to its geometrical isomeride. Catechol inhibits the action of reduced nickel in either case. Since such an action of reduced nickel must be closely related to adsorption, the present work has been contemplated. In the previous paper(1) it was shown that at 20° reduced nickel adsorbs hydrogen bromide slowly but abundantly, giving an indication to an activated adsorption. The present paper records the results of experiments on the sorption of hydrogen bromide at 0°C., of hydrogen chloride, and of hydrogen bromide through carbon tetrachloride.

Materials, Apparatus, and Methods. Reduced nickel was prepared by reducing nickel oxide (Kahlbaum) with hydrogen at 350–400°C. Hydrogen bromide was generated by the action of bromine on hot tetralin, passed through cold tetralin, anhydrous calcium bromide, anthracene, and a tube cooled with ice and salt, condensed in a vessel cooled with solid carbon

---

(1) M. Takebayashi, this Bulletin, **14** (1939), 47.

dioxide and ether, recondensed in a vessel cooled with liquid air, and, after evacuating any uncondensable gases, vaporized, and only the middle fraction was used. Hydrogen chloride was prepared from concentrated hydrochloric acid and concentrated sulphuric acid, dried by passing through concentrated sulphuric acid, condensed in a receiver cooled with liquid air, and then fractionated. Carbon tetrachloride, the purest commercial material, was boiled with alkaline potassium permanganate, washed with water, dried over calcium chloride, and distilled over phosphorus pentoxide. Catechol used was a commercial pure material (Merck).

The apparatus was the same that was used in the previous work. In the experiments on the sorption from carbon tetrachloride a tube as shown in Fig. 1 was used instead of the simple one shown in Fig. 1 of the previous paper.⁽¹⁾

In every experiment 1.00 g. of reduced nickel was used and treated with hydrogen at 350° as described in the previous paper. Sorption took place under 1 atmospheric pressure of the gases in the dark.

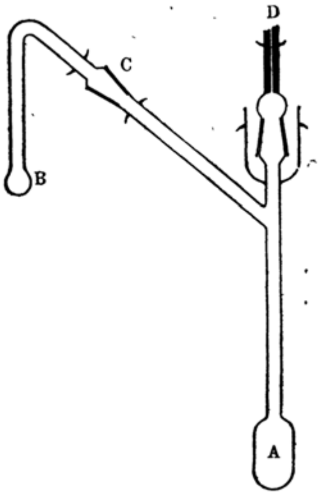

Fig. 1.

Table 1. The Sorption of Hydrogen Bromide on Reduced Nickel (1.00 g.) at 0°C.

Time (min.)	Hydrogen bromide adsorbed (c.c., n.p.t.)
1/2	1.90
1	2.20
2	2.28
3	2.35
5	2.47
10	2.67
20	2.86
30	3.00
50	3.20
70	3.30
100	3.42
130	3.52
160	3.62
190	3.69
1110	4.14
1230	4.12
1545	4.12
2589	4.14

Sorption of Gaseous Hydrogen Bromide. The sorption of hydrogen bromide on freshly reduced nickel was measured at 0°C. The result is given in Table 1. During the first few hours more, but in saturation less, hydrogen bromide is adsorbed at 0°C. than at 20°C. (compare Tables 5 and 6 of the previous paper). This may be another indication to an activated adsorption.

Desorption of hydrogen bromide proceeds slowly in vacuum at 0°C. The reduced nickel which adsorbed 4.14 c.c. of hydrogen bromide at 0°C. to saturation was placed in vacuum for three hours at room temperature; and hydrogen bromide was again introduced at 0°C., when the nickel adsorbed 0.91 c.c. in 1450 minutes and 1.12 c.c. in 1530 minutes. The partial recovery of the capacity of sorption showed that a part of hydrogen bromide adsorbed on reduced nickel could be desorbed in three hours' evacuation.

Sorption of Gaseous Hydrogen Chloride. The sorption of hydrogen chloride on reduced nickel was observed at 20°C. and 0°C. The results are given in Tables 2, 3, and 4. At any time more hydrogen chloride is adsorbed on reduced nickel at 20°C. than at 0°C. and at either temperature more hydrogen bromide is adsorbed than hydrogen chloride.

The reduced nickel, which adsorbed 3.09 c.c. of hydrogen chloride at 0°C. to saturation and stood in vacuum for three hours, adsorbed at 0°C. 0.68 c.c. of hydrogen chloride in 1440 minutes and 0.78 c.c. in 1560 minutes. Thus it was shown that desorption takes place slowly in vacuum as in the case of hydrogen bromide.

Sorption of Hydrogen Bromide on Reduced Nickel through Carbon Tetrachloride. Since it is in liquid media that reduced nickel has been found to exert the peculiar influence on hydrogen bromide, it seemed desirable to study the sorption in such media. Carbon tetrachloride was chosen as the medium, and the sorption of hydrogen bromide on reduced nickel through this medium and the effect of catechol on the sorption were investigated.

The experimental procedure was as follows: Reduced nickel (1.00 g.), prepared as mentioned above, was taken in sorption tube A (Fig. 1), 1.0 c.c. of carbon tetrachloride or a carbon tetrachloride solution of catechol was poured into side tube B, the volume of the liquid was marked on the tube, and further 0.2 c.c. of pure carbon tetrachloride was added. The side tube was cooled with liquid air, and the whole apparatus was evacuated. Then the metal in the sorption tube was heated at 340–350°C. in the atmosphere of hydrogen to refresh the surface and then in vacuum for an hour to remove hydrogen, and cooled to room temperature. After the treatment of the metal was over, the excess of carbon tetrachloride in tube B was distilled off at room temperature through tube D. In this way any traces of water and air were removed. Then the cock nearest to sorption tube A was closed, tube B was revolved by 180° upward, and the contents of the tube were decanted into tube A, while tube A was cooled in liquid air. Then the sorption tube was warmed to 20°, and the sorption of hydrogen bromide was observed at 20°C.

It was first determined with the sorption apparatus that 1 c.c. of carbon tetrachloride absorbs 5.15 c.c. of hydrogen bromide of 1 atmospheric pressure at 20°C. Then 1 g. of reduced nickel was covered with 1 c.c. of pure carbon tetrachloride, and hydrogen bromide was introduced. The total amount of hydrogen bromide absorbed is given in Table 5. By subtracting the amount absorbed by carbon tetrachloride from the value given Table 5, the amount adsorbed on reduced nickel is found to be 4.27 c.c. The concentration of hydrogen bromide in carbon tetrachloride is about five times as large as in the gas, while reduced nickel adsorbed a little less hydrogen bromide from the carbon tetrachloride solution than from the gas.

Table 2. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 20°C.

Time (min.)	Hydrogen chloride adsorbed (c.c., n.p.t.)
1/2	1.64
1	1.92
3	2.13
8	2.42
13	2.58
23	2.68
38	2.86
53	3.04
98	3.16
128	3.24
1418	3.92
1538	3.94

Table 4. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 0°C.

Time (min.)	Hydrogen chloride adsorbed (c.c., n.p.t.)
1/2	1.47
1	1.71
3	1.89
5	2.03
10	2.16
20	2.26
30	2.36
50	2.52
70	2.54
100	2.59
130	2.63
190	2.69
1455	3.09
1590	3.09
1660	3.11
2630	3.09

Table 3. The Sorption of Hydrogen Chloride on Reduced Nickel (1.00 g.) at 20°C.

Time (min.)	Hydrogen chloride adsorbed (c.c., n.p.t.)
1/2	1.68
1	1.90
4	2.18
9	2.38
19	2.54
29	2.67
49	2.77
69	2.84
99	2.93
129	2.98
159	3.02
189	3.06
1470	3.44

Table 5. The Absorption of Hydrogen Bromide by Reduced Nickel (1.00 g.) and Carbon Tetrachloride (1.0 c.c.) at 20°C.

Time (min.)	Hydrogen bromide absorbed (c.c., n.p.t.)
1205	9.26
1440	9.38
1500	9.42

Table 6. The Absorption of Hydrogen Bromide by Reduced Nickel (1.00 g.) and Carbon Tetrachloride (1.0 c.c.) Containing Catechol (2 mg.) at 20°C.

	Time (min.)	Hydrogen bromide absorbed (c.c., n.p.t.)
I	1365	12.50
	1440	12.58
	1500	12.84
II	1320	12.19
	1440	12.43
	1520	12.52

It was first presumed that the inhibiting action of catechol on reduced nickel was caused by poisoning. Hence, the effect of catechol on the sorption of hydrogen bromide on reduced nickel was studied. Because of the small solubility of catechol in carbon tetrachloride, a solution containing 2 mg. of catechol in 1 c.c. was used. The solubility of hydrogen bromide in carbon tetrachloride was found to be hardly affected by such a small amount of catechol: 1 c.c. of the solution absorbed 5.56 c.c. of hydrogen bromide at 20°C. Then reduced nickel (1.00 g.) was covered with 1 c.c. of the solution and hydrogen bromide was introduced. The total amounts absorbed are shown in Table 6. More hydrogen bromide was absorbed in the presence of catechol, and a simple poisoning was not proved. These results as well as those obtained by O. Simamura in the experiments on the action of hydrogen bromide on catechol and reduced nickel will be interpreted by Y. Urushibara elsewhere.(2)

The author expresses his hearty thanks to Prof. Y. Urushibara for his kind guidance and encouragement. Thanks are also due to the Japan Society for the Promotion of Scientific Research and to Ozi Seisi Co. for grants.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(2) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), No. 8.