CCCVIII.—*The Reaction between Sodium Hypobromite and Carbamide.*

By Maxwell Bruce Donald.

The reaction between carbamide and sodium hypobromite may be represented as :

$$CON_2H_4 + 3NaOBr \longrightarrow CO_2 + N_2 + 3NaBr + 2H_2O,$$

but in actual practice it is found that it never goes to completion. The course of the reaction can be followed by estimating (1) the amount of nitrogen evolved, (2) the amount of hypobromite decomposed, or (3) the amount of carbonate formed. All these methods give substantially the same results and indicate that, with the usual methods of performing the experiment, the reaction goes only to about 90% of completion.

The incompleteness of the reaction has been attributed to various causes, such as (1) the solubility of nitrogen in the hypobromite solution, (2) the formation of a compound of carbamide and bromous acid (Hüfner, *J. pr. Chem.*, 1871, **3**, 1), (3) the impurity of the nitrogen (Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, *A*, 187; Rayleigh, *Proc. Roy. Soc.*, 1898, **64**, 95; Krogh, *Z. physiol. Chem.*, 1913, **84**, 379; Hurtley, *Biochem. J.*, 1921, **15**, 11), (4) the formation of oxides of nitrogen in the solution (Fauconnier, *Bull. Soc. chim.*, 1880, **33**, 102; Luther, *Z. physiol. Chem.*, 1889, **13**, 500; Krogh, *loc. cit.*). None of these explanations, however, is adequate (see, for example, Lescœur, *J. Pharm. Chim.*, 1919, **20**, 305; Werner, J., 1922, **121**, 2318; Margosches and Rose, *Biochem. Z.*, 1923, **137**, 542).

The alternative suggestion (Fenton, J., 1878, **33**, 300; P., 1895, 138; see also Lescœur, *loc. cit.*; Margosches and Rose, *loc. cit.*) that the reaction does not go to completion because of the formation of sodium cyanate is supported by the evidence brought forward in the present communication. The work of Margosches and Rose, on which the view was based that the formation of sodium cyanate cannot be the chief cause of the nitrogen deficit, is inconclusive, since no account was taken of the composition of the hypobromite used.

EXPERIMENTAL.

The gasometric method was found to be unsatisfactory for two reasons. The usual solution (40% brominated 10*N*-sodium hydroxide)* was made by adding bromine to a sodium hydroxide solution cooled to below 0° and analysed for hypobromite by sodium arsenite and for total hypobromite and bromate by sodium thiosulphate. The original solution was then kept for 20 hours and analysed again. Although there was no change in the thiosulphate titration, the hypobromite had been half converted into bromate over-night. The old hypobromite solution evolved about 3% more nitrogen from a carbamide solution than the freshly prepared hypobromite. This, as will be seen from subsequent results, is probably due to the decreased ratio of hypobromite to hydroxide.

The other objection to this method is that the reaction between carbamide and hypobromite gives off a considerable amount of heat; in fact, Smith (*Chem. News*, 1895, **71**, 259) used such heat as a basis for determining the amount of carbamide in urine. Wagner (*Z. anal. Chem.*, 1874, **13**, 383) suggests keeping the reaction vessel under water; but the volume of gas only becomes constant 15

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* A hypobromite solution made by adding 25 c.c. of bromine (1 equiv.) to 100 g. of sodium hydroxide (2·5 equivs.) dissolved in water, and making up to 250 c.c. is described as a 40% brominated 10*N*-sodium hydroxide solution.

minutes after the reaction, even when it is kept in a well-stirred thermostat. The factor generally given in text-books for 40% brominated 10*N*-sodium hydroxide is 0·92. Careful measurements with thermostat control, using freshly prepared cool hypobromite and applying all corrections to the volume of gas evolved, gave 0·90, whereas the titration method shows that the factor should be 0·87.

More trustworthy results were obtained by estimating the hypobromite decomposed. The procedure was to add the carbamide solution slowly to the hypobromite, allow the reaction to proceed with occasional shaking for 5 minutes, dilute the reaction mixture to 500 c.c., and add about 20 c.c. of 3*N*-hydrochloric acid and a solution containing about 5 g. of potassium iodide. The solution was kept for 2 minutes and then titrated with thiosulphate, with starch as an indicator. There was a certain tendency to " reblue " on standing. The difference between the amounts of thiosulphate required for this titration and for the hypobromite alone gives the equivalent amount of hypobromite which has been used up in the reaction. The carbamide was recrystallised three times from alcohol and dried at 100°.

A number of experiments were undertaken to determine the chief factors which influenced this reaction at room temperature. Excess of hypobromite had no effect, confirming previous observations on a similar reaction with ammonia (*Analyst*, 1924, **49**, 375). The actual concentration of the hypobromite had no effect at moderate concentrations. Thus a 40% brominated 4*N*-sodium hydroxide solution was diluted in steps down to 0·25*N* without any effect on the reaction. In stronger solutions of hypobromite, there are secondary effects due to time changes in the hypobromite–hydroxide ratio to be allowed for. The chief factor at room temperature was the extent to which the sodium hydroxide had been brominated.

Some of the experimental results obtained with carbamide and various hypobromite solutions are in Table I. The expression " c.c. thio. required " indicates the difference in thiosulphate required for a blank and that required after the carbamide has been added to the hypobromite.

Similar results are obtained with hypobromite solutions prepared from sodium hydroxide as strong as 2*N*. Both titration and gasometric methods show that the nitrogen deficit becomes greater as the percentage bromination increases until the hydroxide is 75% brominated. At this point a sudden change occurs, the amount of gas evolved still decreases, but a slow oxidation sets in. After 30 minutes, an amount of hypobromite is used up which is about equivalent to the

TABLE I.

Sodium thiosulphate 0·1963*N*. Sodium hydroxide 0·496*N*. 5 C.c. of carbamide solution contain 0·075 g., which is equivalent to 38·3 c.c. of thiosulphate.

No. of sol.	% Brominated.	C.c. of thio. required after			Carbamide decomposed %.
		5 mins.	15 mins.	30 mins.	
1	15	34·2	—	—	89·3
2	30	33·8	—	—	88·4
3	45	33·1	—	—	86·4
4	60	31·0	31·1	30·9	81·0
5	75	29·7	29·1	29·4	77·6
6	80	29·2	37·5	38·7	
7	85	33·5	38·6	37·8	
8	90	35·1	37·7	38·7	
9	95	36·5	37·9	38·5	
10	97·5	—	4·2	4·0	

quantity of carbamide taken (*i.e.*, 38·3 c.c. of thio.). When the sodium hydroxide is completely brominated, there is no gas evolution and no hypobromite is used up.

Sodium cyanate was prepared by the method of Leuchs and Geserick (*Ber.*, 1908, **41**, 4171) from urethane and sodium in boiling benzene and was twice recrystallised from pure alcohol. With it and with the same hypobromite solutions as before, the following results were obtained.

TABLE II.

5 C.c. of sodium cyanate taken contain 0·075 g., equiv. to 17·7 c.c. of 0·196*N*-thio.

No. of solution.	% Bromination.	C.c. of thio. after	
		5 mins.	15 mins.
5	75	—	—
6	80	0·4	0·3
7	85	0·4	0·3
8	90	1·0	0·7
9	95	17·9	18·0

There is no action of hypobromite on sodium cyanate below the composition 75% brominated. Above this value the hypobromite reacts slowly with the sodium cyanate, but with 100% brominated solutions there is a vigorous gas evolution from the mixture.

The figures for sodium cyanate (Nos. 7 and 8) do not show complete oxidation, as would be expected from the figures in Table I. Another series of experiments was therefore made with the same hypobromite solutions, using a mixture of carbamide and sodium cyanate.

These figures point to the fact that the deficit of nitrogen is due to the formation of sodium cyanate and that with hypobromite solutions brominated to more than 75% and less than 95% a secondary oxidation of the sodium cyanate is induced only if carbamide is present. They also show that the rate of this secondary oxidation

TABLE III.

5 C.c. of the solution contain 0·0375 g. each of carbamide and sodium cyanate, which are equivalent to 19·15 and 17·7 c.c. of 0·196N-thiosulphate respectively.

		C.c. of thio. required after	
No. of solution.	% Bromination.	5 mins.	15 mins.
4	60	16·2	16·1 carbamide alone
7	85	15·8	28·5
8	90	28·2	28·4

is greater with increase in the amount of bromination of the sodium hydroxide. Carbamide is not acted upon by 100% sodium hypobromite, as there is no excess of sodium hydroxide to decompose the compound which it probably forms with the bromine.

The potential of a platinum electrode dipping into the various solutions shows that there is no marked change in the oxidising power except in the neighbourhood of completely brominated solutions.

TABLE IV.

No. of solution......	1	3	5	7	9	10
E.M.F. volt	+0·756	0·790	0·810	0·830	0·850	0·981

Summary.

The chief factor influencing the deficit of nitrogen in the reaction between carbamide and sodium hypobromite at room temperature is the extent to which the sodium hydroxide has been brominated. The effect of this variable has been studied for all brominations from 0 to 100%. The reaction does not go to completion owing to the formation of sodium cyanate. The amount of sodium cyanate formed becomes greater as the ratio of hypobromite to hydroxide increases until it corresponds to 75% bromination, when it is oxidised in a secondary reaction. Sodium cyanate solutions are not appreciably oxidised by 75 to 90% hypobromite solutions except in the presence of carbamide. With pure hypobromite (*i.e.*, without any excess of sodium hydroxide present) sodium cyanate solutions are vigorously decomposed. The experiments of Margosches and Rose proving that sodium cyanate is not formed in the reaction are inconclusive, since they do not take into account the effect of the composition of the hypobromite. The use of 10N-sodium hydroxide solutions for the estimation of carbamide gasometrically leads to inaccurate results.

The author wishes to thank Professor J. C. Philip, F.R.S., for his kind advice and interest in this research.

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