On the Kinetics of the Decomposition of Cyanic Acid

MOGENS BALLUND JENSEN

The Royal Danish School of Pharmacy, Copenhagen, Denmark

The decomposition of cyanic acid and cyanate into ammonia and carbon dioxide has been investigated kinetically in dilute aqueous solution over the pH-range $0-7$ and in strongly basic medium. The experimental results indicate that the decomposition takes place according to three simultaneous reactions, *viz.* $OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2$ (I), $OCNH + H_2O \rightarrow NH_3 + CO_2$ (II), and $OCN^- + 2H_2O \rightarrow NH_3 + HCO_3^-$ (III). The velocity constants for the reactions I and II were found to be 3.61 (1 $mole^{-1} min^{-1}$) and 0.047 (min^{-1}), respectively, at 18°C. The energy of activation was found to be 15.1 kcal $mole^{-1}$ for reaction I and 19.9 kcal $mole^{-1}$ for reaction II. The velocity constant for reaction III was found to be 0.0017 (min^{-1}) at 94°C with an energy of activation of 23.9 kcal $mole^{-1}$.

Bicarbonate was found to act catalytically on the decomposition.

The acidic dissociation constant of cyanic acid was found to be $10^{-3.54}$ at 18°C.

1. The velocity for the decomposition of cyanate into ammonia and carbon dioxide in aqueous medium has been studied in several cases [1-5]. Most of the investigations have been carried out in strongly acid or basic solution, whereas measurements of the velocity in moderately and weakly acid solution are rather limited.

The present investigation deals with the decomposition of cyanate (meaning cyanic acid and cyanate ion) in dilute solution over the pH range 0—7 and in strongly basic medium.

2. Solutions of potassium cyanate were in most cases prepared by shaking silver cyanate with a solution containing the equivalent amount of potassium iodide. Silver cyanate was prepared by heating 120 g of urea and 68 g of silver nitrate dissolved in about 1 l of water. The needles of silver cyanate, gradually precipitated, were filtered off from time to time and washed until the wash water was almost free from silver ion. The silver cyanate was dried at 60° and stored in a desiccator containing silica gel.

In some experiments solutions prepared from Sodium Cyanate pure (Hopkin and Williams, Ltd.) were used.

Table 1. 20.00 ml 0.1004 M KNCO + 0.1 N AgNO$_3$

Final solution		ml 0.1 N AgNO$_3$ pr. 200 ml	c_{KNCO} found
c_{CH_3COOH}	c_{CH_3COONa}		
0	0	25.00	0.0996
0	0	25.00	0.0994
0	0	50.00	0.1001
0	0	50.00	0.1004
0.025	0.075	50.00	0.0999
0.050	0.050	50.00	0.0993
0.075	0.025	50.00	0.0982

3. The experiments were, unless otherwise stated, carried out in such a way that equal volumes of solutions of potassium cyanate and buffers of the temperature in question were mixed and placed in a thermostat. After an appropriate lapse of time the mixture or a sample of the mixture was brought to pH = approx. 5.5 by the addition of sodium acetate or acetic acid and immediately analysed for cyanate or ammonia.

The method of analysis was in the case of cyanate a procedure analogous to the determination of chloride according to Volhard. The cyanate was precipitated as silver cyanate by the addition of silver nitrate whereupon the excess of silver nitrate was titrated back with ammonium thiocyanate in a quota part of the filtrate acidified with nitric acid.

In Table 1 are listed some determinations of the concentration of cyanate in 20.00 ml of a solution of potassium cyanate prepared by shaking a 0.1004 M solution of potassium iodide with silver cyanate, *i.e.* the concentration of cyanate being 0.1004. The cyanate was precipitated with excess silver nitrate in neutral or in weakly acid medium the total volume being 200 ml.

It is seen from Table 1 that a relative great excess of silver nitrate is required in order to precipitate the cyanate quantitatively. It is furthermore seen that if the pH of the solution is less than approx. 5, more or less cyanate remains unprecipitated.

In the case of ammonia the analysis was carried out in such a manner that the cyanate was precipitated as silver cyanate and the content of ammonia in the filtrate was determined in the usual way by distilling off the ammonia.

4. The velocity constants were calculated on the basis of Napierian logarithms and refer to molar concentrations, the unit of time being the minute. The activity coefficient, f, for a monovalent ion was calculated from the expression of Bjerrum: $-\log f = 0.3 \sqrt[3]{c_{ion}}$.

It should be noted that $c_{cyanate}$ means the total concentration of cyanate, *i.e.* the sum of the concentrations of cyanic acid and of cyanate ion.

5. The values 1.44×10^{-3} and 1.82×10^{-5} for the acidic dissociation constants of chloroacetic acid [6] and acetic acid [7], respectively, and the value 4.01×10^{-7} for the first acidic dissociation constant of carbonic acid [8] were used in the calculations at 18°C.

The solubility of carbon dioxide in water at 18°C and at a pressure of 1 atmosphere was calculated from the data of Harned and Davis [8].

In the case of cyanic acid a calculation of the acidic dissociation constant, K_{OCNH}, was carried out on the basis of determinations of the hydrogen ion activity in solutions containing both cyanic acid and cyanate ion. The solutions were prepared by mixing a solution of sodium cyanate with an appropriate

Table 2. Determination of the acidic dissociation constant of cyanic acid. 18°C.

c_{OCNH}	c_{OCN^-}	c_{ion}	Minutes after mixing	pH	$\dfrac{\Delta pH}{\Delta t}$	pH extrapol.	K_{OCNH}
0.0501	0.0474	0.10	1.5	3.52		3.38	$10^{-3.54}$
			2.5	3.61	0.09		
			3.5	3.70	0.09		
			4.5	3.77	0.07		
0.0334	0.0966	0.13	1.0	3.96		3.84	$10^{-3.53}$
			2.0	4.08	0.12		
			3.0	4.20	0.12		
			4.0	4.31	0.11		
			5.0	4.39	0.08		
0.0167	0.0483	0.065	1.0	3.99		3.88	$10^{-3.54}$
			2.0	4.08	0.09		
			3.0	4.15	0.07		
			4.0	4.20	0.05		
0.0167	0.0483	0.20	1.5	3.94		3.83	$10^{-3.55}$
			2.5	4.01	0.07		
			3.5	4.08	0.07		
			4.5	4.15	0.07		

Mean value of K_{OCNH} $10^{-3.54}$

Table 3. The velocity constant for the reaction $OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2$. 18°C.

Run	Initial solution				Min.	% cyanate	k	k mean	c_H^+ mean
	c_H^+	$c_{NO_3^-}$	c_K^+	$c_{cyanate}$					
4	0.472	0.48	0.02	0.0195	0.5 1.0 1.5 2.0	41.3 17.1 7.2 3.2	1.77 1.76 1.75 1.72	1.75	0.467
3	0.207	0.23	0.02	0.0198	0.5 1.0 1.5 2.0 2.5 3.0	67.2 45.8 30.7 20.7 13.3 8.5	0.794 0.781 0.785 0.787 0.806 0.824	0.797	0.198
2	0.098	0.12	0.02	0.0201	1.0 1.5 2.0 2.5 3.0 4.0	68.8 57.2 47.3 39.0 33.5 23.1	0.375 0.373 0.375 0.378 0.364 0.366	0.373	0.090
6	0.100	0.14	0.04	0.0383	1.0 1.5 2.0 40	68.9 57.2 48.1 0	0.373 0.373 0.366	0.371	0.089
7	0.098	0.22	0.12	0.0182	1.0 1.5 2.0 3.0	66.0 54.0 44.7 30.7	0.414 0.410 0.403 0.398	0.408	0.092
8	0.098	0.32	0.22	0.0182	1.0 1.5 2.0 3.0	67.4 53.4 46.2 31.0	0.394 0.419 0.387 0.391	0.398	0.092
9	0.098	1.12	1.02	0.0182	1.0 2.0 3.0	67.6 46.0 31.0	0.391 0.389 0.389	0.389	0.092
1	0.066	0.09	0.02	0.0199	0.9 2.0 3.0 4.0 5.0 30	79.8 61.0 46.5 36.3 29.0 0.6	0.251 0.246 0.256 0.253 0.249	0.251	0.059

$$k_{OCNH \cdot H_3O^+} = 3.61.$$

Table 4. The velocity constant for the reaction $OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2$. 18°C.

Run	Initial solution			Min.	% cyanate	% CO_2	% NH_4^+	k	k mean	c_{H^+} mean
	c_{H^+}	c_{K^+}	$c_{cyanate}$							
10	0.098[1]	0.02	0.0196	1.0	67.4			0.394	0.385	0.090
				1.5	56.3			0.382		
				2.0	46.8			0.380		
				3.0	31.5			0.385		
				4.0	21.5			0.382		
11	0.098[2]	0.02	0.0196	1.0	66.4			0.410	0.394	0.091
				2.0	45.9			0.389		
				3.0	32.1			0.380		
12	0.096[3]	0.02	0.0205	1.0		30.9		0.368	0.382	0.087
				2.0		54.5		0.394		
				3.0		66.2		0.362		
				4.0		78.2		0.380		
				5.0		87.0		0.408		
13	0.098[3]	0.02	0.0198	1.05			32.8	0.380	0.385	0.090
				2.0			54.3	0.391		
				3.0			68.2	0.382		
				4.0			78.4	0.382		

[1] $c_{ClO_4^-} = 0.12$

[2] $c_{Cl^-} = 0.12$

[3] $c_{NO_3^-} = 0.12$

$k_{OCNH \cdot H_3O^+} = 3.61$

volume of hydrochloric acid which in some cases contained sodium nitrate. The temperature of both solutions was 18°C.

By means of a glass electrode the pH of the solution was determined at intervals of one minute and on the basis of the quantity $\Delta pH/\Delta t$ an extrapolation to zero time was made.

In Table 2 are listed the composition of the solutions and the measured and extrapolated values of pH together with the values of K_{OCNH} calculated from the expression

$$K_{OCNH} = \frac{a_{H^+} \cdot a_{OCN^-}}{a_{OCNH}} = \frac{a_{H^+} \cdot c_{OCN^-} \cdot f}{c_{OCNH}}$$

The mean value of K_{OCNH} obtained in this way is $10^{-3.54}$ at 18°C.

ON THE REACTION: $OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2$

In Tables 3 and 4 are listed the experiments which were carried out in strongly acid solutions at 18°C. In most cases nitric acid was used for the experiments just as some of the solutions contained potassium nitrate.
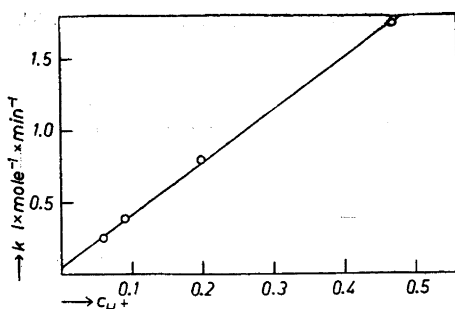
Fig. 1. Velocity constants for the reaction: "cyanic acid → NH_4^+ + CO_2" as a function of the hydrogen ion concentration. 18°C.

In runs 10 and 11 perchloric acid and hydrochloric acid, respectively, was used.

It is seen from Table 4 that nitric acid, perchloric acid and hydrochloric acid yield practically the same results.

In run 11 the method of analysis was modified in the following manner. The chloride and the cyanate were precipitated as silver salts at pH = 5.5 upon addition of silver nitrate. The silver chloride and silver cyanate were filtered off, washed, and boiled with excess of 0.1 N hydrochloric acid whereby: $AgNCO + 2HCl + H_2O = AgCl + CO_2 + NH_4Cl$, and back-titration was carried out with 0.1 N sodium hydroxide.

In runs 12 and 13 the decomposition was followed not by determining the concentration of cyanate but by determining the concentration of carbon dioxide and ammonia, respectively. In the case of carbon dioxide the analysis was carried out in such a manner that sodium hydroxide and barium chloride were added and the barium carbonate precipitated was then determined by acidimetric titration.

It is seen from Tables 3 and 4 that good agreement exists between the content of ammonia and carbon dioxide and the content of cyanate the sum being virtually constant, meaning that cyanate decomposes quantitatively into ammonia and carbon dioxide in strongly acid medium.

Tables 3 and 4 also list the velocity constants calculated from the unimolecular expression: $kt = \ln a/a-x$. It is seen that the velocity constants are almost proportional to the hydrogen ion concentration the mean values of which also are listed in Tables 3 and 4. This indicates a bimolecular reaction between cyanic acid and hydrogen ion.

In Fig. 1 the velocity constants listed in Tables 3 and 4 are plotted against the mean values of the hydrogen ion concentration and a straight line is drawn. The slope of this line is 3.61, meaning that the velocity constant, $k_{OCNH \cdot H_3O^+}$, for the reaction:

$$OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2$$
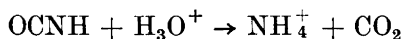
is equal to 3.61 at 18°C. This value is in good agreement with the value 3.75, which was calculated at an ionic strength of 1.0 from the data reported by Lister [3].

Table 5. The temperature dependence of $k_{OCNH \cdot H_2O}^+$

| Run | °C | Initial solution | | | | Min. | % cya-nate | k | k mean | c_{H^+} mean | $k_{OCNH \cdot H_2O}^+$ |
		c_{H^+}	$c_{NO_3^-}$	c_{K^+}	$c_{cyanate}$						
56	10.0	0.181	0.20	0.02	0.0197	1.0	73.4	0.311	0.311	0.173	1.71
						2.0	53.8	0.311			
						3.0	39.2	0.313			
						5.0	21.2	0.309			
55	4.0	0.181	0.20	0.02	0.0197	1.0	84.1	0.173	0.173	0.173	0.986
						2.0	70.6	0.175			
						5.0	42.2	0.172			
						9.0	21.2	0.173			

From Fig. 1 can be seen that the straight line intersects the ordinate axis at 0.05 indicating that also another reaction is taking place, *viz.* a reaction between cyanic acid and water, see next section.

In Table 5 are listed some experiments on the temperature dependence of $k_{OCNH \cdot H_2O}^+$. Table 5 contains the velocity constants, k, calculated from the unimolecular expression. k represents a sum of $k_{OCNH \cdot H_2O}^+$ multiplied with the hydrogen ion concentration and k_{OCNH} (see next section), although the contribution of k_{OCNH} to k is small (about 2—5 %). The value of $k_{OCNH \cdot H_2O}^+$ was obtained dividing the difference between k and k_{OCNH} by the mean value of the hydrogen ion concentration. The values of $k_{OCNH \cdot H_2O}^+$ are 1.71 and 0.986 at 10°C and 4°C, respectively. These values give an average of 15.1 kcal . mole^{-1} for the energy of activation, calculated on the basis of the value of $k_{OCNH \cdot H_2O}^+$ at 18°C. Lister [3] has found the energy of activation to be 14.5 kcal mole^{-1}.

ON THE REACTION: $OCNH + H_2O \rightarrow NH_3 + CO_2$

In Table 6 are listed the experiments which were carried out at 18°C in solutions initially being 0.04 N with respect to nitric acid.

The decomposition takes place through the two simultaneous reactions:

$$OCNH + H_3O^+ \rightarrow NH_4^+ + CO_2 \quad (I)$$

and

$$OCNH + H_2O \rightarrow NH_3 + CO_2 \quad (II)$$
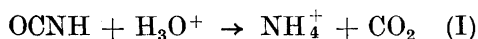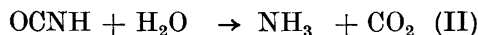
fololwed by the instantaneous reaction $NH_3 + H^+ = NH_4^+$. In more acid solution reaction I predominates but in the less acid solutions listed in Table 6 the velocity of reaction II is about a third of that for reaction I.

The velocity constant for reaction II is denoted k_{OCNH}.

Table 6. The velocity constant for the reaction $OCNH + H_2O \rightarrow NH_3 + CO_2$. 18°C.

Run	Initial solution				Min.	$c_{cyanate}$	k_{OCNH}	k_{OCNH} mean
	c_{H^+}	$c_{NO_3^-}$	c_{K^+}	$c_{cyanate}$				
5	0.0386	0.06	0.02	0.0198	2.0	0.0141	0.0414	
					4.0	0.0106	0.0345	
					6.0	0.0079	0.0391	0.0414
					10.0	0.0046	0.0414	
					15.0	0.0023	0.0461	
14	0.0396	0.06	0.02	0.0196	1.0	0.0164	0.0368	
					2.0	0.0138	0.0414	
					4.0	0.0101	0.0414	0.0414
					6.0	0.0076	0.0414	
					10.0	0.0043	0.0437	
					15.0	0.0021	0.0484	

$$k_{OCNH} = 0.0414$$

The concentration of hydrogen ion varies from approx. 0.04 to 0.02 meaning that practically all of the cyanate exists as cyanic acid and the amount being present as cyanate ion has been neglected in the calculations.

Let a denote the initial concentration of cyanic acid and x the amount decomposed at the time t. The initial concentration of hydrogen ion is denoted b. k_1 stands for $k_{OCNH \cdot H_2O^+}$ and k_2 for k_{OCNH}. For the decomposition of the cyanic acid we have: $dx/dt = (k_1 \cdot c_{H^+} + k_2)(a-x)$.

Introducing $c_{H^+} = b-x$ and integrating we get:

$$k_2 = 1/t \left[\ln \frac{a}{a-x} + \ln \frac{k_1(b-x) + k_2}{k_1 b + k_2} \right] - k_1(b-a).$$

Table 7. The temperature dependence of k_{OCNH}

Run	°C	Initial solution				Min.	$c_{cyanate}$	k_{OCNH}	k_{OCNH} mean
		c_{H^+}	$c_{NO_3^-}$	c_{K^+}	$c_{cyanate}$				
57	10.0	0.0412	0.06	0.02	0.0197	5.0	0.0132	0.0159	
						10.0	0.0092	0.0161	0.0157
						15.0	0.0068	0.0152	
58	4.0	0.0412	0.06	0.02	0.0197	7.0	0.0150	0.0025	
						15.0	0.0113	0.0021	0.003
						30.0	0.0067	0.0044	

The values for k_{OCNH} calculated from the above mentioned expression are also listed in Table 6.

In both experiments the mean value 0.041 for k_{OCNH} was obtained at 18°C. This value is in good agreement with the value 0.05 which was found from Fig. 1.

In Table 7 are listed a few experiments on the temperature dependence of k_{OCNH}, the value of which was calculated from the above mentioned expression inserting the value of $k_{OCNH \cdot H_2O}{}^+$ at the temperature in question. The value of k_{OCNH} is 0.0157 at 10°C corresponding to an anergy of activation of 19.9 kcal mole^{-1}. The value 0.003 found at 4°C is not very accurate since reaction I is by far the predominant at this temperature.

Further experiments on the determination of k_{OCNH} at 18°C were carried out in less acid solutions buffered with a weak acid and its salt. The ionic strength was adjusted to 0.2 by means of sodium nitrate and the samples were analysed for cyanate and ammonia.

For the rate of formation of ammonia we have:

$$\mathrm{d}c_{ammonia}/\mathrm{d}t = (k_{OCNH \cdot H_2O}{}^+ \cdot c_H{}^+ + k_{OCNH}) \cdot c_{OCNH}$$

Introducing $c_{OCNH} = c_{cyanate}/(1 + K_{OCNH}/a_H{}^+ \cdot f)$ and $c_H{}^+ = a_H{}^+/f$ we get:

$$\frac{\mathrm{d}c_{ammonia}}{\mathrm{d}t} = \frac{k_{OCNH \cdot H_2O}{}^+ \cdot a_H{}^+/f + k_{OCNH}}{1 + K_{OCNH}/a_H{}^+ \cdot f} \cdot c_{cyanate} = k \cdot c_{cyanate}$$

k_{OCNH} was calculated from the experimental value of k inserting the mean value of the hydrogen ion activity and the values 3.61 and $10^{-3.54}$ for $k_{OCNH \cdot H_2O}{}^+$ and K_{OCNH}, respectively.

The hydrogen ion activity was calculated from the expression $a_H{}^+ = K_a/f \cdot c_{HA}/c_{A^-}$, where c_{HA} and c_{A^-} denote the mean value of the concentration of the weak acid and its corresponding base, respectively. K_a is the acidic dissociation constant.

The experiments which were carried out in solutions containing chloroacetic acid and sodium chloroacetate are listed in Table 8. It is seen (runs 15 and 16) that the velocity of the decomposition is practically independent of the total amount of chloroacetic acid if the solutions have the same pH-value, i.e. chloroacetic acid shows no appreciable catalytic effect on the decomposition.

It is furthermore observed from Table 8 that the percentages of cyanate and ammonia do not correspond, the sum being less than 100 although the deviations are rather limited. This is probably due to a polymerisation of cyanic acid, cf. that a more concentrated solution of sodium cyanate upon addition of acetic acid yields a precipitate of a polymer.

Since the sum of cyanate and ammonia was not constant the value of k could not be calculated from the unimolecular expression but was obtained from $\Delta c_{ammonia} / \Delta t = k \cdot \bar{c}_{cyanate}$, where $\Delta c_{ammonia}$ is the increase in the concentration of ammonia in the time interval Δt and $\bar{c}_{cyanate}$ is the mean value of the cyanate concentration in that interval. In Table 8 are listed the values of k calculated in this way. There is some decrease in the values of

Table 8. The decomposition of cyanate at pH $= 2.3-3.0$. $c_{ion} = 0.2$. 18°C.

Run	Initial solution c_{HA}[1])	c_{A^-}[2])	$c_{cyanate}$	Min.	% cyanate	% ammonia	k	k mean	pH initial	pH mean	k_{OCNH}
17	0.15	0.02	0.02	2.0	87.4	14.5	0.077	0.067	2.17	2.25	0.0414
				4.0	75.3	23.4	0.055				
				6.0	65.0	33.6	0.073				
				15.0	35.0	61.7	0.062				
15	0.10	0.10	0.02	3.0	84.7	15.0	0.054	0.048	2.63	2.69	0.0484
				6.0	71.7	27.2	0.052				
				10.0	58.2	38.4	0.043				
				15.0	44.4	50.7	0.048				
				25.0	27.7	66.5	0.044				
16	0.06	0.06	0.02	3.0	85.4	15.5	0.056	0.046	2.62	2.70	0.0461
				6.0	73.0	25.5	0.042				
				10.0	60.4	36.7	0.042				
				15.0	47.4	48.6	0.044				
18	0.07	0.13	0.02	5.0	79.6	17.7	0.039	0.035	2.97	3.04	0.0461
				10.0	64.2	30.6	0.036				
				15.0	52.8	40.7	0.035				
				31.0	28.8	60.5	0.030				

[1]) HA $\sim$ CH$_2$ClCOOH
[2]) A$^-$ $\sim$ CH$_2$ClCOO$^-$

k during a run but this is probably mainly due to the variation in the hydrogen ion activity.

Table 8 also lists the values of k_{OCNH} calculated from the mean values of k.

It should be noted that the velocity of reaction II in the experiments listed in Table 8 is 1.5 to 10 times greater than the velocity of reaction I.

In Table 9 are listed some quite analogous experiments carried out in solutions containing acetic acid and sodium acetate. Also in this case no appreciable catalytic effect of the buffer was observed (runs 19 and 20). The discrepancy between the percentage of cyanate and ammonia is a little more pronounced than in the experiments carried out at pH $= 2.3-3.1$. The values for k_{OCNH} listed in Table 9 were calculated in the same manner as for those listed in Table 8.

It should be noted that the velocity of reaction I in the experiments listed in Table 9 is less than 1 % of the velocity of reaction II.

Table 10 shows the experiments which were carried out at 18°C with solutions containing sodium cyanate and sodium bicarbonate saturated with carbon dioxide at a pressure of 1 atmosphere. If there was no catalytic effect of the buffer, the rate of the decomposition should be proportional to the hydrogen

Table 9. The decomposition of cyanate at pH = 4.1—4.8. c_{ion} = 0.2. 18°C.

Run	Initial solution			Min.	% cyanate	% ammonia	k	k mean	pH initial	pH mean	k_{OCNH}
	c_{HA}[1])	c_{A^-}[2])	$c_{cyanate}$								
26	0.15	0.05	0.02	10	90.2	6.7	0.0070				
				20	83.2	12.2	0.0063	0.0062	4.12	4.18	0.0437
				40	70.3	22.2	0.0065				
				60	60.8	28.7	0.0049				
19	0.10	0.10	0.02	20	92.2	6.7	0.0035				
				40	85.3	11.6	0.0027				
				58	81.0	15.9	0.0029				
				99	70.6	23.6	0.0025	0.0026	4.57	4.67	0.0553
				174	56.4	34.9	0.0024				
				297	41.6	46.8	0.0020				
				557	23.0	64.3	0.0021				
				4 132	0						
20	0.06	0.06	0.02	20	92.3	[3])					
				57	80.9				4.56	4.67	
				98	72.7						
				179	58.9						
22	0.07	0.13	0.02	30	92.7	5.3	0.0018				
				60	87.1	9.7	0.0016				
				139	74.1	17.4	0.0012	0.0014	4.83	4.89	0.0484
				242	62.5	26.1	0.0012				
				279	59.0	28.5	0.0011				

[1]) HA $\sim$ CH$_3$COOH
[2]) A$^-$ $\sim$ CH$_3$COO$^-$
[3]) This run has not been analysed for ammonia.

ion activity, *i.e.* inverse proportional to the concentration of bicarbonate (the concentration of carbon dioxide is constant). The results in Table 10 show that the rate increases with increasing concentration of bicarbonate, *i.e.* bicarbonate acts catalytically on the decomposition of cyanate. The following rate expression is proposed:

$$\mathrm{d}c_{cyanate}/\mathrm{d}t = -(k' \cdot c_{HCO_3^-} \cdot c_{OCN^-} + k_{OCNH \cdot H_2O^+} \cdot c_{H^+} \cdot c_{OCNH} + k_{OCNH} \cdot c_{OCNH})$$

where k' is the velocity constant for the process catalyzed by bicarbonate.

Introducing $c_{OCNH} = 1/(1 + K_{OCNH}/a_{H^+} \cdot f) \cdot c_{cyanate} \sim a_{H^+} \cdot f/K_{OCNH} \cdot c_{cyanate}$ and neglecting the term $k_{OCNH \cdot H_2O^+} \cdot c_{H^+} \cdot c_{OCNH}$ which plays practically no part in this case, we get:

$$\mathrm{d}c_{cyanate}/\mathrm{d}t = -(k' \cdot c_{HCO_3^-} + k_{OCNH} \cdot a_{H^+} \cdot f/K_{OCNH}) \cdot c_{cyanate} = -k \cdot c_{cyanate}, \text{ or}$$

$$k \cdot K_{OCNH}/a_{H^+} \cdot f = (k' \cdot K_{OCNH}/a_{H^+} \cdot f) \cdot c_{HCO_3^-} + k_{OCNH} \cdot$$

Table 10. The decomposition of cyanate in carbon dioxide-bicarbonate buffer.
pH = 6.5 — 6.9. c_{ion} = 0.2. 18°C.

Run	Initial solution				Min.	% cyanate	% ammonia	k	k mean	pH mean	$c_{HCO_3^-}$ mean
	pH	c_{CO_2}	$c_{HCO_3^-}$	$c_{cyanate}$							
42	6.38	0.04	0.06	0.02	1 648	86.7	14.0	0.000091	0.000093	6.47	0.075
					3 270	67.9	25.4	0.000091			
					7 232	45.6	44.4	0.000084			
					10 077	32.7	56.0	0.000104			
					12 836	24.3	63.5	0.000095			
40	6.60	0.04	0.10	0.02	1 386	84.7	12.2	0.000095	0.000100	6.66	0.115
					3 107	69.7	25.4	0.000100			
					4 620	58.8	35.8	0.000107			
					5 977	50.7	43.2	0.000099			
					8 454	37.1	54.7	0.000106			
					11 666	26.8	65.5	0.000095			
44	6.82	0.04	0.16	0.02	1 526	82.9	15.4	0.000110	0.000124	6.86	0.178
					2 989	65.7	28.1	0.000117			
					4 581	55.9	41.4	0.000138			
					6 900	40.7	55.2	0.000123			
					9 770	27.8	67.1	0.000117			
					12 657	19.0	76.4	0.000137			

If the quantity $k \cdot K_{OCNH}/a_{H^+} \cdot f$ is plotted against the quantity $(K_{OCNH}/a_{H^+} \cdot f) \cdot c_{HCO_3^-}$ using mean values for the hydrogen ion activity and the bicarbonate ion concentration a straight line can be drawn. The slope of this line gives $k' = $ approx. 0.00060. The line intersects the ordinate axis at 0.062, *i.e.* the value of k_{OCNH} determined in this way is 0.062 which is in relatively good agreement with the value obtained in more acid solution.

It is seen from Table 10 (run 44) that the discrepancy between the percentages of cyanate and ammonia is not so pronounced as in the experiments at pH = 4.1—5.0. The values of k listed in Table 10 were calculated in the same manner as for those listed in Table 8.

The velocity constant, k_{OCNH}, for the reaction:

$$OCNH + H_2O \rightarrow NH_3 + CO_2$$
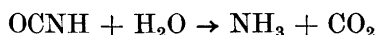
is 0.047 at 18°, which is the mean value for the determinations in this section.

THE DECOMPOSITION OF CYANATE IN STRONGLY BASIC MEDIUM

In Table 11 are listed the experiments which were carried out with solutions containing sodium cyanate and sodium hydroxide. Upon addition of sodium nitrate the initial ionic strength was adjusted to 0.2.

It is seen from Table 11 that the rate of the decomposition is independent of the hydroxyl ion concentration and identical with the rate of formation of ammonia.

Table 11. The decomposition of cyanate at pH = approx. 13. c_{ion} = 0.2.

Run	°C	Initial solution		Min.	% cyanate	% ammonia	k_{OCN^-}	k_{OCN^-} mean
		c_{NaOH}	$c_{cyanate}$					
49	94	0.18	0.018	66	89.0		0.00176	
				121	81.6		0.00169	
				212	70.4		0.00166	0.00171
				285	61.4		0.00171	
				420	48.2		0.00174	
				503	42.1		0.00172	
50	94	0.10	0.019	120	81.9		0.00166	
				301	60.2		0.00169	
				514	42.6		0.00166	0.00169
				617	34.5		0.00172	
				662	32.3		0.00171	
52	94	0.10	0.018	91		14.5	0.00172	
				242		34.4	0.00175	0.00170
				436		51.5	0.00166	
				571		61.8	0.00169	
54	82	0.10	0.020	277	85.3		0.000580	
				578	72.4		0.000562	
				1 346	45.9		0.000578	0.000571
				2 001	31.8		0.000573	
				2 773	20.8		0.000566	
53	70	0.10	0.019	531	91.4		0.000169	
				1 285	80.4		0.000170	
				2 049	71.6		0.000164	0.000170
				2 996	59.4		0.000174	
				4 247	47.8		0.000174	

Table 11 also lists the velocity constant, k_{OCN^-}, for the gross reaction:

$$OCN^- + 2H_2O \rightarrow NH_3 + HCO_3^- \quad (III)$$

calculated from the expression for an unimolecular reaction. The mean value of k_{OCN^-} is 0.00170 at 94°C, 0.000571 at 82°C and 0.000170 at 70°C.

The mean value of the energy of activation for the reaction is 23.9 kcal mole^{-1} calculated on the basis of the value of k_{OCN^-} at 94°C. The value determined by Lister [3] is 23.4 kcal mole^{-1}.

By extrapolation the value $10^{-6.48}$ for k_{OCN^-} is obtained at 18°C.

It should be added that the reactions I and II are too slow to take any appreciable part in the decomposition in strongly basic medium. On the other hand reaction III can be neglected in the more acid solutions investigated in the preceding sections.

REFERENCES

1. Taufel, K., Wagner, C. and Dunwald, H. *Z. Electrochem.* **34** (1928) 115.
2. Masson, O. and Masson, I. *Z. physik. Chem.* **70** (1910) 290.
3. Lister, M. W. *Can. J. Chem.* **33** (1955) 426.
4. Amell, A. R. *J. Am. Chem. Soc.* **78** (1956) 6234.
5. Kemp, I. A. and Kohnstam, G. *J. Chem. Soc.* **1956** 900.
6. Wright, D. D. *J. Am. Chem. Soc.* **56** (1934) 314.
7. Noyes, A. A., Kato, Y. and Sosman, R. B. *Z. physik. Chem.* **73** (1910) 1.
8. Harned, H. S. and Davis, R. *J. Am. Chem. Soc.* **65** (1943) 2030.