CCLXXI.—*The Hydrolysis of Guanidine Carbonate.*

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THE hydrolysis of guanidine in aqueous solution (Bell, J., 1926, 1213) at room temperature gives urea: $CN_3H_5 + H_2O = CON_2H_4 + NH_3$. This is also formed on boiling, but some of it is decomposed by the strongly alkaline solution owing to the dissociation of urea to ammonia and cyanic acid at the high temperature (Werner, J., 1918, **113**, 84). The cyanic acid is then fixed as guanidine cyanate, which is in turn hydrolysed to guanidine carbonate. The prepar-

ation of guanidine cyanate and a detailed examination of its hydrolysis will be dealt with in a future communication.

It is now shown that guanidine carbonate, when heated in aqueous solution to 100°, undergoes similar changes due to its dissociation into the free base and carbonic acid and hydrolysis of the former. A $N/10$-aqueous solution was unchanged after remaining for 10 weeks at room temperature. When it was boiled under reflux, hydrolysis took place to an appreciable extent; urea was first formed (1) and then decomposition to ammonium carbonate took place to a lesser degree (2).

$$(CN_3H_5)_2,H_2CO_3 + 2H_2O = 2CON_2H_4 + (NH_4)_2CO_3 \quad (1)$$

$$CON_2H_4 + 2H_2O = (NH_4)_2CO_3 \quad (2)$$

No cyanate could be detected among the products of this hydrolysis, even by the delicate copper pyridine test (Werner, J., 1923, **123**, 2577). In this respect, the hydrolysis differed from that of free guanidine, where guanidine cyanate accumulated to a considerable degree. However, it was shown (Bell, *loc. cit.*) that guanidine cyanate is also decomposed on further boiling, and since this salt would be formed at a much slower rate in the hydrolysis of the carbonate, its accumulation would be prevented by the fact that its rate of decomposition exceeds that of its formation.

The results in Table I were obtained after boiling a $N/10$-aqueous solution of guanidine carbonate under reflux for various times.

TABLE I.

	Duration of boiling.			
	1 hr.	3 hrs.	6 hrs.	12 hrs.
Urea present *	25·0	25·2	22·7	20·5
Urea converted into $(NH_4)_2CO_3$ *	0·1	11·3	16·5	22·5
Guanidine carbonate unchanged	75·0	62·7	60·9	58·0
Total (%)	100·1	99·2	100·1	101·0

* Estimated as percentage of original guanidine carbonate in accordance with equations (1) and (2).

The rate of hydrolysis diminishes very much after 3 hours' boiling and the reaction appears to stop after 12 hours. This retardation is due to the accumulation of ammonium carbonate in the solution (see Table II).

TABLE II.

	Expt. I.	Expt. II.	Expt. III.
Urea present	25·2	5·6	39·5
Urea converted into $(NH_4)_2CO_3$	11·3	0·0	16·5*
Guanidine carbonate unchanged	62·7	94·7	44·0
Total (%)	99·2	100·3	100·0

* Estimated by difference.

In Experiment I an $N/10$-solution of guanidine carbonate was boiled for 3 hours under reflux. In Experiment II an $N/10$-solution of guanidine carbonate, to which ammonium carbonate equivalent to 5·2 c.c. of N-acid per 100 c.c. of solution had been added, was treated in the same way. In Experiment III an $N/10$-solution of guanidine carbonate was boiled in an open flask for the same length of time, the volume being maintained constant by the addition of water to replace the loss due to evaporation. Under these conditions, ammonium carbonate volatilised as it was formed. The results of Experiment II show that the presence of ammonium carbonate checks the rate of hydrolysis very considerably, and in Experiment III, where the ammonium carbonate was allowed to escape, the change was much greater than in Experiment I.

Ammonium carbonate in solution dissociates into ammonia and carbonic acid and would therefore diminish the dissociation of guanidine carbonate into free guanidine and carbonic acid. This suggests that the hydrolysis of guanidine carbonate in aqueous solution is due to its dissociation into free guanidine and carbonic acid, the free base being hydrolysed in the manner already described. Salts of guanidine, such as the chloride, which undergo no such dissociation in aqueous solution, remain unchanged on boiling.

The ready hydrolysis of guanidine carbonate should not be overlooked in the use of this substance in the preparation of standard acid solutions.

EXPERIMENTAL.

In each experiment involving boiling, 100 c.c. of solution were used. Ten minutes were required to raise the solution to the boiling point and the burner was always adjusted to secure quiet ebullition only.

Urea was estimated by the xanthhydrol method (Fosse, *Compt. rend.*, 1913, **157**, 948). An aliquot part of the liquid was neutralised and evaporated to dryness, and the residue extracted with glacial acetic acid to which one-fourth its volume of water had been added. An excess of xanthhydrol, dissolved in methyl alcohol, was then added and after 12 hours the precipitate of dixanthylurea was collected, washed with alcohol, dried, and weighed. A small correction was applied for the slight solubility of dixanthylurea in the mixture of acetic acid, water, and methyl alcohol, the value of this correction being determined in preliminary control experiments.

The amount of urea converted into ammonium carbonate was determined by the increase in alkalinity after boiling, equation (2) representing the only reaction producing such an increase. This necessitated the estimation, by absorption in a measured volume of standard acid, of any ammonia which escaped through the reflux

condenser. In Experiment III, however, where this procedure was not possible, the change had to be estimated by difference.

Unchanged guanidine carbonate was estimated by warming gently an aliquot portion of the liquid until all ammonium carbonate was driven off, and then titrating the residue with standard acid. Control experiments showed that guanidine carbonate underwent no change during this procedure.

The author gratefully acknowledges his indebtedness to Professor E. A. Werner for advice received.

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Dublin. [*Received, June 4th*, 1928.]