[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LEBANON VALLEY COLLEGE]

# Kinetics of the Hydrolysis of Cyanic Acid

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The rate of hydrolysis of cyanic acid has been determined by measuring the rate of addition of standard hydrochloric acid to maintain a constant *p*H. The rate equation may be expressed as $R_0 = k_1(\mathrm{HOCN}) + (k_2/K_w)(\mathrm{HOCN})^2(\mathrm{OH}^-)$. The reaction intermediates are carbamic acid and a dimer of cyanic acid. No salt effect was found, but the conditions of the experiment may have minimized a salt effect. Studies were made at 20, 28 and 35°. The free energy of ionization of cyanic acid has been determined as 5.0 kcal./mole.

The hydrolysis of cyanic acid in acid solution to give $CO_2$ and $NH_4^+$ has been long recognized. However, kinetic studies made on the reaction are incomplete.[2]

## Experimental

**Materials.**—Solid potassium cyanate reacts with moisture in the air to form potassium carbonate and ammonia. Bottles of the reagent which have been on the shelf for some time smell strongly of ammonia when opened. Addition of $Ba^{++}$ to an aqueous solution of the reagent forms a precipitate of barium carbonate. X-Ray analysis of such samples shows a large % of carbonate. However, newly purchased potassium cyanate does not indicate any carbonate upon X-ray analysis, does not smell of ammonia, and no precipitate is formed upon addition of $Ba^{++}$ to a fresh aqueous solution.

In preliminary experiments three specimens of cyanate were used: (1) C.P. potassium cyanate without any preliminary treatment; (2) C.P. potassium cyanate recrystallized from alcohol and water; (3) potassium cyanate prepared from urea and potassium carbonate.[3] All three samples were stored in a desiccator. The reactions of all appeared identical and so studies were carried out on the C.P. sample without any further treatment.

All other reagents used were C.P. grade used without any further purification. Distilled water was used throughout.

Measurements of *p*H were made with a Beckman Model G *p*H meter with glass-calomel electrodes. The meter was standardized against commercial buffers of *p*H 4.0.

**Analytical Method.**—The stoichiometry of the reaction is shown by the equation

$$OCN^- + 2H^+ + H_2O = CO_2 + NH_4^+$$

The ratio of $H^+$ to $OCN^-$ was checked by adding a weighed sample of potassium cyanate to an excess of standard acid. The solutions were allowed to stand overnight. The excess acid was titrated with standard base. Results are given in Table I. Two moles of acid is used for each mole of cyanate, corresponding to the stoichiometry above. The reaction is complete as written and the formation of urea from $NH_4^+$ and $OCN^-$ does not occur rapidly enough under the conditions of the reaction to change the stoichiometry.

TABLE I

RATIO OF $H^+$ TO $OCN^-$ USED DURING HYDROLYSIS

| Moles $OCN^-$ $\times 10^3$ | Moles $H^+ \times 10^3$ | Moles $H^+$/mole $OCN^-$ |
|---|---|---|
| 3.25 | 6.56 | 2.02 |
| 2.15 | 4.30 | 2.00 |
| 3.60 | 7.20 | 2.00 |
| 4.67 | 9.11 | 1.95 |
| 3.76 | 7.42 | 1.98 |

Kjeldahl determinations were run upon hydrolyzed samples of cyanate to determine the nitrogen content. The $OCN^-$ to N ratio does not indicate anything concerning the reaction since total nitrogen is determined. The theoretical amounts of N were recovered.

The first experiments were followed by the evolution of $CO_2$ from the system. These were abandoned for two reasons: the reaction is so fast that it was felt that the limiting factor might be the evolution of the $CO_2$ and not the hydrolysis, and since there are two moles of $H^+$ used for each mole of $OCN^-$ it was difficult to maintain a constant *p*H, even in a buffered system. It is important that a constant *p*H be maintained because of the critical nature of the *p*H upon the reaction.

Attempts to follow the reaction by the precipitation of the $OCN^-$ as AgOCN were abandoned because of the solubility of the AgOCN and the *p*H change.

Some runs were made by titrating to determine the change in acidity of the sample. In a buffered system the total change is small and the procedure is subject to much error.

A modification of a procedure of Pearson and Piette[4] was finally used. Standard HCl solution was added to the reaction vessel at a rate such that the *p*H was maintained constant. The rate of addition of the HCl can be used to determine the rate of the reaction, as shown below.

The standard HCl was added from either a 50-ml. buret or a 5-ml. buret. The volumes of acid used were between 19 and 40 ml. with the 50-ml. buret and about 4 ml. with the 5-ml. buret, although a few runs were outside of these limits. The normality of the acids varied from 0.01 to 0.5 *N* depending upon the amount of cyanate used.

All reactions were in vessels immersed in a water-bath. The temperature was controlled by a mercury thermal regulator and was constant to within 0.03°. The electrodes of the *p*H meter were immersed in the reaction vessel. A glass stirrer in the reaction vessel ensured complete and rapid stirring during the reaction.

**Procedure.**—The KOCN was added to the reaction vessel containing water at the temperature of the reaction. With rapid stirring the sample would dissolve in 15 to 20 seconds. Standard HCl was then added rapidly to the vessel to bring the *p*H of the solution to the desired value. This addition took from 5 to 10 seconds. The HCl was then added at a rate necessary to keep the *p*H constant. Buret readings were taken as a function of time. After the reaction had proceeded through approximately two half-lifes the temperature was raised to 45-50° to complete the reaction. The total amount of HCl used enabled a calculation of the original concentration of cyanate to be made.

In some experiments weighed quantities of dried NaCl were dissolved in the water before the KOCN was added to study the salt effect on the reaction.

## Results

At a constant *p*H the rate of addition of the HCl is proportional to the rate of hydrolysis. The proportionality constant is found as follows:

Let: $M_t$ = moles of HCl added at time $t$
$M_\infty$ = moles of HCl added at completion of reaction
$M_0$ = moles of HCl added to reach desired *p*H = initial moles of HOCN
$V_t$ = total vol. of HCl added at time $t$
$K_c = \dfrac{(H^+)(OCN^-)}{(HOCN)}$

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[1] Chemistry Department, University of New Hampshire, Durham, New Hampshire.

[2] (a) O. and I. Masson, *Z. physik. Chem.*, **70**, 290 (1910); (b) E. A. Werner, *J. Chem. Soc.*, **113**, 84 (1918); (c) W. R. Fearon and G. C. Dockeray, *Biochem. J.*, **20**, 13 (1926); (d) P. A. H. Wyatt and H. L. Kornberg, *Trans. Faraday Soc.*, **48**, 454 (1952).

[3] "Inorganic Syntheses," Vol. II, McGraw-Hill, Inc., New York, N. Y., 1946. p. 86.

[4] R. G. Pearson and L. H. Piette, THIS JOURNAL, **76**, 3087 (1954).

TABLE II

INITIAL RATE AS A FUNCTION OF INITIAL CONCENTRATION OF CYANATE[a]

Temperature 35°

| pH | 4.0 | | | 4.1 | | | 4.2 | | | 4.3 | | | 4.4 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $c_0$ | $R_0$ | $V_\infty$ | $C_0$ | $R_0$ | $V_\infty$ | $C_0$ | $R_0$ | $V_\infty$ | $C_0$ | $R_0$ | $V_\infty$ | $C_0$ | $R_0$ | $V_\infty$ |
| 0.18 | 0.9 | 19.0 | 0.18 | 0.8 | 19.0 | 0.18 | 0.7 | 19.0 | 0.18 | 0.5 | 19.0 | 0.18 | 0.4 | 19.0 |
| 0.54 | 3.0 | 19.3 | 0.54 | 2.5 | 19.3 | 0.54 | 2.1 | 19.3 | 0.54 | 1.7 | 19.3 | 0.54 | 1.4 | 19.3 |
| 1.09 | 6.3 | 21.4 | 1.03 | 4.9 | 22.0 | 1.09 | 4.3 | 21.4 | 1.09 | 3.7 | 21.4 | 1.09 | 3.1 | 21.4 |
| 1.35 | 8.0 | 38.6 | 1.07 | 5.0 | 23.0 | 1.35 | 5.5 | 38.6 | 1.35 | 4.7 | 38.6 | 1.35 | 4.1 | 38.6 |
| 1.97 | 13.2 | 26.5 | 1.09 | 5.5 | 21.4 | 1.97 | 9.3 | 26.5 | 1.97 | 7.9 | 26.5 | 1.97 | 6.3 | 26.5 |
| 2.11 | 14.6 | 38.0 | 1.35 | 6.9 | 38.6 | 2.11 | 9.3 | 38.0 | 4.26 | 21.7 | 20.8 | 2.11 | 7.0 | 38.0 |
| 2.73 | 19.1 | 48.9 | 1.97 | 11.2 | 26.5 | 4.14 | 22.8 | 20.2 | 5.75 | 31.0 | 28.0 | 4.45 | 19.6 | 21.7 |
| 3.56 | 24.2 | 17.4 | 2.10 | 11.8 | 45.0 | 6.30 | 40.3 | 30.7 | 10.6 | 81.6 | 51.6 | 6.35 | 30.5 | 31.0 |
| 4.00 | 28.4 | 19.5 | 5.70 | 42.7 | 27.8 | 6.78 | 42.0 | 33.1 | 12.1 | 109 | 59.0 | 6.89 | 31.7 | 33.6 |
| 4.77 | 36.8 | 23.3 | 7.69 | 67.0 | 37.5 | 7.17 | 47.4 | 35.1 | | | | 7.17 | 35.2 | 35.1 |
| 4.80 | 37.0 | 23.4 | 9.53 | 88.5 | 46.5 | | | | | | | | | |
| 6.25 | 55.0 | 30.5 | | | | | | | | | | | | |
| 7.17 | 66.7 | 35.1 | | | | | | | | | | | | |

Temperature 28°

| $C_0$ | $V_\infty$ | $R_0$ | | | $C_0$ | $V_\infty$ | $R_0$ | | |
|---|---|---|---|---|---|---|---|---|---|
| pH | | 4.0 | 4.1 | 4.2 | | | 4.0 | 4.1 | 4.2 |
| 0.18 | 3.87[b] | 0.5 | 0.5 | 0.4 | 4.51 | 22.0 | 21.2 | | |
| 0.49 | 18.5 | 1.6 | 1.3 | 1.2 | 5.54 | 27.0 | 27.1 | | |
| 0.97 | 19.0 | 3.3 | 2.9 | 2.2 | 5.62 | 27.4 | | 25.3 | |
| 2.01 | 19.6 | 7.6 | 6.6 | 5.2 | 6.50 | 31.7 | | 30.5 | |
| 2.01 | 9.8 | 6.4 | | | 6.91 | 33.7 | | 33.9 | |
| 2.19 | 10.7 | 8.1 | | | 7.60 | 37.2 | 41.0 | 38.0 | 30.4 |
| 4.04 | 19.7 | | | 12.5 | 8.40 | 41.0 | | 42.8 | |

Temperature 20°

| $C_0$ | $V_\infty$ | $R_0$ 3.8 | 4.0 |
|---|---|---|---|
| 0.21 | 45.3 | 0.7 | 0.5 |
| 0.85 | 18.1 | 2.8 | 1.8 |
| 2.14 | 46.0 | 6.8 | 5.1 |
| 2.22 | 47.6 | 6.8 | 5.0 |
| 4.32 | 42.1 | 14.8 | 11.0 |
| 7.14 | 28.8 | 25.1 | 20.4 |
| 7.72 | 31.2 | 25.8 | 21.0 |

[a] Rates are given as (moles liter$^{-1}$ min.$^{-1}$) × $10^4$ and concentrations in (moles liter$^{-1}$ × $10^2$). $V_\infty$ is total volume of HCl used in reaction. [b] Delivered from 5-ml. buret.

Since $M_\infty/2$ is the total cyanate present at time 0

$$\frac{K_c}{(H^+)} = \frac{\frac{M_\infty}{2} - M_0}{M_0} \tag{1}$$

The HCl that is added reacts in two ways: (1) to combine with $OCN^-$ to form HOCN; (2) to neutralize the $NH_3$ formed in the hydrolysis. For each mole of $NH_4^+$ formed a total of one mole of cyanic acid and cyanate ion has disappeared.

$$-d(NH_4^+) = d(HOCN) + d(OCN^-) \tag{2}$$

The ratio of the decrease in HOCN to $OCN^-$ can be determined from the ionization constant $K_c$

$$\frac{K_c d}{(H^+)}(HOCN) = d(OCN^-) \tag{3}$$

$$-d(NH_4^+) = \frac{K_c d(HOCN)}{(H^+)} + d(HOCN) \tag{4}$$

Since two moles of HCl is used for each mole of $OCN^-$ that disappears but only one for each mole of HOCN

$$-d(M_t - M_0) = \frac{2K_c}{(H^+)} dM_{HOCN} + dM_{HOCN} \tag{5}$$

$$-dM_{HOCN} = \frac{(H^+)}{(H^+) + K_c} dM_{NH_4^+} = \frac{(H^+)}{(H^+) + 2K_c} d(M_t - M_0) \tag{6}$$

Thus, at time $t$

$$M_{HOCN} = M_0 - \frac{(H^+)}{(H^+) + 2K_c}(M_t - M_0) \tag{7}$$

Eliminating $M_0$ between (1) and (7)

$$M_{HOCN} = \frac{(H^+)}{(H^+) + 2K_c}(M_\infty - M_t) \tag{8}$$

Starting with 100 ml. of solution at time 0, at time $t$

$$(HOCN) = \frac{(H^+)(M_\infty - M_t)}{[(H^+) + 2K_c](100 + V_t)} \tag{9}$$

From (6) and (9)

$$R = \frac{d(NH_4^+)}{dt} = -\left(\frac{(H^+) + K_c}{(H^+) + 2K_c}\right) d\left(\frac{M_\infty - M_t}{100 + V_t}\right)/dt \tag{10}$$

The rate of the reaction can be determined by graphing $(M_\infty - M_t)/(100 + V_t)$ *vs.* $t$ and obtaining the slope of the curve. A sample plot is given in Fig. 1. The values of $K_c$ used were obtained from (1) and are given below. Data for the initial rates obtained are given in Table II. The initial rates determined in this way were found to agree with rates determined from the product of the initial concentration of cyanate and the initial first-order rate constant determined graphically.

The log of $R_0$ was plotted *vs.* log $c_0$, the total initial concentration of cyanate. A line with a slight curvature, and a slope changing from 1 to 1.3 was obtained. This suggested that the reaction might be first order in cyanate. However, first-order plots deviated from a straight line and the first-order rate constants determined from the data indicated a linear dependence on the initial concentration with a positive intercept. This dependence might be explainable if the reaction were second order. Second-order plots deviated from a straight line and the rate constants calculated on the basis of second-order dependence again showed a dependence on initial concentration. Because of this and the positive intercept the second-order reaction was eliminated.

It is possible that the dependence is not on initial cyanate concentration but upon ionic strength. To change the ionic strength independently of the cyanate concentration, NaCl was added to some solutions before the start of the reactions. Results

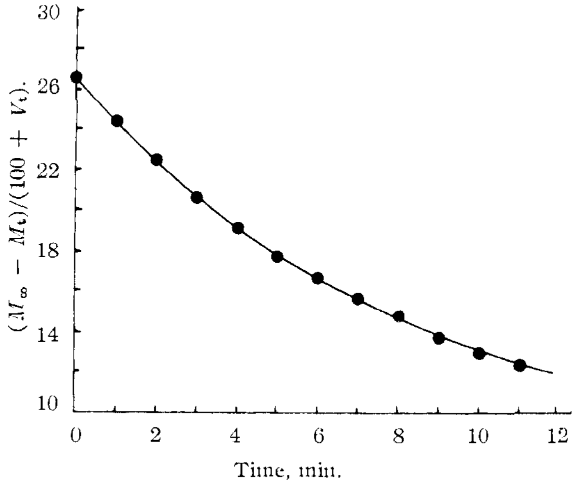

Fig. 1.—Determination of initial rate.

are given in Table III. It is obvious that the rates are dependent upon the cyanate concentration and not upon the ionic strength.

TABLE III

EFFECT OF IONIC STRENGTH UPON INITIAL RATE

Temperature 35°

| $p$H | Total cyanate moles/l. × $10^2$ | Ionic strength[a] × $10^2$ | Experimental rate × $10^4$ | $R_c$[b] | $R_u$[c] |
|---|---|---|---|---|---|
| 4.00 | 1.09 | 4.00 | 6.3 | 6.2 | 29.7 |
| 4.10 | 1.09 | 4.00 | 5.5 | 5.4 | 25.6 |
| 4.20 | 1.09 | 4.00 | 4.3 | 4.5 | 21.2 |
| 4.30 | 1.09 | 4.00 | 3.7 | 4.0 | 19.2 |
| 4.40 | 1.09 | 4.00 | 3.1 | 3.3 | 15.8 |
| 4.10 | 1.07 | 9.13 | 5.0 | 5.3 | 82 |
| 4.10 | 1.03 | 5.77 | 4.9 | 5.1 | 42 |
| 4.10 | 2.10 | 5.52 | 11.8 | 11.5 | 39 |

[a] Ionic strength increased by addition of NaCl. [b] Calculated using $R = ac_0 + bc_0^2$, assuming dependence on initial cyanate concentration. [c] From Fig. 2, 3, or 4 assuming dependence on ionic strength.

The experimental data cannot be explained by either a simple rate equation or a salt effect. The linear dependence of the first-order rate constant upon initial cyanate concentration suggests the form: $k = a + bc_0$ for the rate constant or

$$R_0 = ac_0 + bc_0^2 \qquad (11)$$

for the initial rate. The data were treated by curve fitting methods[5] and found to fit an equation of this form. The values of the parameters $a$ and $b$ were determined from the data by the method of least squares. The agreement with the experimental data is shown in Figs. 2, 3 and 4. Values of $a$ and $b$ determined are given in Table IV.

The significance of the parameters $a$ and $b$ may be investigated further. The initial concentration of HOCN, $A_0$, is related to the initial concentration of total cyanate $c_0$ by

$$K_c = \frac{(H^+)(c_0 - A_0)}{(A_0)} \qquad (12)$$

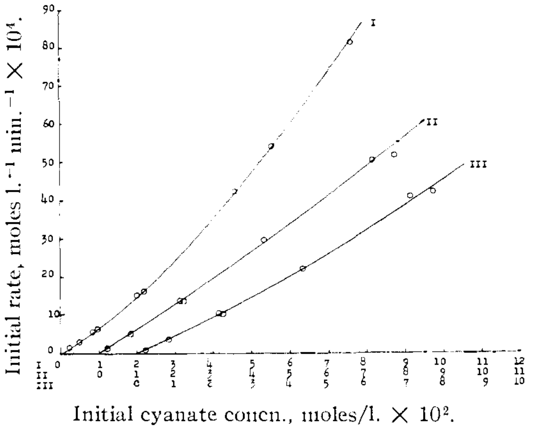

Fig. 2.—Initial rate of hydrolysis as a function of total cyanate concentration: I, $p$H 4.00, 28°; II, $p$H 3.80, 20°; III, $p$H 4.00, 20°.

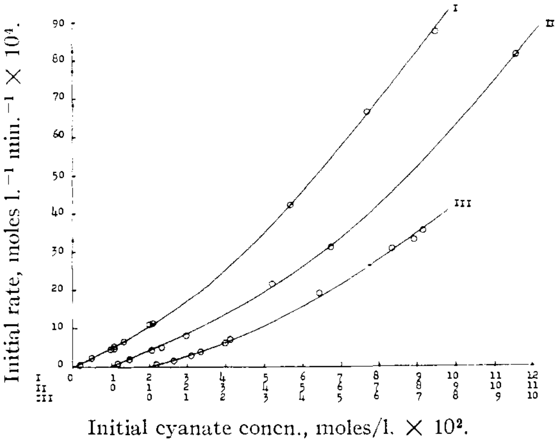

Fig. 3.—Initial rate of hydrolysis as a function of total cyanate concentration: I, $p$H 4.10; II, $p$H 4.30; III, $p$H 4.40; all temperatures 35°.

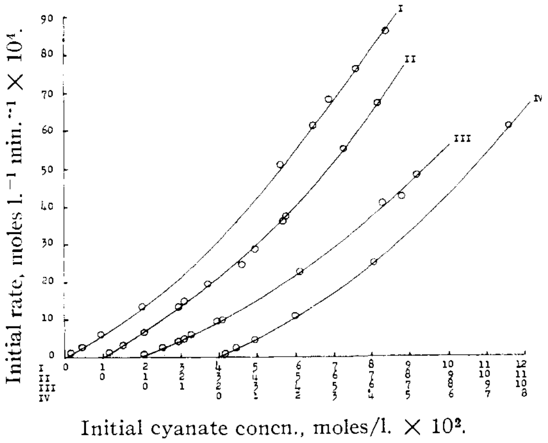

Fig. 4.—Initial rate as a function of total cyanate concentration: I, $p$H 4.10, 28°; II, $p$H 4.00, 35°; III, $p$H 4.20, 35°; IV, $p$H 4.20, 28°.

Solving for $c_0$ and substituting in (11)

$$R_0 = a\left(\frac{(H^+) + K_c}{(H^+)}\right)A_0 + \frac{b\,[(H^+) + K_c]^2}{(H^+)^2}A_0^2 \qquad (13)$$

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[5] I. S. and E. S. Sokolnikoff, "Higher Mathematics for Engineers and Physicists," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y. 1941, Chapter XII.

TABLE IV

VALUES OF PARAMETERS IN $R_0 = ac_0 + bc_0^2$

| Temp., °C. | $p$H | $a \times 10^2$, min.$^{-1}$ | $b$, l. moles$^{-1}$ min.$^{-1}$ |
|---|---|---|---|
| 35.0 | 4.00 | 5.0 | 0.59 |
| 35.0 | 4.10 | 4.4 | .50 |
| 35.0 | 4.20 | 3.7 | .40 |
| 35.0 | 4.30 | 3.2 | .42 |
| 35.0 | 4.40 | 2.7 | .31 |
| 28.0 | 4.00 | 3.0 | .32 |
| 28.0 | 4.10 | 2.7 | .30 |
| 28.0 | 4.20 | 2.1 | .25 |
| 20.0 | 3.80 | 2.9 | .08 |
| 20.0 | 4.00 | 2.2 | .07 |

If the assumption is made that the reacting form is cyanic acid the rate equation should have the form

$$R_0 = k_1(\mathrm{H}^+)^m(\mathrm{HOCN}) + k_2(\mathrm{H}^+)^n(\mathrm{HOCN})^2 \quad (14)$$

From a comparison of (13) and (14) it is seen that

$$(\mathrm{H}^+)^{m+1} k_1 = a[(\mathrm{H}^+) + K_c] = A \text{ and}$$
$$(\mathrm{H}^+)^{n+2} k_2 = b[(\mathrm{H}^+) + K_c]^2 = B \quad (15)$$

A plot of log $A$ or $B$ in (15) against $p$H should give a straight line the slope of which will give the order with respect to $(\mathrm{H}^+)$ and the intercept the rate constant for each step. This plot is shown in Fig. 5. The values of $K_c$ used are given below under the discussion of ionization constants for HOCN.

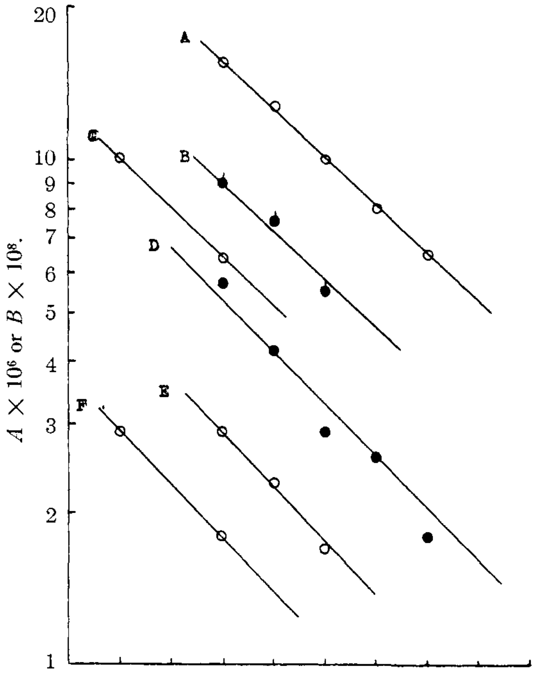

Fig. 5.—Dependence of uni- and bimolecular rate constants upon $p$H: unimolecular, (A) 35°; (B) 28°; (C) 20°; bimolecular, (D) 35°; (E) 28°; (F) 20°. Numerical value × 3 plotted in $F$ on ordinate.

The slopes of all curves in Fig. 5 are 1 within experimental error. The unimolecular reaction is 0 order with respect to $(\mathrm{H}^+)$ and the bimolecular reaction −1 order with respect to $(\mathrm{H}^+)$ or first order with respect to $(\mathrm{OH}^-)$. Values of the rate constants are found to be: 6.4 at 20°, 9.0 at 28° and 15.5 at 35° for $k_1 \times 10^2$ in min.$^{-1}$ and 0.59 at 20°, 2.9 at 28° and 5.3 at 35° for $k_2 \times 10^4$ in (moles/l.)$^{-1}$ min.$^{-1}$.

**Temperature Dependence.**—If log $k$ is plotted *vs.* $1/T$ in the conventional plot for activation energy the curves given in Fig. 6 are obtained. An explanation of the deviation from the normal linear function is given in the discussion.

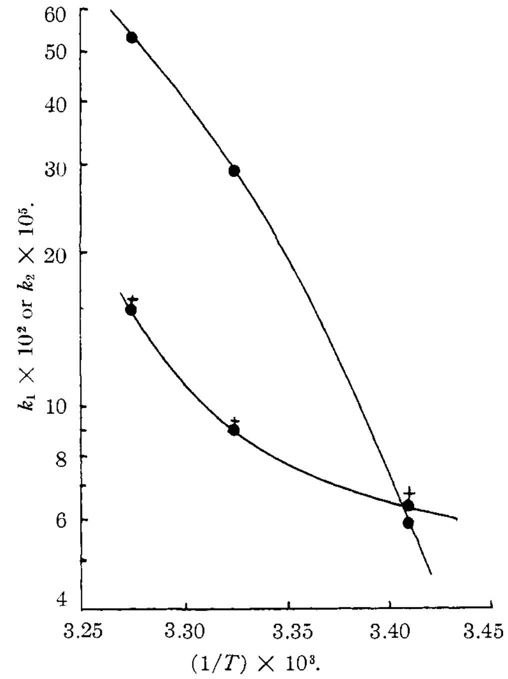

Fig. 6.—Temperature dependence of rate constants: $\dot{\bullet}$, unimolecular rate constant; ●, bimolecular rate constant.

**Ionization Constant of HOCN.**—The ionization constant can be determined from (1). The values increase with ionic strength, although the experimental error is too large to determine the exact dependence. However, in the experiments with the added salt the constant is larger than without the salt, helping to confirm the absence of the salt effect upon the rate.

The best values of the ionization constants calculated at zero ionic strength appear to be: $2.1 \times 10^{-4}$ at 35°, $2.0 \times 10^{-4}$ at 28° and $1.9 \times 10^{-4}$ at 20°. The heat of dissociation and free energy of dissociation are 1.3 and 5.0 kcal./mole. Previously reported values are $2.2 \times 10^{-4}$ for $K_0$ at 25°[6] and 5.0 kcal./mole for $\Delta F$.[7]

## Discussion of Results

The following mechanism is proposed for the hydrolysis

$$\begin{array}{lll}
\mathrm{H}^+ + \mathrm{OCN}^- \rightleftarrows \mathrm{HOCN} \rightleftarrows \mathrm{HNCO} & \text{fast} & (1) \\
\mathrm{HNCO} + \mathrm{H_2O} \longrightarrow \mathrm{NH_2COOH} & \text{slow} & (2) \\
\mathrm{NH_2COOH} \longrightarrow \mathrm{NH_3} + \mathrm{CO_2} & \text{fast} & (3) \\
\mathrm{NH_3} + \mathrm{H}^+ \longrightarrow \mathrm{NH_4}^+ & \text{fast} & (4) \\
2\mathrm{HNCO} \longrightarrow \mathrm{NH_2COOCN} & \text{fast} & (5) \\
\mathrm{NH_2COOCN} + \mathrm{OH}^- \longrightarrow & & \\
\qquad\qquad \mathrm{NH_2COOH} + \mathrm{OCN}^- & \text{slow} & (6)
\end{array}$$

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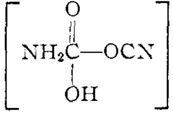
(6) K. Taufel, C. Wagner and H. Dunwald, *Z. Elektrochem.*, **34**, 115 (1928)

(7) J. C. McGowan, *Chemistry and Industry*, 632 (1948).

The rate-determining steps are the formation of the carbamic acid. In the bimolecular mechanism this is from the reaction of a dimer of cyanic acid with an $OH^-$. The existence of a dimer of cyanic acid has been proposed previously to explain reactions of the acid.[8] Werner and Gray, on the other hand, do not feel that there is evidence for the existence of the dimer.[9] It is felt that the rate equation obtained strongly suggests the existence of the dimer, even though it may be in very low concentration. A dimer of phenyl isocyanate is known to exist.[10] Whether the form of the dimer is $NH_2CONCO$ or $NH_2COOCN$ cannot be distinguished from this work. The dimer is attacked by an $OH^-$ to form an intermediate of the form  $\left[\begin{array}{c} O \\ \| \\ NH_2C\text{—}OCN \\ | \\ OH \end{array}\right]$ which then dissociates to carbamic acid and $OCN^-$ in the rate-determining step.

Whether cyanic acid is HOCN or HNCO or a mixture of the two has not been completely determined. Infrared spectra of the vapor and liquid appear to show that the acid is HNCO with less than 0.2% HOCN present.[11] In aqueous solution the tautomerism would be more probable than in the vapor or liquid. Werner and Fearon[12] suggest that the mixture is an equilibrium between the two forms and use the formation of the polymers of the acid as proof. The formation of HNCO is favored as the temperature increases.

Evidence supporting the tautomerism is obtained from the temperature dependence of the rate constants (Fig. 6). If it is assumed that only one form of the tautomer can react by a given mechanism, the total concentration of acid used to determine $k$ should be replaced by the concentration of the reacting form. If $K_t$ is the constant for the tautomerism, $A_0$ = HOCN + HNCO and (HNCO) would be $[K_t/(1 + K_t)]A_0$. This ratio would be included in the rate constant and a linear temperature dependence would not exist. It is believed that the HNCO form is the one that reacts because of steric considerations.

The mechanism proposed is a molecular one and there should be no primary salt effect. Because of the equilibrium which exists between the cyanic acid molecule and the ions, a secondary salt effect might be expected.[13] Since the concentration of $OCN^-$ and HOCN is of the order of 100 times the concentration of $H^+$ the increased dissociation of HOCN because of the added salt will be very small and will not appreciably change the concentration of un-ionized acid. Under these conditions the salt effect will be very small and less than the experimental error.

**Acknowledgment.**—The author is indebted to Drs. J. K. Dixon and G. L. Simard for helpful discussions during the early part of this work, and to Dr. Henry Kuivila who first suggested the dimer as an intermediate in the reaction.

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# A Non-random Disaggregation of Intact Skin Collagen

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Studies of the disaggregation of intact bovine hide collagen show the presence of lateral polypeptide chain cross-linkages of different reactivity and, probably, different distribution along the fibrillar long axis. Under the acid-extraction conditions there appear to be at least two classes of such cross-linkages and the order in which these are broken determines the molecular weight distribution of the solubilized portion. If the extractions are carried out under $p$H and temperature conditions where peptide bond hydrolysis is not significant then discrete soluble fibrillar fragments are obtained which may retain the gross features of the peptide chain configuration present in the native tissue. The onset of peptide bond hydrolysis is readily recognizable.

Various studies of the conversion of collagen to gelatin have had two major objectives: (1) to throw some light on the structure of intact collagen; (2) to explain the variations in the stability of the collagens from different sources.[1-4] Ames' work[1] led him to propose two possible models for collagen, a multi-chain structure in which the peptide chains are held together by non-peptide covalent cross-linkages of some sort and a single chain model in which the peptide chains are too large to be water soluble, but become so as certain particularly weak peptide linkages are broken. In spite of additional data from other quite different points of view[5-7] one could not chose between these alternatives.

Our studies of the mild thermal solubilization of collagen in the acid $p$H range[2] showed, however,

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