

The persistency of type of the rate curve in all these salts, consisting as it does of an ascending and then a descending portion, seems to us of sufficient importance to be taken into account in any explanation of the phenomenon.

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A METHOD FOR THE DETECTION OF CHLORIDES, BROMIDES AND IODIDES.¹

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THE problem of the detection of chlorides, bromides and iodides in presence of each other is one to which a great deal of attention has been devoted, and the present proposal of a new method is justified only by the conviction of the authors that in simplicity of execution, in reliability and in delicacy this method is superior to any hitherto proposed.

Like many of the methods proposed in the past, the one here presented is based upon the varying ease of oxidation of the halogen acids. It arose from a reasonably successful attempt to use dilute nitric acid as the oxidizing agent. Concentrated nitric acid, added dropwise, was employed for this purpose by Kebler,² who states that during a five years' trial by students it gave very satisfactory results. We have found that if nitric acid of suitable dilution is used, it is indeed possible to boil a mixture of the halogen salts with it long enough to liberate and expel all the iodine and bromine without any noticeable loss of chlorine. We may cite here two out of about twenty-five experiments. The acid was of five times molar strength and the quantity used was about half the volume of the solution to be tested:

1. Cl detected in a mixture of 49.9 cc. N KBr and 0.1 cc. N NaCl.
2. Cl detected in a mixture of 10 cc. N/100 KI, 9.8 cc. N/100 KBr, and 0.3 cc. N/100 NaCl.

The substitution of dilute for concentrated nitric acid obviates one defect in Kebler's method, *viz.*, that the concentration of the

¹ Read before the Cincinnati Section of the American Chemical Society, May 13, 1903.

² *J. Anal. Appl. Chem.*, 6, 569 (1892).

acid in the test solution was not well enough controlled, but there are at least two objections that apply to the method, even when the dilute reagent is used, *viz.*, that the separation between iodide and bromide is by no means sharp and that in some instances iodic acid is formed in sufficient quantity to give a precipitate with silver nitrate resembling silver chloride. In the course of the experiments referred to above we observed in several instances that a solution of pure potassium iodide, after boiling with dilute nitric acid until colorless, would give with silver nitrate a white precipitate, soluble in ammonium hydroxide (therefore not iodide) and that this precipitate was not obtained from another portion of the decolorized solution after neutralizing with ammonia, acidifying with oxalic acid, evaporating to dryness and redissolving in nitric acid (therefore iodate). Another fact noticed in the course of these experiments was that a solution containing both potassium bromide and potassium iodide was decolorized somewhat more quickly than a solution of bromide alone. This also pointed to the conclusion that some iodic acid was formed by the action of the nitric acid on the liberated iodine, for the hydrobromic acid would be oxidized more readily by iodic than by nitric acid.

It was the above-mentioned observation that led to the use of the reagent proposed in our present method, *viz.*, iodic acid in the form of potassium iodate. This oxidizing agent will not react with any of the halide ions in neutral solution, but will liberate iodine from potassium iodide in acetic acid solution, while the bromine of potassium bromide is not at all liberated, except upon addition of a stronger acid. As the stronger acid for liberating the bromine we employ nitric acid (dilute) for the two reasons that in the presence of this acid it is easy to eliminate any excess of potassium iodate and that, on the other hand, should the quantity of potassium iodate added be insufficient to react with all the bromide, the nitric acid is itself capable of effecting a complete separation. The first reason is the main one, as, in general, the quantity of potassium iodate added will be sufficient to react with all the bromide.

According to Fresenius,¹ the use of iodic acid or of potassium iodate and hydrochloric acid as a reagent for iodides was proposed by Liebig. Fresenius objects that the reagent "must be

¹ "Qualitative Analysis," Wells' translation (1897), p. 380.

used with the greatest caution" because "an excess of iodic acid will at once put an end to the reaction." It is obvious that this objection applies only to the use of the iodate *with hydrochloric acid*, the liberated iodine combining with the chlorine to form iodine chloride. In the absence of hydrochloric acid no such difficulty exists. Another objection made by Fresenius is that reducing agents will liberate iodine from the reagent, thus causing confusion. In reply to this objection we would point out that the halogen acids can be easily separated from all the other common acids, with the exception of sulphocyanic, by precipitating in presence of nitric acid with silver nitrate and reducing the precipitate with zinc and sulphuric acid.¹ The silver sulphocyanate could easily be destroyed by igniting the precipitate before reducing it, but this is unnecessary. In the presence of sulphocyanate, the test for iodide may be made (after neutralizing) by adding first sodium acetate and then acetic acid and potassium iodate. It is a familiar fact that the acidity of acetic acid is diminished by the addition of sodium acetate, the increase in the concentration of the acetate ion causing a depression of the dissociation of the acid. In such a solution, *i.e.*, in one containing an extremely low concentration of hydrogen ions, the reaction between the sulphocyanate and iodate is entirely prevented, while that between the iodide and iodate still takes place.

Both of the reagents that Fresenius mentions, *viz.*, free iodic acid and potassium iodate with hydrochloric acid, have, of course, the further disadvantage that they cannot be used in presence of bromides, since they liberate bromine as well as iodine. But potassium iodate with acetic acid is free from this objection, as well as from those raised by Fresenius and has the obvious advantages over the commonly employed reagent, chlorine water, that the quantity of iodine liberated is one-fifth greater and that there is absolutely no danger of decolorization of the liberated iodine by excess of the reagent. For the detection of bromides, potassium iodate with nitric acid has similar advantages over chlorine water, the danger of decolorization by excess being absent and six halogen atoms being liberated instead of five, but here we have the additional advantage that the sixth halogen atom is iodine instead of bromine and that consequently the color imparted to the solution, whether in water, carbon disulphide or chloroform, is more intense.

¹ See Bailey and Cady's "Qualitative Analysis," (1901), p. 209.

The superior delicacy of the iodate reagent indicated by the above considerations is amply borne out by the results of actual tests. Thus, using 5 cc. of solution and shaking with about 1 cc. of freshly decolorized carbon disulphide, we were able to detect iodine by use of potassium iodate and acetic acid in an N/60,000 solution of potassium iodide without failure and in one trial out of two in an N/90,000 solution, while chlorine water gave a very faint test upon the third trial with an N/40,000 and failed entirely with an N/50,000 solution. Testing in the same manner for bromides, using potassium iodate and dilute nitric acid, we obtained coloration of the disulphide from an N/16,000 solution of potassium bromide on warming slightly, while chlorine water gave the test in an N/2,500 solution (which is about the delicacy claimed by Fresenius, *viz.*, 1 part of bromine to 30,000 of solution),¹ while it failed entirely with an N/4,000 solution. It would appear from these results that the iodate is nearly twice as delicate a reagent as chlorine water for iodides and four or five times as delicate a reagent for bromides, and with freshly decolorized carbon disulphide is capable of detecting iodine in 5 cc. of a solution containing 1 part of iodine in 500,000 of solution and bromine in 5 cc. of a solution containing 1 part of bromine in 200,000 of solution. It may be remarked in this connection that while the color test for iodine or bromine is decidedly more delicate with carbon disulphide than with chloroform, the latter reagent is sufficiently delicate for ordinary purposes and is, perhaps, preferable as a laboratory reagent because it does not become colored on standing.

METHOD.

The separation of the three halogens can be conveniently accomplished in a rather wide (say 2 cm.) test-tube in which a liquid can be boiled without loss from bumping. The whole analysis does not take more than ten minutes. The reagents used are neutral potassium iodate of one-tenth, potassium iodide of one-fifth, and nitric acid of five times molar concentration. (Specific gravity of the nitric acid = 1.18.) The procedure is the following:

(a) To the neutral solution add potassium iodate and acidify with acetic acid. Coloration shows the presence of iodide, which may be confirmed by shaking a portion with chloroform or carbon disulphide.

¹ *Loc. cit.*, p. 359.

(b) If iodide is found, add a little more potassium iodate to the main portion of the solution and boil. Repeat this procedure until further addition of iodate fails to produce coloration, but avoid more than a slight excess of iodate. Having expelled the liberated iodine by boiling, add to the solution nearly one-half its volume of dilute nitric acid. Coloration shows bromide, which may be confirmed by shaking a portion with chloroform or carbon disulphide.

(c) Boil the main portion of the solution until colorless, add 1 or 2 cc. of potassium iodide and boil again until colorless. The potassium iodide reduces the excess of iodate and the excess of iodide added is destroyed by the nitric acid. Boil again until perfectly colorless, then add an equal volume of concentrated nitric acid and a few drops of silver nitrate. A white precipitate, insoluble on warming, shows chloride. The concentrated nitric acid is added to prevent the precipitation of silver iodate in case there should still be some iodic acid left in the solution after the treatment with potassium iodide.

If sulphocyanate is present, the test for iodide must be made in a small portion of the solution after addition of sodium acetate. (We add an equal volume of the normal solution of the acetate.) The main portion of the solution is treated as above, the sulphocyanic and hydriodic acids being both completely oxidized in the presence of the acetic acid.

If salts of other acids are present, acidify the solution with dilute nitric acid and precipitate with silver nitrate. Digest the washed precipitate with zinc and dilute sulphuric acid. The halogen acids and sulphocyanic acid are thus brought into solution. Neutralize the solution, filter off the precipitate of zinc hydroxide or carbonate and proceed as directed above.

We have made some comparisons of the delicacy of this method for the detection of chlorides in presence of bromides and iodides with that of the commonly employed chromyl chloride distillation method. The limit of the latter method was found to be the detection of chloride in a mixture of 5 cc. N/100 sodium chloride with 10 cc. N/100 potassium bromide. With such a solution, a very faint yellow ring could be recognized at the top of the liquid (ammonium hydroxide solution) in the receiver. With less than 5 cc. of the sodium chloride solution, we failed to obtain any test

by this method, whereas, using our method, we were able to detect chlorine in mixtures of 0.5 cc. N/100 sodium chloride with 20 cc. of N/5 potassium bromide and iodide. In fact, the results of all our qualitative experiments indicate that absolutely no loss of chlorine is suffered in liberating and expelling the iodine and bromine.

To test the adequacy of the above directions we have had first- and second-year students of the University of Cincinnati analyze some forty mixtures of chlorides, bromides, iodides and sulphocyanates. The solutions were of fifth-normal to normal strength. In the reports there was but a single error, one student reporting chlorine when none was present. Some twenty-five mixtures of more dilute solutions, some containing as low as 0.5 cc. of the N/100 solution of one or other of the halide salts, many containing sulphocyanate and some containing salts of other acids, including reducing agents, such as sulphites, ferrocyanides, oxalates, etc., were analyzed by more experienced persons without error.

Bugarszky¹ has employed potassium biiodate and dilute sulphuric acid for the quantitative separation of bromine and chlorine but has not attempted to separate iodine from the other halogen elements. We hope soon to be able to communicate a method for the estimation of all three elements.

THE TESTING OF COAL TAR AND OILS AND AN IMPROVED TESTING STILL.

BY H. W. JAYNE.

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IN the examination of coal tars and oils, and in determining the per cent. of water they contain, it is necessary to distil a considerable quantity of material, from 500 to 1000 cc. at least. In treatises on this subject, it is usual to recommend the use of glass retorts of several liters capacity. As the temperature in making a complete test often rises to 400° C., and as water is usually present, the risk of breakage is very great; and when the distillation is finished, it is impossible to remove the pitch or residue completely.

In our laboratory, where hundreds of these tests are made every

¹ *Ztschr. anorg. Chem.*, 10, 387 (1895).