

Studies on Carbamates

XII. The Carbamates of the Butylamines

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The velocity constants for the reaction "amine + CO₂ → carbamic acid" and the equilibrium constants for the equilibrium "carbamate⁻ + H₂O ⇌ HCO₃⁻ + amine" have been determined for *n*-, *sec*-, *iso*-, *tert*-, di-*n*- and di-*iso*-butylamine. Di-*sec*-butylamine and carbon dioxide form no carbamate in aqueous solution. Di-*tert*-butylamine could not be prepared.

1. The velocity constant for the reaction "amine + CO₂ = carbamic acid" and the equilibrium constant for the reaction "carbamate⁻ + H₂O = HCO₃⁻ + amine" have been determined for the following amines:

1) CH ₃ · CH ₂ · CH ₂ · CH ₂ · NH ₂	<i>n</i> -butylamine
2) CH ₃ · CH ₂ · CHCH ₃ · NH ₂	<i>sec</i> -butylamine
3) (CH ₃) ₂ CH · CH ₂ · NH ₂	<i>iso</i> -butylamine
4) (CH ₃) ₃ C · NH ₂	<i>tert</i> -butylamine
5) (CH ₃ · CH ₂ · CH ₂ · CH ₂) ₂ NH	di- <i>n</i> -butylamine
6) (CH ₃ · CH ₂ · CHCH ₃) ₂ NH	di- <i>sec</i> -butylamine
7) ((CH ₃) ₂ CH · CH ₂) ₂ NH	di- <i>iso</i> -butylamine
but not for	
8) ((CH ₃) ₃ C) ₂ NH	di- <i>tert</i> -butylamine

the synthesis of which failed although several attempts were made.

The experimental and theoretical conditions are analogous to those of the carbamates previously investigated. Detailed information concerning the method of analysis, theory, significance of constants *etc.* is to be found in previous papers¹.

2. The butylamines were purified by distillation through wire gauze columns. The fractions employed for the experiments had the following boiling points: No. 1 (commercial product): 77.4° C (764 mm Hg); No. 2 (prepared by the author): 63.4—63.8° C (768 mm Hg); No. 3 (Eastman Organic Chemicals): 67.6° C (755 mm Hg); No. 4 (Light and Co. Ltd.): 43.8—44.1° C

(749 mm Hg); No. 5 (commercial product): 159.8—160.3° C (765 mm Hg); No. 6 (Light and Co. Ltd.): 136.0—136.8° C (760 mm Hg) and No. 7 (FLUKA AG.): 140.5—140.6° C (765 mm Hg).

Sec.-butylamine was prepared from methyl ethyl ketoxime by reduction with metallic sodium. The oxime was prepared from hydroxylamine hydrochloride and methyl ethyl ketone².

3. An attempt to prepare the carbamate of amine No. 6, *i. e.* di-*sec.*-butylamine, was unsuccessful whereas the carbamates of the other six amines were prepared not only in solution but also as solids in the following manner:

A small portion, *viz.* about 2 ml of butylamine was distributed on the inner surface of a 300 ml Erlenmeyer-flask and carbon dioxide was lead into the flask whereby a white compound was formed; a little more amine was added followed by further carbon dioxide *etc.*

The content of amine in the compounds was determined by acidimetric titration. The content of carbon dioxide was determined by acidimetric titration of the barium carbonate formed when the carbamate was dissolved in a solution of sodium hydroxide and barium chloride and then heated.

The analysis gave the following results. In the case of the four primary amines, *i. e.* Nos. 1, 2, 3 and 4, a content of 76.7 %, 75.0 %, 76.6 % and 76.7 % amine, respectively, was found; the content of carbon dioxide was found to be 23.8 %, 22.0 %, 22.9 % and 23.0 %, respectively. These results correspond to the formula $C_4H_9NHCOOH_3NC_4H_9$ (theoretical values: 76.9 % amine and 23.1 % carbon dioxide).

In the case of di-*n*-butylamine, *i. e.* No. 5, a content of 85.4 % of amine and 14.0 % of carbon dioxide was found. This corresponds to a formula analogous to the above, *viz.* $(C_4H_9)_2NCOOH_2N(C_4H_9)_2$ (theoretical values: 85.4 % amine and 14.6 % carbon dioxide).

In the case of di-*iso*-butylamine, *i. e.* No. 7, a content of 81.2 % amine and 18.5 % carbon dioxide was found. This would be in accordance with the formula $(C_4H_9)_2NCOOH_2N(C_4H_9)_2$, $(C_4H_9)_2NCOOH$ (theoretical values: 81.5 % amine and 18.5 % carbon dioxide).

The solutions of the aminium carbonate, $(AmH)_2CO_3$, were prepared by mixing equivalent amounts of solutions of aminium chloride and sodium carbonate.

4. All the experiments were carried out 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 mono-

valent ion was calculated from Bjerrum's expression $-\log f = 0.3 \sqrt{c_{ion}}$. The data presented in the later tables are corrected for blank values, *viz.* 1—5 units of the percentage.

5. Hall and Sprinkle³ have found the dissociation constants for *n*-butylaminiumion and di-*n*-butylaminiumion at 18° C to be $10^{-10.76}$ and $10^{-11.46}$, respectively. Bredig's⁴ corrected values for the dissociation constants for *sec.*-butylamine, *iso*-butylamine, *tert.*-butylamine and di-*iso*-butylamine at 25° C are $10^{-3.44}$, $10^{-3.58}$, $10^{-3.55}$, and $10^{-3.41}$, respectively. As the heat effect of the reactions is very slight, these values may also be used for 18° C. The value of K_{H_2O} was fixed at $10^{-14.22}$.

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

Amine No.	Initial solution		Absorb. CO ₂ mole/litre	% carbamate	Final solution		Mean		k _{CO₂} · Am	
	c _{NaOH}	c _{Am}			c _{NaOH}	c _{Am}	c _{NaOH}	c _{Am}		Mean
1 <i>n</i> -	0.20	0.10	0.0200	49	0.17	0.09	0.19	0.10	10 ^{5.29}	10 ^{5.29}
	0.10	0.10	0.0224	66	0.07	0.09	0.09	0.09	10 ^{5.28}	
2 <i>sec</i> -	0.10	0.10	0.0189	42	0.07	0.09	0.09	0.09	10 ^{4.85}	10 ^{4.85}
	0.08	0.10	0.0180	48	0.05	0.09	0.07	0.09	10 ^{4.84}	
3 <i>iso</i> -	0.10	0.10	0.0198	61	0.08	0.09	0.09	0.09	10 ^{5.20}	10 ^{5.20}
	0.20	0.10	0.0191	43	0.18	0.09	0.19	0.10	10 ^{5.19}	
4 <i>tert</i> -	0.10	0.20	0.0191	31 *	0.07	0.20	0.08	0.20	10 ^{4.30}	10 ^{4.28}
	0.10	0.40	0.0196	45 *	0.07	0.40	0.08	0.40	10 ^{4.26}	
5 <i>di-n</i> -	0.10	0.022	0.0152	39	0.08	0.016	0.09	0.019	10 ^{5.51}	10 ^{5.49}
	0.10	0.026	0.0140	42	0.08	0.020	0.09	0.023	10 ^{5.47}	
6 <i>di-sec</i> -	0.10	0.04	0.0195	0	0.06	0.04	0.08	0.04		
7 <i>di-iso</i> -	0.10	0.014	0.0199	16	0.06	0.011	0.08	0.013	10 ^{5.13}	10 ^{5.12}
	0.05	0.014	0.0185	28	0.02	0.011	0.04	0.013	10 ^{5.11}	

* Found by analysis: 29 and 43 %, respectively. The listed values are corrected to zero time.

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. Approximately 250 ml of carbon dioxide were substituted for an equal amount of atmospheric air in the gas phase above this solution, and the flask was shaken vigorously for about 2 min to obtain absorption of the carbon dioxide.

The experimental results for the addition of carbon dioxide to the amines together with the calculated velocity constants are listed in Table 1. Since the carbamate of *tert*-butylamine is very rapidly decomposed it was found necessary to delay the conversion to carbonate by the addition of dimethylamine immediately after the shaking with carbon dioxide. If the solution is made 0.5—1 M with regard to dimethylamine, about 98 % of the carbon dioxide dissociated from the carbamate of *tert*-butylamine is converted into the carbamate of dimethylamine, which decomposes very slowly into carbonate⁵. Nevertheless, some decomposition takes place during the 1—2 min which elapse between the shaking with carbon dioxide and the addition of dimethyl-

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

Amino No.	Initial solution				% carbamate	Equilibrium				K_{Eq}	
	c_{Am}	c_{AmH^+}	$c_{(AmH)_2CO_3}$	$c_{AmH\ carbamate}$		c_{AmH^+}	c_{Am}	$c_{carbamate}$	$CHCO_3^-$		Mean
1 <i>n</i> -	0.11	0.10		0.0152	53	0.12	0.11	0.00809	0.00117	$10^{-1.80}$	$10^{-1.79}$
	0.10	0.10	0.0202		51	0.13	0.10	0.0103	0.00167	$10^{-1.78}$	
2 <i>sec</i> -	0.05	0.13		0.0185	25	0.16	0.058	0.00456	0.00413	$10^{-1.28}$	$10^{-1.31}$
	0.05	0.10	0.0203		25	0.13	0.058	0.00499	0.00396	$10^{-1.34}$	
3 <i>iso</i> -	0.10	0.10	0.0203		68	0.12	0.10	0.0133	0.00135	$10^{-2.00}$	$10^{-1.99}$
	0.062	0.14		0.0169	69	0.16	0.058	0.0116	0.00179	$10^{-1.98}$	
4 <i>tert</i> -	0.10		0.10 ^a		< 0.1	0.23	0.07		0.07		$10^{-0.88}$ b
	0.20	0.20		0.02	< 1	0.23	0.21		0.003		
5 di- <i>n</i> -	0.020	0.20	0.0203		4.4	0.24	0.024	0.0009	0.0043		$10^{-0.71}$ b
	0.020	0.20	0.0195		4.8	0.24	0.024	0.0009	0.0041		
6 di- <i>sec</i> -	0.03	0.20	0.0200		0						
7 di- <i>iso</i> -		0.16	0.0203		6.4	0.19	0.013	0.00129	0.0126	$10^{-0.91}$	$10^{-0.92}$
	0.015	0.16	0.0081 ^c		7.0	0.18	0.015	0.00142	0.0115	$10^{-0.92}$	

a The solution was 0.1 M with regard to $NaHCO_3$ corresponding to $CHCO_3^- = 0.10$.

b Calculated from the data on the decomposition of the carbamate, see Table 3.

c The solution was 0.012 M with regard to $NaHCO_3$ corresponding to $CHCO_3^- = 0.012$.

amine; the listed values are corrected to zero time on the basis of the velocity constants determined in section IV.

It is seen from Table 1 that no carbamate was found in the case of di-*sec*-butylamine, nor was it found in another experiment where a solution containing only the amine (0.04 M), but no sodium hydroxide, was shaken with carbon dioxide. In connection with this it should be mentioned that di-*iso*-propylamine does not react with carbon dioxide in aqueous solution either ⁶.

The low value of $k_{CO_2 \cdot Am}$ for *tert*-butylamine compared to that of other primary alifatic amines should also be noted.

No experiments as already mentioned, were carried out with di-*tert*-butylamine, but since neither di-*iso*-propylamine nor di-*sec*-butylamine form carbamates in aqueous solution a similar passivity towards carbon dioxide is to be expected in the case of di-*tert*-butylamine.

The equilibrium 'carbamate \rightleftharpoons carbonate'

In some cases experiments have been carried out from the carbamate side and from the carbonate side, in other cases from the carbonate side only.

Table 3. Velocity constants for the process "carbamate \rightarrow carbonate".
 $p_{\text{H}} = \text{approx. } 13. \text{ } 18^\circ.$

Amine No.	Initial solution			Min.	% carbamate left	k_{amate}		
	$c_{\text{carbamate}}$	c_{NaOH}	c_{Am}			exptl.	calc.	
1 <i>n-</i>	0.018	0.10	0.12	1 122	76.1	0.000106	0.000190	
				1 754	65.8	0.000104		
2 751	52.7	0.000101						
4 285	36.7	0.000102						
7 081	19.5	0.000100						
Mean:		0.000103						
1 207	81.0	0.0000759						
1 845	73.1	0.0000738						
3 008	59.7	0.0000745						
5 778	37.3	0.0000741						
Mean:		0.0000746						
2 <i>sec.-</i>	0.018	0.16	0.08	408	82.3	0.000207	0.000325	
645				72.0	0.000221			
1 528	49.1	0.000202						
2 090	37.0	0.000207						
Mean:		0.000209						
3 <i>iso-</i>	0.011	0.11	0.13	1 413	79.0	0.0000726		0.000104
1 853				70.9	0.0000806			
2 906	60.5	0.0000748						
4 306	46.9	0.0000764						
Mean:		0.0000761						
4 <i>tert.-</i>	0.020	0.066	0.20	3.0	83.7	0.0257	—	
8.0				60.2	0.0276			
13.0	43.9	0.0275						
18.0	31.1	0.0282						
Mean:		0.0273						
3.0	91.5	0.0129						
13.0	71.8	0.0112						
28.0	47.7	0.0115						
48.0	27.3	0.0120						
Mean:		0.0119						
5 <i>di-n-</i>	0.010	0.10	0.02	15	78.4	0.00710	—	
39				52.8	0.00712			
113	18.8	0.00644						
Mean:		0.00698						
27	57.5	0.00893						
51	37.7	0.00831						
114	10.0	0.00882						
Mean:		0.00872						

This Table is continued

Table 3 continued.

7	0.009	0.09	0.009	6	96.2	0.00283	0.00332				
				22	86.0	0.00297					
				42	75.9	0.00286					
				77	59.0	0.00298					
				110	48.5	0.00286					
				169	33.1	0.00284					
				Mean:		0.00289					
				di-iso-							
				0.006	0.11	0.011		6	96.6	0.00251	0.00254
								27	85.3	0.00256	
56	72.4	0.00252									
135	45.7	0.00252									
190	34.0	0.00246									
Mean:		0.00251									

Table 2 shows the composition of the equilibrium solutions and the equilibrium constant, K_{Eq} , for the reaction 'carbamate⁻ + H₂O = HCO₃⁻ + amine'.

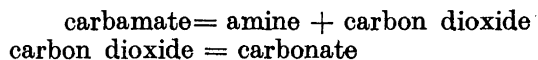
It is seen from Table 2 that measurable amounts of carbamate are formed in the experiments with *n*-butylamine, *sec.*-butylamine, *iso*-butylamine, and *di-iso*-butylamine while only small amounts are formed in the case of *tert.*-butylamine. No detectible amounts of carbamate were found in the experiment with *di-sec.*-butylamine.

In the experiments with *di-n*-butylamine it was not possible to obtain more than a few per cent of carbamate, the amine being slightly soluble in water, *i. e.* the solution was only about 0.02 M with regard to amine.

In the case of *tert.*-butylamine and *di-n*-butylamine the value of K_{Eq} was not calculated from the experiments on equilibrium but this value was obtained in another way, *viz.* indirectly from the data on the velocity of the decomposition of the carbamates in strong alkaline solution, see next section.

The velocity of the conversion 'carbamate →
carbonate'

The decomposition, in alkaline medium, of the carbamates of the amines previously investigated may be explained by assuming that the decomposition is a two-stage reaction, *viz.*



and the velocity constants may be calculated from the expression

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

On the assumption that there is the same two-stage reaction for the decomposition of the carbamates of the butylamines it is possible to calculate, in advance, the velocity constants in the case of *n*-butylamine, *sec.*-butylamine, *iso*-butylamine and di-*iso*-butylamine. The experiments on the decomposition of the carbamates in alkaline medium together with the calculated values of k_{amate} are listed in Table 3. Considering the nature of the experimental conditions the agreement may be described as rather satisfactory.

In the case of *tert.*-butylamine and di-*n*-butylamine the value of K_{Eq} was then calculated from the experimental value of k_{amate} by means of the above expression. The values of K_{Eq} determined in this way correspond to a theoretical content of less than 1 % and 2.6 % carbamate, respectively, in the experiments on equilibrium with *tert.*-butylamine and di-*n*-butylamine (Table 2).

As seen from Table 3 the carbamate of *tert.*-butylamine is rapidly decomposed. The experiments were carried out in such a way that 100 ml of the solution under investigation were quickly adjusted to 0.5—1 M with regard to dimethylamine and the time was noted; on addition of dimethylamine the conversion of carbamate to carbonate was brought to a standstill.

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