

the world for a period of time, while the former gives his at once, and that the latter is, in his original work, seeking for truth that is at once useful as soon as it is worked out, while the former neither knows nor cares whether the truth that he discovers, is either now or at any future time turned to practical or useful effect. Let me not be misunderstood. I am not attempting to belittle in any sense the work of the pure chemists. They are worthy of all honor and respect. But on the other hand, I am not at all willing to have the work of the applied chemists made light of or treated as though it were in an inferior field. To my mind there is no occasion for either to belittle the work of the other. The field of chemistry is so broad, the amount of unoccupied ground in every branch of the science is so great, that there is neither time nor energy for struggling as to who is greatest or who is least, but in whatever line a man's tastes, opportunities, or the force of circumstances may lead him, whether as a pure or an applied chemist, whether organic or inorganic, whether theoretical, physical, or agricultural, whether analytical or synthetic, provided in his mind at all times, the love of the truth is above all, and honest work is being done, he is worthy of recognition, honor, and respect.

ALKYL BISMUTH IODIDES AND BISMUTH IODIDES OF VEGETABLE BASES.¹

BY ALBERT B. PRESCOTT.

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THE common alkyl ammonium iodides, with solutions of the bismuth salts, give bright-colored precipitates. As formed by quaternary methyl or ethyl ammonium iodides, the color is orange-yellow in most cases, usually lighter when obtained with bismuth chloride, and darker when obtained with bismuth nitrate. When fully formed by excess of the organic iodide, in bismuth solution not strongly acid, the precipitation is amorphous and so nearly complete that when the filtrate from a test-tube portion is evaporated to dryness and the residue ignited and treated with solvent acid, hydrogen sulphide fails to

¹ Read before the American Pharmaceutical Association, in the report of a special committee, at Minnetonka Lake, August, 1897, and to be published in the Association Proceedings for this year.

blacken the liquid. Strong mineral acids slowly decompose these colored precipitates, liberating iodine.

What has been known as Drageudorff's reagent for alkaloids is a potassium bismuth iodide, prepared by dissolving precipitated bismuth iodide in a concentrated solution of potassium iodide acidulated with hydrochloric acid, and known as giving reddish-colored precipitates in solution of the salts of the alkaloids. On trial with pyridine salts, a corresponding precipitate was obtained, dark orange-red and voluminous. Kraut¹ has reported the piperidine compound, to which all these are analogous.

These organic bismuth iodides are not perfectly proof against decomposition by much water; they are sparingly soluble in ethyl or amyl alcohol, insoluble in glacial acetic acid, in ethyl ether, in chloroform, and in benzene.

The tetramethyl ammonium bismuth iodide crystallizes from hydrochloric acid, that of sp. gr. 1.19 diluted with an equal measure of water. Also from potassium iodide solution acidulated with hydrochloric acid. The pyridine and the alkaloid bismuth iodides crystallize from alcohol. In all these cases the crystals are clearly hexagonal and easily obtained.

Both the amorphous and crystalline forms are stable in the air. A sample of tetramethyl ammonium bismuth iodide remained constant in weight at 130°; atropine bismuth iodide melts, but at 98° C. holds constant weight.

Reducing agents, as potassium thiosulphate, do not alter these bismuth iodides. Tetramethyl ammonium bismuth iodide, precipitated from ten per cent. solutions both of the organic iodide and bismuth iodide, washed with hydrochloric acidulated water, then with pure water till washings gave no residue, then with alcohol, and lastly with ether, and dried at 110°, gave figures as follows :

Analyses I and II were of the same preparation, III and IV from other preparations made at different times.

	I.	II.	III.	IV.	$N_3(CH_3)_{11}HBiI_7$.
Iodine	58.71	58.29	60.79	59.22
Bismuth	27.08	27.07
Carbon	8.69	8.68	8.58	8.06	8.82
Hydrogen	2.16	2.12	2.30	2.37	2.08
Nitrogen	2.81	2.73	2.81

¹ *Ann. Chem.* (Liebig), 210, 310-327.

The pyridine bismuth iodide, prepared from a pyridine salt by Dragendorff's reagent and crystallized from alcohol, on elementary analysis gave figures as follows :

Different preparations.	I.	II.	III.	$(C_5H_5N)_3(HI)_3Bi_2I_6$.
Iodine	63.98	62.84	62.24	63.59
Bismuth	23.36	23.72	23.18

Kraut¹ found analogous composition for piperidine bismuth iodide.

The corresponding atropine bismuth iodide gave results as follows :

Several preparations.	I.	II.	III.	$(C_{17}H_{23}NO_3)_3 \cdot (HI)_3Bi_2I_6$.
Iodine	46.99	47.03	46.51	46.96
Bismuth	18.82	18.67	18.53	17.22
Carbon.....	23.22	23.62	23.69	25.23
Hydrogen.....	2.87	3.02	2.94	2.96
Oxygen.....	8.10	7.66	8.33	7.63

The carbon is too low for the theory, so that the figures approach to those of $(C_{17}H_{23}NO_3)(HI)BiI_3$.

The brucine compound gave, for $(C_{22}H_{26}N_2O_4)_3(HI)_3Bi_2I_6$, of iodine 41.10 and 40.88 per cent. against 41.56 by calculation from the formula.

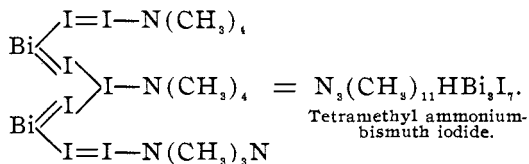
The corresponding strychnine salt gave, for iodine, 44.02 and 44.65 per. cent. against 44.48 by calculation from the formula.

In the results of the work I have done upon the perhalides and double halides of nitrogen bases in the last two or three years, everything goes to support the theory that two or more halogen atoms link to each other with an (uneven) valence of more than one, so as to connect one group of atoms with another. Iodine, especially among the halogens, serves as a binding element in the coupling of other elements with each other, as well as in massing its own atoms together in a heavy periodide, as a swarm of bees hang upon the bough of a tree. In the double iodide structure, where iodine links one base to another base, serving between positive and positive, with iodine not in excess of the "normal" number of its atoms, potassium thiosulphate will not take iodine out of the compound. In the periodide structure where iodine links a base to additive iodine, serving between a positive and a negative group, potassium thiosulphate promptly

¹ *Ann. Chem. (Liebig)*, 210, 310-327.

removes all the additive iodine, leaving a normal single iodide. These generalizations apply to the dipyridine alkyl iodides reported with determinations of molecular weight by Mr. Flintermann and myself in 1895.¹ Also to the various monopyridine alkyl normal iodides² and to the numerous periodides.³ In the compounds of additive iodine, as in double iodides, the results of analysis are in most cases consistent with an uneven valence of iodine, indeed with its trivalence. But there are a very few periodides well determined by Mr. Trowbridge as monopyridine compounds, in which, in our present knowledge, an even numerical valence of iodine is indicated.

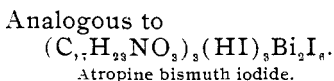
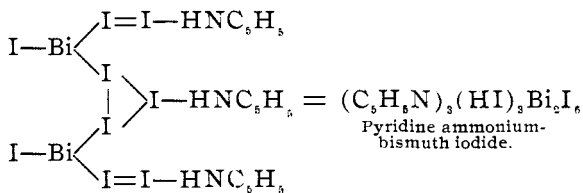
The bismuth iodides of nitrogen bases reported in this paper, both those of fatty alkyls on the one hand and those on the other hand of pyridine and pyridine-derived alkaloids, all evidently conform in their analytical content to the regular iodine-linking structure, the structure common both to double iodides and periodides, as shown in the following proposed constitutional formula. In the case of the quaternary ammonium bismuth compounds, with the prevailing bismuth characteristic of losing halogen in presence of water, the wash-water being found tinged with iodine, each bismuth atom is directly bound to only two atoms of iodine, while in the pyridine-formed compounds the bismuth atom is bound to three atoms of iodine in each instance, bismuth and iodine valencies being always the same. Again, the fatty ammonium compounds, less stable as they are, show a variation from the quaternary to the tertiary base type, in one of the three nitrogen basal groups of the molecule. This doubtless comes about by reaction of water to form methyl alcohol as a by-product, leaving hydrogen in place of methyl in the main product.



¹ This Journal, 18, 28.

² Prescott and Baer, 1896: *Ibid.*, 18, 247.

³ Prescott and Trowbridge, 1895: *Ibid.*, 17, 859; P. F. Trowbridge, 1897: *Ibid.*, 19, 322; Trowbridge and Diehl, 1897: *Ibid.*, 19, 558.



The alkaloidal bismuth iodides are not quantitatively uniform enough to be entirely satisfactory for alkaloidal assay, but are more stable and uniform than the alkaloid mercuric iodides formed by Mayer's reagent. On the other hand, they are more bulky, less easy to gather in a compact mass, less manageable in filtration. On the whole, so far as found, Dragendorff's reagent gives no general advantage over that of Mayer, though I am well aware how unsatisfactory the latter has been found in the hands of analysts.

For the execution of the work upon tetramethyl ammonium bismuth iodide, I am wholly indebted to Mr. H. E. Brown; for that upon the bismuth iodides of pyridine and the alkaloids to Mr. O. C. Diehl. A further study of the reactions of the halides of bismuth upon representative organic bases is now left to Mr. Brown.

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THE ACTION OF SULPHURIC ACID ON MERCURY.

BY J. R. PITMAN.

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THE following statement is made by Messrs. Baskerville and Miller, in a previous number of this Journal (19, 874): "A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C."

As a large amount of my work consists in the use of nitrometers, this statement was of considerable interest to me; however, believing their conclusions to be erroneous, the following simple tests were tried: Apparatus used, a Lunge nitrometer, with separate reading burette; the temperature at all times was