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Studies on Carbamates

IX. The Carbamate of Allylamine

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The equilibrium conditions and reaction mechanism of the formation and decomposition in aqueous medium of the carbamate formed by allylamine have been studied. As the experimental and theoretical conditions are analogous to those of the previous carbamates, we find that, on the whole, it is sufficient here to state the experimental data and the calculated constants, referring for further information to an earlier paper [1].

The allylamine (Eastman Kodak Company) used was distilled through a platinum wiregauze column [2]. The allylamine thus obtained boiled at 53.3°–53.5° C (748 mm Hg) and had a $n_D^{22.2°} = 1.4193$ according to the value of Brühl [3]. A molecular weight of 56.8 and 57.1 was obtained by a bromometric titration and an acidimetric titration, respectively; the theoretical value is 57.09. The above mentioned boiling point is corrected for calibration errors; stem correction has been done.

The carbamate of allylamine, $CH_2 : CH \cdot CH_2 \cdot NH \cdot COONH_3 \cdot CH_2 \cdot CH : CH_2$, in solid form was prepared by treating a solution containing 10 % amine in anhydrous ether with dry carbon dioxide. The precipitate which

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

Initial solution		Absorbed CO_2 mol/litre	% carbamate	Final solution		Mean		$k_{CO_2 \cdot Am}$	
c_{NaOH}	c_{Am}			c_{NaOH}	c_{Am}	c_{NaOH}	c_{Am}		Mean
0.20	0.10	0.0179	37	0.17	0.09	0.19	0.10	$10^{5.07}$	
0.10	0.10	0.0193	54	0.07	0.09	0.09	0.09	$10^{5.07}$	$10^{5.06}$
0.20	0.10	0.0200	35	0.17	0.09	0.18	0.10	$10^{5.03}$	
0.20	0.20	0.0191	54	0.17	0.19	0.19	0.19	$10^{5.08}$	

Table 2. 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
0.05	0.05	0.02		68 [1]	0.054	0.072	0.0137	0.0041	$10^{-1.79}$	
0.02	0.05	0.01		58 [2]	0.024	0.061	0.0058	0.0034	$10^{-1.86}$	$10^{-1.81}$
0.04	0.06	0.02		66 [3]	0.044	0.082	0.0132	0.0049	$10^{-1.78}$	
0.04	0.06		0.02	71 [4]	0.044	0.080	0.0121	0.0044	$10^{-1.80}$	

[1] Mean of 4 determinations: 68.1, 68.3, 68.4, 68.9
[2] » » 4 » 58.7, 57.4, 57.8, 57.2
[3] » » 4 » 66.6, 65.7, 67.2, 64.7
[4] » » 4 » 71.3, 72.1, 69.2, 69.1

Table 3. Velocity constants for the process "carbamate ⇌ carbonate". 18°. pa_H approx. 9.8.

Initial solution			Min.	% carbamate	$k_{amate} + k_{onate}$	
	c_{AmH+}	c_{Am}				
			40	11.7		0.00203
			85	21.0		0.00187
			120	27.6		0.00187
0.020 *M* $(AmH)_2CO_3$	0.05	0.05	260	45.2		0.00181
			∞	68.4	Mean:	0.00190
					k_{amate}:	0.0006
					k_{onate}:	0.0013
			40	14.8		0.00322
			85	25.9		0.00304
			120	33.5		0.00314
0.010 *M* $(AmH)_2CO_3$	0.05	0.02	160	38.9		0.00303
			242	48.0		0.00320
			∞	57.7	Mean:	0.00313
					k_{amate}:	0.0013
					k_{onate}:	0.0017
			40	11.0		0.00197
			80	21.2		0.00211
			120	29.1		0.00210
0.020 *M* $(AmH)_2CO_3$	0.06	0.04	166	34.1		0.00190
			270	49.0		0.00217
			∞	66.0	Mean:	0.00205
					k_{amate}:	0.0007
					k_{onate}:	0.0014

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

Initial solution			Min.	% carbamate left	k_{amate}
$c_{carbamate}$	c_{NaOH}	c_{Am}			
			0	100	
0.020			154	94.9	0.000147
(CO_2			407	87.1	0.000148
in solution	0.08	0.08	1428	62.5	0.000143
of amine)			4293	23.1	0.000148
			8623	4.6	0.000155
			∞	(0)	Mean: 0.00015
			0	100	
			221	93.3	0.000138
			420	86.6	0.000149
0.019			1400	61.5	0.000151
(preparation	0.08	0.08	3065	33.1	0.000157
of carbamate)			5960	12.2	0.000153
			8630	4.9	0.000152
			∞	(0)	Mean: 0.00015
			0	100	
			231	91.6	0.000166
			422	84.8	0.000170
0.022			1573	56.0	0.000160
(preparation	0.08	0.08	3094	32.2	0.000159
of carbamate)			5838	12.6	0.000154
			8948	4.0	0.000156
			∞	(0)	Mean: 0.00016

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		0.00060	0.00067	0.0013	0.0013
0.01		0.05	0.02		0.0013	0.0018	0.0017	0.0018
0.02		0.06	0.04		0.00070	0.00087	0.0014	0.0015
	0.02		0.08	0.08	0.00015	0.00021		
	0.02		0.08	0.08	0.00015	0.00021		
	0.02		0.08	0.08	0.00016	0.00021		

appeared was separated by filtration and dried over concentrated sulphuric acid. We found 72.2 % allylamine (theoretically 72.18 %) by titration with 0.1 *N* HCl of the carbamate. We found 27.6 % (theoretically 27.82 %) by determination of carbon dioxide in the carbamate.

The basic dissociation constant K_{Am} at 18° C of allylamine was fixed at $10^{-4.38}$, the value of which is calculated on the basis of the values at 0°, 25° and 40° C of Hantzsch and Sebaldt [4]. It should be noted that the value at 25° C of Hantzsch and Sebaldt agrees well with the corrected value of Bredig [5].

As the experiments are carried out analogously to those of the *n*-propylamine, and as the addition and equilibrium constants of the two amines have approximately the same quantitative values, it would seem, that the double bond in allylamine has no influence on the conditions of addition and equilibrium.

SUMMARY

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

carbamate = allyl amine + carbon dioxide
carbon dioxide = carbonate

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