

Reactions between Carbon Dioxide and Amino Alcohols

I. Monoethanolamine and Diethanolamine

MOGENS BALLUND JENSEN, ERIK JØRGENSEN and
CARL FAURHOLT

The Royal Danish School of Pharmacy, Copenhagen, Denmark

1. The present investigation deals with the equilibrium conditions and the reaction mechanism for the formation and decomposition of the carbamates of mono- and diethanolamine in aqueous medium. The theoretical conditions are not exactly analogous to those of previously investigated amines¹ because the alcohol groups of the amines may form monoalkyl carbonate simultaneously. The amount is, however, presumed to be negligible and at least cannot be detected in the results obtained. Allowing for errors in the experiments these may be explained by the assumption of a predominant formation of carbamate. This point will be the subject of further investigations.

2. The amino alcohols were purified by distillation, monoethanolamine through a fractionating column at atmospheric pressure, and diethanolamine *in vacuo* without fractionating devices. The fractions used were taken at 172.4—172.6° C at 766 mm Hg and 160° C at 10 mm Hg, respectively. By acidimetric titration, using bromocresol green as an indicator, we obtained results corresponding to a content of 100.0 % and 99.9 %, respectively.

3. No solid carbamate was prepared. Solutions were made by adding carbon dioxide to suitable solutions of the amino alcohols.

4. The method of analysis was as in previous investigations precipitation with barium chloride, causing the precipitation of carbonate, but not of carbamate and contingent monoalkyl carbonate. All of the data presented in the tables are corrected for the blank values unless otherwise stated. "Corr." values are corrected not only with regard to blank values but also with regard to the decomposition mentioned in the next section. The blank values may amount to 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 for a monovalent ion was calculated from the expression of Bjerrum: $-\log f = 0.3 \sqrt[3]{c_{\text{ion}}}$.

6. Hall and Sprinkle² have found the pK 's for monoethanolamine and diethanolamine at 18° C to be 9.58 and 9.02, respectively.

ON THE REACTION "AMINE + CARBON DIOXIDE \rightarrow CARBAMIC ACID"

For a period of 5 minutes atmospheric air containing about 10 % of carbon dioxide was led into solutions containing both amine and sodium hydroxide.

In Table 1 we have listed the experimental results for the addition of carbon dioxide to the amines together with the calculated velocity constant. It has been necessary to correct the found percentages for the decomposition which has taken place before the separation of supernatant and precipitate in the case of diethanolamine.

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

Amine	Initial solution		Absorbed CO ₂ /liter	%carbamate	%carbamate "corr"	$k_{CO_2 \cdot Am}$	
	cNaOH	cAm					Mean
mono-	0.1	0.1	0.0209	47.6		10 ^{4.92}	10 ^{4.92}
	0.2	0.1	0.0194	30.8		10 ^{4.92}	
	0.1	0.2	0.0199	63.8		10 ^{4.92}	
di-	0.1	0.1	0.0168	50.0	52	10 ^{5.01}	10 ^{5.02}
	0.2	0.1	0.0232	35.4	36	10 ^{5.05}	
	0.1	0.2	0.0169	65.7	67	10 ^{4.92}	

THE EQUILIBRIUM "CARBAMATE \rightleftharpoons CARBONATE"

Experiments with monoethanolamine have been done from the carbonate side only, while with diethanolamine experiments have been done from the carbamate side also. The results are listed in Table 2, K_{Eg} being the equilibrium constant.

THE VELOCITY OF THE CONVERSION "CARBAMATE \rightleftharpoons CARBONATE"

Experiments on the velocity have been carried out in buffer solutions of the corresponding amine, see Table 3, and in strongly basic solutions, Table 4.

In Table 5 is given a survey of the experimental and calculated values of the velocity constants.

SUMMARY

The velocity of the addition of carbon dioxide to mono- and diethanolamine has been investigated and may be explained by the assumption of a predominant formation of carbamate.

The decomposition into carbonate of the product formed has been investigated with regard to equilibrium and velocity.

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

Amine	Initial solution				% carb- amate	Equilibrium				K_{Eq}	
	c_{Am}	c_{AmH+}	$C(AmH)_2CO_3$	$c_{carb-amate}$		c_{AmH+}	c_{Am}	$c_{carb-amate}$	$CHCO_3^-$		Mean
mono-	0.10	0.10	0.02		80	0.12	0.10	0.016	0.003	$10^{-1.71}$	$10^{-1.71}$
	0.10	0.10	0.02		78	0.12	0.10	0.016	0.003	$10^{-1.68}$	
	0.01		0.02		45	0.02	0.02	0.009	0.009	$10^{-1.73}$	
di-	0.17	0.04	0.02		47	0.07	0.18	0.009	0.008	$10^{-0.81}$	$10^{-0.82}$
	0.16	0.08		0.013	48	0.08	0.17	0.006	0.005	$10^{-0.82}$	

Table 3. Velocity constants for the process "carbamate \rightleftharpoons carbonate." p_{aH} approx. 9.5. 18°.

Amine	Initial solution				Min.	% carb- amate	$k_{amate} + k_{onate}$
	c_{Am}	c_{AmH+}	$C(AmH)_2CO_3$	$c_{carbamate}$			
mono-	0.10	0.10	0.020		44	13	0.00173
					93	25	0.00178
					140	35	0.00179
					190	43	0.00175
					250	50	0.00174
					350	61	0.00178
					∞	80	Mean: 0.00176
							k_{amate} : 0.00036
		k_{onate} : 0.0014					
di-	0.17	0.04	0.020		40	17	0.00484
					63	24	0.00478
					94	31	0.00479
					119	36	0.00514
					164	41	0.00526
					198	42	0.00458
					∞	47	Mean: 0.0049
							k_{amate} : 0.0026
			k_{onate} : 0.0023				
	0.16	0.08		0.013	23	89	0.00446
					47	80	0.00436
					75	73	0.00424
106					66	0.00432	
142					60	0.00449	
178					58	0.00413	
216	55	0.00411					
∞	48	Mean: 0.0043					
		k_{amate} : 0.0022					
		k_{onate} : 0.0021					

Table 4. Velocity constants for the process "carbamate \rightarrow carbonate". $p_{\text{H}} \text{ approx. } 13. 18^\circ$.

Amine	Initial solution			Min.	% carbamate	k_{amate}
	c_{Am}	c_{NaOH}	$c_{\text{carbamate}}$			
mono-	0.09	0.17	0.007	441	91	0.000100
				1 021	78	0.000104
				1 664	67	0.000104
				2 594	54	0.000106
				4 105	39	0.000100
				5 602	26	0.000105
				Mean: 0.000103		
di-	0.09	0.08	0.009	40	86	0.00166
				82	74	0.00158
				121	65	0.00157
				164	56	0.00153
				207	48	0.00156
				247	43	0.00150
				Mean: 0.0016		
	0.19	0.08	0.011	50	87	0.00126
				89	79	0.00118
				150	69	0.00109
				211	60	0.00104
				274	52	0.00109
				462	34	0.00102
				Mean: 0.0011		
0.09	0.16	0.008	50	86	0.00132	
			80	79	0.00134	
			121	72	0.00117	
			167	66	0.00110	
			223	55	0.00117	
			Mean: 0.0012			

Table 5. Velocity constants, experimental and calculated.

Amine	Initial solution					k_{amate}		k_{onate}	
	c_{Am}	c_{AmH^+}	$c_{(\text{AmH})_2\text{CO}_2}$	$c_{\text{carbamate}}$	c_{NaOH}	exp.	calc.	exp.	calc.
mono-	0.10	0.10	0.020			0.00036	0.00032	0.0014	0.0016
	0.09			0.007	0.17	0.00010	0.00013		
di-	0.17	0.04	0.020			0.0026	0.0018	0.0023	0.0021
	0.16	0.08		0.013		0.0022	0.0019	0.0021	0.0022
	0.09			0.009	0.08	0.0016	0.0019		
	0.19			0.011	0.08	0.0011	0.0012		
	0.09			0.008	0.16	0.0012	0.0013		

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