ART. VII.—*The Use of Selenic Acid in the Determination of Bromine Associated with Chlorine in Haloid Salts;* by

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[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxviii]

WHEN an aqueous solution of bromine is boiled, reaction takes place in slight degree between that element and the water, according to the equation

$$3Br_2 + 3H_2O \rightleftarrows 5HBr + HBrO_3.$$

After the greater part of the bromine has been removed from the system by boiling, a small portion may still remain, in stable equilibrium for a given concentration, as shown in the equation. In further concentration by boiling, more water and free bromine are removed, bromic acid reacts with hydrobromic acid to form bromine, according to the reverse action above, and a new equilibrium is established for each new concentration. Eventually, all the bromic acid might be reduced, and all the bromine be liberated as such, but for the fact that hydrobromic acid also tends to volatilize from the solution.

The satisfactory separation of bromine from chlorine by the action of differential oxidizers upon the haloid salts depends upon the realization of several conditions; first, the presence of a suitable reducing agent in the solution, so that if a bromate is formed, it may be instantaneously decomposed; second, the prevention of the volatilization of hydrobromic acid, by working in sufficiently dilute solution, by condensing the steam with a reflux, or by passing the vapors given off through a fresh solution of the oxidizer; third, the choice of an oxidizer which liberates bromine from bromides with the formation of a reduction product not appreciably active toward bromine under the final conditions. No substance is known which accomplishes the separation at all concentrations, and it is, therefore, necessary to select a suitable oxidizer which will decompose bromides without attacking chlorides in a solution of regulated concentrations. In such action the differential margin must be sufficiently large to admit of the practical discontinuance of the oxidation after the bromine is completely removed, and before the hydrochloric acid is attacked. The concentration of free acid in the solution is of especial importance, since it controls the rate of formation and volatilization of the halogen acids, and the rate of liberation of bromine.

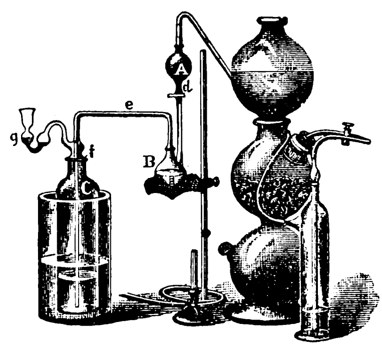
Selenic acid ($H_2SeO_4$) may react with chlorides* and with bromides according to the reversible reactions

$$2HCl + H_2SeO_4 \rightleftarrows H_2SeO_3 + H_2O + Cl_2$$
$$2HBr + H_2SeO_4 \rightleftarrows H_2SeO_3 + H_2O + Br_2$$

* Petterson, Zeitschr. anal. Chem., xii, 287.

Gooch and Evans* find, however, that no chlorine is liberated from solutions of small amounts of selenic acid at the boiling temperature unless the hydrochloric acid present, reckoned as concentrated aqueous acid, amounts to more than ten per cent of the entire volume. Gooch and Scoville† show that the interaction between selenic acid and potassium bromide in the presence of sulphuric acid is proportional to the acid concentration, to the bromide concentration, and to the elevation of temperature. The present paper is an account of an attempt to find conditions under which the reaction of selenic acid with chlorides shall be inappreciable while the oxidizing action upon bromides shall go to the end with the least possible reversal.

FIG. 1.




Selenic acid, now obtainable commercially, was at first used in free condition, since it is capable of performing a twofold service, that of acid, and that of oxidizing agent. Later it was found convenient to substitute a selenate with sulphuric acid to set the selenic acid free.

Solutions of iodine and sodium thiosulphate of approximately N/10 strength were carefully standardized, the iodine against the arsenic solution and the thiosulphate against the iodine, with the use of starch as the indicator. For nearly all these experiments a solution containing 3·9673 grams per liter of purest commercial potassium bromide, and 3·8974 grms. per liter of the best sodium chloride, purified by fractional precipitation from alcohol, were used in the preliminary analyses. In a few cases, the salts were weighed directly. The selenic acid employed was a commercial article of specific gravity 1·387 at 22°–23°, corresponding to that of 40·66 per cent pure selenic acid.‡

* This Journal, [3], 1, 400. † Ibid., [3], 1, 402.
‡ Diemer and Lenher, J. Phys. Chem., xiii, p. 505.

The accompanying illustration, fig. 1, shows the apparatus used in the preliminary tests. The reaction flask was graduated at $5^{cm^3}$ intervals to $50^{cm^3}$, the position of the meniscus being marked on a narrow slip of paper placed upon the flask or by graduation marks etched in with hydrofluoric acid. The alkali halides and $5^{cm^3}$ of selenic acid were introduced into the graduated flask and the total volume of liquid was made up to $50^{cm^3}$. After connecting the receiver, containing 3 to 4 grms. of potassium iodide in $200^{cm^3}$ to $250^{cm^3}$ of water, carbon dioxide was slowly passed through the apparatus and the liquid in the flask, gradually heated to boiling, was kept in a state of gentle ebullition until sufficiently concentrated. In an experiment made under the above conditions, in which the bromide was omitted, 0·2000 grams of sodium chloride caused distinct coloration of the iodide in the receiver when the volume in the flask had decreased to about $20^{cm^3}$, while 0·1000 grm. caused practically no color until the volume had decreased to about $10^{cm^3}$. In the following experiments in which the bromide was associated with chloride, therefore, the amount of sodium chloride was restricted and the final concentration was kept above the limit at which the attack upon the chloride begins. The flask was cooled and disconnected, and the free iodine in the receiver was titrated and taken as the measure of the bromine. Afterward, when the chlorine was to be estimated, connection was made with the receiver freshly charged with iodide and the distillation was continued to secure the evolution of the chlorine, which was estimated by titration of the iodine set free in the second distillation. The results follow in Table I.

The figures for bromine are rather low and somewhat irregular, while those for chlorine, although the concentrations are carried below the point at which the selenic acid itself begins (as was shown in blank tests) to liberate iodine in the receiver, are very irregular and generally low. It does not seem to be feasible to adjust the process so that the chlorine may be estimated by a second distillation, after the removal of the bromine. In the following experiments, therefore, attention was given exclusively to the determination of bromine.

The potassium bromide used in the following experiments was prepared for use from the purest available bromate by ignition, thorough fusion, pouring out upon platinum, cooling, powdering, drying at 105°, boiling and keeping in a sulphuric acid desiccator. A part of this material when dissolved in hot water recrystallized, dried between filters and afterward at 100° and analyzed by the gravimetric silver nitrate process, showed no variation in composition in consequence of this treatment. The results obtained with the bromide alone, and with that substance associated with sodium chloride, are given in Table II.

TABLE I.

*Preliminary Tests with Selenic Acid, Potassium Bromide, and Sodium Chloride.*

| KBr taken grm. | NaCl taken grm. | $H_2SeO_4$ taken (40·66%) cm³. | Initial volume cm³. | Volume for bromine cm³. | Volume for chlorine cm³. | KBr found grm. | Error in terms of KBr grm. | NaCl found grm. | Error in terms of NaCl grm. |
|---|---|---|---|---|---|---|---|---|---|
| ---- | 0·2000 | 5 | 50 | 20 | --- | color | ---- | ---- | ---- |
| ---- | 0·1000 | 5 | 25 | 11 | --- | color | ---- | ---- | ---- |
| 0·1000 | ---- | 5 | 55 | 24 | --- | 0·0979 | −0·0021 | ---- | ---- |
| 0·2000 | ---- | 5 | 58 | 16 | --- | 0·1968 | −0·0032 | ---- | ---- |
| 0·0988 | 0·0970 | 5 | -- | 25 | 2–3 | 0·0985 | −0·0003 | 0·0949 | −0·0021 |
| 0·0990 | 0·0972 | 5 | 48 | 18 | 3–4 | 0·0985 | −0·0005 | 0·0955 | −0·0017 |
| 0·0793 | 0·0779 | 5 | -- | 17 | -- | 0·0788 | −0·0005 | 0·0745 | −0·0034 |
| 0·1389 | 0·1364 | 5 | 55 | 17 | 3 | 0·1380 | −0·0009 | 0·1364 | 0·0000 |
| 0·1389 | 0·1364 | 5 | 55–60 | 12 | 1–2 | 0·1383 | −0·0006 | 0·1377 | +0·0011 |
| 0·0793 | 0·0779 | 5 | 40 | 17 | --- | 0·0785 | −0·0008 | ---- | ---- |
| 0·0991 | 0·0973 | 5 | 70 | 15 | 1–2 | 0·0984 | −0·0007 | 0·0966 | −0·0007 |

TABLE II.

*The Determination of Bromine liberated by Selenic Acid.*

| Br taken as KBr grm. | NaCl taken grm. | $H_2SeO_4$ (40·66%) taken cm³. | Initial volume cm³. | Final volume cm³. | Br found grm. | Error in terms of Br grm. |
|---|---|---|---|---|---|---|
| 0·0749 | .... | 5 | 40 | 15 | 0·0721 | —0·0028* |
| 0·0671 | .... | 5 | 50 | 13 | 0·0762 | —0·0009* |
| 0·0671 | .... | 5 | 55–60 | 6–7 | 0·0760 | —0·0011* |
| 0·0671 | .... | 5 | 50 | 15 | 0·0758 | —0·0013* |
| 0·0673 | .... | 5 | 50 | 16 | 0·0765 | —0·0008† |
| 0·0671 | .... | 5 | . | 12 | 0·0758 | —0·0013† |
| 0·0685 | .... | 5 | 50 | 24 | 0·0672 | —0·0013† |
| 0·2364 | 0·1757 | 5 | 40 | 11 | 0·2332 | —0·0032‡ |
| 0·2026 | 0·1507 | 5 | 40 | 7–8 | 0·2016 | —0·0010‡ |
| 0·1688 | 0·1255 | 5 | 40 | 7–8 | 0·1677 | —0·0011‡ |
| 0·1350 | 0·1003 | 5 | 30 | 7 | 0·1340 | —0·0010‡ |
| 0·1350 | 0·1003 | 5 | 30 | 9 | 0·1345 | —0·0005‡ |
| 0·1350 | 0·1003 | 5 | 30 | 12 | 0·1348 | —0·0002‡ |
| 0·1350 | 0·1003 | 5 | 30 | 12–13 | 0·1346 | —0·0004‡ |
| 0·1013 | 0·0753 | 5 | 25 | 11 | 0·1006 | —0·0007‡ |

* The bromide, made from the bromate, was fused and weighed out in each case.

† The bromide, made from the bromate, was fused, recrystallized, dried, and weighed out in each case.

‡ The bromide, made from the bromate, was made up with sodium chloride in a solution from which aliquot portions were measured.

As in the preliminary tests of Table I, these results run low for bromine, with considerable fluctuations.

An experiment showed that the flask residues of selenic acid, selenious acid, and the potassium salts of these acids were capable of reducing minute amounts of bromate, and of liberating bromine at the boiling temperature. Therefore, the larger of the deficiencies observed cannot be wholly attributed to the retention of bromine in the form of bromic acid or a bromate. Apart from the possibility of trifling losses of liberated iodine due to mechanical transfer in the current of carbon dioxide, the most reasonable explanation of irregularity in results would seem to be the escape of some hydrobromic acid from the reaction flask, without undergoing oxidation. In the subsequent work, therefore, the apparatus was modified to the form shown in fig. 2, so that the vapors escaping from the reaction flask (I) might be forced through another portion of selenic acid, kept hot in a relay flask (II), before passing to the receiver. The selenic acid in the relay flask was kept at 100°

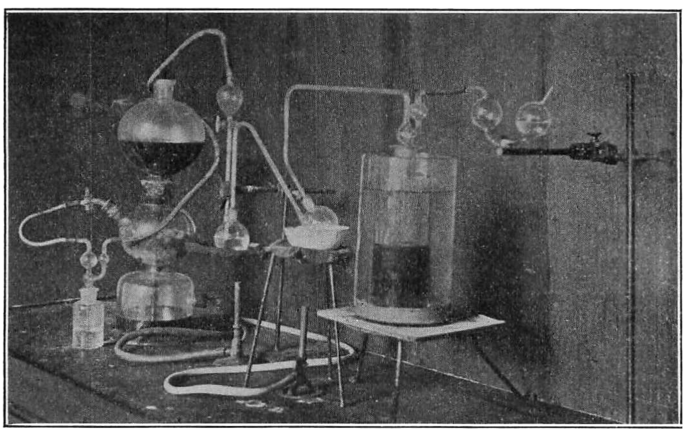
to 110° by means of an oil bath heated to 120° to 130°. The details of experiments with this apparatus are given in the following table:

TABLE III.

*Tests with Selenic Acid, and the Relay Apparatus.*

| Br taken as KBr grm. | Taken NaCl grm. | $H_2SeO_4$ I cm³. | $H_2SeO_4$ II cm³. | Final volume in reaction flask cm³. | Br found grm. | Error grm. |
|---|---|---|---|---|---|---|
| 0·0675 | 0·0050 | 5 | 2·5 | 12–13 | 0·0671 | —0·0004 |
| 0·1350 | 0·0050 | 5 | 2·5 | 15 | 0·1339 | —0·0011 |
| 0·1013 | 0·0050 | 5 | 2·5 | 12–13 | 0·1003 | —0·0010 |
| 0·0675 | 0·1505 | 5 | 2·5 | 15 | 0·0672 | —0·0003 |

FIG. 2.



So far as may be judged from the few results of Table IV, the use of the second voit flask to repeat the contact with selenic acid is favorable, and this evidence is confirmed in the work which follows, in which sulphuric acid and a selenate were used to generate the selenic acid in the reaction flasks. There is still a constant error of deficiency in the bromine. averaging 0·0007 grm., which might suggest that, in reversal of the fundamental reaction by which bromine is set free, the reoxidation of selenious acid by bromine is a possibility even at the final concentration. If this were the case, the addition of more selenic acid and further concentration of the solution in the reaction flask should advance the main reaction; but the addition of $5^{cm^3}$ more of the selenic acid after the estimation of the bromine, and repetition of the boiling to almost the limits at which chloride begins to be evolved, resulted in no appreciable improvement in the results by further evolution of bromine. It must be concluded that the reaction by which selenic acid sets free the bromine is complete under the conditions, or else that the supplementary amount of selenic acid is inadequate to change perceptibly the equilibrium established in the first boiling.

In experiments to be described the conditions of action were somewhat changed by using sulphuric acid and a selenate, in the place of free selenic acid, to effect the liberation of the bromine. The sodium selenate used was prepared in the laboratory and was contaminated with sodium sulphate, though otherwise pure. The selenate content was, however, determined and a solution of the mixed salts was prepared of such strength that $10^{cm^3}$ contained 1 grm. of sodium selenate. A preliminary series of experiments was made to determine the conditions suitable to the use of this reagent. It was found that chlorine is evolved from sodium chloride in presence of sulphuric acid at concentrations much lower than those at which the evolution begins when free selenic acid is the oxidizer in absence of sulphuric acid. The effects observed are shown in Table IV.

TABLE IV.

*Concentrations of Sulphuric Acid, Selenate, and Chloride at which the Evolution of Chlorine begins.*

| NaCl taken grm. | $Na_2SeO_4$ taken grm. | $H_2SO_4$ (1 : 1) taken $cm^3$. | Volume of the reaction liquid at which color appears in the receiver $cm^3$. |
|---|---|---|---|
| 0·1004 | 0·6 | 12 | 35–40 |
| 0·0753 | 0·6 | 12 | 30–35 |
| 0·0500 | 0·6 | 12 | 20–22 |
| 0·0500 | 0·6 | 6 | 16 |
| 0·0500 | 0·6 | 3 | 8–9 |
| 0·0500 | 1·8 | 3 | 9 |

The results of similar preliminary experiments with potassium bromide are shown in Table V.

A comparison of the results of Tables IV and V shows that with $3^{cm^3}$ of sulphuric acid (1 : 1), 1·8 grm. of sodium selenate, and 0·05 grm. of sodium chloride in the reaction flask (I), the concentration may safely reach a volume of $10^{cm^3}$. Determina-

TABLE V.

*The Evolution of Bromine by Sulphuric Acid and Sodium Selenate.*

| Br taken as KBr grm. | $Na_2SeO_4$ taken grm. | $H_2SO_4$ (1 : 1) grm. | Final volume $cm^3$. | Br found grm. | Error grm. |
|---|---|---|---|---|---|
| 0·1041 | 1·2 | 12 | 15–16 | 0·1029 | —0·0012 |
| 0·1041 | 1·2 | 12 | 13–14 | 0·1033 | —0·0008 |
| 0·0694 | 1·2 | 12 | 17–18 | 0·0686 | —0·0008 |
| 0·0694 | 1·2 | 12 | 16–17 | 0·0692 | —0·0002 |
| 0·0694 | 1·2 | 12 | 16–17 | 0·0691 | —0·0003 |
| 0·0694 | 0·6 | 12 | 12–13 | 0·0691 | —0·0003 |
| 0·0694 | 0·6 | 6 | 11–12 | 0·0691 | —0·0003 |
| 0·0694 | 1·8 | 3 | 12–13 | 0·0689 | —0·0005 |
| 0·0694 | 1·8 | 3 | 12 | 0·0691 | —0·0003 |
| 0·0694 | 1·8 | 3 | 12 | 0·0689 | —0·0005 |
| 0·0694 | 1·8 | 3 | 10 | 0·0691 | —0·0003 |
| 0·0694 | 0·6 | 3 | 11–12 | 0·0669 | —0·0025 |

tions of the bromine in potassium bromide associated with sodium chloride, made under these conditions, are recorded in Table VI. In these determinations the relay flask (II) was used, charged with $1^{cm^3}$ to $2^{cm^3}$ of sulphuric acid (1 : 1), 0·2 grm. to 0·3 grm. of sodium selenate, and $10^{cm^3}$ to $15^{cm^3}$ of water.

TABLE VI.

*Determination of Bromine by Selenate-Sulphuric Acid Process.*

| Br taken as KBr | NaCl taken | $Na_2SeO_4$ taken I | $Na_2SeO_4$ taken II | $H_2SO_4$ (1 : 1) taken I | $H_2SO_4$ (1 : 1) taken II | Final volume I | Br found | Error |
|---|---|---|---|---|---|---|---|---|
| grm. | grm. | grm. | grm. | $cm^3$ | $cm^3$ | $cm^3$ | grm. | grm. |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 14 | 0·0683 | —0·0011* |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 13–14 | 0·0690 | —0·0004 |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 13–14 | 0·0690 | —0·0004 |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 12–13 | 0·0693 | —0·0001 |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 12–13 | 0·0693 | —0·0001 |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 11 | 0·0692 | —0·0002 |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 11 | 0·0683 | —0·0011 |
| 0·0694 | 0·0500 | 1·8 | 0·2–0·3 | 3 | 1–2 | 10 | 0·0692 | —0·0002 |

* $CO_2$ was passed for a considerable time after cooling.

The average error in these determinations is 0·0004 grm. in terms of bromine.

According to the procedure which we have found to be effective for the amounts of material dealt with, the haloid salt is introduced into the reaction flask with $30^{cm^3}$ of water. Selenic acid, $5^{cm^3}$ of 40 per cent acid, or the mixture of 1·8 grm. of sodium selenate with $3^{cm^3}$ of sulphuric acid (1 : 1), is diluted with $20^{cm^3}$ of water and put into the separatory funnel. Into the relay flask are put $2{\cdot}5^{cm^3}$ of selenic acid and $10^{cm^3}$ to $15^{cm^3}$ of water, or 0·2 grm. to 0·3 grm. of the selenate with $1^{cm^3}$ to $2^{cm^3}$ of the (1 : 1) sulphuric acid and $10^{cm^3}$ to $15^{cm^3}$ of water. The relay flask is heated in the oil bath kept at 115° to 120°. The receiver is charged with 3 grm. to 4 grm. of potassium iodide dissolved in $200^{cm^3}$ to $250^{cm^3}$ of faintly acidified water, and set in a jar of cold water. The apparatus is connected (as shown in fig. 2), the dilute sulphuric acid is allowed to run into the reaction flask, and a slow current of carbon dioxide replaces the air in the apparatus. The reaction flask is heated until the liquid boils gently, while the oil bath which heats the relay flask is kept at 115° to 120°. The reaction mixture is boiled gently until diminished to a volume of $10^{cm^3}$ to $15^{cm^3}$, when the source of heat is withdrawn and carbon dioxide is passed in a current of sufficient rapidity to prevent back suction of the liquid in the receiver, but regulated to the lowest convenient limit, in order that iodine may not be swept from the receiver and lost to estimation. After the flasks are cool enough to be handled conveniently the apparatus is disconnected, the contents of the receiver and safety bulb are united, and the free iodine is titrated with standard sodium thiosulphate and taken as the measure of the bromine evolved. The entire operation need not occupy more than fifty minutes, and, with practice, may be shortened to forty minutes.

With selenic acid as the active agent it is possible to determine, under the conditions defined, the bromine of 0·25 grm. of bromide in association with 0·15 of chloride in the haloid salts. With sodium selenate and sulphuric acid to bring about the reaction, the separation is shown to be regular and fairly accurate for 0·07 grm. of bromine associated with 0·05 grm. of chlorine in the haloid salts. What the accuracy of the process may be when larger amounts of the salts are handled remains to be determined.