research will deal with weak acids and their neutral salts, with the aim of studying hydrolysis and the dissociation-constant of water. Another line of work to be carried out with the bomb will consist in the determination of the dielectric constant of water up to 306°. Then the attempt will be made to extend all these measurements to the critical temperature.

THE ELECTROLYTIC PREPARATION OF IODOFORM FROM ACETONE.

By J. E. Teeple.

Received December 4, 1903.

There are two general methods in use in organic laboratories for the preparation of iodoform. According to the first one a rather concentrated potassium carbonate solution is treated with alcohol and iodine at a temperature of about 70°. Only 20 to 30 per cent. of the iodine is converted into iodoform. According to the second method[1] a dilute sodium hypochlorite solution (made from bleaching powder and sodium carbonate) is added to a dilute solution of potassium iodide, acetone and sodium carbonate at room temperature. This method gives a very good yield, the ordinary student being easily able to obtain over 80 per cent. of the theoretical yield as computed from the potassium iodide.

At the time E. Schering[2] obtained his patent for the electrolytic preparation of iodoform, only the first of the above methods was in use. So although his claim is broad enough to cover the electrolysis of any warm alkali- or alkali earth-iodide solution in the presence of alcohol, aldehyde or acetone, in practice it seems to have been restricted to the electrolysis of a hot aqueous alcohol solution of potassium iodide and potassium carbonate, through which a current of carbon dioxide was passed. This method has been studied repeatedly and the conditions have been found under which a very satisfactory yield may be obtained, but the preparation from acetone instead of alcohol would be preferable for two reasons: first, when alcohol is used 10 atoms of iodine are required to produce 1 mol. of iodoform, while when acetone is used only 6 atoms of iodine are required per molecule of iodoform, :

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[1] Suilliot and Raynaud: *Bl.*, 1, 4 (1889).

[2] D. R. P. 29,771, March 7, 1884. Friedländer: "Fortschritte der Theerfarbenfabrikation," 1, 576.

$$10I + C_2H_6O + H_2O = CHI_3 + 7HI + CO_2$$
$$6I + C_3H_6O + H_2O = CHI_3 + CH_3COOH + 3HI$$

and second, because acetone is much cheaper than alcohol.

Various attempts to substitute acetone for alcohol in the above method have not been entirely successful. Elbs and Herz[1], using 27 cc. of acetone, 93 cc. of water, 10 to 15 grams of potassium iodide, 3.6 to 12 grams of soda, 0.5 to 4 amperes per square decimeter current density, and working at 20° to 40° obtained no pure iodoform, but instead obtained iodized ketones, free iodine and a little red-brown iodoform. The substitution of sodium hydroxide for the soda did not help matters. During this present year, however, Abbott[2], after a series of experiments, in which he varied the temperature, current density, amount of carbonate and iodide, concentration, rate of adding the acetone, etc., was able to obtain a 59 per cent. yield under the following conditions:

In a porous cup place an anode solution of 10 grams of potassium iodide, 6 grams of sodium carbonate, and 100 cc. of water. For the cathode solution use a 10 per cent. sodium carbonate solution, electrolyze at a temperature of 75° and a current density not above 1.35 amperes per sq. dm., adding 5.5 cc. of acetone to the anode solution in portions of 0.5 cc. each ten minutes.

As will be seen, these investigators have both attempted to make an electrochemical application of the first of the two general laboratory methods for the preparation of iodoform quoted above, simply substituting acetone for alcohol. But the reactions of acetone and alcohol in forming iodoform are essentially different. Alcohol must first be oxidized to aldehyde, a step which is not required when acetone is used; so, if one wished to use acetone for the preparation of iodoform, the obvious thing to do was to apply the method of Suilliot and Raynaud electrochemically, if possible. With regard to their method they suggest that possibly potassium hypoiodite is first formed, which then reacts with the acetone as follows:

$$3KI + KClO = 3KCl + 3KIO$$
$$3KIO + C_3H_6O = CHI_3 + KC_2H_3O_2 + 2KOH.$$

Starting with the assumption that this idea was correct, I attempted to electrolyze potassium iodide in the presence of acetone under conditions that would favor the formation of potassium

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[1] *Ztschr. Electrochem.*, 4, 118.

[2] *J. Phys. Chem.*, 7, 84 (1903).

hypoiodite. As far as one could judge from the work that has been done on the electrolytic formation of hypochlorites, these conditions would be, low anode current density and very high cathode current density, no excess of alkali or alkali carbonate, thorough stirring, and work at room temperature,[1] *i. e.,* have very dilute potassium hydroxide (not carbonate) always acting on a slight excess of iodine.

In the earlier experiments, I attempted to realize these conditions by electrolyzing a neutral solution of potassium iodide containing a small amount of acetone, having the electrodes separated by a diaphragm, and adding dilute alkali to the anode solution as needed to combine with the free iodine; but the current yield here was usually only about 50 per cent. of what would be expected from the above equations. This method, however, was soon abandoned, for experiment showed that when dilute alkali was slowly added to iodine in the presence of acetone a 50 per cent. yield according to the equation

$$2I + 2KOH = KI + KIO$$

was about all that could be obtained; *i. e.,* only about one-fourth of the iodine was transformed into iodoform, the rest forming potassium iodide and iodate. If, however, acid was now added to the filtrate all the iodine lost by the formation of iodate according to the equation

$$6KOH + 6I = 5KI + KIO_3.$$

was set free again according to the equation

$$5HI + HIO_3 = 6I + 3H_2O.$$

The addition of alkali now reconverted about one-fourth of this iodine into iodoform. By repeating the additions of acid and alkali as long as the acid precipitated much iodine, a yield of 92 to 94 per cent. of that theoretically required could be obtained.

From the above experiments it was evident that even very slight excess of alkali must be avoided, since it tended to increase the iodate formation, and that this could not be done when alkali was added as needed to the anode solution. Consequently in all of the following experiments no diaphragm was used. The arrangement of the apparatus was as follows:

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[1] This differs from the observation of N. Lewin (*Ztschr. Electrochem.*, **6**, 464 (1900)), who found that 3 per cent. alkali favored the formation of hypoiodite; and from the statement of Dony-Hénault (*Ztschr. Electrochem.*, **7**, 57, (1900)) who, estimating the amount of hypoiodite by the color and odor of the solution, decided that a temperature of about 65° was most favorable, at least in the presence of alkali carbonate.

The electrolyzing cell was a rather deep crystallizing dish; the anode a piece of platinum foil of 0.4 sq. dm. surface lying on the bottom of the dish; the cathode a piece of platinum wire just dipping beneath the surface of the liquid. A stirrer driven by a small motor kept the solution in active motion. The cell stood in a bath and the temperature was usually kept at about 25° or lower. The solution consisted of 25 to 30 grams of potassium iodine, 200 to 250 cc. of water, and 2 cc. of acetone. The anode current density was 1 to 6 amperes per sq. dm.; the voltage was 3 to 12, according to the concentration and temperature of the solution, the current density, and the distance apart of the anodes. A copper voltameter and an ammeter were connected in series.

A perfectly neutral solution of potassium iodide was now electrolyzed in the presence of acetone without a diaphragm, but again the current yield was only about 50 per cent.

If we imagine the reactions to proceed in the following steps,

$$\begin{aligned} 6KI + 6H_2O &= 6KOH + 6I + 6H \\ 6KOH + 6I &= 3KI + 3KIO + 3H_2O \\ 3KIO + C_3H_6O &= CI_3COCH_3 + 3KOH \\ CI_3COCH_3 + KOH &= CHI_3 + KC_2H_3O_2, \end{aligned}$$

we again see the reason for the low yield, since each 6 molecules of potassium iodide decomposed leaves an excess of 2 molecules of potassium hydroxide, or one-third of the potassium liberated is left in the solution as potassium hydroxide. Evidently we must neutralize this excess of alkali as fast as it is formed. This method led to the desired results, enabling me to obtain almost a theoretical current yield. In selecting the reagent to neutralize this alkali, one has quite a wide range of choice: among others, carbon dioxide, hydrochloric acid, hydriodic acid, and iodine were tried with success.

NEUTRALIZING WITH CARBON DIOXIDE.

200 cc. of water, 25 grams of potassium iodide, 2 cc. of acetone, were electrolyzed for 175 minutes at 25°, the anode current density being 1.8 amperes per sq. dm. A rapid current of carbon dioxide was passed in for fifty-five minutes (about one-third of the total time). Then the electrolysis was continued until the liquid became colorless. 2.43 grams of copper had deposited in the voltameter, corresponding to a theoretical yield of 5.01 grams of iodoform. 4.45 grams of iodoform were obtained, *i. e.*, a cur-

rent yield of 89 per cent. The product, however, was a little darker than usual and had an odor of iodoacetones. In a continuous process the potassium carbonate or bicarbonate would accumulate in the solution, which would be a disadvantage, so it seemed wiser to neutralize the alkali with an acid giving a neutral salt.

NEUTRALIZING WITH HYDROCHLORIC ACID.

200 cc. of water, 30 grams of potassium iodide, and 2 cc. of acetone, were electrolyzed for forty-five minutes, the anode current density being 4.7 amperes per square decimeter. As the solution was not cooled, the temperature rose to 35°. During the electrolysis hydrochloric acid was gradually added in an amount just sufficient to keep the solution colored with iodine, until just before completion of the experiment when it was allowed to become alkaline to remove any iodoacetone that might still been present. 1.66 grams of copper was deposited, corresponding to 3.42 grams of iodoform. 3.05 grams of iodoform were obtained, corresponding to a 90 per cent. current yield. In working with this method potassium chloride and potassium acetate would be the only by-products to accumulate in the solution, as the hydrochloric acid would decompose all iodate formed, setting free the iodine again. If we neutralized with hydriodic acid instead of hydrochloric acid, the only by-product formed would be potassium acetate.

NEUTRALIZING WITH HYDRIODIC ACID.

225 cc. of water, 25 grams of potassium iodide, and 2 cc. of acetone were electrolyzed at 25° for fifty minutes, the anode current density being 2.5 amperes per sq. dm. Hydriodic acid (freed from iodine) was added as needed to keep the iodine color present. In the voltameter 0.995 gram of copper was deposited, corresponding to 2.05 grams of iodoform. 1.96 grams of iodoform was obtained, equivalent to a current yield of 96 per cent.

A still better method, or at least a more practical one, is to neutralize the potassium hydroxide by additions of iodine.

NEUTRALIZING WITH IODINE.

We may consider the iodine to react as follows:

$$2KOH + I_2 = KI + KIO,$$

and the hypoiodite formed then to react with acetone,

$$3KIO + C_3H_6O = CHI_3 + KC_2H_3O_2 + 2KOH,$$

thus setting free more potassium hydroxide. A little consideration shows that the total amount of iodine needed is ${}^1/_3 + {}^1/_9 + {}^1/_{27}$, etc., $= {}^1/_2$, *i. e.,* the amount of iodine needed to be added is just one-half of the amount set free by the electric current. Also one-half of the iodine added should go to form iodoform.

225 cc. of water, 25 grams of potassium iodide, 2 cc. of acetone, were electrolyzed for sixty-five minutes, the anode current density being 2 amperes. 1.56 grams of iodine was added at intervals, keeping the solution just slightly colored. In the voltameter 1 gram of copper was deposited, corresponding to 2.06 grams of iodoform. The iodine added should have produced 0.80 gram more of iodoform, making 2.86 grams in all. 2.70 grams were obtained, equivalent to a current yield of 94.4 per cent.

The yield was always better with an anode current density of 1 to 2 amperes per sq. dm., but when the stirring is thorough this may be increased to 6 to 8 amperes per sq. dm., and still a current yield of 89 to 91 per cent. be obtained. For example, the following experiment was tried with an anode current density of 9 amperes per sq. dm.

250 cc. of water, 35 grams of potassium iodide, 2 cc. of acetone and 1.44 grams of iodine. The iodine in this case was added at the beginning and the solution electrolyzed until colorless. 0.83 gram of copper was deposited, equivalent to 1.71 grams of iodoform. The iodine added should have produced 0.74 gram more, making a total theoretical yield of 2.45 grams. I obtained 2.24 grams, equivalent to a current yield of 91 per cent.

The only factors of much importance then, in the electrolytic formation of iodoform from acetone are, avoidance of an excess of an alkali, the temperature not being allowed to rise enough to cause the formation of much potassium iodate, and a thorough stirring, so that the very dilute solution of iodine produced at the anode may always react with a very dilute solution of potassium hydroxide produced at the cathode, a comparatively low anode current density to prevent the formation of iodate and a high cathode density to prevent the reduction of hypoiodite already formed.

The method of neutralizing the alkali by additions of iodine would likely be easiest to adapt to a continuous process. For every molecule of iodoform formed, one would add 1 molecule of acetone, 1 molecule of potassium iodide and 2 atoms of iodine to the solution to restore it exactly to its original condition, except for the presence of the 1 molecule of potassium acetate.

To see how much this accumulation of potassium acetate in the solution would decrease the yield, the following experiment was tried: 150 cc. of water, 18 grams potasssium iodide, and 2 cc. of acetone were electrolyzed; current density about 2.5 at the anode; 1.685 grams of copper were deposited in the voltameter, corresponding to 3.475 grams of iodoform; 2.89 grams of iodine were added, equivalent to 1.54 grams of iodoform, making a total theoretical yield of 5.015 grams; 4.60 grams were obtained, a yield of 92 per cent. (The stirring in these experiments was not quite as efficient as in most of the preceding ones.)

I now added sufficient potassium iodide and acetone to the filtrate to restore it to its original condition except for approximately 1 gram of potassium acetate which had been formed, and in addition added 18 grams of potassium acetate, and electrolyzed as before: 1.86 grams of copper in the voltameter correspond to 3.84 grams iodoform; 2.68 grams of iodine added should form 1.39 grams iodoform, making in all 5.23 grams; obtained 4.20 grams iodoform, a yield of 80 per cent.; so when the potassium acetate has accumulated until it exceeds the amount of potassium iodide and the solution contains over 12 per cent. of it, the yield is lowered at most not over 15 per cent.

Perhaps the most efficient stirring can be obtained by using a rotating electrode. This was tried in the following experiment, using a rotating anode: 100 cc. of water, 10 grams of potassium iodide, 1 cc. of acetone, electrolyzed at 18° with an anode current density of 5.2 amperes per sq. dm.; copper in voltameter 0.49 gram, corresponding to 1.01 grams of iodoform. Iodine added 0.87 gram which should form 0.45 gram iodoform, making a total of 1.46 gram. I obtained 1.38 grams, being a yield of 94.5 per cent. This corrsponds to 3.34 grams iodoform per ampere-hour as opposed to 1.43 grams from alcohol by Elbs and Herz, and 1.46 grams from acetone by Abbott.

The iodoform obtained, without further purification, melted at 119° and was completely soluble in carbon disulphide.

By working in a similar manner, I have also been able to prepare chloroform, but the yields so far obtained have not been as satisfactory as in the case of iodoform.

CORNELL UNIVERSITY,
November, 1903.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

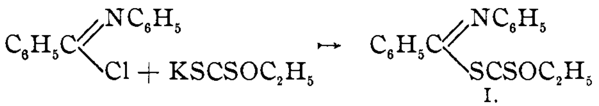
ON SOME THIODIACYLANILIDES.

BY GEORGE S. JAMIESON.

Received December 15, 1903.

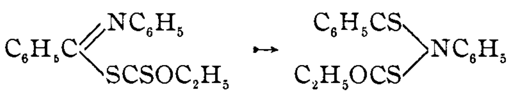
THE object of the work described in this paper was to investigate the compounds formed by the reaction of imide chlorides upon some salts of thioacids and thioanilides.

Tschugaeff[1] has described a series of colored compounds, which he obtained by the action of anilidimide chlorides upon potassium xanthates. He considered these compounds to be imidothioanhydrides, or as he called them, imidoxanthides (Formula I). He represents the reaction, in the case of benzanilidimide chloride as follows:



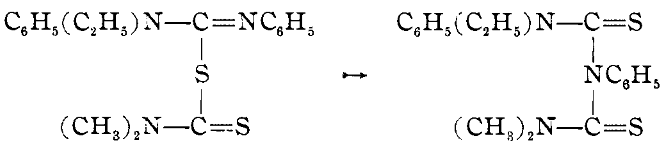
I.

From work done in this laboratory on analogous oxygen compounds[2] it would be expected that a compound having the structure represented by Formula I would undergo a molecular rearrangement, on heating, into the isomeric diacylanilide form as follows:



I. II.

Billeter[3] has shown that a rearrangement takes place in the case of certain imidothiocarbamic anhydrides. He states that dimethylethyl-diphenylpseudodithiobiuret III, at 100° is transformed smoothly into dimethylethyldiphenyldithiobiuret IV.



$$\begin{array}{lcl} C_6H_5(C_2H_5)N-C=NC_6H_5 & & C_6H_5(C_2H_5)N-C=S \\ \qquad\qquad\quad | & & \qquad\qquad\quad | \\ \qquad\qquad\quad S & \longmapsto & \qquad\qquad\quad NC_6H_5 \\ \qquad\qquad\quad | & & \qquad\qquad\quad | \\ (CH_3)_2N-C=S & & (CH_3)_2N-C=S \end{array}$$

III. IV.

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[1] *Ber. d. chem. Ges.*, **35**, 2470 (1902).

[2] Wheeler and Johnson: *Am. Chem. J.*, **30**, 24 (1903).

[3] *Ber. d. chem. Ges.*, **26**, 1688 (1893).