

On the Kinetics of the Reaction of Cyanic Acid with Amines

MOGENS BALLUND JENSEN

The Royal Danish School of Pharmacy, Copenhagen, Denmark

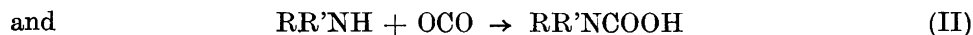
The velocity constants, k_u , for the reactions: $RR'NH_3^+ + OCN^- \rightarrow RR'NCONH_2$ were determined for ammonium ion and a number of aminium ions. Assuming that the formation of urea or substituted urea is a result of a reaction between free ammonia or amine and free cyanic acid the velocity constants, $k_{OCNH \cdot Am}$, for the reactions: $RR'NH + OCNH \rightarrow RR'NCONH_2$ were calculated from $k_{OCNH \cdot Am} = k_u \cdot K_{Am} \cdot K_{OCNH} / K_{H_2O} \cdot f^2$ where K_{Am} , K_{OCNH} and K_{H_2O} are the dissociation constants for the amine, for cyanic acid and for water, respectively. f is an activity coefficient. The values of $k_{OCNH \cdot Am}$ show a simple relationship to the velocity constants, $k_{CO_2 \cdot Am}$, for the analogous reactions between amines and carbon dioxide: $RR'NH + OCO \rightarrow RR'NCOOH$, viz. $\log k' = \log k'' - 1.08$ (18°C), where k' stands for $k_{OCNH \cdot Am}$ and k'' for $k_{CO_2 \cdot Am}$.

The same relation is observed for the velocity constants for the reactions: $OH^- + OCNH \rightarrow NH_2COO^-$ and $OH^- + OCO \rightarrow HCO_3^-$ and for the velocity constants for the reactions: $H_2O + OCNH \rightarrow NH_3 + CO_2$ and $H_2O + OCO \rightarrow H_2CO_3$.

The present investigation is based on the assumption that the rate determining step for the reaction between ammonium ion and cyanate ion leading to the formation of urea in aqueous solution is a reaction between free ammonia and free cyanic acid. In the case of the analogous reactions between aminium ion and cyanate ion yielding substituted urea, the rate determining step is correspondingly assumed to be a reaction between free amine and free cyanic acid.

The purpose of the investigation has been to demonstrate that the velocity constants for the reaction of cyanic acid with amines (*incl.* ammonia) calculated from the velocity constants for the reaction between aminium ion and cyanate ion show a simple relationship to the velocity constants for the reaction of carbon dioxide with amines.

The reactions to compare are



The reaction products are urea or substituted urea and carbamic acid or substituted carbamic acid, respectively.

For reaction I the velocity constants, $k_{\text{OCNH}\cdot\text{Am}}$, were obtained from the velocity constants, k_u , for the gross reaction



upon considering the equilibrium



The following relations will hold:

$$\begin{aligned} \text{rate} &= k_{\text{OCNH}\cdot\text{Am}} \cdot c_{\text{RR}'\text{NH}} \cdot c_{\text{OCNH}} = \\ &k_{\text{OCNH}\cdot\text{Am}} \cdot (K_{\text{H}_2\text{O}}/K_{\text{Am}} \cdot K_{\text{OCNH}}) \cdot f^2 \cdot c_{\text{RR}'\text{NH}_2^+} \cdot c_{\text{OCN}^-} = k_u \cdot c_{\text{RR}'\text{NH}_2^+} \cdot c_{\text{OCN}^-} \end{aligned}$$

$K_{\text{H}_2\text{O}}$ is the dissociation constant of water, K_{Am} is the basic dissociation constant of the amine, and K_{OCNH} is the acidic dissociation constant of cyanic acid. The activity coefficient of the aminium ion is set equal to that of the cyanate ion and is denoted f . The activity coefficients of the free amine and the free cyanic acid are put equal to unity.

From the above relations the following expression is obtained for $k_{\text{OCNH}\cdot\text{Am}}$:

$$k_{\text{OCNH}\cdot\text{Am}} = k_u \cdot K_{\text{Am}} \cdot K_{\text{OCNH}}/K_{\text{H}_2\text{O}} \cdot f^2$$

The values of k_u were determined for ammonia and some primary and secondary amines and the values of $k_{\text{OCNH}\cdot\text{Am}}$ were calculated from the above expression.

The experiments on the determination of k_u are given in the following section.

The velocity constants for reaction II, $k_{\text{CO}_2\cdot\text{Am}}$, have been determined previously for ammonia and a number of amines including the amines¹⁻⁷ here investigated.

The final section gives the results and a discussion.

The experiments were carried out at 18°C. The initial ionic strength was 0.2 and decreased only slightly during an experiment. The velocity constants were calculated on the basis of Napierian logarithms and refer to molar concentration, the unit of time being the minute.



The formation of urea in solutions containing aminium ion and cyanate ion was followed by determining the content of cyanate at different times. The samples to be analyzed were brought to pH = approx. 5.5 by the addition of acetic acid. The cyanate was precipitated as silver cyanate by the addition of a relatively great excess of silver nitrate and back-titration with ammonium thiocyanate was carried out in a quota part of the filtrate from the silver cyanate⁸.

Table 1. The velocity constant for the reaction: $\text{NH}_4^+ + \text{OCN}^- \rightarrow \text{NH}_2\text{CONH}_2$, 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	% carbo- nate	<i>k</i>	<i>k</i> mean	<i>k_u</i>
cNH_4^+	cNH_3	cOCN^-	cNO_3^-	cNa^+						
0.18	0.05	0.02	0.18	0.02	1 501	84.6	1.7	0.000112	0.000101	0.000588
					4 638	62.3		0.000103		
					8 326	43.7	1.9	0.000100		
					12 821	28.8		0.000097		
					21 312	14.2		0.000092		
0.18	0.15	0.02	0.18	0.02	1 694	83.1	0	0.000109	0.000103	0.000595
					4 520	64.4		0.000098		
					6 902	49.8	1.9	0.000101		
					12 788	27.4		0.000102		
0.075	0.095	0.02	0.18	0.125	3 204	88.8	0	0.0000375	0.000040	0.000574
					6 902	75.1		0.0000416		
					12 789	58.3	0.2	0.0000422		
					19 877	45.7		0.0000394		
0.135	0.095	0.02	0.18	0.065	3 203	79.4	0	0.0000720	0.000071	0.000562
					5 990	64.9		0.0000727		
					12 794	39.7	0.1	0.0000725		
					19 874	25.1		0.0000698		
0.18	*	0.02	0.18	0.02	1 778	77.5	5.7	0.000144	0.000119	0.000696
					3 267	65.8		6.9		
					5 762	49.8	9.8	0.000121		
					8 648	36.6		12.6		
					14 264	23.4	12.3	0.000102		
					17 152	16.6		0.000105		

* No ammonia added.

k_u (mean): 0.000577

The experiments with a few exceptions were carried out with solutions containing both ammonium ion and free amine, *i.e.* with solutions being in most cases moderately basic. Under these conditions it was found that the concurrent formation of carbonate was only slight.

The experiments which were carried out in the case of the ammonium ion are listed in Table 1. In all the runs there was a relatively great concentration of ammonium ion compared to that of the cyanate ion, *i.e.* the concentration of ammonium ion varied only slightly during a run meaning that the reaction is approximately of the first order with respect to cyanate ion. The velocity constants, *k*, calculated from $k \cdot t = \ln a/a-x$ are also listed in Table 1. The value of *k_u* was obtained dividing the mean value of *k* with the mean value of the concentration of ammonium ion. The values of *k_u* calculated in this way are also given in Table 1 together with the mean value of the values of *k_u* obtained from the first four experiments.

Table 2. The velocity constant for the reaction:
 $\text{CH}_3\text{NH}_3^+ + \text{OCN}^- \rightarrow \text{CH}_3\text{NH} \cdot \text{CO} \cdot \text{NH}_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c</i> _{AmH⁺}	<i>c</i> _{Am}	<i>c</i> _{OCN⁻}	<i>c</i> _{NO₃⁻}	<i>c</i> _{Na⁺}					
0.18	0.04	0.02	0.18	0.02	903	84.5	0.000186	0.000176	0.00102
					1 255	80.0	0.000178		
					2 260	67.5	0.000174		
					4 003	50.2	0.000172		
					6 988	30.3	0.000171		
0.12	0.10	0.02	0.18	0.08	996	88.1	0.000127	0.000117	0.00104
					2 247	77.0	0.000117		
					3 993	63.6	0.000113		
					6 975	45.5	0.000114		
					11 231	27.6	0.000115		
					4.3 × 10 ⁴	0.1			
0.18	0.15	0.02	0.18	0.02	954	84.1	0.000182	0.000176	0.00102
					1 225	80.5	0.000177		
					2 434	65.2	0.000176		
					3 986	49.6	0.000176		
					8 008	26.2	0.000167		

k_u (mean): 0.00103

Table 3. The velocity constant for the reaction:
 $(\text{CH}_3)_2\text{NH}_2^+ + \text{OCN}^- \rightarrow (\text{CH}_3)_2\text{N} \cdot \text{CO} \cdot \text{NH}_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c</i> _{AmH⁺}	<i>c</i> _{Am}	<i>c</i> _{OCN⁻}	<i>c</i> _{NO₃⁻}	<i>c</i> _{Na⁺}					
0.18	0.04	0.02	0.18	0.02	1 701	37.7	0.000573	0.000556	0.00325
					2 600	23.8	0.000552		
					2 977	19.9	0.000542		
					3 924	11.3	0.000555		
					5 476	4.7	0.000559		
					3.6 × 10 ⁴	0.3			
0.18	0.04	0.04	0.16	0.02	1 124	53.3	0.000566	0.000547	0.00340
					2 440	24.5	0.000576		
					4 517	9.7	0.000517		
					7 120	2.3	0.000530		
0.18	0.04	0.02	0 *	0.02	1 061	54.1	0.000578	0.000575	0.00336
					2 367	24.6	0.000591		
					3 984	10.9	0.000556		
					7 200	0.7			
0.10	0.10	0.02	0.18	0.10	345	89.2	0.000330	0.000318	0.00349
					1 362	64.1	0.000326		
					2 940	39.2	0.000319		
					4 246	26.5	0.000313		
					5 856	15.8	0.000315		
					8 641	7.4	0.000302		

* *c*_{ClO₄⁻} = 0.18

k_u (mean): 0.00338

Table 4. The velocity constant for the reaction:
 $C_2H_5NH_3^+ + OCN^- \rightarrow C_2H_5NH \cdot CO \cdot NH_2$. 18°C.

Initial solution				<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c_{AmH}⁺</i>	<i>c_{Am}</i>	<i>c_{OCN}⁻</i>	<i>c_{NO₃⁻}</i>					
0.18	0.04	0.02	0.18*	1 428	86.7	0.0001000	0.0000998	0.000582
				2 936	74.3	0.0001012		
				5 954	55.0	0.0001004		
				10 079	36.8	0.0000992		
				18 562	16.1	0.0000984		
			4.1×10^4	0.2				
0.132	0.03	0.02	0.18**	1 251	90.8	0.0000775	0.0000725	0.000583
				2 736	82.5	0.0000705		
				6 799	60.8	0.0000731		
				12 730	39.8	0.0000723		
				16 911	29.9	0.0000714		
				22 643	20.3	0.0000702		

* $c_{Na^+} = 0.02$ ** $c_{K^+} = 0.02$; $c_{Na^+} = 0.05$ k_u (mean): 0.000583

Furthermore, from Table 1 can be seen that with exception of the last mentioned experiment only small amounts of carbonate were formed. In the case of the last mentioned experiment the solution contained only ammo-

Table 5. The velocity constant for the reaction:
 $(C_2H_5)_2NH_2^+ + OCN^- \rightarrow (C_2H_5)_2N \cdot CO \cdot NH_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c_{AmH}⁺</i>	<i>c_{Am}</i>	<i>c_{OCN}⁻</i>	<i>c_{NO₃⁻}</i>	<i>c_{Na}⁺</i>					
0.18	0.04	0.02	0.18	0.02	410	94.2	0.000146	0.000154	0.000890
					1 438	79.7	0.000158		
					2 866	63.2	0.000160		
					4 597	48.7	0.000157		
					7 294	33.3	0.000151		
0.18	0.18	0.02	0.18	0.02	1 428	79.5	0.000160	0.000160	0.000934
					2 857	63.2	0.000160		
					4 400	49.3	0.000161		
					7 404	30.3	0.000161		
					13 042	12.5	0.000160		
0.10	0.10	0.02	0.18	0.10	1 421	87.9	0.0000908	0.0000884	0.000946
					2 834	76.7	0.0000936		
					4 564	67.4	0.0000864		
					7 587	50.9	0.0000869		
					13 077	33.2	0.0000844		

 k_u (mean): 0.000923

Table 6. The velocity constant for the reaction:
 $C_6H_5CH_2NH_3^+ + OCN^- \rightarrow C_6H_5CH_2NH \cdot CO \cdot NH_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k_u</i>	<i>k_u</i> mean
<i>c</i> AmH ⁺	<i>c</i> Am	<i>c</i> OCN ⁻	<i>c</i> NO ₃ ⁻	<i>c</i> Na ⁺				
0.04	0.04	0.02	0.18	0.16	218	94.7	0.00691	0.00666
					1 038	77.5	0.00670	
					1 370	72.0	0.00660	
					1 768	65.7	0.00662	
					2 498	56.1	0.00665	
					6 882	25.7	0.00648	
0.02	0.04	0.019	0.18	0.18	458	94.2	0.00674	0.00678
					1 190	86.8	0.00640	
					5 524	57.2	0.00677	
					9 815	42.9	0.00674	
					19 887	27.0	0.00679	
					27 622	20.0	0.00724	

k_u (mean): 0.00672

nium ions and cyanate ions without addition of free ammonia, *i.e.* the pH of this solution was about 6 whereas the pH of the other solutions was about 9.

The formation of considerable amounts of carbonate in more acid solution can be explained through the more rapid decomposition of cyanate into carbon dioxide and ammonia at the lower pH⁸.

The contents of carbonate were determined by acidimetric titration of the barium carbonate precipitated from the solutions upon addition of sodium hydroxide and barium chloride.

Table 7. The velocity constant for the reaction:
 $CH_2 = CH \cdot CH_2 \cdot NH_3^+ + OCN^- \rightarrow CH_2 = CH \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c</i> AmH ⁺	<i>c</i> Am	<i>c</i> OCN ⁻	<i>c</i> NO ₃ ⁻	<i>c</i> Na ⁺					
0.181	0.04	0.02	0.18	0.02	141	91.1	0.000666	0.000618	0.00359
					278	83.2	0.000663		
					1 340	45.0	0.000596		
					2 557	22.3	0.000586		
					2 969	17.6	0.000585		
					4 377	6.8	0.000614		
0.10	0.10	0.02	0.18	0.10	282	90.2	0.000367	0.000332	0.00355
					1 314	64.5	0.000335		
					2 531	49.4	0.000320		
					2 947	40.8	0.000305		
					2×10^4	-0.2			

k_u (mean): 0.00357

Table 8. The velocity constant for the reaction:
 $\text{-OOCCH}_2\text{NH}_3^+ + \text{OCN}^- \rightarrow \text{-OOCCH}_2\text{NH} \cdot \text{CO} \cdot \text{NH}_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c</i> _{AmH⁺}	<i>c</i> _{Am}	<i>c</i> _{OCN⁻}	<i>c</i> _{NO₃⁻}	<i>c</i> _{Na⁺}					
0.14	0.04	0.02	0	0.06	129	89.7	0.000842	0.000833	0.00630
					308	77.3	0.000836		
					438	69.1	0.000846		
					1 425	30.8	0.000825		
					1 792	23.2	0.000814		
0.10	0.04	0.02	0.04	0.10	843	60.3	0.000600	0.000574	0.00630
					1 184	50.2	0.000582		
					1 483	42.4	0.000579		
					2 417	25.8	0.000560		
					3 774	12.5	0.000550		
					2.2×10^4	0.7			
0.14		0.02	0.04	0.06	217	82.7	0.000876	0.000851	0.00650
					359	73.6	0.000854		
					657	56.7	0.000864		
					1 384	31.1	0.000858		
					3 089	8.4	0.000801		

k_u (mean): 0.00637

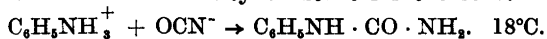
The back-reaction, *viz.* the decomposition of urea into ammonium ion and cyanate ion, was neglected. The equilibrium constant for this reaction is reported⁹ to be $10^{-4.52}$ (25°C).

From the first four experiments the mean value 0.000577 for *k_u* was obtained. Walker and Hambly¹⁰ have determined *k_u* for temperatures between 25°C and 80°C. By extrapolation to 18°C the value 0.00085 is obtained at an ionic strength of 0.1 corresponding to approx. 0.00072 at the ionic strength 0.2. Wyatt and Kornberg¹¹, however, report the values of Walker and Hambly to be about 20 % too large (at 50°C) because of the concurrent formation of carbonate.

Table 9. The velocity constant for the reaction:
 $\text{tert.-C}_4\text{H}_9\text{NH}_3^+ + \text{OCN}^- \rightarrow \text{tert.-C}_4\text{H}_9\text{NH} \cdot \text{CO} \cdot \text{NH}_2$. 18°C.

Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c</i> _{AmH⁺}	<i>c</i> _{Am}	<i>c</i> _{OCN⁻}	<i>c</i> _{NO₃⁻}	<i>c</i> _{Na⁺}					
0.10	0.02	0.02	0.18	0.10	4 018	96.7	(0.00000791)	0.0000102	0.000102
					10 095	89.7	0.0000108		
					21 615	81.1	0.0000096		

Table 10. The velocity constant for the reaction:

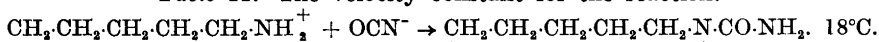


Initial solution					<i>t</i> min.	% cya- nate left	<i>k_u</i>	<i>k_u</i> mean
<i>c</i> AmH ⁺	<i>c</i> Am	<i>c</i> OCN ⁻	<i>c</i> NO ₃ ⁻	<i>c</i> Na ⁺				
0.021	0.10	0.017	0.18	0.18	2.0	87.5	3.49	3.63
					5.0	71.9	3.68	
					8.0	60.9	3.68	
					15.0	43.3	3.78	
					22.1	34.9	3.50	
0.044	0.05	0.016	0.18	0.15	1.5	79.9	3.61	3.67
					4.0	55.4	3.71	
					8.0	32.8	3.73	
					14.0	16.7	3.63	
					1 h	0.8		
0.043	0.10	0.016	0.18	0.15	1.9	72.7	4.10	4.04
					3.9	53.7	4.07	
					6.9	36.6	3.92	
					10.9	21.2	4.06	

k_u (mean): 3.8

In the Tables 2—11 are listed the experiments which were carried out with different aminium ions. In these tables are also given the values of *k_u*. In those experiments where a relatively great excess of aminium ion was applied, the values of *k_u* were obtained dividing the mean value of *k* with the mean value of the aminium ion concentration. The values of *k* were calculated from the expression for an unimolecular reaction. In those experiments where the

Table 11. The velocity constant for the reaction:



Initial solution					<i>t</i> min.	% cya- nate left	<i>k</i>	<i>k</i> mean	<i>k_u</i>
<i>c</i> AmH ⁺	<i>c</i> Am	<i>c</i> OCN ⁻	<i>c</i> NO ₃ ⁻	<i>c</i> Na ⁺					
0.18	0.12	0.02	0.18	0.02	1 102	82.9	0.000170	0.000173	0.000989
					2 530	64.2	0.000176		
					4 192	48.3	0.000174		
0.095	0.10	0.02	0.18	0.09	1 532	87.0	0.0000913	0.0000867	0.000993
					2 976	76.4	0.0000905		
					5 411	61.5	0.0000898		
					9 746	43.7	0.0000851		
					15 452	27.7	0.0000830		
					22 724	16.1	0.0000803		
					3 months	<0.5			

k_u (mean): 0.000992

concentration of aminium ion and the concentration of cyanate ion were of the same order of magnitude the values of k_u were calculated from the expressions for bimolecular reactions.

In the experiments with anilinium ion (Table 10) a few percent of the cyanate was present as free cyanic acid but this was not taken into consideration in the calculation of k_u .

Determinations of the contents of carbonate carried out in some of the experiments showed that only small amounts of carbonate were formed.

From the experiments with methylaminium ion (Table 2) the value 0.00103 was obtained for k_u . This value agrees well with the value 0.00109 calculated by extrapolation from the data of Miller¹² at an ionic strength of 0.082.

RESULTS AND DISCUSSION

In column 1 of Table 12 is given a survey on the values of k_u determined in the preceding section. Column 1 also gives the value of k_u for the reaction between hydrazinium ion and cyanate ion yielding semicarbazide, $H_2N \cdot NH \cdot CO \cdot NH_2$. The value of k_u for this reaction was calculated from the data of Baker and Gilbert¹³.

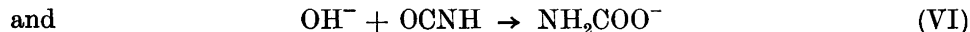
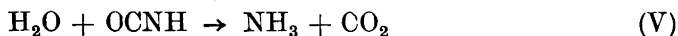
Column 2 of Table 12 contains the pK_{Am} values for the amines. From the columns 1 and 2 can be seen that some correlation appears to exist between the values of k_u and pK_{Am} . The value of k_u for anilinium ion is for instance about 7×10^3 times greater than the value of k_u for ammonium ion. There are, however, large deviations from linearity in a plot of $\log k_u$ against pK_{Am} .

Column 3 of Table 12 presents the values of $k_{OCNH \cdot Am}$ calculated from

$$k_{OCNH \cdot Am} = k_u \cdot K_{Am} \cdot K_{OCNH} / K_{H_2O} \cdot f^2 = k_u \cdot K_{Am} \times 10^{11.03}.$$

The values $10^{-3.54}$ (Ref.⁸) and $10^{-14.22}$ have been used for K_{OCNH} and K_{H_2O} , respectively. From the expression of Svirbely and Warner¹⁴ the value $10^{-0.35}$ is obtained for f^2 in the case of the ammonium ion. This value has been used for the aminium ions as well.

Column 3 also contains the velocity constants⁸ at 18°C for the reactions



The velocity constants for the reactions V and VI are denoted k_{OCNH} and $k_{OCNH \cdot OH^-}$, respectively. The value of $k_{OCNH \cdot OH^-}$ has not been determined directly but was calculated from the previously determined velocity constant, k_{OCN^-} , for the gross reaction: $OCN^- + 2H_2O \rightarrow NH_3 + HCO_3^-$. (k_{OCN^-} is $10^{-6.48}$ at 18°C). Assuming reaction VI to be the rate determining step for this reaction¹⁵ the following equation will hold: $k_{OCNH \cdot OH^-} = k_{OCN^-} \cdot K_{OCNH} / K_{H_2O}$

For $k_{OCNH \cdot Am}$, $k_{OCNH \cdot OH^-}$ and k_{OCNH} the joint designation k' is used.

Column 4 of Table 12 presents the values of $k_{CO_2 \cdot Am}$ at 18°C.

Table 12. Velocity constants for the reactions: $RR'NH^+ + OCN^- \rightarrow RR'NCONH_2$ (k_u),
 $RR'NH + OCNH \rightarrow RR'NCONH_2$ ($k_{OCNH-Am}$) and $RR'NH + OCO \rightarrow$
 $RR'NCOOH$ (k_{CO_2-Am}). 18°C.

Amine	1 k_u	2 pK_{Am}^a	3 $k_{OCNH-Am}$	4 k_{CO_2-Am}
Ammonia	0.000577	4.76	$10^{3.03}$	$10^{4.02}$
Methylamine	0.00103	3.38	$10^{4.66}$	$10^{5.77}$ b
Dimethylamine	0.00338	3.22	$10^{5.34}$	$10^{6.18}$
Ethylamine	0.000583	3.34	$10^{4.46}$	$10^{5.55}$
Diethylamine	0.000923	3.00	$10^{5.00}$	$10^{5.82}$
Benzylamine	0.00672	4.74	$10^{4.12}$	$10^{5.42}$
Allylamine	0.00357	4.38	$10^{4.20}$	$10^{5.42}$
Glycinate ion	0.00637	4.34	$10^{4.32}$ c	$10^{5.41}$
tert.-Butylamine	0.000102	3.55	$10^{3.49}$	$10^{4.64}$
Aniline	3.8	9.46 d	$10^{2.15}$	$10^{3.2}$ e
Hydrazine	0.749 f	6.06	$10^{4.84}$	$10^{5.87}$
Piperidine	0.000992	2.95	$10^{5.08}$	$10^{6.25}$
Hydroxyl ion			$10^{4.20}$	$10^{5.38}$
Water			0.047	1.52 g 0.87 h

a The values of pK_{Am} are, with exception of the pK_{Am} -value for aniline, the same as have been used in the publications on the carbamates.

b Redetermined, not previously published value.

c In the case of glycine the value of $k_{OCNH-Am}$ was calculated from $k_{OCNH-Am} = k_u \cdot K_{OCNH} / K'_{AmH^+} \cdot f$ where $a_{H^+} \cdot c_{-OOC-CH_2NH_2} / c_{-OOC-CH_2NH_2^+} = K'_{AmH^+} = 10^{-9.88}$ and f was put equal to $10^{0.18}$.

d Value of Lundén¹⁹.

e Only small amounts of phenyl carbamate are formed upon addition of carbon dioxide to solutions containing aniline. In a previous paper⁵ values of k_{CO_2-Am} from $10^{2.64}$ to $10^{3.78}$ were reported. The listed value of k_{CO_2-Am} is the mean value of these values.

f Calculated from the data of Baker and Gilbert¹³.

g Value of Faurholt¹. h Value of Pinsent, Pearson and Roughton¹⁶.

Column 4 also contains the velocity constants at 18°C for the reactions^{1,16}



The velocity constants for the reactions VII and VIII are denoted k_{CO_2} and k_{CO_2,OH^-} , respectively.

For k_{CO_2-Am} , k_{CO_2,OH^-} and k_{CO_2} , the joint designation k'' is used.

From the columns 3 and 4 can be seen that the values of k' are about a twelfth of the values of k'' . Roughly, one can still say that the two set of velocity constants are of the same order of magnitude.

Fig. 1 shows that a straight line is obtained if $\log k'$ is plotted against $\log k''$. The slope of the line is approx. 1 and the intersection with the ordinate axis is at -1.08 . This indicates the following relation between k' and k''

$$\log k' = \log k'' - 1.08$$

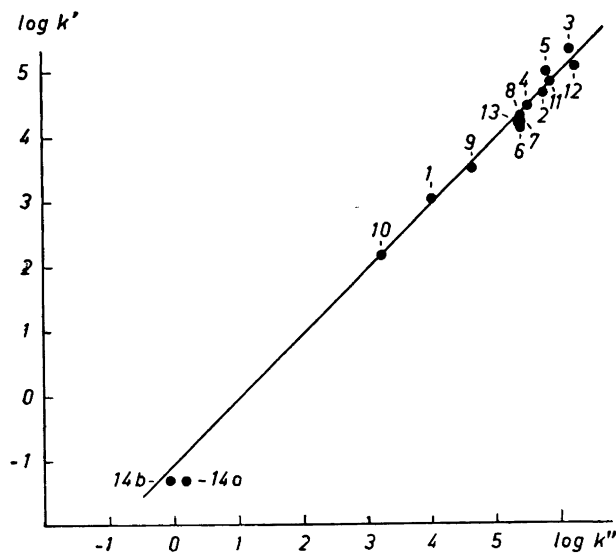
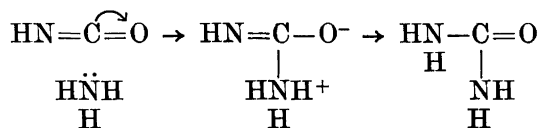


Fig. 1. Plot of $\log k'$ against $\log k''$. k' and k'' are the velocity constants (18°C, min.) for the reactions between cyanic acid or carbon dioxide, respectively, and the following molecules and ions: 1) ammonia, 2) methylamine, 3) dimethylamine, 4) ethylamine, 5) diethylamine, 6) benzylamine, 7) allylamine, 8) glycinate ion, 9) *tert.*-butylamine, 10) aniline, 11) hydrazine, 12) piperidine, 13) hydroxyl ion, 14a) water (k'' : value of Faurholt¹) and 14b) water (k'' : value of Pinsent, Pearson and Roughton¹⁶).

The largest deviations from the straight line are found in the case of the two secondary amines dimethylamine and diethylamine where the deviations amount to approx. + 0.2 units in the logarithm. In the case of the secondary amine piperidine the above stated expression fits well, however. In the case of benzylamine the deviation amounts to approx. - 0.2 units in the logarithm.

It should be noted that the reactions I and III are kinetically indistinguishable, because of the mobile equilibrium indicated in IV. Also the theoretical effect of changing ionic strength and dielectric constant will be the same for both mechanisms. As pointed out by Frost and Pearson¹⁷ reaction I is, however, the most probable, seen from a stereochemical point of view. The reason is supposed to be that this reaction easily can take place by addition of the nitrogen atom's unshared pair of electrons to the positively polarized carbon atom of cyanic acid. In the case of ammonia the reaction is



A simple proton shift completes the transformation to urea. This is similar to a host of reactions involving addition of basic reagents to carbonyl groups.

Reaction II between amines and carbon dioxide is an example of such a reaction.

The above stated analogy between cyanic acid and carbon dioxide requires that at least a part of the cyanic acid exists as the imide form corresponding to the formula OCNH in aqueous medium. Electron diffraction appears to show that the acid has the imide structure (at least mainly)¹⁸. If only a minor part of the cyanic acid is present as OCNH in aqueous solution and if only the OCNH form is the one that reacts the values of $k_{\text{OCNH-Am}}$ have to be multiplied with a common factor greater than 1 in order to give the true values of the velocity constants for reaction I. This is one possible reason which could explain the fact that the velocity constants for the reactions with cyanic acid are smaller than the velocity constants for the reactions with carbon dioxide. Another possibility, or at least a contributory cause, could be that the carbon atom in OCNH is less positively polarized than the carbon atom in OCO, *i.e.* a somewhat weaker attraction exists between the carbon atom and the nitrogen atom in the cyanic acid-amine reactions than is to be found in the carbon dioxide-amine reactions.

It should be added that a detailed discussion of the mechanism of the addition of amines to cyanic acid recently has been given by Johncock, Kohnstam and Speight²⁰,

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