[Contribution from the Department of Chemistry, Grinnell College]

THE ACTION OF SOME OXIDIZING AGENTS ON SULFITE AND ITS DETERMINATION WITH IODATE

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Owing to the apparent confusion in the literature regarding the action of permanganate on sulfite and its determination by this oxidant, the author and L. M. Verbeck[1] took up the study of this reaction more than two years ago. Their results agreed essentially with those of Dymond and Hughes[2] that when sulfite was added to acidified permanganate to the apparent end-point, the oxygen used was 90 to 95% of that required for oxidation to sulfate. Contrary to the statement of Dymond and Hughes, they found about the same deficiency when the sulfite was added to an excess of this oxidant, amounting in some instances to 100% more than the calculated value. Dymond and Hughes accounted for the deficiency on the ground of the formation of dithionic acid. In an experiment on a large scale they passed sulfur dioxide and permanganate into cold water, keeping the sulfur dioxide in excess, until near the end, then adding permanganate until the end-point was reached. From the solution they isolated and analyzed the potassium salt of dithionic acid. In recent experiments the writer found about the same deficiency in oxygen required when sulfite was added to an excess of alkaline permanganate solution.

It seemed to the writer of interest to determine the action of other common oxidants on sulfite and bromate, dichromate and iodate were studied in this order.

Action of Bromate on Sulfite

In all of the work here described the usual precautions against error were observed.

Calibrated flasks, burets and pipets were used. The water was freshly distilled or re-boiled. "Highest purity" potassium bromate, dichromate and iodate were recrystallized, tested and dried; and 0.1 *N* solutions were prepared by weighing the necessary quantities. These solutions were tested against one another and against permanganate through iodide and thiosulfate. The sulfite solution was kept under hydrogen in a vessel connected with a Kipp's apparatus and a buret as represented in a paper by Thornton and Chapman.[3] The solution stood for several days before use and was then standardized every working day by the iodine method of Giles and Shearer. Two solutions thus protected lost only 0.2% in concentration per week. In the earlier experiments of each division of the work titrations were carried out in an atmosphere of carbon dioxide, and to detect loss of sulfur dioxide or halogen, there was attached to the titration flask a small bulb containing a few drops of very dilute iodine in iodide solution, through which must pass the gas forced out when sulfite was added to the solution of

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[1] Hendrixson and Verbeck, *J. Ind. Eng. Chem.*, **14**, 1152 (1922).

[2] Dymond and Hughes, *J. Chem. Soc.*, **71**, 314 (1897).

[3] Thornton and Chapman, This Journal, **43**, 91 (1921).

diluted oxidant of acidity 1 to 3 *N*, usually with sulfuric acid. No change in the depth of color of the iodine was observed, nor was any sulfate formed in the bulb. The sulfite was added at a moderate rate until near the end-point, the flask allowed to stand for several minutes, and the excess of oxidant was determined with iodide and thiosulfate. In some instances the sulfite was added until the end-point was reached as shown electrometrically, without difference in the results. In several experiments titrations in vessels with gas-tight seals were continued to near the end-points, the vessels were heated to boiling in water-baths for about an hour, and the titrations then completed in the usual way with iodide and thiosulfate. No additional oxidation occurred on heating.

Many determinations were carried out, but two series, in which the standard solutions used were wholly different, are given as representative of all. In each series the experiments were carried out within 36 hours of one another. In the same series the results are far from concordant.

1. Five determinations gave 93.4% of oxygen required on the basis of complete oxidation to sulfate, with deviations from the mean of +0.7 and —2%.
2. Six experiments gave a mean of 93.8% of oxygen required, and deviations of +3 and —2%.

It seems clear, therefore, that sulfite cannot be oxidized completely to sulfate in an acid solution of bromate in moderate excess at room temperature or at the boiling point of water. The electrometric titration indicates that bromate and bromine disappear at the same time. Since the curve shows no drop in potential indicating the disappearance of bromate, as is shown for the disappearance of iodate in Fig. 1, when this oxidant is used, it seems probable that the deficiency of oxygen required in titrating sulfite with bromate is due to the formation of dithionic acid which resists further oxidation, as in the titration with permanganate. It is obvious that one-half as much oxygen is required to change sulfite to dithionate as to change it to sulfate, and on the basis of this theory twice the deficiency of oxidation represents sulfite changed to dithionate, and the remainder to sulfate ion.

Quite recently the attention of the writer was called to a paper by Mayr and Peyfuss[4] in which they describe a method of determining sulfurous acid "by oxidation with bromine *in statu nascendi.*" In a special flask, well adapted to its purpose of excluding air and preventing the escape of sulfur dioxide, they boiled a measured solution of potassium bromate and an excess of potassium bromide, passing carbon dioxide through it at the same time. After cooling and by aid of the partial vacuum, they admitted a measured volume of sulfite, then hydrochloric acid. After several minutes an excess of iodide was added and the titration was completed with thiosulfate solution.

The writer has repeated this work, using the same sort of flask, and as nearly as possible the same manipulations, but he has not been able to confirm the results of the three experiments they have recorded showing

[4] Mayr and Peyfuss, *Z. anorg. Chem.*, **127**, 123 (1923).

complete oxidation to sulfate. The most favorable interpretation of his results shows that the oxidation is 2 to 3% short of that required for complete change of sulfite to sulfate. Furthermore, it seems to be a matter of indifference whether the bromate is used alone or with an excess of bromide. The indications are, however, that when even one-fourth of an equivalent of iodide instead of an excess of bromide is used with the bromate the oxidation proceeds completely to sulfate. The author wishes to reserve the details of this part of his work with possible extensions, for another communication.

Action of Dichromate on Sulfite

In general the same methods were used that are described under the discussion of bromate as the oxidant. In this instance, also, the work was begun nearly a year ago, two series of experiments were carried out, and the subject was taken up recently and completed with entirely different standard solutions. As in the case of the work in bromate, it was found to make little difference whether sulfite was added to an excess of oxidant, or only to the end-point, and whether the determination was completed at room temperature or the mixture heated to the boiling point of water, after adding the sulfite, and cooling before completing the titrations with iodide and thiosulfate. The following series show the results, the first at room temperature, the second after heating.

1. Eleven determinations, some of them conducted electrometrically to the end-point, gave for the oxygen required 95.05% of that needed for oxidation to sulfate, with deviations of less than 1% (plus or minus) from this mean.
2. Four determinations after heating gave for the required oxygen 95.2%, with deviations of +1.2 and —0.7% from the mean.

The behavior of dichromate is, therefore, quite analogous to that of permanganate and bromate in the oxidation of sulfite, and the deficiency of oxygen required may be assigned to the same cause—the formation of dithionic acid.

Determination of Sulfite with Iodate

It was anticipated that the action of iodate on sulfite might prove quite different from that of the oxidants already studied, and this view proved to be well founded. An attempt will be made to explain this difference after the experimental results have been presented.

The methods of work were much the same as those described for the work on bromate. Two different sulfite solutions were used, two of iodate and two of iodine. With regard to solutions and dates of doing the work, more than twenty experiments fall into four groups. The 0.1 *N* iodate was diluted with about five volumes of water, and made 1 to 3 *N* in acid, usually with diluted sulfuric acid. The first drop of sulfite gives free iodine which then accumulates till all of the iodate is reduced. In a few instances the last of the iodine was reduced with thiosulfate, but in most experiments the titration was carried to the end with the sulfite, using starch as indicator. Following are the results of the four series of experiments expressed in terms of normality of the sulfite solutions.

1. Five determinations gave the sulfite as 0.1251 *N* with greatest deviations +0.0002 and —0.0. By the iodine method the factor was 0.1249.

2. Seven determinations gave the sulfite as 0.1250 *N* with deviations +0.0001 and —0.0001. The concentration as determined by the iodine method was 0.1249.

3. The material was heated in a water-bath after the addition of sulfite until the end-point had nearly been reached and the titrations were then completed with iodide and thiosulfate. Four determinations gave the factor 0.1242 *N*, with deviations of +0.0002 and —0.0003. By the iodine method the value determined was 0.1245 *N*.

4. Four determinations gave the sulfite as 0.1741 *N*, with the greatest deviations +0.0001 and —0.0001. By the iodine method the value determined was 0.1741 *N*.

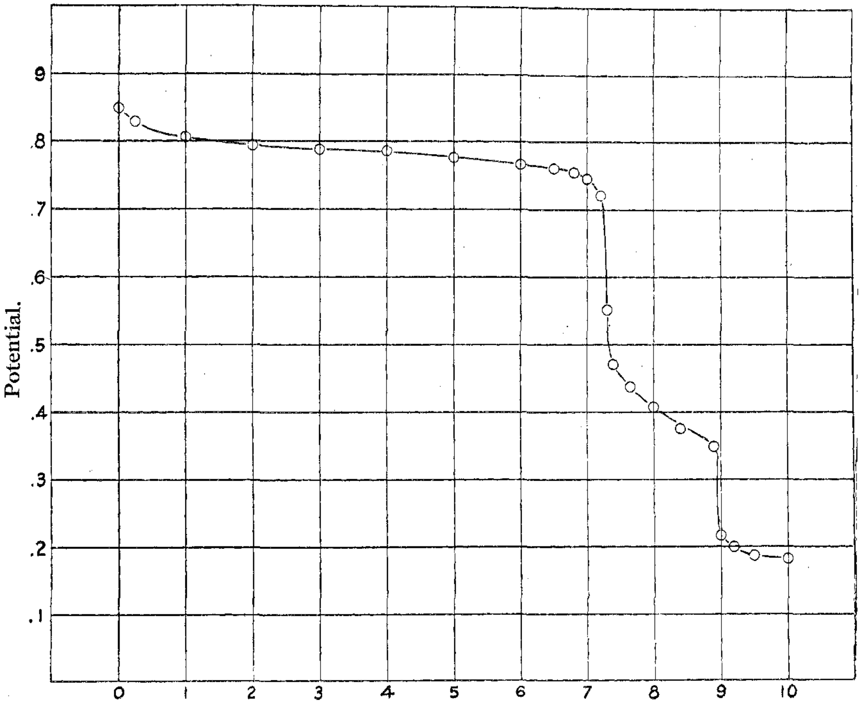

Fig. 1.

From these results it seems that sulfite can be directly determined with iodate, with a degree of accuracy as great as is ordinarily obtainable in volumetric analysis in which delivery from pipets and burets is used. No attempt was made to use weight burets on account of the difficulty of shielding the sulfite solution from the action of the air. The method is one of extreme simplicity. The only standard solution required is that of potassium iodate, which can be very accurately made from pure potassium iodate, and maintains its concentration indefinitely when protected from evaporation and reducing substances.

Several titrations were made of sulfite against iodate by the electrometric method, although the results are not included in the summary. The form of the curve is given in Fig. 1. Experiments with larger volumes than could be well represented by a graph were made, and the agreement was very close between the results of this and the ordinary method of titration. It was thus shown also that the volume represented between the sharp fall indicating the disappearance of the iodate, and that of the last of the iodine at the end of the reaction, was equal to one-sixth of the total volume of the sulfite solution. The electrometric method may obviously be used when desired in the cases of colored solutions of sulfite.

Theoretical Considerations

Many years ago Landolt[5] studied from the point of view of chemical kinetics the oxidation of sulfite in very dilute solutions by an excess of iodate solutions, and divided the oxidation into three steps as follows:

$$IO_3^- + 3SO_3^{--} = I^- + 3SO_4^{--} \qquad (1)$$
$$IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O \qquad (2)$$
$$3I_2 + 3SO_3^{--} + 3H_2O = 6H^+ + 6I^- + 3SO_4^{--} \qquad (3)$$

These are known as the Landolt reactions and they have been since studied from the same point of view by several other chemists. Among the latest researches are two by Anton Skrabal,[6] carried out with great thoroughness both experimentally and theoretically, and formulated mathematically in great detail. In substance it may be said that the slow Reaction (1) represents in its equation the sum of Reactions 2 and 3, and necessarily it must initiate the entire oxidation. Reaction 2 is also very slow near the beginning of the oxidation and is determined by the product of its ions and its constant of Reaction (k). Reaction 3 may be regarded as instantaneous. Even in very dilute solutions of low acidity as in Skrabal's work the speed of Reaction 2 soon exceeds that of Reaction 1, the starch blue appears and thereafter the oxidation proceeds by means of Reactions 2 and 3. Owing to the rapidity of Reaction 2 nearly all the iodine then accumulates as free iodine until the iodate is all used. The influence of Reaction 1 is still further reduced in the initiation of ordinary titrations as described in this paper on account of the high hydrogen-ion concentration in Reaction 2. In experiments of my own it was shown that when an iodate solution as ordinarily used in this work was acidified with one drop of 50% sulfuric acid and a single drop of the sulfite solution added, the blue color appeared suddenly after one minute showing, according to Skrabal, that in the actual oxidation Reaction 3 had superseded Reaction 1.

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[5] Landolt, *Ber.*, **19**, 1317 (1886); **20**, 745 (1887).

[6] Skrabal, *Z. Elektrochem.*, **28**, 224 (1922); **30**, 109 (1924).

From these facts it follows that the titration of sulfite with iodate is virtually the same as its titration with a solution of iodine. If this is so, both methods should give the same results, as in fact they do, so far as can be determined in ordinary volumetric work.

As regards the difference between the oxidation of sulfite by iodate and the action of other oxidants, certain tentative suggestions may be permitted. It seems probable that the type of reaction given for iodate functions at one stage or another in the oxidation by bromate. Although bromate ion is usually regarded as a much stronger oxidant than the iodate ion, and bromine stronger than iodine, hydriodic acid probably excels hydrobromic acid far more as a reducing agent than bromate exceeds iodate as an oxidizing agent. This means that in the case of bromate, Reaction 1 is much faster and Reaction 2 is much slower than in the case of iodate. So great is the difference that Reaction 3 seems to be largely eliminated in the oxidation, provided the sulfite is steadily added to the iodate while the mixture is shaken until the end-point is reached. Anyone can convince himself that free bromine is not formed during this uniform addition of sulfite, but appears only after the addition of a portion of sulfite solution and the elapsing of one to several minutes. In the oxidation with bromate, therefore, it seems that most of the oxidation must take place according to Reaction 1; that is, the oxidation of sulfite is mainly due to the direct transfer of oxygen from the bromate to the sulfite ion.

That the action of permanganate and dichromate on sulfite should differ from that of iodate hardly needs discussion after what has been said of bromate. In their cases no indirect oxidation seems probable. Their action must be considered as of the same general type as Reaction 1, that is, the transfer of oxygen from their negative ions to the sulfite ion.

Why the products of oxidation of sulfite by the other oxidants studied should differ from that by iodine in Reaction 3 is a difficult question. The formula of sulfurous acid seems not to be known with certainty. Following a long series of optical investigations of solutions of sulfur dioxide, its acid, salts and esters, Schaefer and Köhler[7] express the view that a solution of sulfur dioxide in water after an interval of time contains eight different forms of sulfur compounds, including sulfur dioxide itself, the two primary undissociated acids and their ions, all in equilibrium with one another. The two forms of the acids are $(HO)_2SO$ and $HOHSO_2$, and their negative ions may be considered to be SO_3^{--} and HSO_3^-. It seems possible that the milder oxidizing agent iodine might be able to oxidize, through the medium of water, only the first form, and the second only as it shifts into the first form. On the other hand, the more intensive oxidizing agents might oxidize both forms simultaneously, the former by the addition of oxygen. In view of the slight stability of combinations of

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[7] Schaefer and Köhler, *Z. anorg. Chem.*, **104**, 212 (1918).

hydrogen with sulfur, and the tendency of the latter to polymerize, these oxidizing agents might abstract hydrogen from two of the ions HSO_3^{--}, and the two residues might then unite to form the ion of dithionic acid, $S_2O_6^{--}$.

In conclusion it may be stated that the differences in the oxidation of sulfite by iodine and iodate on the one hand and by permanganate, chromate and bromate on the other are due to fundamental differences in the characters of the two classes of oxidants, and these, are not to be altered by varying such secondary conditions as concentrations, temperatures, acidity or excess of the oxidizing agents. It therefore seems that attempts to work out accurate volumetric methods of determining sulfite with permanganate, bromate and dichromate along ordinary lines will probably prove futile.

The writer has received in this work the efficient aid of Mr. Neil L. Crone, a senior in Grinnell College.

Summary

This paper describes the continued work of the author on the oxidation of sulfurous acid, and gives the results obtained with bromate, dichromate and iodate in acid solution. The amounts of bromate and dichromate are less than those required by theory for the complete oxidation to sulfate—to about the same degree as that found for permanganate. The discrepancy is regarded as probably due to the same cause, the formation of some dithionic acid which resists further oxidation. On the other hand, iodate oxidizes completely the sulfite to the sulfate ion; this fact permits the very simple and accurate determination of sulfite by use of this oxidant.

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THE CAPILLARY RISE OF WATER IN TUBES OF VARIOUS METALS

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In a paper published some years ago, Bigelow and Hunter[1] presented results which tended to show that water and benzene rose to greater heights in capillary tubes of various metals than in tubes of glass. Unless metals are able to affect the surface tension of these liquids it is difficult to see how their results can be correct, unless all previous measurements with glass tubes are found to be in error. The most likely source of such an error would be a contact angle between the liquid and the glass, if it were not that it has been fairly well established that this angle of contact is zero. The fact that the magnitude of the effect obtained by Bigelow and Hunter

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[1] Bigelow and Hunter, *J. Phys. Chem.*, **15**, 367 (1911).