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Short Communications

Studies on Carbamates
XIV. On the Catalytic Action of Metal Ammines on the Process "Carbon Dioxide ⇌ Carbonic Acid"

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In a previous investigation [1] from this laboratory it was shown that $Zn(NH_3)_4^{++}$ increases the rate of the process "$NH_2COONH_4 + H_2O = (NH_4)_2CO_3$" which was explained by assuming that the process "$CO_2 + H_2O = H_2CO_3$" is catalyzed by $Zn(NH_3)_4^{++}$.

In the present investigation it is shown that also $Cu(NH_3)_4^{++}$ has some catalytic effect, whereas $Co(NH_3)_6^{+++}$ has no effect.

Experiments with the carbamate of glycine show that the complex zinc glycinate acts as a catalyst to some degree, whereas the complex cupric glycinate has no significant catalytic effect.

1. *Studies on the ammonium carbamate.* In the previous investigation only a single experiment was carried out with $Cu(NH_3)_4^{++}$. The present investigation is supplementary to this experiment. The results of experiments carried out in the buffer 0.5 M NH_4Cl/0.05 M NH_3 are listed in Table 1. The experiments were carried out at 0°C, and the velocity constants were calculated by means of Briggs logarithms. It is seen that the catalytic action is small. Experiments with $Co(NH_3)_6^{+++}$ in the same buffer solution gave no significant effect.

2. *Studies on the carbamate of glycine.* The experiments are carried out in the buffer 0.5 M $+H_3NCH_2COO^-$/0.05 M $H_2NCH_2COO^-$ at 18°C. The reaction was started by addition of K_2CO_3.

The method of analysis was a slight modification of a complexometric titration described by Jørgensen [2].

The reaction was quenched by addition of sodium hydroxide. It was necessary to mask the added catalyst, *e.g.* zinc glycinate or cupric glycinate, in order to titrate excess barium ion. The masking was performed by means of potassium cyanide, since the complex ions, zinc cyanide ion

Table 1. Ca. 0.02 M NH_2COONH_4 in 0.50 M NH_4Cl/0.05 M NH_3 with and without $Cu(NH_3)_4^{++}$. 0°C.

	$c_{metal\ ammine}$	c_{CO_2} total millimole	% carbamate in eq.	$k_{amate} + k_{onate}$	k_{amate}	k_{onate}
$Cu(NH_3)_4^{++}$	0	20.5	15.0	0.0018	0.0015	0.00027
	0.01	20.8	14.5	0.0023	0.0020	0.00033
	0.02	22.9	14.5	0.0040	0.0034	0.00058
	0.04	22.8	12.5	0.0054	0.0047	0.00068
$Co(NH_3)_6^{+++}$	0.04	19.6	18.9	0.0013	0.0010	0.00025

Table 2. 0.02 M K_2CO_3 in 0.50 M $+H_3NCH_2COO^-$/0.05 M $H_2NCH_2COO^-$.

	$c_{metal\ glycinate}$	$c_{CO_3,\ total}$ millimole	% carbonate in eq.	$k_{amate} + k_{onate}$	k_{amate}	k_{onate}
Zinc glycinate	0	21.3	33.5	0.0047	0.0016	0.0031
	0.005	18.3	39.3	0.0058	0.0023	0.0035
	0.01	18.0	34.9	0.0065	0.0023	0.0042
	0.02	18.2	36.7	0.0085	0.0031	0.0054
Cupric glycinate	0.01	18.0	35.6	0.0048	0.0017	0.0031

and cupric cyanide ion, are not titrated together with excess barium ion.

The details are as follows:

20.00 ml of the specimen are run into a flask containing 2.00 ml of a mixture that is 6.4 M in sodium hydroxide and 2 M in potassium cyanide. 8.00 ml of this mixture are precipitated with barium chloride and analysed as described by Jørgensen. It was found that a faint blue colour appeared before the equivalence point was reached, but at the end point a distinct jump in colour intensity was observed.

The complexometric titration gives results which are identical to those obtained by the method previously used.

The experiments are listed in Table 2. It is seen, that the catalytic action of zinc glycinate is significant but it can not be compared in order of magnitude with the catalytic action of zinc tetrammine.

A corresponding experiment with 0.01 M cupric glycinate gave no significant effect.

1. Grønvald, M. and Faurholt, C. *Acta Chem. Scand.* **14** (1960) 1374.
2. Jørgensen, E. *Acta Chem. Scand.* **10** (1956) 747.

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Acid Soluble Cytidine Nuoleotide Linked Amino Acids in Extracts of Rabbit Liver

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In recent papers [1,2] it was reported that ^{32}P-labeled trichloroacetic acid (TCA) extracts of liver and kidneys of the rat and rabbit contained an ultra violet (UV) absorbing peak (X_I) which contained ninhydrin positive substances. After purification by ionophoresis and paperchromatography the material from the peak still gave a ninhydrin positive reaction. A labeled UV-peak in the same position of the elution curve could also be observed in TCA extracts of ^{32}P-labeled tissue homogenates of rat kidneys. The nucleotide-amino acid complex exhibited changes in UV-absorbtion spectrum characteristic of cytidine nucleotide (CMP). Since CMP-linked amino acids do not seem to have been observed in animal cells previously some properties of the fraction will be described briefly.

In Fig. 1 a section of the elution diagram of the TCA extract is presented consisting of the peaks immediately before and after AMP (adenylic acid). The TCA extract of rabbit livers was eluted according to Hurlbert *et al.*[3] The two first labeled UV-peaks (X_I) appearing with formic acid concentration between 0 and 0.23 M were taken to dryness. At paper electropherograms in