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Studies on Carbamates

VI. The Carbamate of Glycine

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In a previous investigation [1], during which was studied the equilibrium conditions and the reaction mechanism of the formation and decomposition in aqueous medium of the carbamates formed by ammonia, methylamine and dimethylamine, a few experiments were done concerning the carbamate of glycine. The present investigation is supplementary to those previous experiments. The equilibrium conditions and reaction mechanism of glycine being analogous to those of the alanines, and the experimental method being similar, we find that on the whole it is sufficient here to state the experimental data and the calculated constants, referring for further information to the investigation of the alanines [2].

The preparation of glycine used in the present investigation was one which fulfilled the demands for purity stated by S. P. L. Sørensen [3], except for a content of 0.05 per cent ammonia, an amount being, however, of no significance in the present investigation.

The following expression was used for the calculations

$$\frac{a_{H^+} \cdot c_{CH_2NH_2 \cdot COO^-}}{c^+_{CH_2NH_3 \cdot COO^-}} = K'_{AmH^+} = 10^{-9.88}\ ^4$$

Table 1. Carbon dioxide in glycine + NaOH . 18°.

Initial solution		Absorbed CO_2 Mol/liter	% carbamate	Final solution		Mean		$k_{CO_2 \cdot Am}$	
c_{NaOH}	c_{Am}			c_{NaOH}	c_{Am}	c_{NaOH}	c_{Am}		Mean
0.20	0.20	0.0191	52.5	0.17	0.19	0.19	0.20	$10^{5,04}$	
0.20	0.10	0.0188	35.6	0.17	0.09	0.18	0.10	$10^{5,04}$	$10^{5,05}$
0.10	0.10	0.0203	55.4	0.07	0.09	0.09	0.09	$10^{5,07}$	

Table 2. The solutions of carbonate-carbamate in equilibrium. 18°.

Initial solution			% carbamate	Equilibrium				K_{Eq}	
$c_{(AmH)_2CO_3}$	c_{AmH^+}	c_{Am}		c_{AmH^+}	c_{Am}	$c_{carbamate}$	$c_{HCO_3^-}$		Mean
0.02	0.05	0.05	55 [1]	0.073	0.056	0.011	0.0064	$10^{-1,48}$	$10^{-1,48}$
0.02	0.05	0.10	64 [2]	0.073	0.104	0.013	0.0041	$10^{-1,47}$	

[1] Mean of 7 determinations: 53.5, 53.5, 53.8, 56.6, 55.6, 55.7, 55.5.
[2] » » 4 » 62.9, 64.6, 63.7, 63.7.

Table 3. Velocity constants for the process: carbamate ⇌ carbonate; pa_H = ca. 10. 18°.

Initial solution			Min.	% carbamate	$k_{amate} + k_{onate}$
	c_{AmH^+}	c_{Am}			
0.02 *M* $(AmH)_2CO_3$	0.05	0.05	41	13.2	0.00287
			80	21.4	0.00263
			160	35.1	0.00269
			261	44.6	0.00267
			1425	56.6	Mean: 0.0027
			1440	55.6	k_{amate}: 0.0012
					k_{onate}: 0.0015

Table 4. Velocity constants for the process: carbamate → carbonate; pa_H = ca. 13. 18°.

Initial solution			Min.	% carbamate left	k_{amate}
$c_{carbamate}$	c_{NaOH}	c_{Am}			
0.011	0.19	0.19	0	100	
			242	92.5	0.000140
			1211	67.8	0.000139
			1680	60.1	0.000131
			2640	43.4	0.000137
			ca. 1 month	0	
					Mean: 0.00014

Table 5. Velocity constants, experimental and calculated.

Initial solution					k_{amate}		k_{onate}	
$c_{(AmH)_2CO_3}$	$c_{carbamate}$	c_{AmH^+}	c_{Am}	c_{NaOH}	exp.	calc.	exp.	calc.
0.02		0.05	0.05		0.0012	0.0013	0.0015	0.0014
	0.011		0.19	0.19	0.00014	0.00019		

SUMMARY

The velocity constant of the reaction "$CH_2NH_2 \cdot COO^- + CO_2 = CH_2NHCOOH \cdot COO^-$" and the equilibrium constant for the reaction "$CH_2NHCOO^- \cdot COO^- + H_2O = HCO_3^- + CH_2NH_2 \cdot COO^-$" have been determined. The velocity of the decomposition of $CH_2NHCOO^- \cdot COO^-$ in basic medium was investigated and may be explained in assuming that the decomposition is a two-stage reaction, *viz.*

carbamate = glycine + carbon dioxide
carbon dioxide = carbonate

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