$AgFO_3$(?) d = 3.37 Tetragonal
$AgClO_3$ d = 4.43 Tetragonal
$AgBrO_3$ d = 5.21 Tetragonal

The above evidence is strongly indicative of the formation of silver fluorate.

The investigation is being continued.

Summary

The treatment of concentrated, cold solutions of fixed alkali hydroxides with fluorine forms a product of comparatively high oxidizing power, and evidence is presented to show that the oxidation cannot be due either to an alkali ozonate, ozone, hydrogen peroxide or fluorine monoxide. When a molten mixture of alkali hydroxides and fluorides is electrolyzed, there is formed an oxysalt of fluorine. Examination of the silver salt of this oxyacid indicates that it is silver fluorate, $AgFO_3$.

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Notes

The Absorption Spectra of *m*-Bromophenol Indophenol, 2,6-Dibromophenol Indophenol and Guaiacol Indophenol

BY MATILDA MOLDENHAUER BROOKS

The absorption curves of *m*-bromophenol indophenol, 2,6-dibromophenol indophenol and guaiacol indophenol have been measured in 0.0001

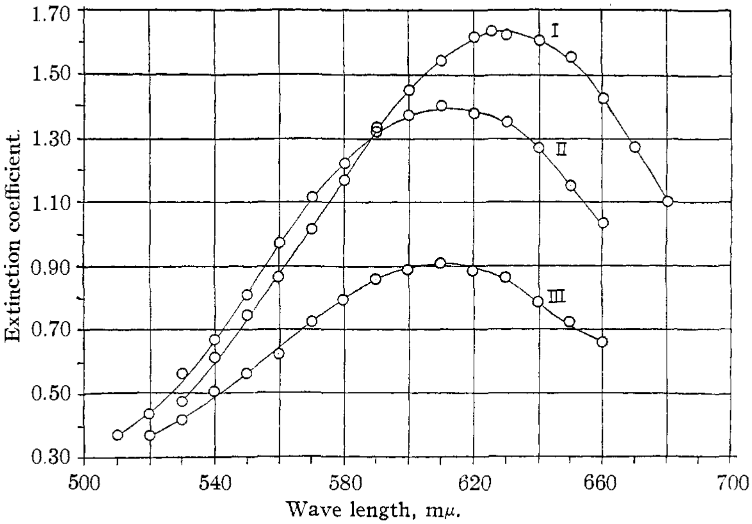

Fig. 1.—I, *m*-bromophenol indophenol; II, 2,6-dibromophenol indophenol; III, guaiacol indophenol.

M aqueous solution and the results are shown in the accompanying figure. The *P*H of the first two solutions was brought to 11.7 and that of the third to 11.8 by the addition of sodium hydroxide, the *P*H values being ascertained by means of the hydrogen electrode. In this range of alkalinity the blue dye ion predominates and there is no noticeable change in the absorption maximum when higher alkalinities are used. Shifting the wave length 2 mμ to one side or the other of the absorption maximum gave reproducible decreases in the absorption index. A Bausch and Lomb instrument was used. The solutions in all cases were freshly prepared from W. M. Clark's dyes and it was found that the absorption maxima did not alter during two days' standing. The absorption maximum of the first dye was at 625 mμ, and that of the second and third at 610 mμ. It was also found that Lambert and Beer's law held for solutions of twice the concentration.

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The Acid Soluble Oxidizing Material from Charcoal

BY M. A. MAYERS

In the course of an investigation of the mechanism of combustion of carbon, it seemed advisable to check the observation of Lamb and Elder[1] that a peroxide-like substance is dissolved out of charcoal by dilute sulfuric acid, which will then liberate iodine from potassium iodide. We applied this test to several commercial charcoals, coal, and ash-free lampblack, and found that an extract capable of liberating iodine from potassium iodide was obtained only from those materials that contained iron in their ash. Measurements on one of the extracts, which liberated about a tenth as much iodine as those of Lamb and Elder, showed that the iodine liberated was equivalent to the ferric ion extracted. These experiments throw some doubt on the existence of the acid soluble peroxide-like material reported to have been extracted from charcoals.

Several commercial charcoals and Edenborn coal[2] were washed with 1.0 *M* sulfuric acid, at which concentration Lamb and Elder found the greatest activity. The filtrates liberated iodine from 10% potassium iodide solution, and decolorized a few drops of potassium permanganate, but did not give the characteristic test for hydrogen peroxide with chromic acid, nor that for ozone with silver.[3] No gas appeared when an inverted test-tube

(1) Lamb and Elder, THIS JOURNAL, **53**, 157 (1931); *cf.* also I. M. Kolthoff, *ibid.*, **54**, 4478 (1932).

(2) U. S. Bureau of Mines, Tech. Paper No. 525 (1932).

(3) Only the first of these tests was considered significant. The reduction of potassium permanganate might have been caused by minute amounts of organic material or by ferrous iron. The peroxide and ozone tests may not have been sufficiently delicate.

filled with solution was exposed to diffuse sunlight for several weeks. When the solution was concentrated, either by boiling or by evacuation at room temperature, there was no loss of activity, but a fine black precipitate separated out when the acid became concentrated. When the solution was evaporated to dryness and the precipitate washed with acid, the reaction with potassium iodide could still be obtained. A trace of iron was indicated by potassium thiocyanate.

Since ferric ion is able to oxidize I^-, it was necessary to use iron-free reagents to show conclusively the presence of a peroxide. Charcoal made from recrystallized sugar could not be obtained iron-free, but a lampblack prepared from natural gas was ashless.[4] Iron-free sulfuric acid was prepared by dissolving pure sulfur trioxide in distilled water. When the experiment was repeated using these pure reagents, no liberation of iodine could be detected.

To identify further the action of ferric ion with that of the active material from charcoal, a solution of ferric chloride was added to a 1.0 *M* sulfuric acid solution to which an excess of thiocyanate had been added until its color matched that of a portion of the acid with which one of the commercial charcoals had been washed. Calculation showed that about 6 mg. of iron had been washed out of each hundred grams of charcoal. Equal amounts of both the iron and the charcoal wash solutions were tested with 10% potassium iodide solution, and titrated with sodium thiosulfate solution (one ml. = 0.383 mg. of iodine), using starch as indicator. The titration showed that the iron solution, which had been made up to contain 0.02 mg. of iron per ml., contained 0.017 mg./ml., while the charcoal wash solution contained 0.016 mg./ml. Since both solutions contained the same concentration of ferric ion, as shown by the thiocyanate color test, and since they both liberate the same amount of iodine, the oxidizing action of the charcoal wash solution must be due entirely to its ferric-ion concentration and not, in part, to the presence of a peroxide.

These results show that evidence previously adduced to show the existence of an acid soluble peroxide of carbon is not conclusive. The oxidation of potassium iodide is shown to be an insufficient test for peroxide in the presence of inorganic ions.

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(4) This lampblack was evacuated to a pressure of 10^{-3} for four hours between 350 and 400°. Howard and Hulett [*J. Phys. Chem.*, **28**, 1082 (1924)] found that such a black had nearly 60% the adsorptive capacity of an activated coconut charcoal.

Colorimetric Determination of Aluminum with Aurintricarboxylic Acid[1]

BY PAUL S. ROLLER[2]

The aurintricarboxylic test of Hammett and Sottery[3] has been shown by Yoe and Hill[4] to be adaptable to the quantitative estimation of aluminum. In the recommended quantitative procedure, as directed for the qualitative test, the reaction mixture is made alkaline with NH_4OH–$(NH_4)_2CO_3$ before colorimetric comparison. The resultant gradual fading and the evolution of bubbles have been found troublesome.[5] By comparison with a slightly acid solution, it is found, as shown below, that the alkaline treatment also greatly reduces the sensitivity. The alkaline solution masks the effect of Cr^{+++}, but since this effect is relatively slight, and since the manner of its complete elimination is indicated, it is proposed that in general the colorimetric determination of aluminum with aurintricarboxylic acid be carried out at a fixed acid *P*H.

The yellow color of the dye in alkaline solution and its red color in acid solution practically neutralize each other at a *P*H of 6.3 in buffered solution. Hence a *P*H of 6.3 was adopted as the fixed acid *P*H at which comparison is made.

In the present procedure, adapted to colorimeter comparison, X cc. of the aluminum solution at about *P*H 6.3 is diluted with $(12-X)$ cc. of water, and 5 cc. of a buffer (*P*H 6.3) is added. The buffer is 4 M ammonium acetate containing some hydrochloric acid. After shaking, 1 cc. (per 0.01 mg. of aluminum) of a 0.1% solution of the ammonium salt of the dye is added and the mixture is again thoroughly shaken. The maximum color intensity is reached in about fifteen minutes. The color is stable over a period of many hours. As in alkaline solution,[5,6] the measured intensity is not linearly proportional to the quantity of aluminum. For amounts of aluminum less than 0.002 mg., comparison must be made in Nessler tubes.

The non-interference of other elements originally observed is found to obtain also under the present conditions. A blank result was given by the following: 10 mg. of Ba^{++}, Ca^{++}, Mg^{++}, Zn^{++}, Pb^{++}; 0.1 mg. of Co^{++}, Cu^{++}; 5 mg. of $PO_4^{\equiv}$. One mg. of SiO_2 from a solution of a crystallized silicate gave a color equivalent to 0.001 mg. of aluminum, no doubt due to an impurity of aluminum.

As is well known, Fe^{+++} is a major source of interference and must be eliminated. Measured in a colorimeter, 0.010 mg. of Fe gave a color equivalent to 0.005 mg. of aluminum.

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(2) Associate chemist, U. S. Bureau of Mines, Nonmetallic Minerals Experiment Station, Rutgers University, New Brunswick, N. J.

(3) Hammett and Sottery, THIS JOURNAL, **47**, 142 (1925).

(4) Yoe and Hill, *ibid.*, **49**, 2395 (1927).

(5) Myers, Mull and Morrison, *J. Biol. Chem.*, **78**, 595 (1928); Schwartze and Hann, *Science*, **69**, 169 (1929).

(6) Winter, Thrun and Bird, THIS JOURNAL, **51**, 2721 (1929).

Cr^{+++} in chrome alum solution was found to react slowly with the dye. The green Cr^{+++} reacts more rapidly than the blue; increase of temperature hastens the reaction. At room temperature, 0.10 mg. of green Cr^{+++} gave after fifteen minutes a color equivalent to 0.0005 mg. of aluminum, after thirty minutes 0.001 mg. of aluminum, and after eighteen hours 0.008 mg. of aluminum. It is seen that Cr^{+++} is but a slight source of interference under the conditions. Complete elimination of this interference is indicated by an increase in *P*H dependent on the quantity of Cr^{+++} with, of course, a resultant decrease in over-all sensitivity of the test.

Under the present conditions, the aurin reaction with aluminum is extremely delicate. A faint pink is obtained with 0.0001 mg. of aluminum, so that the sensitivity is about twenty times that reported by Yoe and Hill under alkaline conditions. Besides the elimination of fading and of carbon dioxide evolution, turbidity in the presence of foreign ions such as that observed by Yoe and Hill is also obviated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Structure of the Chloraloses, Alpha and Beta-Glucochloraloses

BY ANNE WHITE WITH R. M. HIXON

The literature regarding the structure of the chloral derivatives of glucose and of xylose was reviewed in the previous publications[1] of this series. The experimental data of these previous publications as well as the data presented below are summarized for glucose in Table I and for xylose in Table II.

Referring to Table I, the condensation of glucose with chloral under the specified conditions yields a crystalline mixture from which can be isolated dichloralglucose (A), dichloralglucose (C), and dichloralglucose (D). Boiling the mother liquor from this separation causes β-glucochloralose to separate. Neutralization or ether extraction of the mother liquor remaining after the separation of the β-glucochloralose yields α-glucochloralose. The condensation of β-glucochloralose with chloral yields dichloralglucose (A) and dichloralglucose (C). The condensation of α-glucochloralose with chloral yields dichloralglucose (E). A fifth dichloralglucose (B) is reported by Pictet and Reichel.[2]

Repeated methylations[1a] of β-glucochloralose introduced only three methyl groups to give trimethyl-β-glucochloralose. This indicated that

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(1) (a) Coles, Goodhue and Hixon, THIS JOURNAL, **51**, 519 (1929); (b) Goodhue, White and Hixon, *ibid.*, **52**, 3191 (1930).

(2) Pictet and Reichel, *Helv. Chim. Acta*, **6**, 621 (1923). The dichloralglucoses A and B were so designated by Pictet and Reichel. Further descriptions of dichloralglucoses A, C and D are given by Ross and Payne, THIS JOURNAL, **45**, 2363 (1923).