[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE CONSTITUTION OF THIOCHRONIC ACID.[1]

BY C. LORING JACKSON AND S. A. BEGGS.

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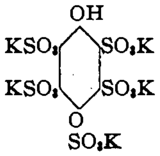
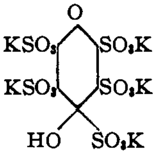
Potassium thiochronate was first prepared by the action of alkaline sulfites on chloroanil by Hesse,[2] and later studied by Grieff[3] and still more fully by Graebe,[4] who assigned to it Formula I, which has been universally adopted, although to make it agree with the analyses it is necessary to assume that this salt retains a molecule of water of crystallization even at 160°.


(I)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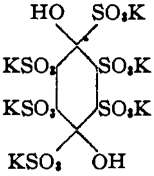
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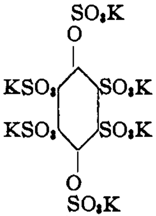
(IV)

Our attention was called to thiochronic acid by encountering it in the course of a research on the action of alkaline sulfites on tetrabromo-*o*-quinone,[5] and we were struck by the fact that Graebe's formula (I) does not explain several of the properties of the acid, thus:

(*a*) It is yellow, but there is no structure, in Formula I, which would account for this yellow color, for sulfonic acids, hydroquinones, and phenol sulfuric esters are all colorless.

(*b*) Baumann[6] has prepared many of the phenol sulfuric esters by the action of potassium pyrosulfate on the potassium salt of the phenol, and has found that, while easily decomposed by acids, the phenol sulfuric ester is very stable toward alkalies, since it can be boiled with a strong solution of potassium hydroxide without decomposition, and decomposes only slowly, even when heated with it in a sealed tube at 150°. The thiochronate therefore can hardly be a phenol sulfuric ester, because it is easily decomposed by potassium hydroxide with only moderate heating.

(*c*) The product of this decomposition is the potassium salt of euthiochronic acid, ($C_6(OH)_2(SO_3H)_2O_2$) an undoubted quinone, the appearance of which would not be expected from Formula I. In fact Graebe,

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Sydney Adams Beggs.

[2] *Ann.*, 114, 324 (1860).

[3] *Jahrb.*, 1863, p. 392.

[4] *Ann.*, 146, 40 (1868).

[5] The results of this research will appear in a later paper.

[6] *Ber.*, 11, 1913 (1878).

in order to explain this transformation, is obliged to assume that SO_3K, splits off from one of the atoms of oxygen and hydrogen from the other, giving acid potassium sulfite and leaving the quinone oxygens of the euthiochronate. While it must be admitted that such a reaction is not impossible, we have not succeeded in finding any similar case in the chemical literature, so that, if this explanation is adopted, it can be only as a strained hypothesis; and yet, this is the only way of explaining this action according to (I), since an experiment tried by us has excluded the more probable theory that the oxygen of the air entered into the reaction, converting into the quinone the potassium salt of the hydroquinone,

$$C_6(SO_3K)_4(OK)_2,$$

which would be the first product of the action of potassium hydroxide on a substance with this formula. We found, however, that the euthiochronate was obtained easily, when the potassium hydroxide acted on the thiochronate in an atmosphere of hydrogen.

(*d*) A fourth objection to Formula I is found in the very slight stability of Baumann's phenol sulfuric esters, when alkalies were not present. Thus the potassium salt of resorcinol monosulfuric ester, the nearest relation to (I), of which Baumann gives the properties, decomposed frequently when its solution stood at ordinary temperature; and the phenol compound was decomposed by moist air, or when the attempt was made to dry it by heat; while the thiochronate is stable under all these conditions. It should be remembered, however, that the behavior of the sulfuric ester group might, perhaps, be modified by the presence of so many sulfonic groups in the thiochronate, and this, to a certain extent, weakens the force of objections (*b*) and (*d*).

These objections to Graebe's formula (I) induced us to consider a second formula (II) for potassium thiochronate, which is formed from quinone tetrasulfonate, $C_6(SO_3K)_4O_2$, by the addition of a molecule of acid potassium sulfite to one of the carbonyl groups of the quinone instead of to both, as in Formula I. The four objections to Graebe's formula do not apply to (II).

(*a*) The yellow color is accounted for by the remaining quinone oxygen. (*b*) The easy decomposition by potassium hydroxide would be expected, for, although we know of no similar quinone derivatives, a substance with Formula II belongs in the same class as the addition compounds of acid potassium sulfite with ketones, or aldehydes, all of which, as is well known, are easily decomposed by alkaline hydroxides.

(*c*) Such decompositions yield the ketone, or aldehyde, just as thiochronic acid yields euthiochronic acid. The fact that such addition compounds of other quinones with acid potassium sulfite are not known may be due to the ease with which the quinone oxygen atoms are reduced by the sulfite; whereas the quinonetetrasulfonate, in our case, might well continue unreduced long enough for the addition to take place, in view of the difficulty with which hydroquinones are formed from quinones highly charged with negative radicals, like the euthiochronate or chloroanilic acid. That the ring structure of the quinone would not prevent the addition of acid potassium sulfite is shown by the formation of addition compounds from cyclopentanone[1] and cyclohexanone.[2]

(*d*) In stability also, the thiochronate stands nearer to this class of compounds than to the phenolsulfuric esters.

The adoption of (II) necessitates the discussion of another set of reactions of the thiochronate. By the action of water at 130°–140°, or heating with hydrochloric acid, or by treatment with reducing agents the thiochronate is converted into the potassium salt of hydroquinonedisulfonic acid, $C_6H_2(SO_3K)_2(OH)_2$, and at first sight this formation of a hydroquinone seems to agree better with (I) than with (II); but this is only apparent, since in all these experiments a reducing agent is present, and this would convert the quinone, formed at first according to (II), into the hydroquinone, which is the final product.

The arguments given above seemed to us to justify the adoption of (II) instead of (I), but, when we had arrived at this point, we were so fortunate as to stumble on new experimental evidence so convincing that it amounts to a proof of the correctness of (II). In the hope of determining the constitution of euthiochronic acid, for use in the research on *o*-quinonesulfonic acids already alluded to, we treated dibromodiphenoxyquinone with acid potassium sulfite. The principal product was potassium thiochronate, so that the experiment threw no light on the structure of euthiochronic acid, but in addition to this we obtained a small quantity of a white salt containing $(SO_3K)_6$, which would be represented by Formula III, if (II) is adopted for the thiochronate. It is formed, therefore, by an addition of acid potassium sulfite to the second quinone carbonyl in the same way that (II) was formed by addition to the first, and such a compound would be expected in this case. On the other hand, we cannot bring this substance into harmony with (I), since according to that formula both the quinone carbonyls have taken part in the formation of the thiochronate, and this has left no way in which acid potassium sulfite can cause the introduction of a sixth SO_3K. And it is no better for Formula I, if we suppose that a compound with $(SO_3K)_6$ could be formed from it in some unexplained way, for this could have only Formula IV. This is inadmissible, because such a compound must give hydroeuthiochronic acid by the action of potassium hydroxide in an atmosphere of hydrogen, that is, under these conditions it could not produce the quinone euthiochronic acid, which was actually obtained by us in an experiment, and is

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[1] Claisen, *Ber.*, 8, 1257 (1875); Pinner, *Ibid.*, 15, 594 (1882).

[2] Baeyer, *Ann.*, 278, 101 (1894).

the natural product, if our acid had the constitution represented by (III). The white color is also explained by this formula, as the last of the chromophoric groups has been modified. We propose for our new compound the name hexachronic acid.

To sum up our arguments, Formula II explains, while (I) does not, the yellow color, the stability especially toward alkalies, the formation of euthiochronic acid and of hexachronic acid.

Other unsuccessful attempts to determine the constitution of euthiochronic acid led to an unexpected result, for, when bromoanilic acid was treated with acid potassium sulfite, both the atoms of bromine were replaced by hydrogen, giving 1,2,4,5-tetrahydroxybenzene. We have been able to find only a few other cases in which bromine has been replaced by hydrogen in aromatic compounds under the influence of sulfites, or sulfurous acid. Stenhouse obtained a partial conversion of bromoanil into tribromohydroquinone, when sulfur dioxide acted on it in boiling water;[1] the formation of dianilino-*p*-quinoneanil from dianilinobromoquinoneanil by an ethereal solution of sulfur dioxide[2] has been observed; likewise the formation of the corresponding dibromo compounds from tribromodinitro- and tribromotrinitrobenzene by alcoholic sodium sulfite.[3]

The marked difference between the action of the acid sulfite on dibromodiphenoxyquinone, giving thiochronate and hexachronate, and on dibromodihydroxyquinone (bromoanilic acid), giving 1,2,4,5-tetrahydroxybenzene, is probably to be ascribed to the presence of free sulfurous acid in the latter case. Accordingly we tried to exclude this by using potassium bromoanilate instead of bromoanilic acid. To our surprise, each addition of the salt to the acid potassium sulfite solution was accompanied by a brisk effervescence of sulfur dioxide, so that the conditions were the same as in the previous experiment, and no light was thrown on the subject. The unexpected evolution of sulfur dioxide is undoubtedly due to the fact that the $C_6Br_2(OK)_2(OH)_2$ formed at first from the bromoanilate is acid enough to decompose the sulfite. That the replacement of the bromine was not due to nascent sulfur dioxide was shown by treating potassium bromoanilate with free sulfur dioxide, when the bromine was eliminated with no more trouble than in the preceding experiment. Bromoanilic acid, on the other hand, when treated with sulfurous acid, loses bromine much less easily than the bromoanilate. It is to be observed that the bromine atoms in bromoanilic acid stand between two atoms of oxygen, and therefore in the position most favorable to their replacement by hydrogen, as has been shown by numerous experiments tried in

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[1] *Ann. Supp.*, 8, 20 (1872). Similar work with chloroanil, *Ibid.*, *Supp.*, 6, 214 (1868).

[2] Jackson and Porter, *Am. Chem. J.*, 30, 518 (1903).

[3] Jackson and Earle, *Ibid.*, 26, 46 (1901).

this laboratory. Whether the loosening of the bromine is due to two hydroxyls, or to a hydroxyl and a quinone oxygen, that is, whether the quinone is reduced before or after the removal of the bromine cannot be decided on our present data.

Tin and hydrochloric acid also convert bromoanilic acid into 1,2,4,5-tetrahydroxybenzene. The two atoms of oxygen therefore produce the same loosening effect on the bromine that has been observed previously with nitro or amino groups alone, or nitro in conjunction with hydroxyl groups.[1]

We found that the 1,2,4,5-tetracetoxybenzene melted at 226–227° (uncorr.) instead of at 217°, as given by Nietzke and Schmidt.[2] The 1,2,4,5-tetrahydroxybenzene yielded a well crystallized black tetrahydroxyquinhydrone, when its solution was exposed to the air after acidification with hydrochloric acid.

Experimental.

Preparation of Potassium Thiochronate.—The following method for preparing thiochronic acid gives a better yield than those previously described:[3] Ten grams of chloroanil were heated with a solution of 50 g. of dipotassium sulfite (prepared just before the experiment) in 100 cc. of water. After boiling for 20 minutes the liquid was allowed to cool and the yellow solid washed with cold water and recrystallized from boiling water. The yield was about 9 g., that is, 32% of the theoretical.

Action of Potassium Hydroxide on Potassium Thiochronate in an Atmosphere of Hydrogen.—A slow stream of hydrogen was passed through two Erlenmeyer flasks, escaping from the last through a Bunsen valve to prevent the entrance of air. The first of these flasks contained the solution of potassium hydroxide, the second 10 g. of potassium thiochronate in 50 cc. of water. After the apparatus was full of hydrogen, the contents of each flask were boiled, until all the dissolved air had been expelled, when, by tipping the first flask, the potassium hydroxide was forced over by the hydrogen into the second. The solution turned very dark at first, and then became light yellow, and deposited a yellow solid, which was filtered out after the liquid had cooled in the atmosphere of hydrogen. The yellow solid was recognized as the tetrapotassium salt of euthiochronic acid by the addition of a drop of dilute hydrochloric acid, which converted it into the very characteristic vivid red tripotassium euthiochronate, which was again changed to the yellow tetrapotassium salt by a few drops of potassium hydroxide.

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[1] Schliepper, *Ber.*, **25**, 553 (1892); **26**, 2465 (1893); Hübner, Petermann, *Ann.*, **149**, 135 (1869); Bässmann, *Ibid.*, **191**, 244 (1878); Zincke, *Ber.*, **5**, 792 (1872); Jackson, Calvert, *Am. Chem. J.*, **18**, 467 (1896).

[2] *Ber.*, **21**, 2378 (1888).

[3] Hesse, *Ann.*, **114**, 324 (1860); Graebe. *Ibid.*, **146**, 40 (1868).

Action of Acid Potassium Sulfite on Dibromodiphenoxyquinone.—One gram of dibromodiphenoxyquinone was heated on the steam bath in an Erlenmeyer flask with a solution of 5 g. of acid potassium sulfite in 10 cc. of water, but, as there was no action, enough potassium hydroxide was added to start a reaction. When the solution had turned brown, it was filtered, and as it cooled it deposited yellow crystals. Seven grams of the dibromodiphenoxyquinone yielded about 6.5 g. of this crude product, which, on crystallization from water, was found to consist principally of a yellow compound mixed with a small amount of a white one. The yellow substance, which contained no bromine, was purified by six crystallizations from water.

Subst. 0.3130, 0.3354; loss at 120° 0.0227, 0.0241.
Calc. for $C_6(SO_3K)_5O_2H.4H_2O$ ($3H_2O$ lost), 7.00; found: H_2O, 7.25, 7.19.
Subst. 0.2891, 0.2854, K_2SO_4 0.1772, 0.1753.
Calc. for $C_6(SO_3K)_5O_2H.H_2O$, K, 27.28; found: K, 27.51, 27.57.

These analyses show that it is potassium thiochronate, which, according to Graebe, contains 4 molecules of water, only 3 of which are given off at 120°; and this conclusion was confirmed by the fact that our substance showed the two characteristic reactions of the thiochronate. An aqueous solution gave a white precipitate with barium chloride, which melted when the supernatant liquid was boiled, and when treated with potassium hydroxide the boiling solution was converted into potassium euthiochronate, recognized by the yellow color of its tetrapotassium salt, which crystallized out on cooling, and the red tripotassium salt obtained when a boiling solution of the yellow salt was treated with a few drops of dilute hydrochloric acid.[1]

Potassium Hexachronate, $C_6(SO_3K)_4((OH)(SO_3K))_2.3H_2O$.—The white part of the product from the action of acid potassium sulfite on dibromodiphenoxyquinone was purified by crystallization from water and air dried. It contained no bromine.

Subst. 0.3035, lost at 120° 0.0200; calc. for $C_4(SO_3K)_6O_2.3H_2O$: H_2O, 6.19; found: 6.59.

Subst. dried at 120° 0.2834, 0.1602; K_2SO_4, 0.1824; $BaSO_4$, 0.2741; Calc. for $C_6(SO_3K)_6O_2$, K, 28.65; S, 23.45; found: K, 29.89; S, 23.51.

We propose for this substance the name hexachronic acid.

Properties of Potassium Hexachronate.—White crystals, which lose crystal water at 120°. Very slightly soluble in cold water, more soluble in hot; soluble in alcohol. Strong hydrochloric acid, or nitric acid, produces no visible effect; strong sulfuric acid dissolves it with evolution of sulfur dioxide.

A little of the salt was dissolved in hot water and two drops of a solution of potassium hydroxide were added, which turned the liquid yellow,

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[1] Graebe, *Ann.*, **146**, 40 (1868); Hesse, *Ibid.*, **114**, 313 (1860).

and on cooling yellow crystals were deposited. These were washed with a little cold water, dissolved in hot water, and treated with a drop of dilute hydrochloric acid, when the solution turned red, and on cooling vivid red crystals separated. There can be no doubt, therefore, that this product was potassium euthiochronate. The same result was obtained when the hexachronate was treated with potassium hydroxide in an atmosphere of hydrogen. The yield of hexachronate is very small, most of the dibromodiphenoxyquinone being converted into thiochronate. For this reason we were unable to study other hexachronates.

In an attempt to determine the constitution of euthiochronic acid the 2,5-dichloro-3,6-dibromoquinone was treated with acid potassium sulfite, and a product obtained which seemed to be a mixture of dibromohydroquinonedisulfonate and the corresponding dichlorocompound, as the percentage of potassium fell between those required by the former compound and the chlorobromohydroquinonedisulfonate. As we found the composition of the product was not changed by 5 crystallizations, we decided it was an isomorphous mixture, and abandoned that line of work.

Action of Acid Potassium Sulfite on Bromoanilic Acid.—This was another of our unsuccessful attempts to determine the constitution of euthiochronic acid. A solution of acid potassium sulfite, containing 5 g. in 10 cc. of water, was warmed in an Erlenmeyer flask on the steam bath, and 1 g. of bromoanilic acid was added in small portions at a time, the solution being kept just warm enough to dissolve the bromoanilic acid at once. Each addition produced an effervescence of sulfur dioxide, and a white solid began to separate, after three-quarters of the acid had been added. At the end of the experiment the liquid was allowed to cool, when the white insoluble product was deposited in quantity, and it was found to contain potassium, but neither bromine nor sulfur. On attempting to crystallize it from water, in which alone it was soluble, it oxidized so rapidly that there was no hope of purifying it in this way. Accordingly, it was dissolved in hot water and treated with strong hydrochloric acid in excess, when, on cooling, yellow crystals were deposited. This behavior made it probable that the colorless crystals were the potassium salt of 1,2,4,5-tetrahydroxybenzene, and the yellow crystals 2,5-dioxyquinone. We proceeded as follows to test this supposition: The yellow crystals were covered with strong hydrochloric acid and heated with tin on the steam bath, till a colorless solution was obtained, which, after the excess of tin had been filtered out gave, on cooling, white crystals free from potassium. As the 1,2,4,5-tetrahydroxybenzene has no sharp melting point and the dioxyquinone does not melt, we converted our product at once into the acet compound by warming 2 g. of it with an excess of acetic anhydride and 2 g. of fused sodium acetate in an Erlenmeyer flask on the steam bath. After 20 minutes 50 cc. of water were added, which threw down the acet compound in practically quantitative yield. It was purified by crystallization from glacial acetic acid, until it showed the constant melting point 226–227° (uncorr.). This was a great surprise to us, as Nietzki and Schmidt[1] found that the 1,2,4,5-tetracetoxybenzene melted at 217°. Since isomers are out of the question, we are of the opinion that the melting point given by Nietzki and Schmidt is wrong, because the following analysis shows that our substance is the tetracetoxybenzene:

Subst. 0.1015; CO_2, 0.2012; H_2O, 0.0444; Calc. for $C_6H_2(OC_2H_3O)_4$: C, 54.20; H, 4.52; found: C, 54.06; H, 4.86.

The same compound was obtained when bromoanilic acid was heated with tin and hydrochloric acid, until the solution became colorless. Enough water was then added to dissolve the white solid with the aid of heat and the solution was filtered hot. On cooling, white crystals separated, which, after drying on a porous plate, were heated with acetic anhydride for half an hour. The product was precipitated with hot water, and after one crystallization from glacial acetic acid it melted at 224–225°. This, with the fact that it contained no bromine, was enough to show that it was the 1,2,4,5-tetracetoxybenzene.

If a solution of the potassium 1,2,4,5-tetrahydroxybenzene was acidified with strong hydrochloric acid and exposed to the air for two days, clusters of small, black, slender plates, terminated by a single plane at an oblique angle and showing a yellow reflex, were deposited, which we supposed were the quinhydrone. As an analysis would show nothing, we tested our hypothesis as follows: A mixture of the tetrahydroxybenzene and dioxyquinone with a little water was heated on the steam bath, when, on cooling, the same black substance crystallized out. Upon heating some of the original black crystals in matched watch glasses a yellow sublimate of dioxyquinone was obtained. There can be no doubt, therefore, that our new substance is a tetrahydroxyquinhydrone.

Action of Acid Potassium Sulfite on Potassium Bromoanilate.—The potassium salt was made by adding potassium hydroxide in excess to bromoanilic acid suspended in warmed water. The salt went entirely into solution at one stage of the experiment, and was then precipitated by an excess of the hydroxide. The solid was sucked out on the filter pump and washed with a little alcohol; the preparation, therefore, could contain no free acid. The acid potassium sulfite was freshly prepared, and warmed, and treated with potassium hydroxide, drop by drop, until the odor of sulfur dioxide had disappeared. To such a solution, prepared from 5 g. of potassium hydroxide in 10 cc. of water, the bromoanilate from 1 g. of acid was added in small portions at a time, while the solution was gently warmed. Each addition gave a vigorous effervescence

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[1] *Ber.*, **21**, 2378 (1888).

of sulfur dioxide and the product was white and crystalline. To this excess of strong hydrochloric acid was added and the mixture exposed to the air, when in two days a fine, black, crystalline precipitate of the quinhydrone was formed, showing that the original product was the 1,2,4,5-tetrahydroxybenzene.

A stream of sulfur dioxide was passed into water containing potassium bromoanilate prepared as above. A red precipitate looking like bromoanilic acid was at first formed, but on longer action a colorless product was obtained, which, on exposure to the air, gave black crystals of a quinhydrone, while the aqueous liquid gave a strong test for a bromide.

Bromoanilic acid warmed with water and exposed to a stream of sulfur dioxide lost bromine, as was shown by a test for hydrobromic acid in the filtrate, but this reduction took place more slowly than in the case of the bromoanilate, and was not complete at the end of the reaction.

CAMBRIDGE, MASS.

THE PREPARATION OF DIMETHYLGLYOXIME WITHOUT THE USE OF HYDROXYLAMINE.

BY J. M. JOHLIN, JR.

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Schramm[1] has made the observation that isonitrosomethylacetone—the monoxime of diacetyl—dissociates, when treated with hydrochloric acid, into hydroxylamine, acetic acid and other unidentified products, yielding upon evaporation 81% of the theoretical amount of hydroxylamine hydrochloride. He also observed the formation of minute quantities of ethylmethylacetoximic acid—the dioxime of diacetyl—by the interaction of the liberated hydroxylamine with the still undissociated monoxime. He prepared larger amounts of the dioxime from the monoxime with hydroxylamine.

v. Pechmann[2] has since shown that, in part, the dissociation products of the isonitrosoketone are hydroxylamine and diacetyl. Diels and Jost[3] adapted this property as the basis of a method for the preparation of the diketone. Since dimethylglyoxime has been given added importance through its employment in the qualitative and quantitative determination of nickel, Gandarin[4] has more recently pointed out that it can be more economically prepared by adding hydroxylamine to the sodium salt of the monoxime without isolating the latter as the acid monoxime.

Operating according to the modified method of Diels and Stephan[5] for the preparation of diacetyl, 850 cc. of methylethylketone are mixed

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[1] *Ber.*, 16, 180 (1883).

[2] *Ibid.*, 20, 3213 (1887).

[3] *Ibid.*, 35, 3290 (1902).

[4] *J. prakt. Chem.*, 77, 414 (1908).

[5] *Ber.*, 40, 4337 (1907).