

some articles cast from a twenty-five per cent. alloy. These low-grade alloys can be used for making luxury articles, statuettes, etc. The metal when polished has a beautiful, and lasting luster. The higher grades and also the lower grades may perhaps be used instead of aluminum in the heating process of Goldschmidt. This process consists of mixing aluminum foil with some substance capable of yielding oxygen, and igniting the mixture at one point. The reaction between the aluminum and the oxygen, if started at one point, gradually proceeds through the whole mass and a heat is produced, which, in intensity, is second only to that of the electric arc. The silicon of the iron silicide may replace the aluminum, and can be made for a lower figure. These silicides are valuable abrasives, being very hard, and still easily crushed.

WILLSON ALUMINUM Co.,  
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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
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### PERHALIDES OF QUINOLINE.<sup>1</sup>

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THE most of the work reported in this paper was completed in the spring of 1897. Publication was delayed because the author hoped soon to be able to complete the study of the halogen salts of quinoline, and the action of the halogens upon these salts and upon the base itself. Other duties have prevented this until it is deemed advisable to present the work in so far as ready, hoping to continue the research during the following year.

The halogen salts of quinoline have been known for a long time, yet only the chloride<sup>2</sup> seems to have been reported. No attempt was made to prepare this salt in crystalline form. For the experiments where the chloride was used it was assumed that it was formed by the addition of an excess of hydrochloric acid to the base. The results confirm this assumption.

An attempt was made to prepare the quinoline hydrobromide in pure condition. A mixture of the acid and base was warmed

<sup>1</sup> Continuation of previous paper. This JOURNAL, 19, 553.

<sup>2</sup> Schiff: *Ann. Chem.* (Liebig), 131, 112.

for some time on the water-bath. Upon cooling, nearly colorless needle-like crystals were obtained. As these were found to be exceedingly deliquescent, and the chief object in the preparation being the study of the further action of the halogens, the attempt at analysis was deferred. (This salt will be investigated later.)

*Quinoline Hydriodide*,  $C_9H_7N.HI$ .—Hydriodic acid (boiling-point  $126^\circ-127^\circ$ ) was added in slight excess to quinoline, and the mixture heated over a small flame in a flask provided with a reflux condenser. Upon cooling, the iodide separated out as yellow needle-shaped crystals. They were recrystallized from absolute alcohol. Melting-point  $135^\circ$ .

	Calculated for $C_9H_7N.HI$ .	I.	Found.	II.
Iodine	49.39	49.44		49.32

*Quinoline Methyl Chloride*,  $C_9H_7N.CH_2Cl$ , has been prepared<sup>1</sup> by heating quinoline, methyl alcohol, and concentrated hydrochloric acid to  $160^\circ$  for ten hours. Perfectly white crystals containing one molecule of water were obtained melting at  $126^\circ$ , and at  $140^\circ$  losing water and becoming deliquescent and rosy red. That used in the following experiments was prepared, without attempt at crystallization, by shaking a watery solution of quinoline methyl iodide with freshly precipitated silver chloride.

*Quinoline Methyl Bromide*,  $C_9H_7N.CH_2Br$ , was prepared by passing methyl bromide into quinoline. An abundance of colorless needle-like crystals were obtained. They were dried and used directly in the following experiments. They are readily soluble in water, alcohol, ether, and chloroform; slightly soluble in acetone, and almost insoluble in petroleum ether and benzene. Melting-point  $70^\circ$ . (Analytical data and other properties will be given in a later paper.)

*Quinoline Methyl Iodide*,  $C_9H_7N.CH_2I$ , has been reported by Williams<sup>2</sup> and La Coste.<sup>3</sup> For the following experiments it was prepared by heating quinoline and methyl iodide, on a water-bath, in a flask provided with a reflux condenser. They are sulphur-yellow crystals, soluble in water, alcohol, chloroform,

<sup>1</sup> Ostermayer: *Ber. d. chem. Ges.*, 18, 593.

<sup>2</sup> *Jsb. d. Chem.*, 1856, 534.

<sup>3</sup> *Ber. d. chem. Ges.*, 15, 192.

and ether. Melting-point  $72^{\circ}$ , agreeing with Williams and LaCoste.

*Quinoline Hydrobromide Tetrabromide*,  $C_9H_7N.HBr.Br_4$ .—Hydrobromic acid was added, in slight excess, to quinoline, and the mixture then saturated with the vapor of pure bromine. A heavy, dark, oily layer separated, which soon solidified as a mass of dark red cubic crystals. They are soluble apparently without decomposition in water, ether, alcohol, and chloroform. Upon exposure to the air they gradually decompose, bromine being given off. Melting-point  $39^{\circ}$ .

	Calculated for $C_9H_7N.HBr.Br_4$ .	I.	Found. II.
Total bromine .....	75.42	75.23	75.10
Bromine by thiosulphate....	60.34	60.61	60.69

A portion of the crystals above described was exposed to the air until constant weight was obtained and no more bromine seemed to be evolved. The compound was then easily soluble in water, alcohol, ether, and chloroform. It crystallized from the last as beautiful red needles, apparently perfectly uniform in composition. Melting-point  $88^{\circ}$ . Analysis shows it to be a mixture of lower perbromides, and not a definite compound.

*Quinoline Hydrobromide Dibromide*,  $C_9H_7N.HBr.Br_2$ .—When an aqueous solution of quinoline hydrochloride was saturated with bromine, a heavy, red oil settled to the bottom, becoming a solid mass of red crystals as soon as separated from the supernatant liquid and exposed to the air. These crystals were dried rapidly between filter-papers and recrystallized from chloroform, fine red crystals melting at  $98^{\circ}$ – $99^{\circ}$ . A qualitative test showed entire absence of chlorine.

	Calculated for $C_9H_7N.HBr.Br_2$ .	I.	Found. II.
Bromine by thiosulphate....	43.20	43.07	43.10
Total bromine .....	64.30	64.29	63.98

*Quinoline Methyl Bromide Dibromide*,  $C_9H_7N.CH_3Br.Br_2$ .—Crystals of quinoline methyl bromide were dissolved in water and the solution saturated with bromine. At first a yellow precipitate formed, gradually changing to a heavy, red oil. When the oil was exposed to the air for the evaporation of the excess of bromine, it became a very hard, yellow, crystalline mass,

almost insoluble in water and ether, sparingly soluble in chloroform, and readily soluble in absolute alcohol, from which it crystallizes as yellow needles. Melting-point  $108^{\circ}$ .

	Calculated for $C_9H_7N.CH_3.Br.Br_2$ .		Found.	
	I.	II.	III.	
Bromine by thiosulphate...	41.39	41.81	41.75	41.72
Total bromine .....	62.44	62.42	62.35	....

*Quinoline Hydriodide Tetraiodide*,  $C_9H_7N.HI.I_4$ .—Fifteen grams of iodine, dissolved in alcohol, were mixed with five grams of quinoline hydriodide, dissolved in water. Upon standing for some time a large bulk of black crystals was obtained. These were found to crystallize best from about sixty per cent. alcohol, from which solution they were obtained as lustrous black plates. Melting-point  $76^{\circ}$ .

	Calculated for $C_9H_7N.HI.I_4$ .		Found.	
	I.	II.	III.	
Iodine by thiosulphate.....	66.36	66.37	....	
Total iodine .....	82.95	82.60	82.87	

This same compound was formed when an alcoholic solution of iodine was added in excess to a solution of quinoline hydrobromide. The crystals first obtained were twice recrystallized from alcohol. Melting-point  $76^{\circ}$ . A qualitative test showed entire absence of bromine.

	Calculated for $C_9H_7N.HI.I_4$ .		Found.	
	I.	II.	III.	
Iodine by thiosulphate .....	66.36	66.31	66.33	
Total iodine .....	82.95	82.51	....	

*Quinoline Methyl Iodide Tetraiodide*,  $C_9H_7N.CH_3.I.I_4$ .—An excess of an alcoholic solution of iodine was added to an aqueous solution of quinoline methyl iodide,  $C_9H_7N.CH_3.I$ . Crystals began to form immediately and after a short time were separated from the mother-liquor, dried, and twice recrystallized from alcohol. Melting-point  $70^{\circ}$ . Analyses I and II are given below.

In another preparation, an alcoholic solution of iodine was added in excess to an aqueous solution of quinoline methyl chloride. Very dark crystals soon formed, which were dried and twice recrystallized from absolute alcohol. A qualitative test showed absence of chlorine, but the analytical results are a little high for the pure quinoline methyl iodide tetraiodide,— III and IV below.

In still another preparation, an alcoholic solution of iodine was added, in excess, to an aqueous solution of quinoline methyl bromide. Crystals began to form at once. After standing for some time the crystals were drained, dried, and recrystallized from alcohol, forming black-green crystals, melting at  $70^{\circ}$ . A qualitative test showed the absence of bromine,—V and VI below.

	Calculated for		Found.				
	$C_9H_7N.CH_3I_4$ .	I.	II.	III.	IV.	V.	VI.
Iodine by thiosulphate..	65.15	65.11	65.06	66.81	66.62	65.08	65.06
Total iodine.....	81.45	81.18	81.26	82.93	82.54	....	....

*Quinoline Hydrochloride Bromide*,  $C_9H_7N.HCl.Br$ .—Chlorine was passed for three hours into a mixture of quinoline and hydrobromic acid dissolved in an abundance of water. The solution became dark-colored and crystals were formed. Gradually the liquid became clear with a voluminous mass of yellow crystals in the bottom of the dish. These were washed with warm water and twice recrystallized from chloroform. They form fine yellow needles melting at  $101^{\circ}$ – $102^{\circ}$ .

	Calculated for	Found.	
	$C_9H_7N.HCl.Br$ .	I.	II.
Halogens by thiosulphate ...	14.42	14.29	14.27
Total halogens.....	46.97	46.73	46.54

*Quinoline Methyl Chloride Bromide*,  $C_9H_7N.CH_3Cl.Br$ .—Quinoline methyl bromide was dissolved in water and saturated with chlorine. A yellow crystalline mass was formed, soluble in chloroform, from which it crystallized as yellow scales. Melting-point  $112^{\circ}$ . A qualitative test showed the presence of bromine.

	Calculated for	Found.	
	$C_9H_7N.CH_3Cl.Br$ .	I.	II.
Halogens by thiosulphate...	11.35	11.10	11.03
Total halogens.....	32.94	32.17	32.11

*Quinoline Hydrochloride Iodochloride*,  $C_9H_7N.HCl.ICl$ .—Quinoline hydriodide dissolved in water, was warmed on the water-bath and then saturated with chlorine. The solution became dark at first, as if from precipitated iodine, then the dark color gradually disappeared with the formation of yellow crystals. These are sparingly soluble in chloroform, but long yellow prismatic crystals were obtained by partial evaporation of the chlo-

reform solution and then setting aside, loosely covered, in a cool place. Melting-point  $112^{\circ}$ .

	Calculated for $C_9H_7N.HCl.ICl.$	I.	Found. II.
Halogens by thiosulphate...	21.61	21.75	21.64
Total halogens.....	60.27	60.04	59.70

*Quinoline Methyl Chloride Iodochloride*,  $C_9H_7N.CH_2Cl.ICl.$ —A watery solution of quinoline methyl iodide was heated on the water-bath and saturated with chlorine. The clear solution rapidly assumed a very dark brown color, gradually changing to a clear solution and a yellow precipitate. The precipitate was collected, dried, and recrystallized from chloroform. Fine yellow crystals were obtained.

	Calculated for $C_9H_7N.CH_2Cl.ICl.$	I.	Found. II.
Halogens by thiosulphate...	20.73	20.60	20.58
Total halogens.....	57.80	57.64	57.48

*Quinoline Hydrobromide Iodobromide*,  $C_9H_7N.HBr.IBr.$ —Quinoline hydriodide was dissolved in water and saturated with bromine. A dark oil, containing crystals, soon settled to the bottom of the liquid. The oily and crystalline mass was carefully separated from the supernatant liquid, and warmed upon the water-bath to drive off excess of bromine. A red crystalline mass was obtained moderately soluble in absolute alcohol, from which solution it crystallizes nicely after partial evaporation. Melting-point  $109^{\circ}$ .

	Calculated for $C_9H_7N.HBr.IBr.$	I.	Found. II.	III.
Halogens by thiosulphate...	38.36	38.40	38.31	38.34
Total halogens.....	68.77	68.52	68.40	....

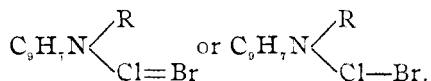
*Quinoline Methyl Bromide Iodobromide*,  $C_9H_7N.CH_2Br.IBr.$ —Heavy, dark red oil is formed upon saturating a watery solution of quinoline methyl iodide with bromine. Upon exposing the oil to the air for the evaporation of the excess of bromine, a mass of reddish crystals was obtained. These crystallized from absolute alcohol as yellow plates containing iodine. Melting-point  $108^{\circ}$ .

	Calculated for $C_9H_7N.CH_2Br.IBr.$	I.	Found. II.	III.
Halogens by thiosulphate...	37.11	37.66	37.32	37.24
Total halogens .....	66.51	66.40	66.37	....

## SUMMARY.

The action of bromine upon quinoline methyl chloride has not been studied, nor the action of the halogens upon the ethyl halides of quinoline. These will be reported later. Iodine completely displaces chlorine from quinoline hydrochloride, but in all cases a tarry-like mass was obtained, which could not be purified for analysis.

The general reactions with quinoline are very similar to those with pyridine<sup>1</sup>. No perchlorides of the normal chlorides are formed. Chlorine seems to displace bromine and iodine from the normal position, and then, with the iodocompounds, to combine with the displaced halogen, forming iodochlorides of the normal chlorides. With the bromides there is but one atom of perhalogen, thus giving other instances of a probable bivalent halogen<sup>2</sup>; *i.e.*,



Bromine displaces chlorine completely, forming perbromides of the normal bromides. It displaces iodine from the normal position and then combines with the displaced iodine to form an iodobromide of a normal bromide. Iodine displaces both chlorine and bromine from the normal position forming periodides of the normal iodides.

The action of the halogens upon quinoline has been studied by Grimaux,<sup>3</sup> Claus and Istel,<sup>4</sup> Ostermayer,<sup>5</sup> and Dittmar<sup>6</sup>; but none of these give the action of reducing agents as showing the probable relation of the halogen atoms. It is proposed to take up this study in the near future.

I wish to express my thanks to Professor A. B. Prescott, in whose laboratory and under whose general supervision the work has progressed; also to Mr. John D. Wombacher, for his assistance in the laboratory at Ann Arbor.

MARBURG, GERMANY, November 24, 1898.

<sup>1</sup> This Journal, 19, 558.

<sup>2</sup> *Ibid.*, 19, 322.

<sup>3</sup> *Bull. Soc. Chim.*, 38, 124

<sup>4</sup> *Ibid.*, 18, 600.

<sup>5</sup> *Ber. d. chem. Ges.*, 15, 824.

<sup>6</sup> *Ibid.*, 18, 1613.