

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

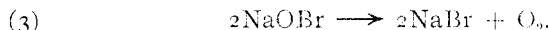
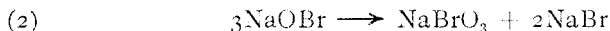
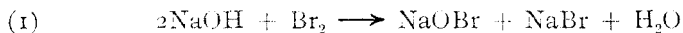
## REACTIONS OF HYPOHALITES WITH ORGANIC COMPOUNDS.<sup>1</sup> REACTIONS WITH DERIVATIVES OF METHANE.

BY WILLIAM M. DEHN.

Received June 29, 1909.

Though much work with the reactions of hypohalites on organic compounds has been reported, the results are scattered; no systematic surveys of the field have been made and no studies of the mechanism of the reactions have been attempted. Furthermore, in many instances,<sup>2</sup> a confusion with other reactions, involving treatment first with bromine and then with fixed alkalis, is observed. The present contribution is one of a series of studies that it is purposed to be made and is here an attempt to throw light on the mechanism of reaction of hypohalites with compounds involving a single atom of carbon.

When a solution of fixed alkali is treated with bromine, the following reactions take place:



Equation (1) indicates the initial and main reaction; equation (2) and (3) indicate the transformation of the sodium hypobromite, partially or completely, into sodium bromide. Under the most favorable conditions<sup>3</sup> and involving only reaction (1), 50 per cent. of the bromine may be found in the form of sodium bromide; the combined effect of the three reactions is to increase the per cent. of bromide from 50-87. Since *not less than 50 per cent. of sodium bromide*, formed by the above reactions, has ever been observed,<sup>4</sup> and since *Br<sub>2</sub> itself is not an ion*, and since *five ions result from two or three ions*, an explanation of these reactions, purely on an ionic basis, cannot be made.

On the basis of "molecular coalescence," as outlined in an earlier contribution,<sup>5</sup> these and many of the following-described organic reactions are more satisfactorily elucidated. For instance in reaction (1) above:

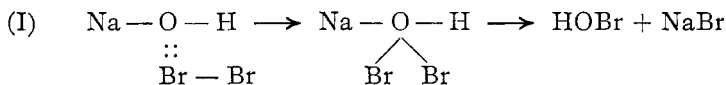
<sup>1</sup> THIS JOURNAL, 30, 1418, 1507.

<sup>2</sup> Notably with Hofmann's reaction.

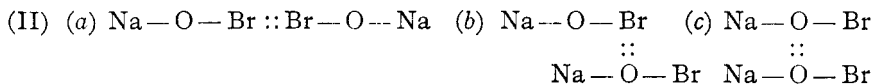
<sup>3</sup> THIS JOURNAL, 31, 526.

<sup>4</sup> Numerous efforts to suppress the sodium ion of the sodium hydroxide at the expense of the hydroxide ion, by adding various sodium salts to the sodium hydroxide, before adding bromine, always gave solutions containing more than 50 per cent. of sodium bromide.

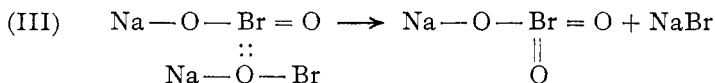
<sup>5</sup> *Am. Chem. J.*, 40, 88-97.



*equimolecular quantities of bromide and hypobromite must first be formed.* Two molecules of hypobromous acid or sodium hypobromite, from this reaction may unite in three different ways, *viz.*:



That *all three modes of union are operative* is indicated by the following: The *color*<sup>1</sup> of the hypobromite solutions argues the formation of (a), whereas the different bromine ions, containing single atoms of bromine, are colorless, perbromides, etc., are colored. The aggregate (b) can dissociate into  $\text{Na}-\text{O}-\text{Br}=\text{O}$  and  $\text{NaBr}$ ; this *bromite*,<sup>2</sup> by the action of more  $\text{NaOBr}$ ,



yielding the *bromate* of equation (2). The aggregate (c) may slowly dissociate into  $\text{Br}_2$  and  $\text{Na}_2\text{O}_2$ , the former with  $\text{NaOH}$  yielding more  $\text{NaOBr}$  and  $\text{NaBr}$ , the latter yielding *oxygen*, according to the equation



and thus quite satisfactorily accounting for equation (3).

When bromoform is treated with sodium hypobromite, the reaction yields nearly quantitatively carbon tetrabromide:



This reaction, like reaction (1) above, though apparently simple, is not easily explained either on the basis of ionization or of "methylene dissociation."<sup>3</sup> On the one hand, the theory of ionization is inadequate for the reason that bromoform itself is a *non-electrolyte* and that the ions of sodium hypobromite are *Na* and *OBr*. On the other hand, the "methylene" theory of chemical mechanics is inadequate for the reasons that it is impossible to conceive of  $\text{CBr}_4$  being formed by the addition to  $\text{Br}_2\text{C}$  = of sodium hypobromite or of its ions. Furthermore, with sodium hypobromite, chloroform yields *bromochloroform*,<sup>4</sup> a fact impossible to explain if, in the alkaline solution of sodium hypobromite, it first dissociates into *dichloromethylene* and hydrochloric acid, as indicated in the equation:

<sup>1</sup> Compare also H. Hantzsch, *Ber.*, **42**, 68-85.

<sup>2</sup> That *bromite* is contained in solutions of hypobromite, slowly increasing in bromate concentration, is indicated in studies made of such solutions by new methods of analysis (*THIS JOURNAL*, **31**, 525). These results are to be announced later.

<sup>3</sup> *Vide*, *THIS JOURNAL*, **26**, 1549-77.

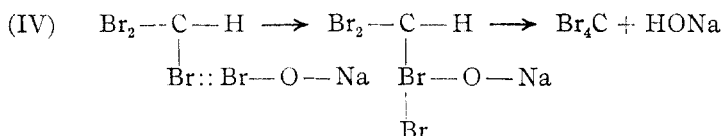
<sup>4</sup> See page 1225.



Furthermore, and opposed to the view of "methylene dissociation," *no polymerized methylene compounds*, as  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_2\text{Br}_4$ , or their halogenized or oxidized derivatives, as oxalic acid,<sup>1</sup> are found among the reaction-products.

The formation of such polymerized products certainly must be expected if "methylene" like "nascent hydrogen," which yields molecular hydrogen in many cases of reduction, is the inevitable intermediate product of reaction.

On the basis of molecular coalescence, we can conceive of the following simple intermediate mechanics:



Here the initial reaction, and indeed the possibility of reaction, is conditioned by the "affinity" of bromoform for sodium hypobromite, the "latent valencies" of the bromine atoms affording the basis for such an assumption. Whereas, the hydrogen atoms of methane, possessing no latent valencies, cannot and do not react with sodium hypobromite, other methane derivatives such as carbon bisulphide, methyl alcohol, formaldehyde, trioxymethylene, formic acid, the cyanides, monohalogen methane, dihalogen methane, trihalogen methane and the amino methane derivatives—all possessing latent valencies—are more or less rapidly acted upon by sodium hypobromite and other hypohalites.

*Methods of Analysis.*—The following qualitative and quantitative methods were employed in these and other studies with hypohalogen acids.

(1) *Hypohalites.*—(a) The color of the solution is usually indicative of the presence of hypohalite. (b) If the solutions are not too dilute, treatment with ammonia or hydrogen peroxide will cause effervescence.

(2) *Oxyhalogen Acids.*—With potassium iodide and hydrochloric acid, all oxyhalogen acids liberate iodine.

(3) *Periodates.*—Solutions containing sodium periodates usually crystallize on standing, especially after heating. The periodate is further identified by the silver salt.

(4) *Fatty Acids.*—(a) Usually detected by the odor of the acid solutions. (b) When treated first with ammonia, to decompose the unchanged sodium hypobromite, then with ferric chloride and finally acidified

<sup>1</sup> As will be shown in a future contribution, oxalic acid is an inevitable product of oxidation by sodium hypobromite of organic compounds containing two linked atoms of carbon.

slightly with hydrochloric acid and boiled, fatty acids yield ferric hydroxide or the corresponding basic ferric salts. Of course, carbonic acid interferes with this reaction and must be expelled. (c) The solutions were treated alternately with ammonia and hydrochloric acid to decompose the oxyhalogen salts, then acidified with hydrochloric acid and distilled. The distillates were treated with an excess of solid lead carbonate, and the filtrates were concentrated, when the lead salts of the lower fatty acids crystallized out.

(5) *Oxalic Acid*.—After decomposing the sodium hypobromite with ammonia, the solutions were first acidified with hydrochloric acid to decompose the carbonate, then treated with calcium chloride, made ammoniacal and boiled. The precipitate was filtered and washed, dissolved in dilute hydrochloric acid, and reprecipitated as calcium oxalate. This was detected or estimated in the usual manner by means of potassium permanganate.

(6) *Halogen Substitution Products of Methane*.—These compounds were usually removed by distilling with steam; some were removed by direct filtering; some, by extraction with ether. They were usually identified by their melting or boiling points.

(7) *Nitric Acid*.—Careful alternate addition of sulphuric acid and fixed alkali or ammonia, sufficient to decompose the oxyhalogen acids, was followed by boiling with silver oxide to precipitate the silver halide. The filtrate was tested for nitric acid in the usual manner.

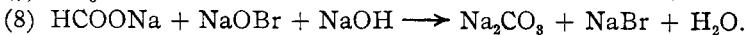
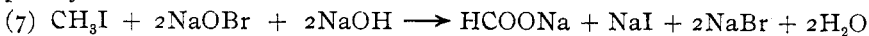
(8) *Carbonic Acid*.—The effervescence with dilute hydrochloric acid was usually sufficiently indicative.

(9) *Cyanic Acid*.—The alkaline solutions were treated with solid caustic soda to the point of saturation, the salts precipitated were filtered on glass wool, dried on a clay plate and the cyanic acid contained therein tested for by the usual methods.

### Reactions.

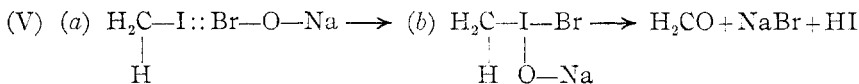
*Methane*.—When methane, freed from ethylene by passing through bromine water, was permitted to stand in nitrometers over strong solutions of sodium hypobromite, no diminution of volumes was observable, even after standing for months. Hence it is concluded that hypohalites, at ordinary temperatures, have no effect on fatty hydrocarbons.

*Methyliodide*.—The iodide was slowly (2–3 days) replaced by some solid sodium periodate; the solution contained the sodium salts of hydriodic, iodic, periodic, formic, and carbonic acids. After standing for some days with an excess of sodium hypobromite, the formate was completely oxidized to carbonate. The reactions involved are:

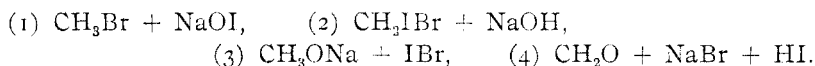


The sodium iodide of (7) was oxidized by the sodium hypobromite to

sodium iodate and sodium periodate. The formation of formate and carbonate may be explained in the following manner:



It may be observed that the intermediate product (b) can dissociate into at least four different sets of end-products:



That dissociations (1), (2) and (3) are not involved, and that form-aldehyde and not sodium methylate is the intermediate product, is evidenced by the non-formation of carbon tetrabromide.<sup>1</sup>

Formula.	State.	Melt. point.	Boil. point.	Sp. gr.	Author.
CCl <sub>4</sub> .....	liquid	-19.5°, at 210	76.7°	1.60, D <sub>25</sub>	Dumas <sup>2</sup>
CBr <sub>4</sub> .....	leaflets	92.5°	189.5°	.....	Bolas <sup>3</sup>
CI <sub>4</sub> .....	solid	...	..	4.32, D <sub>25</sub>	Gustavson <sup>4</sup>
CCl <sub>3</sub> Br.....	liquid	-21°	104°	2.05, D <sub>0</sub>	Löw <sup>5</sup>
CCl <sub>2</sub> I.....	liquid	-19°	142°	2.36, D <sub>17</sub>	Besson <sup>6</sup>
CBr <sub>3</sub> Cl.....	leaflets	55°	160°	2.71, D <sub>17</sub>	Besson <sup>7</sup>
CBr <sub>3</sub> I*.....	solid	35°	..	.....	Dehn <sup>8</sup>
CI <sub>3</sub> Cl.....	..	...	..	.....	.....
CI <sub>3</sub> Br*.....	solid	70-80°	..	.....	Dehn <sup>8</sup>
CCl <sub>2</sub> Br <sub>2</sub> .....	needles	22°	135°	2.42, D <sub>25</sub>	Arnhold <sup>9</sup>
CCl <sub>2</sub> I <sub>2</sub> .....	scales	85°	..	.....	Höland <sup>10</sup>
CBr <sub>2</sub> I <sub>2</sub> .....	..	...	..	.....	.....
CCl <sub>2</sub> BrI.....	..	...	..	.....	.....
CBr <sub>2</sub> CI.....	..	...	..	.....	.....
CI <sub>2</sub> CIBr.....	..	...	..	.....	.....

There are in all 35 tetrahalogen derivatives of methane. Excluding the compounds of fluorine, of which 20 are possible and 2 are known,<sup>11</sup> there are 15 tetrahalogen derivatives involving chlorine, bromine and iodine. These are shown in the above table; compounds indicated by the asterisk are new compounds herewith contributed. It will be

<sup>1</sup> Vide, Methyl Alcohol, page 1228.

<sup>2</sup> *Ann.*, **33**, 187; Regnault, *Ibid.*, **33**, 332.

<sup>3</sup> *Z. Chem.*, **1870**, 441; **1871**, 432; *Ann.*, **156**, 60.

<sup>4</sup> *Ann.*, **172**, 173; **231**, 264; *Bull. soc. chim.* [2], **24**, 733.

<sup>5</sup> *Z. Chem.*, **1869**, 624; *Jsb. Chem.*, **1871**, 259; *Bull. soc. chim.*, **17**, 538; *Ber.*, **10**, 678; *J. Chem. Soc.*, **37**, 203.

<sup>6</sup> *Bull. soc. chim.* [3], **9**, 179.

<sup>7</sup> *Ber.*, **25** R, 188.

<sup>8</sup> Vide, page 1227.

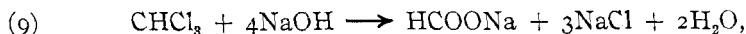
<sup>9</sup> *Ann.*, **240**, 208; *Ber.*, **25** R, 188.

<sup>10</sup> *Ann.*, **204**, 233.

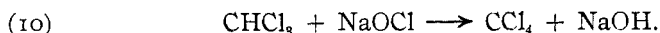
<sup>11</sup> "Carbon Tetrafluoride," Fumy, *Ann.*, **92**, 247; Moissan, *Ann. chim. phys.* [6], **19**, 272. "Fluorochloroform," Swartz, *Ber.*, **26** R, 291.

observed that *the hypohalites afford a general method of preparation of methane tetrahalides.*

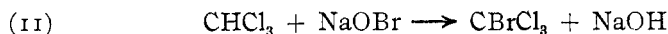
*Chloroform.* (a) *With NaOCl.*—When 10 grams of chloroform were mixed with an excess of sodium hypochlorite, shaken 20 hours and let stand 6 days, 7.5 grams of oil were obtained. It boiled mostly below 66°; only about 0.5 gram boiled above 70°. The solution contained formic and carbonic acids. The main reaction is one of saponification,



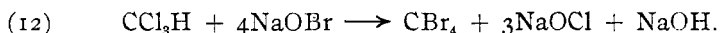
and is followed by reaction (29). The following reaction is very slow and is incomplete:



(b) *With NaOBr.*—When 10 grams of chloroform were treated with an excess of sodium hypobromite, shaken for 20 hours and then let stand for a number of days, 13 grams of an oil, boiling at 102–5°, were obtained (bromochloroform boils at 104°). About 0.5 gram each of a higher boiling oil and a white crystalline solid melting at 88° were obtained. The solution contained formic and carbonic acids. The main reaction was



and for the calculated quantity of CBrCl<sub>3</sub> was 16.6 grams. Evidently the higher-boiling oil was dichlorodibromomethane (b. 150°) or chlorobromoform (b. 160°) and the solid was carbon tetrabromide (m. 92.5°). These probably were formed by displacement reactions illustrated by the equation



(c) *With NaOI.*—Iodine was gradually added to a solution of sodium hydroxide in contact with 10 grams of chloroform. After standing for some time, the mixture was shaken and then more iodine was added. This process was repeated during the course of a number of days and then the oil was removed and distilled. About two-thirds of the oil (6 grams) distilled below 70° (unchanged chloroform), 1.8 grams distilled up to 142° (mostly 140–142°) and 0.52 gram oil remained in the distilling flask. The higher oils became violet on standing. By the Carius method, 0.2420 gram of the oil<sup>1</sup> boiling at 142° gave 0.6630 gram of silver salt and required 0.6830 gram of AgNO<sub>3</sub>:

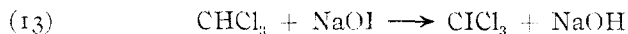
Calculated for CCl <sub>3</sub> I:	Cl, 43.39; I, 51.74.
Found:	Cl, 45.00; I, 49.79.

By the Carius method, 0.2083 gram of the residual oil gave 0.5249 gram of silver salt and required 0.5202 gram of AgNO<sub>3</sub>:

Calculated for CCl <sub>2</sub> I <sub>2</sub> :	Cl, 20.76; I, 75.37.
Found:	Cl, 36.10; I, 57.38.

<sup>1</sup> *Vide, Bull. soc. chim.* [3], 9, 179.

Evidently the oil boiling at  $142^{\circ}$  was iodochloroform and the residual oil was a mixture of the same with diiododichloromethane.<sup>1</sup> The slowness of the reaction:



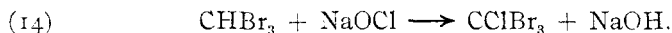
is accounted for by the instability of the sodium hypoiodite.

*Bromoform.* (a) *With NaOCl.*—Bromoform (10 grams) was placed in a bottle with an excess of sodium hypochlorite and the mixture was shaken repeatedly during 7 days. The oil was separated and distilled; about equal weights of each fraction were taken: (a) to  $152^{\circ}$ , (b)  $152-157^{\circ}$ , (c)  $157-160^{\circ}$ . From the higher fractions by distillation with steam a white crystalline solid melting at  $53^{\circ}$  was obtained (chlorobromoform melts at  $55^{\circ}$ ). By the Carius method 0.2162 gram of this solid substance yielded 0.5295 gram of silver halide and required 0.5125 gram of  $\text{AgNO}_3$ :

Calculated for  $\text{CBr}_3\text{Cl}$ : Cl, 12.34; Br, 83.47.

Found: Cl, 13.59; Br, 80.85.

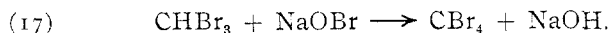
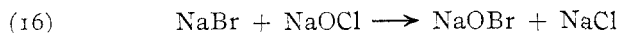
Evidently chlorobromoform was formed:



After standing for three months with an excess of sodium hypochlorite, another 10 grams portion of bromoform yielded an oil and a white crystalline solid. The mixture was distilled with steam; the oil obtained was dried with calcium chloride and then fractionated. About equal weights of each fraction were taken: (a) to  $160^{\circ}$ , (b)  $160-170^{\circ}$ , (c)  $170-175^{\circ}$ , (d)  $175^{\circ}$ . The residue in the flask was distilled with steam and dried on a clay plate; it was found to melt at  $65.5^{\circ}$ . The following analyses were made:

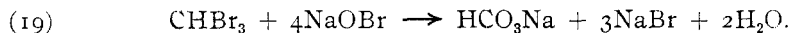
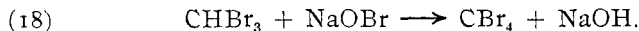
Fraction.	State.	Weight.	$\text{AgNO}_3$ required.	$\text{AgNO}_3$ for 1 g. substance.	Calc. $\text{AgNO}_3$ .	Required for
(b).....	liquid	0.5761	1.2883	2.2362	2.0153	$\text{CHBr}_3$
(c).....	liquid	0.5228	1.1305	2.1624	2.3668	$\text{CClBr}_3$
(c).....	solid	0.2105	0.4627	2.1943	2.0496	$\text{CBr}_4$
(d).....	liquid	0.4122	0.8887	2.1560	2.8001	$\text{CBr}_2\text{Cl}_2$

The *residue* and the *solid* (c) were evidently mixtures of chlorobromoform and carbon tetrabromide. The liquids were evidently mixtures of unchanged bromoform, chlorobromoform and possibly dichlorodibromomethane. In the first experiment no carbon tetrabromide was indicated; its formation in the second experiment is accounted for by the following equations:



<sup>1</sup> *Ann.*, 204, 233.

(b) *With NaOBr.*—When shaken with an excess of sodium hypobromite, bromoform was slowly (24 hours) and nearly quantitatively replaced by solid carbon tetrabromide. From 3.92 grams were obtained 5.01 grams of  $\text{CBr}_4$ ; theory, 5.064 grams. The solution contained traces of formic acid. The reactions involved are:

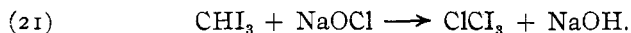


(c) *With NaOI. Iodobromoform.*—When bromoform in sodium hydroxide solution was treated slowly with free iodine, a golden yellow crystalline precipitate replaced the liquid bromoform. This substance is best prepared, however, by adding with constant shaking to a solution of potassium iodide in contact with the bromoform, either a solution of hypochlorite or a solution of hypobromite. The colorless oil is first replaced by a golden-colored oil, then by the golden-colored crystalline precipitate of *iodobromoform*. When freed from an admixture of  $\text{Na}_2\text{H}_3\text{IO}_6$  by treatment with dilute sodium hydroxide, washing with water and drying on a clay plate, the substance became ochre-yellow in color. However, it was easily purified by dissolving in absolute alcohol, filtering and reprecipitating the alcoholic solution with dilute sodium hydroxide. By the Carius method, 0.1057 gram required 0.1852 gram of  $\text{AgNO}_3$ ; calculated for  $\text{CIBr}_3$ , 0.1870 gram. *Iodobromoform* darkens and decomposes at  $35^\circ$  and is formed according to the equation:



When a large quantity of iodine was used in the preparation of this compound, both carbon tetraiodide and iodoform were detected in the red-yellow reaction-product.

*Iodoform. (a) With NaOCl.*—When 10 grams of iodoform were treated with an excess of sodium hypochlorite, shaken for 20 hours and let stand for 5 days, 9.5 grams of unchanged iodoform were recovered. Another sample, permitted to stand for 2 months, yielded a mass of brick-red colored crystals intermixed with white crystals. The mixture was decomposed by organic solvents, hence could not be purified. If the following reaction took place, it was only partial:



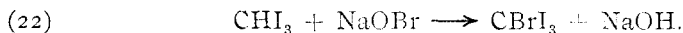
(b) *With NaOBr.*—When 10 grams of iodoform were treated with an excess of sodium hypobromite, shaken for 20 hours and let stand for 5 days, 12 grams of a brick-red amorphous solid were obtained. After removing and drying on a clay plate, the substance was found to soften at  $75^\circ$  and to melt at  $113^\circ$ . By the Carius method: (a) 0.3541 gram of substance required 0.5151 gram of  $\text{AgNO}_3$ ; (b) 0.4876 gram required 0.6903 gram of  $\text{AgNO}_3$ ; (c) 0.4202 gram, after extracting with ammonia, yielded 0.6230 gram of  $\text{AgI}$ .



Calculated for  $\text{CBrI}_3$ : I, 80.14;  $\text{BrI}_3$ , 97.46.

Found: I, 80.55;  $\text{BrI}_3$ , 98.62, 96.00.

*Bromiodoform* is a very unstable substance toward organic solvents; it may be boiled with water with only a partial volatilization. In sunlight it decomposes into iodine and a light yellow solid. The above reaction was nearly quantitative as follows:

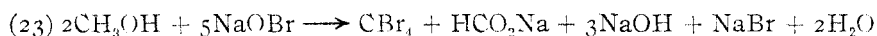


(c) *With NaOI.*—The dark red crystals of carbon tetraiodide<sup>1</sup> could not be obtained; formic acid was detected in the alkaline solution.

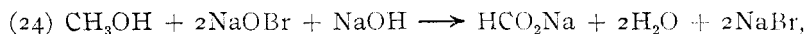
*Carbon Tetrabromide. With NaOBr.*—After 4 days the oil gave no increased boiling point; the solution contained some formic acid.

*Carbon Tetrabromide. With NaOCl.*—No detectable effect.

*Methyl Alcohol. With NaOBr.*—(a) When the reagent was added to dilute aqueous solutions of methyl alcohol, an immediate and voluminous precipitate of carbon tetrabromide was formed. In solutions more concentrated than 1 per cent., this precipitate was heavy; in 1/2–1 per cent. solutions, it appeared as a white opaqueness; in 1/10–1/2 per cent. solutions, as a faint opalescence. Since ethyl alcohol does not precipitate carbon tetrabromide immediately when treated with sodium hypobromite, *this reagent is useful for the purpose of detecting wood alcohol in methylated spirits and other mixtures.* Though the precipitate formed by the reaction

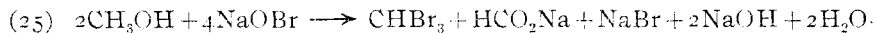


is apparently voluminous, it has been separated only to the extent of 4 per cent. of the theory—13.7 grams of the alcohol gave 5 grams of  $\text{CBr}_4$ . Evidently the main reaction yields formic acid,

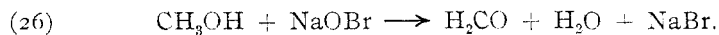


and much free alkali favors this reaction.

(b) When an excess of methyl alcohol was added gradually to sodium hypobromite, an oil was precipitated. It was found to contain both bromoform and carbon tetrabromide:



(c) When an excess of dilute methyl alcohol was treated with sodium hypobromite and the alkaline mixture was distilled, an aqueous distillate, possessing the odor of methylal, was obtained. When warmed with ammoniacal silver nitrate, this distillate gave a dark precipitate of silver; when no excess of silver nitrate was used, the filtrate from the silver bromide gave good tests for formic acid. The presence of methylal was thereby indicated; hence formaldehyde must be an intermediate product of the action of sodium hypobromite on methyl alcohol:



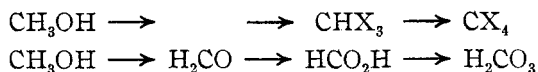
<sup>1</sup> *Ann.*, 172, 173; 231, 264; *Bull. soc. chim.* [2], 24, 733.

(d) A solution of methyl alcohol containing potassium iodide was gradually treated with sodium hypobromite; iodoform<sup>1</sup> was precipitated and finally the odor of carbon tetraiodide was detected. The solution contained formic acid. Here, of course, the sodium hypobromite reacted first with the potassium iodide in the following manner:



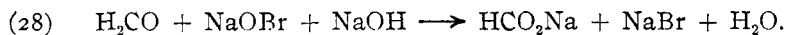
and this hypoiodite reacted with the alcohol in the same manner as the sodium hypobromite.

From the foregoing it is evident that methyl alcohol, when treated with hypohalites, is either progressively halogenized or progressively oxidized:

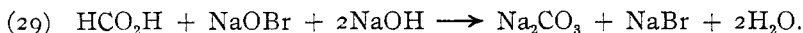


and that oxidation is the main reaction.

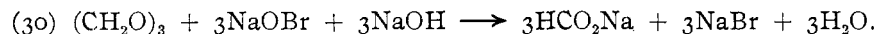
*Formaldehyde.*—When treated with a little sodium hypobromite, formaldehyde causes an immediate decolorization of the former; formic acid can be detected in the solution. When treated with an excess of sodium hypobromite, only carbonic acid can be detected in the solution. The reactions are (29) below and



*Formic Acid.*—When treated with a small quantity of sodium hypobromite, formic acid causes the color of the former to disappear rapidly; when an excess of the hypobromite is used, much carbonic but no formic acid can be detected in the solution:



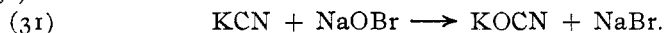
*Trioxymethylene.*—Heat and rapid decolorization indicated energetic reaction. Formic and carbonic acids were detected:



*Carbon Disulphide.*—The oil disappeared rapidly and enough heat was developed to boil the unchanged carbon disulphide. When treated with different quantities of sodium hypobromite, solutions were obtained containing sulphide, sulphite, sulphate, formate and carbonate. An excess of sodium hypobromite yielded quantitatively the sulphur as sulphate.

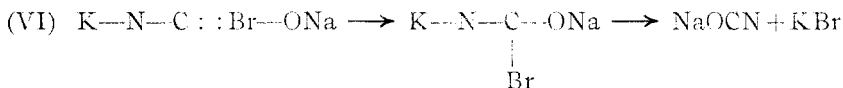
### Cyanogen Acids.

*Potassium Cyanide.*—When treated with an excess of sodium hypobromite, solutions of potassium cyanide became very warm and gave good tests for cyanic, formic and carbonic acids. The reactions are (32) below and

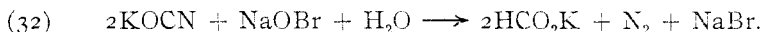


<sup>1</sup> With acetone, potassium iodide and NaOCl, Suilliol and Raynard obtained iodoform. *Bull. soc. chim.*, 51, 4.

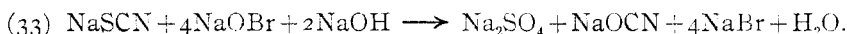
*Potassium Cyanate.*<sup>1</sup>—When treated in the cold with sodium hypobromite, decolorization of the latter was very slow. At ordinary temperature nitrogen was slowly evolved: 0.2591 gram KOCN<sup>1</sup> in a nitrometer gave 0.1 cc. N<sub>2</sub> in 10 min., 0.5 cc. in 3 hrs., 40 cc. in 5 days, calculated vol. 41.5 cc. N<sub>2</sub>. Formic and carbonic acids were detected. Cyanic acid may be considered the intermediate product of action of sodium hypobromite on potassium cyanide. If the isocyanide formula of potassium cyanide be used, we may have the following initial reaction:



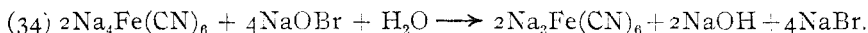
and the cyanic acid formed is oxidized as shown in the equation:



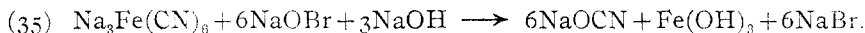
*Potassium Thiocyanate.*—Intense warming and rapid decoloration of the sodium hypobromite were observed. When a solution containing 0.1240 gram of potassium thiocyanate (KSCN),<sup>2</sup> estimated by means of 0.1 *N* silver nitrate, was treated with an excess of sodium hypobromite, it yielded 0.2970 gram of barium sulphate, the theoretical quantity.<sup>3</sup> Since cyanic acid was detected we have the equation



*Sodium Ferrocyanide.*—When this salt was treated at ordinary temperature with an excess of sodium hypobromite, ferricyanide was formed:



*Sodium Ferricyanide.*—When boiled with sodium hypobromite, solutions of ferricyanide gradually yielded a beautiful amorphous, deep brown-red precipitate, intermixed with iridescent scales. The precipitate was dried in a desiccator and was found to contain iron and formic acid. By ignition, 0.0986 gram lost 0.0091 gram or 9.32 per cent. Evidently the substance was a basic ferric formate intermixed with ferric oxide. The reaction is largely indicated<sup>4</sup> by the equation



#### Amino Derivatives.

*Methylamine.*—When 0.1970 gram of the hydrochloride was treated in a nitrometer with sodium hypobromite, it *slowly* evolved nitrogen.<sup>5</sup>

<sup>1</sup> Cf. Reychler, *Bull. soc. chim.* [3], 9, 427.

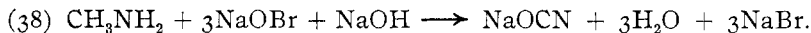
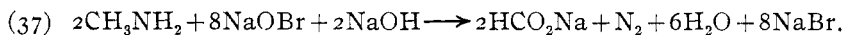
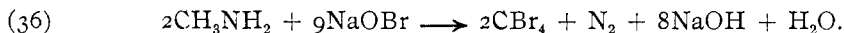
<sup>2</sup> Since it will be shown later that cyanic acid and methyl cyanide react alike toward NaOBr, the  $\text{---C} \equiv \text{N}$  structure in each is probable.

<sup>3</sup> Since thiocyanates are quantitatively oxidized to sulphate by NaOBr, their solutions may be standardized by oxidation with this reagent and precipitation as BaSO<sub>4</sub>. Cf. action of KMnO<sub>4</sub>. Péan, *Jsb. Chem.*, 1858, 585.

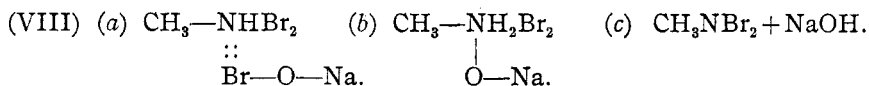
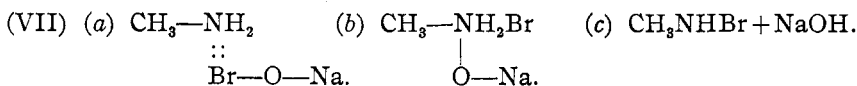
<sup>4</sup> Since no oxalic acid could be detected in the solutions, structural formulas of ferrocyanides and ferricyanides involving linkings of two carbon atoms are improbable.

<sup>5</sup> Cf. de Coninck, *Compt. rend.*, 126 1042.

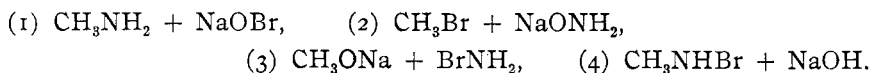
At 760 mm. and 20° it yielded 8.0 cc. in 4 hours, 15.6 cc. in 16 hours, 17.2 cc. in 24 hours and 27 cc. in 5 days—calculated volume of nitrogen at 760 mm. and 20° was 37.8 cc. Since carbon tetrabromide, cyanic acid and formic acid were detected, the main reactions are:



When a concentrated solution of methylamine was treated with sodium hypobromite, at first a red-yellow oily precipitate, volatile with steam and of a tear-producing odor, was formed. With an excess of sodium hypobromite this oil was replaced by carbon tetrabromide (1.0 gram of  $\text{CH}_3\text{NH}_2\text{HCl}$  gave 0.3 gram of  $\text{CBr}_4$ —calculated, 4.9 grams). The oil was methylmonobromamine or methyl dibromamine described by Hofmann.<sup>1</sup> The formation of this compound is easily explained by the following reactions:

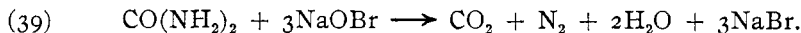


Theoretically the aggregate (VII) (b) can yield four different sets of cleavage products:

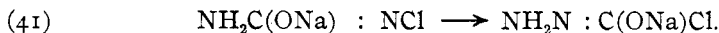


That at least dissociations (3) and (4) are involved is indicated by the formation of carbon tetrabromide and methylbromamine. Since the reaction of formation of methyl dibromamine is slowly reversible and cyanic acid is slowly decomposed by sodium hypobromite, the slowness of evolution of nitrogen is accounted for.

*Urea.*—The familiar end-reaction is:

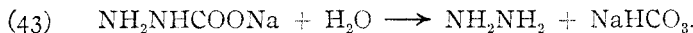


That intermediate compounds are formed is proven by Schestakow.<sup>2</sup> He gave the following reactions:

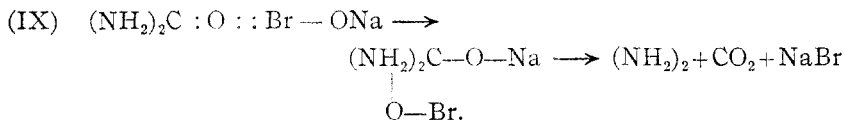


<sup>1</sup> *Ber.*, 15, 767. For the chloramines, *vide* Koehler, *Ber.*, 12, 771; Berg, *Ann. chim. phys.* [7], 3, 318; Bamberger, Renauld, *Ber.*, 28, 1683.

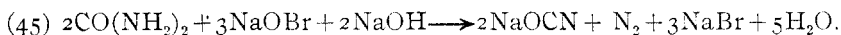
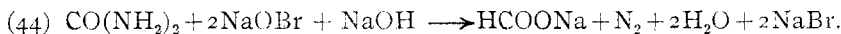
<sup>2</sup> *Z. angew. Chem.*, 1903, 1061; *J. Russ. Phys. Chem. Soc.*, 37, 1; *Chem. Centr.*, 1905, I, 1227; *J. prakt. Chem.*, 76, 438.



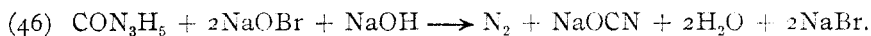
and was able to separate 60.5 per cent. of the calculated hydrazine. That no such complicated reactions as the above need be imagined to account for the hydrazine, is seen in the following proposed equation:



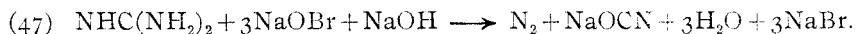
When an excess of urea was treated with sodium hypobromite, the above-described methods detected formic acid and cyanic<sup>1</sup> acid:



*Semicarbazide.*<sup>2</sup>—Nitrogen was evolved; formic and cyanic acids were detected. In a nitrometer, 0.0226 gram of the hydrochloride gave 5.2 cc.  $\text{N}_2$  at 760 mm. and  $20^\circ$ —calculated volume, 7.8 cc.  $\text{N}_2$ —or  $2/3$  of the nitrogen was evolved. On standing for a number of days the volume of nitrogen slowly increased. The above observations harmonize with the equation.



*Guanidine.*<sup>3</sup>—When the hydrochloride was treated in a nitrometer with sodium hypobromite it evolved  $2/3$  of its nitrogen. Solutions containing 0.1145 gram gave at 747 mm. and  $22^\circ$  (a) 11.6 cc. and (b) 11.0 cc. or (a) 21.29 per cent.  $\text{N}_2$  and (b) 21.10 per cent.  $\text{N}_2$ —calculated  $\text{N}_2$  was 31.86 per cent. Since formic and cyanic acids were detected, the following equation is justified:



Though not properly belonging to this communication, the reactions of sodium hypobromite with urethane, hydroxylamine and ammonia are given below so that comparisons with the above compounds may be made.

*Urethane.*—When 0.0632 gram of urethane was permitted to react with sodium hypobromite in a nitrometer only 0.9 cc. was evolved in 5 days.

*Hydroxylamine.*—When 0.0557 gram of the hydrochloride was permitted to stand in a nitrometer with sodium hypobromite for 16 hours, 5.8 cc. of  $\text{N}_2$  were evolved at 760 mm. and  $20^\circ$ —0.0062 gram  $\text{N}_2$ , calculated  $\text{N}_2$ ,

<sup>1</sup> Others have observed the formation of cyanic acid. Smolka, *Monatsh.*, 8, 67; Emich, *Monatsh.*, 10, 331; Hamburger, *Rec. trav. chim.*, 2, 188; Haller, *Ann. chim. phys.* [6], 9, 276.

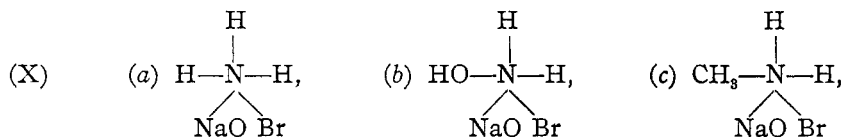
<sup>2</sup> For the reaction of semicarbazide with hypochlorite, *vide* Darapsky, *J. prakt. Chem.*, 76, 450.

<sup>3</sup> For the reaction of guanidine with hypochlorite, *vide* de Coninck, *Compt. rend.*, 126, 1042.

0.0115 gram—or 55 per cent.<sup>1</sup> of the nitrogen was evolved. Nitric acid<sup>2</sup> was found in the solution.

*Ammonia.*—When 1 cc. of ammonium chloride solution, standardized by 0.1 *N* silver nitrate and containing 0.00613 gram ammonia, was treated in a nitrometer with sodium hypobromite at 742 mm. and 21.5°, (a) 4.66 cc. N<sub>2</sub> and (b) 4.64 cc. N<sub>2</sub> were obtained—calculated volume was 4.65 cc. N<sub>2</sub>.

Now since urea and ammonia quantitatively evolve nitrogen, since guanidine and semicarbazide evolve two-thirds of their nitrogen, since hydroxylamine evolves about one-half of its nitrogen, since methylamine slowly evolves its nitrogen, and since urethane almost fails to evolve nitrogen, it is concluded that, when treated with sodium hypobromite, the mere presence in a compound of the *amino group* is not a criterion of evolution of nitrogen. *The influence of other groups* in the compound mentioned is a greater factor. If the reaction of sodium hypobromite with these compounds were purely *ionic*, certainly greater similarity of reaction is expected. However, if there are formed different aggregates as



either representing respectively different stabilities, or ease of dissociation, or representing in the same aggregate tendencies to dissociate in more than one direction, a more rational basis of interpretation of these organic reactions is revealed. Studies will be continued along these lines with compounds containing two atoms of carbon.

SEATTLE, WASH., June 24, 1909.

## ACTION OF AMINES ON DIBASIC ALIPHATIC ACIDS. FIFTH COMMUNICATION ON AMIDIC ACIDS.<sup>3</sup>

BY J. BISHOP TINGLE AND S. J. BATES.

Received September 4, 1909.

With the exception of the work on succinic acid, described in the first paper of this series, attention has, hitherto, been directed exclusively to the interaction of amines with phthalic acid and its substitution products. In the present communication we describe the results which we

<sup>1</sup> Cf. with NaOCl, *Ber.*, 20, 1504.

<sup>2</sup> All of the other nitrogen-containing compounds failed to give solutions containing nitric acid.

<sup>3</sup> The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, 37, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, 38, 642 (1907); Bishop Tingle and Rolker, *THIS JOURNAL*, 30, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, 31, 1157 (1909).