ACTA CHEMICA SCANDINAVICA 6 (1952) 398—403

Studies on Carbamates

VII. The Carbamates of *n*-Propylamine and *iso*-Propylamine

JØRGEN OLSEN, KNUD VEJLBY and CARL FAURHOLT

The Royal Danish School of Pharmacy, Copenhagen, Denmark

1. In previous investigations were studied the equilibrium conditions and the reaction mechanism of the formation and decomposition in aqueous medium of ammonium carbamate as well as of the carbamates formed by amines and other amine compounds, *e.g.* the alanines. The present investigation deals with the corresponding conditions for the carbamates formed by n-propylamine and iso-propylamine. The conditions have been shown to be analogous to those found for the carbamates previously investigated, only differing somewhat quantitatively. The experimental method likewise being similar, we refer to previous investigations [1] for information on method, theory, significance of the constants *etc.* It should be noted, though, that "Am" means propylamine and "AmH^+" propylammonium ion.

2. The following preparations were used in the experiments:

n-propylamine was prepared by catalytic reduction of 1-nitropropan by means of hydrogen of a pressure of 2 to 3 atm. at room temperature, and with Raney-nickel as a catalytic agent. It was purified through the acid oxalate by recrystallizations, until the constant melting point, 135—136°, was attained. The molecular weight of the acid oxalate, crystallizing with half a molecule crystal water [2], is theoretically 158.16. The preparation obtained showed the following molecular weight: by distilling off the amine and titrating it was found 157.5, by titration with permanganate was found 157.5, and by titration with base was found 159.1. From the acid oxalate was prepared an aqueous solution of *n*-propylamine by distilling it off with sodium hydroxide.

The *iso*-propylamine was obtained from the Rubber Industries and Sherman Chemicals Ltd. It was likewise purified through the acid oxalate, also crystallizing with half a molecule crystal water, and having a melting point of 164—165°; by titrating with base the molecular weight was found to be 159.5.

3. No attempt was made to obtain the carbamates or the carbonates as substances. The solutions of carbamates were prepared by dissolving carbon dioxide in solutions of the pure amine, practically all of the carbon dioxide thus being converted to carbamate "$CO_2 + 2C_3H_7NH_2 = C_3H_7NHCOONH_3C_3H_7$". The solutions of carbonate were prepared by mixing equivalent amounts of solutions of propylammonium chloride and sodium carbonate "$2C_3H_7NH_3Cl + Na_2CO_3 = (C_3H_7NH_3)_2CO_3 + 2NaCl$", *i. e.* the resulting solutions contain some sodium chloride too, but this is insignificant in the present investigation.

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 the values of blank experiments, *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 Brigg's 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. For the acidic dissociation constants K_{AmH^+} were used the values $10^{-10,81}$ and $10^{-10,86}$ for *n*-propylammonium ion and *iso*-propylammonium ion, respectively. The corrected values of Bredigs[3] for the basic dissociation constants at 25° C are $3,9 \cdot 10^{-4}$ and $4,3 \cdot 10^{-4}$ for *n*-propylamine and *iso*-propylamine, respectively. The heat effect at the reactions being very slight, these values may be used for 18° C as well. By conversion to the acidic dissociation constants K_{H_2O} was fixed at $10^{-14,22}$.

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

About 240 ml of carbon dioxide were dissolved in 500 ml of solution containing both propylamine and sodium hydroxide and placed in a 2 liter flask.

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

	Initial solution		Absorb. $CO_2\frac{\text{mol.}}{\text{liter}}$	% carbamate	Final solution		Mean		$k_{CO_2 \cdot Am}$	
	c_{NaOH}	c_{Am}			c_{NaOH}	c_{Am}	c_{NaOH}	c_{Am}		Mean
n-	0.20	0.10	0.0216	45	0.167	0.090	0.183	0.095	$10^{5.21}$	$10^{5.20}$
	0.20	0.10	0.0185	43	0.171	0.092	0.185	0.096	$10^{5.19}$	
	0.20	0.148	0.0207	36	0.166	0.141	0.183	0.144	$10^{4.86}$	
iso-	0.20	0.10	0.0182	25	0.160	0.096	0.180	0.098	$10^{4.81}$	$10^{4.83}$
	0.20	0.10	0.0097	25	0.183	0.098	0.192	0.099	$10^{4.82}$	

The carbon dioxide is reacting partly with the amine, partly with the hydroxyl ion. The mixture was immediately analyzed, see Table 1, where "% carbamate" indicates how many per cent of the carbon dioxide absorbed have been converted to carbamate.

From the values of $k_{CO_2 \cdot Am}$, the velocity constant of the reaction "$C_3H_7NH_2 + CO_2 \rightarrow C_3H_7NHCOOH$", it is seen that carbon dioxide is added to *n*-propylamine about twice as fast as it is to *iso*-propylamine.

The equilibrium "carbamate ⇌ carbonate"

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

	Initial solution				% carbamate	Equilibrium				K_{Eq}	
	$c_{(AmH)_2CO_3}$	$c_{carbamate}$	c_{AmH^+}	c_{Am}		c_{AmH^+}	c_{Am}	$c_{carbamate}$	$c_{HCO_3^-}$		Mean
n-	0.02		0.10	0.10	54 [1]	0.128	0.101	0.0108	0.0014	$10^{-1.88}$	$10^{-1.88}$
		0.021	0.10	0.099	55 [2]	0.128	0.101	0.0118	0.0015	$10^{-1.88}$	
iso-	0.02		0.10	0.096	18 [3]	0.134	0.099	0.0035	0.0023	$10^{-1.18}$	$10^{-1.20}$
		0.018	0.10	0.10	19 [4]	0.130	0.103	0.0038	0.0023	$10^{-1.21}$	

[1] Mean of 3 determinations: 53.6, 53.6, 53.7.
[2] » » 3 » 55.1, 54.6, 54.8.
[3] » » 3 » 17.4, 18.0, 17.4.
[4] » » 3 » 19.5, 18.6, 20.2.

Experiments have been done from the carbonate side as well as from the carbamate side, see Table 2, and the pa_H of the solutions is fixed about 10.8 by means of propylammoniumion-propylamine-buffers. The initial composition of the solution *e.g.* in the experiment "0.02 *M* $(AmH)_2CO_3$, 0.10 *M* AmH^+, 0.10 *M* Am" was 0.14 *M* AmHCl, 0.10 *M* Am, and 0.02 *M* Na_2CO_3. The initial composition of the solution *e.g.* in the experiment "0.021 *M* carbamate, 0.10 *M* AmH^+, 0.10 *M* Am" was 0.10 *M* AmHCl, 0.14 *M* Am, and 0.0205 (*i. e.* 0.021) *M* CO_2. The constitution of the equilibrium solutions was calculated from the equations:

$$\frac{c_{Am} \cdot c_{HCO_3^-}}{c_{AmH^+} \cdot c_{CO_3^{--}} \cdot f^2} = \frac{K_{AmH^+}}{K_{HCO_3^-}}$$

$c_{Am} = c_{Am}$ (column 5 of the table) $+ c_{HCO_3^-}$
$c_{carbamate} + c_{HCO_3^-} + c_{CO_3^{--}} =$ total concentration of CO_2
$c_{carbamate} + c_{AmH^+} + c_{Am} =$ total concentration of amine.

Furthermore the equilibrium constant K_{Eq} for the reaction "carbamate$^-$ + $H_2O \rightleftharpoons HCO_3^-$ + Am" or in other words "$C_3H_7NHCOO^- + H_2O \rightleftharpoons HCO_3^- + C_3H_7NH_2$", was calculated.

The velocity of the conversion "carbamate ⇌ carbonate"

In Table 3 are presented the experiments on velocity, which have been carried out in a propylammoniumion-propylamine buffer, where an easily measurable

Table 3. Velocity constants for the process "carbamate ⇌ carbonate", pa_H = ca. 10.8. 18°.

	Initial solution			Min.	% carbamate	$k_{amate} + k_{onate}$
		c_{Am}	c_{AmH^+}			
n-	0.02 *M* $(AmH)_2CO_3$	0.10	0.10	186	8.9	0.00043
				310	13.7	0.00041
				434	18.3	0.00042
				771	28.8	0.00043
				1467	42.3	0.00046
						Mean: 0.00043
						k_{amate}: 0.00020
						k_{onate}: 0.00023
iso-	0.02 *M* $(AmH)_2CO_3$	0.096	0.10	57	2.7	0.00130
				92	4.4	0.00138
				190	7.6	0.00129
				330	11.3	0.00135
				784	15.8	0.00126
						Mean: 0.00131
						k_{amate}: 0.00108
						k_{onate}: 0.00023
	0.018*M* solution of carbamate	0.10	0.10	0	100	
				47	89.5	0.00132
				82	82.5	0.00133
				212	62.4	0.00132
				431	41.8	0.00134
				622	32.0	0.00136
						Mean: 0.00133
						k_{amate}: 0.00107
						k_{onate}: 0.00026

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}			
n-	0.019	0.181	0.081	0	100	
				240	95.3	0.000087
				464	91.5	0.000083
				696	86.8	0.000089
				1339	76.8	0.000086
				1676	71.8	0.000086
				3600	49.1	0.000086
				∞	(1)	
						Mean: 0.000086
iso-	0.009	0.191	0.090	0	100	
				172	90.3	0.000256
				352	82.5	0.000237
				712	67.9	0.000237
				1455	45.7	0.000234
				1834	38.3	0.000227
				2320	29.2	0.000230
				∞	(0)	
						Mean: 0.000237

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, where carbamate is converted practically completely to carbonate, *e. g.* in the experiment "0.019 *M* carbamate, 0.081 *M* Am, 0.181 *M* NaOH", the initial composition of the solution was 0.10 *M* Am, 0.20 *M* NaOH, and 0.019 *M* CO_2; it was prepared by dissolving the carbon dioxide in a pure solution of amine, and subsequently add sodium hydroxide.

k_{amate} and k_{onate} are the velocity constants for the decomposition of the carbamate and the carbonate, respectively, and may, provided the decomposition takes place through the reactions

$$\text{carbamate} \rightleftharpoons \text{amine} + CO_2$$

$$CO_2 \rightleftharpoons \text{carbonate}$$

be calculated from the expressions:

$$k_{\text{amate}} = \frac{k_{CO_2 \cdot Am} \cdot K_{Eq} \cdot K_{H_2O} \cdot 1/K_{CO_2}}{c_{OH^-} + \frac{k_{CO_2 \cdot Am}}{k_{CO_2 \cdot OH^-}} \cdot c_{Am}}, \quad k_{\text{onate}} = \frac{k_{HCO_3^-}}{1 + \frac{a_{H^+}}{K_{H_2CO_3}} \cdot f + \frac{K_{HCO_3^-}}{a_{H^+}} \cdot \frac{1}{f}}$$

In Table 5 is given a survey of the experimental and calculated values of the velocity constants. Considering the nature of the conditions the agreement may be described as satisfactory.

Table 5. Velocity constants, experimental and calculated.

	Initial solution					k_{amate}		k_{onate}	
	$c_{(AmH)_2 CO_3}$	$c_{\text{carbamate}}$	c_{AmH^+}	c_{Am}	c_{NaOH}	exp.	calc.	exp.	calc.
n-	0.02		0.10	0.10		0.00020	0.00027	0.00023	0.00028
		0.019		0.081	0.181	0.000086	0.00013		
iso-	0.02		0.10	0.096		0.0011	0.0014	0.00023	0.00028
		0.018	0.10	0.10		0.0011	0.0013	0.00026	0.00026
		0.009		0.090	0.191	0.00024	0.00034		

SUMMARY

The velocity constant of the reaction "$CH_3 \cdot CH_2 \cdot CH_2NH_2 + CO_2 = CH_3 \cdot CH_2 \cdot CH_2NHCOOH$" and the equilibrium constant for the reaction "$CH_3 \cdot CH_2 \cdot CH_2NHCOO^- + H_2O = HCO_3^- + CH_3 \cdot CH_2 \cdot CH_2NH_2$" have been determined. The velocity of the decomposition of $CH_3 \cdot CH_2 \cdot CH_2NHCOO^-$ in basic medium was investigated and may be explained in assuming that the decomposition is a two-stage reaction, *viz.*

carbamate = propylamine + carbon dioxide
carbon dioxide = carbonate

The carbamate of *iso*-propylamine was studied in a similar way.

REFERENCES

1. Lund, V., and Faurholt, C. *Dansk Tids. Farm.* **22** (1948) 109.
2. Chancel, M. F. *Bull. Soc. Chim. Paris* **7** (1892) 406.
3. Bredig, G. *Z. physik. Chem.* **13** (1894) 289.

Received July 2, 1951.