VII.—*Action of Sulphuric Acid on the Bromides of Potassium, Sodium, and Hydrogen.*

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ON page 1320 of the Abstracts, 1891, is an abstract from a paper on the "Preparation of Hydrobromic Acid," by Feit and Kubierschky. Seeing that the method there given is nearly identical with the one which has been used by me, from time to time, during the last three years, I decided to publish at once the results obtained so far in this research.

The object in view has been to determine to what extent hydrogen bromide is oxidised by sulphuric acid under varying conditions of mass and dilution. The experiments may, for the sake of convenience, be divided into two sets :—

I. Where concentrated sulphuric acid, in varying quantities, is allowed to act on potassium bromide.

II. Where the sulphuric acid used is dilute.

The difference between these two cases is at once apparent when it is considered that in the second case all the products of the reaction remain in solution, thus finding a position of equilibrium between the two reactions :—

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2,$$

and

$$SO_2 + 2H_2O + Br_2 = H_2SO_4 + 2HBr.$$

In the first case, on the other hand, the gaseous substances are partially or wholly removed; so that the sulphuric acid acts much more completely.

These two sets of experiments are in no way comparable.

Action of Concentrated Sulphuric Acid on Potassium Bromide.

In order to determine the quantitative result of this reaction, several descriptions of apparatus were used, which either collected the bromine evolved, in tubes of amorphous phosphorus and water, or else collected all the products in bulbs containing strong potash. In the first case, the amount of phosphoric acid formed was determined by means of magnesia mixture; in the second, the sulphurous anhydride was oxidised by bromine and estimated as barium sulphate. The first of these methods gave such unsatisfactory results that it was soon discarded, and the results here given were always obtained by the barium sulphate method.

The apparatus at first used for working this method consisted of a flask with a reflux condenser attached, through which the gases might pass into U-tubes containing broken glass and bromine-water. The reason for using a condenser was to prevent any sulphuric acid from distilling over. But this was soon discarded as unnecessary; because, in the first place, it was found that the reaction takes place without any evolution of heat; and, secondly, because the last traces of bromine evolved were easily driven off by heating gently. In no case was the temperature raised above 110°.

The set of experiments of which the results are now published was therefore performed, for the most part, in a flask with a very long neck, the body being of about 200 c.c. capacity, and the neck about 16 inches in length. About 3 inches from the body of the flask a side tube was inserted, which was bent up and down into the shape of a W to prevent any sulphuric acid from being carried over mechanically. This was connected with a Will and Varrentrapp bulb tube, containing strong caustic potash solution, to collect all the gaseous products of the reaction.

The potassic bromide was weighed out and placed in the dry flask, then the concentrated sulphuric acid, sp. gr. 1·84, was poured, from a beaker in which it had been weighed, down the long neck, the beaker with the adhering acid being immediately and rapidly reweighed. A stopper was inserted into the top of the neck of the flask and the reaction allowed to proceed until effervescence stopped. On gently warming, the fumes came off more rapidly but got lighter in colour until at last they became colourless: a slow current of air was then aspirated through the apparatus. This experiment in all cases where 11·9 grams of potassic bromide were used occupied about 35 minutes. The potash was removed to a beaker, and bromine added in excess, then barium chloride was added and the barium sulphate weighed.

It has been found most convenient, for comparison's sake, to act upon the supposition that the whole of the bromine is first liberated as hydrogen bromide and that some of this is then decomposed. Reasons for believing this to be true will be given hereafter. The results of the experiments are, therefore, expressed in terms of the percentage of hydrogen bromide which has been decomposed.

No. of expt.	Weight of H_2SO_4 used.	Weight of KBr used.	Approximate molecular ratio of H_2SO_4 to KBr.	Weight of $BaSO_4$.	Per cent. of HBr decomposed.
1*	10·0510	11·9000	1 : 1	0·9864	8·55
2*	5·2460	11·9000	1 : 2	0·3746	3·22
3	9·7510	11·9034	1 : 1	0·8500	7·30
4	9·6050	11·9062	1 : 1	0·9682	8·31
5	14·8080	11·8996	3 : 2	1·8236	15·53
6	19·5230	11·9000	2 : 1	2·3168	19·88
7	24·6140	11·9000	5 : 2	3·1346	26·91
8	28·9360	11·9070	3 : 1	3·6408	31·30

If this were represented in the form of a curve with the percentage of HBr decomposed for the abscissæ and the number of molecules of H_2SO_4 to one of KBr for ordinates, we should get very nearly a straight line, or, in other words, the amount of decomposition is very nearly proportional to the amount of sulphuric acid used.

The materials in Experiment No. 8 were as large in amount as the apparatus would hold, and as experiments with larger quantities gave

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* Condenser used.

results varying with the shape of the vessel employed, it was thought that when so large an excess of sulphuric acid was present that the water formed in the reaction caused no sensible dilution, the hydrogen bromide at first formed was decomposed in quantities varying with the amount of sulphuric acid with which it came in contact. Thus a higher percentage would be decomposed in a deep than in a shallow vessel. To test this, the following experiment was devised :—

1·4035 grams of potassium bromide was passed up into a graduated tube standing over mercury and 10·6 grams of sulphuric acid was passed up after it by means of a graduated syringe having a long curved end. The bromine formed was absorbed by the mercury to form mercurous bromide, which was not acted upon by the sulphuric acid. This was allowed to stand for a week, shaking every day, and then the gas was transferred to a tube having a stopcock above and thence bubbled through silver nitrate slightly acidified with nitric acid. Only the faintest trace of a precipitate was given, showing that the hydrogen bromide had been entirely decomposed.

This experiment was performed in a graduated tube with the intention of measuring the gases, but the absorption of sulphurous anhydride by sulphuric acid is so great that this was found to be useless; it was therefore repeated several times in a plain tube with a stopcock. In one case it gave no trace whatever of hydrogen bromide, in two others very small traces.

Action of Dilute Sulphuric Acid on the Bromides of Hydrogen, Sodium, and Potassium. Preparation of Pure Hydrobromic Acid.

Method 1.—Barium carbonate was dissolved in crude hydrobromic acid, the solution evaporated to dryness, and the barium bromide extracted with hot alcohol, from which, after filtering, it was allowed to crystallise out. From these crystals of pure barium bromide, pure bromine was obtained. This was effected by distilling it with manganese peroxide and strong sulphuric acid, in a retort which had been fused on to a condenser so as to avoid india-rubber joints.

This pure bromine, after washing and redistillation, was converted into hydrobromic acid by means of amorphous phosphorus and water in the ordinary way.

Method 2.—A saturated solution of barium bromide in water was prepared as in the last method, and 60 per cent. sulphuric acid (sp. gr. = 1·50) added in quantity not quite sufficient to precipitate all the barium. The precipitate of barium sulphate was allowed to subside, the liquid decanted off, and then distilled. The first portion of the distillate was rejected as containing scarcely any acid. The distillation is conducted with a thermometer in the vapour; at first very dilute acid comes over. When, the thermometer being a little over 100°, the temperature begins to rise, as it does rather rapidly after a time, the distillate may be collected. At 122°, acid comes over containing 47 per cent. HBr.

Method 3.—This is very similar to that of Feit and Kubierschky, mentioned at the beginning of this paper. Potassium bromide (which has been heated with bromine to remove iodine, and recrystallised) is dissolved in the requisite quantity of 30 per cent. sulphuric acid (sp. gr. = 1·22) calculated according to the equation

$$H_2SO_4 + KBr = KHSO_4 + HBr.$$

To effect this, it was necessary to heat nearly to boiling. On allowing the solution to cool in an open dish, potassium hydrogen sulphate crystallised out, together with a certain amount of unaltered potassium bromide, which is much less soluble in hydrobromic acid than in water. The liquid was poured off into a retort, and distilled to about one-third of its bulk, when it began to turn yellow. This yellow liquid was next mixed with half its bulk of water, and returned whilst warm to the dish containing the crystals, and, after cooling, was again poured off and distilled until the distillate began to be yellow.

The acid thus prepared always contained traces of sulphuric acid, partly carried over mechanically, and partly formed by the passing over together of bromine and sulphurous anhydride. This sulphuric acid was precipitated by pure barium bromide, and the liquid redistilled. When strong acid was required, the portion boiling at 122° was collected; this contained about 47 per cent. HBr.

It will be found, on referring to Experiments 12, 49, 77, and 89, that 30 per cent. sulphuric acid has no action upon hydrogen bromide, whereas 40 per cent. acid, as used by Feit and Kubierschky, has some slight action (Experiments 16, 54, 80, 81, 93, 94). This was my reason for using the more dilute acid. But as, in all cases, redistillation was necessary, the 40 per cent. sulphuric acid would be just as good.

Method of Experiment.—A solution of hydrogen bromide, or of potassium or sodium bromide, was made up to a certain strength, varying in different experiments. 5 c.c. of this was measured out into a tube, concentrated sulphuric acid added in varying quantities from a tap-burette, and sometimes also water, and the whole mass gradually mixed with a glass stirrer. An exactly similar tube was then filled up to the same level with water, and freshly prepared dilute bromine-water (free from iodine or chlorine) added, until the intensity of colour in the two tubes was the same. Potassium iodide was then added in excess to this aqueous solution, and centi-normal sodic thiosulphate run in until the colour disappeared; the end of the reaction being shown more clearly by adding a little starch-paste when the solution was nearly colourless. In this way the amount of bromine formed was determined. In these experiments, the highest results were obtained when the mixture had stood for about 12 hours, after which it slowly decreased, either from the absorption of water or from the evaporation of bromine.

Experiments with Hydrogen Bromide Solution.

5 c.c. HBr solution contains 0·81 gram HBr.

No. of experiment.	Volume of HBr solution.	Volume of H_2SO_4, 98 per cent.	$\frac{N}{100}$ $Na_2S_2O_3$ required.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4 in solution (calculated).
	c.c.	c.c.				
9	5	0·3	—	—	—	—
10	„	0·5	—	—	—	—
11	„	0·7	—	—	—	20·79
12	„	1·0	—	trace	—	27·27
13	„	1·2	0·2	0·00016	0·04	31·03
14	„	1·4	0·2	0·00016	0·04	34·43
15	„	1·6	0·2	0·00016	0·04	37·50
16	„	1·8	0·3	0·00024	0·06	40·30
17	„	2·0	0·3	0·00024	0·06	42·86
18	„	2·2	0·4	0·00032	0·08	45·20
19	„	2·4	0·4	0·00032	0·08	47·37
20	„	2·6	0·5	0·00040	0·10	49·37
21	„	2·8	0·6	0·00048	0·12	51·22
22	„	3·0	0·8	0·00064	0·16	52·94
23	„	3·2	1·2	0·00096	0·24	54·55
24	„	3·4	1·2	0·00096	0·24	56·04
25	„	3·6	1·8	0·00144	0·36	57·45
26	„	3·8	2·1	0·00168	0·42	58·76
27	„	4·0	2·7	0·00216	0·54	60·00
28	„	4·2	2·8	0·00234	0·56	61·17
29	„	4·4	2·7	0·00216	0·54	62·26
30	„	4·6	—	—	—	63·30
31	„	4·8	2·8	0·00224	0·56	64·29
32	„	5·0	2·7	0·00216	0·54	65·22
33	„	5·2	2·8	0·00224	0·56	66·10
34	„	5·4	2·9	0·00232	0·58	66·94
35	„	5·6	2·9	0·00232	0·58	67·74
36	„	5·8	3·0	0·00240	0·60	68·50
37	„	6·0	2·9	0·00232	0·58	69·23
38	„	6·2	2·9	0·00232	0·58	69·92
39	„	6·4	2·9	0·00232	0·58	70·59
40	„	6·6	2·8	0·00224	0·56	71·22
41	„	6·8	2·8	0·00224	0·56	71·83
42	„	7·0	2·9	0·00232	0·58	72·41
43	„	7·2	3·0	0·00240	0·60	72·97
44	„	7·4	3·0	0·00240	0·60	73·51
45	„	7·6	3·1	0·00248	0·62	74·02
46	„	7·8	3·2	0·00256	0·64	74·52
47	„	8·0	3·2	0·00256	0·64	75·00

In using this method, the greatest possible care had to be taken that no trace of iodine might get into the bromide. For this reason, many of the earlier experiments, performed with commercially pure sodium bromide (giving no coloration with chlorine-water and starch-paste), were entirely spoiled. If iodine be present in the slightest traces, as it was in the experiments here referred to, the colour of the solution when mixed with sulphuric acid was slightly redder than that of the bromine-water, and it was quite impossible to get trustworthy results, all the results being far too high. This slight difference in colour was used in the later experiments as a most delicate test for iodine.

Experiments with stronger Hydrogen Bromide Solution.

5 c.c. of solution contains 1·62 grams HBr.

No. of experiment.	Volume of HBr.	Volume of H_2SO_4.	$Na_2S_2O_3$.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4.*
	c.c.					
48	5	0·5	—	—	—	—
49	,,	0·9	—	—	—	—
50	,,	1·0	0·3	0·00024	0·027	27·27
51	,,	1·2	0·6	0·00048	0·054	31·03
52	,,	1·4	0·7	0·00056	0·062	34·43
53	,,	1·6	1·1	0·00088	0·097	37·50
54	,,	1·8	1·2	0·00096	0·106	40·30
55	,,	2·0	1·3	0·00104	0·115	42·86
56	,,	2·2	1·4	0·00112	0·125	45·20
57	,,	2·4	1·5	0·00120	0·133	47·37
58	,,	2·6	1·6	0·00128	0·142	49·37
59	,,	2·8	1·7	0·00136	0·151	51·22
60	,,	3·0	1·8	0·00144	0·160	52·94
61	,,	3·2	2·0	0·00160	0·177	54·55
62	,,	3·4	2·0	0·00160	0·177	56·04
63	,,	3·6	2·2	0·00176	0·195	57·45
64	,,	3·8	2·3	0·00184	0·207	58·76
65	,,	4·0	3·6	0·00288	0·323	60·00
66	,,	4·2	5·2	0·00416	0·467	61·17
67	,,	4·4	4·9	0·00392	0·440	62·26
68	,,	4·6	5·4	0·00432	0·485	63·30
69	,,	4·8	5·5	0·00440	0·494	64·29
70	,,	5·0	6·3	0·00504	0·566	65·22
71	,,	5·2	6·0	0·00480	0·539	66·10
72	,,	5·4	6·1	0·00488	0·548	66·94
73	,,	5·6	7·0	0·00560	0·628	67·74
74	,,	5·8	9·3	0·00744	0·835	68·50
75	,,	6·0	10·8	0·00864	1·212	69·23

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* The percentages of sulphuric acid are not calculated out anew for the slight difference made by the stronger hydrobromic acid, and hence are only approximate in this table.

Experiments with Potassium Bromide.

5 c.c. of solution contains 1·19 grams KBr.

No. of experiment.	Volume of KBr solution.	Volume of H_2SO_4.	$Na_2S_2O_3$ required.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4 in solution.
	c.c.	c.c.				
76	5	1·0	—	—	—	—
77	„	1·2	—	trace	—	—
78	„	1·4	—	trace	—	—
79	„	1·6	0·3	0·00024	0·03	—
80	„	1·8	0·4	0·00032	0·04	—
81	„	2·0	0·4	0·00032	0·04	—
82	„	2·0	0·6	0·00048	0·06	—
83	„	2·4	1·0	0·00080	0·10	—
84	„	2·6	1·2	0·00096	0·12	—
85	„	2·8	*	—	—	—
86	„	3·0	*	—	—	—

Experiments with Sodium Bromide.

5 c.c. of solution contains 1·03 grams NaBr.

No of experiment.	Volume of NaBr solution.	Volume of H_2SO_4.	$Na_2S_2O_3$.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4 in solution.
	c.c.	c.c.				
87	5	0·5	—	—	—	—
88	„	0·7	—	—	—	—
89	„	1·0	—	—	—	26·90
90	„	1·2	—	trace	—	30·63
91	„	1·4	—	trace	—	34·00
92	„	1·6	0·3	0·00024	0·03	36·27
93	„	1·8	0·3	0·00024	0·03	39·85
94	„	2·0	0·4	0·00032	0·04	42·40
95	„	2·2	0·5	0·00040	0·05	44·74
96	„	2·4	0·6	0·00048	0·06	46·90
97	„	2·6	1·0	0·00080	0·10	48·32
98	„	2·8	1·7	0·00136	0·17	50·70
99	„	3·0	3·1	0·00248	0·31	52·47
100	„	3·2	3·2	0·00256	0·32	54·08

* In these two, crystals of potassium hydrogen sulphate began to form as soon as the solution cooled; this spoilt the experiment.

Experiments with Similar Proportions of Sulphuric Acid and Sodium Bromide variously diluted.

Each experiment is with 5 c.c. sodium bromide solution containing 1·03 grams NaBr.

No. of experiment.	Volume of H_2SO_4.	Volume of H_2O.	$Na_2S_2O_3$.	Br liberated.	Per cent. of Br decomposed.	Per cent. of H_2SO_4 in solution.
	c.c.	c.c.				
101	3·7	—	2·7	0·00216	0·27	59·01
102	,,	0·2	2·1	0·00168	0·21	58·00
103	,,	0·4	2·0	0·00160	0·20	57·03
104	,,	0·6	1·7	0·00136	0·17	56·09
105	,,	0·8	1·3	0·00104	0·13	55·17
106	,,	1·0	1·1	0·00088	0·11	54·20
107	,,	1·2	1·0	0·00080	0·10	53·45
108	,,	1·4	1·1	0·00088	0·11	52·62
109	,,	1·6	0·9	0·00072	0·09	51·82
110	,,	1·8	0·7	0·00056	0·07	51·04
111	,,	2·0	0·6	0·00048	0·06	50·29
112	,,	2·2	0·6	0·00048	0·06	49·56
113	1·84	—	0·3	0·00024	0·03	41·72
114	,,	0·2	0·3	0·00024	0·03	40·71
115	,,	0·4	0·2	0·00016	0·02	39·76
116	,,	0·6	0·3	0·00024	0·03	38·84
117	,,	0·8	0·2	0·00016	0·02	37·97
118	,,	1·0	0·2	0·00016	0·02	37·14
119	,,	1·2	0·2	0·00016	0·02	36·34
120	5·5	—	crystals	of $NaHSO_4$	formed.	68·13
121	,,	0·2	,,	,,	,,	67·24
122	,,	0·4	4·2	0·00336	0·42	66·36
123	,,	0·6	3·8	0·00304	0·38	65·50
124	,,	0·8	3·5	0·00280	0·35	64·66
125	,,	1·0	3·3	0·00264	0·33	63·85
126	,,	1·2	3·0	0·00240	0·30	63·05
127	,,	1·4	2·6	0·00208	0·26	62·26
128	,,	1·6	2·5	0·00200	0·25	61·52
129	,,	1·8	2·4	0·00192	0·24	60·77
130	,,	2·0	2·1	0·00168	0·21	60·06
131	,,	2·2	1·9	0·00152	0·19	59·35
132	,,	2·4	1·9	0·00152	0·19	58·67
133	,,	2·6	1·7	0·00136	0·17	57·99
134	,,	2·8	1·6	0·00128	0·16	57·34
135	,,	3·0	1·5	0·00120	0·15	56·68
136	,,	3·2	1·5	0·00120	0·15	56·07
137	,,	3·4	1·3	0·00104	0·13	55·45
138	,,	3·6	1·0	0·00080	0·10	54·85
139	,,	3·8	0·8	0·00064	0·08	54·26

In most of these experiments the sulphuric acid was in excess. With more concentrated hydrogen bromide solutions, a modification of this process must be used.

Experiments upon the action of sulphuric acid upon hydrogen bromide when the latter is in excess are now in progress.