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Studies on Carbamates

VIII. The Carbamates of Benzylamine, Piperidine and Aniline

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1. The equilibrium conditions and reaction mechanism of the formation and decomposition in aqueous medium of ammonium carbamate and of the carbamates formed by amines, the most recent being *n*-propylamine and *iso*-propylamine [1], and a few amino acids [2] have been studied in previous investigations.

The present investigation deals with the corresponding conditions with regard to the carbamates formed by benzylamine, piperidine and aniline. The conditions have been shown to be analogous to those of the carbamates previously investigated, only differing somewhat quantitatively. The experimental methods likewise being the same, we refer to previous investigations [1-3] for the detailed information concerning method, theory, significance of constants *etc.* It should be noted, however, that "Am" means amine and "AmH^+" aminium ion. $c_{\text{carbamate}}$ signifies the concentration of $C_6H_5CH_2NHCOO^-$, $C_5H_{10}NCOO^-$ or $C_6H_5NHCOO^-$, and $c_{\text{AmHcarbamate}}$ signifies the concentration of $C_6H_5CH_2NHCOONH_3CH_2C_6H_5$ or $C_5H_{10}NCOONH_2C_5H_{10}$.

2. The following preparations were used in the experiments:

Benzylamine and piperidine (both from Fischer Scientific Co.) were purified by distillation through a wiregauze column with 55 sets of platinum plates [4], provided with a sodalime tube to prevent the admission of carbon dioxide from the atmosphere. For the experiments with benzylamine we used a fraction with a boiling point 184.5—184.8° C (759 mm Hg), $n_D^{20.0°} = 1.5439$, and by acidimetric titration with 0.1 *N* HCl we obtained a result corresponding to a

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content of 99.4 % $C_6H_5CH_2NH_2$. For the experiments with piperidine we used a fraction with a boiling point 106.2—106.4° C (757 mm Hg), $n_D^{20.0°} = 1.4537$, and by titration with 0.1 *N* HCl we obtained a result corresponding to a content of 99.7 % $C_5H_{10}NH$.

Aniline (puriss. Merck) was distilled from zinc dust in an ordinary distiller. The fraction used had a boiling point of 184.4° C (760 mm Hg), $n_D^{20.0°} = 1.5860$, and gave a result corresponding to a percentage of 100.4 by a bromometric titration, according to Vaubel [5].

The applied phenyl isocyanate was an Eastman Kodak Company product.

The above-mentioned boiling points are corrected for calibration errors; stem corrections have been done.

3. The carbamates of benzylamine and piperidine were prepared partly in solution by leading a deficit of carbon dioxide to aqueous solutions of amines, practically all of the carbon dioxide thus being converted to carbamate "$CO_2 + 2C_6H_5CH_2NH_2 = C_6H_5CH_2NHCOONH_3CH_2C_6H_5$" and "$CO_2 + 2C_5H_{10}NH = C_5H_{10}NCOONH_2C_5H_{10}$", and partly as substances. The carbamate of aniline was only prepared in solution.

Solutions of the carbonates of benzylamine and piperidine were prepared by mixing equivalent amounts of solutions of benzylammonium chloride (piperidinium chloride, respectively) and sodium carbonate "$2C_6H_5CH_2NH_3Cl + Na_2CO_3 = (C_6H_5CH_2NH_3)_2CO_3 + 2\,NaCl$" and "$2C_5H_{10}NH_2Cl + Na_2CO_3 = (C_5H_{10}NH_2)_2CO_3 + 2NaCl$", *i.e.* the resulting solutions contain some sodium chloride, but this is insignificant in the present investigation.

a) The carbamate of benzylamine, $C_6H_5CH_2NHCOONH_3CH_2C_6H_5$, was prepared mainly according to Fichter and Becker [6]. 10 g benzylamine were gradually dissolved in 100 g anhydrous ether — added in portions of about 1 g. After each addition the solution was saturated with dry carbon dioxide, whereby a microcrystalline precipitate of the carbamate was formed. The precipitate was collected on a filter and after the evaporation of the ether it was placed in an exsiccator over concentrated sulphuric acid. It should be noted, that the precipitate turns gelatinous, if all the benzylamine is dissolved in the ether at the beginning. With regard to the solubility of the carbamate it should be stated, that 100 g of the mother liquor contains amine corresponding to approx. 0.5 g carbamate. 82.7 % af amine (theoretically 83.0 %) was found by titration of the carbamate with 0.1 *N* HCl, and by the method of analysis, stated under 4, 17.4 % of carbon dioxide in the form of carbamate (theoretically 17.0 %) was found.

b) An attempt was made to prepare the carbamate of piperidine by the same method as that used in the preparation of the carbamate of benzylamine, but no precipitate appeared by saturation of the etheric piperidine solution with carbon dioxide. If on the other hand a solution of piperidine in ether containing a little water is saturated with carbon dioxide, a precipitate of carbamate at once appears. 17 g piperidine and 1.8 g water, *i.e.* half a mole of water per mole of piperidine, were dissolved in about 150 g anhydrous ether, and by saturation of the solution with carbon dioxide a distinctly crystalline precipitate of carbamate was formed. With regard to the solubility of the carbamate it should be stated that 100 g of the mother liquor contains amine corresponding to approx. 1 g carbamate. 73.1 % of amine was found by titration of the carbamate with 0.1 *N* HCl, and by the method of analysis, stated under 4, 18.8 % of carbon dioxide in the form of carbamate was found. This corresponds with the compound $C_5H_{10}NCOONH_2C_5H_{10},H_2O$, *i.e.* with a mole of crystal water, the theoretical contents of which are 73.3 % of amine and 18.9 % of carbon dioxide.

The carbamate of piperidine — as well as the carbamate of benzylamine — can, at least for some time, be stored in closed bottles in an exsiccator with concentrated sulphuric acid.

c) Solutions of the carbamate of aniline are prepared according to Mohr [7]. 0.04 mole of phenyl isocyanate is shaken for twenty minutes with 1 litre of approx. 0.24 *N* NaOH, whereby all the phenyl isocyanate is dissolved and converted to $C_6H_5NHCOO^-$, *viz.* "$C_6H_5NCO + OH^- = C_6H_5NHCOO^-$". After the twenty minutes all smell of phenyl isocyanate has disappeared, and no phenyl isocyanate can be extracted by ether. The solution remains limpid by the addition of barium chloride showing that no carbonate is formed — or at any rate to an extremely small extent.

4. The method of analysis was as in previous investigations precipitation with barium chloride, *i.e.* barium chloride is added to 100 ml of the solution, if necessary previously made alkaline by the addition of sodium hydroxide. In this way the carbonate is precipitated, whilst the carbamate remains dissolved. The precipitate and the supernate are separated as quickly as possible by centrifugation. If the supernate is left standing or is heated, the carbamate decomposes forming a precipitate of barium carbonate, the amount of which can be determined by titration with 0.1 *N* HCl.

Since the solutions containing only carbonate, and no carbamate, upon precipitation with barium chloride yield a supernate precipitating a small amount of barium carbonate, it was found necessary to carry out blank experiments.

All of the data presented in later tables are corrected, unless otherwise stated, for the blank values, *viz.* about 3 units of the percentage.

5. All of the experiments were done 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: $-\log f = 0.3\sqrt[3]{c_{\text{ion}}}$.

6. Hantzsch and Sebaldt[8] have found the basic dissociation constant for benzylamine at 0° C to be $10^{-4.82}$ and at 25° C $10^{-4.71}$, the latter being in good agreement with Bredigs[9] corrected value of $10^{-4.70}$. By interpolation the value for the basic dissociation constant of benzylamine is calculated to $10^{-4.74}$ at 18° C. Hantzsch and Sebaldt[10] for piperidine have the values $10^{-2.95}$ and $10^{-2.94}$ at 15° C and 20° C, respectively. At 25° C they have the value $10^{-2.92}$, and this one is in good agreement with Bredigs[9] corrected value of $10^{-2.92}$. The value $10^{-2.95}$ may here be used for 18° C.

It should be noted, that the basic dissociation constants for benzylamine and piperidine are called "K_{Am}".

The basic dissociation constant for aniline is for 18° C approx. $10^{-9.3}$. The exact value is insignificant in the present investigation, all the solutions in the experiments being so basic, that practically all the aniline is present as $C_6H_5NH_2$.

For the value of K_{H_2O} at 18° C $10^{-14.22}$ has been used.

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

500 ml of an aqueous solution containing both amine and sodium hydroxide, were placed in a 2 litre flask. In the gas phase above this solution approximately 250 ml of carbon dioxide were substituted for an equal amount of atmospheric air, and the flask was shaken vigorously for about 2 minutes to obtain absorption of the carbon dioxide. The carbon dioxide reacts partly with the amine "carbon dioxide + amine → carbamic acid", partly with the hydroxyl ion "carbon dioxide + hydroxyl ion → bicarbonate ion".

The mixture was immediately analysed, see Table 1, where "% carbamate" indicates how many per cent of the carbon dioxide absorbed have been converted to carbamate. In the case of benzylamine and piperidine considerable amounts of carbamate are formed, while only small, but undoubtedly measurable amounts are formed in the case of aniline. In order to illustrate how much importance may be attached to the determinations as to aniline the amount of 0.1 N HCl used in the experiments as well as in the blank experiments is presented as a footnote of the table.

In Table 1 are also listed the values of $k_{CO_2 \cdot \text{Am}}$ calculated from the experiments, where $k_{CO_2 \cdot \text{Am}}$ is the velocity constant of the reaction "carbon dioxide + amine → carbamic acid".

To get a better determination of $k_{CO_2 \cdot \text{Am}}$ for aniline we made another experiment in a far less basic solution than the ones listed in Table 1. The solution

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

	Initial solution		Absorb. mol CO_2/litre	% carba-mate	Final solution		Mean		$k_{CO_2 \cdot Am}$	
	c_{NaOH}	c_{Am}			c_{NaOH}	c_{Am}	c_{NaOH}	c_{Am}		Mean
$C_6H_5CH_2NH_2$	0.20	0.10	0.0195	37	0.17	0.09	0.18	0.10	$10^{5.06}$	$10^{5.06}$
	0.10	0.10	0.0176	54	0.07	0.09	0.09	0.10	$10^{5.04}$	
	0.10	0.05	0.0178	39	0.07	0.04	0.08	0.05	$10^{5.08}$	
$C_5H_{10}NH$	0.20	0.10	0.0189	79[1]	0.18	0.09	0.19	0.09	$10^{5.89}$	$10^{5.89}$
	0.20	0.05	0.0175	65[2]	0.18	0.04	0.19	0.04	$10^{5.91}$	
	0.20	0.05	0.0197	63[3]	0.17	0.04	0.19	0.04	$10^{5.88}$	
$C_6H_5NH_2$	0.08	0.22	0.0202	5.6[4]	0.04	0.22	0.06	0.22	$10^{3.23}$	[9]
	0.05	0.24	0.0189	4.6[5]	0.01	0.24	0.03	0.24	$10^{2.80}$	
	0.10	0.10	0.0212	3.1[6]	0.06	0.10	0.08	0.10	$10^{3.42}$	
	0.10	0.12	0.0210	2.5[7]	0.06	0.12	0.08	0.12	$10^{3.26}$	
	0.10	0.12	0.0200	3.6[8]	0.06	0.12	0.08	0.12	$10^{3.42}$	

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[1], [2], [3] found by the analysis: 77.2, 62.7, 60.3 respectively.

Since the piperidine-carbamate is comparatively rapidly decomposed, it was necessary — by means of the velocity constants determined in section IV — to correct the analytically determined percentage of carbamate for the decomposition taken place during the 7 to 9 minutes passing between the start of the shaking with carbon dioxide and the separation of precipitate and supernate by centrifugation. Similar corrections are done in Tables 2,3 and 4. The correction amounts at most 4 units of the percentage.

		Blank experiments	Corrected data
[4]	3.18 ml 0.1 N HCl	0.93 ml 0.1 N HCl	2.25 ml 0.1 N HCl
[5]	2.74 » » » »	0.99 » » » »	1.75 » » » »
[6]	2.06 » » » »	0.76 » » » »	1.30 » » » »
[7]	1.96 » » » »	0.91 » » » »	1.05 » » » »
[8]	2.08 » » » »	0.65 » » » »	1.43 » » » »

[9] See in the end of this chapter the value $10^{2.28}$, which is more accurate and, therefore, used for the calculations in Table 5.

contained 0.2 *M* aniline, approx. 0.11 *M* triethylamine and approx. 0.09 *M* triethylaminium chloride. It should be mentioned that tertiary amines do not react with carbon dioxide. The pa_H of the buffer was measured by means of a glass electrode and found to be 11.07, corresponding to a c_{OH^-} of $10^{-3.02}$; the addition of carbon dioxide is calculated to decrease the c_{OH^-} to $10^{-3.16}$, *i.e.* the mean value of c_{OH^-} being $10^{-3.09}$. In the course of 1 minute atmospheric air containing 10 % of carbon dioxide was lead into the solution in the form of fine bobbles under vigorous stirring. Immediately hereafter the solution was made strongly basic and analysed. 0.013 moles of carbon dioxide was absorbed per litre, 31 % as carbamate corresponding to a $k_{CO_2 \cdot Am} = 10^{2.28}$.

The equilibrium "carbamate ⇌ carbonate"

For all three amines experiments have been done from the carbonate side as well as from the carbamate side, see Table 2. In the case of benzylamine and piperidine the pa_H of the solutions was fixed at about 9.5 and 11, respectively, by means of aminiumion-amine-buffers of the amines concerned. In the case of aniline, the pa_H in two experiments is fixed at about 10—11 by means of bicarbonate-carbonate-buffers. In the case of benzylamine, a considerable amount of carbamate was found in the equilibrium, while only small, but undoubtedly measurable amounts were found in the case of piperidine and aniline.

Furthermore, in Table 2 is presented the calculated constitution of the equilibrium. For information on the method of calculation concerning benzylamine and piperidine we refer to a previous investigation[1]; in the case of aniline the following equations are valid:

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

	Initial solution							% carbamate	Equilibrium				K_{Eq}	Mean
	c_{Am}	c_{AmH^+}	$c_{(AmH)_2CO_3}$	c_{AmH} carbamate	$c_{HCO_3^-}$	$c_{CO_3^{--}}$	$c_{carbamate}$		c_{AmH^+}	c_{Am}	$c_{carbamate}$	$c_{HCO_3^-}$		
$C_6H_5CH_2NH_2$	0.10	0.10	0.02					86[2]	0.121	0.102	0.0173	0.0021	$10^{-1.90}$	$10^{-1.91}$
	0.02	0.05	0.01					64[3]	0.060	0.023	0.0066	0.0033	$10^{-1.93}$	
	0.05	0.10		0.02				80[4]	0.121	0.056	0.0158	0.0035	$10^{-1.90}$	
$C_5H_{10}NH$	0.05	0.10		0.02				7.8[5]	0.137	0.0526	0.0016	0.0025	$10^{-1.08}$	$10^{-1.09}$
	0.05	0.10	0.02					7.4[6]	0.136	0.0523	0.0015	0.0023	$10^{-1.09}$	
$C_6H_5NH_2$	0.10				0.05	0.10	0.02	12[7]	0	0.117	0.0023	0.0664	$10^{0.53}$	$10^{0.55}$[10]
	0.10				0.05	0.10		2.7[8]	0	0.099	0.0013	0.0480	$10^{0.56}$	
	0.12[1]						0.02	1.9[9]	0	0.144	0.0004	0.0159	$10^{0.76}$	

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[1] pa_H = approx. 10
[2] Mean of 3 determinations: 86.5, 86.3, 86.4.
[3] » » » » 64.4, 64.2, 63.9.
[4] » » » » 79.0, 80.0, 79.8.
[5] » » 2 » 7.58, 8.01.
[6] » » 4 » 7.93, 7.81, 6.62, 7.23.
[7] » » » » 11.3, 11.4, 11.5, 11.8.
[8] Percentage of bicarbonate converted into carbamate.
Mean of 3 determinations: 2.68, 2.73, 2.75.
[9] » » 4 » 2.27, 1.80, 1.69, 1.66.
[10] The value of $10^{0.76}$ is not taken into consideration in the calculation of the mean-value. The concentration of carbamate in this experiment has been very small and the determination consequently being encumbered with especially great error.

$c_{\mathrm{Am}} = c_{\mathrm{Am}}$ (column 2 of the Table) $+ c_{\mathrm{carbamate}}$ (column 8 of the Table) $- c_{\mathrm{carbamate}}$.

$c_{\mathrm{HCO_3^-}} = c_{\mathrm{HCO_3^-}}$ (column 6 of the Table) $+ c_{\mathrm{carbamate}}$ (column 8 of the Table) $- c_{\mathrm{carbamate}}$.

The solutions initially containing carbamate were, in the case of benzylamine and piperidine, prepared by dissolving the preparations of carbamates, see 3a and 3b, in the aminiumion-amine-buffers. In the case of aniline, phenyl isocyanate was shaken with a solution of sodium hydroxide for twenty minutes and then — in two experiments — an adequate amount of potassium bicarbonate and a solution of aniline were added and — in a third experiment — a solution of aniline and hydrochloric acid until $pa_{\mathrm{H}} = 10.3$. No aniline was allowed to be added before all of the phenyl isocyanate was converted into carbamate ion, since aniline and phenyl isocyanate react with each other forming diphenylurea.

The equilibrium constants K_{Eq} of the reaction carbamate$^-$ "$+ H_2O \rightleftharpoons HCO_3^- +$ amine" were also calculated.

The velocity of the conversion "carbamate ⇌ carbonate"

Experiments on velocity in weakly basic medium have, in the case of benzylamine, been done from the carbonate side, and in the case of piperidine and aniline from the carbamate side. The pa_{H} of the solutions was in the case of benzylamine and piperidine fixed by means of aminiumion-amine-buffers of the amines concerned, in the case of aniline by means of bicarbonate-carbonate-buffer. In the experiments from the carbamate side the solution was prepared, in the case of piperidine, by dissolving the preparation of carbamate, see 3b, in the aminiumion-amine-buffer. In the case of aniline, phenyl isocyanate was shaken with a solution of sodium hydroxide for twenty minutes, to which was added an adequate amount of potassium bicarbonate together with a solution of aniline. In Table 3 are presented the experiments on velocity in these weakly basic solutions, where a measurable equilibrium is established between carbamate and carbonate.

In Table 4 are presented those experiments, which have been carried out in a medium containing sodium hydroxide; in these solutions carbamate is converted practically completely to carbonate. The solutions were, in the case of benzylamine and piperidine, prepared partly by dissolving carbon dioxide in a pure solution of amine and subsequently adding sodium hydroxide and partly by dissolving the preparations of carbamate, see 3a and 3b, in the solutions containing amine and sodium hydroxide. In the case of aniline,

Table 3. Velocity constants for the process "carbamate ⇌ carbonate". p_{aH} = approx. 9—11. 18°.

	Initial solution							p_{aH}	Min.	% carbamate	$k_{\text{amate}} + k_{\text{onate}}$
	c_{Am}	c_{AmH^+}	$c_{(\text{Am})_2\text{CO}_2}$	$c_{\text{AmH carbamate}}$	$c_{\text{HCO}_3^-}$	$c_{\text{CO}_3^{--}}$	$c_{\text{carbamate}}$				
$C_6H_5CH_2NH_2$	0.10	0.10	0.02					approx. 9.6	40	14.6	0.00200
									80	30.1	0.00233
									95	33.0	0.00220
									124	40.1	0.00218
									160	46.7	0.00211
									261	63.4	0.00220
									∞	86.4	Mean: 0.0022
											k_{amate}: 0.0003
											k_{onate}: 0.0019
	0.02	0.05	0.01					approx. 9.2	44	18.2	0.00331
									65	26.9	0.00364
									121	40.6	0.00360
									312	58.7	0.00343
									∞	64.2	Mean: 0.0035
											k_{amate}: 0.0013
											k_{onate}: 0.0022
$C_5H_{10}NH$	0.05	0.10		0.02				approx. 11.0	0	100	
									57	72.8	0.00266
									134	51.0	0.00246
									219	35.0	0.00242
									312	23.3	0.00248
									∞	7.8	Mean: 0.0025
											k_{amate}: 0.0023
											k_{onate}: 0.0002
$C_6H_5NH_2$	0.10				0.05	0.10	0.02	approx. 10.6	0	100	
									12	30.0	0.0563
									25	17.2	0.0477
									43	12.5	0.0452
									∞	11.5	Mean: 0.050
											k_{amate}: 0.049
											k_{onate}: 0.00066

phenyl isocyanate was shaken with a solution of sodium hydroxide for twenty minutes to which was added water or a solution of aniline.

In addition to the experimental data presented in Table 3 and 4 are listed the velocity constants calculated from the experiments. k_{amate} is the velocity constant for the conversion "carbamate → carbonate" and k_{onate} the one for the reversed reaction. k_{amate} are, in the experiments in strong basic medium, the values of $\frac{1}{t}\log\frac{a}{a-x}$. In weakly basic solution $k_{\text{amate}} + k_{\text{onate}}$ are the values of $\frac{1}{t}\log\frac{K\cdot a}{K\cdot a-(1+K)x}$, the expression for a process which is mono-

Table 4. Velocity constants for the process "carbamate → carbonate". pa_H = approx. 13. 18°.

	Initial solution			Min.	% carbamate left	k_{amate}
	$c_{\text{carbamate}}$	c_{NaOH}	c_{Am}			
$C_6H_5CH_2NH_2$	0.019 (CO_2 in solution of amine)	0.10	0.08	0	100	
				218	94.4	0.000114
				633	83.6	0.000123
				1402	68.6	0.000117
				4060	33.8	0.000116
				5985	20.9	0.000114
				∞	(0)	Mean: 0.00012
	0.020 (preparation of carbamate)	0.10	0.08	0	100	
				748	83.1	0.000108
				1835	60.8	0.000118
				5681	22.3	0.000115
				7531	13.5	0.000116
				∞	(0.8)	Mean: 0.00011
$C_5H_{10}NH$	0.017 (CO_2 in solution of amine)	0.11	0.08	0	100	
				45	90.3	0.00098
				117	75.7	0.00103
				270	53.4	0.00101
				384	41.3	0.00100
				1319	4.8	0.00100
				∞	(0)	Mean: 0.0010
	0.020 (preparation of carbamate)	0.10	0.08	0	100	
				94	79.1	0.00108
				210	59.1	0.00109
				278	50.6	0.00107
				347	43.6	0.00104
				680	21.0	0.00100
				745	17.7	0.00101
				∞	(0)	Mean: 0.0011

This Table is continued.

molecular from both sides and which does not run to completion. The constant K signifies the relation between the equilibrium values of the concentrations of carbamate and carbonate. The sum "$k_{\text{amate}} + k_{\text{onate}}$" is approximately constant within each experiment. By means of

Table 4 continued.

$C_6H_5NH_2$	0.020 (preparation of carbamate)	0.11	0	0	100	
				150	91.7	0.000249
				462	78.0	0.000233
				1078	55.9	0.000235
				1347	48.1	0.000236
				1594	41.9	0.000237
				2561	24.1	0.000241
				3015	18.4	0.000244
				∞	(0)	Mean: 0.00024
	0.020 (preparation of carbamate)	0.11	0.12	0	100	
				150	91.6	0.000253
				463	78.2	0.000231
				1079	56.1	0.000233
				1348	48.6	0.000232
				1592	42.0	0.000237
				2562	24.2	0.000241
				3015	17.8	0.000249
				∞	(0)	Mean: 0.00024
	0.043 (preparation of carbamate)	0.20	0	0	100	
				1340	58.2	0.000175
				2500	34.7	0.000184
				3880	21.1	0.000174
				∞	(0)	Mean: 0.00018

$\frac{k_{\text{onate}}}{k_{\text{amate}}} = \frac{\text{equilibrium value of } c_{\text{carbamate}}}{\text{equilibrium value of } c_{\text{carbonate}}} = K$, the values of k_{amate} and k_{onate} are obtained.

The experiments can be interpreted in a way similar to the one used by carbamates previously examined allowing a margin for the ones regarding aniline. The conversion is a two-stage reaction

$$\text{carbamate} = \text{amine} + CO_2$$
$$CO_2 = \text{carbonate}$$

and it is possible to calculate in advance the velocity constants.

The conversion of the carbon dioxide into carbonate and the reciprocal conversion take place through the two reactions:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \tag{1}$$

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \tag{2}$$

If pa_H of the solution is > about 10, the conversion takes place through reaction (2) only. This is the case with all the solutions containing piperidine or aniline, together with those containing benzylamine and sodium hydroxide and k_{amate} and k_{onate} may be calculated from the expression:

$$k^{11}_{\text{onate}} = \frac{k_{\text{HCO}_3^-}}{1 + \dfrac{a_{\text{H}^+}}{K_{\text{H}_2\text{CO}_3}} \cdot f + \dfrac{K_{\text{HCO}_3^-}}{a_{\text{H}^+}} \cdot \dfrac{1}{f}}$$

$$k^{3}_{\text{amate}} = \frac{k_{\text{CO}_2\cdot\text{Am}} \cdot K_{Eq} \cdot K_{\text{H}_2\text{O}} \cdot \dfrac{1}{K_{\text{CO}_2}}}{c_{\text{OH}^-} + \dfrac{k_{\text{CO}_2\cdot\text{Am}}}{k_{\text{CO}_2\cdot\text{OH}^-}} \cdot c_{\text{Am}}}$$

If pa_H of the solution is < about 10, process (1) must also be taken into consideration. In this case k_{onate} and k_{amate} have to be calculated from the expressions previously deduced[12].

For the conversion of carbonate we have:

$$\frac{dc_{\text{carbonate}}}{dt} = - \frac{k_{\text{H}_2\text{CO}_3}}{1 + \dfrac{K_{\text{H}_2\text{CO}_3}}{a_{\text{H}^+}} \cdot \dfrac{1}{f} \cdot (1 + \dfrac{K_{\text{HCO}_3^-}}{a_{\text{H}^+}} \cdot \dfrac{1}{f})} \cdot c_{\text{carbonate}} = - k_{\text{a}} \cdot c_{\text{carbonate}}$$

$$\frac{dc_{\text{carbonate}}}{dt} = - \frac{k_{\text{HCO}_3^-}}{1 + \dfrac{a_{\text{H}^+}}{K_{\text{H}_2\text{CO}_3}} \cdot f + \dfrac{K_{\text{HCO}_3^-}}{a_{\text{H}^+}} \cdot \dfrac{1}{f}} \cdot c_{\text{carbonate}} = - k_{\text{b}} \cdot c_{\text{carbonate}}$$

Since both processes take place simultaneously, we have:

$$\frac{dc_{\text{carbonate}}}{dt} = - (k_{\text{a}} + k_{\text{b}}) \cdot c_{\text{carbonate}} = - k_{\text{onate}} \cdot c_{\text{carbonate}}.$$

For the conversion of carbamate we have:

$$\frac{dc_{\text{carbamate}}}{dt} = - (k_{\text{CO}_2} + k_{\text{CO}_2\cdot\text{OH}^-} \cdot c_{\text{OH}^-}) \cdot c_{\text{CO}_2} = k_{\text{carbon dioxide}} \cdot c_{\text{CO}_2} =$$
$$- k_{\text{carbon dioxide}} \cdot c_{\text{carbamate}} \cdot \alpha_{\text{CO}_2} = - k_{\text{amate}} \cdot c_{\text{carbamate}}.$$

α_{CO_2} indicates the part of the carbamate being dissociated into CO_2, and it is calculated by means of

$$\frac{c^2_{\text{Am}} \cdot c_{\text{CO}_2}}{c_{\text{AmH}^+} \cdot c_{\text{carbamate}} \cdot f^2} = \frac{K_{\text{H}_2\text{O}} \cdot K_{Eq}}{K_{\text{Am}} \cdot K_{\text{CO}_2}}$$

i.e.

$$k_{\text{amate}} = (k_{\text{CO}_2} + k_{\text{CO}_2 \cdot \text{OH}^-} \cdot c_{\text{OH}^-}) \frac{K_{Eq} \cdot \dfrac{1}{K_{\text{CO}_2}}}{c_{\text{Am}}} \cdot a_{\text{H}^+} \cdot f$$

K_{CO_2} ($10^{-6.52}$) is the equilibrium constant for the process "$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$" $K_{H_2CO_3}$ ($10^{-3.7}$) the one for the process "$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$" and $K_{HCO_3^-}$ ($10^{-10.3}$) the equilibrium constant for the process "$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$".

k_{CO_2} (0.66) is the velocity constant for process (1) from left to right and $k_{H_2CO_3}$ (426) the one for process (1) from right to left. $k_{CO_2 \cdot OH^-}$ ($10^{5.02}$) is the velocity constant for process (2) from left to right and $k_{HCO_3^-}$ ($10^{-2.74}$) is the one for process (2) from right to left.

Table 5 contains a survey of the experimental and calculated values of k_{amate} and k_{onate}. Considering the nature of the conditions the agreement may be described as satisfactory in the case of benzylamine and piperidine. In the case of aniline, the calculated values of k_{amate} are not so good, but when estimating the results it should be taken into consideration that the determinations of $k_{CO_2 \cdot \text{Am}}$ as well as the one of K_{Eq} in this case may be encumbered with especially great errors.

Table 5. Velocity constants, experimental and calculated.

	Initial solution								k_{amate}		k_{onate}	
	c_{Am}	c_{AmH^+}	$c_{(\text{AmH})_2\text{CO}_3}$	c_{NaOH}	$c_{\text{carbamate}}$	$c_{\text{AmH carbamate}}$	$c_{\text{HCO}_3^-}$	$c_{\text{CO}_3^{--}}$	exp.	calc.	exp.	calc.
$C_6H_5CH_2NH_2$	0.10	0.10	0.02						0.00030	0.00028	0.0019	0.0017
	0.02	0.05	0.01						0.0013	0.0014	0.0022	0.0025
	0.08			0.10	0.019				0.00012	0.00015		
	0.08			0.10	0.020				0.00011	0.00015		
$C_5H_{10}NH$	0.05	0.10				0.020			0.0023	0.0033	0.00020	0.00022
	0.08			0.11	0.017				0.0010	0.0016		
	0.08			0.10	0.020				0.0011	0.0017		
$C_6H_5NH_2$	0.10				0.020		0.05	0.10	0.049	0.03	0.00066	0.00066
	0			0.11	0.020				0.00024	0.00014		
	0.12			0.11	0.020				0.00024	0.00014		
	0			0.20	0.043				0.00018	0.00008		

SUMMARY

The velocity constants of the reaction "amine + CO_2 = carbamic acid" and the equilibrium constant for the reaction "carbamate$^-$ + H_2O = HCO_3^- + amine" have been determined. The velocity of the decomposition of carbamate ion in basic medium was investigated and may be explained for piperidine and benzylamine in assuming that the decomposition is a two-stage reaction, *viz.*

carbamate = amine + carbon dioxide
carbon dioxide = carbonate

In the case of aniline there is a relatively great difference between the experimental and calculated velocity constants, not excluding that the decomposition also here is the same two-stage reaction, because the experiments, on which the calculations are based, in this case may be encumbered with particularly great errors.

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