NOTES ON SOME VANADIUM REACTIONS.

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The following notes are the outcome of some work I have recently done for a firm of ink manufacturers; and as some of them have an analytical bearing, I have thought them of sufficient interest to bring before the Society.

It has long been known that ammonium vanadate forms a dark soluble compound with gallo-tannic acid, which has the reputation of being an excellent permanent ink, and has been so described in different standard text-books (*e.g.*, Miller's "Elements of Chemistry"). The discovery of this fact is attributed to Berzelius (*Dingler's polyt. J.*, 1835, lvi., 237), but I have been unable to discover any reference to the subject in the "Jahresberichte" or "Lehrbuch" of Berzelius.

Appelbaum (*Dingler's polyt. J.*, 1889, cclxxi., 423), on making experiments with gall extracts and solutions of gallo-tannic acid, found that both the writing and ink faded in a short time, and hence doubted whether Berzelius had ever made any experiments with the ink.

I have repeated Appelbaum's work, and can confirm what he says about gall vanadium ink, though I find that gallo-tannic acid gives an ink of somewhat greater permanency than was found to be the case by him.

In making experiments with other substances, I have found that the law established by Schluttig and Neumann ("Die Eisengallustinten," p. 33) for iron salts also applies to ammonium vanadate—viz., that it yields an ink with substances containing three adjacent hydroxyl groups. Thus, gallic acid, logwood extract, and hæmatoxylin combine with ammonium vanadate to form black inks, whilst phenol, benzoic acid, saccharin, etc., do not form such compounds.

Unfortunately, none of these inks has proved to be satisfactory as regards permanency, the writing in each case becoming more or less yellow with the lapse of time, and hence ammonium vanadate, apart from its expense, is not a suitable constituent of writing inks.

In the course of this work I made a number of experiments on the reducing action of organic acids upon ammonium metavanadate. Though all that I tried gave a lemon-yellow coloration, probably due to the formation of metavanadic acid (HVO_3), only a few showed marked reducing properties, the most notable of these being oxalic acid.

If a 1 per cent. solution of oxalic acid be mixed with an ammonium metavanadate solution of the same strength, the liquid becomes bright yellow, and on heating is rapidly reduced to a brilliant blue solution, which when concentrated deposits blue crystals, presumably consisting of hypovanadic oxalate, a compound of the oxide V_2O_4.

This reduction is also brought about by tartaric, citric, and, to a much smaller extent, by malic acid, similar blue colorations being produced in each case.

If a solution of ammonium metavanadate be first treated with an ordinary hydrochloric acid solution of hydrogen peroxide, and then a few drops of a solution of oxalic acid be added, there is an immediate ruby-red coloration. Apparently in this reaction the hydrogen peroxide oxidizes the metavanadate to a higher vanadate, and then on adding the oxalic acid reduction takes place, with the formation of vanadic salts (compounds of vanadium pentoxide, V_2O_5), which have a red colour.

This red solution can also be produced by first forming the blue reduction compound with oxalic acid, and then oxidizing this with hydrogen peroxide.

In the absence of inorganic reducing agents, such as sulphur dioxide, this reaction can be applied as a test for oxalic acid. Thus, on adding 2 drops of hydrogen peroxide to 1 c.c. of a 0·5 per cent. solution of ammonium vanadate and 0·2 c.c. of a 1 per cent. solution of oxalic acid, an unmistakable ruby-red colour is immediately formed. In the case of tartaric acid, however, there is only a very faint indication of red when 2 c.c. of a 10 per cent. solution are added; or, in other words, oxalic acid has 1,000 times the reducing power of tartaric acid. The reducing power of citric acid is less than that of tartaric acid, whilst malic acid is weaker still.

In the case of succinic and phthalic acids, the formation of the red reduction compound can only be brought about by using a hot saturated solution of the acids.

This reaction can also be used as a simple test for distinguishing between chromates and vanadates, which may be very similar in colour. If hydrogen peroxide be cautiously added to a solution of potassium chromate, the solution is oxidized to bichromate, and on now adding a solution of oxalic acid there is an evolution of oxygen, and a blue solution of the hypothetical perchromic acid is formed, which is speedily reduced to a green solution, probably consisting of a mixture of the yellow chromate and blue compound, and finally to a violet or pale green chromium salt, the exact nature of the change depending upon the relative amounts of the different substances present.

DISCUSSION.

The PRESIDENT (Mr. Fairley) said it happened that on the previous evening he had been lecturing on inks before the Bradford Society of Dyers and Colourists, and had then shown a number of experiments with vanadium inks. Salts containing certain heavy metals commonly produced dark-coloured solutions with many of the hydroxyl derivatives and with many of the hydroxyl and carboxyl derivatives of phenol, such, for instance, as salicylic acid and pyrogallic acid, which latter had not been mentioned by Mr. Mitchell, though it produced a very deep colour with ammonium vanadate. So far, however, as modern experience went, inks of this kind appeared not to have so great a degree of permanence as they were stated by many older authorities to possess. In fact, he had come to the conclusion that, in order to make a durable ink, it was best to add a little finely-divided carbon, such as lamp-black, thus insuring the presence in the ink of a marking substance at least as permanent as the paper. Phenol itself did not strike a dark colour with many iron and other solutions, though it produced a blue colour with ferric chloride, and in that respect came within the same category as the hydroxyl derivatives referred to.