

# HALIDES AND PERHALIDES OF THE PICOLINES.

BY PAUL MURRILL.<sup>1</sup>

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THE history of the periodides has been given in papers previously published from this laboratory,<sup>2</sup> and work upon various phases of the problem has been in progress here since 1895.<sup>3</sup> For our present knowledge of picoline we are chiefly indebted to the labors of Anderson,<sup>4</sup> Baeyer,<sup>5</sup> Dewar,<sup>6</sup> and Ramsay.<sup>7</sup> This research was undertaken as an extension of the work of Prescott and Trowbridge on pyridine and quinoline, and for the purpose of studying the homologues in the series, inasmuch as the presence of a side-chain can be considered as being a step nearer to the composition of the vegetable alkaloid.

## EXPERIMENTAL PART.

### I. NORMAL IODIDES.

*α-Picoline Methyl Iodide*,  $C_6H_4(CH_3)N.CH_3I$ .—This compound was prepared and described by Ramsay<sup>8</sup> in 1876, and the same method of preparation was used. Picoline and methyl iodide unite readily at ordinary temperatures with evolution of heat, so that a reflux condenser is necessary to prevent loss of methyl iodide. The product soon solidifies to a yellowish mass, and is recrystallized from absolute alcohol, from which solvent it comes out in long white needles, melting at  $224^\circ$  (Ramsay  $227^\circ$ ).

	Calculated for $C_6H_7N.CH_3I$ .	Found.
Iodine .....	53.97	53.5 <sup>9</sup>

The isomeric  $\beta$ - and  $\gamma$ -compounds were not obtained pure but

<sup>1</sup> A thesis presented to the council of the graduate school of the University of Michigan, for the Degree of Doctor of Philosophy, June, 1899.

<sup>2</sup> A. B. Prescott: The Periodides, this Journal, 17, 775 (1895); Periodides of the Alkaloids, *Pharm. Review*, 14, 172 (1896).

<sup>3</sup> Prescott and Trowbridge: Periodides of Pyridine, this Journal, 17, 859, and 19, 322; Trowbridge and Diehl: Halides and Perhalides of Pyridine, this Journal, 19, 558; Trowbridge: Perhalides of Quinoline, this Journal, 21, 66; Gomberg: Perhalides of Caffeine, this Journal, 18, 347; Prescott and Gordin, Alkaloidal Periodides, this Journal, 20, 706.

<sup>4</sup> *Ann. Chem.* (Liebig), 60, 86 (1846); 70, 32 (1849); 80, 44 (1851); 94, 358 (1855); *Edinb. Phil. J.*, 146 and 291 (1846); *Phil. Mag.*, (3), 33, 174 and (4), 9, 291.

<sup>5</sup> *Ber. d. chem. Ges.*, 2, 398 (1869).

<sup>6</sup> *Chem. News*, 23, 38 (1871)

<sup>7</sup> *Phil. Mag.*, (5) 2, 269 (1876); 4, 241 (1877); 6, 19 (1878); *Ber. d. chem. Ges.*, 11, 1836.

<sup>8</sup> *Phil. Mag.*, (5), 2, 277.

<sup>9</sup> For methods of analysis see last part of this paper.

the results show that their melting-points are in all probability considerably lower than that of the  $\alpha$ -compound. Five grams of picoline boiling at  $137^{\circ}$ – $140^{\circ}$  (the last fraction of  $\approx 400$  grams lot) were converted into the methiodide and crystallized once from absolute alcohol. These crystals appeared to be a mixture of two or more kinds, and melted at  $183^{\circ}$ . It was further converted into the triiodide described further on, and in view of later facts appears to have been a mixture of the  $\alpha$ - and  $\gamma$ -compounds. A mixture of the  $\alpha$ - and  $\beta$ -compounds was obtained as an oil, and this was also used in the preparation of periodides.

*$\alpha$ -Picoline Ethyl Iodide*,  $C_6H_7N.C_2H_5I$ .—This compound was prepared by Anderson<sup>1</sup> in 1855, and by him the melting-point is said to be below  $100^{\circ}$ , but is not definitely stated. He prepared it by heating picoline and ethyl iodide in a sealed tube, but this has been found to be unnecessary, and instead the constituents were heated on a water-bath under reflux condenser. The reaction is complete in two hours, and on cooling the oil solidifies to a yellowish mass. The excess of ethyl iodide is distilled off, and the residue dissolved in hot absolute alcohol. When cooled slightly, ether is added as long as the precipitate redissolves on shaking, and then it is allowed to crystallize. From this it comes out in large feathery plates, colorless or faintly yellow. It melts at  $123^{\circ}$ , and contains 50.8 per cent. iodine; theory 50.93 per cent.

*Picoline Propyl Iodide*,  $C_6H_7N.C_3H_7I$ .—Prepared by heating the constituents on the water-bath under reflux condenser. The action is complete in about two hours, and a thick sirup is formed, which solidifies to a crystalline mass on cooling. A portion was dried on porous plates in a desiccator, and the remainder crystallized from a very small amount of hot absolute alcohol. Yellowish needles formed, melting at  $77^{\circ}$ .

	Calculated for $C_6H_7N.C_3H_7I$ .	Crude.	Found. Crystallized.
Iodine .....	48.23	45.2	48.3

*Picoline Isopropyl Iodide*,  $C_6H_7N.C_3H_7I$ .—Prepared in same manner as preceding, using instead isopropyl iodide. Needles which melt at  $142^{\circ}$ , and contain 48.4 per cent. iodine.

*Picoline Butyl Iodide*,  $C_6H_7N.C_4H_9I$ .—Preparation same as the pre-

<sup>1</sup> *Phil. Mag.*, (4), 9, 214; *Ann. Chem.* (Liebig), 94, 361.

ceding. The residue was crystallized once from a very small amount of absolute alcohol, washed with ether and dried on a porous plate in a vacuum desiccator. These were straw-colored crystals, melting at  $98^{\circ}$ .

	Calculated.	Found.
Iodine.....	45.79	45.8

*Picoline Isobutyl Iodide*,  $C_6H_7N.C_4H_9I$ .—A light yellow sirup, not solidifying at  $-15^{\circ}$ . Prepared by allowing a mixture of the constituents to stand at room temperature for two weeks, also by heating the same mixture for six hours at  $100^{\circ}$ . If either the mixture or the addition-product is heated much above  $100^{\circ}$ , decomposition takes place, and on cooling crystals of picoline hydriodide appear. It is very hygroscopic, and no analysis of this compound was made, but these products were used in the preparation of the periodides described later.

*Picoline Secondary Butyl Iodide*,  $C_6H_7N.C_4H_9I$ .—This compound was prepared in the same manner as the preceding, but it is much more unstable, and it is doubtful if it was obtained entirely free from hydriodide. When heated, or even if kept on a porous plate in a desiccator, it gradually disappears, breaking up into picoline, hydriodic acid, and (probably) pseudo-butylene. When prepared by allowing the constituents to stand two weeks at room temperature it is a light yellow sirup, which becomes crystalline on cooling to  $0^{\circ}$ . When prepared by heating the constituents for six hours at  $100^{\circ}$ , it is obtained as a straw-colored crystalline solid, which could not be dried sufficiently to obtain a melting-point. Both preparations were converted into periodides described later.

	Calculated.	Found.
Iodine.....	45.79	44.64

*Picoline and Tertiary Butyl Iodide*.—Picoline reacts with tertiary butyl iodide at  $100^{\circ}$  in the same way that pyridine<sup>1</sup> does; *i. e.*, with formation of the hydriodide, and liberation of isobutylene. The resulting compound melted at  $98^{\circ}$ , and seemed to be a mixture, so that perhaps a little of the butyl iodide was formed. Analysis showed 51.76 per cent. of iodine.

Picoline and tertiary butyl chloride do not react at the boiling-point of the mixture.

<sup>1</sup> Lippert: *Ann. Chem. (Liebig)*, 276, 184.

*Picoline Isoamyl Iodide*,  $C_7H_7N.C_5H_{11}I$ .—Amyl iodide (boiling at  $148^\circ$ ) was heated with picoline on a sand-bath under reflux condenser. When cold the residue was dissolved in a very small quantity of hot absolute alcohol, placed in a vacuum desiccator and set aside in the cold. Straw-colored cubical crystals formed, which were washed with ether containing a little alcohol, and were dried on a porous plate in a desiccator. It melts at  $120^\circ$ , and turns brown on keeping.

	Calculated.	Found.
Iodine .....	43.58	43.2

*Picoline Allyl Iodide*,  $C_6H_7N.C_3H_5I$ .—This preparation is reported by Ramsay,<sup>1</sup> who states: "All the picoline allyl compounds (of which the iodide, chloride, nitrate, sulphate, and oxalate were made) are sirupy liquids," but this seems to be somewhat inaccurate, in that it does not express all the facts.

Allyl iodide was purified by shaking with dilute potash, drying over calcium chloride, and rectifying. When this is mixed with picoline, the colorless liquid rapidly becomes turbid and yellowish oily drops separate. The reaction proceeds readily at ordinary temperatures, and no heating is necessary. It is complete in about an hour, and a light straw-colored sirup is the resulting product. This rapidly becomes brown on standing, but if cooled to  $0^\circ$  solidifies to a yellowish crystalline mass. Recrystallized from small quantity of hot absolute alcohol it yields cubes, transparent and almost colorless. Melting-point  $70^\circ$ .

	Calculated.	Found.
Iodine.....	48.603	48.5

*Picoline Hydriodide*,  $C_6H_7N.HI$ .—Prepared by conducting dry hydriodic acid gas into picoline kept in a freezing-mixture, and drying on a porous plate over sulphuric acid. A white snowy mass which is rather unstable, and separates readily into its proximate constituents, for which reason the melting-point could not be taken. It was also prepared by adding fuming hydriodic acid (sp. gr. 1.96) to picoline kept in a freezing-mixture, and inducing crystallization by means of the previous preparation. This preparation was attempted by Ramsay,<sup>2</sup> but he obtained it only in solution.

<sup>1</sup> *Phil. Mag.*, (5), 2, 279.

<sup>2</sup> *Ibid.*, (5), 2, 271.

	Calculated.	Found.
Iodine.....	57.41	57.62

## II. PERIODIDES.

*Picoline Hydrogen Diiodide*,  $C_6H_7N.HI.I$ .—Obtained by adding one equivalent of iodine to one of hydriodide, both in alcohol. As the alcohol evaporates, a dark brown oil separates, which on exposure to low temperatures crystallizes in prisms, dark brown, hard and gritty. The melting-point is about  $95^\circ$  but not sharp.

	Calculated for $C_6H_7N.HI.I$ .	Found.
Total iodine .....	72.94	72.5
Additive iodine .....	36.47	36.25

Crystalline bodies of varying composition were also obtained, giving figures of analysis lower than the above, but no definite formula could be ascribed to them except that they were mixtures of  $C_6H_7N.HI.I$  with  $C_6H_7N.HI$  in varying proportions.

It is worthy of note that *although the hydriodide is unstable, and the odor of picoline is always noticeable about it, the periodides are quite stable, and no odor is perceptible either of picoline or iodine*. A peculiarity of this and all other perhalides of picoline hydriodide or hydrobromide, is that they all become liquid in contact with water, in which, however, they are almost entirely insoluble. Upon standing in a desiccator at low temperature the liquid will again solidify, the composition and properties being unchanged. This fact was observed by Ramsay in connection with the compound described below, but no explanation is offered to account for it.

*Picoline Hydrogen Triiodide*,  $C_6H_7N.HI.I_2$ .—Dark brown octahedral crystals, melting at  $44^\circ$ . It is prepared by adding two equivalents of iodine to one of hydriodide, both in alcohol. After evaporation of the alcohol the oil that remains is exposed to low temperatures when it crystallizes and is dried on a porous plate.

	Calculated for $C_6H_7N.HI.I_2$ .	Found.
Total iodine .....	80.17	79.97
Additive iodine .....	53.45	53.10

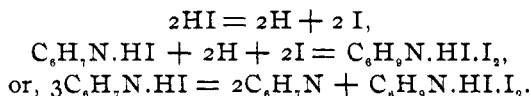
A compound was prepared by Ramsay<sup>1</sup> to which he assigns the same formula. He says "when picoline is mixed with strong

<sup>1</sup> *Phil. Mag.*, (5), 2, 273.

aqueous hydriodic acid, and distilled after excess of water has been removed by evaporation, the temperature rises rapidly and the mass turns brown and viscid. If the distillation be continued picoline distils over, and the residue when cool solidifies to a mass of reddish brown needles.' These were soluble in alcohol and ether but did not crystallize from them; were insoluble in carbon disulphide and became liquid in contact with water.

	Calculated for		Found.
	$C_6H_7N.HI.I_2$	$C_6H_9N.HI.I_2$	
Total iodine.....	80.17	79.83	80.14
Additive iodine .....	53.45	53.22	....

The melting-point is given as  $79^\circ$ , and it is evidently a different compound from that obtained by the writer. It is possible that it is from a different one of the isomeric picolines, but to the writer it appears more probable that the compound obtained by Ramsay is a periodide not of picoline but of a hydropicoline. It is known that the pyridine bases are readily reduced to hydro-compounds, and that hydriodic acid is an active reducing agent at high temperatures. In view of this the following equations would show the probable reactions:



This might be proved or disproved by the preparation of the free base from the periodide, but that compound is obtained in such small quantities as to obstruct such a procedure.

*Picoline Hydrogen Pentiodide*,  $C_6H_7N.HI.I_4$ .—A thick greenish black oil obtained by adding picoline hydriodide to the theoretical amount of alcoholic iodine, and allowing the alcohol to evaporate. The oil was washed with dilute arsenite and with water and dried in a desiccator. It did not solidify at  $-25^\circ$ .

	Calculated.	Found.
Total iodine .....	87.08	87.12
Additive iodine .....	69.66	69.58

*$\alpha$ -Picoline Methyl Triiodide*,  $C_6H_7N.CH_3.I_3$ .—Blue-black feathery plates, melting at  $134^\circ$ . This compound, or rather a mixture of its isomers, was prepared by Ramsay<sup>1</sup> by dissolving iodine in an alcoholic solution of the normal iodide. He says

<sup>1</sup> *Phil. Mag.*, (5), 2, 278.

that on cooling it crystallized out in bluish-black feathery plates which transmitted red light, and gives the melting-point as  $129^{\circ}$ . For the preparation of the  $\alpha$ -compound, picoline was fractionated very slowly, carefully, and repeatedly, and the fraction boiling at  $131.5^{\circ}$ – $132.5^{\circ}$  was used. This was converted into the methiodide, which was crystallized once from absolute alcohol. A portion of this was treated with the theoretical amount of iodine in hot alcohol, heated to dissolve the periodide formed and allowed to crystallize. The periodide was then recrystallized once from absolute alcohol, and found to melt at  $134^{\circ}$  as given above (preparation I). It was also prepared by adding iodopotassium iodide to an aqueous solution of picoline methyl iodide, keeping the latter in excess. By this means an abundant powdery precipitate is formed, which was washed with water, dried, and found to melt at  $133^{\circ}$  (preparation II). Recrystallized from alcohol it was identical with I in appearance and melting-point.

It was obtained once as short brown needles, melting at  $135^{\circ}$  (preparation III), but on subsequent recrystallization it yielded feathery plates.

	Calculated for $C_6H_7N.CH_3.I.I_2$ . (Ramsay)	I.	Found. II.	III.
Total iodine . . . . .	77.81	77.59	77.81	77.62
Additive iodine . . . . .	51.87	52.26	51.50	52.29

*$\beta$ -Picoline Methyl Triiodide*,  $C_6H_7N.CH_3.I.I_2$ .— $\beta$ -Picoline was prepared by following the directions of Schwartz<sup>1</sup> in what is usually known as Baeyer's<sup>2</sup> synthesis. A yield of 15 grams was obtained from 220 grams glycerine, 87.5 grams ammonium phosphate, and 175 grams phosphorus pentoxide. This was distilled and collected in three fractions, and each fraction converted into the methiodide, but as none could be obtained crystalline, they were separately converted into the triiodide by addition of the theoretical amount of alcoholic iodine. A number of products were obtained differing in physical properties (oils, plates, needles, etc.), but all gave figures of analysis agreeing with the formula  $C_6H_7N.CH_3.I.I_2$ , and on purification by alcohol and repeated recrystallization were separated into two lots. One of these melted sharply at  $134^{\circ}$  and agreed in every way with the  $\alpha$ -compound described above. The other after several re-

<sup>1</sup> Ber. d. chem. Ges., 24, 1676; Chem. Centrbl., (1891), ii, 172.

<sup>2</sup> Ber. d. chem. Ges., 2, 398; Chem. Centrbl., (1870), 14.

crystallizations yielded light brown feathery plates, melting at  $36^{\circ}$ .

These results agree with those of Schwartz, who found that his product contained five per cent. of  $\alpha$ -picoline.

	Calculated for $C_6H_7N.CH_3I.I_2$ .	$\alpha$	Found. $\beta$
Total iodine .....	77.81	78.50	77.62
Additive iodine .....	51.87	51.78	51.73

*$\gamma$ -Picoline Methyl Triiodide*,  $C_6H_7N.CH_3I.I_2$ .— $\alpha$ -Picoline methyl iodide is less soluble in alcohol than its isomers, and the same is true of the corresponding triiodides. A portion of picoline boiling at  $137^{\circ}$ – $140^{\circ}$  (the final fraction, from a 400 grams lot) was converted into the methiodide and triiodide, and the latter was crystallized from alcohol. The first crops of crystals were the feathery plates of the  $\alpha$ -compound, but finally crystals of another kind were seen, very different in color, shape, and appearance, and easily picked out by hand. These were recrystallized and came out as light brown hexagonal plates which melted at  $101^{\circ}$ . Repeated recrystallizations from alcohol did not alter the melting-point or crystalline form. The same compound was obtained from other fractions of the picoline, and by exclusion it is reasoned that this must be the  $\gamma$ -compound. On account of the small amount obtained it was not studied as thoroughly as could be desired, but there hardly seems reason to doubt its identity.

	Calculated.	Found.
Total iodine .....	77.81	78.04
Additive iodine .....	51.87	51.53

*$\alpha$ -Picoline Methyl Pentiodide*,  $C_6H_7N.CH_3I.I_4$ .—Flat needles, blue-black, melting at  $60^{\circ}$ . It is prepared by adding the corresponding normal iodide to the theoretical amount of alcoholic iodine, or prepared from the triiodide by boiling with the calculated amount of alcoholic iodine. It is also obtained by adding an aqueous solution of the normal iodide to iodopotassium iodide, keeping the latter in excess.

	Calculated.	I.	Found. II.
Total iodine .....	85.43	85.7	85.6
Additive iodine .....	68.34	68.5	68.7

*$\beta$ -Picoline Methyl Pentiodide*,  $C_6H_7N.CH_3I.I_4$ .—A brown-black



oil not solidifying at  $-25^{\circ}$ . Prepared from the corresponding triiodide by boiling with the theoretical amount of alcoholic iodine. The alcohol is then allowed to evaporate, and the oil washed with dilute arsenite and with water, and dried in a desiccator.

	Calculated.	Found.
Total iodine .....	85.43	85.62
Additive iodine .....	68.34	68.44

*$\gamma$ -Picoline Methyl Pentiodide*,  $C_8H_7N.CH_3.I_5$ .—Slender steel-blue needles, melting at  $63^{\circ}$ . It is prepared from the corresponding triiodide by boiling with the calculated amount of alcoholic iodine.

	Calculated.	Found.
Total iodine .....	85.43	85.51
Additive iodine .....	68.34	68.42

*$\alpha$ -Picoline Methyl Heptiodide*,  $C_8H_7N.CH_3.I_7$ .—Dark green, feathery plates, melting at  $57^{\circ}$ . It gives off iodine on exposure to air, and pentiodide remains. Prepared by dissolving the calculated amounts of normal iodide and iodine in hot alcohol, and boiling fifteen minutes under reflux condenser. On cooling an oil separates which soon solidifies, and at the same time crystals are formed.

	Calculated.	Found.
Total iodine .....	89.146	88.05
Additive iodine .....	76.411	76.04

*$\gamma$ -Picoline Methyl Heptiodide*,  $C_8H_7N.CH_3.I_7$ . Small, flat needles, dark green, melting at  $81.5^{\circ}$ . It is more stable than the preceding compound. Prepared by treating the corresponding triiodide with the theoretical amount of iodine, and boiling for fifteen minutes under a reflux condenser.

	Calculated.	Found.
Total iodine .....	89.146	89.14
Additive iodine .....	76.411	76.11

*$\alpha$ -Picoline Ethyl Triiodide*,  $C_8H_7N.C_2H_5.I_3$ .—Dark brown oil, obtained by adding two equivalents or less of iodine to one equivalent of the normal iodide, both in alcohol. The oil is separated, washed with dilute arsenite and with water, and dried in desiccator. It remained liquid at  $-25^{\circ}$ .

	Calculated.	Found.
Total iodine .....	75.70	76.10
Additive iodine .....	50.47	50.62

*α-Picoline Ethyl Pentiodide*,  $C_6H_7N.C_2H_5.I_4$ .—A green-black oil, obtained by adding one equivalent of normal iodide to four of iodine, both in alcohol. It was washed and dried as the preceding. It did not solidify at  $-25^\circ$ .

On standing several weeks at  $0^\circ$  and below, a few crystals formed (about 0.1500 gram). These were very long needles, almost black. Dried on porous plate they were found to melt at  $80^\circ$ , and gave figures of analysis under column II below. This is probably the  $\gamma$ -picoline compound.

	Calculated for $C_6H_7N.C_2H_5.I_4$ .	I.	Found. II.
Total iodine .....	83.85	83.4	82.9
Additive iodine.....	67.08	67.1	66.8

*Picoline Propyl Triiodide*,  $C_6H_7N.C_3H_7.I_3$ .—Brown oil obtained by adding iodine to normal iodide in theoretical proportions, both in alcohol. It was washed and dried as the preceding. On standing several days at low temperature it crystallized in fine needles, melting at  $16^\circ$ .

	Calculated.	Found.
Total iodine .....	73.65	73.45
Additive iodine .....	49.10	49.07

*Picoline Propyl Pentiodide*,  $C_6H_7N.C_3H_7.I_5$ .—A green-black oil, obtained by adding normal iodide to alcoholic iodine in proper proportions. It was washed and dried as the preceding. It did not solidify at  $-25^\circ$ .

	Calculated.	Found.
Total iodine .....	82.32	82.1
Additive iodine.....	65.86	65.7

*Picoline Isopropyl Diiodide*,  $C_6H_7N.C_3H_7.I_2$ .—Light brown cubes, melting at  $106^\circ$ . Obtained as the final crop of crystals from the addition of one equivalent of iodine to one of normal iodide. The triiodide is formed at the same time, and in larger quantity, and is separated in crystallization. The diiodide appears to be rather unstable, its alcoholic solution passing to triiodide on warming. The diiodide was also obtained from a portion of normal iodide, containing some alcohol, that had been allowed to stand for about a year, when it was observed that the

sirupy liquid had become brown and crystals had been deposited. These were collected, dried on a porous plate, and recrystallized from alcohol without heating.

	Calculated for $C_6H_7N.C_3H_7.I.I.$	I.	Found. II.
Total iodine .....	65.076	65.10	64.82
Additive iodine .....	32.538	32.61	32.51

*Picoline Isopropyl Triiodide*,  $C_6H_7N.C_3H_7.I.I.$ .—Light brown needles, long and silky, melting at  $60^\circ$ . They are formed when alcoholic iodine is mixed with a solution of normal iodide in any proportion. It is readily prepared free from admixture by mixing in theoretical proportions and allowing to crystallize.

	Calculated for $C_6H_7N.C_3H_7.I.I.$	I.	Found. II.	III.
Total iodine.....	73.65	72.78	73.74	73.01
Additive iodine.....	49.10	48.66	49.18	48.9

*Picoline Isopropyl Pentiodide*,  $C_6H_7N.C_3H_7.I.I.$ .—Greenish black oil, liquid at  $-25^\circ$ . It was obtained by adding normal iodide to the calculated amount of iodine in alcohol, and boiling a few minutes under a reflux condenser. When cold the oil is separated, washed, and dried as in previous preparations.

	Calculated.	Found.
Total iodine .....	82.33	82.40
Additive iodine .....	65.86	65.77

*Picoline Butyl Triiodide*,  $C_6H_7N.C_4H_9.I.I.$ .—Light brown needles, long and flat, melting at  $33^\circ$ . They were prepared by adding iodine to the normal iodide in proper proportions, both in alcohol, and allowing to crystallize at low temperature.

	Calculated.	Found.
Total iodine .....	71.70	71.81
Additive iodine .....	47.80	47.82

*Picoline Butyl Pentiodide*,  $C_6H_7N.C_4H_9.I.I.$ .—Dark brown oil, not solidifying at  $-20^\circ$ . Formed by adding normal iodide to alcoholic iodine in proper proportions.

	Calculated.	Found.
Total iodine .....	80.856	81.01
Additive iodine .....	64.685	64.67

*Picoline Isobutyl Triiodide*,  $C_6H_7N.C_4H_9.I.I.$ .—Prepared from the normal iodide in the usual manner. It is a dark brown oil, not solidifying at  $-15^\circ$ .

	Calculated	Found.
Total iodine .....	71.705	71.56
Additive iodine .....	47.803	48.04

*Picoline Isobutyl Pentiodide*,  $C_6H_7N.C_4H_9I_5$ .—A brown-black oil, not solidifying at  $-20^\circ$ . It was prepared from the normal iodide by adding it to alcoholic iodine in proper proportions and boiling under reflux condenser for a few minutes.

	Calculated.	Found.
Total iodine .....	80.856	80.95
Additive iodine .....	64.685	64.73

*Picoline Secondary Butyl Triiodide*,  $C_6H_7N.C_4H_9I_3$ .—Brown oil, not solidifying at  $0^\circ$ . It was prepared in the usual manner from the normal iodide previously described. The picoline hydrogen periodide which accompanies it is much more soluble in alcohol, so that as the alcohol evaporates the butyl periodide separates out first, and quite pure. This also applies to the pentiodide described next.

	Calculated for $C_6H_7N.C_4H_9I_3$ .	I.	Found. II.
Total iodine .....	71.705	71.56	71.63
Additive iodine .....	47.803	48.04	47.92

*Picoline Secondary Butyl Pentiodide*,  $C_6H_7N.C_4H_9I_5$ .—A green-black oil, not solidifying at  $0^\circ$ . It was obtained in the usual manner from the normal iodide.

	Calculated for $C_6H_7N.C_4H_9I_5$ .	I.	Found. II.
Total iodine .....	80.856	80.73	81.21
Additive iodine .....	64.685	64.56	64.77

*Picoline Tertiary Butyl Salts* are not formed. (See preceding part of this paper under normal iodides.)

*Picoline Isoamyl Diiodide*,  $C_6H_7N.C_5H_{11}I_2$ .—Light brown plates, melting at  $96^\circ$ . They were prepared from the normal iodide previously described by adding alcoholic iodine in theoretical quantity. The triiodide is formed at the same time and crystallizes out first.

	Calculated.	Found.
Total iodine .....	60.71	60.35
Additive iodine .....	30.355	30.12

*Picoline Isoamyl Triiodide*,  $C_6H_7N.C_5H_{11}I_3$ .—Light brown, overlapping plates, melting at  $22^\circ$ . They are obtained when—

ever alcoholic iodine is mixed with normal iodide. Prepared pure by mixing in theoretical quantities, and allowing to crystallize at low temperature.

	Calculated.	Found.
Total iodine .....	69.86	69.5
Additive iodine .....	46.57	46.3

*Picoline Isoamyl Pentiodide*,  $C_6H_7N.C_5H_{11}I_5$ .—Brown-black oil, not solidifying at  $-25^\circ$ . It was obtained by mixing alcoholic iodine with normal iodide in theoretical proportions, and boiling a few minutes under reflux condenser.

	Calculated.	Found.
Total iodine .....	79.44	80.1
Additive iodine .....	63.55	63.3

*Picoline Allyl Triiodide*,  $C_6H_7N.C_3H_5I_3$ .—Purplish brown needles, melting at  $62^\circ$ . Also obtained as light brown feathery plates, of same composition and melting-point, which on recrystallization came out as needles. It is obtained as an oil by adding iodine to the normal iodide in theoretical proportions. On cooling to  $0^\circ$  the oil solidifies, is dried on a porous plate and recrystallized, coming out as above. Ramsay<sup>1</sup> states that no diiodide of the allyloiodide was obtained, but goes on to say that by adding iodine to the normal iodide he obtained an oil, insoluble in carbon disulphide, and from which this solvent does not extract iodine. He reports no analysis of it.

	Calculated.	Found.
Total iodine .....	73.94	73.875
Additive iodine .....	49.29	49.25

*Picoline Allyl Pentiodide*,  $C_6H_7N.C_3H_5I_5$ .—A green-black oil, not solidifying at  $-25^\circ$ . It was obtained by adding normal iodide to alcoholic iodine in proper proportions, and heating a short time under reflux condenser.

	Calculated	Found.
Total iodine .....	82.35	82.25
Additive iodine .....	65.88	65.76

### III. NORMAL CHLORIDES.

*Picoline Hydrochloride*,  $C_6H_7N.HCl.\frac{1}{2}H_2O$ .—Prepared by Anderson<sup>2</sup> in 1846, and again by Ramsay<sup>3</sup> in 1876, but no analyses

<sup>1</sup> *Phil. Mag.*, (5), 2, 279.

<sup>2</sup> *Ibid.*, (4), 9, 145 and 214; *Ann. Chem.* (Liebig), 60, 86.

<sup>3</sup> *Phil. Mag.*, (5) 2, 271.

are reported by either. White crystals, extremely deliquescent, very stable, and sublime or distil unchanged except for loss of water. Prepared by acidifying picoline with hydrochloric acid and distilling after excess of water has been expelled; or water can be expelled, and the residue which remains on cooling is dried on porous plates in a vacuum desiccator.

Preparation I was made by acidifying picoline with concentrated hydrochloric acid, evaporating to a thick sirup and allowing to crystallize in desiccator. Crystals were dried on a porous plate in the desiccator, and analyzed. Preparation II is the same, allowed to remain two weeks in the desiccator. Preparation III is the same heated for several hours at  $110^{\circ}$ , when it was observed that the compound was liquid, and a large part of it had sublimed away. The remainder was cooled in a desiccator and analyzed.

	Calculated for			Found.	
	$C_6H_7N \cdot HCl \cdot \frac{1}{2}H_2O$	$C_6H_7N \cdot HCl$	I.	II.	III.
Chlorine ..	25.58	27.36	25.42	25.60	26.81

The melting-point given by Anderson is  $160^{\circ}$ , but this is only partially verified. Preparation I melted at  $165^{\circ}$ ; II became liquid at  $168^{\circ}$ , but did not melt to a clear liquid until a temperature of  $198^{\circ}$  was reached; III became liquid at  $80^{\circ}$  and cleared up at  $85^{\circ}$ . From this it would appear that the melting-point of the *hydrated* salt is about  $200^{\circ}$ , and of the *anhydrous* about  $80^{\circ}$ , certainly a very remarkable difference.

*α-Picoline Methyl Chloride*,  $C_6H_7N \cdot CH_2Cl \cdot H_2O$ .—Prepared by Ramsay<sup>1</sup> by treating picoline methyl iodide in aqueous solution with freshly precipitated silver chloride. On evaporation to dryness a white, crystalline deliquescent mass was obtained. No analysis or melting-point was reported. When prepared in this manner, crystallized once from absolute alcohol, and dried on a porous plate in a vacuum desiccator it was found to melt in the neighborhood of  $70^{\circ}$ , but not sharply, on account of its great hygroscopic power. The crystals contain one molecule of water of crystallization.

	Calculated for		
	$C_6H_7N \cdot CH_2Cl \cdot H_2O$	$C_6H_7N \cdot CH_2Cl$	Found.
Chlorine .....	21.94	23.045	21.72

<sup>1</sup>*Phil. Mag.*, (5), 2, 277.

## IV. NORMAL BROMIDES.

*Picoline Hydrobromide*,  $C_6H_7N.HBr$ .—Prepared by Ramsay<sup>1</sup> in the same manner as the hydrochloride, and also by brominating picoline and distilling the resulting oil. It was prepared by the writer by conducting dry gaseous hydrobromic acid into picoline, and drying in a desiccator on porous plates. It recrystallized from a very small quantity of absolute alcohol (preparation I) and formed very deliquescent white crystals, melting at  $187^\circ$  (Ramsay). At  $306^\circ$  the compound distils unchanged, coming over as a thick viscid sirup, which on standing in a desiccator gradually solidifies (preparation II).

	Calculated for $C_6H_7N.HBr$ .	I.	Found. II.
Bromine .....	45.94	45.06	46.27

*Picoline Methyl Bromide*,  $C_6H_7N.CH_3Br$ .—Prepared by conducting methyl bromide into picoline. Union takes place readily, with evolution of some heat, and the product soon solidifies to a flesh-colored mass. This was dried on porous plates *in vacuo* over sulphuric acid to remove excess of picoline, and recrystallized from a small quantity of absolute alcohol. It forms long colorless needles, which on keeping gradually turn pink. It melts at  $217^\circ$ .

	Calculated.	Found.
Bromine.....	42.52	42.47

*Picoline Ethyl Bromide*,  $C_6H_7N.C_2H_5Br$ .—Prepared by heating the constituents together under a reflux condenser. The formation is not as ready as with the corresponding iodide, but the union is complete in three or four hours. On standing in the cold it gradually solidifies, and is crystallized from a small quantity of absolute alcohol, from which it comes out as transparent colorless crystals. It is somewhat deliquescent and is dried on a porous plate in a desiccator. It melts at  $97^\circ$ .

	Calculated.	Found.
Bromine.....	39.56	38.9

## V. PERBROMIDES.

*Picoline Hydrogen Dibromide*,  $C_6H_7N.HBr.Br$ .—Red rhombohedral crystals, melting at  $76^\circ$ . It was prepared by mixing the normal hydrobromide with the corresponding tribromide in equi-

<sup>1</sup> *Phil. Mag.*, (5), 2, 271.

molecular proportions, in presence of a small amount of absolute alcohol. On standing the dibromide crystallizes out and is dried on porous plates.

	Calculated.	Found.
Total bromine .....	62.95	62.2
Additive bromine.....	31.47	31.1

*Picoline Hydrogen Tribromide*,  $C_6H_7N.HBr.Br_2$ .—Transparent oil, deep red in color, not solidifying at  $-15^\circ$ . It was prepared by adding bromine to an aqueous solution of the hydrobromide, or by aspirating vapors of bromine through the same.

	Calculated for $C_6H_7N.HBr.Br_2$ .	Ramsay's analyses.		Found.
Total bromine.....	72.00	71.17	68.04	72.74
Additive bromine.....	48.00	...	....	48.21

Ramsay<sup>1</sup> describes a compound to which he assigns the same formula, and which he obtained by heating the constituents in a sealed tube to  $190^\circ$ , and also by adding bromine to a solution of the hydrobromide. His compound crystallized from hot water in yellow crystals, melting at  $85^\circ$  with loss of bromine. The second method could not be verified, and the first was not tried by the writer. Picoline hydrogen tribromide should melt lower than the corresponding triiodide ( $44^\circ$ ); and if a solid, should be liquefied by water. In view of these and other facts it appears that Ramsay must have had quite a different compound, perhaps  $C_6H_5BrN.HBr.Br_2$ , which although differing in empirical formula by only one hydrogen atom would have properties very different from the compound obtained by the writer.

*$\alpha$ -Picoline Methyl Tribromide*,  $C_6H_7N.CH_3Br.Br_2$ .—When vapors of bromine are aspirated through an aqueous solution of picoline methyl bromide to saturation, a red oil is precipitated, which soon solidifies. On recrystallizing from alcohol it comes out as orange-yellow plates, melting at  $111^\circ$ , and having a faint odor of bromine.

	Calculated for $C_6H_7N.CH_3Br.Br_2$ .	I.	Found.	II.
Total bromine .....	68.94	67.99		69.21
Additive bromine .....	45.96	45.50		45.42

*Picoline Ethyl Tribromide*,  $C_6H_7N.C_2H_5Br.Br_2$ .—On aspirating vapors of bromine through an aqueous solution of picoline ethyl

<sup>1</sup> *Phil. Mag.*, (5), 2, 275.



bromide, a transparent deep red oil separates as before, but in this case it remains liquid in a freezing-mixture.

	Calculated.	Found.
Total bromine .....	66.26	66.34
Additive bromine.....	44.17	44.22

#### VI. IODOBROMIDES.

*Picoline Hydriodide Bromide*,  $C_6H_7N.HI.Br$ .—Dark red crystals, melting at  $68^\circ$ . Prepared by mixing equimolecular portions of picoline hydriodide and picoline hydriodide dibromide; or of picoline hydrogen diiodide with the corresponding dibromide, in presence of a small quantity of absolute alcohol.

	Calculated for $C_6H_7N.HI.Br$ .	Found.
Total halogens.....	68.726	68.57
Total iodine .....	42.156	41.93
Total bromine .....	26.570	26.64
Additive halogen (bromine).....	26.570	26.72

*Picoline Hydriodide Dibromide*,  $C_6H_7N.HI.Br_2$ .—Dark red crystals melting at  $58^\circ$ . It was obtained in a number of ways. I. Two molecular portions of tribromide and one of triiodide were mixed in presence of a small quantity of absolute alcohol. II. Picoline is diluted with water and acidified with hydrobromic acid, potassium iodide is added and vapors of bromine are aspirated through to saturation. By this means a red oil is obtained which solidifies to a crystalline mass, and melts at  $57^\circ$ . III. Vapors of bromine were aspirated through water in which was suspended picoline hydrogen diiodide. Red crystals were obtained, melting at  $48^\circ$ .

	Calculated for $C_6H_7N.HI.Br_2$ .	I.	Found. II.	III.
Total halogens .....	75.295	74.08	75.47	73.45
" iodine.....	33.31	29.09	29.63	21.99
" bromine.....	41.985	44.82	45.50	51.29
Additive halogen.....	41.985	42.15	41.94	42.21
Atomic ratio, I : Br .....	1 : 2	1 : 2.4	1 : 2.4	1 : 3.7

*$\alpha$ -Picoline Methyl Iodide Dibromide*,  $C_6H_7N.CH_3I.Br_2$ .—When vapors of bromine are aspirated through an aqueous solution of picoline methyl iodide (or any normal iodide), the first thing noticed is a brownish precipitate, evidently a triiodide, resulting from the displaced iodine which *immediately* combines with the

normal iodide still in excess. As the process is continued the precipitate becomes lighter in color (due to its conversion into iodobromide), and the supernatant liquid becomes clear. A portion of the precipitate was removed at this point and recrystallized from alcohol (I), and the remainder further treated with bromine for a considerable time and then recrystallized (II). I melted at  $121^{\circ}$ , and II at  $110^{\circ}$ .

That the triiodide is converted into iodobromide was shown by suspending it in water and aspirating vapors of bromine through it for some time. The product was then crystallized from alcohol and yielded fine orange-red needles, melting at  $121^{\circ}$  (III).

Prepared purest and best by mixing two molecular portions of tribromide with one of triiodide, and crystallizing from alcohol. Slender orange-red needles formed, two to three inches long, melting at  $121.5^{\circ}$  (IV).

	Calculated for $C_6H_7N.CH_3I.Br_2$ .	I.	II.	Found. III.	IV.
Total halogens.....	72.630	71.46	70.35	70.21	71.83
“ iodine .....	32.136	27.36	18.02	16.30	31.70
“ bromine .....	40.494	43.90	51.71	53.91	40.28
Additive halogen ...	40.494	40.87	40.53	40.50	40.48
Atomic ratio I : Br ..	1 : 2	1 : 2.2	1 : 4.5	1 : 5.2	1 : 2

The compound is perfectly stable and does not decompose at  $220^{\circ}$ , although a faint odor of bromine is usually noticeable in the bottle.

On gently warming a solution of potassium iodide, in which is suspended any one of the above preparations, the orange-red color immediately disappears, and the crystals become brown. Recrystallized from alcohol they then melt at  $133^{\circ}$ .

	Calculated for $C_6H_7N.CH_3I.I_3$ .	Found.
Total iodine .....	77.81	77.63
Additive iodine .....	51.87	51.20

*$\alpha$ -Picoline Methyl Iodide Iodobromide*,  $C_6H_7N.CH_3I.IBr$ .—Long, flat, interlaced needles, reddish brown in color, melting at  $113^{\circ}$ . It was prepared by mixing two molecular portions of  $\alpha$ - $C_6H_7N.CH_3I.I_3$ , with one of  $\alpha$ - $C_6H_7N.CH_3Br.Br_2$  and crystallizing from hot alcohol.

	Calculated for $C_8H_7N.CH_2I.Br.$	Found.
Total halogen .....	75.525	75.53
" bromine .....	18.097	18.15
" iodine .....	57.428	57.24
Atomic ratio I:Br .....	2:1	2:1

*Picoline Allyl Iodide Dibromide*,  $C_8H_7N.C_3H_5I.Br_2$ .—Orange-yellow plates, melting at  $84^\circ$ , perfectly stable and odorless. It was prepared by aspirating bromine through an aqueous solution of the normal iodide, and crystallizing from alcohol. The allyl group does not become saturated by the bromine.

	Calculated for $C_8H_7N.C_3H_5I.Br_2.$	Found.
Total halogen.....	68.13	68.27
" bromine .....	37.99	38.15
" iodine .....	30.14	29.93

#### VII. AMINE PERHALIDES.

*Picoline Dibromide*,  $C_8H_7N.Br_2$ .—These compounds were prepared by Ramsay,<sup>1</sup> and are given here for the sake of completeness. The dibromide is formed by addition of bromine to picoline in chloroform, and evaporating the chloroform in a vacuum desiccator. Small interlaced needles formed which lose bromine on standing.

*Picoline Iodochloride*,  $C_8H_7N.ICl$ .—Prepared by Ramsay<sup>1</sup> in the same manner as the preceding by adding iodine chloride to picoline in chloroform. Long yellow needles formed.

*Picoline Periodide*,  $C_8H_7N.I_2$ .—The existence of compounds analogous to pyridine tetriodide is indicated, although they were not obtained by the writer in a pure form. It is well known that a solution of iodine in chloroform is violet. If now a drop of picoline be added, the color at once changes to brown. On allowing the chloroform to evaporate, a thick sirup remained, but crystals were not obtained.

#### DISCUSSION.

The compounds described in the preceding pages are in every way analogous to those of pyridine, and with few exceptions agree with generalizations based upon a study of the pyridine compounds.<sup>2</sup>

<sup>1</sup> *Phil. Mag.*, (5), 2, 275.

<sup>2</sup> Prescott: Pyridine Alkyl Iodides, *This Journal*, 18, 91.

In each case where a melting-point could be taken, the normal iodides of picoline were found to melt higher than the corresponding pyridine compound, and the same is generally but not invariably true of the periodides. Also, the addition-products with methyl bromide follow the rule, but the reverse is true with ethyl bromide; while the other normal bromides and chlorides do not give melting-points sufficiently sharp for comparison. The relation existing between the boiling-points of the alkyl iodides and the melting-points of their pyridine addition-products is found to hold true with picoline in all cases except the isopropyl, amyl, and various butyl compounds, in which cases the melting-points are more or less anomalous.

The generalizations of Carnally<sup>1</sup> in regard to isomeric compounds were found to apply in nearly all instances. These are: "Of two isomers, that is most soluble which has the lower melting-point." "Of two or more isomeric compounds, those whose atoms are the most symmetrically or compactly arranged, melt higher than those in which the arrangement is asymmetric or in long chains." "Those compounds melt highest which have the greatest number of side chains; and compactness sometimes overbalances increase in atomic weight." Exceptions to these are observed in the case of the butyl and isobutyl compounds, both normal and superiodides. Also, compounds of  $\gamma$ -picoline should melt highest of the three isomers, but this is not the case with the methyl triiodides, and probably not with the normal methiodide.

From a practical or analytical point of view, perhaps the most important result of this research is the separation or the identification of the three isomeric picolines by means of their methyl triiodides. The separation has not been studied in all its aspects and possibilities on account of the scarcity of material and difficulty of preparation of the  $\beta$ - and  $\gamma$ -picolines. The picoline drawn upon for the preceding preparations was a Kahlbaum article, boiling at  $130^{\circ}$ – $134^{\circ}$ . It consisted very largely of  $\alpha$ -picoline, but contained some pyridine and some  $\gamma$ -picoline. The larger part distilled over between  $131^{\circ}$  and  $133^{\circ}$ , but on slow and careful fractionation a small amount (six grams from a 400 grams

<sup>1</sup> *Phil. Mag.*, (5), 13, 116 and 180; *J. Chem. Soc.*, 53, 782.

lot) was obtained which boiled at  $137^{\circ}$ – $140^{\circ}$ , and yielded the  $\gamma$ -picoline compounds previously described.

At present there is no ready method of obtaining the tertiary base in this series after it has once combined with an alkyl iodide to form a salt of the quaternary base, for on distilling the hydroxide of the quaternary base decomposition takes place, the ring is broken down and an aliphatic amine is produced, along with other products of decomposition, and no odor of picoline could be detected in the distillate. The use of the method as a *separation* is therefore diminished, but it is promising as a means of identification of the picolines.

In regard to the conditions of formation of the various periodides, it appears that the lower periodides (usually a triiodide) are formed whenever iodine is added to a normal iodide, or when the iodine is not in excess; and that the pentiodides are formed whenever these conditions are reversed. For formation of the heptiodides it is necessary to boil for some time with a considerable excess of iodine. The heptiodides are unstable, giving off iodine on standing and becoming pentiodides. The diiodides are also unstable (except  $C_6H_5N.HI.I$ ) as on boiling their alcoholic solutions they change to triiodides and normal iodides.

In solution the additive halogens are very reactive, and rearrange themselves with the greatest readiness. Lower periodides take up more iodine and change to pent- and heptiodides on boiling with alcoholic iodine; and these can be changed to triiodides with equal readiness by boiling with normal iodide. This readiness of rearrangement is most noticeable in the case of the complex perhalides, and was studied thoroughly in connection with the picoline methyl- and allyl-iodobromides.

The study of the complex perhalides, those with more than one halogen element, is of interest as bearing upon questions of constitution and the structural character of the halogens. When solutions of a periodide and a perbromide are mixed, or when a mixture of the two is dissolved in alcohol, reaction appears to be instantaneous, and an iodobromide results. The iodobromides are isomorphous with the perbromides, and if the latter be in excess it will crystallize out with the iodobromide in homogeneous crystals, so that different products may vary widely in composition, and yet be identical in appearance and even in

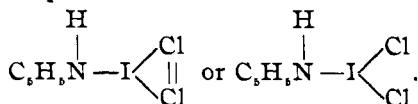
melting-point. The same results are obtained when bromine is aspirated through a solution of normal iodide or through a suspension of a periodide. At one time the question was raised in this research whether the complex perhalides were not in reality *mixtures* of the *simple* perhalides, but this now appears to be improbable. In view of these conclusions it will be seen that isomerism in the arrangement of the halogens is impossible, and that of the two formulas  $C_6H_7N.CH_3I.Br_2$  and  $C_6H_7N.CH_3Br.IBr$  only one can exist, and only one such compound is known.

The proof of the structure of the complex perhalides is perhaps not complete, but from a careful consideration of the facts at hand, the writer takes the view that *in every case it is the halogen of higher atomic weight that is next to the nitrogen*. The facts bearing on this question are as follows :

1. The great ease of formation and stability<sup>1</sup> of the periodides, and the power of iodine to hold a large number of additive atoms of iodine.<sup>2</sup>
2. The non-existence<sup>3</sup> of perchlorides.
3. The intermediate position of perbromides; the limit of the number of additive atoms being usually two, but in some cases four<sup>2</sup> atoms of bromine.<sup>4</sup>
4. Iodobromides are more stable than perbromides.
5. Iodine displaces bromine or chlorine completely, and bromine displaces chlorine completely,<sup>5</sup> a reversal of the usual reactions of these elements ; while bromine or chlorine displaces *all but one* of the iodine atoms in the molecule, and chlorine displaces *all but one* of the bromine atoms.

Since no perchlorides are formed, chlorine cannot hold chlo-

rine, and the formula  $C_6H_7N : Cl \begin{array}{c} H \\ | \\ I \\ || \\ Cl \end{array}$  is untenable, and the compound of that composition would have the constitution



<sup>1</sup> See under Picoline Hydrogen Diiodide, in previous part of this paper.

<sup>2</sup> Atropine Enneaiodide,  $C_{17}H_{23}NO_9.HI.I_8$ , Prescott and Gordin: This Journal, 20, 711.

<sup>3</sup> Trowbridge and Diehl: This Journal, 19, 571.

<sup>4</sup> Quinoline Hydrogen Pentabromide,  $C_9H_7N.HBr.Br_4$ , Trowbridge : This Journal, 21, 68.

<sup>5</sup> Trowbridge and Diehl: This Journal, 20, 563.

The general properties of these periodides and perhalides are much the same as those of the corresponding pyridine compounds. All the pentiodides, except two of the picoline methyl pentiodides are oils, while the triiodides with few exceptions are nicely crystalline. They are all insoluble in water, but are soluble in alcohol or chloroform. They are soluble in hot solutions of alkali carbonates without color (formation of iodate and iodide), and from such solution they are reformed and precipitated by addition of acids. They are soluble in caustic alkalies with more or less decomposition; and on boiling with alkalies iodoform appears to be formed. Normal halides of the tertiary base (picoline hydrochloride) are decomposed by solutions of alkali bicarbonates, yielding the free base. Solutions of potassium iodide convert all perhalides to pure periodides. The perhalides of the quarternary base are in general very stable, and some of the liquid periodides may be boiled for hours with decinormal arsenite before solution takes place.

#### METHODS OF ANALYSIS.

In analyzing the compounds described, volumetric processes were used almost exclusively, although the results were checked frequently by gravimetric estimations.

##### I. ANALYSIS OF COMPOUNDS CONTAINING ONLY ONE HALOGEN.

For estimating halogens in the normal halides, the Volhard method was used, precipitating with decinormal silver nitrate and retitrating with thiocyanate. The volumetric silver solution was standardized and tested at intervals by precipitating a definite portion and weighing the silver chloride formed.

In perhalides containing only one halogen, the additive or exterior halogen, was estimated with decinormal arsenious acid in sodium bicarbonate, retitrating with iodine. The arsenite was made by weighing resublimed arsenic, dissolving in sodium bicarbonate and when cold diluting to required volume. Arsenite has this advantage over thiosulphate, that both the arsenate and arsenite of silver are soluble in nitric acid, so that there are no products of reaction to interfere with the estimation by the Volhard method of the total halogen present in the same solution. When thiosulphate is used there are products which do interfere.

For estimating the total halogen, the easiest and most rapid method is to dissolve the perhalide in alkaline arsenite, with or without the aid of alcohol, precipitate with decinormal silver nitrate, and titrate the excess of silver with thiocyanate. This was compared with the zinc dust reduction and found to give identical results, with the advantage that no filtering is necessary.

The method of analysis for both additive and total halogen in a simple periodide or perbromide is as follows: A weighed portion is covered with about 10 cc. of alcohol, and decinormal arsenite is added till the perhalide is dissolved and the color destroyed, and the excess of arsenic is titrated with iodine in the ordinary way using starch paste as an indicator. The difference, multiplied by the decinormal factor of the halogen gives the weight of *additive halogen* present in the original sample.

After the titration with iodine, the total halogen can be estimated in the same portion, provided it is known how much iodine was added in the first titration. For this purpose a convenient solution is made by dissolving 12.685 grams iodine and 24.8925 grams potassium iodide in a small amount of water, and diluting to one liter. One cc. of this solution, reduced with arsenic, is equal to two and five-tenths cc. of decinormal silver nitrate, or in other words the solution is decinormal to arsenic and fourth-normal to silver.

## II. ANALYSIS OF MIXTURES OF TWO HALOGEN ELEMENTS.

When two halogens are present, their separate estimation is not quite so easy, but may be accomplished in the following manner: A weighed portion of the complex perhalide is reduced with zinc dust or arsenic as preferred, or any compound containing two halogens, is converted to the condition of a soluble iodide, etc. The halides in the clear solution or filtrate are precipitated with a known amount of standard silver nitrate, the precipitate is collected in the usual manner and weighed, and the filtrate containing the excess of silver is titrated with thiocyanate. By means of the following formulas the percentages are calculated.



Given :

$a$  = weight of substance taken for analysis.

$b$  = weight of silver halides obtained.

$c$  = no. of cc. of  $\frac{N}{10}$  silver nitrate required.

To find :

$p$  = percentage of total halogen.

$r$  = atomic ratio of halogens.

$p'$  = percentage of one halogen.

$p'' = p - p'$  = percentage of the other halogen.

For iodine and bromine the formulas are :

$$p = \frac{100 b - 1.0792 c}{a} \quad [1]$$

$$r = \frac{0.023477 c - b}{b - 0.018787 c} = \frac{\text{atoms of bromine}}{\text{atoms of iodine}} \quad [2]$$

$$p' = \frac{126.85 (b - 0.018787 c)}{0.469 a} = \text{per cent. iodine} \quad [3]$$

$$p'' = \frac{79.95 (0.023477 c - b)}{0.469 a} = \text{per cent. bromine} \quad [4]$$

For iodine and chlorine they are :

$$r = \frac{0.023477 c - b}{b - 0.014337 c} = \frac{\text{atoms of chlorine}}{\text{atoms of iodine}} \quad [2a]$$

$$p' = \frac{126.85 (b - 0.014337 c)}{0.914 a} = \text{per cent. iodine} \quad [3a]$$

$$p'' = \frac{35.45 (0.023477 c - b)}{0.914 a} = \text{per cent. chlorine} \quad [4a]$$

For bromine and chlorine they become :

$$r = \frac{0.018787 c - b}{b - 0.014337 c} = \frac{\text{atoms of chlorine}}{\text{atoms of iodine}} \quad [2b]$$

$$p' = \frac{79.95 (b - 0.014337 c)}{0.445 a} = \text{per cent. bromine} \quad [3b]$$

$$p'' = \frac{35.45 (0.018787 c - b)}{0.445 a} = \text{per cent. chlorine} \quad [4b]$$

The deduction of the formulas for iodine and bromine is as follows :

Let  $m$  = weight of silver in  $b$   
 $n$  = weight of halogen in  $b$

$$m + n = b$$

$$m = 0.010792 c$$

$$n = b - m = b - 0.010792 c$$

but  $a : n :: 100 : p$

$$\text{or } p = \frac{100 n}{a} = \frac{100 b - 1.0792 c}{a} \quad [1]$$

Also let  $w$  = combining weight of mixed halogens.

$x$  = number of atoms of iodine in one molecule of  $a$ .

$y$  = " " " " bromine in one " "  $a$

$r = \frac{y}{x}$  = atomic ratio of bromine to iodine.

$$\text{then } w = \frac{126.85 x + 79.95 y}{x + y} = \frac{126.85 + 79.95 r}{1 + r}$$

$$r = \frac{126.85 - w}{w - 79.95}$$

but  $m : n :: 107.92 : w$

$$\text{or } w = \frac{107.92 n}{m} = \frac{107.92 (b - 0.010792 c)}{0.010792 c}$$

$$w = \frac{10000 (b - 0.010792 c)}{c} = \frac{10000 b}{c} - 107.92$$

$$r = \frac{234.77 - 10000 b}{10000 b - 187.87 c} = \frac{0.023477 c - b}{b - 0.018787 c} \quad [2]$$

Also:

$$0.010792 \left( \frac{1}{1 + r} \right) c = \text{weight of silver combined with iodine in } b$$

$$0.010792 \left( \frac{r}{1 + r} \right) c = \text{ " " " " " bromine " } b$$

$$\text{then } \frac{0.012685 c}{1 + r} = \text{ " " iodine in } b \text{ or in } a$$

$$\frac{0.007995cr}{1+r} = \text{weight of bromine in } b \text{ or in } a$$

$$p' = \frac{100}{a} \times \frac{0.012685c}{1+r} = \frac{126.85(b - 0.018787c)}{0.469a} \quad [3]$$

$$p'' = \frac{100}{a} \times \frac{0.007995cr}{1+r} = \frac{79.95(0.023477c - b)}{0.469a} \quad [4]$$

In conclusion profound thanks are expressed to Prof. A. B. Prescott, in whose laboratory and under whose supervision the work has been done.

CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN,  
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## THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

BY GEO. WM. SARGENT.

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THE results obtained in this laboratory by the following method have been such as to warrant my placing it before fellow-chemists, who, I believe, will find the method more reliable and more pleasant to work than most procedures now in vogue for the determination of nickel in steel.

The method in detail is as follows: Dissolve two grams of the steel in hydrochloric acid (1.1 sp. gr.), add one cc. of strong nitric acid to oxidize the iron, and evaporate to hard dryness. Take up the residue in twenty cc. hydrochloric acid (1.1 sp. gr.), evaporate to ten cc. volume, and transfer the solution to a 250 cc. separatory funnel.<sup>1</sup> Use warm hydrochloric acid (1.1 sp. gr.) for washing the contents of the beaker into the funnel, taking care to keep the volume as small as possible. Cool the funnel and its contents under the spigot, then introduce forty cc. of ether free from alcohol, which has just been thoroughly shaken with five cc. of strong hydrochloric acid, and shake vigorously for ten minutes, keeping the temperature from rising by frequently holding the funnel under the running water. Allow the funnel to stand a few minutes, draw off the lower aqueous layer containing the nickel, copper, manganese, and other chlorides not held by the ether, wash down the sides of the separatory funnel with hydrochloric acid (1.1 sp. gr.), shake with the

<sup>1</sup> See method of Chase for the "Determination of Nickel and Aluminium in Steel" in the appendix of "The Chemical Analysis of Iron," by Blair, third edition.