LXXIII.—*Electrolysis of Hydrogen Bromide in Liquid Sulphur Dioxide.*

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THE work to be described in this paper was suggested by some results previously published by Bagster and Steele (*Trans. Faraday Soc.*, 1912, **8**, 51), who found that, although dry solutions of hydrogen bromide in liquid sulphur dioxide were practically non-conducting, the addition of water, which itself in solution is also non-conducting, allowed current to flow freely, hydrogen being discharged at the cathode and bromine at the anode, whilst water was carried from anode to cathode and deposited there. The conclusion drawn was that combination between the two solutes preceded conduction, and comparison with the similar behaviour of organic compounds led to the suggestion that the water and hydrogen bromide united to form an oxonium compound which was electrolytic in character.

The present work was undertaken in order to examine the nature of this phenomenon carefully, and in particular to obtain quantitative information regarding the products formed during electrolysis and regarding the compound from which the products are derived. As an alternative explanation to that already offered, it may be suggested that a simple hydrate type of compound is formed analogous to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and that the deposition of water at the cathode is brought about during electrolysis by the loss of the hydrogen bromide holding it in solution. The experimental evidence, however, renders this suggestion untenable.

The experiments to be described were carried out at the temperature of boiling liquid ammonia, which was used as

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refrigerant. The solutions were prepared and the experiments carried out in large test-tubes immersed in the ammonia contained in Dewar flasks. The tubes were closed by rubber stoppers carrying the electrodes and tubes for introducing the gaseous sulphur dioxide, which condensed to liquid at the temperature of the ammonia. Water was placed in the tube before placing the latter in the ammonia. The water remained as a solid at the bottom of the test-tube after the introduction of the sulphur dioxide, but on passing gaseous hydrogen bromide into the liquid, two layers were formed, the lower one consisting of a solution of sulphur dioxide and hydrogen bromide in water, and the upper one of a solution of water and hydrogen bromide in sulphur dioxide.

In the course of preliminary experiments, it was found that if the upper layer were syphoned off and used for the electrolysis, the current soon fell in value, whilst no water was deposited at the cathode, sulphur being liberated there in quantity. When the lower layer was allowed to remain in the vessel during the electrolysis, the current maintained its initial value, whilst water appeared at the cathode, very little sulphur being deposited. The water deposited at the cathode collected as small drops, which fell to the bottom of the apparatus.

The probable explanation of the need for the presence of the second layer is that it serves to maintain a saturated solution, and that otherwise the solution near the electrodes becomes depleted of water and hydrogen bromide, a different type of reaction then setting in. In the electrolysis experiments to be described, the second layer was present, but the electrodes were so arranged that conduction and electrolysis took place in the upper solution with the sulphur dioxide as solvent.

Two series of quantitative investigations were carried out, namely, (1) solubility determinations, and (2) determination of the quantity of water deposited at the cathode. In both cases the following method of analysis was adopted for the mixtures and solutions obtained, which contained water, sulphur dioxide, and hydrogen bromide. The sample was introduced into a weighed vessel, and most of the sulphur dioxide and some of the hydrogen bromide boiled off at a temperature below 0° , the gases being absorbed in sodium hydroxide solution. The bromide and sulphite in the hydroxide solution were determined by standard methods. Trial showed that the water was not appreciably distilled and could be estimated in the residue. For this purpose, a weighed quantity of concentrated sodium hydroxide solution was added to the already weighed vessel containing the water and residual sulphur dioxide and hydrogen bromide, the vessel then being re-

weighed. A determination of the bromide and sulphite in the solution enabled the water to be calculated by difference. Tests with known quantities of the constituents showed that the method was accurate to about 1 per cent.

For the solubility determinations, the solutions were prepared by adding excess of water to the sulphur dioxide and passing into the liquid varying amounts of hydrogen bromide. The solutions were well shaken and allowed to settle, the clear, upper layer being syphoned off for analysis. The results of the analyses are given in the following table:

Hydrogen bromide. Gram.	Water. Gram.	Gram-mol. of hydrogen bromide.	Gram-mol. of water.	Dissolved in x grams of sulphur dioxide.
0.568	0.126	0.0070	0.0070	10.2
0.970	0.214	0.0120	0.0119	15.6
0.435	0.096	0.0054	0.0053	11.0
0.650	0.145	0.0080	0.0080	9.7

It will be seen that the water and hydrogen bromide are found in the solutions in equimolecular proportion, and as water itself is but sparingly soluble in sulphur dioxide, it may be concluded that a compound, $\text{H}_2\text{O} \cdot \text{HBr}$, is formed. Whether this compound is an oxonium derivative or a simple hydrate can be decided from observation during electrolysis. If the deposit of water at the cathode were formed by precipitation of dissolved water as the hydrogen bromide holding it in solution was destroyed by electrolysis, a similar deposit should appear at the anode. In no case was the slightest indication of such deposit observed, and it may be concluded that a true oxonium compound is formed:

and as the hydrogen and water liberated during electrolysis both appear at the cathode, this compound must ionise as follows:

the H_3O^+ ion losing its charge at the electrode during electrolysis and forming hydrogen and water.

This formula and mechanism of reaction have been previously suggested by Bagster and Steele, but no quantitative evidence was available, and the formula adopted was based on speculation. It was also shown in the paper referred to that Faraday's law holds for solutions in sulphur dioxide, and it is to be expected that the water and hydrogen liberated will correspond with the quantity of silver deposited in a silver voltameter. It was shown, however,

that in the case of the hydrogen this expectation was not realised, and further careful experiments lately carried out gave no better result. As the solutions were always coloured yellow, probably by traces of bromine, it is probable that the hydrogen was destroyed by reaction at the electrode. The water deposited, however, has been estimated, and found to correspond closely with the quantity predicted by the theory put forward. For this determination, the cathode consisted of a platinum wire sealed through the bottom of a glass tube, the deposited water being collected in a small glass cup suspended underneath. At the end of the experiment, the cup was transferred to the weighed vessel and its contents analysed, as already described.

Two experiments were carried out, with the following results:

Silver in voltameter. Gram.	Water deposited. Gram.	Milligram equivalent of silver.	Milligram equivalent of water.
0.120	0.022	1.11	1.22
0.224	0.037	2.08	2.06

It will be seen from the results that one equivalent of water is liberated at the cathode in the sulphur dioxide solution for every equivalent of silver deposited in the voltameter. This is the result to be expected if the explanation offered as to the mechanism of reaction is correct.

This work has seemed of sufficient importance to publish, as it is probable that similar compounds exist in aqueous solutions of halogen hydrides, quite apart from hydrates of the ordinary type, and that they may take part in the electrolysis and reactions of such solutions.

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