

## On the Kinetics of the Decomposition of Cyanic Acid

## II. The Carbonate Catalysis

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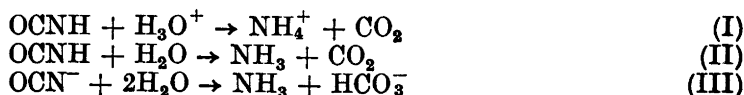
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The uncatalyzed decomposition of cyanate in dilute aqueous solution takes place according to the reactions:  $\text{OCNH} + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{CO}_2$  (I),  $\text{OCNH} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$  (II) and  $\text{OCN}^- + 2\text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{HCO}_3^-$  (III). Reaction III has been shown to be catalyzed by bicarbonate ion:  $\text{OCN}^- + 2\text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{HCO}_3^-$  (catalyzed by  $\text{HCO}_3^-$ ) (IV). The results can also be interpreted in that way that reaction II is catalyzed by carbonate ion:  $\text{OCNH} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$  (catalyzed by  $\text{CO}_3^{--}$ ) (V). The rate expression for the decomposition of cyanate in the presence of carbonate ( $\text{HCO}_3^-$  or  $\text{CO}_3^{--}$ ) is:  $d\text{OCN}^-/dt = -(k\text{OCNH} \cdot a_{\text{H}^+} \cdot f / K\text{OCNH} + k\text{OCN}^- + k' \cdot c_{\text{HCO}_3^-}) \cdot \text{OCN}^- = -(k\text{OCNH} + k\text{OCN}^- \cdot K\text{OCNH} / a_{\text{H}^+} \cdot f + k'' \cdot c_{\text{CO}_3^{--}}) \cdot \text{OCN}^-$ . In this expression  $k'$  and  $k''$  are the velocity constants for reactions IV and V, respectively.  $k''$  is equal to  $k' \cdot K\text{OCNH} / K\text{HCO}_3^-$ , where  $K\text{OCNH}$  is the acidic dissociation constant for cyanic acid and  $K\text{HCO}_3^-$  is the acidic dissociation constant for the bicarbonate ion.  $k\text{OCNH}$  ( $0.047 \text{ min}^{-1}$ ) at  $18^\circ\text{C}$ ) and  $k\text{OCN}^-$  ( $10^{-6.46} \text{ min}^{-1}$ ) at  $18^\circ\text{C}$ ) are the previously determined velocity constants for reactions II and III, respectively.  $f$  is an activity coefficient.

The uncatalyzed decomposition will take place mainly according to reactions II and III in solutions where the carbonate catalysis is appreciable. The decomposition after I has therefore been disregarded in the above stated expression. (The velocity constant for reaction I is  $3.61 \text{ l mole}^{-1} \text{ min}^{-1}$ ) at  $18^\circ\text{C}$ ).

$k'$  ( $\text{l mole}^{-1} \text{ min}^{-1}$ ) was found to be  $4.76 \times 10^{-4}$  ( $18^\circ\text{C}$ ),  $9.21 \times 10^{-4}$  ( $25^\circ\text{C}$ ) and  $76.2 \times 10^{-4}$  ( $50^\circ\text{C}$ ) yielding an energy of activation of  $16.2 \text{ kcal mole}^{-1}$ . The corresponding value of  $k''$  is  $10^{3.54}$  ( $\text{l mole}^{-1} \text{ min}^{-1}$ ) at  $18^\circ\text{C}$ .

In a previously published paper<sup>1</sup> the decomposition of cyanic acid and cyanate in dilute aqueous solution was found to take place according to three simultaneous reactions:



In the experiments carried out in carbon dioxide-bicarbonate buffers at pH = approx. 6.7 it was observed that the decomposition was catalyzed by the bicarbonate ion. In this pH-range the uncatalyzed decomposition will take place mainly according to reaction II. The rate in the presence of bicarbonate was found to be

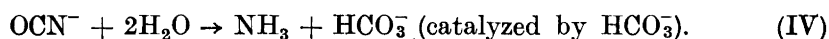
$$dc_{\text{OCN}^-}/dt = -(k_{\text{OCNH}} \cdot a_{\text{H}^+} \cdot f/K_{\text{OCNH}} + k' \cdot c_{\text{HCO}_3^-}) \cdot c_{\text{OCN}^-} \quad (1)$$

Eqn. (1) can also be written

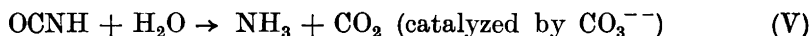
$$dc_{\text{OCN}^-}/dt = -(k_{\text{OCNH}} + k'' \cdot c_{\text{CO}_3^{--}}) \cdot c_{\text{OCNH}} \quad (2)$$

$$\text{where } k'' = k' \cdot K_{\text{OCNH}}/K_{\text{HCO}_3^-}.$$

$k_{\text{OCNH}}$  is the velocity constant for reaction II.  $f$  is an activity coefficient.  $K_{\text{OCNH}}$  and  $K_{\text{HCO}_3^-}$  are the acidic dissociation constants for cyanic acid and for the bicarbonate ion, respectively.  $k'$  is the velocity constant for the reaction



Reaction IV can also be written



$k''$  is the velocity constant for reaction V. The experiments do not give any information about the actual reaction being IV or V. The value of  $k'$  was previously found to be approx. 0.0006 at 18°C.

The present investigation deals with the decomposition of cyanate in the presence of bicarbonate or carbonate, or both, under more varied conditions.

The method of analysis was the same as has been used previously, *viz.* an argentometric titration of the cyanate.

The velocity constants refer to molar concentration, the unit of time being the minute. The solutions were prepared at room temperature.

Sodium Cyanate Pure (Hopkin and Williams Ltd.) was used for the experiments. The salt was found to contain only a slight trace of carbonate.

## RESULTS

The experiments on the decomposition of cyanate in solutions containing bicarbonate (pH = approx. 8.4) are listed in Table 1. The solution contained both carbonate and bicarbonate (pH = approx. 10) in runs 4 and 9.

The uncatalyzed decomposition will take place mainly according to reactions II and III in this pH-range. The rate expression may be written

$$dc_{\text{OCN}^-}/dt = -(k_{\text{OCNH}} \cdot a_{\text{H}^+} \cdot f/K_{\text{OCNH}} + k_{\text{OCN}^-} + k' \cdot c_{\text{HCO}_3^-}) \cdot c_{\text{OCN}^-} \quad (3)$$

identical with

$$dc_{\text{OCN}^-}/dt = -(k_{\text{OCNH}} + k_{\text{OCN}^-} \cdot K_{\text{OCNH}}/a_{\text{H}^+} \cdot f + k'' \cdot c_{\text{CO}_3^{--}}) \cdot c_{\text{OCNH}} \quad (4)$$

Table 1. The velocity constant,  $k'$ , for the reaction:  $\text{OCN}^- + 2\text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{HCO}_3^-$  (catalyzed by  $\text{HCO}_3^-$ ).

Run	°C	Initial solution			$t$ min.	% $\text{OCN}^-$ left	$k$	$k' = \frac{k}{c_{\text{HCO}_3^-}}$
		$c_{\text{HCO}_3^-}$	$c_{\text{CO}_3^{2-}}$	$c_{\text{OCN}^-}$				
1	18	0.108		0.021	1 430	92.5	0.0000540	0.000482
					7 499	67.2	0.0000532	
					14 246	47.1	0.0000529	
					18 391	38.0	0.0000526	
mean:							0.0000532	
2	18	0.179		0.020	1 313	89.7	0.0000828	0.000470
					3 076	76.7	0.0000861	
					7 467	53.0	0.0000850	
					14 169	29.8	0.0000855	
mean:							0.0000878	
mean:							0.0000854	
3	25	0.188		0.020	1 185	81.9	0.000169	0.000911
					2 690	62.9	0.000172	
					4 365	46.5	0.000176	
					5 647	36.8	0.000177	
mean:							0.000174	
mean:							0.000174	
4	25	0.100	0.050	0.019	1 299	88.2	0.0000961	0.000931
					4 051	67.6	0.0000966	
					7 046	50.1	0.0000979	
					11 211	32.4	0.0001006	
mean:							0.0000978	
9	50	0.100	0.050	0.020	162	87.8	0.000799	0.00762
					292	79.7	0.000780	
					405	72.2	0.000805	
					1 508	26.2	0.000890	
mean:							0.000818	

$k'$  (mean): 0.000476 (18°C) 0.000921 (25°C) 0.00762 (50°C).

$k_{\text{OCN}^-}$  is the velocity constant for reaction III. The velocity of the uncatalyzed decomposition, however, is negligible in comparison with that of the catalyzed in the experiments listed in Table 1. Consequently eqn. (3) will be reduced to

$$dc_{\text{OCN}^-}/dt = -k' \cdot c_{\text{HCO}_3^-} \cdot c_{\text{OCN}^-} = -k \cdot c_{\text{OCN}^-}.$$

The concentration of bicarbonate is approximately constant during each experiment and  $k$  was obtained from the expression for a unimolecular reaction:  $k \cdot t = \ln a/a-x$ .  $k$  and  $k'$  are listed in Table 1 ( $k' = k/c_{\text{HCO}_3^-}$ ).  $k'$

is 0.000476 (18°C), 0.000921 (25°C) and 0.00762 (50°C). The energy of activation is 16.2 kcal mole<sup>-1</sup> calculated from the data at 18°C and 25°C, and 16.1 kcal mole<sup>-1</sup> calculated from the data at 25°C and 50°C. The corresponding value of  $k''$  is 10<sup>3.54</sup> at 18°C. The values 10<sup>-3.54</sup> (Ref.<sup>1</sup>) and 10<sup>-10.40</sup> (Ref.<sup>2</sup>) for  $K_{\text{OCNH}}$  and  $K_{\text{HCO}_3^-}$ , respectively, have been used.  $k' = 0.000476$  at 18°C is in a relatively good agreement with 0.0006 found previously in the above mentioned experiments in more acid solution.

It should be noted that ammonium ions are formed during the process, *i.e.* the gross reaction:  $\text{NH}_4^+ + \text{OCN}^- \rightarrow \text{NH}_2 \cdot \text{CO} \cdot \text{NH}_2$  will also occur in solutions containing initially only cyanate. From the velocity constant for this reaction (0.000577 at 18°C<sup>3</sup>) can be estimated that only a small amount of urea is formed in the experiments listed in Table 1 (the concentration of  $\text{NH}_4^+$  does not exceed 0.02).

The experiments on the decomposition of cyanate in strongly alkaline solutions of sodium carbonate and sodium hydroxide are listed in Table 2.

We get

$$\begin{aligned} dc_{\text{OCN}^-}/dt &= -(k_{\text{OCNH}} \cdot a_{\text{H}^+} \cdot f/K_{\text{OCNH}} + k_{\text{OCN}^-} + k' \cdot c_{\text{HCO}_3^-}) \cdot c_{\text{OCN}^-} \simeq \\ &\quad -(k_{\text{OCN}^-} + k' \cdot c_{\text{HCO}_3^-}) \cdot c_{\text{OCN}^-} = \\ &\quad -(k_{\text{OCN}^-} + (k' \cdot K_{\text{H}_2\text{O}}/K_{\text{HCO}_3^-}) \cdot c_{\text{CO}_3^{--}}/c_{\text{OH}^-}) \cdot c_{\text{OCN}^-} \end{aligned}$$

if we assume that the decomposition still takes place in accordance with eqn. (3). (The term  $k_{\text{OCNH}} \cdot a_{\text{H}^+} \cdot f/K_{\text{OCNH}}$  is without significance in strongly alkaline solution).

Substituting  $p = k' \cdot K_{\text{H}_2\text{O}}/K_{\text{HCO}_3^-}$  we get

$$dc_{\text{OCN}^-}/dt = -(k_{\text{OCN}^-} + p \cdot c_{\text{CO}_3^{--}}/c_{\text{OH}^-}) \cdot c_{\text{OCN}^-} \quad (5)$$

or

$$dc_{\text{OCN}^-}/dt = -k \cdot c_{\text{OCN}^-}$$

where  $k = k_{\text{OCN}^-} + p \cdot c_{\text{CO}_3^{--}}/c_{\text{OH}^-}$ .

The concentration of carbonate and hydroxyl ion is approximately constant during each experiment. The values of  $k$  listed in Table 2 were hence calculated from the expression for a unimolecular reaction.

The experimental results in Table 2 show clearly that  $k$  depends not only upon the concentration of carbonate ion but also upon the concentration of hydroxyl ion as required from eqn. (5). The values of  $p$  calculated from  $p = (k - k_{\text{OCN}^-}) \cdot c_{\text{OH}^-}/c_{\text{CO}_3^{--}}$  are also listed in Table 2 ( $k$ ,  $c_{\text{OH}^-}$  and  $c_{\text{CO}_3^{--}}$  are mean values). The previously determined values 0.00170 at 94°C and 0.000170 at 70°C for  $k_{\text{OCN}^-}$  have been used. Although the difference between  $k$  and  $k_{\text{OCN}^-}$  is rather small a fairly constant value for  $p$  is obtained in runs 5, 6, and 11 yielding the mean value 0.00031 for  $p$  at 94°C. The value found in run 7 has been disregarded. The difference between  $k$  and  $k_{\text{OCN}^-}$  is very small in this run ( $c_{\text{OH}^-} = 0.2$ ). At 70°C the value 0.000032 was found for  $p$ .

Run 8 shows that the addition of sulfate instead of carbonate has very little influence on the velocity. Run 12 shows that the velocity in strongly alkaline medium is not affected by the addition of ammonia (0.1 M).

Table 2. The decomposition of  $\text{OCN}^-$  in  $\text{NaOH} + \text{Na}_2\text{CO}_3$ .

Run	°C	Initial solution					t min.	% $\text{OCN}^-$ left	k	$p =$ $(k - k_{\text{OCN}^-})$ $\times \frac{c_{\text{OH}^-}}{c_{\text{CO}_3^{--}}}$ *
		$c_{\text{OH}^-}$	$c_{\text{CO}_3^{--}}$	$c_{\text{NH}_3}$	$c_{\text{SO}_4^{--}}$	$c_{\text{OCN}^-}$				
11	94	0.040	0.070			0.018	83	82.5	0.00231	0.00034
							220	57.9	0.00248	
							306	46.9	0.00247	
							403	35.4	0.00258	
								mean:		
								0.00246		
5	94	0.100	0.070			0.020	121	79.1	0.00194	0.00030
							265	59.4	0.00197	
							368	49.5	0.00191	
							525	36.7	0.00191	
								mean:		
								0.00194		
6	94	0.100	0.150			0.019	120	78.2	0.00205	0.00030
							280	54.2	0.00219	
							392	41.0	0.00227	
							430	37.5	0.00228	
								mean:		
								0.00220		
7	94	0.200	0.070			0.019	174	73.9	0.00174	(0.00016)
							329	55.8	0.00177	
							392	50.4	0.00175	
							493	41.5	0.00178	
								mean:		
								0.00176		
8	94	0.100			0.150	0.020	158	77.2	0.00164	
							252	65.7	0.00167	
							336	57.7	0.00164	
							1 139	14.2	0.00171	
								mean:		
								0.00167		
12	94	0.180		0.10		0.018	76	88.1	0.00167	
							141	77.9	0.00178	
							207	70.2	0.00171	
							362	55.6	0.00162	
								mean:		
								0.00171		
10	70	0.100	0.149			0.019	1 189	76.7	0.000223	0.000032
							1 534	71.0	0.000222	
							2 625	56.2	0.000219	
							4 339	37.8	0.000225	
								**		
								mean:		
								0.000222		

\*  $k_{\text{OCN}^-}$  (0.00170 at 94°C 0.000170 at 70°C) is the velocity constant for the uncatalyzed reaction.

\*\* In this run the ammonia was distilled from the filtrate from the silver cyanate and titrated. The following percentages of ammonia were found: 22.0 29.1 44.0 62.7.

An extrapolation from the data at 94°C and 70°C gives  $p = 3.8 \times 10^{-6}$  at 50°C.  $k'$  calculated from this value of  $p$  by means of  $k' = p \cdot K_{\text{HCO}_3^-} / K_{\text{H}_2\text{O}}$  is 0.0047 (for  $K_{\text{HCO}_3^-} = 6.73 \times 10^{-11}$  (Ref.<sup>2</sup>)) or 0.0062 (for  $K_{\text{HCO}_3^-} = 8.98 \times 10^{-11}$  \*); cf. the value 0.00762 found in run 9 (Table 1). In view of the small differences on which this calculation is based the agreement between  $k'$  calculated from  $p$  and  $k'$  found in run 9 is regarded as satisfactory. This means that eqn. (3) (or eqn. (4)) accounts for the catalyzed decomposition as well in moderately acid or basic medium as in strongly basic medium.

#### DISCUSSION

The catalytic effect of carbonate on the decomposition of cyanate was first observed by Masson and Masson<sup>6</sup> who found the formation of carbonate from sodium cyanate to be autocatalytic. More recently Lister<sup>7</sup> and Kemp and Kohnstam<sup>8</sup> have examined the carbonate catalysis.

Lister finds that the decomposition of cyanate conforms to the equation

$$dc_{\text{OCN}^-}/dt = -(k_1' \cdot c_{\text{OCN}^-} + k_2' \cdot c_{\text{CO}_3^{--}})$$

in solutions containing sodium carbonate and approximately equal moles of sodium hydroxide and sodium cyanate. This near-equality will hold throughout the reaction (the gross reaction is:  $\text{OCN}^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_3^{--}$ ). Eqn. (5) in this case takes the form

$$dc_{\text{OCN}^-}/dt = -(k_{\text{OCN}^-} \cdot c_{\text{OCN}^-} + p \cdot c_{\text{CO}_3^{--}})$$

*i.e.* eqn. (5) is under the stated experimental conditions consistent with the expression of Lister. Lister has  $k_2'$  ( $= p$ ) =  $6.2 \times 10^{-4}$  at 100°C. An extrapolation to 100°C from the data listed in Table 2 gives  $p = 5.2 \times 10^{-4}$ .

The expression proposed by Kemp and Kohnstam is in agreement with eqn. (3). At 60.1°C Kemp and Kohnstam have  $k' = 0.0175$ , which agrees well with  $k' = 0.0164$  obtained by extrapolation from the data listed in Table 1.

The author wishes to thank Professor, Dr. phil. Carl Faurholt for his very kind interest in this investigation.

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\*  $K_{\text{HCO}_3^-} = 8.98 \times 10^{-11}$  at 50°C was obtained by extrapolation from  $5.70 \times 10^{-11}$  at 25°C and  $7.15 \times 10^{-11}$  at 37°C<sup>4</sup>.  $K_{\text{H}_2\text{O}} = 5.47 \times 10^{-14}$  has been used at 50°C<sup>5</sup>.