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Studies on Carbamates

XIII. On the Catalytic Action of Zinc Tetrammine on the Process 'Carbon Dioxide ⇌ Carbonic Acid'

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$Zn(NH_3)_4^{++}$ catalyses the process 'carbamate ⇌ carbonate'. The effect is explained by the catalysis of the $Zn(NH_3)_4^{++}$ on the process '$CO_2 + H_2O \rightleftharpoons H_2CO_3$'.

1. The rate of equilibration of the process '$NH_2COONH_4 + H_2O \rightleftharpoons (NH_4)_2CO_3$' in aqueous medium has previously been studied[1,2]. The decomposition is a two-step reaction, *viz.*

carbamic acid ⇌ ammonia + carbon dioxide
carbon dioxide ⇌ carbonic acid

and for a moderately basic solution the last step will be the rate determining step exclusively.

The zinc-containing enzyme carbonic anhydrase, isolated by Meldrum and Roughton[3], catalyses the process '$CO_2 + H_2O \rightleftharpoons H_2CO_3$'. It was therefore of interest to know if other zinc complexes also could have such an effect. This was examined by means of the process '$NH_2COONH_4 + H_2O \rightleftharpoons (NH_4)_2CO_3$'. We have in the present investigation used zinc tetrammine in NH_4Cl/NH_3 buffers.

2. The method of analysis was in principle that described in previous investigations[4]. The samples were adjusted to 0.1 N with regard to hydroxyl ion. Carbonate but not carbamate was precipitated when barium chloride was added. The barium carbonate was removed by centrifugation. The supernatant was in the previous method heated until the carbamate had been decomposed and precipitated as barium carbonate. The carbonate was then titrated acidimetrically. However, in the presence of zinc tetrammine it appears that the precipitate involves zinc, probably in the form of zinc hydroxide. The supernatant therefore was analysed for carbon dioxide by means of an apparatus introduced by Tovborg-Jensen[5]. The supernatant was acidified by means of hydrochloric acid and the carbamate decomposes practically instantaneously to carbon dioxide. The carbon dioxide was absorbed in 0.1 N sodium hydroxide. This solution was titrated using a Radiometer-titrigraf, type TTT 1 a. The amount of 0.05 N hydrochloric acid used from pH 8.4 to 4.5 corresponds to the content of carbamate since 1 mole HCl $\sim$ 1 mole CO_2 $\sim$ 1 mole carbamate.

It was necessary to correct all the determinations for blank values since the air in the apparatus at the beginning contains a small amount of carbon dioxide.

The method of analysis was tested by means of solutions containing per litre 0.4 mole NH_4Cl, 0.2 mole NH_3, 0.01 mole $Zn(NH_3)_4(CH_3COO)_2$ and about 0.02 mole carbonate + carbamate. Zinc tetrammine did not interfere with the precision of the method.

3. Ammonium carbamate was prepared from dry ice and liquid ammonia [6]. Anhydrous liquid ammonia was placed in a Dewar flask and powdered dry ice was slowly added. The excess of ammonia was allowed to evaporate, when the mixture had attained a slushy consistency. This material was transferred to a desiccator and kept under slightly reduced pressure for 24 h. The ammonium carbamate was stable when kept in a desiccator over dry calcium chloride. It contained about 5 % carbonate.

The concentrations of zinc acetate and zinc perchlorate were determined by complexometric titrations.

The salts of zinc tetrammine have not been prepared in the solid state. The solutions of zinc tetrammine were prepared by adding zinc acetate or zinc perchlorate to the NH_4^+/NH_3 buffers. In the calculation of the concentrations of ammonia we have taken into account the ammonia used by the process '$Zn^{++} + 4NH_3 = Zn(NH_3)_4^{++}$'.

4. All the experiments were carried out at 0°C. The data presented in the tables were corrected for blank values, *viz.* about 3 units of the percentage. The velocity constants were calculated by means of Brigg's logarithms, the unit of time being the minute. The activity coefficient f was calculated as in earlier investigations from the expression of Bjerrum [7]: $-\log f = 0.3\sqrt[3]{C_{\text{ion}}}$.

The experiments concerning the process 'carbamate ⇌ carbonate'

Two different NH_4^+/NH_3 buffers, 0.40 M NH_4Cl/0.20 M NH_3, and 0.50 M NH_4Cl/0.05 M NH_3 have been used. Experiments were carried out with zinc acetate and zinc perchlorate and, within the experimental error, we attained the same results under the same conditions. Experiments were carried out with and without zinc tetrammine.

Some of the experiments are listed in Tables 1 and 2 and illustrate the precision of the method. The values $k_{\text{amate}} + k_{\text{onate}}$ are calculated from the expression $k_{\text{amate}} + k_{\text{onate}} = 1/t \cdot \log \dfrac{Ka-b}{Ka-b-(1+K)x},$ the expression for a process which is unimolecular from both sides. a and b represent the starting

Table 1. 0.02 M NH_2COONH_4 in 0.4 M NH_4Cl + 0.2 M NH_3

without $Zn(NH_3)_4^{++}$			with 0.04 M $Zn(NH_3)_4^{++}$		
min.	% carbamate left	$k_{\text{amate}} + k_{\text{onate}}$	min.	% carbamate left	$k_{\text{amate}} + k_{\text{onate}}$
3	94.8	—	0.5	96.4	—
36	93.4	(0.000285)	7.0	91.3	0.00460
171	86.3	0.000357	36	73.7	0.00432
303	80.2	0.000363	96	53.5	0.00377
463	76.3	0.000310	155	39.8	0.00381
1 420	49.3	0.000361	238	32.5	0.00331
1 860	42.8	0.000365	329	27.2	0.00312
3 230	33.2	0.000367	413	23.0	0.00339
∞	28.9	mean: 0.00035	∞	20.0	mean: 0.0038
$k_{\text{amate}} = 0.00025$; $k_{\text{onate}} = 0.00010$; $K = 2.46$			$k_{\text{amate}} = 0.00304$; $k_{\text{onate}} = 0.00076$; $K = 4.00$		

values of carbamate and carbonate, respectively. The constant K signifies the ratio between the equilibrium values of the concentrations of carbonate and carbamate.

It is seen from the tables that the influence of zinc tetrammine is greatest at lower pH values.

It should be pointed out that the value of K is not constant in analogous experiments with and without $Zn(NH_3)_4^{++}$. This may be explained by the fact that the determination of carbamate is relatively inexact in the equilibrium where the percentage of carbamate is rather small. But there is a marked drift, so it is possible that other factors come into play, *e.g.* the formation of zinc carbonato ions.

All experiments are listed in Table 3.

An experiment with $Cu(NH_3)_4^{++}$ is furthermore listed in Table 3, but the effect is small and therefore not reliable. Further experiments are necessary to state a catalytical effect of $Cu(NH_3)_4^{++}$.

Table 2. 0.02 M NH_2COONH_4 in 0.5 M NH_4Cl + 0.05 M NH_3.

without $Zn(NH_3)_4^{++}$			with 0.04 M $Zn(NH_3)_4^{++}$		
min.	% carbamate left	$k_{\text{amate}} + k_{\text{onate}}$	min.	% carbamate left	$k_{\text{amate}} + k_{\text{onate}}$
0.75	96.8	—	0.50	84.0	—
8.75	93.3	0.00234	5.10	60.2	0.0357
27.0	89.0	0.00166	9.3	42.2	0.0397
57.0	82.1	0.00153	15.8	33.0	0.0319
107	71.6	0.00151	25.0	21.1	0.0322
172	59.9	0.00152	45.5	12.3	0.0288
284	47.2	0.00200	∞	8.50	
∞	15.0	mean: 0.0018			mean: 0.034
$k_{\text{amate}} = 0.0015$; $k_{\text{onate}} = 0.00027$; $K = 5.66$			$k_{\text{amate}} = 0.0308$; $k_{\text{onate}} = 0.0029$; $K = 10.7$		

Table 3.

$c_{Zn(NH_3)_4^{++}}$	$c_{NH_4^{++}}$	c_{NH_3}	c_{CO_2} total	% carbamate in equilibrium	$k_{amate} + k_{onate}$	k_{amate}	k_{onate}
—	0.4	0.2	0.0209	28.9	0.00035	0.00025	0.00010
0.005	0.4	0.2	0.0210	27.1	0.00078	0.00057	0.00021
0.01	0.4	0.2	0.0209	25.7	0.00100	0.00074	0.00026
0.015	0.4	0.2	0.0197	24.0	0.00140	0.00106	0.00034
0.020	0.4	0.2	0.0195	22.4	0.0019	0.00147	0.00043
0.040	0.4	0.2	0.0194	20.0	0.0038	0.00304	0.00076
—	0.5	0.05	0.0205	15.0	0.0018	0.00153	0.00027
0.02	0.5	0.05	0.0191	11.5	0.018	0.0160	0.0020
0.04	0.5	0.05	0.0225	8.5	0.034	0.0308	0.0029
$c_{Cu(NH_3)_4^{++}}$							
0.01	0.4	0.2	0.197	27.3	0.00050	0.00037	0.00013

Calculations on the experiments concerning the process 'carbamate ⇌ carbonate'

Without zinc the conversion of the carbon dioxide into carbonate and the reciprocal conversion take place through the two reactions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

and between pH 8 and 10 the velocity of the processes proceeds with the same order of magnitude.

We have the following expression for the conversion of carbamate:

$$\frac{dc_{carbamate}}{dt} = -(k_{CO_2} + k_{CO_2 \cdot OH^-} \cdot c_{OH^-}) \cdot c_{CO_2}$$
$$= -(k_{CO_2} + k_{CO_2 \cdot OH^-} \cdot c_{OH^-}) \cdot a \cdot c_{carbamate} = -k_{amate} \cdot c_{carbamate}$$

where a indicates the part of the carbamate being dissociated into CO_2. a is calculated from:

$$a = \frac{c_{CO_2}}{c_{carbamate}} = \frac{K_{NH_4^+} \cdot K_{Eq}}{K_{CO_2}} \cdot \frac{c_{NH_4^+} \cdot f^2}{c^2_{NH_3}}$$

and then we have

$$k_{amate} = \frac{(k_{CO_2} + k_{CO_2 \cdot OH^-} \cdot c_{OH^-}) \cdot K_{NH_4^+} \cdot K_{Eq} \cdot c_{NH_4^+} \cdot f^2}{K_{CO_2} \cdot c^2_{NH_3}}$$

In the presence of zinc tetrammine the expression must be:

$$\frac{\mathrm{d}c_{\text{carbamate}}}{\mathrm{d}t} = -\left(k_{\text{CO}_2} + k_{\text{CO}_2\cdot\text{OH}^-}\cdot c_{\text{OH}^-} + k'_{\text{Zn}}\cdot c_{\text{Zn(NH}_3)_4^{++}}\right)\cdot c_{\text{CO}_2}$$

$$= -k_{\text{amate}}\cdot c_{\text{carbamate}}$$

This can be transformed to:

$$k_{\text{amate}} = \frac{\left(k_{\text{CO}_2} + k_{\text{CO}_2\cdot\text{OH}^-}\cdot c_{\text{OH}^-} + k'_{\text{Zn}}\cdot c_{\text{Zn(NH}_3)_4^{++}}\right)\cdot K_{\text{NH}_4^+}\cdot K_{\text{Eq}}\cdot c_{\text{NH}_4^+}\cdot f^2}{K_{\text{CO}_2}\cdot c^2_{\text{NH}_3}}$$

For the conversion of carbonate we have:

$$\frac{\mathrm{d}c_{\text{carbonate}}}{\mathrm{d}t} = -k_{\text{H}_2\text{CO}_3}\cdot c_{\text{H}_2\text{CO}_3} - k_{\text{HCO}_3^-}\cdot c_{\text{HCO}_3^-} = -k_{\text{onate}}\cdot c_{\text{carbonate}}$$

By means of

$$c_{\text{carbonate}} = c_{\text{H}_2\text{CO}_3} + c_{\text{HCO}_3^-} + c_{\text{CO}_3^{--}}$$

$$a_{\text{H}^+}\cdot c_{\text{HCO}_3^-}\cdot f = K_{\text{H}_2\text{CO}_3}\cdot c_{\text{H}_2\text{CO}_3}$$

$$a_{\text{H}^+}\cdot c_{\text{CO}_3^{--}}\cdot f^2 = K_{\text{HCO}_3^-}\cdot c_{\text{HCO}_3^-}\cdot f$$

and

$$a_{\text{H}^+}\cdot c_{\text{NH}_3} = K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f$$

the expression is transformed to

$$k_{\text{onate}} = \frac{\dfrac{k_{\text{H}_2\text{CO}_3}\cdot K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}{c_{\text{NH}_3}} + k_{\text{HCO}_3^-}\cdot K_{\text{H}_2\text{CO}_3}}{\dfrac{K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}{c_{\text{NH}_3}} + K_{\text{H}_2\text{CO}_3} + \dfrac{K_{\text{H}_2\text{CO}_3}\cdot K_{\text{HCO}_3^-}\cdot c_{\text{NH}_3}}{K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}}$$

In the presence of zinc tetrammine we have:

$$\frac{\mathrm{d}c_{\text{carbonate}}}{\mathrm{d}t} = -\left(k_{\text{H}_2\text{CO}_3}\cdot c_{\text{H}_2\text{CO}_3} + k_{\text{HCO}_3^-}\cdot c_{\text{HCO}_3^-} + k''_{\text{Zn}}\cdot c_{\text{H}_2\text{CO}_3}\cdot c_{\text{Zn(NH}_3)_4^{++}}\right)$$

$$= -k_{\text{onate}}\cdot c_{\text{carbonate}}$$

which can be transformed into:

$$k_{\text{onate}} = \frac{\dfrac{k_{\text{H}_2\text{CO}_3}\cdot K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}{c_{\text{NH}_3}} + k_{\text{HCO}_3^-}\cdot K_{\text{H}_2\text{CO}_3} + k''_{\text{Zn}}\cdot c_{\text{Zn(NH}_3)_4^{++}}\cdot\dfrac{K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}{c_{\text{NH}_3}}}{\dfrac{K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}{c_{\text{NH}_3}} + K_{\text{H}_2\text{CO}_3} + \dfrac{K_{\text{H}_2\text{CO}_3}\cdot K_{\text{HCO}_3^-}\cdot c_{\text{NH}_3}}{K_{\text{NH}_4^+}\cdot c_{\text{NH}_4^+}\cdot f^2}}$$

Table 4.

c_{NH_4Cl}	c_{NH_3}	$c_{Zn(NH_3)_4^{++}}$	k_{amate} exptl.	k_{amate} calc.	k_{onate} exptl.	k_{onate} calc.	k'_{Zn}	$k''_{Zn} \times 10^{-4}$
0.4	0.2	—	0.00025	0.00025	0.00010	0.00012	—	—
		0.005	0.00057		0.00021		147	11.5
		0.010	0.00074		0.00026		115	8.6
		0.015	0.00106		0.00034		127	8.6
		0.020	0.00147		0.00043		146	9.2
		0.040	0.00304		0.00076		171	9.5
0.5	0.05	—	0.0015	0.0012	0.00027	0.00022	—	—
		0.02	0.0160		0.0020		126	8.3
		0.04	0.0308		0.0029		132	6.8

The ratio $c_{NH_4^+}/c_{NH_3}$ is not constant during the experiments with $c_{NH_4Cl}/c_{NH_3} = 0.5/0.05$. The ratio $c_{NH_4^+}/c_{NH_3}$ is in the equilibrium 0.52/0.065, 0.52/0.065 and 0.52/0.068 for $c_{Zn(NH_3)_4^{++}} = 0.00$, 0.02 and 0.04, respectively.

K_{Eq} ($10^{-0.48}$) is the equilibrium constant for the process ’$NH_2COO^- + H_2O \rightleftharpoons HCO_3^- + NH_3$’, K_{CO_2} ($10^{-6.65}$) is the equilibrium constant for ’$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$’, $K_{H_2CO_3}$ ($10^{-3.7}$) for ’$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$’ and $K_{HCO_3^-}$ ($10^{-10.5}$) for ’$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$’. For K_{H_2O} and $K_{NH_4^+}$ are used $10^{-14.93}$ and $10^{-10.08}$, respectively. k_{CO_2} (0.078) is the velocity constant for ’$CO_2 + H_2O \rightleftharpoons H_2CO_3$’ from left to right and $k_{H_2CO_3}$ (69.6) from right to left. $k_{CO_2 \cdot OH^-}$ (2.43×10^4) is the velocity constant for ’$CO_2 + OH^- \rightleftharpoons HCO_3^-$’ from left to right and $k_{HCO_3^-}$ (15.6×10^{-5}) from right to left.

The experimental and calculated values for k_{amate} and k_{onate} are listed in Table 4. Furthermore are listed k'_{Zn} and k''_{Zn} calculated from experimental values of k_{amate} and k_{onate}. The ratio $c_{NH_4^+}/c_{NH_3}$ may be regarded as constant in the experiments with $c_{NH_4Cl}/c_{NH_3} = 2$, but not in the experiments with $c_{NH_4Cl}/c_{NH_3} = 10$. The mean value therefore is used in the calculation.

Table 5.

Metal ammine, M	Initial solution c_{NaOH}	Initial solution c_{NH_3}	Absorbed CO_2 mole/l	% Carbamate	Final solution c_{NaOH}	Final solution c_{NH_3}	Mean c_{NaOH}	Mean c_{NH_3}	log $k_{CO_2 \cdot NH_3}$
	0.2	0.5	0.0191	23.6	0.17	0.5	0.185	0.5	3.45
	0.2	1.0	0.0187	31.9	0.17	1.00	0.185	1.0	3.33
	0.2	1.0	0.0191	31.9	0.17	1.00	0.185	1.0	3.33
0.01 Zn	0.2	0.5	0.0186	26.1	0.17	0.5	0.185	0.5	3.51
0.01 Zn	0.2	1.0	0.0137	33.7	0.18	1.0	0.190	1.0	3.38
0.01 Cu	0.2	1.0	0.0204	32.6	0.17	1.0	0.185	1.0	3.34
0.01 Co	0.2	1.0	0.0209	35.1	0.17	1.0	0.185	1.0	3.39
0.02 Ag	0.2	1.0	0.0194	35.8	0.17	1.0	0.185	1.0	3.40

It is seen that the process '$CO_2 + H_2O \rightleftharpoons H_2CO_3$' in 1 M $Zn(NH_3)_4^{++}$ solution proceeds about 2 000 times faster than in a solution without $Zn(NH_3)_4^{++}$.

Some experiments in strongly basic solution

500 ml of an aqueous solution containing both ammonia and sodium hydroxide were placed in a 2 litre flask. Approximately 225 ml of carbon dioxide were substituted for an equal amount of atmospheric air in the gas phase above this solution, and the flask was shaken vigorously for about 2 min. to obtain absorption of the carbon dioxide.

Other experiments were carried out with the same concentrations of ammonia, sodium hydroxide and carbon dioxide. The solutions furthermore contained 0.01 M $Zn(NH_3)_4(CH_3COO)_2$, 0.01 M $Cu(NH_3)_4Cl_2$, 0.01 M $Co(NH_3)_6Cl_3$ and 0.02 M $Ag(NH_3)_2NO_3$, respectively.

The solutions were immediately analysed in order to determine, how many per cent of the carbon dioxide absorbed had been converted to carbamate and carbonate, respectively. The results are presented in Table 5. It is seen from the table that the influence of the metal ammines is very little. The lack of influence may be due to the predominance of the process '$CO_2 + OH^- \rightleftharpoons HCO_3^-$' in strongly basic solution. Neither the process '$H_2O + CO_2 \rightleftharpoons H_2CO_3$' nor the zinc tetrammine catalysed process can manifest itself appreciably. Furthermore probably all $Zn(NH_3)_4^{++}$ is transformed to $Zn(OH)_4^{--}$.

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