

Studies on Carbamates

XI. The Carbamate of Ethylenediamine

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The velocity constants of the reaction $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-$ and the equilibrium constant for the reaction $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 + \text{HCO}_3^-$ have been determined. The velocity of the decomposition of $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-$ in basic medium was investigated and may be explained in assuming that the decomposition is a two stage reaction, *viz.* 1) carbamate \rightleftharpoons amine + carbon dioxide, 2) carbon dioxide \rightleftharpoons carbonate.

It is to be noticed that the carbamate has been prepared not only in solution by leading CO_2 into a diluted solution of $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, but also as a solid. This substance consists of equal moles of $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ and CO_2 , so that the gross composition corresponds with both monocarbamate, $+\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-$, and dicarbamate, $+\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 + ^-\text{OOCNH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-$. The carbamate showed by analysis that it did not contain monocarbamate exclusively, approx. 20 % CO_2 being present as dicarbamate. The experiments on equilibrium and velocity have been calculated as if all the carbamate was present as monocarbamate.

1. The equilibrium conditions and reaction mechanism of the formation and decomposition in aqueous medium of the carbamate formed by ethylenediamine have been studied. As the experimental and theoretical conditions are practically analogous to those of the carbamates previously investigated, we confine ourselves, with some exceptions, to refer to an earlier paper^{1,2} for the detailed information concerning method, theory, significance of constants, *etc.* It should be noted, though, that "Am" means $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ and "AmH⁺" $+\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$.

2. Two different preparations of ethylenediamine were used in the experiments. One preparation was purified through the acid oxalate by recrystallization, until constant molecular weight was obtained. The molecular weight of the acid oxalate, crystallizing with one molecule of crystal water, is theoretically 258.20. The preparation obtained showed the following molecular weight: By titration with permanganate it was found to be 256.8, and by a Kjeldahl

analysis it was found to be 262.1; the melting point was about 210°C. From the acid oxalate was prepared an aqueous solution of ethylenediamine by distilling it off with sodium hydroxide.

The other preparation was purified by distillation in an ordinary stiller at atmospheric pressure after drying with metallic sodium; the fraction used had a boiling point of 117.3—117.7°C (768 mm Hg), $n_D^{25.0^\circ} = 1.4548$, and by titration with 1.0 *N* HCl a molecular weight of 61.7 (theoretically 60.1) was found. Presumably this difference in the molecular weight is due to small contents of water.

The two preparations gave the same results in the experiments concerning the formation and decomposition of carbamate.

3. The carbamate of ethylenediamine was prepared partly in solution by leading a deficit of carbon dioxide to aqueous solutions of the amine, practically all of the carbon dioxide thus being converted to carbamate, and partly as a solid.

The solid substance, the gross composition of which corresponds with equal moles of $H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$ and CO_2 was prepared in the following way. Carbon dioxide was lead through a mixture of 80 g amine and 20 g water, cooled to 0°C, for an hour; after ten hours at 0°C a microcrystalline precipitate was formed, which increased for the following fifty hours at 20°C. It was dried and stored over concentrated sulphuric acid in an exsiccator, in which it, at least for some time, showed no sign of decomposition. 58.0 % of amine (theoretically 57.73 %) was found by titration of the carbamate with 0.1 *N* HCl, and by the method of analysis, stated under 4, 42.0 % of carbon dioxide (theoretically 42.27 %) in the form of carbamate was found.

The gross composition corresponds with two compounds, *viz.* $+H_3N \cdot CH_2 \cdot CH_2 \cdot NHCOO^-$ and $+H_3N \cdot CH_2 \cdot CH_2 \cdot NH_3^+ \cdot -OOCHN \cdot CH_2 \cdot CH_2 \cdot NHCOO^-$. Katchalski, Berliner-Klibanski and Berger³⁻⁵ have recently shown that a carbamate they prepared as a solid substance was a mixture of approx. equal parts by weight of monocarbamate and dicarbamate.

We have examined the same problem but after quite another method than the one used by the above-mentioned authors. Our principle has been to dissolve the preparation of carbamate in excess of 1.0 *N* NaOH. By this method 1 mole of amine was liberated from 1 mole of dicarbamate but no amine was liberated from monocarbamate. The solution was immediately shaken with *n*-amyl alcohol whereupon the concentration of $H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$ in the layer of *n*-amyl alcohol was determined by titration. Approximately, the partition coefficient of $H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$ between *n*-amyl alcohol and 1.0 *N* NaOH was found equal to 0.10. By means of the titration results and the partition coefficient the concentration of liberated amine was calculated. The indicator was bromophenol blue, and the layer of *n*-amyl alcohol was dissolved in enough *iso*-propyl alcohol to ensure homogeneity after titration. The examination showed that approx. 20 % CO_2 was present as a dicarbamate, *i.e.* approx. 80 % CO_2 was present as a monocarbamate.

4. The method of analysis was as in previous investigations precipitation with barium chloride, causing the precipitation of carbonate, but not of carbamate. All of the data presented in the later tables are corrected for blank values, *viz.* 3—5 units of the percentage.

5. All of the experiments were performed at 18° C, and the velocity constants were calculated by means of Briggs' logarithms, the unit of time being the minute. As in previous investigations the activity coefficient f for a monovalent ion was calculated from the expression of Bjerrum $-\log f = 0.3 \sqrt{c_{\text{ion}}}$.

6. For the calculation of certain experiments we have needed the value of the equilibrium constant of $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+ \rightleftharpoons \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 + \text{H}^+$. Since the values of K_{AmH^+} stated in the literature⁶⁻⁸ not agree very well, we have used a value determined by us. This constant was calculated (Table 1) on the basis of determinations of the hydrogen ion activity in solutions containing equal moles of corresponding acid and base, prepared by the mixing of ethylene diamine with half the number of moles of hydrochloric acid. The investigations were carried out both by means of a hydrogen electrode against a 0.1 *N* calomel electrode and by means of a glass electrode. By the hydrogen electrode the hydrogen ion activity was calculated from the expression $\text{p}a_{\text{H}} = -\log a_{\text{H}^+} = (E - E_0) \frac{F \log e}{RT}$, E_0 being fixed at 0.3360⁹, and the adjustment of the glass electrode was carried out by means of buffer solutions of phosphate, borate and sodium hydroxide, according to Sørensen. No corrections were made for the diffusion potentials, these being insignificant.

Table 1. Determination of the second acidic dissociation constant of ethylenediamine 18°.

| C _{acid} | C _{base} | p _{aH} | |
|-------------------|-------------------|-----------------|--------------------|
| | | Glass electrode | Hydrogen electrode |
| 0.198 | 0.198 | 10.19 | 10.22 |
| 0.148 | 0.148 | 10.17 | 10.21 |
| 0.099 | 0.099 | 10.16 | 10.19 |
| 0.079 | 0.079 | 10.14 | 10.18 |
| 0.060 | 0.060 | 10.21 | 10.18 |
| 0.049 | 0.049 | 10.13 | 10.16 |
| 0.039 | 0.039 | 10.19 | 10.17 |

The results are found in Table 1, from which it appears that the expression

$$\frac{a_{\text{H}^+} \times c_{\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2}}{c_{\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+}} = K'_{\text{AmH}^+}$$

has a practically constant value independent of the ion concentration. We have used $K_{\text{AmH}^+} = 10^{-10.17}$ in the calculations.

The acidic dissociation constant for $^+\text{H}_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+ \rightleftharpoons \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+ + \text{H}^+$ was calculated by us on the basis of similar determinations as mentioned before and was found to be about $10^{-7.2}$. In the calculations of our experiments we have only used K'_{AmH^+} , since the solutions are so basic, that they contain practically nothing of the ion $^+\text{H}_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$.

7. The acidic dissociation constant

$$K'_{\text{amate}} = \frac{c_{\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-} \times a_{\text{H}^+}}{c_{^+\text{H}_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-}}$$

for the process: ${}^+\text{H}_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^- \rightleftharpoons \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^- + \text{H}^+$ has been determined in the following way. By dissolving the carbamate, ${}^+\text{H}_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-$, as quickly as possible in a deficit of sodium hydroxide solution, we made solutions containing acid and corresponding base, and in these solutions we determined $\text{p}a_{\text{H}}$ by means of a glass electrode in the course of a few minutes. It should be noted, that we, during this short time, took the liberty of ignoring the decomposition of the carbamate. The results are found in Table 2, from which it appears, that

$$K'_{\text{amate}} = \frac{c_{\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-} \times a_{\text{H}^+}}{c_{{}^+\text{H}_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCOO}^-}}$$

is independent of the ion concentration analogous to the conditions of the alanines ¹.

Table 2. Determination of the acidic dissociation constant of the carbamate 18°.

| cacid | Cbase | p a_{H} | p K'_{amate} |
|--------|--------|------------------|-----------------------|
| 0.0025 | 0.0025 | 10.09 | 10.09 |
| 0.005 | 0.005 | 10.10 | 10.10 |
| 0.0125 | 0.0375 | 10.58 | 10.10 |
| 0.025 | 0.025 | 10.10 | 10.10 |

i. e. p K'_{amate} : 10.10

On the reaction "amine + carbon dioxide → carbamic acid"

500 ml of an aqueous solution containing both amine and sodium hydroxide were shaken vigorously for two minutes with a deficit of a gaseous mixture of 15 % carbon dioxide and 85 % atmospheric air. We also tried in the course of approx. 15 minutes to lead atmospheric air containing about 1 % carbon dioxide into the solution of both amine and sodium hydroxide, the decomposition of the carbamate going so slowly, that we can disregard it. The mixture was immediately analysed, and the two methods gave practically the same results. The analytical data obtained in the experiments are listed in Table 3, where "% carbamate" indicates how many per cent of the carbon

Table 3. Carbon dioxide in amine + NaOH, 18°.

| Initial solution | | Absorbed CO ₂ $\frac{\text{mole}}{\text{litre}}$ | % carba- mate | Final solution | | Mean | | k _{CO₂} · Am | |
|------------------|------|---|---------------------|----------------|------|-------|------|----------------------------------|--------------------|
| cNaOH | cAm | | | cNaOH | cAm | cNaOH | cAm | | Mean |
| 0.20 | 0.10 | 0.0178 | 51 | 0.18 | 0.09 | 0.19 | 0.10 | 10 ^{5.34} | 10 ^{5.30} |
| 0.20 | 0.10 | 0.0266 | 48 | 0.16 | 0.09 | 0.18 | 0.09 | 10 ^{5.37} | |
| 0.20 | 0.10 | 0.0116 | 50 | 0.18 | 0.10 | 0.19 | 0.10 | 10 ^{5.30} | |

Table 4. The solution of carbonate-carbamate in equilibrium, 18°.

| Initial solution | | | | % carbamate | Equilibrium | | | | K_{Eq} | |
|------------------|-------------|-------------------|-----------------|-----------------|-------------|-------------|-----------------|---------------|---------------------|---------------------|
| c_{Am} | c_{AmH^+} | $c_{(AmH)_2CO_3}$ | $c_{carbamate}$ | | c_{Am} | c_{AmH^+} | $c_{carbamate}$ | $c_{HCO_3^-}$ | | Mean |
| 0.01 | 0.00 | 0.04 | | 74 ¹ | 0.020 | 0.015 | 0.0089 | 0.0023 | 10 ^{-2.29} | 10 ^{-2.32} |
| 0.01 | 0.01 | | 0.02 | 79 ² | 0.0057 | 0.0186 | 0.0042 | 0.0033 | 10 ^{-2.34} | |

¹ Mean of 5 determinations: 73.1 73.7 73.3 74.3 74.1.

² » » 5 » » 78.2 78.4 79.2 78.8 79.2.

dioxide absorbed have been converted to carbamate. Furthermore, the velocity constant $k_{CO_2, Am}$ for the reaction $H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2 + CO_2 \rightarrow H_2N \cdot CH_2 \cdot CH_2 \cdot NHCOOH$ was calculated.

The equilibrium "carbamate \rightleftharpoons carbonate"

Experiments with ethylenediamine have been done from the carbonate side as well as from the carbamate. In Table 4 are listed the compositions of the solutions and the equilibrium constant K_{Eq} for the reaction $H_2N \cdot CH_2 \cdot CH_2 \cdot NHCOO^- + H_2O \rightleftharpoons H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2 + HCO_3^-$.

It should be noted that in the experiments

$c_{Am} = C_{H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2}$, $c_{AmH^+} = C_{H_2N \cdot CH_2 \cdot CH_2 \cdot NH_3^+}$ and $c_{amate} = C_{H_2N \cdot CH_2 \cdot CH_2 \cdot NHCOO^-}$, c_{amate} being calculated on the basis of $c_{H_2N \cdot (CH_2)_2 \cdot NHCOO^-}$, α_{H^+} and K'_{amate} .

Table 5. Velocity constants for the process "carbamate \rightleftharpoons carbonate"; $p_{aH} = \text{approx. } 10-11$; 18°.

| Initial solution | | | Min. | % carbamate | $k_{amate} + k_{onate}$ |
|---|-------------|----------|----------------|-----------------------|-------------------------|
| | c_{AmH^+} | c_{Am} | | | |
| 0.020 M (AmH) ₂ CO ₃ | 0.05 | 0.11 | 40 | 5.5 | 0.000707 |
| | | | 100 | 13.3 | 0.000712 |
| | | | 150 | 18.2 | 0.000673 |
| | | | 210 | 24.7 | 0.000682 |
| | | | 325 | 36.5 | 0.000716 |
| | | | Mean : 0.00070 | $k_{amate} : 0.00085$ | $k_{onate} : 0.00061$ |
| 0.020 M (AmH) ₂ CO ₃ | 0.10 | 0.13 | 80 | 11.4 | 0.000711 |
| | | | 170 | 23.5 | 0.000745 |
| | | | 260 | 33.2 | 0.000740 |
| | | | 365 | 43.4 | 0.000748 |
| | | | 470 | 52.2 | 0.000762 |
| | | | Mean : 0.00075 | $k_{amate} : 0.00055$ | $k_{onate} : 0.00070$ |

The velocity of the conversion "carbamate
 \rightleftharpoons carbonate"

In Table 5 are presented the experiments on velocity, which have been carried out in a buffer solution consisting of $^+H_3N \cdot CH_2 \cdot CH_2 \cdot NH_2 / H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$, where a measurable equilibrium is established between carbamate and carbonate. In Table 6 are presented those experiments which have been carried out in a medium containing sodium hydroxide, where carbamate is converted almost completely to carbonate.

The velocity constants calculated from the experiments are listed in Table 5 and 6. These velocity constants may be calculated in advance, provided the decomposition takes place through the reactions

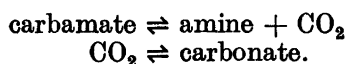


Table 6. Velocity constants for the process "carbamate \rightarrow carbonate"; p_{aH} = approx. 13; 18°.

| Initial solution | | | Min. | % carbamate left | k_{amate} |
|---|-------------------|-----------------|-------|------------------|-------------|
| c _{carbamate} | c _{NaOH} | c _{Am} | | | |
| 0.022 M (CO ₂ in solution of amine) | 0.08 | 0.08 | 0 | 100 | |
| | | | 180 | 96.2 | 0.0000917 |
| | | | 1494 | 73.1 | 0.0000913 |
| | | | 2892 | 54.4 | 0.0000909 |
| | | | 4295 | 42.1 | 0.0000876 |
| | | | 5764 | 31.2 | 0.0000878 |
| | | | 10057 | 12.6 | 0.0000894 |
| Mean: | | | | | 0.000090 |
| 0.021 M (preparation of carbamate) | 0.08 | 0.05 | 0 | 100 | |
| | | | 399 | 89.7 | 0.000118 |
| | | | 1426 | 69.3 | 0.000112 |
| | | | 2855 | 49.9 | 0.000106 |
| | | | 5742 | 25.4 | 0.000104 |
| | | | 7289 | 17.7 | 0.000103 |
| | | | 8819 | 13.0 | 0.000101 |
| 10233 | 8.9 | 0.000103 | | | |
| Mean: | | | | | 0.000107 |

Table 7. Velocity constants, experimental and calculated.

| Initial solution | | | | | k_{amate} | | k_{onate} | |
|-------------------------------------|------------------------|------------------------------|-----------------|-------------------|-------------|----------|-------------|---------|
| c(AmH) ₂ CO ₂ | c _{carbamate} | c _{AmH⁺} | c _{Am} | c _{NaOH} | exptl. | calc. | exptl. | calc. |
| 0.02 | | 0.05 | 0.11 | | 0.000085 | 0.000087 | 0.00061 | 0.00066 |
| 0.02 | | 0.10 | 0.13 | | 0.000055 | 0.000076 | 0.00070 | 0.00079 |
| | 0.022 | | 0.08 | 0.08 | 0.000090 | 0.000079 | | |
| | 0.021 | | 0.05 | 0.08 | 0.000107 | 0.000098 | | |

In Table 7 is given a survey of the experimental and calculated values of the velocity constants.

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REFERENCES

1. Jensen, A. and Faurholt, C. *Acta Chem. Scand.* **6** (1952) 385.
2. Jensen, A., Jensen, M. B. and Faurholt, C. *Acta Chem. Scand.* **6** (1952) 1073.
3. Mulvaney, J. F. and Evans, R. L. *Ind. Eng. Chem.* **40** (1948) 393.
4. Siefken, W. *Ann.* **562** (1948) 96.
5. Katchalski, E., Berliner-Klibanski, C. and Berger, A. *J. Am. Chem. Soc.* **73** (1951) 1829.
6. Bredig, G. *Z. physik. Chem.* **13** (1894) 289.
7. Lowry, T. M. and Lloyd, W. V. *J. Chem. Soc.* **1932** 1623.
8. Philpot, J. P., Rhodes, E. C. and Davies, C. W. *J. Chem. Soc.* **1940** 84.
9. Bjerrum, N. and Unmack, A. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **9** (1929) 1.

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