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## PERIODIDES OF CARBONYL COMPOUNDS.

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Some years<sup>1</sup> ago the writer showed that several different types of organic substances, all possessing the carbonyl group in common, united readily with iodine and potassium iodide to form fairly stable triple addition compounds which crystallized readily, were possessed of a strong metallic lustre and could easily be separated into their components. Pure compounds were prepared with benzophenone, benzoic anhydride and other anhydrides, and it was pointed out that there was evidence of the existence of similar compounds of benzanilide and of methyl oxalate. Careful analyses of several of the pure compounds showed that the formulas of some were relatively simple while those of others were complex; and it was also found that a different combining proportion existed for each of the different bodies which were analyzed. In no case was a perfectly stable substance found, that is, there was always noted at least a slow disengagement of iodine at ordinary temperature and in all cases the iodine of the compounds was readily removed by means of very weak reducing agents.

The results which were obtained in this former investigation naturally brought to mind the well known class of periodides of the alkaloids and other organic bases. Concerning the structure of the periodides derived from these strongly basic substances and the essential function of the nitrogen in their constitution, there can be little doubt. When we compare these with the compounds referred to in the previous paragraph, we find that in the latter case we have generally nonbasic, or at the most, feebly basic substances which may take on a metallic iodide in place of the hydriodic acid of an alkaloidal salt, a further addition of iodine in either case giving rise to periodides, or bodies containing loosely combined iodine. It becomes clear that there must be a fundamental difference between the carbonyl periodides and those derived from strong bases.

In 1891, Scholvien<sup>2</sup> described a substance which he supposed to be a periodide of acetophenetidine, having the composition  $C_{20}H_{25}N_2O_4I_3$ . This was patented by Riedel<sup>3</sup> and known as *Iodophenin*. Emery<sup>4</sup> has recently shown that the formula assigned by Scholvien is incorrect and that the latter had a wrong conception of the molecular structure of *Iodophenin*. Emery has proved the correct formula of the body to be  $(C_2H_5OC_6H_4NHC(O)CH_3)_2HI.I_4$  and regards it as an addition compound of

<sup>1</sup> *Am. Chem. J.*, **31**, 256 (1904).

<sup>2</sup> *Pharm. Zentralhalle*, **32**, 311 (1891).

<sup>3</sup> D. R. P. 58409, *Ber.*, **25**, 235 Ref. (1892).

<sup>4</sup> THIS JOURNAL, **38**, 140 (1916).

the 3 constituents. He considers it a periodide of the hydriodide of acetophenetidine and classes it with the well known basic periodides.

The results of Emery's investigation are not surprising in view of the work of Wheeler and Walden<sup>1</sup> who in 1896 showed that acetanilide combines with iodine and hydriodic acid to form the crystalline addition compounds  $(C_6H_5NHCOCH_3)_2HI.I_2$  and  $(C_6H_5NHCOCH_3)_2HI.I_4$ . These compounds they considered analogous to the periodides of substituted ammonium salts.

Wheeler and Walden naturally made no mention of the acetophenetidine periodide of Scholvien and Riedel for, as has already been stated, the discoverers of this substance, through failure to understand its true constitution, had not properly described it. Shortly afterward, Piutti<sup>2</sup> in attempting to prepare other periodides similar to the product obtained by Scholvien and Riedel from acetophenetidine, was able to isolate crystalline periodides, which were composed of *p*-ethoxy- or *p*-methoxy-phenylsuccinimide, potassium iodide and iodine and represented as follows:  $(C_4H_4O_2NC_6H_4OC_2H_5)_2.KI.I_2$  and  $(C_4H_4O_2NC_6H_4OCH_3)_2.KI.I_2$ . Extending his experiments beyond the scope originally intended, he isolated a similar crystalline derivative of succinimide to which he assigned the formula  $(C_4H_5O_2N)_4KI.I_3$ . This formula has been found by the author to be incorrect, as will appear from the experimental part of this article. However, Piutti undoubtedly isolated a crystalline addition compound between succinimide, potassium iodide and iodine which was more or less contaminated with impurities and with 2 of the derivatives of succinimide he isolated analogous compounds which we may assume to have been pure. The discovery of bodies of this type containing potassium iodide in the molecule was of course not expected by Piutti, and he made no attempt to explain their formation. He concluded, however, that the derivatives of a dibasic acid behaved differently from those of a monobasic acid and was misled into this conclusion by assuming the incorrect formula of Scholvien.

Moore and Thomas,<sup>3</sup> in 1914, isolated periodides of benzamide, triple compounds containing as the third constituent sodium iodide, potassium iodide or hydriodic acid. The writer has examined only the potassium iodide compound and as will appear in the experimental part of this article, a different composition must be assigned to it, from the one given by Moore and Thomas. This is a matter of secondary importance, however, and the work of these authors has shown more clearly the relation existing between the periodides of the amide type which had been previously described. They also pointed out that the product described by Curtius<sup>4</sup> in 1890

<sup>1</sup> *Am. Chem. J.*, 18, 85 (1896).

<sup>2</sup> *Gazz. chim. ital.*, 25, 11, 518 (1895).

<sup>3</sup> *THIS JOURNAL*, 36, 1928 (1914).

<sup>4</sup> *Ber.*, 23, 3040 (1890).

and by him represented by the questionable formula



was very likely the benzamide sodium iodide periodide. This substance appears to have been the first of its type to have been isolated.

In 1906, Morgan and Micklethwait<sup>1</sup> described an addition compound of cumarin, hydriodic acid and iodine having the composition  $(\text{C}_9\text{H}_6\text{O}_2)_4 \cdot \text{HI} \cdot \text{I}_3$  and considered it comparable to the periodides  $(\text{C}_7\text{H}_8\text{O}_2)_2 \cdot \text{HI} \cdot \text{I}_2$  and  $(\text{C}_9\text{H}_{12}\text{O}_2)_2 \cdot \text{HI} \cdot \text{I}_2$ , derived from dimethyl pyrone and tetramethyl pyrone respectively by Collie and Steele.<sup>2</sup> More recently Dox and Gaessler<sup>3</sup> have described a periodide of cumarin formed by treating the latter with iodine and potassium iodide and they conclude as the result of their experiments that their product is likely an addition compound of iodine and cumarin. H. Simonis<sup>4</sup> has found that the compound of Dox and Gaessler contains potassium iodide as one of its chemical constituents and has assigned to it the formula  $(\text{C}_9\text{H}_6\text{O}_2)_4 \cdot \text{KI} \cdot \text{I}_3 \cdot \text{H}_2\text{O}$ . He has also prepared similar compounds with other metallic iodides and has pointed out that these are only modifications of the periodide which Morgan and Micklethwait obtained with hydriodic acid.

The periodides of cumarin obviously are closely related to those described earlier by the writer. The other periodides which have been considered here are all those of weak bases and have been generally regarded as analogous to the periodides of the ammonium bases and of the alkaloids. The periodides of a ketone, anhydride, ester or a lactone which contain no nitrogen cannot be classed with the above and it is desirable to explain their structure. The authors who have described the periodides of cumarin have overlooked their similarity to those described by the writer. So far as known Simonis attempted no explanation of structure and, as already stated, Morgan and Micklethwait compared their periodide to the pyrone derivatives of Collie and Steele or the periodides of oxonium salts.

Further study of this entire subject has convinced the writer that the power to form periodides is one common to nearly all types of organic substances, containing the carbonyl group. The difficulty in the investigation of the subject is that of obtaining these periodides in pure condition and to do this it is necessary to choose carefully the proper solvent, or mixture of solvents. In solution the compounds are probably broken up to a limited extent into their constituents, any one of which according to its solubility, may separate with, and contaminate the compound. Many of the compounds are very largely broken up by liquids in which they are only sparingly soluble. This difficulty in purification undoubtedly pre-

<sup>1</sup> *J. Chem. Soc.*, 89, 866 (1906).

<sup>2</sup> *Ibid.*, 77, 1114 (1900).

<sup>3</sup> *THIS JOURNAL*, 39, 114 (1917).

<sup>4</sup> *C. A.*, 12, I, 700 (1918); *Ber.*, 50, 1137 (1917).

vents the isolation of a large number of bodies of this class although evidence of their formation may be obtained in several ways: (1) by grinding the constituents together in a mortar or by fusing them together in a test-tube, whereupon a strong metallic lustre will be developed; (2) by bringing the constituents together in a solvent which although not suitable for purification of the compound, will leave a lustrous residue upon evaporation; (3) by grinding in a mortar then spreading in the air and noting whether the iodine is held in combination or readily volatilizes.

Another difficulty is that most carbonyl compounds of relatively low melting point form liquid products with iodine and potassium iodide and of course there is no way of isolating the pure compounds.

Many common organic liquids which, according to their structures, may belong to one of the classes of ketones, anhydrides, esters, etc., will dissolve a mixture of iodine and potassium iodide to a very large extent, whereas the solubility of either of these latter substances, especially that potassium iodide, is usually limited. Ordinary acetone, acetic ester and even olive oil may be given as examples.

A new type of periodide, that of an ester, methyl oxalate, has been isolated and will be described in the experimental part. Crystals of an acetone periodide separate under certain conditions from a solution of iodine and potassium iodide in the solvent. Most of the members of the barbituric acid group readily form pure periodides. With barbituric acid, itself, 2 distinct bodies have been isolated, this result corresponding, in a way, to that of Wheeler and Walden<sup>1</sup> with acetanilide and of Emery<sup>1</sup> with acetophenetidine. A pure triple compound of diethyl-barbituric acid (*Veronal*) has also been studied.

There can be no other conclusion than that in the case of the periodides derived for organic substances containing no nitrogen we have a class quite distinct from the well known one, derived from amine and alkaloidal bases. The evidence is sufficient to conclude that the carbonyl group is the one which is essentially involved in the structure of these substances and the writer proposes that they be designated as *carbonyl periodides*. He would include in this group all derivatives of amides, anilides, etc., which have heretofore been considered as amino or basic derivatives. The reason for this proposed classification is that the acid amides, anilides, etc., are only weak bases and their periodides formed with hydriodic acid or a metallic iodide are very similar in properties to those of the periodides which contain no nitrogen.

The periodides of dimethyl pyrone and tetramethyl pyrone, to which previous reference has been made, were considered by Collie and Steele to be exactly analogous to the periodides of substituted ammonium compounds and the formation of such periodides was considered by these

<sup>1</sup> *Loc. cit.*

authors as very strong evidence of the existence of oxonium salts,<sup>1</sup> compounds of oxygen analogous to ammonium salts. From the facts presented in this article one would be led to consider the bodies of Collie and Steele as carbonyl periodides for the reason that the carbonyl group in general shows such a tendency to form just such compounds and also that no such compounds derived from oxygen differently combined, are known. This matter, along with that of a satisfactory explanation of the structure of the carbonyl periodides, the writer hopes to be able to take up in the near future.

### Experimental Part.

#### Cumarin Potassium Iodide Periodide.

This substance was evidently discovered by Leach,<sup>2</sup> who employed its formation as a delicate test for cumarin. Dox and Gaessler<sup>3</sup> studied its composition and concluded that while potassium iodide was necessary to its formation, the amount found to be present was too small to be considered in assigning a chemical formula. The writer was led to suspect the true nature of the compound at the time of the appearance of Dox and Gaessler's article and the experimental results described here were finished shortly before the publication of the work of Simonis.<sup>3</sup> The analytical results of the latter differ somewhat from those obtained by the writer, consequently the same formula is not assigned. Water was used by Simonis as a solvent for purification, while the writer used ether mixed with alcohol or ethyl acetate.

If the ingredients, including powdered potassium iodide, are added to ether, they may be brought into solution by boiling the ether under a reflux condenser. On filtering and cooling the solution, the periodide crystallizes readily. Preliminary analyses of a product made in this way showed approximately its composition, but it was further found that the percentages of iodine and potassium iodide were not close enough to a simple molecular ratio for the product to be considered pure. When the ingredients were first dissolved in a small amount of alcohol, or ethyl acetate, and warm ether was added until the periodide just began to separate, the crystalline product obtained, after filtering and cooling the solution, gave much better analytical results. The periodide is only sparingly soluble in ether and probably suffers considerable dissociation in this solvent. The addition of alcohol or ethyl acetate, in which the substance is very soluble, tends to overcome this difficulty.

**Sample I.**—Five and three-tenths g. of cumarin, 3.1 g. of iodine and 1.5 g. of potassium iodide were dissolved completely in 10 cc. of alcohol, and warm ether was added gradually until the point of precipitation was

<sup>1</sup> Collie and Tickle, *J. Chem. Soc.*, **75**, 710 (1899).

<sup>2</sup> Leach, "Food Inspection and Analysis," 3rd Ed., p. 862.

<sup>3</sup> *Loc. cit.*

reached. The warm solution was filtered and the periodide allowed to separate by cooling the solution. In order to remove the solvent as completely as possible, the crystals were pressed tightly while being filtered, and were closely packed upon a porous plate. The dry crystals were washed by covering them with a small amount of the solvent mixture and again packed tightly on a porous plate. Before analysis, the crystalline mass was well broken up by means of a spatula and placed in a vacuum for one-half hour.

Subs., 0.4208; 9.8 cc. 0.1 *N* thiosulfate soln.

Subs., 0.4771; KI, 0.0740.

Subs., 0.3441; cumarin, 0.1853 g.

Subs., 1.7; 0.0037 loss in weight after remaining in a vacuum 2 hrs.

**Sample II.**—The same amounts of the constituents were dissolved in about 20 cc. of ethyl acetate and about 3 volumes of ether was then added. The other details of the operations were the same as in the previous experiment.

Subs., 0.4833; 11.25 cc. 0.1 *N* thiosulfate soln.

Subs., 0.3789; KI, 0.0584.

Subs., 0.3896; cumarin, 0.2075 g.

**Sample III.**—Still another sample was prepared just as the last one, except that a 15% excess of iodine was used. The result was that there was no substantial increase in the percentage of active iodine in the compound.

Subs., 0.5326; 12.75 cc. 0.1 *N* thiosulfate soln.

Subs., 0.5988; 14.45 cc. thiosulfate soln.

	Calc. for $(C_9H_6O_2)_3(KI)_2I_6.H_2O$ .		Found.
	%		%
Active Iodine.....	29.48	I	29.58
		II	29.54
		III	30.51
Potassium Iodide.....	15.43	I	15.51
		II	15.41
Cumarin.....	54.27	I	53.85
		II	53.26

Active iodine was determined by titration with thiosulfate solution. The substance was added to a solution of potassium iodide and the liberation of the iodine was facilitated by warming the solution and by the addition of ethyl acetate to it.

Potassium iodide was determined by heating a sample in an oven at 160° for 2 hours, and weighing the residue. To insure the removal of all of the cumarin, the residue was dissolved in a few drops of water and again heated until it was dry.

Cumarin was determined by dissolving a sample in a small amount of freshly distilled ether with the addition of a couple drops of water; then "molecular" silver was added and the mixture was shaken until the

solution was decolorized. The residue of cumarin obtained from the solution and washings was weighed. The loss of cumarin in a blank experiment was found to be negligible.

### Methyl Oxalate Potassium Iodide Periodide.

Two and one-half g. of methyl oxalate was dissolved in 50 cc. of water. Six g. of iodine and 5 g. of potassium iodide were made into a water solution amounting to 20 cc. About  $\frac{1}{3}$  of the iodine solution was added to the whole of the former. Crystals of periodide soon appeared and were allowed to settle. The mother liquor was poured off and the crystals were packed tightly upon a porous plate. When nearly dry, they were removed, mixed with a little water and again packed upon a fresh plate. They were finally dried by spreading them in the air for a couple of hours.

#### SAMPLE I.

Subs., 0.4453; 21.45 cc. 0.1 *N* thiosulfate soln.  
Subs., 0.5992; KI, 0.0940.

A second crop was obtained from the mother liquor of the previous experiment by again adding about the same amount of the iodine solution.

#### SAMPLE II.

Subs., 0.3813; 18.50 cc. 0.1 *N* thiosulfate soln.  
Subs., 0.5400; KI, 0.0860.

	Calc. for $(C_4H_4O_4)_2.KI.I_2$ %		Found, %
Active Iodine.....	61.23	I	61.17
		II	61.61
Potassium Iodide.....	16.00	I	15.69
		II	15.93
Methyl Oxalate (by diff.)....	22.76	I	23.14
		II	22.46

The active iodine was determined by direct titration in water with thiosulfate solution. The potassium iodide was weighed as a residue after evaporation in a dish placed on a steam-bath. It was heated until the weight was constant, a drop of water having been added toward the end of the operation.

This periodide is relatively unstable. During a couple of hours exposure in the air, the loss of iodine is not sufficient to affect the analytical results decidedly, but in a vacuum the loss is rapid. When spread out in a thin layer in the air, the product becomes nearly colorless in 3 days. The crystals are very fine and have a dark bluish-gray lustre. When heated, they begin to melt at about  $55^\circ$  but are not completely fused until  $75^\circ$  is reached. The substance is only sparingly soluble in water but dissolves readily in alcohol, acetone or ether. Crystals may be obtained by adding chloroform to the ether solution,

### Periodides of Acetone.

Five g. of iodine and 2.5 g. of potassium iodide were dissolved in about 8 cc. of acetone. On cooling the solution in ice-water, it was converted into a semisolid mass of crystals. The product was quickly removed to a porous plate and as the mother liquor was absorbed, needle-shaped, dark green crystals remained. They were very unstable and, after a couple of hours, a residue of potassium iodide alone remained.

A similar compound of sodium iodide is more conveniently prepared. A saturated solution of iodine in acetone was added to a saturated solution of sodium iodide in the same solvent. The periodide soon separated in very fine needles. These were filtered off, pressed on a porous plate, and washed with acetone in which they are only sparingly soluble. The crystals are not so heavy as those formed with potassium iodide. They are lighter in color and show a golden lustre. When the substance was about free from mother liquor, decomposition began so quickly that an analysis was not considered worth while.

### Benzamide Potassium Iodide Periodide.

This substance is especially difficult to purify on account of its dissociation in solution. On the other hand, the dry crystals are very stable. Moore and Thomas<sup>1</sup> purified the compound and also the one derived from sodium iodide, by dissolving it in ether and adding benzene to this solution. They assigned the formulas  $(C_6H_5CONH_2)_3.KI.I_2$  and  $(C_6H_5CO-NH_2)_3.NaI.I_2$  to the salt derivatives. The analytical results of Moore and Thomas are not in good agreement with the theoretical percentages and it seemed desirable to determine the true composition of this representative compound.

It was found that a satisfactory molecular ratio between iodine and potassium iodide could not be obtained by the use of ether and benzene, probably due to the decomposition brought about by the benzene. Better results were obtained when a saturated ethereal solution was cooled in ice-water. The results which were finally found to be acceptable were obtained by bringing the constituents into solution in ether, concentrating this solution as far as possible, then filtering it and cooling it in ice-water.

**Sample I.**—Two g. of benzamide, 1.2 g. of iodine and 1.0 g. of powdered potassium iodide were gently warmed for a few minutes with about 100 cc. of ether. The solution was filtered and concentrated to about 45 cc. which was again filtered and cooled in ice-water. The crystals are very fine and must be pressed in the funnel to remove mother liquor and finally packed tightly on a porous plate. To wash them, they were covered with a small amount of ether and again packed on a porous plate. When dry, the product was broken up with a spatula and placed in a vacuum for

<sup>1</sup> *Loc. cit.*



a couple of hours. The loss in weight in a vacuum was found to be very slow. The substance melted at 130°, but began to soften a few degrees below this point.

Subs., 0.3176; 0.3131; 8.2 cc. 8.05 cc. 0.1 *N* thiosulfate soln.

Subs., 0.2797; 10.05 cc. 0.1 *N* AgNO<sub>3</sub> soln.

Subs., 0.2726; benzamide, 0.1387.

**Sample II.**—Two and one-half g. of benzamide, 1.65 g. of iodine and 0.85 g. of powdered potassium iodide were dissolved in about 2.5 cc. of alcohol with careful warming. Fifty cc. of ether was added and the solution was filtered and cooled in ice-water. If much more than the specified amount of alcohol be used, the periodide will fail to separate. This sample was prepared for analysis just as the previous one.

Subs., 0.2994; 7.9 cc. 0.1 *N* thiosulfate soln.

Subs., 0.2667; 10.0 cc. 0.1 *N* AgNO<sub>3</sub> soln.

	Calc. for (C <sub>7</sub> H <sub>7</sub> NO) <sub>3</sub> KI <sub>2</sub> I.		Found.
	%.		%.
Active Iodine.....	32.79	I	32.78
		II	32.65
		III	33.51
Potassium Iodide.....	17.16	I	16.19
		II	17.77
Benzamide.....	50.04		50.88

The active iodine was determined in the same manner as that of the cumarin periodide. To determine the total iodine, water was first added, then a few drops of sulfur dioxide solution sufficient to cause complete decolorization. The iodine in the clear solution was then treated with silver nitrate and ammonium thiocyanate in the usual manner. The potassium iodide was of course calculated from the difference between active iodine and total iodine. The benzamide was weighed directly after dissolving a small sample of periodide in freshly distilled ether and adding a couple of drops of water and sufficient "molecular" silver to decolorize it.

#### Succinimide Potassium Iodide Periodide.

The compound is readily obtained pure and with a good yield when the constituent parts are dissolved in hot alcohol and the solution is then cooled. On varying the proportion of the components considerably, it has not been possible to affect the composition of the periodide as shown by analysis. When dil. acetic acid is used as a solvent, the yield of periodide is poor and under certain conditions the product is not pure. It seems likely that the product described by Piutti<sup>1</sup> contained free iodine.

The substance has several interesting peculiarities. It is unusually stable and in a stoppered bottle may be preserved indefinitely. It is not perfectly stable, however, and it shows a very slow loss in weight when it is

<sup>1</sup> *Loc. cit.*

spread out well and placed in a vacuum or exposed for a long time in the air. The crystals are light brown in color but lack the metallic lustre which characterizes the other compounds described. This deficiency cannot be due to the relatively small percentage of iodine in the compound, for the analogous body formed from succinic anhydride does show a metallic lustre. The periodide dissolves very readily in water, but it is decomposed by the solvent and a part of its active iodine separates from the solution. It dissolves readily in glacial acetic acid and to a moderate extent in alcohol. The pure substance begins to melt at  $141^{\circ}$ , but the fusion is not complete until  $149^{\circ}$  is reached.

**Sample I.**—Five g. of iodine and 3.2 g. of potassium iodide were added to 6 cc. of water and the solution was filtered to remove a small amount of iodine which remained undissolved. A solution of 4 g. of succinimide in 20 cc. of glacial acetic acid was then added. It was necessary to cool the solution in ice-water and wait for several minutes for the separation of the periodide. The latter was filtered quickly with suction and washed with a few drops of cold acetic acid.

Subs., 0.3702; 9.05 cc. 0.1 *N* thiosulfate soln.

Subs., 0.4044; 15.00 cc. 0.1 *N*  $\text{AgNO}_3$  soln.

The active iodine was titrated directly. Total iodine was determined by means of silver nitrate and ammonium thiocyanate after decolorizing the solution with a small amount of sulfurous acid.

**Sample II.**—Two g. of pulverized potassium iodide, 3.1 g. of iodine and 4.9 g. succinimide were dissolved in about 40 cc. of hot alcohol and the solution filtered. The crystals were washed with alcohol.

Subs., 0.2550; 9.35 cc. 0.1 *N*  $\text{AgNO}_3$  soln.

Subs., 0.5150; 12.55 cc. 0.1 *N* thiosulfate soln.

	Calc. for $(\text{C}_4\text{H}_5\text{NO}_2)_4\text{KI}_2$ .		Found.
	%.		%.
Active Iodine.....	31.13	I	31.04
		II	30.94
Potassium Iodide.....	20.34	I	20.99
		II	20.42
Succinimide (by difference)...	48.53	I	47.97
		II	48.64

#### Succinic Anhydride Potassium Iodide Periodide.

This compound was previously isolated in an impure condition by the writer<sup>1</sup> and a formula assigned which was only in fairly good agreement with the analyses. It was desired to make sure of the correctness of this formula for comparison with the succinimide periodide just described. A pure product has now been obtained by using as a solvent a mixture of chloroform and acetic ether in the proportion of 2 to 1, respectively, by volume.

<sup>1</sup> *Loc. cit.*

Six g. of succinic anhydride, 4 g. of iodine and 3 g. of pulverized potassium iodide were shaken well with a mixture of equal volumes of ethyl acetate and chloroform. An additional volume of chloroform was then added and the solution filtered. Only a part of the anhydride had gone into solution. On cooling the solution in a freezing mixture, crystals separated readily. These were filtered quickly and pressed compactly on a porous plate where they remained until dry. The yield was about 2 g. The mother liquor contained an excess of free iodine and, for this reason, the product was broken up and spread out in the air for 6 hours before analysis. The determinations were made in the same manner as those of the succinimide compound.

	Subs., 0.3197; 7.5 cc. 0.1 <i>N</i> thiosulfate soln.	
	Subs., 0.4451; 15.8 cc. 0.1 <i>N</i> AgNO <sub>3</sub> soln.	
	Calc. for (C <sub>4</sub> H <sub>4</sub> O <sub>3</sub> ) <sub>4</sub> .KI.I <sub>2</sub> .	Found.
	%.	%.
Active Iodine.....	30.97	29.79
Potassium Iodide.....	20.24	20.00

After exposure to the air overnight, the same sample showed an active iodine content of 29.23%. The compound is unstable compared with that of succinimide. The crystals are very fine and show a decided greenish lustre. The result of the analysis shows clearly the molecular ratio existing between the constituents. This ratio is the same as that found for the succinimide compound.

#### Periodides of Barbituric Acid.

Barbituric acid and its derivatives readily form periodides which are fairly stable and which generally crystallize from an aqueous solution on the addition of Wagner's reagent. With barbituric acid, itself, it has been possible to isolate in a pure state, 2 different substances whose formation is dependent upon the relative amount of iodine used.

**Yellow Crystals, (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O<sub>3</sub>)<sub>7</sub>, (KI)<sub>2</sub>.I<sub>5</sub>.**—Two grams of iodine and 4 g. of potassium iodide were dissolved in about 15 cc. of water and the solution was filtered. This solution was added to one containing 3 g. of anhydrous barbituric acid in 100 cc. of warm water. Crystals appeared at once, the amount of which was increased by cooling the solution in ice-water. They were filtered, washed with a little water and dried on a porous plate. Yield (Sample I), 4.7 g. Another sample was prepared by adding 3 g. of barbituric acid, 2 g. of iodine and 2 g. of potassium iodide to 100 cc. of water and by warming this mixture in a glass stoppered flask until a clear solution resulted. After filtering this solution, the remainder of the operation was carried out as in the previous case. Both samples were exposed to the air a few hours before analysis. In the determination of active iodine it was found best to add an excess of potassium iodide to the solution as iodine shows a tendency to unite with barbituric acid to form a colorless compound.

Sample I. Subs., 0.4085; 10.85 cc. 0.1 *N* thiosulfate soln.  
 Subs., 0.4462; 16.7 cc. 0.1 *N* AgNO<sub>3</sub> soln.  
 Sample II. Subs., 0.5804; 15.55 cc. 0.1 *N* thiosulfate soln.  
 Subs., 0.5151; 19.2 cc. 0.1 *N* AgNO<sub>3</sub> soln.

	Calc. %		Found. %
Active Iodine.....	34.08	I	33.73
		II	34.02
Potassium Iodide.....	17.82	I	18.04
		II	17.39

A 2 g. sample was spread out on a watch-glass and placed in a desiccator over calcium chloride for 3 weeks. It lost 6 mg. in weight. The substance is only sparingly soluble in alcohol and crystallizes from a hot solution on cooling.

**Green Crystals, (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O<sub>3</sub>)<sub>2</sub>, (KI)<sub>2</sub>, I<sub>5</sub>.**—In the preparation of the previous compound the amount of iodine was purposely limited. By using a large excess of the latter, it is possible to isolate green crystals of the composition given above. Although a good yield is obtained, this substance separates only from a solution containing a considerable excess of iodine. The crystals are quickly decomposed by water and as it is impossible to remove the mother liquor completely, the dried product is contaminated with iodine and potassium iodide.

A sample was well packed on a porous plate and allowed to dry. On removing and breaking up the mass of crystals, the presence of uncombined iodine was evident. After exposure of the crystals to the air for 5 hours, the percentage of active iodine in the compound was found to be 52.96; after 24 hours, 52.63; after 3 days, 51.23. From these results the compound appears to be fairly stable. The analyses of this sample and also of a second sample which are used in the calculations were made after the products had been exposed for 24 hours. As would be expected, the percentage of potassium iodide was found to be high.

The samples were prepared as follows: Five g. of iodine and 10 g. of potassium iodide were dissolved in sufficient water to make 12 cc. of solution, which was then filtered through glass wool. One-half g. of anhydrous barbituric acid was dissolved in 20 cc. of hot water. The latter solution was poured quickly into the former and the product was then cooled in ice-water.

Sample I. Subs., 0.3366; 13.95 cc. 0.1 *N* thiosulfate soln.  
 Subs., 0.3702; 21.75 cc. 0.1 *N* AgNO<sub>3</sub> soln.  
 Sample II. Subs., 0.4746; 19.40 cc. 0.1 *N* thiosulfate soln.  
 Subs., 0.4671; 27.25 cc. 0.1 *N* AgNO<sub>3</sub> soln.

	Calc. %		Found. %
Active Iodine.....	51.92	I	52.63
		II	51.92
Potassium Iodide.....	27.15	I	28.73
		II	28.98

It seems remarkable that in these closely related substances we have such a great difference in the number of molecules of barbituric acid contained in the triple compounds.

#### Diethyl-barbituric Acid Potassium Iodide Periodide.

One g. of diethyl-barbituric acid was dissolved in about 150 cc. of water. One g. of potassium iodide was dissolved in 10 cc. of water and the resulting solution saturated with iodine. On mixing the 2 solutions, the periodide separated at once. The crystals were removed by filtration and transferred to a porous plate. When nearly dry they were washed by moistening them with water, then were again dried thoroughly on a porous plate. Before analysis they were placed in vacuum for  $1\frac{1}{2}$  hour.

The potassium iodide in Sample I was determined by heating the substance, spread out thinly in a dish, at  $150^{\circ}$  for 2 hours and weighing the residue after it had been washed well with pure ether. Diethyl-barbituric acid was weighed directly after removing the iodine and potassium iodide. The sample was dissolved in pure ether, a couple of drops of water were added and the solution was shaken with sufficient "molecular" silver to effect complete decolorization. The ether solution was carefully removed and evaporated.

Sample I.	Subs., 0.3180; 12.1 cc. 0.1 <i>N</i> thiosulfate soln.
	Subs., 0.2358; diethyl-barbituric acid, 0.0847.
	Subs., 0.2553; potassium iodide, 0.0405.
Sample II.	Subs., 0.4200; 16.05 cc. 0.1 <i>N</i> thiosulfate soln.
	Subs., 0.4244; diethyl-barbituric acid, 0.1504.
	Subs., 0.4672; 22.3 cc. 0.1 <i>N</i> AgNO <sub>3</sub> soln.

	Calc. for (C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> .KLI <sub>4</sub> .		Found.
	%.		%.
Active Iodine.....	48.75	I	48.29
		II	48.49
Potassium Iodide.....	15.93	I	15.86
		II	15.80
Diethyl-barbituric acid.....	35.51	I	35.92
		II	35.46

The crystals have a steel-blue lustre and remain unfused when heated to  $200^{\circ}$ . They dissolve readily in alcohol and acetic acid but only sparingly in water and ether. On varying the proportions of the constituents no other compound could be obtained. The substance is a fairly stable one.