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STUDIES ON HALOGEN-CYANIDES I.

THE MOLECULAR WEIGHT, THE STABILITY AND THE BASIC HYDROLYSIS OF CYANOGEN BROMIDE

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1). Introduction.

It has been shown by SERULLAS[1] and by NEF[2] that cyanogen chloride and cyanogen bromide are decomposed quantitatively into potassium cyanate and potassium halide by the action of potassium hydroxide. Iodine cyanide, however, is decomposed by potassium hydroxide with the formation of potassium cyanide. potassium cyanate, potassium iodide and potassium iodate in variable proportions depending upon the concentration and the temperature of the reacting solutions.

This difference in behaviour may be due to a difference in the structure of the two substances, such as it is indicated by the names, i. e. that in cyanogen bromide bromine is the electronegative part of the molecule (CN^+Br^-), while in iodine cyanide the iodine forms the electropositive part of the molecule (I^+CN^-). This, however, without assuming anything else concerning the structure of the two molecules.

The basic hydrolysis of cyanogen bromide might then result in the formation of a cyanate and a bromide, while iodine cyanide would give, as the first products of the reaction, a cyanide and a hypoiodite. The hypoiodite, however, would for a part undergo a decomposition into an

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[1] SERULLAS. A. chim. phys. [2]. **35** (1827) 345.

[2] NEF. A. **287** (1895) 316.

iodide and an iodate and for a part oxidize some of the cyanide into a cyanate.

As the transformation velocity of a hypoiodite into an iodate is known to be very much greater than the velocity with which a hypobromite is transformed into a bromate, it might also be possible that the basic hydrolysis of cyanogen bromide yields a hypobromite and a cyanide as the first products of the reaction, but that the hypobromite, which does not get time to become transformed into a bromate, oxidizes the cyanide quantitatively into cyanate.

Dixon & Taylor[1] have accepted the last point of view and formulate the reaction in the following manner:

$$K_2O + {=}C{=}NBr \rightarrow KO{-}CK{=}NBr \rightarrow$$
$$KBrO + KCN \rightarrow KOCN + KBr.$$

It should, however, also be born in mind that tautomeric changes, such as shown by hydrocyanic acid, are not excluded and may be the cause of the complexity of the basic hydrolysis of iodine cyanide.

2). The Preparation of Cyanogen Bromide and its Purity.

The cyanogen bromide was prepared according to Scholl[2] from sodium cyanide and bromine, and it was then purified and dried according to Steinkopf[3] by distillation over calcium chloride and metallic sodium.

The preparation and purification proceed smoothly and the product is perfectly pure.

1.3983 gram of cyanogen bromide was dissolved in a

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[1] Dixon & Taylor. Trans. Chem. Soc. **103** (1913) 974.

[2] Scholl. B. **29** (1896) 1822. B. **41** (1908) 523.

[3] Steinkopf. J. prak. Chem. **109** (1925) 347.

100 ccs. volumetric flask and the volume made up to the mark. This solution is 0.1320 molal.

10.00 ccs. of this solution were added to a mixture of 2 grams of potassium iodide and 20 ccs. of a 5 % acetic acid, and the liberated iodine titrated with thiosulphate according to Chattaway & Wadmore[1]. 26.98 ccs. of a 0.09783 N. sodium thiosulphate solution were consumed, and the cyanogen bromide solution thus is 0.1320 molal.

10.00 ccs. of the same cyanogen bromide solution were added to a conc. solution of sodium hydroxide (halogenfree, analytical reagent). After the decomposition nitric acid was added to acid reaction and then 37.10 ccs. of a 0.04397 N. solution of silver nitrate. After filtration and washing of the precipitate the excess of silver nitrate was found to be equivalent to 6.20 ccs. of a 0.04992 N. solution of potassium thiocyanate. The total consumption is therefore 30.06 ccs. of the 0.04397 N. silver nitrate solution. From this it is calculated that the cyanogen bromide solution is 0.1322 molal.

10.00 ccs. of the same cyanogen bromide solution were runned into 20 ccs. of sodium hydroxide lye for ammonia distillation. After a while an excess of sulphuric acid was added, and the reaction mixture boiled to hydrolyse the cyanate. After cooling the mixture was made alkaline with sodium hydroxide, and the ammonia distilled over into 53.04 ccs. of a 0.02524 N. solution of hydrochloric acid. The excess of acid was found to be equivalent to 0.93 cc. of a 0.02035 N. solution of sodium hydroxide. The consumption of acid is therefore 52.29 ccs. of a 0.02524 N. hydrochloric acid, and the cyanogen bromide solution is 0.1320 molal.

The results of the three estimation methods are in

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[1] Chattaway & Wadmore. J. Chem. Soc. 81 (1902) 196.

agreement and show that the substance is perfectly pure. Since the amount of ammonia obtained in the last experiment is in agreement with the theoretical quantity, this experiment also shows that cyanogen bromide in a basic hydrolysis is transformed quantitatively into a cyanate.

3). The Stability of Cyanogen Bromide.

When completely dry, such as it is on distillation over calcium chloride and metallic sodium, cyanogen bromide is able to keep for 1 to 1$^1/_2$ month at ordinary temperature, even if the bottle is opened up now and then, and it keeps much longer in fused off phials.

If it contains moisture a decomposition soon sets in. Hydrogen bromide is evolved, and this catalyzes the polymerization of the undecomposed cyanogen bromide into cyanuric bromide, $(BrCN)_3$, which is a white substance insoluble in water. However, simultaneously an orange-yellow, water soluble, volatile substance is formed, which passes over with the cyanogen bromide on distillation and seems to induce a rapid decomposition. Only on distillation over metallic sodium may it be removed. When the orange-yellow cyanogen bromide is dissolved in water and added with sodium hydroxide, sodium cyanide or hydrocyanic acid the orange-yellow colour disappears. There seems to be some evidence therefore, that the orange-yellow colour is due to traces of free bromine dissolved in the cyanogen bromide crystals. The formation of bromine may be due to that the reaction:

$$Br_2 + HCN \rightleftarrows BrCN + Br^- + H^+$$

is reversible, but with the equilibrium attained far to the right hand side. This will be taken up for discussion in a later paper.

4). The Molecular Weight of Cyanogen Bromide in the Gaseous State.

In a investigation on the Friedel-Craft's reaction between benzene and cyanogen bromide KARRER & ZELLER[1] have found that the nitrile is readily formed with freshly prepared cyanogen bromide, while 3 weeks old cyanogen bromide does not react at all.

This behaviour might be due to a gradual polymerization, the final product of which is cyanuric bromide.

In a series of measurements with Victor Meyers apparatus applying cyanogen bromide of different ages, from freshly made to $1^1/_2$ month old preparations, all of which had shown no sign of decomposition (no fumes of hydrobromic acid and no discolouration), the following results were obtained:

Freshly made	BrCN.	Molecular	weight	106.7
One week old	„	„	„	107.7
Two weeks old	„	„	„	105.1
Three „ „	„	„	„	107.8
Four „ „	„	„	„	104.1
Six „ „	„	„	„	107.8
			Mean...	106.6. Theory 105.9.

These results do not indicate any polymerization in the gaseous state.

5). The Molecular Weight of Cyanogen Bromide in Aqueous Solution and the Electric Conductivity.

The polymerization, however, may be reversible at the temperature of the VICTOR MEYER apparatus (100°), and the molecular weight in aqueous solution was therefore estimated by the freezing point method. For an about 2 months

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[1] KARRER & ZELLER. Helv. Chim. Ac. 2 (1919) 484.

old preparation, which showed no sign of decomposition, the molecular weight was found to 100.7 as an average of 6 estimations.

This value is lower than the theoretical, such as it might also be expected from the fact that cyanogen bromide is hydrolyzed by the action of water. The result, however, induced the wish to investigate the electric conductivity of freshly made aqueous solutions of freshly made cyanogen bromide, to ascertain whether or not it undergoes a reversible hydrolysis followed by an irreversible reaction.

0.2850 g of cyanogen bromide was dissolved to 250 ccs. with water at 25°, and the conductivity measured 8 minutes later and found to $2.73 \cdot 10^{-6}$. On subtraction of the conductivity of the water, which was found to be $1.46 \cdot 10^{-6}$, this result gives a conductivity due to the cyanogen bromide of $1.27 \cdot 10^{-6}$, or a molecular conductivity of 0.118 at 25°.

However, the conductivity of the solution gradually increases, and by plotting the corrected values (conductivity of solution ÷ conductivity of water) the conductivity-time curve may be extrapolated to the moment the cyanogen bromide was added to the water, and it appears that this very closely and quite unstrained gives the conductivity zero. There is no indication of a reversible hydrolysis.

In the course of the measurements it appeared, that the conductivity varied quite regularly with the time, when the conductivity vessel remained quiet in the thermostate. On shaking the conductivity decreased instantaneously, but began immediately a slow increase as before. This effect, perhaps, may be due to a catalytic action of the platinum electrodes.

6). The Molecular Weight of Cyanogen Bromide in Benzene.

Since many substances show polymerization in benzene solutions, it was of interest to investigate the molecular weight of cyanogen bromide in benzene. This for the reason that Karrer & Zeller[1] have worked with benzene solutions, and also for the reason that benzene solutions of cyanogen bromide are applied in a following investigation, which will be published later.

A series of freezing point estimations with freshly made cyanogen bromide in Beckmann's apparatus and with pure, dehydrated (with metallic sodium), distilled benzene gave the results in table I.

Table I.

Benzene in grams	BrCN in grams	Freezing point depression	Molecular weight
14.90	0.2501	0.790°	109.0
16.02	0.1912	0.569	107.6
16.30	0.1504	0.437	108.3
15.23	0.1023	0.325	106.0
16.07	0.08791	0.261	107.5
		Mean...	107.7

This table and the following have been calculated with a normal freezing point depression of 5.13° for one gram-molecule dissolved in 1000 grams of benzene.

Table II.

Benzene in grams	BrCN in grams	Freezing point depression	Molecular weight
15.89	0.2563	0.744°	111.2
16.04	0.1321	0.384	110.0
17.30	0.1011	0.273	109.8
		Mean...	110.3

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[1] (l. c.).

The results for a two month old preparation, containing about 0.1 % of a substance which is insoluble in benzene (cyanuric bromide), are given in table II.

The results in table II are somewhat higher than the theoretical molecular weight (105.9), and the deviation is slightly higher than the experimental error. It may be due to a polymerization, but this can only be slight. The quantity in per cent which had undergone such a polymerization should be:

$$p = \frac{m}{m-1} \cdot \frac{(110.3 - 105.9)\,100}{110.3} = 3.99\,\frac{m}{m-1}.$$

For a polymerization in which cyanuric bromide is formed the value of m is 3. Cyanuric bromide, however, is insoluble in benzene, while of the substance applied only 0.1 % is insoluble. Cyanuric bromide may exist in two modifications with different solubility, but it is more probable that m in the equation above is smaller than 3, i. e. $m = 2$. For this value of m we have:

$$p = 2 \cdot 3.99 = 7.98.$$

This means that about 8 % of the cyanogen bromide should have undergone a polymerization with the formation of the molecule $(BrCN)_2$.

Even if actually a polymerization of this type takes place, it does not explain the results of Karrer & Zellers (l. c.) experiments. They have probably used a preparation of cyanogen bromide which has not been perfectly dehydrated and therefore, in the course of some few weeks, has undergone a partial hydrolysis, with the formation of hydrobromic acid, and a partial polymerization to cyanuric bromide. When heated a rapid polymerization occurs, catalyzed by the hydrobromic acid, before the reaction with benzene sets in.

7). The Basic Hydrolysis of Cyanogen Bromide.

For the question of the constitution of cyanogen bromide an investigation of the basic hydrolysis is of importance. If it could be proved that a hypobromite is an intermediate product of the hydrolysis, this would indicate that the bromine atom is the electropositive part of the cyanogen bromide molecule, or that cyanogen bromide shows a case of tautomerism:

$$Br^{-}CN^{+} \rightleftarrows Br^{+}CN^{-}.$$

For this reason the basic hydrolysis of cyanogen bromide was investigated in three cases, a) by the action of silver hydroxide, b) by the action of mercuric oxide and water, and c) by the action of sodium hydroxide.

a). The Basic Hydrolysis of Cyanogen Bromide by the Action of Silver Hydroxide.

Silver oxide was prepared from 10 grams of silver nitrate by precipitation with pure sodium hydroxide. The precipitate was washed very carefully and suspended in 100 ccs. of water. The mixture was stirred with a rapidly rotating stirrer, and 2 grams of freshly made and pure cyanogen bromide added. The stirring was continued until no odour of cyanogen bromide could be observed. The mixture was filtered to remove the excess of silver oxide and the silver bromide, the silver cyanide and silver cyanate formed in the reaction.

To the filtrate was added nitric acid, and the mixture boiled for some time to transform into silver bromate and silver bromide any silver hypobromite which might have been formed. But not the slightest precipitate of silver bromide was observed in several experiments, i. e. no silver hypobromite is formed, or it must have been transformed into silver bromate in the course of the hydrolysis. The nitric acid solution was boiled, therefore, with a solution of sulphurous acid, but no precipitate of silver bromide could be observed.

b). The Basic Hydrolysis of Cyanogen Bromide by the Action of Mercuric Oxide and Water.

Yellow mercuric oxide was suspended in water and cyanogen bromide was added with constant stirring, which was continued until no odour of cyanogen bromide could be observed. This, however, takes about 48 hours. The reaction thus proceeds very slowly and no trace of mercuric hypobromite or mercuric bromate could be detected.

c). The Basic Hydrolysis of Cyanogen Bromide by the Action of Sodium Hydroxide.

These experiments were made in order to estimate the reaction order and the velocity constant of the basic hydrolysis of cyanogen bromide.

The experiments were made in a flask with a wide neck of about 1800 ccs. capacity. It was fitted with a rubber stopper having a bore for a rotating stirrer fixed with an ordinary mercury valve to prevent the air from the outside, contaminated with carbon dioxide, to pass into the flask and to prevent the evaporation of cyanogen bromide. The stopper had also a bore for a glass tube down to the bottom of the flask. This tube was used for an aeration of the content with air freed from carbon dioxide and for taking out samples. Further, the stopper had a bore fitted with a short, wide glass tube ordinarely closed with a rubber stopper. This was used for adding one of the reacting substances to the other in the reaction flask. Finally the stopper had a bore for a soda-lime tube.

As the sodium hydroxide solutions, which were applied in these experiments, are very dilute, it is necessary to be very carefull not to get a great percentic contamination with carbonate by exposure to the laboratory air.

The sodium hydroxide solutions for the kinetic experiments were made from a concentrated, carbonate-free sodium hydroxide lye with aerated water. The sodium hydroxide lye was made by the method of SÖRENSEN[1], and according to BJERRUM[2] such a solution contains only about 0.5 equivalent of carbonate per 100 equivalents of sodium hydroxide.

The standard solution was estimated by means of pure sodium carbonate (through a hydrochloric acid titration) and by means of potassium biphthalat to be 0.4559 N. All other sodium hydroxide solutions were made from this by dilution.

The experiments were made in the following manner: A certain quantity of aerated water (calculated to have the desired volume at 0°) was weighed out in the reaction flask. The stopper with the stirrer was fixed and the flask placed in a water-ice mixture. Air, freed from carbon dioxide by passing through tubes with soda-lime, was bubbled through a gas washing flask filled with pure water and placed in the ice-water mixture, and then through the water in the reaction flask. This aeration was continued for 3 hours. A calculated volume of the standardized sodium hydroxide

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[1] SÖRENSEN. Comp. rend. Lab. Carlsberg. Copenhagen. 8 (1909) 36.

[2] BJERRUM. Det kgl. danske Videnskab. Selsk. math.-fysiske Medd. IX, 1. 85.

solution was now added and the mixture stirred from time to time to bring the temperature of the solution down to zero again.

The cyanogen bromide solution was made by weighing out a certain quantity of pure, freshly made cyanogen bromide in a small phial, dropping the content into a measuring flask with pure, ice-cold water and again weighing the phial with adhering crystals. The solution was made up to the desired volume, cooled to zero and then standardized by the method of CHATTAWAY & WADMORE (l. c.).

A velocity experiment was started by rapidly rotating the stirrer in the reaction flask, and adding the desired volume of cyanogen bromide solution. The stirring was continued for about 2 min. after the addition of cyanogen bromide, when the first sample was taken out. The pipettes employed were surrounded by a wide glass tube containing ice and water. The reaction was stopped short by running the sample into a mixture of 20 ccs. of a 5 percentic acetic acid and 2 grams of potassium iodide, however, if the volume of the sample exceeded 100 ccs. the quantities of acetic acid and potassium iodide were doubled.

The time was calculated from the moment when the half of the first sample had been added to the stop-short mixture, and until the half of one of the following samples had been stopped short.

The results of a series of measurements are given in table III. Here x is the quantity in grammolecules of the cyanogen bromide which has reacted to the time t, while a is the initial concentration of cyanogen bromide, and b the initial concentration of sodium hydroxide.

If the velocity is expressed by means of the equation:

$$\frac{dx}{dt} = K \cdot (a - x) \cdot (b - 2x)$$

this gives for K, the velocity constant, the following value:

$$K = \frac{2.303}{t \cdot (b - 2a)} \cdot \log \frac{a\,(b - 2x)}{b\,(a - x)}.$$

Table III.

The alkaline hydrolysis of cyanogen bromide by sodium hydroxide. Temperature 0° C.

Initial concentration of cyanogen bromide 0.0006006 molal.
Initial concentration of sodium hydroxide 0.004545 molal.

t sec.	ccs. taken out	ccs. $Na_2S_2O_3$ 0.01016 N	BrCN $(a - x)10^4$	$x \cdot 10^5$	NaOH $(b - 2x)10^3$	$K\,10^4$	
0	100	10.88	5.527	0.479	4.449		
184	100	10.27	5.221	0.785	4.388	704	not included in mean.
439	100	9.20	4.647	1.359	4.273	905	
778	100	8.02	4.075	1.931	4.159	912	
1382	200	12.66	3.215	2.791	3.987	935	
2275	200	9.20	2.340	3.666	3.812	926	
3209	200	6.69	1.699	4.307	3.684	924	
4390	200	4.56	1.158	4.848	3.575	917	
5600	200	3.08	0.7836	5.222	3.501	917	
7430	200	1.75	0.4444	5.561	3.433	914	
∞		0.000	0.0000	6.006	3.344		
					Mean . . .	920	

The values of K have been calculated and are given in the table.

It appears from the results in the table (and from many other similar experiments) that the values of K, calculated by means of the formula given above, are faily constant when the initial period is excepted. In a series of experiments with various concentrations of cyanogen bromide and sodium hydroxide the average value of $K \cdot 10^4$ was found to 930 at 0° C., when in all cases the initial value was excluded. The results are given in table IV.

Table IV.

NaOH $N \cdot 10^3$	BrCN $M \cdot 10^4$	$K \cdot 10^4$
4.559	6.183	919
4.559	6.471	935
4.449	5.527	920
4.545	3.201	935
3.102	3.507	937
3.092	3.417	923
7.021	3.527	929
7.030	3.511	938
	Mean...	930

The reaction undoubtly consists of two consecutive reactions, one of which proceeds exceedingly fast, while the other proceeds with a measurable velocity, the velocity which defines the reaction velocity of the entire reaction.

The structural formula of cyanogen bromide may be either Br–C≡N, or, with divalent carbon, such as it has been proposed by Nef[1], Br–N=C. The reaction, therefore, may be explained either by the scheme:

$$\begin{aligned} &\mathrm{Br{-}C{\equiv}N + OH^- \rightarrow Br^- + HO{-}C{\equiv}N} \quad &&\text{(slow)} \\ &\mathrm{HO{-}C{\equiv}N + OH^- \rightarrow H_2O + OCN^-} \quad &&\text{(very fast),} \end{aligned}$$

or by the scheme:

$$\begin{aligned} &\mathrm{Br{-}N{=}C + OH^- \rightarrow Br{-}N{=}C{-}OH^-} \quad &&\text{(slow)} \\ &\mathrm{Br{-}N{=}C{-}OH^- + OH^- \rightarrow Br^- + N{\equiv}C{-}O^- + H_2O} \quad &&\text{(very fast).} \end{aligned}$$

Cyanogen bromide may also exist in tautomeric forms, and the transformation of one to the other may be the

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[1] (l. c.).

reason why the experiments show an initial disturbance, with a reaction velocity slower than in the later stages of the reaction.

A final conclusion as to the mechanism of the reaction cannot be drawn, and a further discussion of the problem will be taken up in a later paper in the connection with the alkaline hydrolysis of iodine cyanide.

8). Conclusions.

1). It has been shown, that cyanogen bromide may be prepared in a very pure state by Scholl's method and a following distillation over calcium chloride and metallic sodium.

2). That pure cyanogen bromide is fairly stable when it is kept in the dry state, and that moisture produces a hydrolysis with the formation of hydrobromic acid, which catalyzes the polymerization of cyanogen bromide into cyanuric bromide. Simultaneously very small quantities of an orange substance are formed, which seems to be free bromine.

3). Pure cyanogen bromide, which has not started to undergo a slight hydrolysis by the action of the moisture of the air, does not show any sign of polymerization. The molecular-weight in gaseous state, in aqueous solution and in benzene solution has the theoretical value.

4). From the conductivity of freshly made solutions of cyanogen bromide it may be concluded, that no reversible hydrolysis takes place to any measurable extent in the aqueous solution.

5). In the alkaline hydrolysis of cyanogen bromide no hypobromite can be detected as an intermediate product of the reaction.

6). The alkaline hydrolysis of cyanogen bromide proceeds as a process of two consecutive reactions, one of which has a great reaction velocity, while the other proceeds slowly enough to be measured. The reaction further shows an initial disturbance, which may be due to a tautomeric change in the cyanogen bromide molecule.

This investigation has been made in the Kent Chemical Laboratory of the University of Chicago, and it is a dear duty to me to express my thanks to the Head of the Department Professor Dr. JULIUS STIEGLITZ for the readiness, with which materials were placed to my disposal.

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