

VIII. *On a new Equiatomic Compound of Bicyanide with Binoxide of Mercury.* By
 JAMES F. W. JOHNSTON, *Esq. M.A. F.R.S., Professor of Chemistry and Mineralogy in the University of Durham.*

Received March 21,—Read April 11, 1839.

WHEN hydrocyanic acid of considerable strength (10 to 20 per cent.) is agitated with red oxide of mercury in large excess, a white compound is obtained, intermixed with the red oxide, on which cold water has very little action. If the mixture be collected on the filter and treated with boiling water, the new compound is separated from the excess of oxide, and, as the solution cools, is deposited on the sides of the vessel in the form of a white incrustation, adhering strongly, and consisting of an aggregation of colourless transparent four sided acicular prisms. In favourable circumstances, I have obtained it in such prisms half an inch in length, but not sufficiently perfect to admit of measurement.

This salt is remarkably distinguished from the bicyanide by its sparing solubility in cold water, by the strong alkaline reaction exhibited by its solution, and by its relations to heat. Heated gently in the air, it blackens slightly and then explodes with little noise, but if it be heated in larger quantity (5 to 10 grs.), and in a close tube, it explodes with a loud detonation, and shivers the tube into fragments. It does not explode under the blow of a hammer.

Burned with bichromate of potash or oxide of copper it gives off a gas which consists of nitrogen and carbonic acid, in the proportion of one volume to two. Thus

1. 131 vols. treated with caustic potash left	47
239 vols. treated with caustic potash left	79
2. 122 vols. treated with caustic potash left	40
91 vols. treated with caustic potash left	31·5
<hr/>	<hr/>
590	197·5

and $197·5 \times 3 = 592·5$.

The formation of this new salt therefore is not due to any decomposition of the cyanogen.

Dissolved in dilute muriatic acid and gently heated, it emits the odour of prussic acid. If sulphuretted hydrogen be passed through the solution in water, a precipitate, at first white and afterwards becoming black, is thrown down. To the solution filtered and heated to drive off the excess of hydrosulphuric acid, sulphate of iron and afterwards caustic potash were added, when a precipitate of Prussian blue fell. The salt therefore contains

MDCCCXXXIX.

Q

1. Cyanogen, since its solution when decomposed by hydrosulphuric and hydrochloric acid gives hydrocyanic acid.

2. Its alkaline reaction indicates an excess of mercury.

3. That this excess is in the state of oxide is shown by the detonating property of the salt, the sudden decomposition being due to the action of the oxygen on a portion of the carbon of the cyanogen.

Heated to incipient decomposition the salt loses no weight, it is therefore anhydrous.

29.275 grains dissolved in hydrochloric and precipitated by hydrosulphuric acid gave 29.245 grains of bisulphuret of mercury = 86.191 grains of metallic mercury per cent.

29.27 grains gave 29.15 grains bisulphuret = 85.933 Hg per cent.

34.93 grains gave 34.68 grains bisulphuret = 85.674 Hg per cent.

The last result, as we shall see, is nearest the truth.

Burned with oxide of copper,

63.55 grains gave $\ddot{C} = 11.96 = 5.203$ carbon per cent.

$\dot{H} = 0.60$

43.94 grains gave $\ddot{C} = 8.00 = 5.034$ carbon per cent.

The small quantity of water obtained in the first analysis was obviously accidental, and therefore the water was neglected in the second. And since the nitrogen is to the carbon, as already shown, in the proportion of one volume or atom to two, 5.203 carbon, the result of the two very approximate ones, which should be nearest the truth, indicates 6.025 of nitrogen, since,

$$152.875 : 177.036 :: 5.203 : 6.025.$$

Therefore the salt consists by analysis of

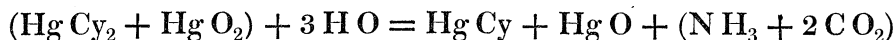
Carbon	=	5.203
Nitrogen	=	6.025
Mercury	=	85.674
Oxygen	=	3.098
		100

This composition agrees with the formula ($\text{Hg Cy}_2 + \text{Hg O}_2$) which gives

		per cent. calculated.	per cent. by experiment.
2. Cyanogen .	{	4 carbon = 305.750 =	5.162 5.203
		2 nitrogen = 354.072 =	5.977 6.025
		2 mercury = 5063.288 =	85.483 85.674
		2 oxygen = 200.000 =	3.378 3.098
		5923.110 100	100

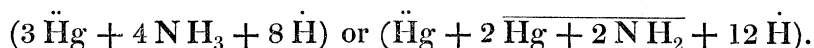
This salt exhibits many very interesting reactions.

1. Heated over a lamp, under water, it becomes yellow, and a portion of a yellow powder (Hg Cy?) ultimately remains undissolved, mixed with protoxide and a little metallic mercury; that is, a portion of it is decomposed, probably according to the following formula

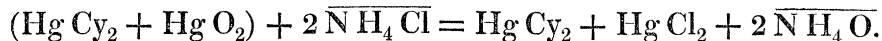


the reduction of the mercury being the consequence of a second reaction.

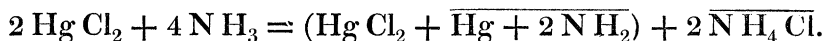
2. Caustic ammonia throws down from a cold solution of this salt, a copious and bulky white precipitate; from a hot solution, the precipitate is slightly yellowish. The supernatant liquid, on evaporation, gives pure bicyanide of mercury. The precipitate when dried at 212° FAHR. and heated in a close tube over a lamp, gives off ammonia, water, and metallic mercury. It is probably the same compound which is obtained by digesting red oxide of mercury in caustic ammonia, and which is *supposed* to be represented by one or other of the formulæ



3. A solution of sal ammoniac throws down a yellow precipitate, the supernatant liquid having a strong alkaline reaction. On heating, the precipitate is redissolved, ammonia is given off, and the alkaline reaction disappears. The *direct* action here is the change of the binoxide into bichloride and the liberation of ammonia, according to the formula



The white precipitate is a secondary result, due to the action of the free ammonia (as above mentioned), and which consequently disappears when the ammonia is driven off by heat. In this case, however, since bichloride is present, the white precipitate will not be the same as is produced by the action of ammonia on the new salt (2.), but may consist in part or in whole of the long-known *hydrargyrum precipitatum album*, the true composition of which ($\text{Hg Cl}_2 + \overline{\text{Hg}} + 2 \overline{\text{N H}_2}$) has been recently established by Dr. KANE. This reaction is represented by the formula



4. The fixed alkaline chlorides render the solution of the new salt milky, and throw down a small quantity of a white precipitate, the liquid becoming more strongly alkaline. In this case also, the chloride gives up its chlorine to the mercury, and the free alkali causes the increased causticity of the solution. The milkiness I attribute to the presence in small quantity either of ammonia, or of some neutral salt (formiate?) of mercury, the decomposition of which by the alkaline chloride causes the formation of an equivalent portion of calomel. It is known how readily formic acid and ammonia are produced at the expense of cyanogen, when water is present*, and it would appear that the action of heat upon this new double salt in water very frequently gives rise to these products. In treating with boiling water the mixture of

* The reaction is thus represented: $\text{N C}_2 + 4 \text{H O} = (\text{H C}_2 \text{O}_3 + \text{N H}_3).$

oxide of mercury and this salt, (which is produced on digesting prussic acid with the latter in excess,) in order to obtain the salt in solution, copious bubbles of gas are evolved, the smell of ammonia becomes perceptible, and much metallic mercury is precipitated*. On concentrating the solutions also, decomposition takes place, with deposition of metallic mercury; and when the crystallized salt is dissolved in boiling water, a black sediment in greater or less quantity is generally observable. In the solution therefore when cold, the presence either of a trace of a formiate or of any ammoniacal salt would account for the slight deposit which occurs when chloride of potassium is added to it. When chloride of magnesium is employed, the milkiness is more speedy and more distinct, a light bulky hydrate of magnesia being thrown down, as is to be expected, when we consider that on parting with its chlorine the magnesium is oxidized, and set at liberty in a liquid which can retain very little of it in solution.

If the salt be added in successive quantities to a concentrated boiling solution of chloride of potassium, it is largely dissolved, and on cooling, the beautiful pearly scales of the compound of bichloride of mercury with chloride of potassium fall down. The supernatant liquid contains bichloride of mercury and caustic potash.

A solution of iodide of potassium produces analogous compounds and reactions, as does also a solution of cyanide of potassium.

5. The solution of this new salt (oxycyanide), as has been already stated, has a strong alkaline reaction. If it be added to a very dilute solution of nitric acid till the solution ceases to redden litmus, it will be found to dissolve with great ease and in large quantity. The solution by careful evaporation gives long, delicate, transparent, colourless, quadrangular prisms, or hexagonal plates and pearly scales, and crystallizes to the last drop.

At 212° FAHR. these crystals lose nothing, and therefore contain no water. Over the lamp in the open air they decompose with a flash of white light, giving off metallic mercury, and leaving a yellow residue. In a close tube they are decomposed with a slight detonation, and with the emission of red fumes.

38·334 grains of the oxycyanide, cautiously treated in this way, gave beautiful crystals, weighing 40·53 grains, equal to an increase of 5·728 per cent. The new compound therefore consists of

		Calculated.	Found.
One equivalent of oxycyanide ($\text{Hg Cy}_2 + \text{Hg O}_2$)	= 59·23	94·285	94·272
One half equivalent of nitric acid, $\frac{1}{2} \text{N O}_5$	= 3·38	5·715	5·728
	<hr/>	<hr/>	<hr/>
	62·61	100	100

This salt is readily soluble in water. What is chiefly interesting in regard to its constitution and properties is, that the alkaline reaction of the oxycyanide should be fully

* This second reaction is due to the decomposition of the formiate of ammonia by the agency of the binoxide of mercury thus: $(\text{H C}_2 \text{O}_3 + \text{N H}_3) + \text{Hg O}_2 = (\text{N H}_3 + \text{C O}_2) + \text{C O}_2 + \text{Hg}$.

destroyed by so small a quantity of nitric acid. This fact would seem to show, that the bicyanide of mercury, and consequently other compounds of the same class, do really possess something of the characters of the true acids, having the power, if not of completely neutralizing a metallic oxide, at least of so far modifying its basic character as materially to weaken its neutralizing action on the oxygen acid.

6. This is further illustrated by the action of acetic acid on the oxycyanide. A weak solution of this acid dissolves it in large quantity, and if carefully saturated, the solution gives, on evaporation, a white salt having the odour of acetic acid, which loses nothing at 220° FAHR., but when heated in a close tube, blackens and gives off cyanogen, metallic mercury, and a strong odour of acetic acid. In preparing this salt, it is difficult so perfectly to neutralize the acetic acid, that, during the evaporation*, any excess that may be present should not, as it becomes concentrated, decompose some of the bicyanide which the solution contains. On the following results, therefore, I do not place much reliance, though they serve to show by how small a quantity of this acid the oxycyanide may be perfectly neutralized.

	Increase.
49 grains of oxycyanide gave 49.94 of the new salt	= 1.918 per cent.
34.567 grains of oxycyanide gave 35.36 of the new salt	= 2.294 per cent.
54.00 grains of oxycyanide gave 54.92 of the new salt	= 1.704 per cent.

Taking the atom of acetic acid at 623, these results indicate the addition of *one-sixth* of an equivalent of this acid to each equivalent of the oxycyanide, or that the new compound is $(\text{Hg Cy}_2 + \text{Hg O}_2 + \frac{1}{6} \bar{\text{A}})$. Thus we have

	Calculated per cent.	Found per cent.
One equivalent of the oxycyanide = 5923	= 98.23	98.296
One-sixth equivalent of acetic acid = 643 = 107	= 1.77	1.704
<hr style="width: 50%; margin: 0 auto;"/> 6 6030	<hr style="width: 50%; margin: 0 auto;"/> 100	<hr style="width: 50%; margin: 0 auto;"/> 100

Though this is not a solitary instance in which one of acetic acid combines with six of base, the subacetate of lead ($6 \text{Pb O} + \bar{\text{A}}$) being an analogous salt, yet I would be understood as representing the constitution above given for this salt as open to future correction.

I have tried also several other organic acids, and have found that with the benzoic and citric acids, soluble and crystallizable salts may be obtained, and with tartaric acid, a compound which, after being crystallized, is decomposed by water into a soluble and an insoluble portion. Oxalic acid gives a white precipitate, and the filtered solution, on evaporation, two salts; one in white prisms, the other in yellowish crystals. I have not subjected any of these compounds to analysis.

7. When an acid solution of nitrate of silver is poured into a hot saturated solution of the oxycyanide, a shower of beautiful pure white prismatic crystals falls.

* When a solution of the bicyanide is heated with acetic acid the odour of prussic acid becomes distinctly perceptible.

These crystals dissolve readily in hot water and re-crystallize on cooling. Heated in a close vessel they give off water, become opaque, melt, and finally explode, with the beautiful purple flame characteristic of burning cyanogen.

Heated on the Water Bath.

33·125 grains lost 2·63 grains = 7·939 per cent.

31·075 grains lost 2·46 grains = 7·916 per cent.

On standing in a moist atmosphere for a few days, the dry salt recovers the whole of its water of crystallization.

The 33·125 grains, after drying as above, were dissolved in water and precipitated by muriatic acid. The chloride of silver obtained weighed 10·48 grains, = 23·834 per cent., or 37·533 of nitrate of silver. This salt therefore is the compound discovered by WÖHLER ($\text{Hg Cy}_2 + \text{Ag O} \cdot \text{N O}_5 + 4 \text{H O}$), and which is composed of

	Calculated per cent.	Found per cent.
Bicyanide of mercury, 1 equivalent = 2991·46	53·709	54·540
Nitrate of silver, 1 equivalent . . . = 2128·64	38·214	37·533
Water, 4 equivalents = 449·92	8·077	7·927
	<hr/>	<hr/>
	5570·02	100
	100	100

Many of the other interesting reactions of the oxycyanide may be predicted from its constitution, and its use as a reagent will occasionally be valuable to the chemist, from its affording a solution in which binoxide of mercury exists as such, and possessed of alkaline properties.

Durham, February 1839.