The decomposition of cyanate ions in aqueous solution

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THESIS

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entitled

THE DECOMPOSITION OF CYANATE IONS IN AQUEOUS SOLUTION

Being an account of research carried out in the Chemistry Department of the University of Durham, (Durham Division), during the period, October, 1951, to July, 1954, under the supervision of Dr. G. Kohnstam.

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191. *The Decomposition of Inorganic Cyanates in Water.*

By I. A. KEMP and G. KOHNSTAM.

The simultaneous formation of urea and carbonate from aqueous solutions of ammonium, barium, or sodium cyanate has been studied near 60° and 80°. The ionic strength was virtually constant at 0·25, and [OH^-] ranged from 4×10^{-7} to 2×10^{-3}. The rate of reaction was given by

$$\begin{aligned} -\,d[NCO^-]/dt &= [NCO^-](k_1'[NH_4^+] + k_3' + k_4'[H_3O^+] + k_5'[HCO_3^-]) \\ &= [HNCO](k_1[NH_3] + k_3[OH^-] + k_4 + k_6[CO_3^{2-}]) \end{aligned}$$

where the first term accounts for urea formation and the others are responsible for the production of carbonate. A first-order decomposition of urea to cyanate sometimes contributes slightly, and must be taken into account when considering the overall reaction. These rate equations permit an explanation of earlier observations, and other evidence indicates that they can be expected to apply whenever the pH is greater than 2. Borate ions and triethylamine do not affect the rate specifically.

The Brönsted relations for acid and base catalysis apply to k and k', respectively, but general acid or base catalysis is not observed. It therefore seems likely that all the reactions involve nucleophilic addition to cyanic acid in the rate-determining step, with formation of carbonate occurring *via* carbamic acid or the carbamate ion. This mechanism is subject to the restriction that the addition complex resulting from this nucleophilic attack must be capable of forming urea, carbamic acid, or the carbamate ion by proton transfer and bond rupture. Any reactions of these complexes with water or hydroxide ions appear to be too slow to prevent return to the initial reactants. This accounts for the absence of catalysis by borate ions, triethylamine, or cyanate ions in the reactions of cyanic acid.

INORGANIC cyanates decompose in aqueous solution to form urea and *carbonate*.* When it is borne in mind that reactants and products will be partly present as their conjugate acids or bases, the reactions may be represented by the stoicheiometric equations

$$NCO^- + 2H_2O \rightleftharpoons CO_3^{2-} + NH_4^+ \quad . \quad (i) \qquad NCO^- + NH_4^+ \rightleftharpoons CO(NH_2)_2 \quad . \quad (ii)$$

The kinetics of the formation of urea in aqueous solutions have frequently been studied.[1, 2] The reaction is of the first order with respect to ammonium and cyanate ions, but this has only been established over a limited pH range, as all the work was carried out with solutions of ammonium cyanate. According to Wyatt and Kornberg [3] the rate coefficients previously reported for the reaction in water are appreciably in error owing to neglect of the concomitant production of *carbonate*. Many workers have assumed that the reaction involves the combination of ammonium and cyanate ions in the rate-determining step, and the results of kinetic investigations have often been employed to test theories of ionic reactions; [2, 4] the good agreement between theory and experiment was accepted as confirmatory evidence of this ionic mechanism. It was, however, pointed out long ago [5] that the observed kinetics are equally consistent with reaction between ammonia and cyanic acid (these are in equilibrium with ammonium and cyanate ions) and it has since been shown that purely kinetic evidence cannot distinguish between the ionic and non-ionic reactions as both will show the same salt effect, and the same sensitivity to changes in the dielectric constant of the solvent.[6] This problem has been discussed in detail by Frost and Pearson,[7] who drew attention to the analogy between this reaction and the formation of substituted ureas from organic *iso*cyanates, and regarded the non-ionic mechanism as the more probable.

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* Throughout this paper the term *carbonate* is used collectively, and refers to all forms in which carbonates may be present, *i.e.*, carbonate ions, hydrogen carbonate ions, carbonic acid, and carbon dioxide. Similarly, *cyanate* refers to cyanate ions and cyanic acid, and *ammonium* to ammonium ions and ammonia.

(calculated from the conventional form of the absolute rate equation for reactions in solution [14]) are given in Table 1.

TABLE 1. *Kinetic data for reaction at ionic strength* 0·25.

(Each rate coefficient is the mean from the results of *n* different reaction mixtures.)

	n		Rate coefficients		*E*	ΔS *
	60·10°	80·10°	60·10°	80·10°	(kcal.)	(cal. °K⁻¹)
$10^3k_1'$	20	3	1·250 †	9·22 †	23·3	− 4·07
$10^{-2}k_1$	20	3	0·992 †	2·61 †	11·3	−17·8
10^7k_2	6	—	2·62 ‡	—	—	—
$10^6k_3'$	10	2	1·060 ‡	8·67 ‡	24·6	−14·5
$10^{-3}k_3$	10	2	2·204 †	6·88 †	13·3	− 5·69
$10^{-2}k_4'$	10	2	0·67 †	2·33 †	14·6	− 8·82
10^2k_4	10	2	2·70 ‡	9·91 ‡	15·2	−22·5
$10^3k_5'$	10	2	0·292 †	1·187 †	16·1	−28·7
$10^{-3}k_5$	10	2	0·389 †	1·479 †	15·4	− 3·20

† In sec.⁻¹ mole⁻¹ l. ‡ In sec.⁻¹.

k_1' is probably more reliable than k_1, as the latter involves the dissociation constant of cyanic acid which has only been determined at temperatures appreciably lower than those of the present investigation.[9, 10, 15] Following previous workers,[3] we assumed it to be 2×10^{-4}, irrespective of temperature, and though this may lead to errors in k_1 it does not affect the reliability of the rate equations, as any such errors are cancelled by similar errors in [HNCO]. Other possible errors in the rate coefficients are discussed in the Experimental section (p.   ), but these are probably not very important, as consistent results were obtained under a wide variety of conditions. In any one run the average discrepancy between the observed value of U and that calculated from the mean rate coefficient given in Table 1 was never greater than 3%, and usually less. This is illustrated below for a typical run (a similar comparison for the *carbonate* concentration, *C*, has also been included; the appropriate rate equations are given on p.   ).

Run 18, initially 0·0496M-NaNCO + 0·0017M-NaOH; temp. 60·10°.

$10^{-2}t$ (sec.) ...	0	86	193	314	665	1109	1399	1653	1740	2005	2278	2541	2632
10^4U obs. ...	—	—	—	—	5	18	24	35	41	52	59	71	75
10^4U calc. ...	—	—	—	1	6	17	27	38	41	52	63	71	74
10^4C obs. ...	3	8	15	21	52	96	129	159	171	204	231	261	271
10^4C calc. ...	—	8	14	21	48	91	123	153	164	195	225	252	260

Previous work in this field was carried out with solutions of ammonium cyanate. In water, Wyatt and Kornberg [3] found that k_1' was appreciably less than previously reported,[16] and ascribed this observation to the neglect of *carbonate* formation in the earlier studies. This is now confirmed; at 70° and zero ionic strength * our values and theirs agree within the limits of experimental error, and the assumption of negligible *carbonate* in the decomposition of ammonium cyanate leads to a " rate coefficient " which is in good agreement with the earlier, erroneous values (this can be readily verified from the data for Run 1, Table 4). The resulting percentage error in k_1' is virtually the same at 60° and 80°, and the activation energy should therefore not be affected by the neglect of *carbonate* formation; we found E = 24·0 kcal. at zero ionic strength; Svirbely and Warner [2] reported 23·3.

In the decomposition of urea solutions at 60° significant amounts of *carbonate* were formed before the *cyanate* concentration, *Cy*, became stationary. This is illustrated below.

Run 24, initially 0·1990M-urea; temp. 60·10°.

$10^{-2}t$ (sec.)	0	245	865	1173	1753	2013	2561	2880	3719
10^4Cy	22	29	45	48	50	48	48	47	42
10^5C	30	49	77	101	156	183	233	262	356

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* Rate coefficient at zero ionic strength $k^\circ = kf_x/f_af_b$, where k is the rate coefficient corresponding to the activity coefficients f. The subscripts a and b refer to the " reactants " (the species whose concentrations appear in the appropriate kinetic term), and x refers to the activated complex which is assumed to carry a charge equal to the sum of the charges of the " reactants."

these observations can be explained, but as the predicted value of C was always greater than that observed, there is no evidence for the direct formation of *carbonate* from urea. This is in agreement with the views of other workers.[19]

Our rate equations for *carbonate* formation account for others which have previously been found to apply over more limited ranges of pH. Thus, in strongly alkaline solutions equation (3) reduces to $\mathrm{d}C/\mathrm{d}t = k_3'[\mathrm{NCO}^-]$, a rate law which has already been proposed for such systems.[9, 10] The earlier rate coefficients at 100° are in good agreement with our extrapolated value of k_3', and the activation energies are within 1 kcal. At 0°, k_4 agrees closely with the rate coefficient found for the first-order decomposition of cyanic acid; [10] the activation energies differ by less than 1 kcal. At 70°, our value of k_4 is less than that reported by Wyatt and Kornberg,[3] who assumed that only the term involving this parameter is concerned in the production of *carbonate* from unbuffered solutions of ammonium cyanate. We did not find this to be the case, but these authors stressed the approximate nature of their result.

The third term in equation (3) has not been proposed before. It is, however, supported by the results of Masson and Masson,[8] who found *carbonate* formation from sodium cyanate to be autocatalytic (about 65% of the *carbonate* is present as hydrogen carbonate), strongly accelerated by " $\mathrm{NH_4CO_3^-}$ " ions and weakly by carbonate ions (small amounts of hydrogen carbonate result from the addition of these ions to water). Their observation of first-order *carbonate* formation from barium cyanate is consistent with our observation that the pH only varies between 7·72 and 7·92 over the course of the reaction at 60° ($[\mathrm{HCO_3^-}]$ is very small in this system), and their smaller first-order rate coefficient for the initial *carbonate* formation from sodium cyanate is now seen to arise from the greater pH of this system (cf. Run 14, Table 2).

Lister [10] found that in strongly alkaline cyanate solutions containing added carbonate ions

$$\mathrm{d}C/\mathrm{d}t = k_3'[\mathrm{NCO}^-] + k''[\mathrm{CO_3}^{2-}]$$

This is now seen to result from the experimental conditions employed. Initially $[\mathrm{NCO}^-] \doteq [\mathrm{OH}^-]$, and this near-equality holds throughout the reaction. As $[\mathrm{HCO_3}^-] \ll [\mathrm{CO_3}^{2-}]$ at high pH values, equation (3) can easily be shown to take the form

$$\mathrm{d}C/\mathrm{d}t = k_3'[\mathrm{NCO}^-] + k_5'K_v[\mathrm{CO_3}^{2-}]$$

under these conditions.* Lister found $10^5k'' = 1{\cdot}1$ sec.$^{-1}$ at 100°; we calculate $10^5k_5'K_v = 1{\cdot}7$ at this temperature and ionic strength 0·25. In view of the large and variable ionic strength of the earlier work, this is regarded as satisfactory.

The combination of our results with those observed in more acid [10] and alkaline solutions [9, 10] thus shows that equations (3) and (4) account for the rate of *carbonate* formation from cyanates and cyanic acid, provided the pH is greater than 2.

DISCUSSION

Catalysis by Acids and Bases.—The rate laws for the decomposition of cyanates can be written in the form

$$-\,\mathrm{d}Cy/\mathrm{d}t = \{\mathrm{NCO}^-\}[(k_1')^\circ\{\mathrm{NH_4}^+\} + (k_2')^\circ + (k_4')^\circ\{\mathrm{H_3O}^+\} + (k_5')^\circ\{\mathrm{HCO_3}^-\}] \quad . \quad . \quad (5)$$

$$= \{\mathrm{HNCO}\}[k_1{}^\circ\{\mathrm{NH_3}\} + k_3{}^\circ\{\mathrm{OH}^-\} + k_4{}^\circ + k_5{}^\circ\{\mathrm{CO_3}^{2-}\}] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the braces { } refer to activities, and the superscript ° to zero ionic strength.

It seems likely that the first-order terms represent reaction with water, and equation (6) can then be considered to imply reactions of cyanic acid with bases. The rate coefficients increase with increasing base strength and, the activity of water being taken as unity, the " best " Brönsted relation for base catalysis [20] can be written in the form

$$\log_{10}(k^\circ/q) = -\,1{\cdot}447 + 0{\cdot}3764\log_{10}(p/qK_a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k° refers to a base of strength $1/K_a$, K_a is the thermodynamic dissociation constant of its conjugate acid, q the number of centres in the base which can accept a proton with

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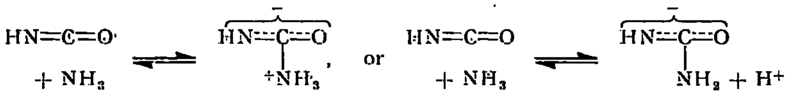
* The kinetic term $k_4'[\mathrm{H_3O^+}][\mathrm{NCO}^-]$ is extremely small.

with about the same accuracy as equation (7) predicts k°, and it can similarly be shown that the reactions of cyanate ions are not subject to general acid catalysis.

Reaction Mechanism.—The observed kinetics suggest that the four reactions which contribute to the decomposition of *cyanate* involve either a cyanate ion or cyanic acid in the rate-determining step. As each set of rate coefficients follows the Brönsted relation, it seems likely that the reactions occur by the same mechanism irrespective of whether they yield urea or *carbonate*, and the absence of general acid or base catalysis indicates that the reagents do not act by virtue of their ability to donate or accept protons. The connection between nucleophilic activity and base strength [24] allows us to consider another general reaction mechanism, nucleophilic addition to cyanic acid, which permits rate coefficients to follow the Brönsted relation for base catalysis, and it seems probable that this mechanism is operating in the present reactions. This view can only be advanced tentatively at present. It is based on the possibly fortuitous observation that four rate coefficients follow the Brönsted relation, and further work is necessary before it can be finally accepted. On the other hand, our interpretation is consistent with the present findings and also with those of other workers (see next paragraph).

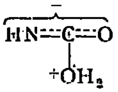
Nucleophilic attack on cyanic acid will occur at the carbon atom, the point of lowest electron density, and the reaction with ammonia can therefore be visualised to occur in the following manner : [25]



$HN{=}C{=}O + NH_3 \rightleftharpoons HN{=}C({-}{}^{+}NH_3){=}O^{-}$ (I), or $HN{=}C{=}O + NH_3 \rightleftharpoons HN{=}C(NH_2){=}O^{-} + H^+$ (II)

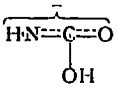
(I) (II)

A rapid proton transfer [prototropic change in (I), or proton addition to (II)] then yields urea. Confirmatory evidence for this scheme is supplied by studies of the formation of substituted ureas. As expected, the rates increase with increasing base strength of the amine [7, 26, 27] and with increasing capacity for attracting electrons by substituents in aryl *iso*cyanates.[27] The addition complex resulting from nucleophilic attack by water or hydroxide ions (III or IV) can similarly be expected to undergo rapid proton transfer yielding carbamic acid, and this acid will break down into *carbonate* as soon as it is formed.



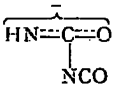
$HN{=}C({}^{+}OH_2){=}O^{-}$

(III)



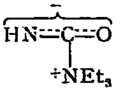
$HN{=}C(OH){=}O^{-}$

(IV)



$HN{=}C(NCO){=}O^{-}$

(V)

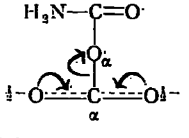


$HN{=}C({}^{+}NEt_3){=}O^{-}$

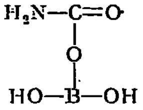
(VI)

It seems likely that this ability of the addition complex to form the product, or a species which is readily converted into it, by simple proton transfer is an essential requirement for reaction. Equation (7) predicts a significant catalysis of *carbonate* formation by cyanate ions and triethylamine (cf. Runs 1 and 20, Table 4), but this was not observed. Steric factors do not oppose the formation of the addition complex (V) or (VI), but this complex can only be converted into carbamic acid or a carbamate ion (which would also readily yield *carbonate* at our reaction temperatures) by a further reaction with water or hydroxide ions (cf. Baker *et al.*[28]). Proton transfer can be expected to occur much more rapidly than reaction with the solvent or its anions, and it seems reasonable to suppose that the intrinsically unstable addition complex has a much greater chance of acquiring a proton

(VII)



$H_2N{-}C({=}O){-}O_\alpha{-}C_\alpha(O^{\frac{1}{2}-})_2$



$H_2N{-}C({=}O){-}O{-}B(OH)_2$

(VIII)

before it reverts to the initial reactants than of forming a bond with oxygen, either before or after protonation of the imino-group. This view provides an explanation of the catalysis by carbonate ions and the absence of a measurable reaction with borate ions, although such a reaction is predicted by equation (7) (cf. Run 21, Table 4). In the amounts of one base from another. Allowing for all the added substances employed, we can therefore write

$$X = 2C + Cy + [NH_3]_i + [NEt_3]_i + [OH^-]_i - [HCO_3^-]_i$$

where the subscript i refers to the concentrations of added species before their participation in acid–base equilibria.

Tubes containing samples of the reaction mixture were cleaned, broken under 200 ml. of neutral acetone, treated with excess of standard hydrochloric acid, then a further 200 ml. of neutral acetone, and titrated with standard sodium hydroxide (lacmoid). Good end-points were obtained if the water content of the titration mixtures was kept low; the acid was therefore made up in 70% (v/v) acetone, and the alkali added from a microburette. The accuracy was 0·4% at $2C + Cy = 0{\cdot}004$M, and better at higher concentrations.

(b) *Determination of* C. Except in solutions of barium cyanate, C was evaluated by similarly determining the basicity, Y, of a sample from which the cyanate had been removed by precipitation as the silver salt:

$$Y = 2C + [NH_3]_i + [NEt_3]_i + [OH^-]_i - [HCO_3^-]_i$$

5 ml. of approx. 0·1N-silver nitrate, containing ammonium nitrate (40 g. $l.^{-1}$) to prevent the precipitation of silver carbonate, were added to a sample of the reaction mixture, which was made up to 25 ml. After being shaken, some of this mixture was centrifuged and 5 ml. of the supernatant liquid were removed. The basicity of this solution was determined as before, after a few crystals of sodium chloride had been added to precipitate the silver ions present. *Cyanate* was not completely precipitated by this method, and the necessary correction was found by carrying out similar experiments with a solution of approximately the same *cyanate* concentration and with the same solution after it had been diluted five-fold. The quality of the end-point in the final titration could be improved by using less ammonium nitrate, and this was done when the reaction mixtures contained relatively small amounts of *carbonate*. The method could be employed up to $C = 0{\cdot}035$M; its accuracy, which was independent of Cy, was 5% at $C = 0{\cdot}001$M, and better at higher concentrations.

In the decomposition of barium cyanate, virtually all the *carbonate* was precipitated as the barium compound—the correction for the *carbonate* in solution is discussed on p. . Here, C was determined by dissolving the washed precipitate from three samples in excess of hydrochloric acid and back-titrating with alkali.

(c) *Determination of* Cy. In the early stages of the decomposition of urea solutions, C was too small for reliable estimation by the methods described above. It was therefore more convenient to evaluate Cy. The method was essentially that proposed by Werner,[31] and the absorption coefficient of the cupric cyanate–pyridine complex in chloroform was examined at 690 mμ, a Unicam S.P. 500 spectrophotometer being used. Nitrate ions interfered slightly, and the " blank cell " was therefore prepared from a solution of the same $[NO_3^-]$ as the solution under test. The accuracy was 5% at $Cy = 0{\cdot}001$M, and better at higher concentrations.

When the reactant was barium cyanate, Cy was determined directly from the supernatant liquid by the method described in (a).

Calculation of Concentrations.—The various species present in a reaction mixture are concerned in the usual acid–base equilibria, and their concentrations can be calculated from the analytical results if $[OH^-]$ and the appropriate equilibrium constants are known. $[OH^-]$ was obtained by the following method. In the first place it is assumed that reactants and products are in the form in which they appear in equations (i) and (ii), and that any other substances are present at their " added " concentrations, *i.e.*, before their participation in any equilibria. The following reactions must then be considered:

$$NCO^- + H_2O \rightleftharpoons HNCO + OH^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iii)}$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \quad . \; . \; . \; . \; . \; . \; . \quad \text{(iv)}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad . \; . \; . \; . \; . \; . \; . \quad \text{(v)}$$

$$CO_3^{2-} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^- \quad . \; . \; . \; . \; . \; . \quad \text{(vi)}\,*$$

$$H_2CO_3 \rightleftharpoons CO_2(g) + H_2O \quad . \; . \; . \; . \; . \; . \quad \text{(vii)}\,*$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \quad . \; . \; . \; . \; . \; . \; . \quad \text{(viii)}$$

$$NEt_3 + H_2O \rightleftharpoons Et_3NH^+ + OH^- \quad . \; . \; . \; . \; . \; . \quad \text{(ix)}$$

$$H_3BO_3 + OH^- \rightleftharpoons H_2BO_3^- + H_2O \quad . \; . \; . \; . \; . \; . \; . \quad \text{(x)}$$

$$BaCO_3 \rightleftharpoons Ba^{++} + CO_3^{2-} \quad . \; . \; . \; . \; . \; . \; . \quad \text{(xi)}$$

* All dissolved carbon dioxide is assumed to be present as carbonic acid.

k_3', k_4', and k_5' were determined by the following method. Integration of equation (2) gives

$$\alpha = (C - C_0 - k_4'\beta)/\gamma = k_3' - k_5'\delta/\gamma$$

where $\beta = \int_0^t [H_3O^+][NCO^-].dt$, $\gamma = \int_0^t [NCO^-].dt$, and $\delta = \int_0^t [HCO_3^-][NCO^-].dt.[H_3O^+]$ is small in Run 13 (cf. Table 3), and provisional values of k_3' and k_5' were obtained from the results as the intercept and slope of the straight-line plot of $(C - C_0)/\gamma$ against δ/γ. These, in conjunction with Run 1, gave a provisional value of k_4'; α in Run 13 could thus be determined, and hence improved values of k_3' and k_5' which, in turn, led to an improved value of k_4'. A repetition of this procedure did not alter the rate coefficients. When sodium cyanate was the reactant, the kinetic term in $[H_3O^+]$ had only a small effect on the rate of carbonate formation, and k_3' and k_5' were determined from the results of such reaction mixtures with the aid of the value of k_4' from Run 1. The mean values of these rate coefficients were then employed in the calculation of k_4' from the observations on systems containing ammonium cyanate as the initial reactant.

The rate coefficients k were obtained from the corresponding values of k' and the equilibrium constants.

The most likely errors in k and k' arise out of the ionic activity coefficients which were employed. These were calculated from the equation proposed by Davies,[33] which is only accurate up to an ionic strength of 0·1.* Any such errors would, however, not be great, and it also seems that they largely cancel each other; our values of k_1 and k_1' agree very closely with those of Wyatt and Kornberg,[3] who used the same equation but did not work at ionic strengths greater than 0·1. It can easily be shown that, although the ionic strength decreases over the course of some of our reactions, this decrease is not large enough to cause significant errors in rate coefficients calculated on the assumption of constant ionic strength.

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* This equation leads to 0·700 for f_1 at 60°. The use of this figure instead of 0·705 does not alter the values of k', and the change in k is never greater than 1·5%.

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CHAPTER I

HISTORICAL

(a) Introduction

Probably one of the most outstanding advances in chemistry was the discovery by Liebig and Wohler (1-7) that ammonium cyanate decomposes on heating to form urea and that the reaction is reversible. This synthesis of the "organic" urea from substances of "inorganic" origin was largely responsible for the destruction of the "vital force" theory of organic chemistry. The general chemistry of the cyanates is reviewed by Williams (8).

By the year 1910, it was generally recognized that the modes of decomposition of cyanates in aqueous solution could be divided into three main classes:

(a) Ammonium Cyanate decomposes quantitatively to form urea, with the possibility that a very small side reaction forming carbonate may also be present.

(b) Sodium Cyanate decomposes to form both carbonate and urea, the former product predominating.

(c) Barium Cyanate decomposes to form urea and carbonate in almost equal proportions.

Lewis (9) recognized that during the decomposition of ammonium cyanate, urea is not the ultimate product but that urea decomposes in aqueous solutions to form carbonate and, at equilibrium - reached only after a long time at ordinary temperatures - the species present is almost all ammonium carbonate.

Despite the lack of knowledge concerning the nature and behaviour of strong electrolytes, early investigators did establish the general principles of the kinetics of the decomposition of ammonium cyanate, as will be shown in the next section.

It is now generally accepted that cyanates decompose in aqueous solutions according to the stoichiometric equations:

$$CNO^- + 2H_2O \rightleftharpoons CO_3^= + NH_4^+ \quad .. \quad .. \quad I, 1$$

$$CNO^- + NH_4^+ \rightleftharpoons CO(NH_2)_2 \quad .. \quad .. \quad I, 2$$

In solutions of initially pure sodium cyanate, urea is formed by reaction between ammonium ions, produced as shown in eqn. I, 1, and unchanged cyanate, as in eqn. I, 2.

In the following review of the investigations into the kinetics and mechanism of these two reactions, the work will be considered under the following headings:

(a) The decomposition of ammonium cyanate to form urea, and the reverse reaction.

(b) The carbonate formation from cyanates.

Such a division is not ideal by any means, since, as has already been stated, some carbonate may be formed during ammonium cyanate decomposition and some considerable urea formation accompanies the hydrolysis of cyanates to carbonate.

It is, however, convenient when writing a literature survey, to keep to these divisions, since in the past, the tendency has been to consider the decompositions of sodium and ammonium cyanates separately, rather than as a whole.

(b) Urea formation from ammonium cyanate and the reverse reaction

In the early part of this century, J. Walker and his co-workers (10-14) extensively examined the formation of urea and alkyl urea from ammonium and alkyl ammonium cyanates.

During the decomposition of ammonium cyanate in aqueous solution, Walker (10) recognized that a small proportion of carbonate bi-product is formed, estimating it at about 4% of the total cyanate decomposed, although any possible effect of the carbonate on the kinetics of the decomposition was ignored in the subsequent calculations. From the effect of added cyanate ions, ammonium ions and ammonia on the rate of decomposition, it was concluded that the reaction is bimolecular between ammonium and cyanate ions, the alternative possibilities of ammonia and cyanic acid, or two undissociated ammonium cyanate molecules, being considered unlikely.

Good second order rate constants were obtained in any one run but the value of the constant increased with increasing dilution and decreased in the presence of added electrolyte. To-day, this would be accepted as reasonable in view of known effects of ionic strength on activity coefficients of ionic species, but these authors tried to account for this by assuming incomplete ionization of ammonium cyanate. An investigation of the reaction in aqueous alcohol (12) attempted to account for this by writing the rate equation:

$$\text{rate} = k\alpha^2 [NH_4^+][CNO^-]$$

where the degree of ionization, α, was determined conductometrically by the usual method, it being assumed that the effect of solvent change on Λ_∞ of ammonium cyanate was the same as for diethylammonium chloride.

Rate constants determined by this method were independent of the dilution and thus appeared to confirm their earlier interpretation. Present day views on the nature of strong electrolytes assume complete ionization and Miller (26) has pointed out that Walker's value of α corresponds closely to the value of the mean ionic activity coefficients of a 1 - 1 electrolyte and, hence, his results are not inconsistent with what would have been expected on the basis of more modern theories.

The equilibrium constant of the system urea-ammonium-cyanate was also determined by these authors at 30°C. and 100°C. from which it is deduced that the heat of the reaction is about 5,000 cals. A calorimetric determination of the heat of reaction by J. Walker (15) gave a value of 7,500 cals.

The rate of decomposition of ammonium cyanate in aqueous alcoholic solution is accelerated by increasing the alcoholic content of the solvent. This was thought to be due to an increased rate of reaction of the ions, more than counterbalancing the decrease due to the smaller ionization of ammonium cyanate under these conditions. Nowadays, such a result would be expected when a reaction between two ions, leading to a decrease in the ionic charge in the transition state, takes place in a medium of lower dielectric constant.

A comparison of the rates of decomposition of some alkyl ammonium cyanates with ammonium cyanate showed no increase in rate for the monomethyl salt but a doubling of the rate for the dimethyl compound.

The principal conclusion of J. Walker's work is, then, that the reaction is ionic:

$$NH_4^+ + CNO^- \rightleftharpoons CO\,(NH_2)_2 \qquad .. \qquad .. \qquad I, 2$$

This was criticized in 1912 by Chattaway (16), who considered that the mechanism of the reaction is:

$$HCNO + NH_3 \rightleftharpoons HNC\,(OH)NH_2 \rightleftharpoons CO(NH_2)_2$$

i.e., addition of ammonia to the carbonyl group of cyanic acid as occurs in aldehyde-ammonia formation. This type of mechanism was considered by J. Walker to be unlikely, since the addition of ammonia to solutions of ammonium cyanate causes no appreciable acceleration in the rate of urea formation. However, in an appended note to this Paper by D. L. Chapman, it was pointed out that this non-ionic mechanism is not inconsistent with the experimental results of J. Walker in view of the known equilibria between ammonium ions and ammonia and/cyanate ions and cyanic acid: i.e., the rate equation

$$\text{Rate} = k[NH_4^+][CNO^-]$$

can be written

$$\text{Rate} = \frac{k\ K_A\ K_B}{K_W}[NH_3][HCNO]$$

where
$$K_B = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_A = \frac{[H^+][CNO^-]}{[HCNO]}$$

$$K_W = [H^+][OH^-]$$

Normand and Cumming (17) represent the decomposition of cyanic acid in two ways, depending on the experimental conditions.

(a) In acid solution:-

$$CNO^- + 2H^+ + H_2O \rightleftharpoons NH_4^+ + CO_2$$

(b) In neutral solution:-

$$2CNO^- + 2H^+ + H_2O \rightleftharpoons CO(NH_2)_2 + CO_2$$

i.e., proceeding via cyanate ions in each case.

Yet another mechanism was proposed by Werner in 1913 (18). This author stressed the importance of the two possible forms of cyanic acid, HOCN and HNCO. Ammonium cyanate was assumed to be a true cyanate which dissociated according to the equation:

$$NH_4OCN \rightleftharpoons NH_3 + HOCN$$

whilst urea was formed by the interaction of ammonia with isocyanic acid:

$$NH_3 + HNCO \rightleftharpoons CO(NH_2)_2$$

The rate of urea formation thus depends on the tautomeric equilibrium between the two forms of cyanic acid, a rise in temperature favouring the iso form of the acid. During the decomposition of pure cyanic acid, it was observed that the proportion of urea to ammonium cyanate formed, increased as the temperature of reaction was raised. This was considered a strong argument in favour of this scheme.

Nowadays, it is very difficult to accept such a mechanism which does not treat ammonium cyanate as a strong electrolyte. Furthermore, it is now generally accepted that cyanic acid exists almost completely in the iso form (see p.64) although the presence of a small quantity of HOCN cannot be absolutely ruled out. Admittedly these conclusions refer to the pure cyanic acid but there is little reason to suppose different behaviour in aqueous solution. At the same time, it is worth noting that when this mechanism was proposed, the Arrhenius equation for the temperature dependence of rate constants was already 20 years old.

E. E. Walker (19) suggested that the rate constants of the reaction in various aqueous solvents could only be compared if they were calculated on the basis of equal water concentrations in each medium. His reason for suggesting this is obscure, and, in any case, the rate thus calculated should be zero in non-aqueous solution, a conclusion which was not confirmed experimentally by Ross (20). Ross reported a continuous increase in rate in changing the solvent from 90% aqueous alcohol to absolute alcohol. Obviously, water cannot be involved in the rate determining stage, (or necessarily, any stage), in the urea formation from cyanates.

E. E. Walker, however, reported that during the decomposition of ammonium cyanate in aqueous solution, as much as 10% carbonate bi-product is formed - much more than previously reported. An attempt to allow for this side reaction was made when calculating the rates of urea formation (cf. p. 33).

Moelwyn Hughes (21) quotes results of Doyle (22) in which second order rate constants independent of dilution are reported. This was considered as evidence for the collision of two unionised molecules of ammonium cyanate. It is difficult to see why this should be the case, or even how the results were obtained, since the dependence on dilution of the second order constant has been clearly demonstrated, both at that time and more recently.

The theory of the influence of neutral salts and dielectric constant of the media on the velocity of reactions in solution has been developed from the Debye-Hückel theory by Bjerrum (23) and Christiansen (24). These theories have been applied by a number of workers to the kinetics of urea formation from cyanates.

Miller (26-28) and her co-workers examined the rate of transformation of a number of cyanates in various aqueous alcoholic media. They showed the dependence of rate on dilution, assuming that the reaction is ionic as in eqn. I, 2, to be in accordance with the predictions of the Brönsted eqn. (29)[*] and, at high dilutions, with the limiting Debye-Hückel theory.

More recently, many American authors (30-37) have examined the transformation of ammonium cyanate in various aqueous media. They show that the effect of dilution and dielectric constant (affecting the forces between the two reacting ions) on the rate of reaction, is in accordance with predictions, assuming that the reaction is ionic. For a complete survey of this, see Amis (30) and Warner (25).

The two important points apparent from this work are:

(a) Both Miller and the American authors considered carbonate formation to be sufficiently small to be

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[*] The Brönsted eqn. assumes that the reactants form an intermediate complex, which is treated as a normal molecule in equilibrium with the reactants:

$$A + B \rightleftharpoons X \longrightarrow \text{Products}$$

negligible over the reaction ranges examined.

(b) The extent of the agreement between the predicted and observed effect on the rate and Arrhenius parameters of the reaction of variations in ionic strength and dielectric constant of the media, was considered to show conclusively that the reaction is ionic as expressed by eqn. I, 2.

However, Weil and Morris (40), re-stated (cf. Chapman (16) p. 6) that the agreement between the kinetics of the reaction and expected salt effects, etc., for ionic reactions do not conflict with a non-ionic mechanism in any way.

The rate equation:

$$\frac{d[\mathrm{Urea}]}{dt} = k_U[NH_4^+][CNO^-]$$

can be written

$$\frac{d[\mathrm{Urea}]}{dt} = k_U'[NH_3][HCNO]$$

where

$$k_U = \frac{k_U' \; K_W \; f_1^2}{K_A K_B}$$

and

$$K_A = \frac{[H^+][CNO^-]f_1^2}{[HCNO]}$$

$$K_B = \frac{[NH_4^+][OH^-]f_1^2}{[NH_3]}$$

$$K_W = [H^+][OH^-]f_1^2$$

Both reactions would show the same primary salt effect. Thus, on the basis of the kinetic evidence, the rate determining stage of the reaction could involve either ionic or non-ionic species.

The kinetics of the reverse reaction, cyanate and carbonate formation from urea, have not been examined in any detail in this investigation, but certain general points are essential to the interpretation of the mechanism of carbonate and urea formation from cyanates.

The kinetics of urea decomposition were investigated by Fawsitt (41) and Burrows and Fawsitt (42), who found that the rate of decomposition of urea in both aqueous and aqueous alcoholic solution was first order in urea. The reaction is accelerated by small concentrations of mineral acid, but with the addition of larger concentrations the rate reaches a virtually constant limiting value. These authors, therefore, proposed that the decomposition proceeds:

$$CO(NH_2)_2 \rightleftharpoons NH_4^+ + CNO^-$$

$$CNO^- + 2H_2O \rightleftharpoons NH_4^+ + CO_3^=$$

the limiting rate corresponding to a point at which the decomposition of the cyanate is very rapid, the decomposition being controlled by the slow hydrolysis of the urea to cyanate.

Werner (43), however, attributed this maximum velocity to the equilibrium:

$$CO(NH_2)_2 + HCl \rightleftharpoons CO(NH_2)_2HCl ;$$

only the free urea decomposing to form cyanate. (In this respect, it would be interesting to know whether or not the maximum rate is dependent on the urea concentration, but as far as is known, these data are not available). Ingold (67, p. 786) has suggested that the similar maximum in the rate of amide hydrolysis with strong acids* is attributable to a decrease in the activity of water at high acid concentrations.

The addition of strong alkali to urea also increases the rate of hydrolysis, but here in a regular manner with increasing alkali concentration. Fawsitt considered this to be a direct hydrolysis of urea, not by way of an intermediate cyanate, but Werner writes the reaction:

$$CO(NH_2)_2 + NaOH \rightleftharpoons NH_3 + NaCNO + H_2O$$

$$NaCNO + 2H_2O \rightleftharpoons NH_3 + NaHCO_3$$

still with intermediate cyanate. The precise course of the alkaline hydrolysis of urea does not seem to have been established with any certainty.

Davis and Blanchard (44) showed that the products of the decomposition of various substituted ureas are in accordance

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* Urea is the amide of carbamic acid.

with a primary dissociation to cyanic acid and an amine:

$$C_6H_5NHCONH_2 \rightleftharpoons C_6H_5NH_2 + HNCO$$

$$HNCO + C_6H_5NH_2 \rightleftharpoons C_6H_5NHCONH_2$$

$$C_6H_5NHCONH_2 \leftrightharpoons C_6H_5NCO + NH_3$$

$$C_6H_5NCO + C_6H_5NH_2 \Longrightarrow C_6H_5NHCONHC_6H_5$$

All these possible products were found.

Krasil'shchikov and Nefedova (45) investigated the rate of cyanate formation from urea. They showed that the reaction followed a unimolecular law, the rate constants decreasing with increasing urea concentration. Plots of the negative logarithm of the rate constant as a function of the activity of urea are linear.

Dirnhuber and Shültz(46) showed that cyanate is formed from urea by hydrolysis at ordinary temperatures (below 38°C.) but only very slowly.

In a recent investigation, Mukaiyama and Matsumaga (47) examined the rate of urea decomposition in fatty acid solvents, and found that that the rate was first order, increasing with a rise in acidity of the solvent. A maximum rate of decomposition, with 1.5 moles of sulphuric acid, was reported, analogous to that found by Fawsitt in aqueous solution. They considered a cyanate to be formed as an intermediary in the reaction.

The equilibrium between urea, carbon dioxide, ammonia and water was studied by Lewis and Burrows (9) at 132°C. They showed that, at equilibrium, only carbonate is present in appreciable quantities (at 77°C. between 0.9 and 1.1% urea only; no detectable cyanate).

There would, then, seem to be no certain evidence that urea does decompose wholly via cyanate under normal conditions. It was considered desirable in our investigation to confirm that direct carbonate formation from urea was negligible compared with the carbonate formation from cyanate.

(c) Carbonate formation from cyanates

The first kinetic examination of the decomposition of sodium and potassium cyanate in aqueous solution was that of I. and O. Masson (48). These authors found that both urea and carbonate were formed during the decomposition, which they represented by the stoichiometric equations:

$$CNO^- + 2H_2O \rightleftharpoons NH_4^+ + CO_3^=$$

$$NH_4^+ + CNO^- \rightleftharpoons CO(NH_2)_2$$

i.e., ammonium ion produced during carbonate formation is intermediate in the urea formation. The ratio of urea to carbonate formed was approximately constant throughout the decomposition, 0.33.

The course of the reaction indicated autocatalysis of the decomposition, and these authors considered that the "$NH_4CO_3^-$" ion was largely responsible, although the $CO_3^=$ ion showed some catalytic effect. Re-interpretation of these conclusions suggests that the bicarbonate ion is probably the species involved.

Normand and Cumming (49) showed that the only products from the decomposition of alkali cyanates in the presence of mineral acids are ammonia and carbon dioxide, the reaction being very rapid even at ordinary temperatures.

Werner (50) interpreted the mechanism of the decomposition in terms of his hydrolytic dissociation theory (see p. 7). He considered the decomposition of metallic cyanates to be:

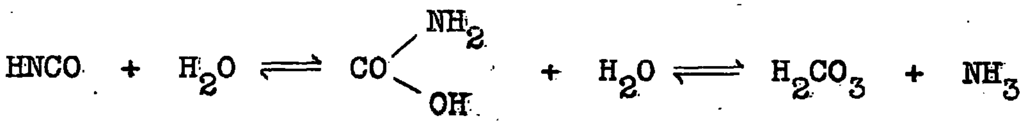
$$KOCN + H_2O \rightleftharpoons KOH + (HOCN \rightleftharpoons HNCO)$$

$$HOCN + H_2O \rightleftharpoons NH_3 + CO_2$$

$$HNCO + NH_3 \rightleftharpoons CO(NH_2)_2$$

As has already been explained, this can no longer be maintained in the light of recent investigations of the structure of cyanates, which show that alkali cyanates are ionic in character, and that the existence of the enol form of the acid is doubtful. (See p.64).

Fearon and Dockeray (51), on the other hand, considered the keto acid to be more susceptible to hydrolysis:



$$HNCO + H_2O \rightleftharpoons CO\begin{matrix}\diagup NH_2 \\ \diagdown OH\end{matrix} + H_2O \rightleftharpoons H_2CO_3 + NH_3$$

Carbamic acid

The formation of carbamic acid as an intermediate in the reaction was considered likely, since during the decomposition of N/5 cyanic acid at 5 - 7°C., greater concentrations of carbamate were shown to be present than could be accounted for on the basis of equilibria with the ammonium carbonate formed:

$$H_2O + NH_4CO_2NH_2 \rightleftharpoons 2NH_4^+ + CO_3^=$$

Täufel, Dünwald and Wagner (52) examined the hydrolysis of metallic cyanates in strongly alkaline solution. They calculated first order rate constants which, although constant in any one run, decreased with increasing alkali concentration. They proposed a kinetic equation:

$$\frac{d[CO_3^=]}{dt} = k_1 [H^+][CNO^-] + k_2[CNO^-] .$$

The small decreasing contribution from the first term corresponds to the dependence of the first order constants on alkali concentration.

Cyanates which form insoluble carbonates, i.e., barium calcium and lead cyanates, decompose somewhat differently, however. Cumming (53) reported that the decomposition of lead cyanate can be quantitatively represented by:

$$Pb(CNO)_2 + 2H_2O \longrightarrow PbCO_3 + CO(NH_2)_2$$

and considered that there was no evidence for a cyanate intermediate in the urea formation. I. and O. Masson, however, in a kinetic investigation of the decomposition of calcium and barium cyanates in aqueous solution, considered the reaction to proceed by way of a slow hydrolysis of cyanate to ammonium and carbonate ion, followed by rapid reaction between cyanate and ammonium ion to form urea. The products of the reaction, urea and carbonate, were shown to be formed in approximately equal amounts - not as in the decomposition of sodium cyanate.

The main conclusions that can be drawn from the work relating to carbonate formation from cyanates, prior to this investigation, are then:

(1) The rate of carbonate formation is increased by increasing acidity.

(2) The reaction is autocatalytic, bicarbonate ion probably being the species responsible.

(3) Carbamate may be an intermediate in the reaction.

(d) Conclusions

Treating the problem of the decomposition of cyanate as a whole, the position at the commencement of this investigation was as follows:

(a) The bimolecular nature of the transformation of ammonium cyanate into urea had been clearly established, although the question of whether the reaction was ionic or non-ionic was still unsolved, there being no conclusive evidence either way.

(b) Various workers reported differing amounts of carbonate formed during ammonium cyanate decomposition (E. E. Walker reported approx. 10%, Svirbely and Warner reported negligible carbonate).

(c) The kinetics of carbonate formation from sodium and barium cyanates had only been investigated in outline while the nature of the autocatalytic decomposition of sodium cyanate had not been established and the kinetics of carbonate formation (if any?) during ammonium cyanate decomposition were quite unknown.

(d) The kinetics of urea formation from metallic cyanates had not been examined.

The aim of this investigation was to try to answer these questions, i.e., to treat the decomposition as a whole and investigate urea and carbonate formation from ammonium, sodium and barium cyanates.

Shortly after the commencement of this investigation, results were published by Wyatt and Kornberg (54) pointing out the very serious consequences of the neglect of carbonate formation during ammonium cyanate decomposition.

Since the completion of this work, the results of an investigation of the decomposition of cyanates and cyanic acid has been reported by Lister (110).

The decomposition of solutions of cyanic acid both with and without added acid was examined, the reactions proceeding qualitatively according to the equations:

$$HNCO + H_3O^+ \longrightarrow CO_2 + NH_4^+$$

$$HNCO + 2H_2O \longrightarrow NH_4^+ + HCO_3^-$$

Rate constants for the first order decomposition of cyanic acid and the second order reaction of cyanic acid and hydrogen ions are reported.

The decomposition of alkali cyanates in strongly alkaline solution was found to proceed in accordance with the rate equation:

$$\frac{dC}{dt} = k_1[CNO^-] + k_2[CO_3^=]$$

An examination of the effects of added borate and acetate ions showed that the catalytic action represented by the second term of the equation is specific to carbonate ions.

CHAPTER II

THE KINETICS OF UREA AND CARBONATE FORMATION

(a) Introduction

The decomposition of cyanate ions in aqueous solution can be represented by the stoichiometric equations:-

$$CNO^- + 2H_2O \rightleftharpoons CO_3^= + NH_4^+ \quad .. \quad .. \quad \underline{I,\ 1}$$

$$NH_4^+ + CNO^- \rightleftharpoons CO(NH_2)_2 \quad .. \quad .. \quad \underline{I,\ 2}$$

The kinetics of these two reactions are discussed in this Chapter; full details of the runs carried out are given in pages 132 et seq..

The decomposition of ammonium, sodium and barium cyanate has been examined, in some cases with the addition of small amounts of sodium carbonate, sodium bicarbonate, ammonia, hydroxyl ion, triethylamine and boric acid. All runs were carried out in sealed tubes to prevent loss of carbon dioxide which is formed from the products of reaction in the more acid solutions, the volume of gas and liquid phases being made approximately equal.

In order to permit the use of concentration units in the rate equations, all runs were carried out at the same, virtually constant, ionic strength. This was achieved by using an initial cyanate concentration not greater than 0.05 M. and adding sufficient potassium nitrate to bring the total ionic strength to 0.25. Under these conditions the largest variation of ionic strength encountered throughout any one run was 10% (NH_4CNO run) corresponding to a 2% change in the activity coefficient of a univalent ion. In the majority of cases, where additions to the cyanate solutions had been made, the variation was even less than this.

The analytical methods employed and the calculation of the concentration of the various species present are discussed in the appropriate Chapter (IV). Rate constants were calculated from the rate equations by graphical integrations.

(b) Results

The three cyanates used (sodium, ammonium and barium cyanate) lead to different relative amounts of the two products, urea and carbonate. Illustrations of this, taken from typical runs, are given in Table II, 1 below.

Table II, 1 60°C. I = 0.25

0.05 M. Cyanate	% decomp.	[Urea]	C*	$\frac{[\text{Urea}]}{C}$
Ammonium Cyanate	20	0.009	0.0022	4.1
	40	0.021	0.0032	6.6
	60	0.026	0.0043	6.1
Barium Cyanate	20	0.0034	0.0060	0.57
	40	0.0086	0.0104	0.83
	60	0.0143	0.0172	0.83
Sodium Cyanate	20	0.0022	0.0083	0.27
	40	0.0044	0.0120	0.37
	60	0.0073	0.0240	0.30
Sodium Cyanate + 0.0075 M. triethylamine	20	0.0011	0.010	0.11

* C = Total carbonate formed per unit volume

$= [CO_3^{=}] + [HCO_3^{-}] + [H_2CO_3] + [CO_2]$ gas

($[H_2CO_3]$ includes dissolved CO_2)

A graph showing the carbonate produced as a function of time (Figs. 2 and 3)* also shows that the three cyanates behave in a different manner and the pH range covered during decomposition depends on the particular cyanate (fig. 1).

The range of hydrogen ion concentration oovered by the reaction mixtures employed is thus 10^{-7}–8×10^{-11} and it can be seen that apparently the ratio of urea to carbonate formed decreases as $[H^+]$ decreases.

It has been found that under all these experimental conditions:

(a) The rate of urea formation is represented by

$$\frac{d[\text{Urea}]}{dt} = k_U[NH_4^+][CNO^-] - k_R[\text{Urea}] \quad .. \quad .. \quad \underline{II, 1}$$

(b) The rate of carbonate formation by

$$\frac{dC}{dt} = k_H[H^+][CNO^-] + k_C[HCO_3^-][CNO^-] + k_W[CNO^-] \quad \underline{II, 2}$$

The average values of the constants found in this investigation are listed in Table II, 2, together with the corresponding values of the Arrhenius parameters calculated from

$$\ln k = B - E_A/RT$$

The kinetic equations will now be considered in detail.

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* following pages 41 and 42.

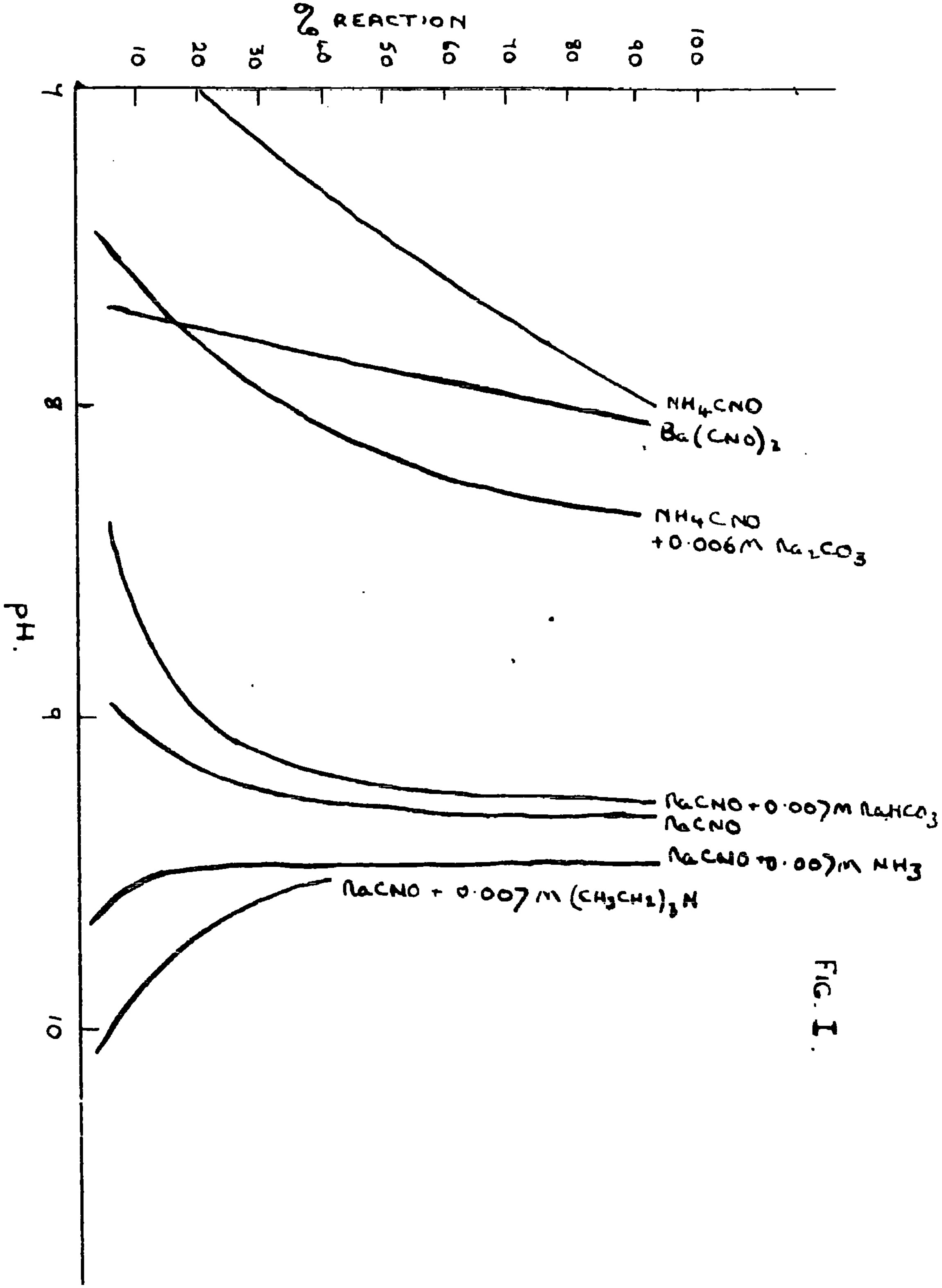
% REACTION
10
20
30
40
50
60
70
80
90
100
pH.
7
8
9
10
NH4CNO
Ba(CNO)2
NH4CNO +0.006M Na2CO3
NaCNO + 0.007M NaHCO3
NaCNO
NaCNO + 0.007M NH3
NaCNO + 0.007M (CH3CH2)3N

FIG. I.

Table II. 2 60°C. $I = 0.25$

	Rate constants			E_A(K cals.)		B/2.303	
	40°	60.1°	80.1°	40°-60°	60°-80°	40°C.	60°C.
(k_H)		4.0 x 10^{3} *	1.40 x 10^{4} *	-	14.6	-	13.2
(k_C)		1.75 x 10^{-2} *	6.96 x 10^{-2} *	-	16.1	-	8.8
(k_W)		6.36 x 10^{-5} ‡	5.20 x 10^{-4} ‡	-	24.5	-	11.9
(k_U)	0.00814	0.0748 *	0.553 *	22.9	23.3	14.0	14.2
(k_R)	-	1.6 x 10.$^{-5}$ ‡	-	-	-	-	-

* In min^{-1} mol.$^{-1}$ L. ‡ In min^{-1}.

(c) The Kinetics of Urea Formation

(i) Rate Constants

As already has been stated, the rate of urea formation is given by

$$\frac{d[\text{Urea}]}{dt} = k_U[NH_4^+][CNO^-] = k_R[\text{Urea}] \quad .. \quad \text{II, 1}$$

The value of the constant for the reverse reaction, k_R, is obtained from a study of the decomposition of pure urea solutions as described on p. 115.

Values for k_U for some of the runs are listed in Table II, 3, together with the hydrogen ion concentration range during each run.

It has been the aim of this investigation to determine the value of each constant over as wide a range of experimental conditions as possible. Consequently, urea constants have been determined not only in pure ammonium cyanate solutions at a hydrogen ion concentration of $10^{-7} - 10^{-8}$, but in solutions with added carbonate and ammonia. There has been some tendency in the past to consider the decomposition of ammonium and sodium cyanates separately, but here, the urea formation during the decomposition of sodium cyanate and barium cyanate[*] are examined also, confirming that the same

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[*] Ammonium ions formed as in eqn. I, 1, react with unchanged cyanate as in eqn. I, 2.

Table II, 3 RATE CONSTANTS FOR UREA FORMATION AT I = 0.25

Temp.	Run No.	Details of Run	$[H^+]$ range	k_U ‡
60°C.	1	0.05 M. Ammonium Cyanate, no additions	$14-1 \times 10^{-8}$	0.0754
	4	" " " + approx. 0.002 M. Na_2CO_3	$8-0.8 \times 10^{-8}$	0.0721
	2	" " " " 0.005 M. "	$5-0.5 \times 10^{-8}$	0.0746
	3	" " " " 0.006 M. "	$3-0.5 \times 10^{-8}$	0.0728
	7	" " " " 0.007 M. NH_3	$3-0.6 \times 10^{-8}$	0.0741
	14	0.05 M. Sodium Cyanate, no additions	$\sim 6 \times 10^{-10}$	0.075
	13	" " " " "	"	0.072
	15	" " " " "	"	0.078
	12	" " " + approx. 0.007 M. $NaHCO_3$	$4-0.6 \times 10^{-9}$	0.074
	17	" " " " " 0.007 M. NH_3	$\sim 3 \times 10^{-10}$	0.079
	18	" " " " " 0.002 M. NaOH	$1-5 \times 10^{-10}$	0.075*
	20	" " " " " .008 M. $(CH_3CH_2)_3N$	$0.8-3 \times 10^{-10}$	0.075*
80°C.	9	0.05 Ammonium Cyanate, no additions	$2 \times 10^{-7}-3 \times 10^{-8}$	0.554
	8	" " " + approx. 0.002 Na_2CO_3	$1 \times 10^{-7}-2 \times 10^{-8}$	0.551
40°C.	10	0.05 Ammonium Cyanate, + approx. 0.002 Na_2CO_3	$1 \times 10^{-7}-4.0 \times 10^{-9}$	0.00810

* Shown by comparison of observed and predicted urea values on the basis of eqn. II, 1

‡ $Min.^{-1}$ $mol.^{-1}$ L.

rate law for urea formation holds as in ammonium cyanate solutions.

Values of k_U are listed over a pH range of 7 - 10, the fraction of total ammonium $[NH_4^+] + [NH_3]$ present as NH_4^+ varying from 0.98 - 0.02. The results are in satisfactory agreement over this range.

The usual spread from the mean value of k_U in any one ammonium cyanate run is 4%. The values derived from the sodium cyanate decomposition are of a considerably lower order of accuracy, since the small urea concentration (not more than 0.011 M.) is calculated as the difference between two much larger quantities (cf. p.92) and a small error in either of the analytical determinations leads to an appreciable error in urea concentration. In any one run, the usual spread from the mean value of k_U is ± 12%; the mean values, however, agree within ± 5%.

(ii) Earlier work

Although the formation of urea from ammonium cyanate in water has been frequently examined (e.g., Svirbely and Warner (32)), a direct comparison of our results with those of other workers is impossible except for the data of Wyatt and Kornberg (54) which was published after the beginning of this investigation. This arises out of the fact that most of these workers considered only the reaction:

$$CNO^- + NH_4^+ \rightleftharpoons CO(NH_2)_2 \qquad .. \qquad \underline{I, 2}$$

and ignored carbonate formation by reaction I, 1.

This was originally justified by reporting negligible carbonate formation[*] but this conclusion cannot be maintained in view of the results of Wyatt and Kornberg (54), and of this investigation, where it was found that for 90% decomposition of 0.05 M. ammonium cyanate, approximately 15% of the products were in the form of carbonate.

If reaction I, 2, only is taken into consideration, we have:

$$[\text{Urea}] = [\text{CNO}^-]_o - [\text{CNO}^-] \; ; \quad [\text{NH}_4^+] = [\text{CNO}^-]$$ [‡]

where subscript "o" refers to initial concentrations. (Of course, neither of these assumptions is actually justified).

Hence the rate equation:

$$\frac{d[\text{Urea}]}{dt} = k_U^*[\text{NH}_4^+][\text{CNO}^-]$$

reduces to

$$-\frac{d[\text{CNO}^-]}{dt} = k_U^*[\text{CNO}^-]^2 \qquad \ldots \qquad \underline{\text{II, 3}}$$

where k_U^* is the "rate constant" calculated on the assumption of no carbonate formation, a conclusion which has already been

---

[*] Analysis for carbonate was carried out by adding $Ba(NO_3)_2$. At the pH prevailing in Ammonium Cyanate runs, however, most of the carbonate is present as HCO_3^- and H_2CO_3 and precipitation would not occur or be incomplete. (This has been confirmed by experiments here.) (Cf. also Wyatt and Kornberg (54)).

[‡] pH of the solution is such that virtually all ammonia is present as NH_4^+ if no carbonate is formed.

shown to be inadmissible. A calculation of $k_U^{\ddagger}$ from the results of this investigation shows that, due to a partial cancellation of errors, this quantity is sensibly constant in any one run. This is demonstrated in Appendix I and has also been pointed out by Wyatt and Kornberg (54).

Table II, 4 below, shows values of $k_U^{\ddagger}$ and k_U, (the "true" rate constant) for a number of ammonium cyanate runs:-

<u>Table II, 4</u> 60°C. $I = 0.25$

Run No.	Details of conditions	k_U	$k_U^{\ddagger}$
1.	0.05 M. NH_4CNO no additions	0.075	0.097
2.	" " + approx. 0.005 M. Na_2CO_3	0.075	0.074
3.	" " " " 0.006 M. "	0.073	0.071
7.	" " " " 0.007 M. NH_3	0.074	0.078

It can be seen that $k_U^{\ddagger}$ depends on the concentration of added carbonate and ammonia, while k_U is constant. Furthermore, the disagreement between k_U and $k_U^{\ddagger}$ is most serious in the reaction mixture containing no added substances, the very conditions investigated by earlier workers.

In order to compare our $k_U^{\ddagger}$ values, which are obtained at an ionic strength of 0.25, with those of other workers, the method employed by Svirbely and Warner (32) was used. These workers applied the Brönsted equation (29):

$$k = \frac{k^{o} f_{a} f_{b}}{f_{x}}$$

where k^{o} is the rate constant at zero ionic strength and f_a, f_b and f_x are the activity coefficients of the reacting species and activated complex respectively, at an ionic strength which leads to a rate constant, k.

The activated complex is assumed to have a charge equal to the sum of the charges of the reacting species, i.e., zero, and hence its activity coefficient was taken as unity: f_a and f_b, the activity coefficients of the univalent ions, were calculated here by means of the Davies' Equation (95).

Values of $(k_U^{*})^{o}$ obtained in this investigation are compared with those of Svirbely and Warner in Table II, 5 below, at 80°, 60° and 40°C.

<u>Table II, 5</u>

Rate constant (gm. mol^{-1}. L. min^{-1})		80°C.	60°C.	40°C.
$(k_U^{*})^{o}$	Svirbely and Warner	-	0.202	0.0222
	This investigation	1.53	0.196	0.0217
$(k_U)^{o}$	This investigation	1.17	0.149	0.0161

It can be seen that, when they can be compared, $(k_U^*)^o$ values are in good agreement and differ by 24 - 27% from the values of $(k_U)^o$, irrespective of temperature. This means that Arrhenius activation energies suggested by Svirbely and Warner are in agreement with those found in this investigation although their values are calculated from erroneous rate constants.

As Svirbely and Warner utilize their results to discuss ionic reactions in terms of the Brönsted-Christiansen-Scatchard theory (55, 56), it can be concluded, at this stage, that the conclusions of these authors cannot be maintained if they depend on the values of rate constants, but that they may be of importance when only the activation energies are involved.

Similar objections apply to the results of other workers (e.g., J. Walker (10)). Admittedly, E. E. Walker (19) observed and allowed for carbonate formation in his investigation but he assumed all ammonia to be present as NH_4^+. This will not be the case at the pH prevailing in such systems and his rate constants will, therefore, be too high.

Reference has already been made to the work of Wyatt and Kornberg (54) who also examined this reaction in the absence of any added substances. These authors allowed for the carbonate formation in the calculation of their k_U values, but, as they themselves point out, their results are not particularly accurate for the following reasons:-

(1) The analysis of their reaction mixtures was carried out by a gasometric method which made the accurate determination of small changes in carbonate content difficult.

(2) Their rate constants represent instantaneous values obtained from the slope of the [Urea] -time curve at various points.

They estimate their error in k_U values to be ± 10%. It must also be pointed out that these authors sampled their reaction mixture by pipetting and this occasional opening of the reaction vessel might have resulted in loss of gaseous carbon dioxide at the beginning of a run where the pH is at its lowest value.

Most of this work was carried out at 70°C. where they report $(k_U)^{o}$ values of 0.41 - 0.47 gm. mol.$^{-1}$. L. min^{-1}. The corresponding value from this investigation is 0.44, (calculated from values at 60°C. and 80°C.), i.e., the agreement is good.

(iii) Arrhenius Parameters

The Arrhenius parameters for the formation of urea have already been quoted (Table II,2). It is worth noting that the value of these quantities depends on the temperature interval involved: e.g.,

	40° - 60°	60° - 80°
$(E_A)_U$	22.9 (k.cal.)	23.3 (k.cal.)

In view of the accuracy of individual rate constants (see p. 29), the small number of runs at 40°C. and 80°C., and the fact that the calculations involve a knowledge of equilibrium constants, which in some cases have been extrapolated from values at a lower temperature, it may well be that the variation is fortuitous. On the other hand, the experimental error is estimated to be such that this variation is only just within its limits and may, therefore, well be genuine.

Similar variations were reported by Svirbely and Warner (32), who considered that the temperature dependence of $(E_A)_U$, together with the experimentally observed "salt effects", provided good evidence that the stoichiometric equation:

$$NH_4^+ + CNO^- \rightleftharpoons CO(NH_2)_2$$

also represented the nature of the kinetic process, i.e., an ionic mechanism. They argued that, as a result of the destruction of the formal electronic charges as the system passes into the transition state, such a process will be affected by the dielectric constant of the medium. Hence activation energy will vary with temperature due to variation of the dielectric constant of the solvent medium with temperature. Application of the Christiansen-Scatchard equation and work with iso-dielectric solvents* gave good agreement between the observed and calculated values of the activation energy.

Although the rate constants of these authors have been criticised, it was pointed out at the same time that activation energies obtained in pure water are in agreement with these of this investigation. No data have been obtained here for mixed solvents, which these authors used extensively, but it is surprising that the dielectric constant, a macroscopic property of the solvent medium, should affect the short range forces between two oppositely charged ions as they pass into the activated state. This objection becomes even stronger in mixed solvents. In this connection, Eyring and Ri (57), in a discussion of the nitration of benzene with NO_2^+ as the attacking agent, were able to treat the system on the assumption that forces between charged particles under these conditions were controlled by a dielectric constant of unit value.

At present, the ionic mechanism proposed by Svirbely and Warner (32) cannot be regarded as by any means certain, but even if this mechanism operates, the positive temperature coefficient of the energy of activation is open to an alternative explanation. On the basis of Eyring's rate equation (58) it can be shown that

$$\frac{dE_A}{dt} = Cp^{*} + R$$

---

* Solvents - usually alcohol-water mixtures - chosen in such a way that they had the same dielectric constant at all temperatures investigated.

where $C_p^{\ddagger}$, the heat capacity of activation, represents the difference in heat capacity between the activated complex and initial reactants. The ionic mechanism requires a decrease in electronic charge as the activated complex is formed, thus implying a decrease in solvation, i.e., fewer solvent molecules will have their motion restricted, and hence a larger amount of heat can be absorbed.

Thus if the temperature dependence of E_A is genuine, it can be accounted for in a qualitative manner by the assumption of an ionic mechanism for this reaction. On the other hand, if this ionic mechanism is not operating, it may be that even a genuine temperature dependence of the present E_A values is due to the existence of a number of pre-equilibria involving ΔH^o values with large temperature coefficients.

(d) The Kinetics of Carbonate Formation

(i) The Kinetic Equation

It has already been pointed out that in all reaction mixtures investigated, the rate of carbonate formation can be represented by the equation:

$$\frac{dC}{dt} = k_H[H^+][CNO^-] + k_C[HCO_3^-][CNO^-] + k_W[CNO^-] \quad .. \quad \underline{II,2}$$

This equation contains three unknown constants, but their values may be determined by utilizing the fact that the relative contributions of the three terms depend on the particular cyanate examined (see Chap. VI). Thus:

(a) The first term usually makes negligible contribution in runs involving sodium cyanate.

(b) The second term only makes a small contribution in runs involving ammonium cyanate and no added substances, and obviously no contribution at all in the presence of Ba^{++} ions where the greater part of the carbonate formed is precipitated as barium carbonate.

These points are illustrated in Table II, 7.

Values of the rate constants are given in Table II, 8, for a number of the runs. It is worth noting at this stage that the agreement between the values of any one rate constant for different runs is not as good as the corresponding agreement in the case of k_U. This is a consequence of the mode of

Table II, 7 60°C. I = 0.25

Contribution to total carbonate of each mechanism

0.05 M. NH_4CNO	% Reaction	Carbonate concentration due to *			% contribution of term in k_H
		1st term (k_H)	2nd term (k_C)	3rd term (k_W)	
Run 1	15	0.0005	2×10^{-5}	8×10^{-5}	84
	25	0.0011	6×10^{-5}	0.00016	79
	60	0.0020	0.0003	0.0005	72
	70	0.0022	0.0007	0.0008	60
0.05 M. NaCNO Run 13	10	0.00014	0.0011	0.0020	4-5
	16	0.00021	0.0026	0.0034	3
	40	0.00032	0.0090	0.0062	2
	70	0.00038	0.0169	0.0085	1.5

* The carbonate concentrations quoted are those formed after the arbitrary zero time, i.e., 16 mins. in the case of Run 1 and 168 mins. in the case of Run 13.

Table II, 8 60°C. $I = 0.25$

Rate Constants for Carbonate Formation

Temp.	Run No.	Details of Run	$10^{-3}k_H$ *	$10^{2}k_C$ *	$10^{5}k_W$ ‡
60°C.	14	0.05 M. Sodium Cyanate, no additions		1.77	6.3
	13	" " " " "		1.66	6.1
	15	" " " " "		1.74	6.4
	16	0.025 " " " "		1.59	6.6
	17	0.05 M. Sodium Cyanate + 0.007 M. NH_3		1.78	6.4
	12	" " " + 0.007 M. $NaHCO_3$		1.72	6.4
	1	0.05 M. Ammonium Cyanate, no additions	4.0		
	2	" " " + 0.005 Na_2CO_3	4.0		
	3	" " " + 0.006 "	3.8		
	4	" " " + 0.002 "	4.1		
	7	" " " + 0.007 M. NH_3	4.1		
80°C.	23	0.05 M. Sodium Cyanate, no additions		6.96	51.5
	9	" Ammonium Cyanate, no additions	13.8		
	8	" " " + 0.002 M. Na_2CO_3	14.1		

* gm. mol.$^{-1}$ L. min.$^{-1}$

‡ min.$^{-1}$

calculation of the rate constants; (full details in experimental section). Values of k_C and k_W were obtained from the slope and intercept of a straight line calculated from the experimental results, and k_H from the relatively small amounts of carbonate formed in ammonium cyanate runs.

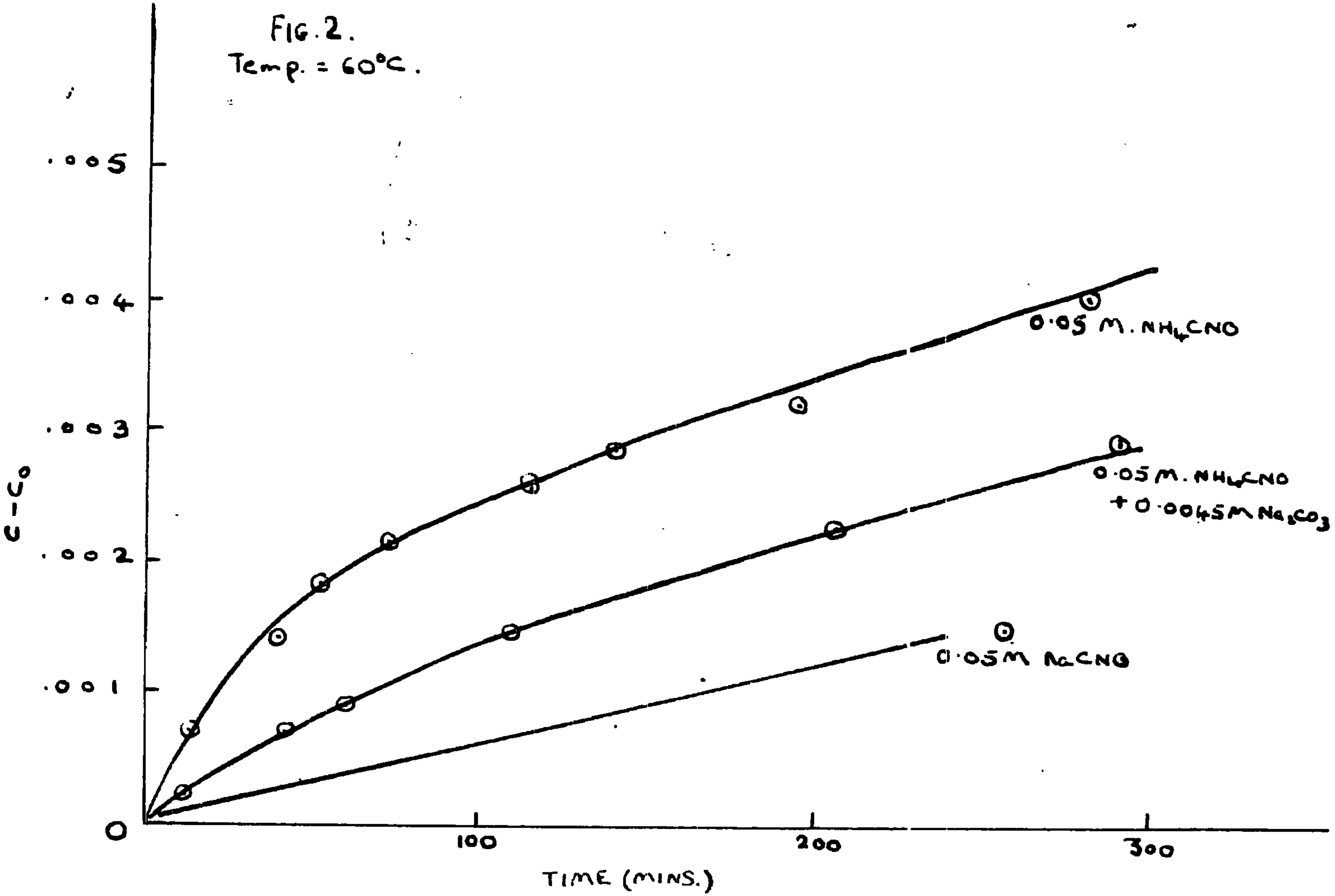
Runs carried out in the presence of barium ions have not been included in Table II, 8. Full details of these runs can be obtained by reference to Run 19, where, although large amounts of carbonate are accounted for by the first term of equation II, 2, the results cannot be used to obtain a reliable value of k_H since calculation of $[H^+]$ requires a knowledge of the total ammonia present in solution. This quantity has a low value in such systems, and can only be obtained as a difference between two very much larger quantities. Consequently, rather than calculate values for k_H, the results of such runs are expressed as a comparison between total carbonate calculated on the basis of eqn. II, 2, and that found experimentally. The good agreement is taken as confirmatory evidence of the values assigned to the rate constants.

The rate expression was originally derived from the following considerations.

The rate of carbonate formation from sodium and ammonium cyanate solutions can be compared in Figs. 2 and 3. The

FIG. 2.

Temp. = 60°C.



approximate hydrogen ion concentrations of these solutions are listed below.

Table II, 6

Cyanate	$[H^+]$
Ammonium Cyanate	$1.5 \times 10^{-7} - 2 \times 10^{-8}$
" " + 0.005 Na_2CO_3	$5 \times 10^{-8} - 5 \times 10^{-9}$
Barium Cyanate	1.4×10^{-8}
Sodium Cyanate	6×10^{-10}

It can be seen that:-

(1) There is a considerable decrease in the rate of carbonate formation from ammonium cyanate with decreasing acidity. The much more alkaline sodium cyanate solutions show even lower initial rates. (Fig. 2)

(2) The rate of carbonate formation from sodium cyanate is autocatalytic (Fig. 3, curve B) and the pH is virtually constant over the reaction range examined.

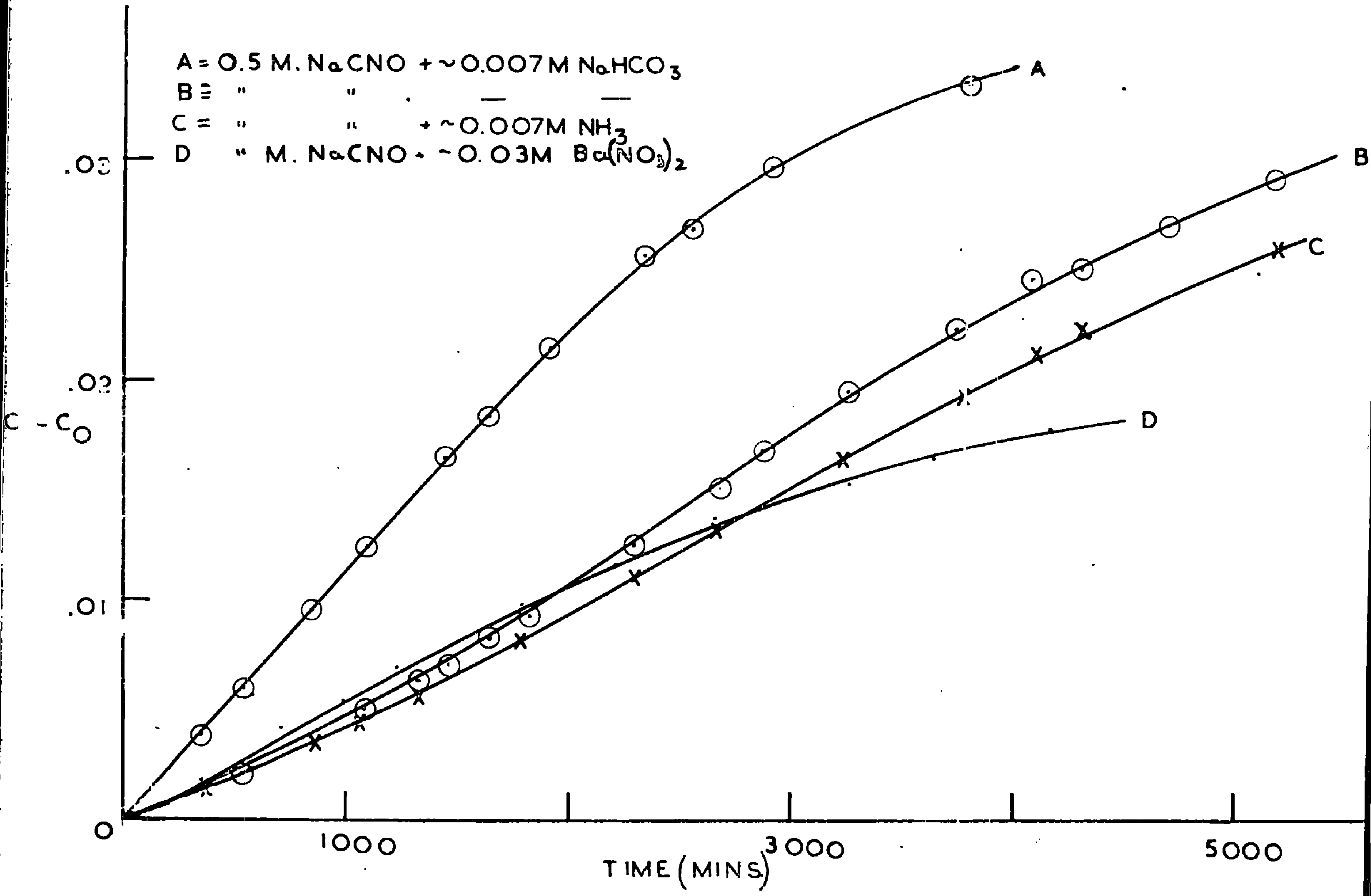
(3) The rate of carbonate formation from barium cyanate is approximately first order with respect to cyanate. Here the pH is again constant and virtually no carbonate is present in solution.

This indicates the likelihood that the rate equation contains:-

(1) a term involving $[H^+]$

(2) a term involving one of the products of the reaction

FIG. 3


A = 0.5 M. NaCNO + ~0.007M NaHCO$_3$
B = " " . — —
C = " " + ~0.007M NH$_3$
D " M. NaCNO + ~0.03M Ba(NO$_3$)$_2$
A
B
C
D
.03
.02
.01
0
C - C$_0$
1000
3000
5000
TIME (MINS)

(3) a term involving only $[CNO^-]$.

Bicarbonate ion is, of course, a product of the reaction formed from interaction between carbonate and the solvent.

In runs involving sodium and ammonium cyanate, the pH is such that, to a first approximation,

$$[HCO_3^-] = [NH_3]$$

It might, therefore, appear that the second term in the rate equation could equally well be written as:

$$k_C[NH_3][CNO^-],$$

the constant having the same value as before. This possibility was excluded by carrying out runs with sodium cyanate in the presence of small additions of ammonia and bicarbonate ions. (Runs 12 and 17).

The runs in the presence of barium ions involve relatively low values of $[NH_4^+]$ and hence confirm that no term involving this quantity contributes to the carbonate formation. This possibility could not be entirely excluded before, as all other runs in which the first term in eqn. II, 2 contributes appreciably, also involve relatively large $[NH_4^+]$ values.

It is interesting to note that in the reaction mixture containing barium ions, the values of N do not reach a stationary state (cf. I. and O. Masson, p. 16) but tend to increase throughout the run; whereas if this quantity is calculated assuming all carbonate to be precipitated as barium carbonate, a value more nearly constant results. A quantitative examination of this problem (cf. Appendix II) shows that the ammonium ion concentration calculated from the rate constants k_W, k_H and k_U is in good agreement with this stationary (but incorrect) value for N if it assumed that all carbonate is precipitated as barium carbonate. This serves as a useful comparison between this and the earlier work of I. and O. Masson, direct comparison being difficult because of temperature and ionic strength differences.

A run was carried out in which the initial sodium cyanate concentration was half the usual value of 0.05 M. (Cf. Run 16). The rate constants have the usual value and thus indicate that the proposed rate equation is not due in some way to a cancellation of errors resulting from the same initial cyanate concentration being employed in all runs.

The addition of a number of substances to the reaction mixture, particularly in the case of sodium cyanate runs, does not affect the general result, i.e., the rate of carbonate formation can always be represented by eqn. II, 2 and these substances only affect the rate by their effect on hydrogen and bicarbonate ion concentration via the normal acid-base equilibria.

The following substances were investigated in this connection:-

Table II, 9

Run No.		Addition
17	..	0.05 M. Sodium Cyanate + NH_3
18	..	" " " " OH^- ions
12	..	" " " " HCO_3^- ions
20	..	" " " " $N(CH_2CH_3)_3$
21	..	" " " " H_3BO_3

These conclusions are of importance in view of the possibility (cf. later discussion, p. 73) that the formation of carbonate from cyanate ions is subject to general acid or base catalysis.

Thus all the results are consistent with a postulate that the rates of carbonate and urea formation are defined by equations II, 1 and II, 2, respectively.

(ii) Comparisons with the results of earlier workers

I. and O. Masson (48) examined the decomposition of barium calcium and sodium cyanates in water at 70°C. Quantitative comparison is not possible, since these authors did not work at constant ionic strength. A number of qualitative comparisons, however, can be made:

(1) Although not stated as such, their results are in agreement with an auto-catalytic effect of bicarbonate ions, as expressed by eqn. II, 2*.

(2) Masson reported that, during the decomposition of

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* I. and O. Masson reported that the autocatalysis was due to the "$NH_4CO_3^-$" ion and to a smaller extent, the $CO_3^=$ ion.

sodium cyanate, the ratio of urea to carbonate formed reached a constant limiting value of 0.33. It can be seen that the same is found in this investigation*. (Cf. Table II, 1).

(3) A quasi-stationary ammonium concentration was reported during the decomposition of barium and calcium cyanate. The mean value, 0.0020 M., is in good agreement with that found here. (Cf. Run 19).

Täufel, Wagner and Dünwald (52) examined the rate of hydrolysis of alkali cyanates in strongly alkaline solution. They calculated a first order rate constant with respect to cyanate which, although virtually constant in any one run, decreased with increasing initial hydroxyl ion concentration of the reaction mixture. They proposed the rate expression:

$$\frac{dC}{dt} = k_1[H^+][CNO^-] + k_2[CNO^-]$$

and reported a limiting first order rate constant of 0.0028 gm. mol.$^{-1}$ L. min.$^{-1}$ at 100°C. (The value of the first order constant at high alkali concentration).

This is, however, open to re-interpretation. Whereas these authors consider the decrease in the value of the first order rate constant with increasing alkali concentration to be due to the decrease in the $[H^+]$, it can equally well be accounted for on the basis of eqn. II, 2 by the decrease in the small

---

* I. and O. Masson considered this to have some fundamental significance but this is considered fortuitous since the value of the ratio is dependent on additions that have been made to the reaction mixture: cf. Table II, 1.

fraction of the total carbonate which is present as HCO_3^- under these conditions.

If this is so, the limiting first order velocity constant reported by these authors, of 0.0028 gm. mol.$^{-1}$ L. min.$^{-1}$ at 100°C., should be the k_W of II, 2 at this temperature. As k_W extrapolated to 100°C. gives a value of 0.0031 gm.mol.$^{-1}$L. min.$^{-1}$ the agreement, considering the uncertainty in ionic strength, etc., is good. In any case, a hydrogen contribution at all apparent at these high pH values, would predict a rate of carbonate formation at a pH of 7 - 8 (in ammonium cyanate runs) many times that observed. Their rate equation, therefore, cannot be accepted as being generally applicable.

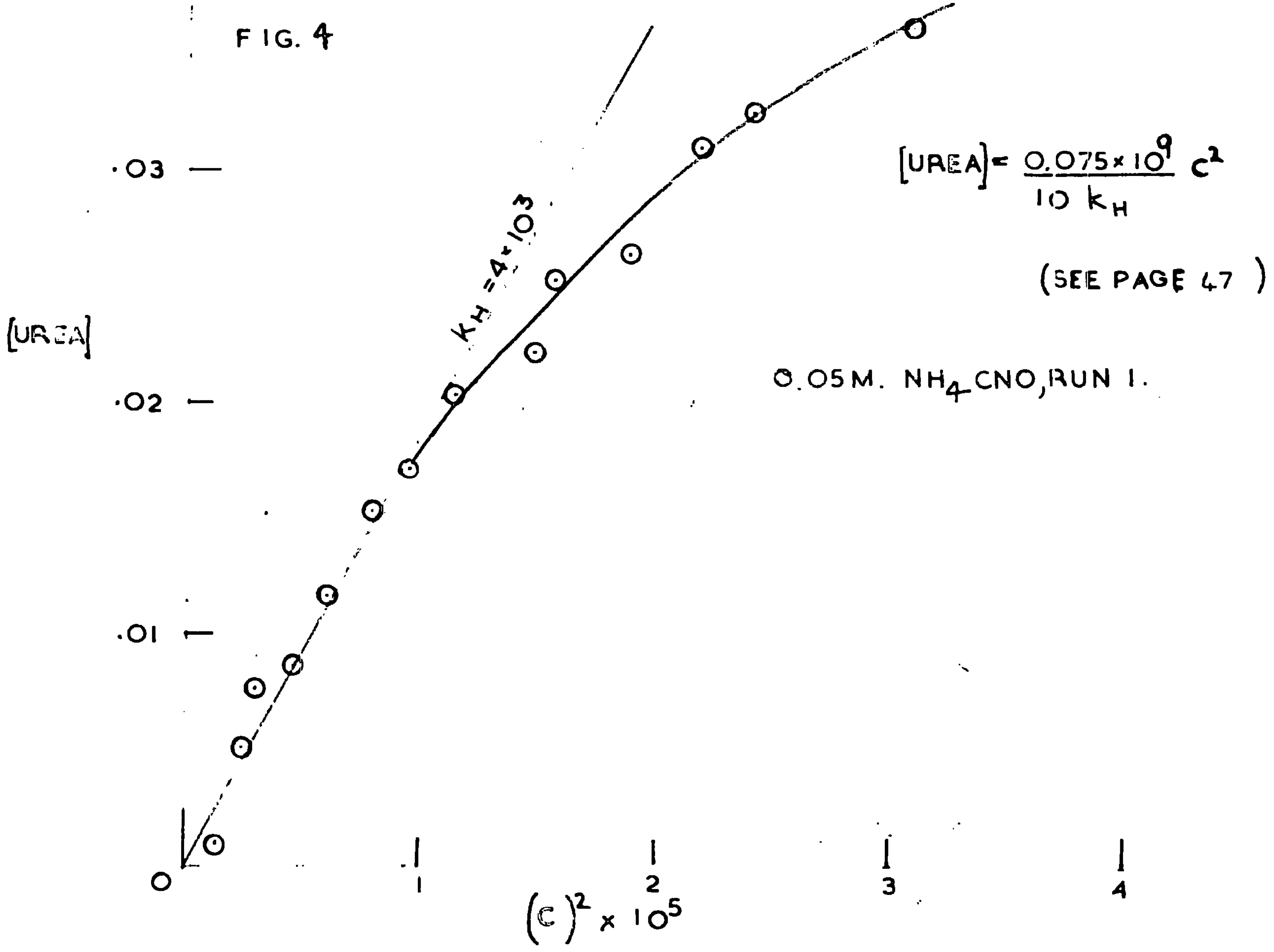
Wyatt and Kornberg (54) proposed that, in solutions of ammonium cyanate, the rate of carbonate formation is given by:

$$\frac{dC}{dt} = k'[H^+][CNO^-]$$

Following the treatment of Wyatt and Kornberg, this rate equation requires a straight line relationship between [Urea] and C^2, in any one run. At 60°C., $I = 0.25$, this line should have a slope of $\frac{10^9 k_U}{10k'}$ where k' is the rate constant of carbonate formation.

Within their experimental error, this is obeyed. However, the treatment applied to Run 1 of this investigation, is shown in Fig. 4. The straight line is drawn such that $k' = k_H =$ 4×10^3. The initial slope agrees well with the points plotted since here most of the carbonate is produced by the first term

FIG. 4



$$[\text{UREA}] = \frac{0.075 \times 10^9}{10\ k_H}\, c^2$$

(SEE PAGE 47)

0.05M. NH_4CNO, RUN 1.

in eqn. II, 2. (See Table II, 7) but considerable deviations later in the run are apparent. The rate equation is totally unable to account for the considerable carbonate formation in the carbonate added ammonium cyanate runs. This rate equation is therefore, not accepted, although it is correct within Wyatt and Kornberg's experimental error.

Lister (110) has examined the decomposition of cyanic acid and cyanate ions in acid and alkaline solutions respectively. In the presence of strong mineral acid, the rate is represented by:

$$-\frac{d[HCNO]}{dt} = k_1[H^+][HCNO] \quad .. \quad \text{II, 3.}$$

and in solutions of the pure acid:

$$-\frac{d[HCNO]}{dt} = k_2[HCNO] \quad .. \quad \text{II, 4.}$$

reaction II, 4, being faster at pH>2.

At the lowest pH (7) encountered during this investigation, a term $k_H[H^+][CNO^-]$ in equation II, 2, plays an important part in carbonate formation, (cf. Table II, 7, p. 39, Run 1), and

$$\frac{dC}{dt} = k_H[H^+][CNO^-] \quad \text{under Lister's conditions.}$$

$$\text{i.e.,} \quad \frac{dC}{dt} = k_H K_A[HCNO] \quad \text{where } K_A = \frac{[H^+][CNO^-]}{[HCNO]}$$

whence k_2 from equation II, 4 should be comparable with the constant $k_H K_A$. Lister quoted k_2 as 3.7×10^{-2} at 12°C. The value of $k_H K_A$ at 12°C., extrapolated from the rate constants and Arrhenius parameters quoted in Table II, 2, is 7.0×10^{-2}(min.$^{-1}$).

Considering the uncertainty in ionic strength, etc., the agreement is satisfactory.

The rate equation for the decomposition of cyanate ions in alkaline solutions (urea formation negligible) was proposed as:

$$\frac{dC}{dt} = k_1[CNO^-] + k_2[CO_3^=]$$

However, under the conditions employed, $[CNO^-] \simeq [OH^-]$ in any one run and the term in k_H in eqn. II, 2, may be neglected.

Writing $[HCO_3^-] = \dfrac{[CO_3^=]}{K_2[OH^-]}$ this becomes:-

$$\frac{dC}{dt} = k_W[CNO^-] + \frac{k_c}{K_2}\frac{[CO_3^=][CNO^-]}{[OH^-]} \quad *$$

$$= k_W[CNO^-] + \frac{k_c}{K_2}[CO_3^=]$$

Lister quoted k_2 to be 6.6×10^{-4} (mins^{-1}) at 100°C. The value of $\frac{k_c}{K_2}$ at 100°C., extrapolated from the results quoted in Table II, 2, is 1×10^{-3} at $I' = 0.25$. Considering the uncertainty in ionic strength, etc., the agreement is satisfactory.

The effect on the rate of carbonate formation of acetate and borate ions was also studied but in complete agreement with this investigation, they were found to exert no specific catalytic effect.

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* $K_2 = \dfrac{[CO_3^=]}{[HCO_3^-][OH^-]}$ See Table V, 2.

(e) The Kinetics of Urea Decomposition

(i) The rate constant for Urea decomposition

Urea is known to hydrolyse in aqueous solution, the ultimate products being ammonium carbonate, although it is generally held that ammonium cyanate is first formed. In order to determine the effect of this reaction on the rate of decomposition of cyanates, the rate of hydrolysis and the nature of the immediate decomposition products must be known.

The results of a few experiments designed to answer these questions are described below.

The hydrolysis of urea was examined only at 60°C. under the usual conditions, i.e., in sealed tubes at an ionic strength of 0.25, the reaction mixture being analysed by estimating the amount of cyanate and carbonate formed.

The results showed clearly that NH_4^+ and CNO^- ions are first formed, no carbonate being detected till some time after the beginning of the reaction. (Cf. Fig. 5).

The rate constant for the hydrolysis reaction, k_R, was determined from the equation:

$$-\frac{d[\text{Urea}]}{dt} = k_R\,[\text{Urea}] - k_U[NH_4^+][CNO^-]$$

though, in practice, the second term was ignored and the resulting first order rate constants extrapolated back to zero time, thus giving k_R.

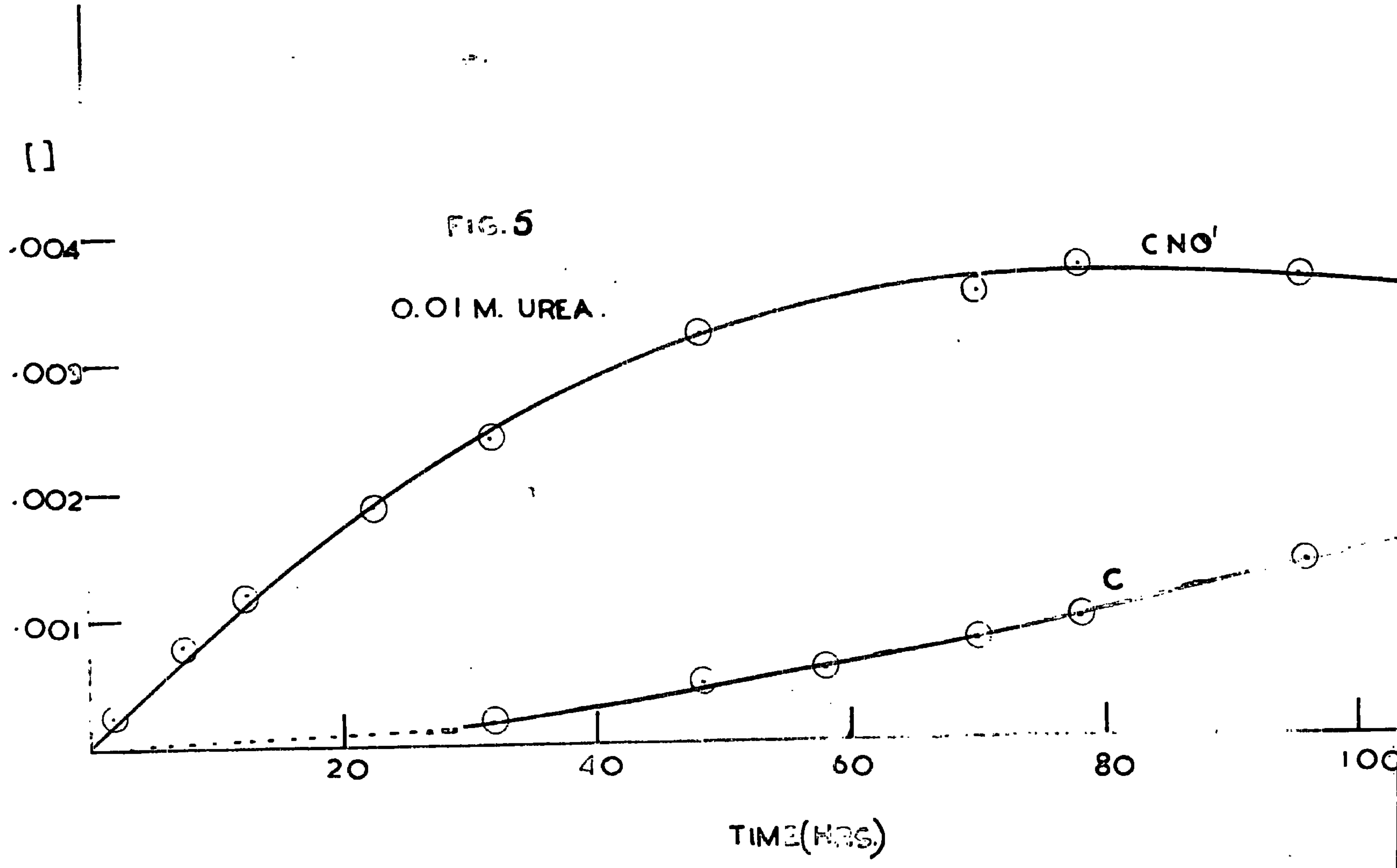


FIG. 5

0.01 M. UREA.

Values of k_R, determined from a number of reaction mixtures, are given below:

Table II, 10

Run No.	Details of Run	gm. mol.$^{-1}$ L. min.$^{-1}$ $k_R \times 10^5$	~pH
24	0.2 M. Urea	1.48	7
25	0.1 " "	1.63	7
26	0.1 " "	1.61	7
27	0.1 " " + 0.0035 M. Na_2CO_3	1.55	10
28	0.1 " " + 0.0014 " "	1.60	9

It will be noted that k_R would seem to be independent of pH over this range, in general agreement with the work of Krasil'shchikov and Nefedova (45).

This value of k_R is such that the hydrolysis of urea need only be taken into account in the decomposition of cyanates when large amounts of urea have been formed, i.e., after 80% reaction for 0.05 M. ammonium cyanate. (see p. 115).

(ii) Equilibrium between Urea and Ammonium Cyanate

A number of authors have reported equilibrium constants between urea and ammonium cyanate in aqueous solutions, from the data obtained by examining appropriate mixtures for a sufficiently long time: (Cf. J. Walker (10); Wyatt and Kornberg (54)). It is difficult to see how such an equilibrium could have been observed as cyanate ions in such systems will decompose to give carbonate. However, as can be seen from Fig. 5, this decomposition to carbonate is relatively slow, the cyanate ions are in a quasi-stationary state, and, presumably, the small quantities of carbonate present escaped the detection of the other workers.

The true equilibrium constant of this system can, of course, never be observed directly, but its value is given by:

$$K = \frac{k_R(f_1)^2}{k_U}$$

and can be used to calculate the standard Gibbs Free Energy change for the reaction:

$$NH_4^+(aq.) + CNO^-(aq.) \rightleftharpoons Urea(aq.)$$

A pseudo-equilibrium constant, K', can be obtained by assuming that the flat portion of the $[CNO^-]$ - t curve (Fig. 5) corresponds to equilibrium. If carbonate formation is ignored:

$[CNO^-] = [NH_4^+]$ and K' may be calculated.

Presumably this corresponds to the constant reported by earlier workers. Values of K at zero ionic strength are compared with those of K' in Table II, 11 below. Our values of K' were obtained from the maximum of the $[CNO^-]$-t curve. (Cf. Fig. 5).

Table II, 11 60°C. $I = 0$

	K	K'
This investigation	1.1×10^{-4}	-
This investigation Runs 24, 25, 26	-	0.7×10^{-4}
Walker and Kay (12)*	-	1.2×10^{-4}

* Extrapolated from data at 30° and 100°C. quoted by these authors. Wyatt and Kornberg (54) quote a value at 70°C. in substantial agreement with an extrapolated value from the data of Walker and Kay at that temperature.

Considerable deviations between K and K' in this investigation are apparent, as would be expected in view of the facts already discussed. The value of Walker and Kay (12) was obtained by using a conductivity method and would thus be especially sensitive to carbonate formation[‡]. The K' value obtained from their data is high compared with K' obtained here, as is to be expected in view of their probable over-estimate of cyanate at equilibrium.

(iii) Carbonate formation from Urea

As urea decomposes to form cyanate ions, carbonate will be formed from them and it should be possible to check the consistency of the general scheme proposed, by calculating the quantity of carbonate formed by means of eqn. II, 2, and comparing with that observed experimentally.

This is only possible when the reaction has been taking place for some time, as the use of eqn. II, 2, requires a knowledge of the hydrogen ion concentration which in turn can only be obtained from a knowledge of the total carbonate content, C. (Chap. IV). The value of this quantity is very small in runs starting with 0.1 M. urea and must, moreover, be determined by the difference of two much larger quantities – $[CNO^-]$, which is determined spectrophotometrically, and the "total basicity" (cf. p. 34) – and thus cannot be determined very accurately.

The observed carbonate may, therefore, well be in error and this has a serious effect on the calculated value. Thus, an observed value which is too low, results in too high a

---

[‡] The conductivity corresponding to known concentrations of ammonium cyanate had been determined by separate experiment. Carbonate formation would result in a higher conductivity being observed with consequent over-estimation of cyanate.

value for hydrogen ion concentration. In the decomposition of pure Urea, the term in $[H^+]$ is the most important term in eqn. II, 2 for the carbonate formation and the initial error leads to a comparison of too high a calculated value with too low an observed value.

This is taken to account for the discrepancies observed in Run 25 listed in the Table below.

Table II, 12 60°C. I = 0.25

Run 25 0.10 M. Urea

Time (hrs.)	t	C (observed)	C (calculated)	$[H^+]$
22	0	-	-	
30	8	0.0002	0.0003	7×10^{-8}
70	48	0.0008	0.0017	2.5×10^{-8}
120	198	0.0019	0.0032	1.4×10^{-8}

Much better agreement is observed in the case of Run 27, which was carried out in the presence of 0.0035 M. sodium carbonate, resulting in a lower value for $[H^+]$ and a smaller inaccuracy in the calculated value of the total carbonate. Analogous considerations apply to Run 24, where the initial urea concentration was 0.2 M. resulting in a more accurate figure for the total carbonate in view of the larger quantities involved. Both of these runs are illustrated in Tables II, 13 and II, 14 below.

Table II, 13 60°C. I = 0.25

Run 27 0.10 M. Urea + 0.0035 M. Na_2CO_3

Time (hrs.)	t	C (observed)	C (calculated)
41.9	0	-	-
51.5	9.6	0.0003	0.00029
112	70	0.0023	0.00217
150	108	0.0038	0.00420
188	146	0.0053	0.00563

Table II, 14 60°C. I = 0.25

Run 24 0.20 M. Urea

Time (hrs.)	t	C (observed)	C (calculated)
4.9	0	-	-
15	10.1	0.0002	0.0002
39	34	0.0007	0.0012
85	80	0.0023	0.0032
118	113	0.0035	0.0042

As a further check, the pH of the solution during the initial period of an 0.1 M. Urea run at 60°C., was calculated from the pH of samples of the run mixture cooled to room temperature. (See p. 112). The results are shown in Fig. 6 (upper curve).

An initial rapid fall in hydrogen ion concentration is observed, the value reaching $3 - 4 \times 10^{-8}$ after twenty-four hours, whereas that calculated from the observed carbonate and ammonia concentration in Run 25 does not reach this value until 40 hours.

The hydrogen ion concentration may be calculated theoretically[*] by assuming the rate of formation of all species to be given by eqns. II, 1 and II, 2. The derivation is described in Appendix III. Values of hydrogen ion concentration calculated theoretically, and the measure of agreement between the value observed experimentally and the value so calculated can be seen from Fig. 6.

It has been suggested by some workers (cf. Mukaiyama and Matsumaga (47)) that biuret is formed in appreciable quantities during the decomposition of urea:-

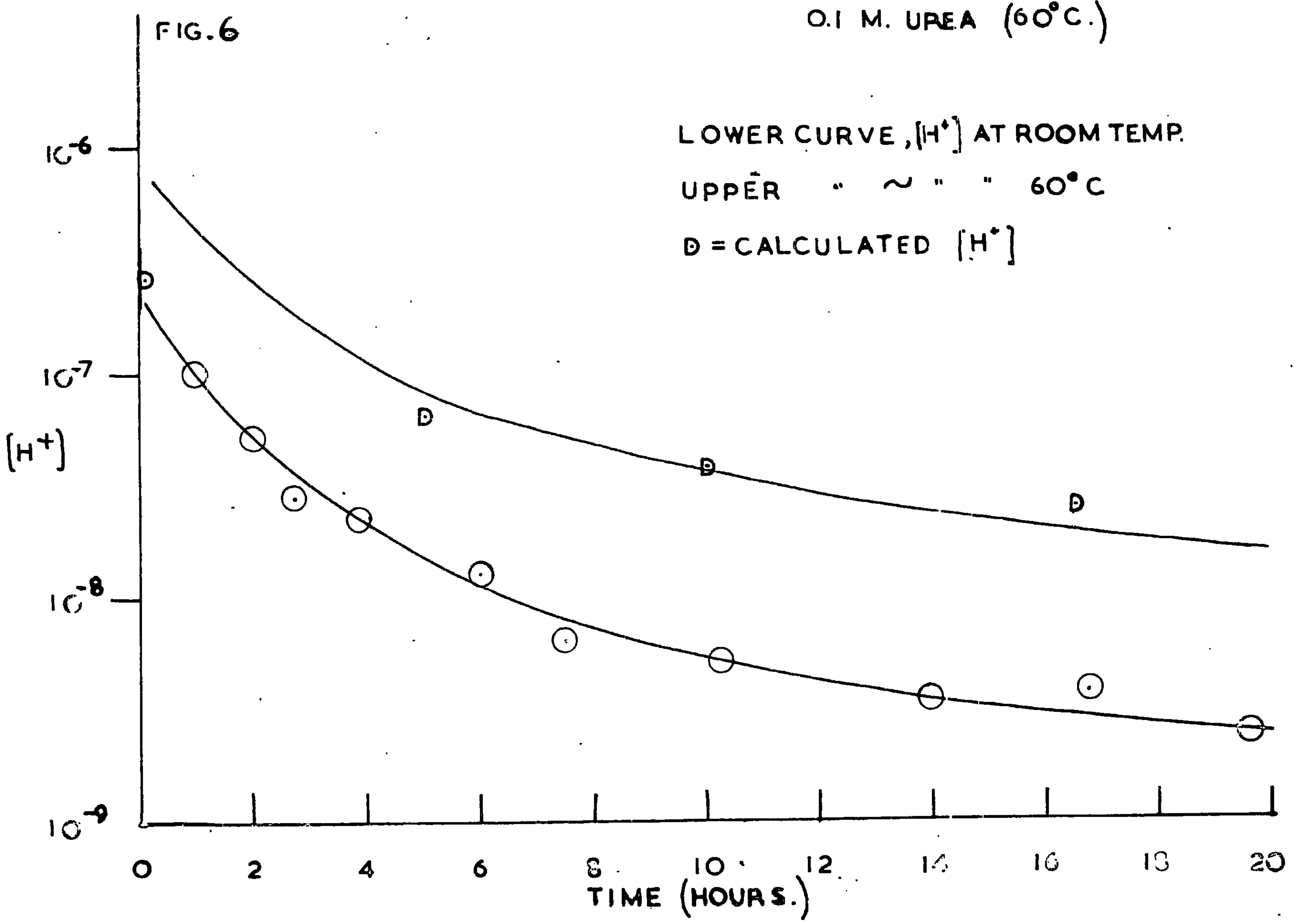
$$NH_4^+ + CNO^- \rightleftharpoons NH_3 + HCNO + CO(NH_2)_2 \rightleftharpoons NH_2CONHCONH_2$$

---

[*] The value of $[H^+]$ is given by

$$[H^+] = \frac{1.35 \times 10^{-6}}{t^{1/2}} \quad .. \quad .. \quad \text{Appendix III, 10}$$

FIG. 6


0.1 M. UREA (60°C.)
LOWER CURVE, [H⁺] AT ROOM TEMP.
UPPER " " " 60°C
D = CALCULATED [H⁺]
10⁻⁶
10⁻⁷
[H⁺]
10⁻⁸
10⁻⁹
D
D
D
0
2
4
6
8
10
12
14
16
18
20
TIME (HOURS.)

If this were so here, in appreciable quantities, it could account for the high pH, and consequently low rate of carbonate formation observed, due to the accumulation of ammonia in solution. However, the examination of 1 M. Urea solution at 60°C. showed that no biuret could be detected here (the concentration of biuret was shown to be less than 5×10^{-4}) and the quantities formed in the 0.1 and 0.2 M. solutions would be quite negligible.

It is concluded, then, that it is probable that carbonate is formed in accordance with the kinetic equation already established (eqn. II, 2), the low order of accuracy of some of the analytical determinations of the very dilute solutions involved, leading to seemingly divergent results.

(f) The Alternative Rate Equation

Ignoring the decomposition of urea, the rate equation for the decomposition of cyanate ions:

$$-\frac{d[CNO^-]}{dt} = [CNO^-]\left[k_U[NH_4^+] + k_W + k_H[H^+] + k_C[HCO_3^-]\right]$$

II, 5

may, with equal validity, be written in an alternative form. Thus eqn. II, 5 may be written:

$$-\frac{d[CNO^-]}{dt} = [H^+][CNO^-]\left[k_U\frac{[NH_4^+]}{[H^+]} + \frac{k_W}{[H^+]} + k_H + k_C\frac{[HCO_3^-]}{[H^+]}\right]$$

$$= K_{HCNO}[HCNO]\left[\frac{k_U}{K_{NH_4^+}}[NH_3] + \frac{k_W}{K_W}[OH^-]\right.$$

$$\left. + k_H + \frac{k_C}{K_{HCO_3^-}}[CO_3^=]\right]$$

$$= [HCNO]\left[k_U'[NH_3] + k_W'[OH^-] + k_H' + k_C'[CO_3^=]\right]$$

II, 6

where K_{HCNO}, $K_{NH_4^+}$ and $K_{HCO_3^-}$ are the acid dissociation constants of these species and K_W the dissociation constant for water, all expressed in concentration units.

On the basis of the kinetic data alone, no distinction is possible between the reaction mechanisms implied by these two rate equations. This applies not only to the present work, where all experiments were carried out at the same ionic strength, but also when the ionic strength - and hence activity coefficients of the ionic species - varied throughout a run. The activity coefficients, which are included in the initial rate constants k, in eqn. II, 5, are also included in the alternative formulation in eqn. II, 6, since the acid dissociation constants of the species are in concentration units. (Cf. Weil and Morris (40), p. 11).

At the ionic strength used in this investigation, the alternative rate constants, k', may be obtained from the values of k via the acid dissociation constants of the species, which, in turn, may be calculated from the data recorded in Table V, 2. Values of k' are shown in Table II, 15, together with the corresponding Arrhenius factors.

The difference in the values of the Arrhenius parameters for any term on the basis of both formulations is often considerable. For instance, the rate of urea formation expressed in terms of k_U and k_U' shows a difference in activation energy of 12 k.cals., due to the large temperature dependence of K_W compared with the relatively small temperature dependence of the other constants. (See Table V, 2).

Table II. 15 60°C. $I = 0.25$

	Rate Constants			E_A(K cals.)		B/2.303	
	40°C.	60.1°C.	80.1°C.	40-60°C.	60-80°C.	40-60°C.	60-80°C.
k_H		4.0×10^3	1.40×10^4	-	14.6	-	13.2
k_H'		1.62 *	5.95 *	-	15.2	-	10.2
k_C		1.75×10^{-2} ‡	6.96×10^{-2} ‡	-	16.1	-	8.8
k_C'		2.32×10^4 ‡	8.18×10^4 ‡	-	14.7	-	16.8
k_W		6.36×10^{-5} *	5.20×10^{-4} *	-	24.5	-	11.9
k_W'		1.32×10^5 ‡	4.13×10^5 ‡	-	13.3	-	13.9
k_U	0.00814	0.0748 ‡	0.553 ‡	22.9	23.3	14.0	14.2
k_U'	2.21×10^3	5.95×10^3 ‡	1.57×10^4 ‡	10.1	11.3	10.4	11.2

* Min.^{-1} ‡ $\text{Min.}^{-1}\ \text{mol.}^{-1}\ \text{L.}$

Both values are reasonable and no indication of mechanism can be obtained from their consideration.

A variation of Arrhenius parameters with temperature is still shown in the alternative formulation although now this may very well be fortuitous since lack of data with regard to a value of the dissociation constant of cyanic acid has led to the adoption of an approximate extrapolated value, independent of temperature over the range considered.

CHAPTER III

THE MECHANISM OF UREA FORMATION

It has already been seen in Chapter II that the kinetics of urea formation, in all the solutions examined, are given by:

$$\frac{d[\text{Urea}]}{dt} = k_U[NH_4^+][CNO^-] - k_R[\text{Urea}] \quad .. \quad \underline{\text{II, 1}}$$

or $$\frac{d[\text{Urea}]}{dt} = k_U'[NH_3][HCNO] - k_R[\text{Urea}] \quad .. \quad \underline{\text{II, 2}}$$

The kinetic data are, therefore, consistent with either an ionic or a non-ionic mechanism. The discussion in this Chapter is an attempt to establish which of these alternative mechanisms is actually operating.

(i) The Ionic Reaction

As has already been discussed in Chapter II, many workers consider the reaction to be truly ionic, involving ammonium and cyanate ions in the rate determining stage. In no case has a detailed mechanism for the ionic reaction been proposed and such a mechanism is very hard to visualise. Miller (28) quotes a suggestion by Lowry that the reaction involves proton transfer:

$$NH_4^+ + CNO^- \rightleftharpoons NH_3 + HNCO \rightleftharpoons CO(NH_2)_2$$

but recent work (cf. Bell and Pearson (59)) indicates that the rate of proton transfer in all cases, except the ionization of a C-H bond, is too fast for direct observation. Consequently, it would seem probable that the rate determining step in this reaction would involve the non-ionic species, HCNO and NH_3.

It will be seen that, whereas no satisfactory ionic mechanism can be proposed, the presentation of a plausible non-ionic mechanism is ppssible.

(ii) The Non-ionic Reaction

As has already been explained, Werner (18) considered urea formation to proceed by this mechanism, but his scheme is complicated both by insistence on the importance of the tautomeric equilibria:

$$HOCN \rightleftharpoons HNCO$$

and by lack of knowledge concerning the nature and behaviour of strong electrolytes. Much work has been done recently on the structure of cyanic acid and the cyanic esters, the main conclusions of which are:

(i) Hendricks and Pauling (60) and Goubeau (61) showed that, on the basis of Raman spectra, the cyanates may be divided into two classes:

(a) The cyanates of silver and mercury; the free acid and cyanic esters, have identical spectra and are undoubtedly covalent and nitrogen linked (iso-cyanates).

(b) Those of potassium and lead are ionic (not oxygen linked as suggested by Werner; (see p.17)).

(ii) Gillete and Brockway (62) examine the structure of methyl cyanate and cyanic acid (at -20°C.) by an electron diffraction method. Their results show that the covalent isocyanate group contains contributions from the three structures:

$$R{-}N{=}C{=}O \qquad R{-}\overset{-}{N}{-}C\equiv\overset{+}{O} \qquad R{-}\overset{+}{N}\equiv C{-}\overset{-}{O}$$

The three possible oxygen linked forms:

$$R{-}\overset{+}{O}{=}C{=}\overset{-}{N} \qquad R{-}O{-}C\equiv N \qquad R{-}\overset{++}{O}\equiv C{-}\overset{=}{N}$$

cannot be detected and are considered improbable, since in neither of the charged forms are the formal charges distributed in accordance with the relative electronegativity of the oxygen and nitrogen atoms. (Cf. thiocyanic acid with stable enol esters).

It would, therefore, appear that cyanic acid is present almost exclusively in the iso-form, and thus the tautomeric equilibria postulated by Werner has no effect on the rate*.

The assumption of the non-ionic mechanism receives support

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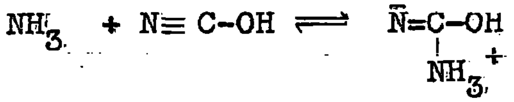
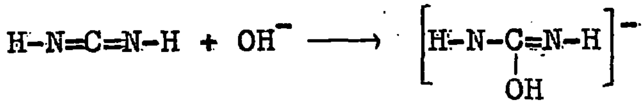
* A reaction between the enol form of the acid and ammonia can be visualized, however, by the addition of ammonia to the carbon-nitrogen triple bond:



$$NH_3 + N\equiv C{-}OH \rightleftharpoons \overset{-}{N}{=}\underset{\overset{+}{N}H_3}{\underset{|}{C}}{-}OH$$

in an analogous manner to that proposed for urea formation from cyanamide in strongly alkaline solution



$$H{-}N{=}C{=}N{-}H + OH^- \longrightarrow \left[H{-}N{-}\underset{OH}{\underset{|}{C}}{=}N{-}H\right]^-$$

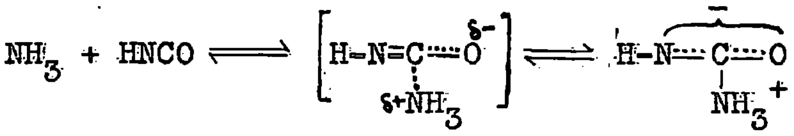
(See Hammett (63) p. 338)

from the fact that the formation of substituted ureas by the action of ammonia on isocyanic esters cannot proceed by any other mechanism; a rate determining step involving cyanate ion is highly unlikely.

$$NH_3 + RNCO \rightleftharpoons RNHCONH_2$$

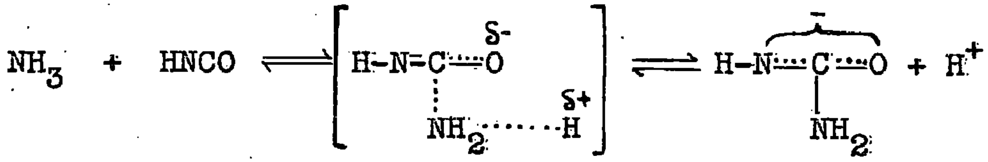
It would seem probable that the first stage in the formation of urea involves the nucleophilic addition of an ammonia molecule to the carbonyl group of isocyanic acid. This can be visualized with or without simultaneous loss of a proton: i.e.,

(a)



$$NH_3 + HNCO \rightleftharpoons \left[H{-}N{=}\underset{\delta+NH_3}{C}\cdots\overset{\delta-}{O} \right] \rightleftharpoons H{-}\overset{-}{\overbrace{N\cdots\underset{NH_3^{+}}{C}\cdots O}}$$

or (b)



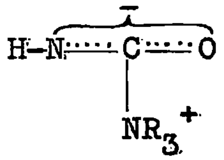
$$NH_3 + HNCO \rightleftharpoons \left[\begin{array}{l} H{-}N{=}C\cdots\overset{\delta-}{O} \\ \quad\;\, \vdots \qquad\quad \delta+ \\ \quad NH_2\cdots\cdots H \end{array} \right] \rightleftharpoons H{-}\overset{-}{\overbrace{N\cdots\underset{NH_2}{C}\cdots O}} + H^+$$

The mesomeric ion produced in (a) can form urea by a prototropic change, while in (b), urea formation occurs by addition of a proton. These processes will be expected to occur very rapidly, the overall reaction rate being controlled by the initial step. Under these conditions, this mechanism leads to the rate law:

$$\frac{d[Urea]}{dt} = k_U'[NH_3][HCNO]$$

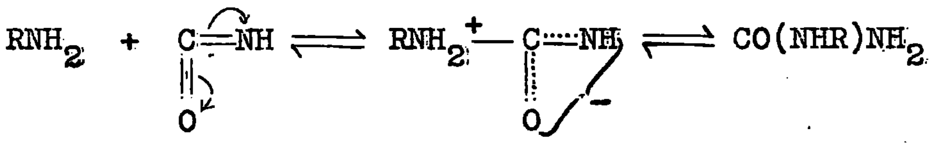
in agreement with the experimental observations.

Primary and secondary amines may form the corresponding substituted ureas in an analogous manner. Tertiary bases, however, do not react. Evidence is presented in Chapter IV, that the corresponding complex between the strong tertiary base triethylamine and isocyanic acid:



is not formed in appreciable amounts, the $C-\overset{+}{N}R_3$ link being very unstable*. This would tend to suggest that proton loss from the ammonia-isocyanic acid complex must be either synchronous with the nucleophilic addition or follow immediately after it.

Davis and Blanchard (64) and Packer, Vaughan and Watts (65) studied substituted urea formation from nitro-urea and amines in aqueous solution. They proposed that cyanic acid is formed by reaction between nitro-urea and the solvent, which then reacts with the amine:



in the same manner as proposed here.

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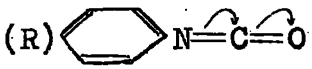
[*] It will be seen in Chapter IV, that if a complex of this type were appreciably stable, then some specific contribution of triethylamine to carbonate formation would be expected, i.e., eqn. II, 2 should contain a term $[NR_3H^+][CNO^-]$ when triethylamine is present in the reaction mixture.

Evidence in favour of this mechanism can be obtained from the work of Naegeli, Tyabji and Conrad (66) who investigated the rate of substituted urea formation from various amines, and substituted aryl isocyanates in benzene solution:

$$\varphi NCO + RNH_2 \rightleftharpoons \varphi NHCONHR$$

On the basis of the above mechanism, we would expect the presence of electron attracting groups in the benzene ring to facilitate the reaction by increasing the unsaturation of the carbonyl group, reducing the tendency for the unsaturation to be satisfied by an internal conjugation of the unshared electron pair on the nitrogen atom, i.e.,

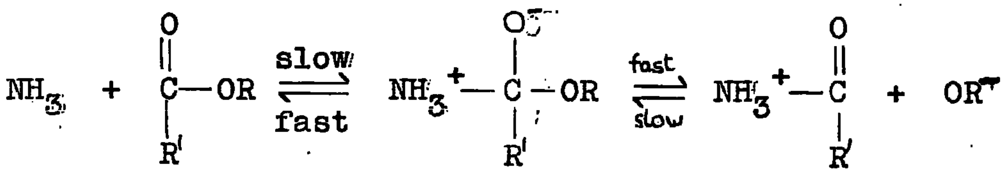


These authors observe the reactivity of substituents in the benzene ring of the aryl isocyanate to increase in the order:

$R = 4.\text{-}OMe < 4.Me < H < 3.OMe < 3\text{-}NO_2 < 4\text{-}NO_2 < 3.5(NO_2)_2 < 2.4.6.(NO_2)$

in accordance with these predictions. The reaction of various arylamines with ioscyanates showed the reverse order of reactivity to be the case for substituents in the aryl amine. This again is in concord with the proposed mechanism, since the basic strength of the amine, and hence its ability as a nucleophilic reagent, will decrease with increasing conjugation of the nitrogen unshared electron pair.

Many similar types of nucleophilic addition to a carbonyl group are known, among which may be mentioned the ammonolysis of esters:

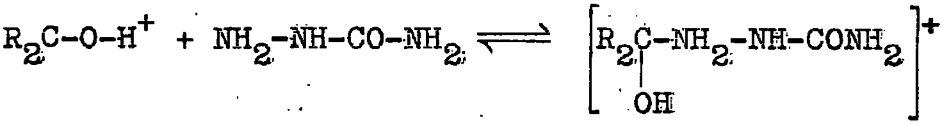


$$NH_3 + \underset{R'}{\overset{O}{\overset{\|}{\underset{|}{C}}}}-OR \underset{fast}{\overset{slow}{\rightleftharpoons}} NH_3^{+}-\underset{R'}{\overset{O^-}{\overset{|}{\underset{|}{C}}}}-OR \underset{slow}{\overset{fast}{\rightleftharpoons}} NH_3^{+}-\underset{R'}{\overset{O}{\overset{\|}{\underset{|}{C}}}} + OR^-$$

(See Ingold (67) p.783)

The formation of semicarbazones, however, seems to proceed by a somewhat different mechanism. The reaction has been studied by Conant and Bartlett (68) and Stempel, Jr. and Shaffel (69) and shown to be subject to general acid catalysis. It is proposed that the first stage of the reaction is the addition of a proton to the carbonyl group of the ketone, followed by reaction of this intermediate with semicarbazide.

$$R_2C=O + HA \rightleftharpoons R_2C-O-H^+ + A^-$$



$$R_2C-O-H^+ + NH_2-NH-CO-NH_2 \rightleftharpoons \left[R_2\underset{OH}{\underset{|}{C}}-NH_2-NH-CONH_2\right]^+$$

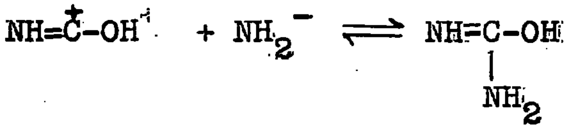
Proton removal from this complex is rate determining. Similar considerations would seem to apply to the formation of oximes, (Olander (70) and Barrett and Lapworth (71), Acree and Johnson (72)) although in strongly alkaline solutions, there is evidence of $[H_2NO]^-$ ion attack on the protonated carbonyl group.

Betts and Hammett (73) have examined the kinetics of the ammonolysis of methylphenylacetate in alcohol solution. The overall reaction, due to two processes, can be expressed by the equation:-

$$\text{Rate} \propto [RCO_2CH_3][NH_3] + [RCO_2CH_3][NH_2^-]$$

i.e., reaction with ammonia and amide ion.

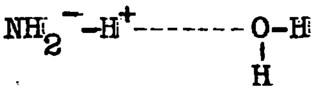
In the case of urea formation from cyanates investigated here, the kinetics would not be inconsistent with an amide ion attack on a protonated carbonyl group:



$$NH{=}\overset{+}{C}{-}OH + NH_2^- \rightleftharpoons \underset{\displaystyle NH_2}{NH{=}\underset{|}{C}{-}OH}$$

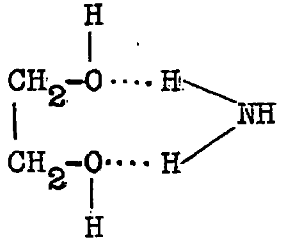
although there is no evidence for a dual mechanism, in this case. There seems, however, to be no independent evidence for the existence of the amide ion in aqueous solution, and such a mechanism must be considered improbable under the present experimental conditions.

Gordon, Miller and Day (74)(75) suggest, that instead of reaction involving amide ion, ammonolysis of esters proceeds via an attack on the ester molecule of a hydrogen bonded ammonia:

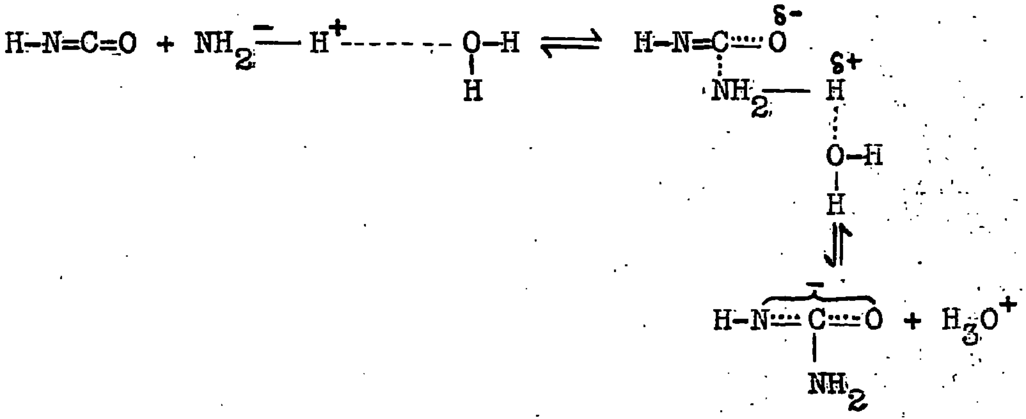


$$NH_2^-{-}H^+{-}{-}{-}{-}{-}{-}{-}\underset{\displaystyle H}{\underset{|}{O}}{-}H$$

The $NH_2^-{-}H^+$ bond is stretched to a point stimulating ionization by hydrogen bonding with the solvent. The catalytic effect of hydroxylic substance on the rate of ammonolysis is explained by the formation of a hydrogen bonded complex such as:



Urea formation might well involve attack by such species, since it has already been mentioned that loss of a proton is probably synchronous with ammonia addition:



The observation of J. Walker (12) that a 10% solution of cane sugar (a hydroxylic substance) increases the rate of urea formation by 36% may possibly be evidence for this mechanism.

CHAPTER IV

THE MECHANISM OF CARBONATE FORMATION

(a) General considerations

The rate equations for carbonate formation may be written in the form:-

$$\frac{dC}{dt} = \frac{k_W}{[H_2O]}[CNO^-][H_2O] + k_H[CNO^-][H^+] + k_C[CNO^-][HCO_3^-] \qquad \underline{IV, 1}$$

or

$$\frac{dC}{dt} = k_W'[HCNO][OH^-] + \frac{k_H'}{[H_2O]}[HCNO][H_2O] + k_C'[HCNO][CO_3^=] \qquad \underline{IV, 2}$$

We see the reaction is represented as occurring between:

(1) Cyanate ion and various acids, H_2O, HCO_3^- and H^+

or (2) Cyanic acid and various bases, H_2O, $CO_3^=$ and OH^-.

Considering first Case (1), it is difficult to visualize any mode of reaction other than proton donation by the acid to the cyanate ion. If this were so, however, the reaction should be subject to general acid catalysis, not specific to the three acids HCO_3^-, H^+ and H_2O. For example, the results of this investigation clearly show that ammonium ion takes no specific part in carbonate formation, there being no term in the kinetic equation for carbonate formation involving $[NH_4^+][CNO^-]$.

A base reaction as in (2) can be considered in two ways:

(i) The base reacts by removal of a proton, the converse of (1) or (ii) the base reacts by virtue of its nucleophilic properties, adding on to isocyanic acid or some intermediary in the reaction.

Case 2 (i) similarly cannot be maintained, since any such reaction would be expected to be generally base catalysed, i.e., triethylamine should exert some specific catalytic effect on the rate of carbonate formation analogous to the effect of carbonate ion.

Case 2 (ii), however, involves the actual addition of the base to the acid and could, therefore, be specific to certain bases depending on their structure.

The basic strength of a species is a measure of its efficiency as a nucleophilic reagent and in Table IV, 1 below, the basic strength of the species involved in both urea and carbonate formation are compared with the corresponding rate of reaction[*]. The concentration of water is taken as 55.5 M. in agreement with general convention (this is actually correct only at room temperature, but the error involved is negligible here).

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[*] In agreement with general convention, the basic strength of a species is defined as the reciprocal of the acid dissociation constant of the corresponding conjugate acid, i.e., for any base B'

$$\frac{1}{K_A} = \frac{[HB]}{[H^+][B']}$$

Thus for water, $\frac{1}{K_A} = \frac{1}{[H_2O]}$ and for OH', $\frac{1}{K_A} = \frac{[H_2O]}{[H^+][OH']}$

Table IV, 1 $60^\circ C$. $I = 0.25$ $[H_2O] = 55.5M$.

Base	$^1/_{K_A}$	Rate constant for bimolecular reaction with HCNO ($mins^{-1}$)
OH^-	2.87×10^{14}	1.32×10^5
$CO_3^=$	3.31×10^9	2.32×10^4
NH_3	1.96×10^8	5.90×10^3
H_2O	0.0180	0.0288

It is clear that there is a parallel between basic strength and rate of reaction, irrespective of whether the reaction is urea or carbonate formation.

That there exists a relationship between acid or base strength of a species and its ability to catalyse a particular reaction has been known for some time. Brönsted and Pedersen (76) proposed a relationship:

$$k_A = G_A K_A^{\alpha} \quad \text{for acid catalysis}$$

$$k_B = G_B K_B^{\beta} \quad \text{for base} \quad "$$

where G_A, α and G_B, β are constants for any given reaction, solvent, temperature and series of similar reactants.

This expression must be modified in the case when the acid-base system has more than one acid-base centre, and Brönsted (77) proposed:

$$\frac{k_A}{p} = G_A\left(\frac{qK_A}{p}\right)^{\alpha} \qquad \ldots \quad \ldots \quad \ldots \qquad \underline{\text{IV, 3}}$$

$$\frac{k_B}{q} = G_B\left(\frac{p}{qK_A}\right)^{\beta} \qquad \ldots \quad \ldots \quad \ldots \qquad \underline{\text{IV, 4}}$$

where for any conjugate acid-base pair A and B, A has p dissociable protons and B, q equivalent points to which a proton can be attached. The values assigned to p and q are often arbitrary, but since the relation only holds with any accuracy in a series with the same p and q values, they are not important; (cf. Bell (78), p. 85). If equation IV, 4 is obeyed, then a graph of log. $\left(\frac{(k)^{o}}{q}\right)$ as a function of log. $\left(\frac{p}{q(K_A)^{o}}\right)$ will be linear.

In Table IV, 2 below, are listed values of these functions for the terms in the kinetic equations of urea and carbonate formation. In all cases, p and q are taken as unity, except for carbonate ion, where clearly $p = 1$ and $q = 3$. The corresponding plot is shown in Fig. 7A.

FIG. 7A

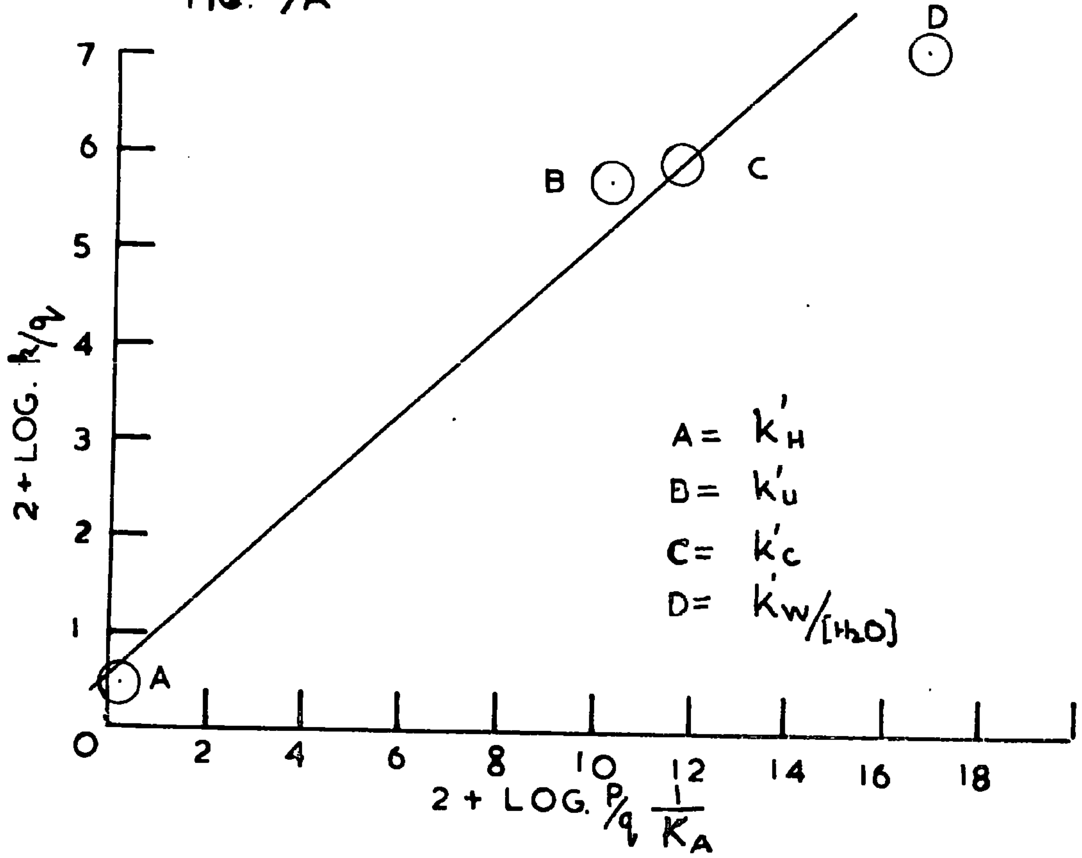

2 + LOG. k/q
0
1
2
3
4
5
6
7
2
4
6
8
10
12
14
16
18
2 + LOG. $p/q \frac{1}{K_A}$
A
B
C
D
A = k'_H
B = k'_u
C = k'_c
D = $k'_W/[H_2O]$

FIG. 7B

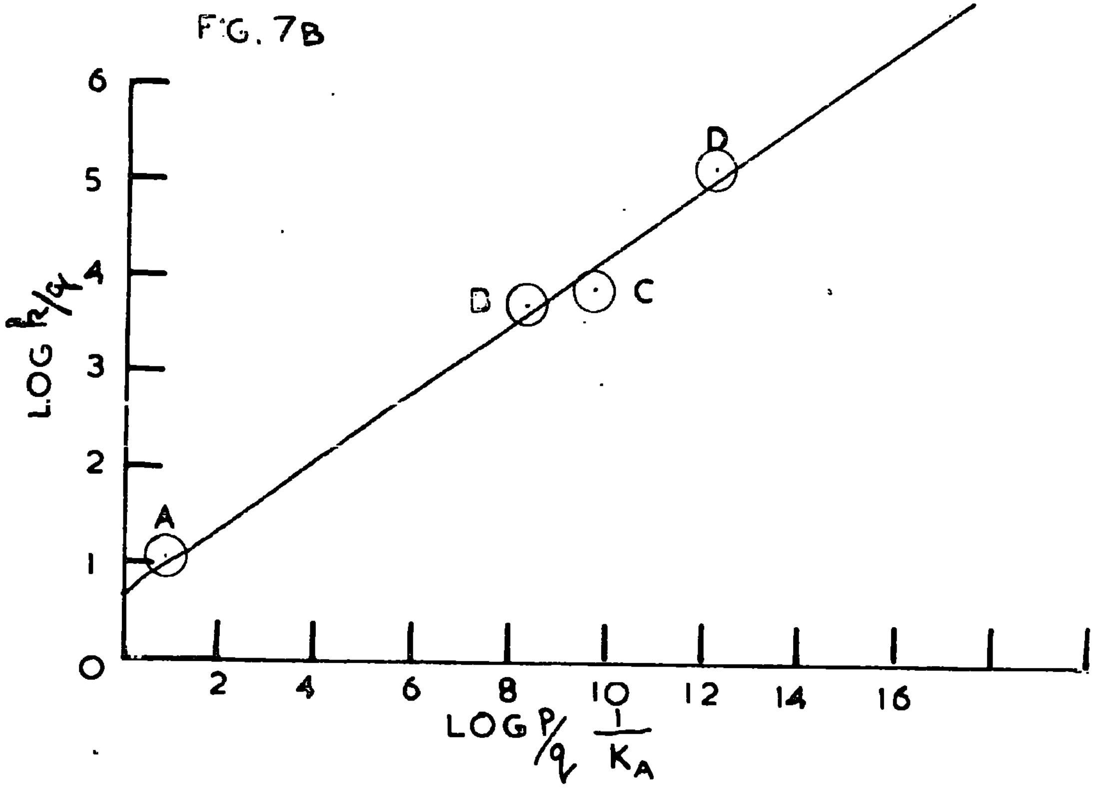

LOG k/q
0
1
2
3
4
5
6
2
4
6
8
10
12
14
16
LOG $p/q \frac{1}{K_A}$
A
D
C
D

Table IV, 2 60°C. $I = 0$ $[H_2O] = 55.5$ M.

Base	$\log.\left(\frac{p}{q(K_A)^o}\right)$	$\log.\left(\frac{(k')^o}{q}\right)$
OH^-	14.762	5.121
$CO_3^=$	9.663	3.884
NH_3	8.297	3.771
H_2O	-1.750	-1.541

Although agreement is not good, it is probably as good as can be expected over such a wide range of base strengths and differing types of reactants. (Brönsted originally only proposed equations IV, 3 and IV, 4 for a series of similar reactants, although they are often applied more generally).

In the values quoted in both Tables IV, 1 and IV, 2, the concentration of water has been made equal to 55.5 M., in agreement with general convention. Bell, (79), however, points out that the observed velocity of hydroxyl ion reaction is always lower by several powers of ten than that predicted on the basis of the Brönsted relation. Any relation between the catalytic power of an unassociated species such as OH' with the thermodynamic properties of the highly associated water, cannot be justified, and he suggests that the "effective" concentration of water should more nearly be represented by 0.13 M. Thus:

$$\frac{k'_H}{[H_2O]} = \frac{k'_H}{0.13}$$

For water: $\frac{1}{K_A} = \frac{1}{0.13}$

For OH^- $\frac{1}{K_A} = \frac{0.13}{K_W}$

the remainder of the rate and dissociation constants remain unaltered.

Table IV, 3 below, shows log. $\left(\frac{p}{q(K_A)^o}\right)$ and log. $\left(\frac{(k')^o}{q}\right)$ values calculated assuming $[H_2O] = 0.13$ M. and Fig.7B, the corresponding Brönsted plot.

Table IV, 3 60°C. $I = 0$ $[H_2O] = 0.13$ M.

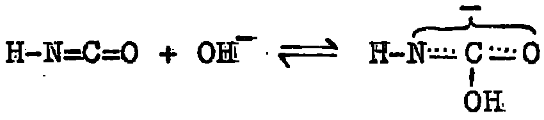
Base	log. $\left(\frac{p}{q(K_A)^o}\right)$	log. $\left(\frac{(k')^o}{q}\right)$
OH^-	12.130	5.120
$CO_3^=$	9.663	3.884
NH_3	8.297	3.771
H_2O	0.887	1.090

The agreement with equation IV, 4 is now quite good. It is concluded then that there is a relationship between the base strength of these species and their rate of reaction with cyanic acid.

Moreover, the relationship holds, irrespective of whether the reaction is urea or carbonate formation, and this would suggest that the rate determining stage in both cases is similar, i.e., the addition is governed essentially by the nucleophilic power of the reacting base[*].

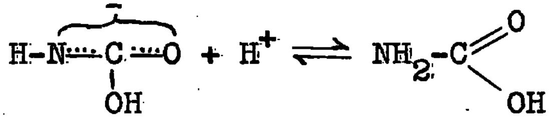
(b) The mechanism of the reaction

It would, therefore, appear likely that carbonate formation results from a nucleophilic addition of a base to the carbonyl group of cyanic acid, just as urea was considered to be formed by the addition of NH_3 to this group. For attack by OH^- ions, this can be represented:



$$H{-}N{=}C{=}O + OH^- \rightleftharpoons H{-}\overbrace{N \cdots \underset{\underset{OH}{|}}{C} \cdots O}^{-}$$

followed by rapid proton addition to form the hypothetical carbamic acid[‡].



$$H{-}\overbrace{N \cdots \underset{\underset{OH}{|}}{C} \cdots O}^{-} + H^+ \rightleftharpoons NH_2{-}C\begin{matrix}{=}O\\ \diagdown OH\end{matrix}$$

---

[*] It is clear that an exactly similar relationship would apply if the acid dissociation constants of NH_4^+, HCO_3', H^+ and H_2O were compared with the corresponding rate of reaction of these species with cyanate ion, but in this case the reaction should be generally acid catalysed.

[‡] Carbamic acid has already been proposed by Fearon and Docheray (51) as a possible intermediate in the reaction.

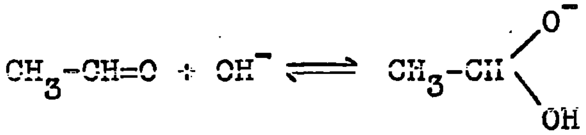
Carbamic acid is not known; all reactions that might be expected to form it give only ammonia and carbon dioxide. The decomposition of ammonium carbamate in acid solution has been investigated by Faurhoult(80), who has shown that the primary products in the decomposition are ammonia and carbon dioxide, the rate of hydration of the latter being rate determining. There can be no doubt that at the temperatures used during this investigation (> 40°C.), the decomposition of carbamate and the hydration of carbon dioxide can be regarded as instantaneous. (Cf. Mills and Urey (81)).

The nucleophilic addition of hydroxyl ions to carbonyl groups has been investigated by Bell and his co-workers, (82-83) who show that the hydration of acetaldehyde:

$$CH_3\text{-}CH{=}O + H_2O \rightleftharpoons CH_3\text{-}CH\text{-}(OH)_2$$

is subject to both general acid and base catalysis.

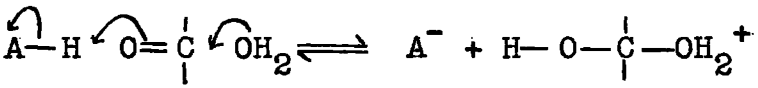
They propose that the base catalysed reaction consists primarily of the addition of a hydroxyl group to the aldehyde:



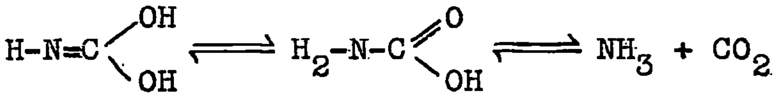
$$CH_3\text{-}CH{=}O + OH^- \rightleftharpoons CH_3\text{-}CH\begin{matrix} O^- \\ OH \end{matrix}$$

followed by rapid proton addition. The general base B^- acts on the solvent water to generate hydroxyl groups synchronously with the addition of the latter:

and similarly for acid catalysis:

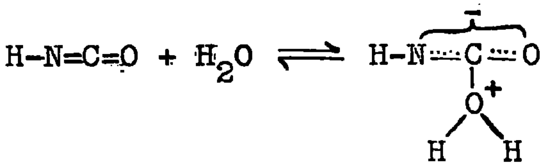


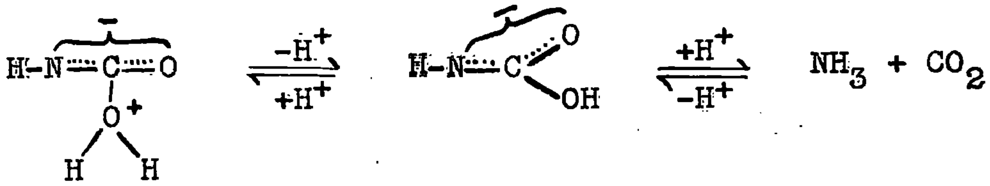
In the case of carbonate formation from cyanates, however, hydroxyl addition is not generally acid and base catalysed. The reaction could conceivably involve a carbonyl hydrate, tautomeric with carbamic acid:



but in the light of the work of Bell, the initial hydration should be subject to general acid and base catalysis, it being very improbable that the subsequent prototropic re-arrangements would proceed at a measurable speed.

On the basis of the mechanism proposed here, reaction with water can be represented by

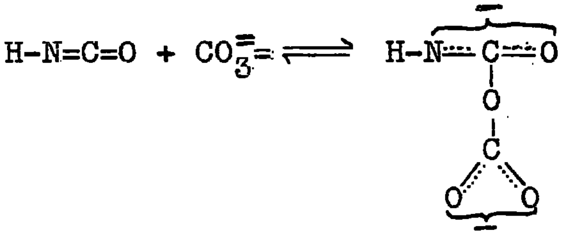




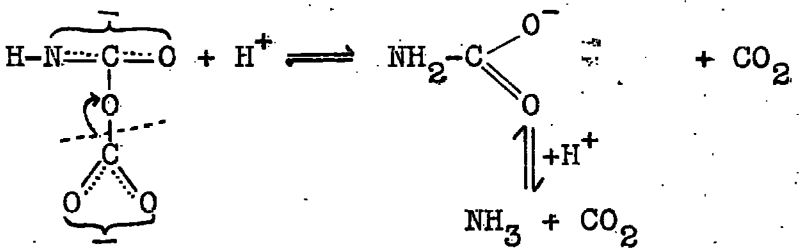
although, again, the work of Bell would indicate the addition of water, per se, is improbable.

Thus, although the kinetic data would appear to be consistent only with a nucleophilic addition of hydroxyl ion and water to the carbonyl group of cyanic acid, a reconciliation of this view with the recent work of Bell seems difficult.

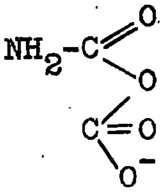
A similar specific nucleophilic addition of carbonate ion may be written:



With subsequent decomposition of this intermediate in a number of possible ways, e.g., it may decompose by reaction with hydrogen ions:



or, with addition of a proton, this intermediate becomes a mixed anhydride of carbamic acid and the acid bicarbonate ion:



The general instability of mixed anhydrides is well known and this would be expected to decompose rapidly to the corresponding acids, carbamic acid and bicarbonate ion[*]. These reactions must be considered to be very hypothetical, although they do present a reasonable scheme for the specific carbonate catalysis.

(c) <u>The bicarbonate ion as a basic catalyst</u>

In Eqn. IV, 1, there appears no term involving the bicarbonate ion as a basic catalyst. On the basis of the scheme proposed above, it would seem probable that the bicarbonate ion should exert some specific catalytic effect analogous to that of carbonate ion (a possible intermediate would be a mixed anhydride of carbamic and carbonic acid).

In terms of the Brönsted relation (Eqn. IV, 4), the catalytic effect of a basic catalyst is expressed in terms of the

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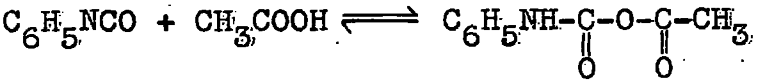
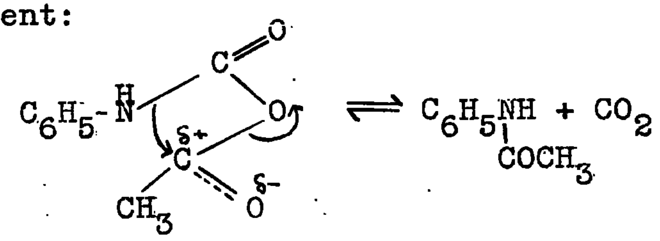
[*] It is interesting in this respect that Hoshino and Hoshino, (84-86), in an investigation of the decomposition of aryl ureas in organic acid solvents, proposed a mixed anhydride as an intermediary in the reaction:



$$C_6H_5NCO + CH_3COOH \rightleftharpoons C_6H_5NH-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3$$

which, they postulate, decomposes by an internal nucleophilic displacement:



acid strength of the corresponding conjugate acid. In the case of the bicarbonate ion, obviously it is important to distinguish between the carbon dioxide which is present in solution as carbonic acid and that present as dissolved carbon dioxide. It has been pointed out by Roughton and Booth (87) and Olson and Youle (88) that the usually accepted value for the first dissociation constant of carbonic acid:

$$\frac{[H^+]\,[HCO_3^-]}{[\text{total } CO_2 \text{ in solution}]} = 4 \times 10^{-7}$$

leads one to expect a catalytic activity of the bicarbonate ion (as a basic catalyst) much greater than that actually observed. Olsen and Youle (88) suggest that the value:

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 2 \times 10^{-4}$$

more nearly represents the true catalytic activity of carbonic acid.

An increase in the first dissociation constant of carbonic acid of three powers of ten is adopted here. Thus, from the Brönsted plot, (Fig. 8), the expected rate constant of carbonate formation by a term $[HCO_3^-][HCNO]$ is 95 gm. mol.$^{-1}$ L. min.$^{-1}$.

Thus we have:

$$R = \frac{\text{Rate of carbonate formation by } CO_3^{=} \text{ catalysis}}{\text{'' \quad '' \quad '' \quad '' \quad } HCO_3^{-} \text{ \quad ''}}$$

$$= \frac{10^2[CO_3^{=}]}{[HCO_3^{-}]}$$

$$= 3.7 \times 10^5[OH^-]$$

In Table IV, 4 below, are listed for various runs, the ratios of the rates of carbonate formation by the two terms (R) and the approximate % contributions of an $[HCO_3^-][HCNO]$ term.

Table IV, 4 60°C. $I = 0.25$

Run No.	Conditions	$[OH^-]$	R	% contribution to total carbonate due to $CO_3^{=}$ catalysis	% contribution expected from HCO_3^- catalysis
1.	NH_4CNO	10^{-6} 2×10^{-5}	0.38 7.6	negligible 16%	negligible 2.1%
2.	NH_4CNO + 0.004 M. Na_2CO_3	5×10^{-6}	1.85	10.14%	5.5%
		3×10^{-5}	11.1	40%	3.6%
13.	NaCNO	3×10^{-4}	111	80%	0.7%

The contribution of HCO_3^- catalysis will always be negligible except in the case of Run 2, which represents the most favourable conditions encountered for the observation of this contribution. However, here the concentration of carbonate involved is sufficiently small for it to be improbable that it could have been detected, especially as the carbonate formed is calculated by difference from the concentration added initially. Consequently, there might well be a contribution from a bicarbonate mechanism, although, equally well, it might be absent.

(d) The effect of added boric acid and triethylamine: the results of Baker and his co-workers

It has already been pointed out that boric acid and triethylamine exert no specific effect on the rate of carbonate formation. In Tables IV, 5 and IV, 6, the carbonate that should be formed, calculated on the basis of Eqn. II, 2, and that found experimentally in runs with boric acid and triethylamine added, are compared. The contribution to be expected from $[NR_3][HCNO]$ and $[H_2BO_3^-][HCNO]$ terms are calculated from the Brönsted plot, (Fig. 7b), assuming the usual values for the basic strengths of these species.

Table IV, 5 60°C. $I = 0.25$

Run 20 0.05 M. NaCNO with 0.0075 M. triethylamine added

Time (mins.)	t	$C - C_o$ observed	$C - C^o$ calculated	approx. calculated catalytic contribution from NEt_3
129	0	-	-	-
1072	943	0.0037	0.0034	-
1288	1159	0.0044	0.0043	1.8×10^{-3}
2344	2215	0.0093	0.0094	3.1×10^{-3}
3236	3107	0.0149	0.0146	4.0×10^{-3}
3715	3586	0.0180	0.0175	5.0×10^{-3}

Table IV, 6 $60^{o}C$. $I = 0.25$

Run 21 0.05 M. NaCNO with 0.015 M. Boric Acid added

Time (mins.)	t	$C - C_o$ observed	$C - C_o$ calculated	approx. calculated catalytic contribution from $H_2BO_3^-$
162	0	-	-	-
1349	1187	0.00940	0.00898	2.0×10^{-2}
2344	2182	0.0178	0.0171	2.9×10^{-2}
3548	3386	0.0250	0.0242	3.2×10^{-2}
4266	4104	0.0274	0.0269	3.5×10^{-2}

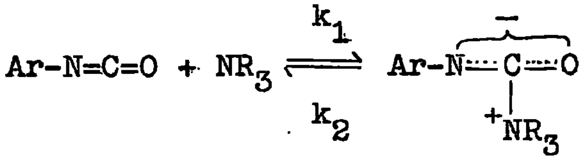
The agreement between observed and calculated total carbonate is satisfactory in both cases, and the expected contribution of the terms $[H_2BO_3^-][HCNO]$ and $[NR_3][HCNO]$ is appreciable. This is especially so in the case of Run 20 (triethylamine added) where, over the range considered, most of the observed carbonate is produced by the "spontaneous reaction", and errors in the determination of pH, etc., would not have any very serious effect. The expected contribution of a term $[NR_3H^+][CNO^-]$ is well outside the experimental error of the analytical determination.

In a similar manner, the carbonate that would be expected from catalysis by the two bases CNO^- and NH_3 may be calculated. In the case of Run 1, the carbonate concentration produced by CNO^- catalysis would vary from 2 - 5 x 10^{-3} M. and that by NH_3 catalysis , 5 - 30 x 10^{-3} M. during the course of the run - i.e., neither is negligibly small and it can safely be concluded that no such mechanism of basic catalysis occurs.

In the calculation of the expected contribution of boric acid to the rate of carbonate formation, it has been assumed that the rate is proportional to the accepted value for the acid strength of boric acid. This, however, may well not be justified, since it would seem probable that solutions of boric acid contain all kinds of ions which can be formed from boric acid, e.g., BO_2^-, $H_2BO_3^-$, and $B_4O_7^=$ (see Ephraim (89)), and considerations similar to those discussed for the catalytic effect of bicarbonate ion may apply, i.e., the catalytic effect of borate may be very much less than that expected from its acid strength.

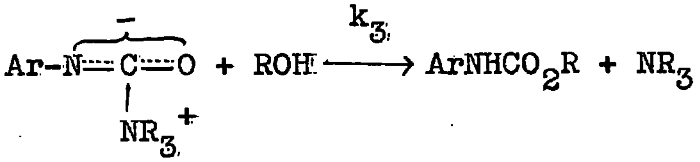
Baker and his co-workers (90-94), however, have shown that the reaction of aryl iso-cyanates with alcohols in non-aqueous solvents is subject to general basic catalysis, triethylamine exerting a catalytic effect proportional to its basic strength. The product of the reaction, urethane, is a stable ester of the unstable carbamic acid and, consequently, it might be expected that carbonate formation from cyanates and urethane formation proceed by similar mechanisms, subject to similar catalysis by tertiary amines. Baker proposed a base catalysed mechanism:

(i)



$$\mathrm{Ar{-}N{=}C{=}O + NR_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ar{-}\overbrace{N{=}\underset{{}^{+}NR_3}{\underset{|}{C}}{=}O}^{-}}$$

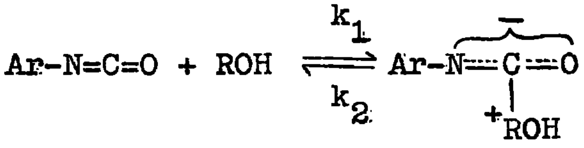
(ii)



$$\mathrm{Ar{-}\overbrace{N{=}\underset{NR_3{}^{+}}{\underset{|}{C}}{=}O}^{-} + ROH \xrightarrow{k_3} ArNHCO_2R + NR_3}$$

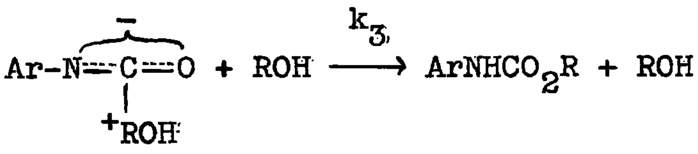
and a "spontaneous" reaction:

(iii)



$$\mathrm{Ar{-}N{=}C{=}O + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ar{-}\overbrace{N{=}\underset{{}^{+}ROH}{\underset{|}{C}}{=}O}^{-}}$$

(iv)



$$\mathrm{Ar{-}\overbrace{N{=}\underset{{}^{+}ROH}{\underset{|}{C}}{=}O}^{-} + ROH \xrightarrow{k_3} ArNHCO_2R + ROH}$$

Direct re-arrangement of the alcohol-cyanate complex in (iii) is ruled out by the kinetics. It would seem then, rather surprisingly, that carbonate formation and urethane formation proceed by different mechanisms.

Baker showed that the rate of urethane formation increases with increasing electron attraction from the cyanate group, i.e.,

$$\text{Rate} = \text{cyclohexyl} < p - MeOC_6H_4 < p - MeC_6H_4 < Ph < p.NO_2C_6H_4$$

(See p.68)

The possibility that the observed difference in mechanism is due to the decrease in electron attraction when the aryl group is replaced by hydrogen, possibly favouring direct rearrangement of the intermediate in Stage (iii), is improbable, since Baker showed that the reaction of the cyclohexyl ester of cyanic acid was subject to basic catalysis by triethylamine. The differences in electron attraction of the cyclohexyl and hydrogen groups would be negligible. Also, a charged intermediary of the type proposed by Baker would be expected to be more stable in the polar solvent water than in the di-n-butyl ether used by Baker.

The reasons for these differences in mechanism are not clear, and it would seem that either the two mechanisms are dissimilar[*] or that some cancellation of error has occurred in this investigation, possibly due to the complications involved in accurate calculation of pH, etc., in aqueous solution. Much further work is required to establish this point with any certainty.

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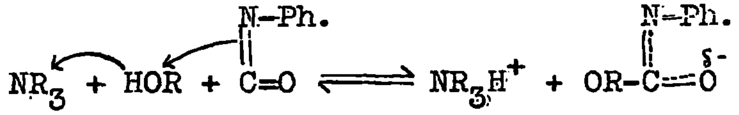
[*] Baker found that, contrary to the requirements of the proposed mechanism, k_1 (see p. 88 (1)), is not independent of the reacting alcohol. It was proposed that either the alcohol solvates the highly polar complex and thus plays an important part in the energetics of its formation, or reaction occurs partly with a hydrogen bonded complex of the type $NR_3 \cdots\cdots HOR$.

This might suggest that, in fact, the mechanism is termolecular, of the type proposed by Bell (82-83) and discussed already on p. 79.



$$NR_3 + HOR + \overset{\overset{\text{N-Ph.}}{\|}}{C{=}O} \rightleftharpoons NR_3H^+ + OR\text{-}\overset{\overset{\overset{\delta-}{\text{N=Ph.}}}{\|}}{C}{=}\overset{\delta-}{O}$$

although, again, if this were so, a similar generally catalysed mechanism would be expected for carbonate formation in aqueous solution.

CHAPTER V

ANALYTICAL METHODS AND CALCULATIONS

(a) Introduction

During the decomposition of aqueous solutions of cyanates, the determination of the concentration of the various species present at any time in the reaction mixture is complicated. The principles underlying the methods employed in this investigation are discussed below and the experimental details may be found by reference to the appropriate section.

The decomposition of cyanate ions may be represented by the following stoichiometric equation:

$$CNO^- + 2H_2O \rightleftharpoons NH_4^+ + CO_3^= \quad .. \quad .. \quad \underline{I, 1}$$

$$NH_4^+ + CNO^- \rightleftharpoons CO(NH_2)_2 \quad .. \quad .. \quad \underline{I, 2}$$

In some cases NH_4^+ ions are present initially; in others, they are produced by hydrolysis of cyanate ions as in eqn. I, 1.

As the ions NH_4^+, CNO^- and $CO_3^=$ are capable of reacting, not only with each other, but also with the aqueous solvent and its ionization products, H^+ and OH^-, it is convenient to define the following quantities whose values are amenable to direct experimental observation:

Total carbonate, $C = [CO_3^{=}] + [HCO_3^-] + [H_2CO_3]_T$ [*] V, 1

Total ammonia, $N = [NH_4^+] + [NH_3]$ .. .. V, 2

Total cyanate $= [CNO^-] + [HCNO] \simeq [CNO^-]$ [‡] V, 3

Hence it follows from the stoichiometric eqns. I, 1 and I, 2, that at any time - t,

$$U - U_o = [CNO^-]_o - [CNO^-] - (C - C_o) \quad .. \quad .. \quad \text{V, 4}$$

$$N - N_o = 2(C - C_o) - ([CNO^-]_o - [CNO^-]) \quad .. \quad \text{V, 5}$$

where $U = [CO(NH_2)_2]$ and the subscript "o" refers to initial concentrations of the species.

The validity of expressions V, 4 and V, 5 is demonstrated in Table V, 1 below, where it is shown that the experimental urea concentration is the same as that predicted by eqn. V, 4,

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[*] $[H_2CO_3]_T = [H_2CO_3] + [CO_2]$ gas. as liquid and gas phases have equal volumes. (H_2CO_3 includes dissolved CO_2).

$$[H_2CO_3]_T = s([H_2CO_3])$$

where "s" can be calculated from the known solubility of CO_2 in aqueous solutions. (See Table V, 2).

[‡] In all experiments carried out in this investigation, $[H^+] < 10^{-7}$ and hence $[HCNO] \ll [CNO^-]$.

within experimental error.[*]

Table V, 1 [‡]

Cyanate	$[CNO^-]_o - [CNO^-]$	$C - C_o$	$U - U_o$	
			calc.	observed
Ammonium Cyanate	0.~~0~~04261	0.00481	0.03780	0.0370) 0.0379)
Sodium Cyanate	0.03960	0.0283	0.0113	0.0116) 0.0114)

It can thus be seen that the decomposition of cyanate ions can be followed by analysing the reaction mixture for only cyanate ions and total carbonate. A knowledge of these quantities allows the concentration of all species present to be calculated, provided their initial concentration and the pH of the solution are known.

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[*] Wyatt and Kornberg (54) have also demonstrated that this is so for ammonium cyanate decomposition, within their experimental error (3%).

[‡] These results do not refer to any particular run but were isolated experiments.

(b) Determination of Cyanate Ion Concentration and Total Carbonate

The concentration of cyanate ion and total carbonate in a given reaction mixture were determined by a method which is an extension of that used by E. E. Walker (19).

It can be seen from the stoichiometric equations I, 1 and I, 2, that the only basic species whose concentrations are altered by reaction are CNO^- and $CO_3^=$. Admittedly, some of these will be converted into their corresponding acids by reaction with the solvent or other acids present in the solution, but these reactions only result in the formation of one base from another. The total basicity of the solution, i.e., the combined normality of all bases present, is thus unaltered as a result of the normal acid-base equilibria in aqueous solution. Hence, the total change in basicity of the reaction mixture over a given time interval will be:

$$X - X_o = [CNO^-] - [CNO^-]_o + 2(C - C_o) \quad .. \quad \underline{V, 6}$$

where X is the total basicity. Also,

$$\begin{aligned} Y - Y_o &= X - X_o - ([CNO^-] - [CNO^-]_o) \\ &= 2(C - C_o) \quad .. \quad .. \quad .. \quad .. \quad \underline{V, 7} \end{aligned}$$

where Y is the total basicity of the solution other than that due to cyanate.

In the experimental determination of X, we utilise the fact that weak acids do not interfere in the titration of H^+ ions with sodium hydroxide, provided that the titration is carried out in a large excess of acetone. X was, therefore, determined by adding excess hydrochloric acid to a sample of the reaction mixture in a large excess of acetone - HCNO does not decompose under these conditions[*] - and back titrating with sodium hydroxide. Lacmoid was used as indicator. Y was determined in an analogous manner, using a sample from which the cyanate had been removed by precipitation as silver cyanate in the presence of sufficient ammonium ions to prevent precipitation of silver carbonate. Hence, C, $[CNO^-]$, U and N were evaluated by means of eqns. V,4, V,5, V,6, and V,7 and a knowledge of the initial values of these quantities.

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[*] This was shown by "blank" experiments; cf. p.123.

(c) Calculation of the Concentration of Various Species

While the methods described in the preceding section allow the estimation of such quantities as total ammonia, N, etc., these quantities are not sufficient for a full analysis of experimental results.

For example, it has been confirmed in this investigation that during the formation of urea, given by the equation:

$$\frac{dU}{dt} = k_U[NH_4^+][CNO^-] - k_R[Urea]$$

the approximation:

$$[NH_4^+] = N \qquad (N.B.\ N = [NH_3] + [NH_4^+])$$

is only justified in the more acid solutions and not in the alkaline solutions examined here.

The concentrations of all the species present can be calculated from the observed values of N, C, $[CNO^-]$, a knowledge of the pH of the solution and the equilibrium constants for the appropriate acid-base reaction. The method employed for all the conditions encountered in this investigation is considered below.

It is found convenient to define a number of parameters $\alpha, \beta, \gamma, \delta, \varepsilon$ and η such that:

(i) $[NH_3] = \alpha([NH_3] + [NH_4^+]) = \alpha N$

$[NH_4^+] = (1-\alpha)N$ .. .. V, 8

Defining $K_1 = \frac{[NH_4^+][OH^-]}{[NH_3]}$

we have $\alpha = \frac{1}{1 + \frac{K_1}{[OH^-]}}$ .. .. <u>V, 9</u>

(ii) $[CO_3^=] = (1 - \beta - \gamma)\left[[CO_3^=] + [HCO_3^-] + [H_2CO_3]_T\right]^* = (1 - \beta - \gamma)C$

where $[HCO_3^-] = \beta\ C$ .. .. .. <u>V, 10</u>

$[H_2CO_3]_T = \gamma\ C$ .. .. .. <u>V, 11</u>

whence $\beta = \frac{1}{1 + K_2[OH^-] + \frac{sK_3}{[OH^-]}}$ .. <u>V, 12</u>

$\gamma = \frac{\frac{sK_3}{[OH^-]}}{1 + K_2[OH^-] + \frac{sK_3}{[OH^-]}}$ .. <u>V, 13</u>

where $K_2 = \frac{[CO_3^=]}{[HCO_3^-][OH^-]}$

$K_3 = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$

$s = \frac{[H_2CO_3]_T}{[H_2CO_3]}$ *

---

* Cf. p. 92.

(iii) $$[HCNO] = \delta\Big[[CNO^-] + [HCNO]\Big] = \delta[CNO^-]$$

whence $$\delta = \frac{K_4}{[OH^-]} \qquad \ldots \quad \ldots \quad \ldots \qquad \underline{V,\ 14}$$

where $$K_4 = \frac{[HCNO][OH^-]}{[CNO^-]}$$

(IV) $$[H_3BO_3{}^{-}] = \varepsilon\Big[[H_2BO_3{}^-] + [H_3BO_3]\Big] = \varepsilon[H_3BO_3]_o$$

$$[H_2BO_3^-] = (1 - \varepsilon)[H_3BO_3]_o$$

where the subscript "o" refers to the concentration prior to any acid-base reaction, i.e., the concentration added initially.

$$\varepsilon = \frac{K_5}{K_5 + [OH^-]} \qquad \ldots \quad \ldots \quad \ldots \qquad \underline{V,\ 15}$$

where $$K_5 = \frac{[H_3BO_3][OH^-]}{[H_2BO_3{}^-]}$$

(v) $$[NEt_3H^+] = \eta\Big[[NEt_3] + [NEt_3H^+]\Big] = \eta[NEt_3]_o$$

$$[NEt_3] = (1 - \eta)[NEt_3]_o$$

$$\eta = \frac{K_6}{K_6 + [OH^-]} \qquad \ldots \quad \ldots \quad \ldots \qquad \underline{V,\ 16}$$

where $K_6 = \frac{[NEt_3H^+][OH^-]}{[NEt_3]}$

(vi) Employing the notation defined above

$$[OH^-] = \frac{K_W}{[H^+]}$$

where $K_W = [H^+][OH^-]$

It must be pointed out that all the equilibrium constants quoted above are in concentration units. Their values are obtained from the known thermodynamic equilibrium constants, the ionic product of water, and the appropriate activity co-efficients which are calculated from the Davies Equation (95), viz.,

$$\log._{10} f_i = - \Theta Z_i^2 \left\{ \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2\ I \right\} \quad .. \quad \underline{V,\ 17}$$

where f_i is the activity co-efficient of the species "i",
where Z_i is the valency of the ion,
where Θ is a constant depending on solvent and temperature only
and I the ionic strength.

Values of K_W, $K_1 - K_6$ thus obtained are listed below in Table V, 2 for the ionic strength used in this investigation, (0.25). * The value of K_7 is also given as it will be required later.

It can be seen that the expressions V, 9 to V, 16 for the concentration of the various species, all involve the unknown quantity $[OH^-]$. Its calculation is discussed in the next section. The values of α and β at various values of $[OH^-]$ are given in Tables V, 3, 4, and 5 below, at the three temperatures used in this investigation. The value of $\frac{\beta + 2\gamma}{\alpha}$, which is useful in the calculation of $[OH^-]$, is also given. (Cf. next section).

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* This equation gives a value of 0.700 for f_1 at 60°C. Due to an arithmetical error, 0.705 has been used in all calculations. The effect, however, is quite negligible in every case.

Table V, 2

Constant	Value at I = 0.25			Reference and remarks
	40°C.	60°C.	80°C.	
K_1	3.91×10^{-5}	3.82×10^{-5}	3.57×10^{-5}	(96)
K_2	$4.07 \times 10^{+3}$	1.56×10^{3}	6.35×10^{2}	(97)
K_3	5.86×10^{-8}	1.85×10^{-7}	5.25×10^{-7}	(98)
K_4	1.4×10^{-10}	4.81×10^{-10}	1.26×10^{-9}	Approximate value from data at 0°C. (99)
K_5		1.04×10^{-4}		Extrapolated value from data listed (100)
K_6		1.29×10^{-3}		(96)
K_7		1.87×10^{-7}		Extrapolated value
K_W	5.770×10^{-14}	1.936×10^{-13}	5.357×10^{-13}	(101) (100)
	0.522	0.547	0.577	(100)
s	3	4	4.5	Calculated from solubility of CO_2 in aq. soln. (102)
f_1	0.711	0.700	0.686	Calculated from the Davis Eqn. (95)
f_2	0.256	0.240	0.222	

Calculation of $[H^+]$, α and β , etc.

(a) Table V, 3 I = 0.25 Temp. = 40°C.

$[H^+]$	$[OH^-]$	α	β	γ	$\frac{\beta + 2\gamma}{\alpha}$
1.15×10^{-7}	5.0×10^{-7}	0.013	0.739	0.260	96.8
9.61×10^{-8}	6.0	0.015	0.772	0.226	81.6
7.96	7.0	0.0177	0.797	0.200	67.6
7.21	8.0	0.0200	0.818	0.180	58.9
5.77	1.0×10^{-6}	0.0249	0.847	0.149	46.0
3.85	1.5	0.0369	0.890	0.104	29.8
2.89	2.0	0.0485	0.912	0.0803	22.1
1.92	3.0	0.0712	0.934	0.0551	14.7
1.44	4.0	0.0928	0.943	0.0415	11.05
1.16	5.0	0.113	0.947	0.0332	8.964
9.61×10^{-9}	6.0	0.133	0.969	0.0281	7.71
7.96	7.0	0.152	0.973	0.0244	6.72
7.21	8.0	0.170	0.948	0.0209	5.70
5.77	1.0×10^{-5}	0.204	0.944	0.0170	4.79
3.85	1.5	0.277	0.932	0.0112	3.40
2.89	2.0	0.337	0.917	0.0081	2.74
1.92	3.0	0.435	0.887	0.0052	2.06

(b) Table V, 4 I = 0.25 Temp. = 60°C.

$[H^+]$	$[OH^-]$	α	β	$\left(\frac{\beta + 2\gamma}{\alpha}\right)$
3.87×10^{-7}	5.0×10^{-7}	0.01291	0.4031	123.5
3.22	6.0	0.01546	0.4476	100.3
2.76	7.0	0.01800	0.4859	84.08
2.42	8.0	0.02051	0.4192	72.13
1.93	1.0×10^{-6}	0.02551	0.7574	55.81
1.29	1.5	0.03779	0.6688	35.15
9.67×10^{-8}	2.0	0.04976	0.7283	25.47
6.45	3.0	0.07283	0.7994	16.39
4.83	4.0	0.09479	0.8394	12.13
3.87	5.0	0.1157	0.8651	9.69
3.22	6.0	0.1357	0.8834	8.113
2.76	7.0	0.1549	0.8961	7.009
2.42	8.0	0.1732	0.9050	6.193
1.93	1.0×10^{-5}	0.2075	0.9174	5.076
1.29	1.5	0.2830	0.9320	3.618
9.67×10^{-9}	2.0	0.3436	0.9363	2.921
6.45	3.0	0.4399	0.9337	2.227
4.83	4.0	0.5115	0.9251	1.875
3.87	5.0	0.5669	0.9149	1.662
3.22	6.0	0.6109	0.9049	1.517
2.76	7.0	0.6468	0.8929	1.410
2.42	8.0	0.6770	0.8818	1.326
1.93	1.0×10^{-4}	0.7236	0.8598	1.206
1.29	1.5	0.797	0.810	1.019
9.67×10^{-10}	2.0	0.840	0.762	0.909
8.79	2.2	0.852	0.744	0.875
8.06	2.4	0.863	0.727	0.844
7.44	2.6	0.872	0.711	0.819
6.91	2.8	0.880	0.696	0.791
6.45	3.0	0.887	0.681	0.768
6.04	3.2	0.894	0.667	0.746
5.69	3.4	0.899	0.653	0.726
5.37	3.6	0.904	0.640	0.708
5.09	3.8	0.908	0.628	0.691
4.84	4.0	0.912	0.615	0.675
4.61	4.2	0.917	0.604	0.659
4.40	4.4	0.920	0.593	0.645
4.21	4.6	0.923	0.582	0.630
4.03	4.8	0.926	0.572	0.617
3.87	5.0	0.929	0.562	0.605

(c) Table V, 5 I = 0.25 Temp. = 80°C.

$[H^+]$	$[OH^-]$	α	β	$\frac{\beta + 2\gamma}{\alpha}$
3.57×10^{-7}	1.5×10^{-6}	0.0403	0.391	39.97
2.68	2.0	0.0530	0.461	29.03
1.79	3.0	0.0775	0.562	18.55
1.34	4.0	0.101	0.629	13.5
1.07	5.0	0.123	0.677	10.66
8.93×10^{-8}	6.0	0.144	0.719	8.88
7.65	7.0	0.164	0.747	7.59
6.70	8.0	0.183	0.770	6.68
5.36	1.0×10^{-5}	0.219	0.806	5.41
3.57	1.5	0.296	0.858	3.804
2.68	2.0	0.359	0.885	3.04
1.79	3.0	0.457	0.912	2.310
1.34	4.0	0.529	0.923	1.95
1.07	5.0	0.585	0.927	1.73
8.93×10^{-9}	6.0	0.627	0.928	1.59
7.65	7.0	0.662	0.928	1.495
5.36	1.0×10^{-4}	0.737	0.920	1.307
2.678	2.0	0.848	0.871	1.051
2.23	2.4	0.871	0.864	1.006
1.913	2.8	0.887	0.843	0.966
1.786	3.0	0.894	0.834	0.947
1.575	3.4	0.904	0.817	0.924
1.410	3.8	0.914	0.802	0.883
1.280	4.2	0.992	0.786	0.862
1.164	4.6	0.928	0.771	0.838
1.071	5.0	0.933	0.756	0.818
9.236×10^{-10}	5.8	0.942	0.729	0.780
8.928	6.0	0.944	0.722	0.766
8.370	6.4	0.947	0.709	0.755
7.877	6.8	0.950	0.703	0.746
7.652	7.0	0.951	0.690	0.731
6.867	7.8	0.956	0.668	0.703
6.696	8.0	0.957	0.661	0.695
6.30	8.5	0.960	0.652	0.683
5.952	9.0	0.962	0.635	0.663
5.698	9.4	0.963	0.625	0.652
5.466	9.8	0.965	0.616	0.641
5.357	1×10^{-5}	0.966	0.610	0.635

(d) Calculation of pH

(1) Ba^{++} ions absent

In any reaction mixture, the occurrence of the following reactions with the solvent or OH^- ions will affect the pH:

$$H_2O \rightleftharpoons H^+ + OH^- \quad .. \quad \underline{V.\ 18}\ (a)$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \quad .. \quad .. \quad (b)$$

$$CO_3^= + H_2O \rightleftharpoons HCO_3^- + OH^- \quad .. \quad .. \quad (c)$$

$$CO_3^= + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^- \quad .. \quad .. \quad (d)$$

$$CNO^- + H_2O \rightleftharpoons HCNO + OH^- \quad .. \quad .. \quad (e)$$

$$H_3BO_3 + OH^- \rightleftharpoons H_2BO_3^- + H_2O \quad .. \quad .. \quad (f)$$

$$NEt_3 + H_2O \rightleftharpoons NEt_3H^+ + OH^- \quad .. \quad .. \quad (g)$$

It will be seen that OH^- ions are removed by reactions (b) and (f) and produced by reactions (a), (c), (d), (e) and (g).

Thus, we have:

$$\begin{aligned}[OH^-] - [OH^-]_o = {} & [H^+] - [H^+]_o + [HCO_3^-] - [HCO_3^-]_o + 2[H_2CO_3] \\ & - 2[H_2CO_3]_o + [HCNO] - [HCNO]_o - [NH_3] \\ & + [NH_3]_o - [H_2BO_3^-] + [H_2BO_3^-]_o \\ & + [NEt_3H^+] - [NEt_3H^+]_o \quad .. \quad .. \quad \underline{V,\ 19}\end{aligned}$$

where the subscript "o" refers to initial values, i.e., prior to occurrence of reactions V, 18, (a) - (g). In this investigation, H_2CO_3, HCNO, NEt_3H^+ and $H_2BO_3^-$ were never added to the reaction mixture in that form. Equation V, 19, therefore, reduces to:

$$[OH^-] - [OH^-]_o = [H^+] - [H^+]_o + [HCO_3^-] - [HCO_3^-]_o + 2[H_2CO_3] + [HCNO] + [NEt_3H^+] - [NH_3] + [NH_3]_o - [H_2BO_3^-] \qquad .. \quad .. \quad .. \ \underline{V, 20}$$

Substituting in this equation for α, β, γ, δ, ε and η, we have:

$$[OH^-] - [OH^-]_o = [H^+] - [H^+]_o + (\beta + 2\gamma)C + \delta[CNO^-] + \eta[NEt_3]_o - \alpha N - (1-\varepsilon)[H_3BO_3]_o + [NH_3]_o - [HCO_3^-]_o$$

Re-arranging, we have:

$$\frac{N}{C} = \frac{\beta + 2\gamma}{\alpha} - \frac{[OH^-]}{\alpha C} + \frac{\delta[CNO^-]}{\alpha C} + \frac{[OH^-]_o - [H^+]_o + [H^+]}{\alpha C} + \frac{[NH_3]_o - [HCO_3^-]_o}{\alpha C} + \frac{\eta[NEt_3]_o - (1-\varepsilon)[H_3BO_3]_o}{\alpha C} \qquad .. \ \underline{V, 21}$$

From a definition of the parameters α, β, γ, δ, ε and η, (eqns. V, 9-16), it can be seen that eqn. V, 21 is a polynomial in $[OH^-]$, the only unknown quantity, and its value may be determined by solving this equation. This solution appears at first sight to be a laborious process although it can be carried out graphically. It may, however, be considerably simplified by considering individual cases. These are discussed below.

(i) The last two terms are obviously only involved when the appropriate species have been added to the reaction mixture. In this connection, it is worth noting that the addition of $CO_3^=$ or NH_4^+ ions does not require any additional terms.

(ii) The third term is negligible.

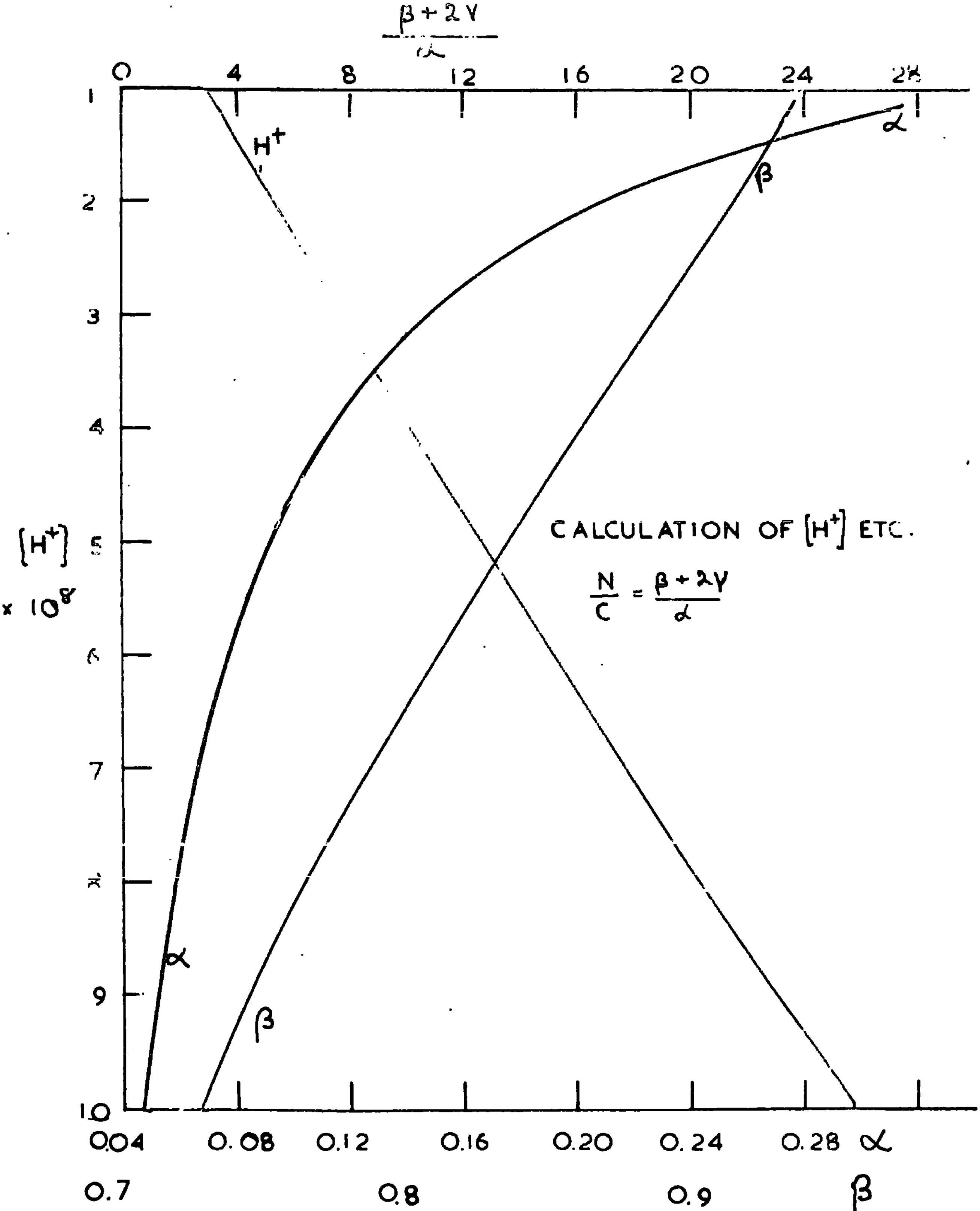
(iii) The fourth term can be neglected except when OH^- ions have been added to the reaction mixture.

(iv) The second term can be neglected when $[OH^-] < 3 \times 10^{-5}$. Under these conditions, V, 21 reduces to:

$$\frac{N}{C} = \frac{\beta + 2\gamma}{\alpha} \quad .. \quad .. \quad .. \qquad \underline{V,\ 22}$$

and thus $[OH^-]$ can be obtained directly from Tables 3, 4 and 5 or from a graph showing $\frac{\beta + 2\gamma}{\alpha}$ as a function of $[OH^-]$, as is drawn in Fig. 8 for the 10^{-7} - 10^{-8} $[H^+]$ range. These simplifications are illustrated below for two typical reaction mixtures based on NH_4CNO and NaCNO Runs respectively.

FIG. 8



CALCULATION OF $[H^+]$ ETC.

$$\frac{N}{C} = \frac{\beta + 2\gamma}{\alpha}$$

Table V, 6 I = 0.25 Temp. = 60°C.

AMMONIUM CYANATE

From Table V, 4

$[CNO^-]$	N	C	$[OH^-]$	αC	$N/C = \frac{\beta + 2\gamma}{\alpha}$	$\frac{[OH^-]}{\alpha C}$	$\frac{\delta[CNO^-]}{\alpha C}$	$\frac{[H^+]}{\alpha C}$
0.044	0.045	0.00177	2×10^{-6}	8.8×10^{-4}	25.5	2×10^{-3}	0.01	10^{-4}
0.010	0.018	0.00616	2×10^{-5}	0.00212	2.92	10^{-2}	10^{-3}	10^{-6}

It is clear that all but the first term of equation V, 21, are negligible and the $[H^+]$ concentration may be read directly from a graph as in Fig. 8.

Table V, 7 I = 0.25 Temp. = 60°C.

SODIUM CYANATE

From Table V, 4

$[H^+]$	$[OH^-]$	$\frac{[OH^-]}{\alpha C}$	$\frac{\beta + 2\gamma}{\alpha}$	$\frac{\delta[CNO^-]}{\alpha C}$	$\frac{[H^+]}{\alpha C}$	$\frac{\beta + 2\gamma}{\alpha} - \frac{[OH^-]}{\alpha C}$
6.91×10^{-1}	2.8×10^{-4}	0.034	0.791	$< 10^{-6}$	$< 8 \times 10^{-8}$	0.757
6.45 "	3.0 "	0.036	0.768	"	"	0.732
6.04 "	3.2~~3~~	0.038	0.746	"	"	0.708

It can be seen that only the first two terms contribute: Extrapolating graphically to an $^N/C$ ratio of 0.747,

$$[OH^-] = 2.88 \times 10^{-4}$$

Once $[OH^-]$ is known, the parameters α, β, γ, etc., which are functions of this quantity, can be calculated and hence the concentration of all the species which are present.

(2) Barium Ions present

When Ba^{++} ions are present in the solution, a certain amount of Barium Carbonate will be precipitated. $[OH^-]$ is still given by eqn. V, 21, if we assume C, the total carbonate concentration, to refer now to the value of the carbonate in solution, excluding that precipitated. Experimental determinations of the total carbonate in solution, in reaction mixtures containing barium ions, showed that the value was small compared with that precipitated, i.e., precipitation was largely complete and accurate experimental determination of carbonate in solution was not possible.* At any stage of the reaction then:

$$[Ba^{++}] = [Ba^{++}]_0 - C \quad \ldots \quad \ldots \qquad \underline{V, 23}$$

(C still refers to total carbonate, including that precipitated, where the subscript "o" has the usual meaning.)

---

* The $[HCO_3^-]$ varies from 0.00019 M. at t = 0 to 0.00083 M. at t = 5706 mins.

Hence $$[CO_3^{=}] = \frac{K_7}{[Ba^{++}]_o - C}$$

where $$K_7 = [Ba^{++}][CO_3^{=}] \quad \cdot\cdot \quad \cdot\cdot \qquad \underline{V,\ 24}$$

and from the definition of K_2 (p.101)

$$[HCO_3^{-}] = \frac{K_7}{([Ba^{++}]_o - C)\ K_2[OH^{-}]} \quad \cdot\cdot \qquad \underline{V,\ 25}$$

and from the definition of K_3

$$[H_2CO_3]_T = \frac{S\ K_7\ K_3}{([Ba^{++}]_o - C)\ K_2\ [OH^{-}]^2} \qquad \underline{V,\ 26}$$

Substituting these values for $[H_2CO_3]_T$ and $[HCO_3^{-}]$ in eqn. V, 20 and for $[NH_3]$ and $[HCNO]$ from eqns. V, 8 and V, 14, (remembering that in all the runs carried out with added barium ions, only CNO^-, NO_3^- and alkali metal ions were initially present);

$$[OH^{-}] - [OH^{-}]_o = [H^{+}] - [H^{+}]_o - \alpha N + \delta[CNO^{-}]$$

$$+ \frac{K_7\left(1 + \frac{2SK_3}{[OH^{-}]}\right)}{([Ba^{++}]_o - C)K_2[OH^{-}]} \qquad \underline{V,\ 27}$$

or

$$N([Ba^{++}]_o - C) = \frac{K_7}{K_2[OH^-]} \left(1 + \frac{2SK_3}{[OH^-]}\right) \frac{1}{\alpha}$$

$$+ \frac{([Ba^{++}]_o - C)}{\alpha} \left\{ \delta[CNO^-] + [OH^-]_o \overset{-[OH]}{\wedge} - [H^+]_o + [H^+] \right\}$$

V, 28

It is found that under the experimental conditions employed, only the first term need be taken into account. This is illustrated below.

Table V, 8 $\qquad I = 0.25 \qquad$ Temp. = 60°C.

$[Ba^{++}]_o$ = 0.03 M. $\qquad$ N. = 0.0021

$[CNO^-]$	C	$[H^+]$	$[OH^-]$	1st term on r.h.s.	2nd term on r.h.s.
0.048	0.00143	2.4×10^{-8}	8.0×10^{-6}	1.0×10^{-4}	-1×10^{-6}
0.003	0.0243	9.67×10^{-9}	2.0×10^{-5}	1.9×10^{-5}	-3×10^{-7}

Hence, as a first approximation, values of $[H^+]$ may be calculated from a graph showing

$$\frac{K_7}{K_2[OH^-]} \left\{ 1 + \frac{2SK_3}{[OH^-]} \right\} \frac{1}{\alpha}$$

as a function of $[OH^-]$ The necessary data is shown in Table V, 9. This value of $[OH^-]$, however, assumes that all carbonate is precipitated as barium carbonate, which, as has already been stated, is not so. The observed values for N and C are, therefore, low and $[CNO^-]$ too large by an amount $[HCO_3^-]$ (carbonate in solution). A value of $[HCO_3^-]$ was calculated from the preliminary value of $[OH^-]$ and hence improved values of N and C. An improved value of $[OH^-]$ can then be calculated from eqn. V, 21 as described in (d). A further approximation was found unnecessary in this case.

Table V, 9

Calculation of hydrogen ion concentration, etc., in the barium-added runs

$[H^+]$	$[OH^-]$	α	β	$\frac{K_7}{K_2[OH^-]}\left(1 + \frac{2SK_3}{[OH^-]}\right)\frac{1}{\alpha}$
3.87×10^{-7}	5.0×10^{-7}	0.01291	0.4031	7.4×10^{-2}
2.42	8.0	0.02051	0.4192	2.1×10^{-2}
1.93	1.0×10^{-6}	0.02551	0.7574	1.2×10^{-2}
9.67×10^{-8}	2.0	0.04976	0.7283	2.1×10^{-3}
3.87	5.0	0.1157	0.8651	2.7×10^{-4}
2.42	8.0	0.1732	0.9050	1.0×10^{-4}
1.94	1.0×10^{-5}	0.2075	0.9174	6.6×10^{-5}
9.67×10^{-9}	2.0	0.3436	0.9363	1.9×10^{-5}

(e) The calculation of $[H^+]$ at 60°C. from pH measurements at room temperatures

The pH at various times throughout the decomposition of 0.1 M. urea was determined, using a Cambridge pH meter, on samples cooled to room temperature. It was necessary to calculate the corresponding pH at 60°C.

In the range of N and C values encountered ($N > 10C$), the hydrogen ion concentration is given by:

$$\frac{N}{C} = \frac{\beta + 2\gamma}{\alpha} \quad \text{(cf. p.107)}$$

Consequently, from the observed value of the pH at room temperature, the values of $\frac{N}{C}$ may be calculated at 20°C. The pH corresponding to this same $\frac{N}{C}$ ratio at 60°C. will be the required value at this temperature. In practice, it is sufficiently accurate to use Tables V, 3 and V, 5 at 40°C. and 80°C.; the increase in hydrogen ion concentration over this range corresponds approximately with that over the 20° - 60°C. range.

CHAPTER VI

THE CALCULATION OF RATE CONSTANTS

(a) Evaluation of rate constants

It has already been pointed out that the rates of urea and carbonate formation are given by:

$$\frac{d[\text{Urea}]}{dt} = k_U[NH_4^+][CNO^-] - k_R[\text{Urea}] \quad .. \quad .. \quad \underline{\text{II, 1}}$$

and $$\frac{dC}{dt} = k_W[CNO^-] + k_H[H^+][CNO^-] + k_C[HCO_3^-][CNO^-] \quad \underline{\text{II, 2}}$$

respectively. Neither of these equations can be integrated directly.

Rate constants are calculated by graphical integration, since these are considered more accurate than instantaneous values obtained from the slopes of [Urea] - t and C - t curves, although more laborious to calculate.

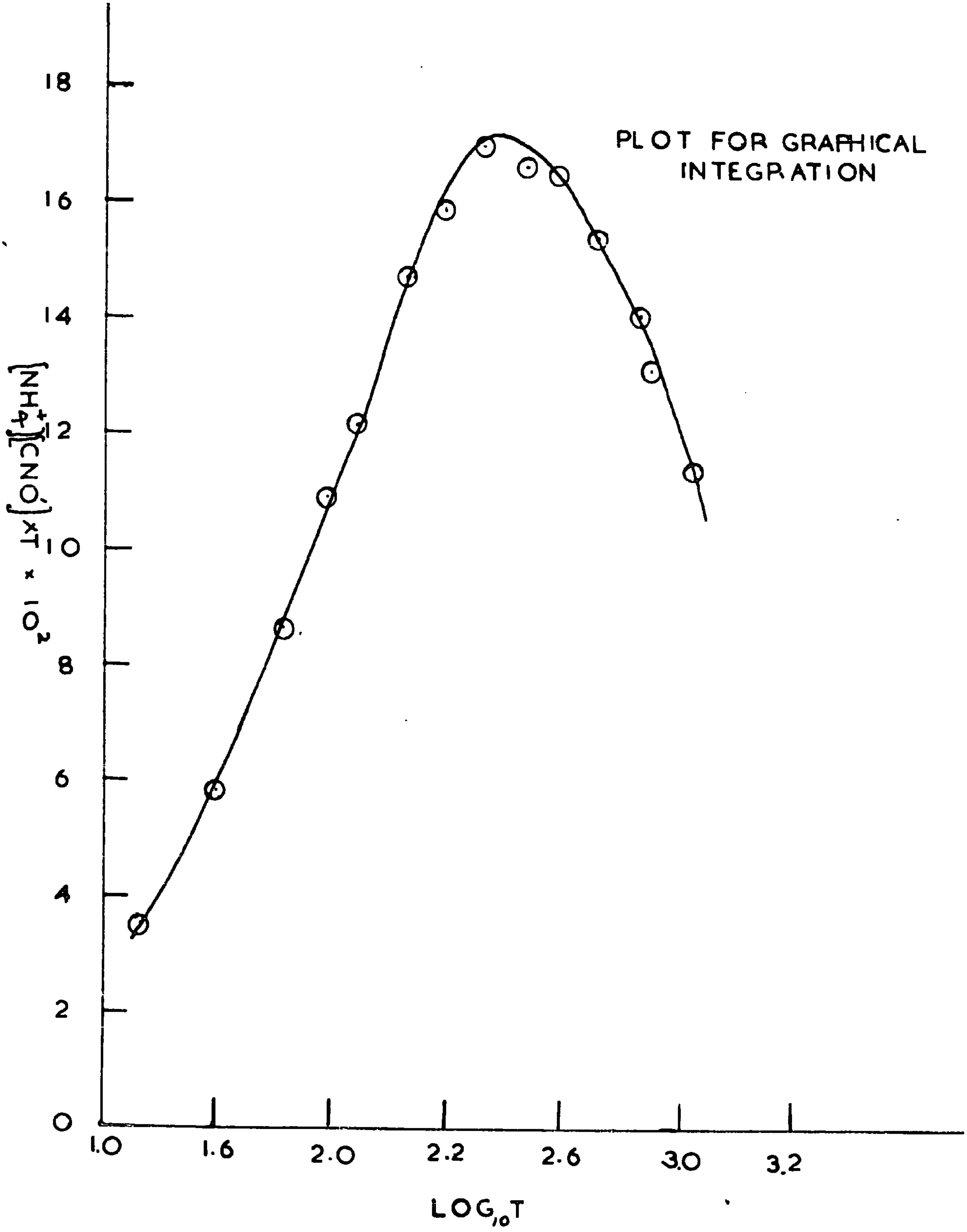
Integrals of the type $\int_0^t xy\,dt$

are evaluated by taking the area under a graph of xyt as a function of $\log_{10}t$, when

$$\int_0^t xy\,dt = 2.303 \times \text{Area}$$

This procedure was found more convenient than the more obvious one - the area under the curve xy as a function of t - in view of the long tail of such a curve for large values of t. A typical curve for Run 2 is shown in Fig. ~~10~~.9.

FIG. 9


PLOT FOR GRAPHICAL INTEGRATION
$[NH_4^+][CNO']\times T \times 10^2$
18
16
14
12
10
8
6
4
2
0
1.0
1.6
2.0
2.2
2.6
3.0
3.2
$LOG_{10}T$

(b) The rate constants of urea formation (k_U)

The rate of urea formation is given by:

$$\frac{d[\text{Urea}]}{dt} = k_U[NH_4^+][CNO^-] - k_R[\text{Urea}] \quad .. \quad .. \quad \underline{II, 1}$$

i.e., $[\text{Urea}] - [\text{Urea}]_o = k_U \int_o^t [NH_4^+][CNO^-]\,dt - k_R \int_o^t [\text{Urea}]\,dt$

from which k_U can be calculated if k_R is known. The value of k_R can be obtained from independent experiment (p.116) and, for the experimental conditions employed, it can be shown that the term involving this quantity can be neglected in the calculation of k_U up to 80% reaction. This is illustrated in Table VI, 1 below for typical runs:

<u>Table VI, 1</u> I = 0.25 60°C.

	% reaction	$k_U\int_o^t [NH_4^+][CNO^-]dt$	$k_R\int_o^t [\text{Urea}]dt$
0.05 NH_4CNO (Run 2)	60	0.029	0.00012
	70	0.034	0.00030
	80	0.038	0.00045
0.05 NaCNO (Run 14)	80	0.01	0.00036

(c) The rate constants for carbonate formation (k_W, k_H and k_C)

The rate of carbonate formation is given by:

$$\frac{dC}{dt} = k_W[CNO^-] + k_H[H^+][CNO^-] + k_C[HCO_3^-][CNO^-]$$

or, on integration:

$$C - C_o = k_W\int_o^t [CNO^-]dt + k_H\int_o^t [H^+][CNO^-]dt + k_C\int_o^t [HCO_3^-][CNO^-]dt \quad .. \quad \underline{VI,\ 1}$$

This involves the evaluation of three constants from about twelve experimental points, and although this can be done by an extension of the least squares method, the contribution of the term in k_H is so small that its value is less than the standard deviation and hence meaningless.

An approximate value of k_H was available (10^{+4} gm. mol.$^{-1}$ L. min.$^{-1}$ at 70°C., by Wyatt and Kornberg (54)). If this value is not greatly in error, the contribution of the term in k_H to the total carbonate formation from sodium cyanate can be neglected, as here $[H^+]$ is small (10^{-9} - 10^{-10}). Hence, approximately:

$$C - C_o = k_W\int_o^t [CNO^-]dt + k_C\int_o^t [HCO_3^-][CNO^-]dt$$

$$\text{or} \quad \frac{C - C_o}{\int_o^t [CNO^-]dt} = k_W + \frac{k_C \int_o^t [HCO_3^-][CNO^-]dt}{\int_o^t [CNO^-]dt} \quad \cdot\cdot \quad \underline{VI, 2}$$

Approximate values of k_C and k_W may thus be obtained from the results of a sodium cyanate run by plotting:

$$\frac{C - C_o}{\int_o^t [CNO^-]dt} \quad \text{as a function of} \quad \frac{\int_o^t [HCO_3^-][CNO^-]dt}{\int_o^t [CNO^-]dt}$$

when these constants can be calculated from the slope and intercept of the resulting straight line. An example, for a typical run, is illustrated in Fig. 1D*. The substitution of these values (for k_W and k_C) in eqn. VI, 1, then allows an approximate value of k_H to be obtained from the results of an ammonium cyanate run, where the term involving this constant contributes appreciably to the total carbonate formation. The use of this value of k_H in conjunction with the results of a sodium cyanate run, leads to improved values for k_C and k_W, which in turn, give an improved value of k_H from the results of an ammonium cyanate run. A repetition of this procedure does not appreciably alter the value of these constants. The difference between the approximate and improved values is illustrated in Table VI, 2.

---

* In Fig. 1D

$$A = \int_o^t [CNO^-]dt$$

$$B = \int_o^t [HCO_3^-][CNO^-]dt$$

$$C' = C - C_o - k_H \int_o^t [H^+][CNO^-]dt$$

FIG. 10

(Run 18)

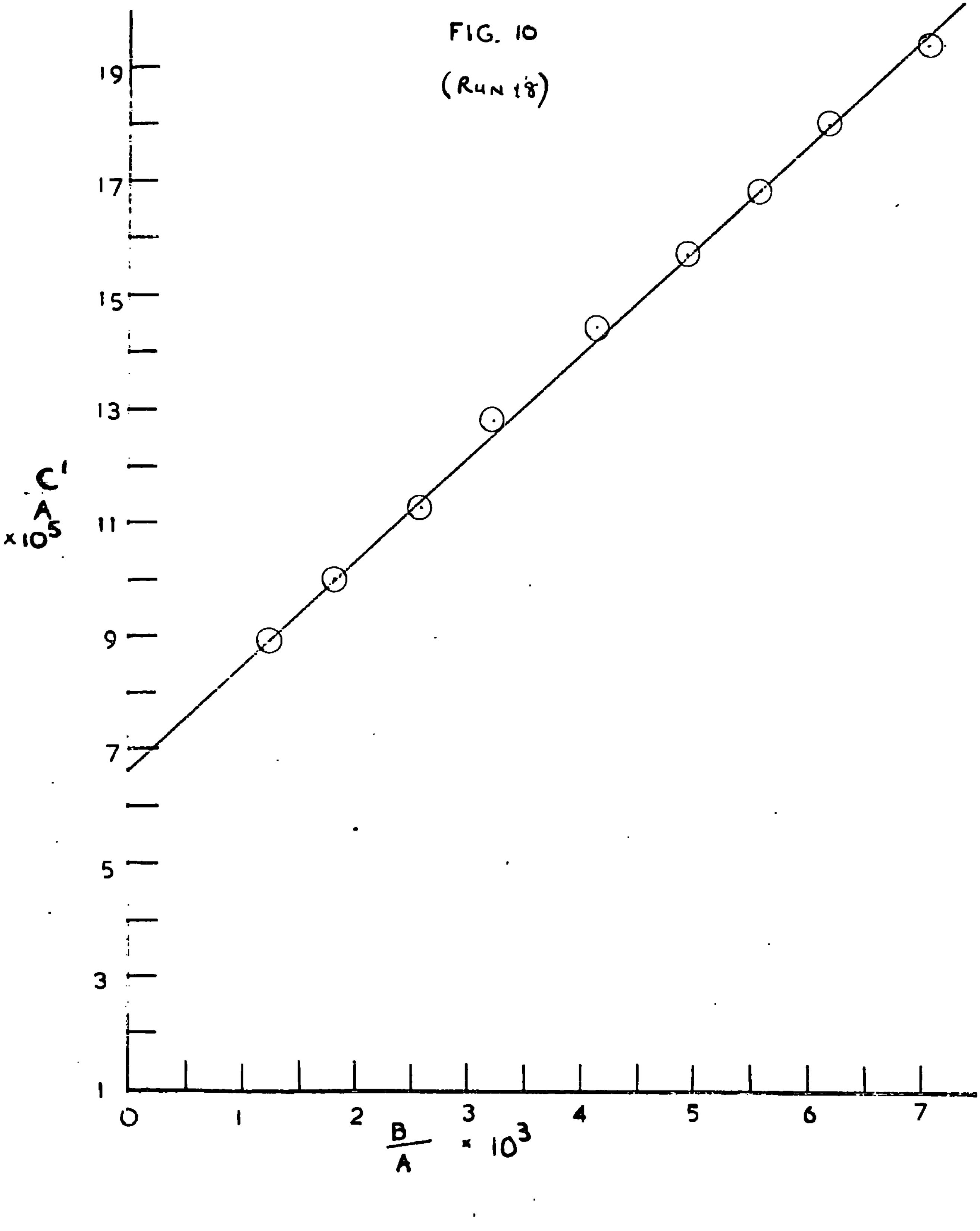

19
17
15
13
11
9
7
5
3
1
$\frac{C'}{A} \times 10^5$
0
1
2
3
4
5
6
7
$\frac{B}{A} \times 10^3$

Table VI, 2 $I = 0.25$ 60°C.

	$k_H(10^{-3})$	$k_C(10^2)$	$k_W(10^5)$
Determination of approx. values of k_C and k_W (NaCNO, Run 13)	-	1.63	6.7
Determination of approx. value of k_H (NH_4CNO, Run 2)	3.7		
Recalculation of k_C and k_W applying a correction for k_H term	-	1.67	6.2
Recalculation of k_H assuming corrected values of k_W and k_C	4.0	-	-
% change	8%	3%	8%

(d) The rate constants for Urea decomposition (k_R)

The rate of urea decomposition is given by:

$$- \frac{d[\text{Urea}]}{dt} = k_R[\text{Urea}] - k_U[NH_4^+][CNO^-]$$

The last term (involving k_U) was neglected and the equation integrated directly. First order rate constants were calculated from an approximate form of the first order rate expression:

$$k = \frac{[\text{Urea}] - [\text{Urea}]_0}{[\text{Urea}]_0 \, t}$$

which holds with sufficient accuracy over the range considered here.*

Values of k_R can be calculated by extrapolating the values of k back to zero time, i.e., when the effect of the reverse reaction is negligible. In practice, it was not found necessary to extrapolate graphically, in fact, the accuracy of determination of the small $[\text{Urea}]_t - [\text{Urea}]_0$ values would not allow this, but a mean value over the first 12 hours of a run at 60°C. is sufficiently accurate for this purpose. Table VI, 3 below, shows the effect of urea formation over this time to be negligible.

Table VI, 3 I = 0.25 60°C.
Run 25

Time (mins)	$k_R \int_0^t [\text{Urea}]dt \times 10^5$	$k_W \int_0^t [NH_4^+][CNO^-]dt \times 10^5$
288	-	-
737	71.5	5
978	108	6.5

---

* Accurate if $\frac{[\text{Urea}] - [\text{Urea}]_0}{[\text{Urea}]_0} \ll 1$

This function is always less than 5×10^{-2} over the range considered here and the error caused by the approximation less than 1% in k_R.

CHAPTER VII

EXPERIMENTAL DETAILS

(a) Preparation of Materials

Sodium Cyanate

Approximately 20 gms. of B.D.H. commercial sodium cyanate was dissolved in 100 ml. water at 40-50°C. and the solution filtered. The filtrate was cooled as rapidly as possible to room temperature and re-filtered. After one hour in a refrigerator, 4-5 gms. of white crystaline sodium cyanate separated, and this was filtered off and dried in a vacuum dessicator over P_2O_5. It was found to contain not more than 0.8% carbonate (and usually less than 0.5%) and no detectable cyanide or ferric ion.

It is important for the heating period to be short and the filtrate cooled as quickly as possible. The method, although wasteful of crude material, is simpler than other methods described and does yield a satisfactorily pure product. The pH of an 0.05 M. solution of the cyanate was found to be approx. 8.3 (theoretical value 8.1).

Ammonium Cyanate

The method adopted by the majority of previous workers was found satisfactory, i.e., double decomposition between ammonium chloride and silver cyanate.

Silver cyanate was prepared by heating a solution of silver nitrate ($^N/10$) with five times the equivalent quantity of urea. The first dark batch of crystals was filtered off and discarded and the remainder - formed after two hours' heating - filtered off and dried in a vacuum desiccator.

1.33 gms. of "Analar" ammonium chloride and approx. 4 gms. of silver cyanate in 50 mls.water were shaken together until no appreciable chloride could be detected in a few drops of the supernatant liquid (approx. 20 mins.). The precipitate was filtered off and the 0.5 M. ammonium cyanate solution diluted to the required strength*.

Urea

A batch of Messrs. B.D.H. Analar grade urea was found to contain approx. 1% biuret but to be otherwise pure. This urea was recrystalised twice from alcohol and dried in a vacuum desiccator; M.P. 132°C. (after re-crystalisation, no biuret could be detected).

Biuret

A small sample was prepared by the method of Haworth and Mann (104).

Acetone

Commercial Acetone was purified by the method of Conant and Kirner (105), i.e., refluxed for two hours over caustic soda and potassium permanganate, and distilled. Acetone, which had already been used contained ammonium salts and was, therefore, distilled with acid (2 l. acetone + 10 Ml. dil. H_2SO_4)

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* Bader, Dupre and Schutz (103) criticise this method of preparation, considering the product to be contaminated with as much as 14% carbonate. The max. encountered during the present investigation is 1% (see Run 1).

in order to ensure the absence of ammonia in the final product.

Lacmoid (indicator)

A stock solution was made up by dissolving approx. 1 gm. lacmoid in 250 mls. acetone. Approx. 4 mls. of this was added to each Winchester of acetone.

Standard Hydrochloric Acid

Constant boiling mixture HCl was prepared by the usual procedure. This was diluted (by weighing) to give an approx. 0.01 M. solution of accurately known strength. In the first instance, the strength was checked by titration with silver nitrate, standardised against sodium chloride. All sodium hydroxide was standardised against this standard hydrochloric acid.

(b) Determination of Total Basicity

The total basicity - $[CNO^-] + 2C$ - of a solution was determined by adding excess hydrochloric acid in the presence of a large amount of acetone and back-titrating with sodium hydroxide, lacmoid being used as indicator. The general principles underlying the method have already been discussed (cf. p.94) and consistent results were obtained, provided that the amount of water present was small. The following procedure was, therefore, adopted.

A tube containing 3.749 mls.[*] of the reaction mixture was placed in approx. 200 mls. neutralised acetone, the tube broken

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[*] At 0°C.

after the appropriate amount of HCl had been added, and the total volume made up to 400 mls. with more neutralised acetone. The sodium hydroxide was added from a semi-micro burette and the HCl made up in 70% aqueous acetone.

The reliability of the method is illustrated in Tables VII, 1 and VII, 2 below, the solution being made up by weight from the pure salt. On the whole, the results are slightly higher than expected but this is consistent with a small amount of carbonate in the "pure" cyanate.

Table VII, 1

Determination of Cyanate concentrations in the absence of carbonate

1.997 mls. of cyanate solution of known strength was titrated with 0.00919 N. NaOH after the addition of 2.03 mls. of 0.05396 N. HCl.

$[CNO^-]$	Titre (mls)	$[CNO^-]$ found	% Error
0.04681	1.46*	0.04687	+ 0.1
0.03580	4.09	0.03603	+ 0.6
0.01221	9.26	0.01224	+ 0.3
0.003580	9.97‡	0.003584	+ 0.1

* In this experiment 0.01170 N. NaOH and 0.05454 N. HCl were employed.

‡ In this experiment 5.006 mls. of cyanate solution were used.

Table VII, 2

Determination of $[CNO^-] + 2C$.

1.997 mls. of cyanate-carbonate solution of known strength weretitrated with 0.00919 N. NaOH after the addition of 2.03 mls. of 0.5396 N. HCl.

$[CNO^-]$	C	$[CNO^-] + 2C$	Titre	$[CNO^-] + 2C$ found	% error
0.04876	0.01895	0.09667*	2.85	0.09661	-
0.04876	0.00379	0.05634*	11.65	0.05610	- 0.4
0.04876	0.00190	0.05256	0.46	0.05272	+ 0.2
0.01761	0.00210	0.02181	7.18	0.02180	-

* In these experiments, 4.06 mls. HCl were added.

(c) Determination of Total Carbonate

The total carbonate, C, was determined in the same manner as that used for basicity, except that the cyanate was first removed from the solution. The following method was finally adopted.

5 mls. of a solution containing 40 gms. ammonium nitrate and 17 gms. of silver nitrate per litre were added to 3.749 mls. of the reaction mixture, made up to 25 mls. and shaken. Under these conditions, no appreciable amount of silver carbonate is precipitated, provided the carbonate concentration of the sample is less than 0.035 M. A portion of the mixture was

centrifuged and 5 mls. of the supernatant liquid withdrawn and titrated as before, with sodium hydroxide in acetone after the addition of excess hydrochloric acid. A few crystals of sodium chloride were added prior to the titration to remove the silver ions.

The end point was not as sharp as might have been desired. This appeared to be due to the relatively large amounts of ammonium ion necessarily present to avoid precipitation of carbonate. The light conditions prevailing during the titration also affected the value of the end point, but by working under standard conditions, it was possible to obtain results reproducable within 0.005 mls. alkali.

Before each series of titrations, "blank" titres were determined to allow for the incomplete precipitation of silver cyanate and the prevailing light conditions. Blanks were determined in two ways:-

(a) by carrying out the procedure with standard solutions of cyanate containing no carbonate. (Cf. Table VII, 3).

or (b) by analysing a carbonate-cyanate mixture in the normal manner and again after it had been diluted prior to precipitation of the silver cyanate. (Cf. Run 2).

The reliability of the method is illustrated in Table VII, 3 below. It can be seen that the accuracy of the method is independent of the amount of cyanate present and decreases with decreasing carbonate concentration.

Table VII, 3

Determination of Total Carbonate

5 mls. of a solution containing known amounts of sodium cyanate and carbonate (made up by weight) were employed. Cyanate was precipitated, the mixture made up to 25 mls. and 5 mls. of the supernatant solution reacted with 2 mls. of 0.02024 N. hydrochloric acid and titrated with 0.01048 N. NaOH

The sodium cyanate contained negligible carbonate, as the same titre was obtained by analysing solutions of different strengths.

Blank titre = 3.817 mls.

By weight		Titre*	C (found)	% Error
$[CNO^-]$	C			
0.04876	0.01895	0.200	0.0189	-
0.01621	0.01895	0.210	0.0189	-
0.04876	0.00379	3.088	0.00382	+ 1
0.01621	0.00379	3.069	0.00392	+ 3
0.04876	0.00190	3.462	0.00183	- 4
0.04876	0.000948	3.630	0.00980	+ 4

* Each value is the mean of four titrations.

(d) The Calorimetric Determination of Cyanate

The accuracy of the method for the determination of C decreases as the total carbonate decreases and cannot, therefore, be employed in the investigation of the decomposition of urea where small quantities of cyanate and carbonate have to be estimated. Under these conditions, it was found more convenient to determine cyanate concentration instead. This can be done spectrophotometrically, using Werner's modification of the Spatu test (106), which involves the calorimetric determination of a copper-pyridene-cyanate complex soluble in chloroform, also used by Bailey and Bailey (107) for the determination of cyanate solutions of about 0.01 M.

The following method was adopted.

5 mls. of the cyanate solution were shaken with 2 mls. of a 2% Copper Sulphate pentahydrate solution, 2 mls. of A.R. pyridene and 10 mls. of A.R. chloroform. 2 mls. of the chloroform layer were run off through a Watmann No. 1 filter paper*, into a 1 cm. photometer cell (larger cells would have increased the accuracy, but none was available at this time). The percentage transmission at 690 $m\mu$ was determined, using a Unicam S.P. 500 spectrophotometer, separate experiments having shown that the maximum adsorption occurred at this wave length.

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* To remove a slight aqueous suspension.

It was found that nitrate ion interfered very slightly in the determination and the "blank" cell was, therefore, filled with a solution which had undergone the same treatment and contained the same amoumt of potassium nitrate as the cyanate solution. The calibration curve for known cyanate concentration is shown in Fig. 11. (This is dependent on the particular pair of cells used). The accuracy of the method is estimated at about ± 5% at a cyanate concentration of 0.005 M. and ± 10% at 0.001 M. Ammonium ion, carbonate, urea and biuret were shown not to interfere to any detectable extent.

(e) Determination of Biuret (Usual "biuret test")

Only a very rough estimate of biuret was required. In fact, none could be detected in any of the solutions examined. 2 mls. of a 2% copper sulphate solution and 2 mls. of a 2% NaOH solution were added to 5 mls. of the solution to be examined. The precipitated cupric hydroxide was centrifuged down and the supernatant liquid examined at 560 mμ, for biuret colour. 5×10^{-4} M. biuret could be detected.

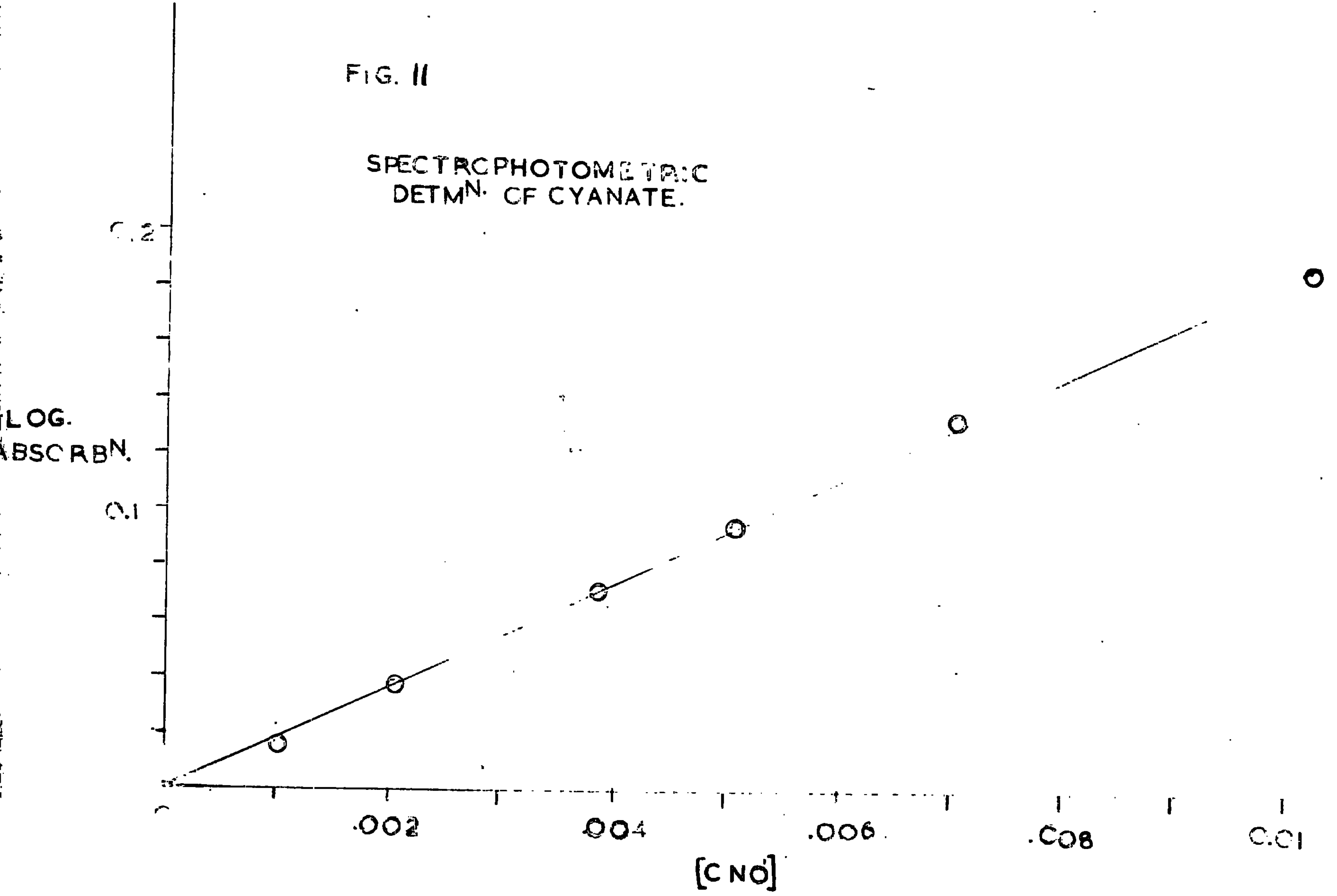
(f) The Determination of Precipitated Carbonate

In Run 19, barium nitrate was added to the cyanate solution and it was necessary to estimate that carbonate which was precipitated as barium carbonate.

The following technique was adopted.

The tube, containing 10 mls. of solution, was broken open at the top and the solution drawn off with a Miller type

FIG. II



SPECTROPHOTOMETRIC DETM$^{N.}$ OF CYANATE.

filter stick (108) containing a pulp of "Watmann Accelerator" inside the raised lip. The precipitate and filter stick were washed with barium nitrate solution and excess hydrochloric acid added. After warming for ten minutes at 60°C., (to ensure complete reaction of the carbonate with the acid), the excess acid was determined by back titration with sodium hydroxide.

(g) The Determination of Urea

It was considered desirable to show that the stoichiometric equation of carbonate and urea formation were, in fact, obeyed and results to this effect have already been quoted (p.93).

Urea was estimated by the method of Fosse (109). A 10 mls. sample of the solution (sealed in boiling tube) was cooled to room temperature and diluted with three volumes of glacial acetic acid and 0.5 vols. of a 10% solution of Xanthhydrol in methyl alcohol. After one hour, the precipitated Xanthhydrol-urea was filtered off in a semi-micro sintered glass crucible, washed with alcohol and weighed. The accuracy of the method at a urea concentration of 0.01 M. was estimated at ± 2%.

Two solutions, which originally contained ammonium and sodium cyanates, were examined. (Cf. Table V, 1).

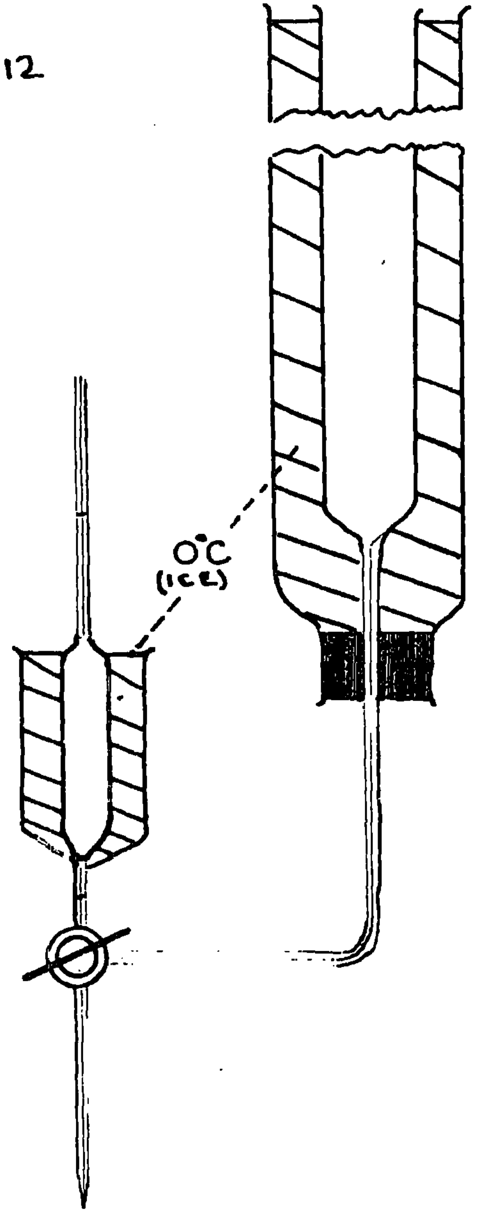
(h) Technique of Runs

All runs were carried out using the usual closed tube technique, care being taken to ensure that gas and liquid volumes were approximately equal. Tubes were filled at 0°C., using the apparatus shown in Fig. 12, which delivered 3.749 mls. at 0°C.

The thermostat was the usual oil-water variety, controlled to ± 0.02°C. at 60°C. by a mercury-toluene regulator. Temperatures were corrected against standard N.P.L. thermometers.

Preliminary experiments showed that after an initial warming up period of two minutes at 60°C. and three minutes at 80°C., the tubes had reached thermostat temperature. Tubes were placed in the thermostat in groups of eight and, after the warming up period, two were withdrawn and cooled in a dewar of solid CO_2 and alcohol. Tubes were thus withdrawn from time to time in pairs (one for $[CNO^-]$ + 2C and one for C determination) and frozen until required for analysis.

FIG 12



CHAPTER VIII

DETAILS OF RUNS

In the following pages, details are given of the runs carried out.

Full details (all major steps in the calculation) are shown for Runs 2 and 12. In the majority of cases, only the concentrations at each time of N, CNO^-, C and Urea are recorded, together with final results of the runs. For the remainder - repeat runs which show no new effects - only final results have been quoted.

The following remarks apply to all runs:-

(a) All runs were carried out at an initial ionic strength of 0.25.

(b) All times are in minutes unless specifically stated to the contrary (a few urea decomposition runs).

(c) All rate constants are in gm. mol.$^{-1}$ L. min.$^{-1}$ units unless it is specifically stated to the contrary.

(d) In all runs, the urea concentration recorded is that formed after zero time. There will, of course, have been some urea formed during the initial warming up period and preparation of the materials, but since urea does not affect either the pH or ionic strength of the solution, and the correction to be applied to allow for the reverse reaction is very small, its absolute concentration does not need to be known.

Run 1 Temp. = 60.12°C.

0.0519 M. Ammonium Cyanate (No additions)

Time	N	[CNO⁻]	C	[Urea]*
0	0.05252	0.0519	0.00031	0.0
16	0.05266	0.0504	0.00113	0.0007
27.6	0.04852	0.0454	0.00156	0.0052
40.3	0.04614	0.0427	0.00172	0.0078
53.1	0.04540	0.0411	0.00215	0.0089
72.8	0.04292	0.0380	0.00246	0.0117
105	0.03968	0.0340	0.00284	0.0154
141	0.03826	0.0321	0.00310	0.0170
168	0.03502	0.0285	0.00326	0.0204
196	0.03260	0.0265	0.00350	0.0222
281	0.03003	0.0213	0.00435	0.0265
437	0.02586	0.0165	0.00468	0.0310
525	0.02452	0.0147	0.00491	0.0326
1428	0.01856	0.0060	0.00628	0.0399

$k_U = 0.0754$

$k_H = 3.99 \times 10^{+3}$

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* See p. 131.

Run 2

0.05566 M. Ammonium Cyanate with 0.00448 M. Sodium Carbonate added. Temp. = 60.13°C.

Table A (Basicity)

The tube, containing 3.749 mls. of reaction mixture, was broken into neutral acetone containing an excess of HCl - the number of mls. of 0.05324 N. HCl added are shown in Col. 2. The excess acid was back titrated with 0.01119 N. NaOH (Col.3)

Table A (Carbonate)

The tube, containing 3.749 mls. of reaction mixture, was made up to 25 mls. with $AgNO_3$ - NH_4NO_3 solution (p.125). 5 mls. of supernatant liquid were removed and reacted with 1.980 mls. of 0.02036 N. HCl and back titrated with 0.01119 N. NaOH. Then:

$$2C + "y" = \left(\frac{1.98 \times 0.02036}{0.01119} - \text{Titre}\right) \frac{0.01119 \times 5}{3.749}$$

where "y" is that cyanate remaining in solution and also includes "light factors", etc., (see p.125). Its value is determined from two similar titrations of the original reaction mixture:-

(1) A sample of the cyanate solution analysed for carbonate as above: Titre = 2.740 mls.

(2) The same solution diluted five times and re-analysed: Titre = 3.419 mls.

Thus: (1) gives $2C + y$

(2) gives $\frac{2}{5}C + y$

and hence:

$$y = \left\{ \frac{1.98 \times 0.02036}{0.01119} - \left(2.740 + \frac{5}{4}(3.419 - 2.740)\right) \right\} \frac{0.01119 \times 5}{3.749}$$

and hence:

$$2C = (3.588 - \text{Titre}) \frac{0.01119 \times 5}{3.749}$$

Run 2 (continued)

Table A

Basicity				Carbonate		
Time (mins)	ml. HCl	Titre (mls)	2C + [CNO$^-$]	ml. HCl	Titre (mls)	C
0.0	5	2.07	0.06484	2	2.974	0.00458
13.9	5	2.92	0.06232	2	2.943	0.00481
25.0	5	3.50	0.02412	-	-	-
42.3	5	4.43	0.05781	2	2.886	0.00524
60.6	3.970	0.28	0.05553	2	2.851	0.00550
76.5	"	1.03	0.05329	-	-	-
113.3	"	2.17	0.04990	2	2.780	0.00603
156.2	"	3.33	0.04644	-	-	-
212.2	"	4.39	0.04326	2	2.676	0.00680
300.7	"	5.66	0.03950	-	-	-
390.7	"	6.55	0.03683	2	2.536	0.00785
524.5	"	7.34	0.03445	2	2.455	0.00846
750.5	"	8.21	0.03187	2	2.365	0.00913
819.2	"	8.44	0.03119	-	-	-
1112.5	"	8.94	0.02968	2	2.250	0.00999

Run 2 (continued)

Table B

Time (mins)	N	[CNO$^-$]	[Urea]
0.0	0.05586	0.05566	0.00
13.9	0.05336	0.0527	0.00273
25.0	0.05161	0.0507	(0.00463)
42.3	0.04888	0.0473	0.00770
60.6	0.04654	0.0445	0.0102
76.5	0.04433	0.0420	(0.0125)
113.3	0.04090	0.0378	0.0164
156.2	0.03748	0.0335	(0.0209)
212.2	0.03430	0.0297	0.0238
300.7	0.03054	0.0245	(0.0283)
390.7	0.02780	0.0211	0.0313
524.5	0.02546	0.0175	0.0342
750.5	0.02290	0.0136	0.0375
819.2	0.02223	0.0127	(0.0378)
1112.5	0.02072	0.0097	0.0406

(   ) = calculated from extrapolated values of C.

Run 2 continued

Calculation of $[H^+]$ and ionic concentrations (see p.105).

Table C

Time	Ratio $^N/_C$	$[H^+]$ (10^{-8})	α	β	$[HCO_3^-]$	$[NH_4^+]$
0.0	12.1	4.85	0.094	0.838	0.00384	0.0506
13.9	11.1	4.45	0.102	0.850	0.00409	0.0479
25	10.42	4.20	0.108	0.857	0.00424	0.0460
42.3	9.32	3.74	0.119	0.869	0.00455	0.0443
60.6	8.46	3.39	0.181	0.880	0.00484	0.0405
76.5	7.84	3.13	0.140	0.886	0.00501	0.0381
113.3	6.79	2.69	0.160	0.899	0.00542	0.0344
156.2	5.79	2.25	0.187	0.910	0.00589	0.0304
212.2	5.04	1.93	0.211	0.917	0.00624	0.0271
300.7	4.07	1.50	0.258	0.928	0.00696	0.0237
390.7	3.55	1.27	0.285	0.933	0.00731	0.0199
524.5	3.01	1.05	0.343	0.936	0.00792	0.0168
750.6	2.51	0.777	0.395	0.935	0.00854	0.0139
1112.5	2.08	0.525	0.489	0.928	0.00927	0.0106

Run 2 continued

Rate constant of Urea formation (see p.115).

Table D

Time	t	$\int_0^t [NH_4^+][CNO^-]dt$	$[Urea] - [Urea]_o$	$k_R\int_0^t [Urea]dt$ ($[CNO^-]$ from reverse reaction)	k_U
13.9	0				
24.6	10.7	0.0247	0.00186		0.0753
33.9	20.0	0.0458	0.00310		(0.0677)
64.6	50.7	0.1057	0.0077		0.0729
115.0	101.1	0.177	0.0136		0.0768
155.0	141.1	0.227	0.0170		0.0749
214	200	0.280	0.0210	0.00005	0.0753
295	281	0.336	0.0252	0.00008	0.0753
389	375	0.382	0.0285	0.00012	0.0749
501	487	0.419	0.0309	0.00017	0.0740
708	694	0.474	0.0344	0.00029	0.0732
977	963	0.517	0.0377	0.00045	0.0738

Mean k_U = 0.0746

Run 2 continued

Calculation of k_H

Table E

t	$k_W \int_0^t [CNO^-]\,dt$ *	$k_C \int_0^t [CNO^-][HCO_3^-]\,dt$ ‡	$C - C_o$	$\int_0^t [H^+][CNO^-]\,dt$ ($\times 10^{-8}$)	k_H ($\times 10^3$)
0					
10.7	0.000035	0.000036	0.00013	2.48	2.4
20.0	0.000092	0.000071	0.00037	4.34	4.8
50.7	0.000156	0.000168	0.00069	9.48	3.9
101.1	0.000280	0.000341	0.00124	15.26	4.1
141.1	0.000377	0.000490	0.00166	19.09	4.1
200	0.000492	0.000690	0.00206	23.02	3.8
281	0.000632	0.000941	0.00263	25.84	3.9
375	0.000770	0.000991	0.00304	29.93	4.3
487	0.000922	0.001215	0.00356	32.29	4.4
694	0.001120	0.001660	0.00418	35.61	3.9
963	0.001340	0.002130	0.00486	37.97	3.7

* $k_W = 6.36 \times 10^{-5}$ (mins^{-1})

$k_C = 1.75 \times 10^{-2}$

Mean value = $\underline{4.0 \times 10^3}$

Run 3 Temp. = 60.13°C.

0.0530 M. Ammonium Cyanate with 0.006098 M. Sodium Carbonate added.

Time	N	$[CNO^-]$	C	[Urea]
0	0.05332	0.0530	0.00626	0.00
13	0.05118	0.0498	0.00679	0.0027
28	0.04903	0.0473	0.00696	0.0050
40	0.04728	0.0451	0.00719	0.0070
65	0.04458	0.0419	0.00747	0.0099
91	0.04237	0.0389	0.00783	0.0125
119	0.04025	0.0363	0.00809	0.0149
150	0.03816	0.0336	0.00838	0.0173
180	0.03630	0.0314	0.00854	0.0194
210	0.03500	0.0296	0.00879	0.0209
284	0.03217	0.0259	0.00924	0.0242
346	0.03038	0.0235	0.00954	0.0263
407	0.02875	0.0213	0.00984	0.0281
467	0.02773	0.0198	0.01008	0.0294
517	0.02661	0.0182	0.01030	0.0307
560	0.02631	0.0176	0.01048	0.0312
685	0.02512	0.0154	0.01097	0.0329
811	0.02410	0.0133	0.01149	0.0345
983	0.02332	0.0117	0.01191	0.0357
1138	0.02261	0.0099	0.01244	0.0370

$k_U = 0.0728$

$k_H = 3.8 \times 10^{+3}$ *

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* The values calculated for k_H from this run, drift from $4.4 \times 10^3 - 3.3 \times 10^3$, but the contribution to the total carbonate from the term in k_H is small (max. 0.0007 M.) and hence, this variation is probably due to experimental error.

Run 4 Temp. = 60.13°C.

0.0514 M. Ammonium Cyanate with 0.00207 M. Sodium Carbonate added.

k_U = 0.0721

k_H = 4.1×10^3

Run 5 Temp. = 60.15°C.

0.0506 M. Ammonium Cyanate with 0.00366 M. Sodium Carbonate added.

k_U = 0.0754

k_H = 3.9×10^3

Run 6 Temp. = 60.13°C.

0.0508 M. Ammonium Cyanate with 0.00762 M. NH_3 added.

k_U = 0.0762

Run 7 Temp. = 60.13°C.

0.0507 M. Ammonium Cyanate with 0.00650 M. NH_3 added.

Time	N.	$[CNO^-]$	C	[Urea]
0	0.05838	0.0507	0.00059	0.000
13	0.05601	0.0481	0.00070	0.00251
30	0.05336	0.0453	0.00080	0.00526
51	0.05022	0.0419	0.00092	0.0085
75	0.04750	0.0389	0.00105	0.0114
114	0.04375	0.0348	0.00124	0.0153
142	0.04156	0.0323	0.00137	0.0176
175	0.03886	0.0293	0.00151	0.0205
202	0.03767	0.0283	0.00162	0.0214
279	0.03435	0.0241	0.00190	0.0254
339	0.03227	0.0217	0.00207	0.0275
404	0.03054	0.0196	0.00222	0.0296
464	0.02903	0.0179	0.00234	0.0311
524	0.02788	0.0164	0.00247	0.0324
698	0.02515	0.0131	0.00280	0.0355
853	0.02388	0.0114	0.00301	0.0369
1018	0.02273	0.0097	0.00328	0.0384

$k_U = 0.0741$

$k_H = 4.1 \times 10^3$ (mean of values of k_H after t = 114 mins.)

Run 8 Temp. = 80.13°C.

0.0434 M. Ammonium Cyanate with 0.00148 Sodium Carbonate added.

Time	N	[CNO$^-$]	C	[Urea]
0	0.04422	0.04342	0.00188	-
3	0.04182	0.0402	0.00229	0.0028
6	0.03950	0.0372	0.00265	0.0055
10	0.03706	0.0340	0.00300	0.0083
15	0.03480	0.0308	0.00348	0.0111
20	0.03268	0.0282	0.00371	0.0134
25	0.03086	0.0259	0.00395	0.0154
30	0.02922	0.0240	0.00409	0.0172
40	0.02700	0.0210	0.00448	0.0199
50	0.02541	0.0188	0.00478	0.0217
60	0.02404	0.0170	0.00498	0.0233
70	0.02277	0.0153	0.00520	0.0248
85	0.02135	0.0132	0.00558	0.0266
115	0.01962	0.0113	0.00574	0.0283

$k_U = 0.551$

$k_H = 1.41 \times 10^4$

Run 9 Temp. = 80.12°C.

0.0498 M. Ammonium Cyanate

Time (Mins)	N	[CNO$^-$]	C	[Urea]
0	0.05198	0.0498	0.00109	-
3	0.04878	0.0447	0.00205	0.0041
6	0.04491	0.0400	0.00244	0.0084
10	0.04200	0.0363	0.00285	0.0117
15	0.03720	0.0307	0.00325	0.0169
20	0.03623	0.0288	0.00372	0.0184
25	0.03430	0.0265	0.00390	0.0205
30	0.03382	0.0257	0.00406	0.0211
40	0.02966	0.0205	0.00460	0.0258
50	0.02767	0.0179	0.00489	0.0281
60	0.02596	0.0156	0.00516	0.0301
70	0.02458	0.0140	0.00543	0.0315
85	0.02323	0.0118	0.00573	0.0334
115	0.02134	0.0094	0.00596	0.0355
145	0.02000	0.0078	0.00609	0.0370

$k_U = 0.554$

$k_H = 1.38 \times 10^{+4}$

Run 10 Temp. = 39.99°C.

0.0584 M. Ammonium Cyanate with 0.00148 M. Sodium Carbonate added.

Time	N	[CNO^-]	C	[Urea]
0	0.05843	0.05835	0.00152	-
95	0.05660	0.0562	0.00166	0.0020
205	0.05444	0.0535	0.00194	0.0044
360	0.05144	0.0498	0.00227	0.0078
505	0.04888	0.0466	0.00260	0.0107
902	0.04303	0.0395	0.00326	0.0172
1121	0.04118	0.0372	0.00347	0.0192
1402	0.03849	0.0338	0.00380	0.0223
1551	0.03737	0.0324	0.00395	0.0235
1760	0.03560	0.0301	0.00418	0.0256
2347	0.03248	0.0263	0.00454	0.0291
2700	0.03097	0.0243	0.00479	0.0308
2915	0.03004	0.0232	0.00490	0.0318
3256	0.02901	0.0217	0.00513	0.0331
3783	0.02716	0.0191	0.00548	0.0354
4144	0.02662	0.0182	0.00568	0.0360
5231	0.02439	0.0148	0.00629	0.0388

$k_U = 8.10 \times 10^{-3}$ *

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* Values of k_C and k_W were not obtained at this temperature (due to the very slow decomposition of NaCNO) and hence no values of k_H can be calculated.

Run 11 Temp. = 39.99°C.

0.0471 M. Ammonium Cyanate with 0.00148 M. Sodium Carbonate added.

Time	N	[CNO$^-$]	C	[Urea]
0	0.04726	0.0471	0.00153	0.00
95	0.04579	0.0453	0.00174	0.0011
201	0.04413	0.0432	0.00191	0.0035
355	0.04232	0.0407	0.00226	0.0056
502	0.04076	0.0387	0.00252	0.0075
700	0.03880	0.0362	0.00277	0.0097
910	0.03683	0.0339	0.00292	0.0118
1110	0.03523	0.0318	0.00317	0.0137
1407	0.03340	0.0295	0.00340	0.0158
1497	0.03273	0.0287	0.00347	0.0164
1769	0.03132	0.0270	0.00362	0.0180
2353	0.02832	0.0232	0.00405	0.0215
2718	0.02723	0.0217	0.00423	0.0227
2911	0.02670	0.0208	0.00437	0.0235
3315	0.02574	0.0192	0.00455	0.0250
3824	0.02401	0.0172	0.00489	0.0266
4147	0.02369	0.0166	0.00501	0.0271
5283	0.02162	0.0133	0.00561	0.0297

$k_U = 8.21 \times 10^{-3}$

Run 12 Temp. = 60.12°C.

0.05163 M. Sodium Cyanate with 0.007224 M. Sodium Bicarbonate added.

Experimental methods are exactly as already described for Run 2.

Strength of NaOH = 0.01224 N.

" " HCl = 0.05351 N.

$$\text{and} \quad 2C = (4.049 - \text{Titre}) \frac{5 \times 0.01224}{3.749}$$

Run 12 continued

Table A

	Basicity			Carbonate		
Time (mins)	ml. HCl	Titre (mls.)	"Total Basicity" *	ml. HCl	Titre (mls.)	C ‡
0	5	3.79	0.05899	1.980	3.598	0.00729
68	5	3.58	0.05968	"	3.493	0.00816
163	5	3.28	0.06066	"	3.377	0.00910
348	5	2.83	0.06213	"	3.126	0.01115
538	5	2.33	0.06376	"	2.851	0.01339
840	5	1.62	0.06605	"	2.433	0.01680
1089	5	1.01	0.06808	"	2.066	0.01980
1375	5	0.34	0.07026	"	1.707	0.02272
1449	6.326	6.00	0.07072	"	1.579	0.02385
1649	6.326	5.58	0.07208	"	1.286	0.02616
1910	6.326	5.04	0.07385	"	0.960	0.02882
2348	6.326	4.26	0.07640	"	0.445	0.03303
2547	6.326	4.03	0.07715	"	0.300	0.03422
2990	6.326			3.96	4.020	0.03740
3809	6.326	2.66	0.08163	3.96	3.570	0.04064

*"Total Basicity" = $[CNO^-] + 2C - [HCO_3^-]_0$

‡ $C = [CO_3^=] + [HCO_3^-] + [H_2CO_3]$ as before.

Run 12 continued

Table B

Time (mins)	N*	[CNO^-]	[Urea]
0	0.00007	0.05163	-
68	0.00077	0.05059	0.00017
163	0.00138	0.04969	0.00050
348	0.00322	0.04706	0.00071
538	0.00485	0.04420	0.00132
840	0.00710	0.03967	0.00245
1089	0.00920	0.03571	0.00341
1375	0.0113	0.03203	0.00417
1449	0.0118	0.03025	0.00482
1645	0.0132	0.02698	0.00578
1910	0.0149	0.02342	0.00668
2348	0.0175	0.01760	0.00829
2547	0.0182	0.01593	0.00877
2990	0.0205	0.01180	0.00972
3809	0.0227	0.00758	0.01070

* In the calculation of N, the assumption is made that all carbonate in excess of that added as bicarbonate (0.007224 M.) is present with an equivalent quantity of ammonia.

Run 12 continued

Evaluation of k_W and k_C

Time	t	$\int_0^t [CNO^-]\,dt$	$\int_0^t [HCO_3^-][CNO^-]\,dt$	$k_H\int_0^t [H^+][CNO^-]\,dt$	$C - C_o$	* C'/A (10^{-4})	* B/A ($\times 10^{-2}$)
68	0						
163	95	4.67	0.034	6×10^{-6}	0.0009	1.88	0.728
355	287	13.86	0.116	0.00015	0.0030	2.06	0.836
537	469	22.07	0.198	0.00020	0.0052	2.28	0.897
851	783	34.98	0.355	0.00026	0.0086	2.39	1.01
1072	1004	43.51	0.468	0.00030	0.0110	2.47	1.08
1350	1282	53.25	0.614	0.00033	0.0142	2.61	1.15
1862	1794	65.86	0.875	0.00037	0.0199	2.96	1.33
2344	2276	75.88	1.087	0.00039	0.0249	3.28	1.43
2950	2882	84.77	1.303	0.00042	0.0288	3.35	1.54
3890	3822	93.68	1.542	0.00044	0.0325	3.43	1.65

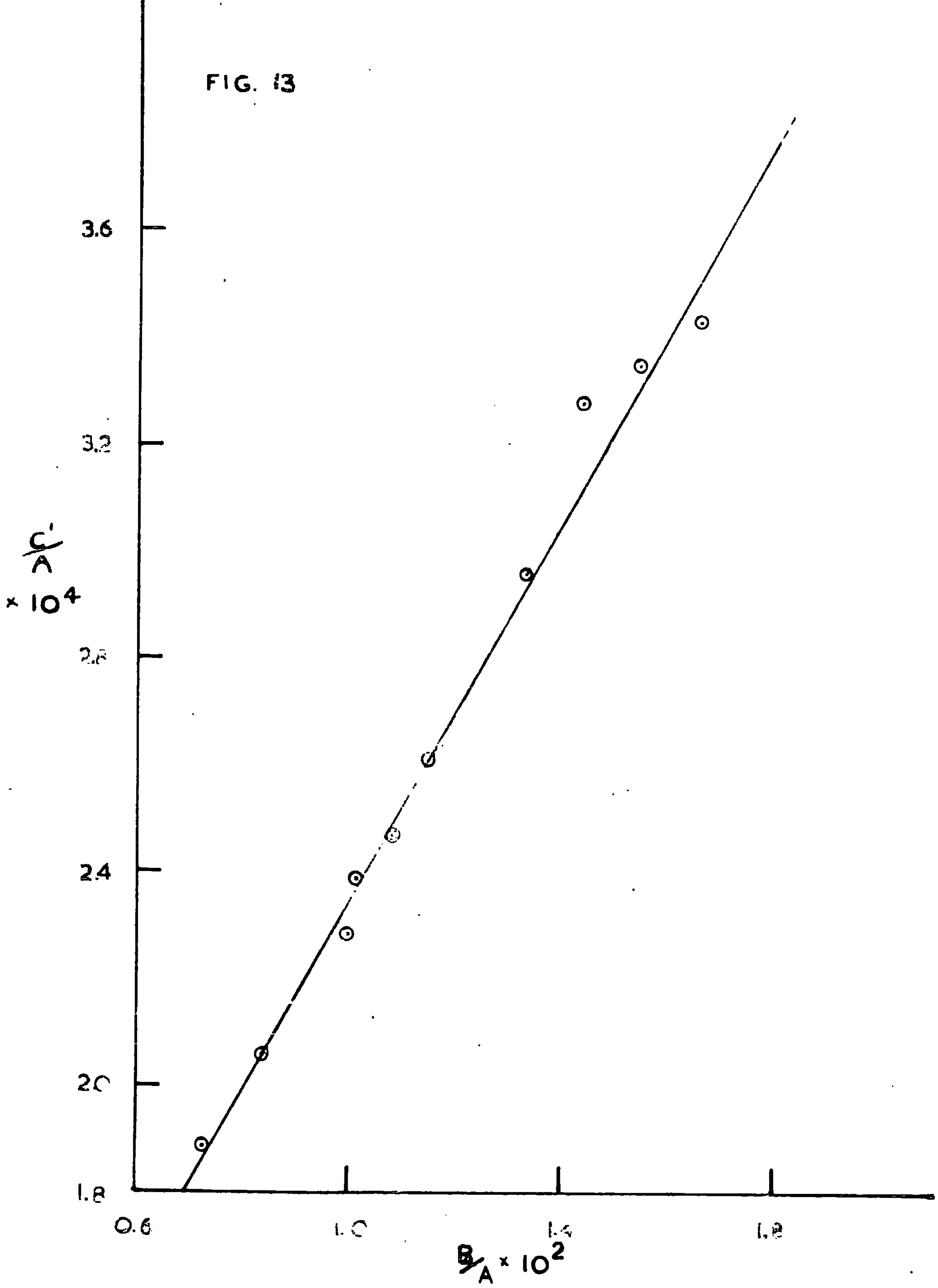
The corresponding plot is shown in Fig. 13.

$k_c = 1.72 \times 10^{-2}$

$k_w = 6.4 \times 10^{-5}$ (mins^{-1})

* See p. 117

FIG. 13



Run 12 continued

Table D

Rate constants of urea formation

Time	t	$\int_0^t [NH_4^+][CNO^-]dt$ $(\times 10^{-2})$	$[Urea]-[Urea]_0$* (extrapolated)	k_U
68	0		(0.00010)	
163	95	0.254	0.00025	(0.095)
335	267	0.992	0.00070	0.071
538	470	1.809	0.00126	0.070
851	783	3.386	0.00235	0.070
1122	1054	4.781	0.0033	0.070
1480	1412	6.612	0.00490	0.074
2042	1974	9.169	0.00750	0.082
2692	2624	11.49	0.0091	0.079
3800	3732	14.01	0.0104	0.074

Mean k_U = 0.074

* [Urea] at t = 0 is assumed to be 0.00010 M.

Run 13 Temp. = 60.14°C.

0.0505 M. Sodium Cyanate

Time	N	[CNO$^-$]	C	[Urea]
0	0.00040	0.0505	0.00040	
168	0.00085	0.0496	0.00105	0.0002
357	0.00176	0.0489	0.00186	0.0001
533	0.00242	0.0479	0.00272	0.0003
863	0.00355	0.0453	0.00455	0.0010
1081	0.00428	0.0438	0.00568	0.0014
1340	0.00560	0.0419	0.00730	0.0017
1511	0.0060	0.0403	0.00834	0.0023
1839	0.0077	0.0374	0.01056	0.0029
2306	0.0105	0.0331	0.01410	0.0037
2704	0.0125	0.0296	0.01690	0.0044
2906	0.0128	0.0277	0.01802	0.0052
3251	0.0150	0.0247	0.02055	0.0056
3763	0.0166	0.0197	0.02388	0.0073
4110	0.0183	0.0169	0.02614	0.0078
4374	0.0187	0.0152	0.02724	0.0085
4687	0.0198	0.0127	0.02903	0.0092
5223	0.0215	0.0102	0.03110	0.0096
5578	0.0221	0.0082	0.03235	0.0103

$k_U = 0.072$

$k_W = 6.1 \times 10^{-5}$ (mins^{-1})

$k_C = 1.66 \times 10^{-2}$

Run 14 Temp. = 60.13°C.

0.0489 M. Sodium Cyanate

Time	N	[CNO⁻]	C	[Urea]
0	0.0003	0.0492	0.00028	
168	0.00052	0.0489	0.00052	
289	0.00010	0.0484	0.00010	~~0.00068~~
547	0.00176	0.0469	0.00217	0.00041
884	0.00283	0.0441	0.00413	0.0013
1070	0.00397	0.0433	0.00507	0.0011
1335	0.00485	0.0416	0.00635	0.0015
1463	0.00632	0.0408	0.00798	0.0016
1647	0.00648	0.0394	0.00828	0.0018
1825	0.00696	0.0377	0.00936	0.0024
2300	0.00870	0.0330	0.0126	0.0039
2685	0.0106	0.0299	0.0151	0.0045
2887	0.0126	0.0285	0.0168	0.0042
3263	0.0132	0.0237	0.0195	0.0063
3753	0.0149	0.0198	0.0223	0.0074
4070	0.0163	0.0174	0.0242	0.0079
4321	0.0162	0.0153	0.0252	0.0090
4717	0.0173	0.0128	0.0270	0.0097
5183	0.0182	0.0093	0.0292	0.0110

$k_U = 0.075$

$k_C = 1.77 \times 10^{-2}$

$k_W = 6.3 \times 10^{-5}$ (mins^{-1})

Run 15 Temp. = 60.12°C.

0.0513 M. Sodium Cyanate

$k_C = 1.74 \times 10^{-2}$

$k_W = 6.4 \times 10^{-5}$ (mins^{-1})

$k_U = 0.078$

Run 16 Temp. = 60.13°C.

0.0260 M. Sodium Cyanate

Time	N	[CNO⁻]	C	[Urea]
0	0.00019	0.02603	0.00019 *	
142	0.00040	0.0261	0.00040 *	
481	0.00094	0.0255	0.00094 *	
902	0.00180	0.0240	0.00200	0.0002
1387	0.00264	0.0226	0.00314	0.0005
1611	0.00318	0.0216	0.00388	0.0007
2333	0.00433	0.0195	0.00553	0.0012
2734	0.00528	0.0177	0.00688	0.0016
3080	0.00590	0.0169	0.00760	0.0017
3784	0.00726	0.0147	0.00936	0.0021
4134	0.00768	0.0133	0.01027	0.0026
5213	0.00980	0.0102	0.01290	0.0031

$$k_C = 6.6 \times 10^{-5}$$

$$k_W = 1.69 \times 10^{-2} \ (\text{mins}^{-1})$$

* A number of discrepancies in the first three values are apparent. Since the values at zero time are the mean of a number of determinations, this value is assumed to be correct in the calculation of N, etc.

Run 17 Temp. = 60.12°C.

0.0496 M. Sodium Cyanate with 0.00658 M. NH_3 added

Time	N	[CNO^-]	C	[Urea]
0	0.00658	0.04963	-	-
172	-	-	0.00077	-
362	0.00715	0.04755	0.00137	0.0008
543	0.00793	0.04684	0.00215	0.0008
861	0.00844	0.04470	0.00346	0.0016
1068	0.00903	0.04329	0.00445	0.0020
1344	0.00968	0.04181	0.00554	0.0024
1792	0.00992	0.03781	0.00814	0.0048
2317	0.01271	0.03345	0.01123	0.0051
2659	0.01388	0.03043	0.01330	0.0060
2899	0.01461	0.02968	0.01403	0.0060
3250	0.01612	0.02620	0.01654	0.0070
3778	0.01637	0.02073	0.01939	0.0096
4120	0.01861	0.01912	0.02133	0.0093
4325	0.01998	0.01830	0.02240	0.0090
5201	0.02250	0.01363	0.02600	0.0101

$k_C = 1.78 \times 10^{-2}$

$k_W = 6.4 \times 10^{-5}$ (mins^{-1})

$k_U = 0.079$

Run 18 Temp. = 60.15°C.

0.0496 M. Sodium Cyanate with 0.00170 NaOH added

Time	N	[CNO⁻]	C	[Urea]
0	0.0003	0.0496	0.0003	
144	0.0008	0.0493	0.0008	
321	0.0015	0.0487	0.0015	
523	0.0021	0.0481	0.0021	
890	0.0038	0.0461	0.0038	
1109	0.0047	0.0442	0.0052	0.0005
1426	0.0061	0.0428	0.0066	0.0005
1849	0.0078	0.0385	0.0096	0.0018
2332	0.0105	0.0346	0.0129	0.0024
2755	0.0124	0.0305	0.0159	0.0035
2900	0.0130	0.0287	0.0171	0.0041
3342	0.0152	0.0243	0.0204	0.0052
3796	0.0172	0.0209	0.0231	0.0059
4235	0.0190	0.0167	0.0261	0.0071
4387	0.0197	0.0154	0.0271	0.0074
5284	0.0223	0.0100	0.0311	0.0088

Run 18 continued

Time	t	C'/A * (10^{-5})	B/A * (10^{-3})	[Urea]-$[\text{Urea}]_0$ (predicted)‡	[Urea]-$[\text{Urea}]_0$ (observed) (extrapolated)
144	0				
525	381	8.04	0.51		
871	727	8.85	0.93		
1096	952	9.00	1.25		
1445	1301	10.00	1.83		≠
1820	1676	11.3	2.57	0.0006	0.0007
2291	2147	12.9	3.26	0.0009	0.0013
2884	2740	14.5	4.24	0.0029	0.0029
3311	3167	15.8	4.89	0.0039	0.0039
3802	3658	17.05	5.56	0.0050	0.0049
4365	4221	18.27	6.27	0.0062	0.0061
5248	5104	19.77	7.09	0.0076	0.0076

$$k_W = 6.6 \times 10^{-5} \quad (\text{mins}^{-1})$$

$$k_C = 1.78 \times 10^{-2}$$

≠ [Urea] at Time 1445 is taken as 0.0011 M., an extrapolated value.

* See p. 117

‡ Calculated on basis of Eqn. IV, 1

Run 19

0.0491 M. Sodium Cyanate + 0.0299 M. Barium Carbonate

Temp. = 60.12°C.

Time	N* (apparent)	N	$[CNO^-]$	C	[Urea]	$[HCO_3^-]$
0	-	-	0.0491	-	-	-
156	0.0007	0.0009	0.0476	0.00110	0.0002	0.0002
353	0.0002	0.0016	0.0447	0.00233	0.0017	0.00039
539	0.0010	0.0012	0.0434	0.00335	0.0023	0.00037
756	0.0012	0.0016	0.0410	0.00473	0.0031	0.00043
984	0.0022	0.0026	0.0393	0.00603	0.0034	0.00043
1247	0.0020	0.0024	0.0358	0.00760	0.0052	0.00045
1787	0.0013	0.0018	0.0296	0.0104	0.0086	0.00048
2221	0.0016	0.0010	0.0264	0.0121	0.0101	0.00050
2646	0.0029	0.0024	0.0249	0.0133	0.0109	0.00053
3257	0.0025	0.0019	0.0194	0.0148	0.0129	0.00056
3650	0.0022	0.0029	0.0170	0.0172	0.0143	0.00067
4173	0.0022	0.0029	0.0142	0.0186	0.0157	0.00071
5706	0.0037	0.0045	0.0082	0.0223	0.0178	0.00083

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* Calculated assuming all carbonate precipitated.

Run 19 continued.

Time	t	$C - C_o$ (observed)	$C - C_o$ * (calculated)
156	0		
355	199	0.0012	0.0012
741	585	0.0034	0.0037
977	821	0.0055	0.0048
1288	1132	0.0072	0.0077
1778	1622	0.0094	0.0090
2239	1983	0.0114	0.0121
2692	2536	0.0132	0.0135
3715	3559	0.0166	0.0170
4266	4110	0.0179	0.0182
5129	4973	0.0209	0.0196
5623	5467	0.0218	0.0208

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* See p. 109.

Run 20 Temp. = 60.14°C.

0.0499 M. Sodium Cyanate with 0.00746 M. triethylamine added

Time	N	$[CNO^-]$	C	[Urea]
0	-	0.0499	-	
129	0.00054	0.0494	0.00054	
291	0.0011	0.0487	0.0012	
497	0.0019	0.0481	0.0018	
852	0.0032	0.0469	0.0030	
1048	0.0040	0.0461	0.0038	
1299	0.0048	0.0448	0.00496	0.0002
1501	0.0054	0.0435	0.00589	0.0005
1829	0.0068	0.0417	0.00744	0.0006
2291	0.0087	0.0391	0.00977	0.0011
2677	0.0105	0.0367	0.01187	0.0014
2965	0.0118	0.0344	0.01385	0.0016
3729	0.0149	0.0278	0.01851	0.0036

Run 20 continued

Time	t	$C - C_o$ (observed)	$C - C_o$ (calculated)
129	0	-	-
295	166	0.00056	0.0006
490	361	0.00136	0.00120
852	723	0.0027	0.00256
1072	943	0.0037	0.00342
1288	1059	0.0044	0.00431
1862	1733	0.0069	0.00691
2344	2215	0.0093	0.00937
2692	2563	0.0113	0.01135
3236	3107	0.0149	0.01460
3715	3586	0.0180	0.01750

Run 20 continued

Time	t	$[\text{Urea}]-[\text{Urea}]_o$ (observed)	$[\text{Urea}]-[\text{Urea}]_o$ (calculated)
129	0	-	-
2291	2062	0.0011	0.0013
2677	2548	0.0013	0.0018
2965	2836	0.0020	0.0025
3729	3600	0.0036	0.0032

Run 21 Temp. = 60.15°C.

0.0504 M. Sodium Cyanate with 0.0153 M. Boric Acid added

Time	N	C	[CNO$^-$]	[Urea]
0	0.0001	0.00013	0.0504	
162	0.0015	0.00177	0.0485	0.0003
353	0.0020	0.00310	0.0463	0.0011
557	0.0024	0.00452	0.0439	0.0021
853	0.0036	0.00726	0.0396	0.0037
1077	0.0044	0.00898	0.0369	0.0046
1359	0.0057	0.01138	0.0335	0.0057
1802	0.0079	0.01511	0.0282	0.0072
2301	0.0096	0.01930	0.0215	0.0097
2672	0.0111	0.02189	0.0178	0.0108
2871	0.0118	0.02308	0.0161	0.0113
3223	0.0128	0.02510	0.0134	0.0123
3740	0.0143	0.02761	0.0096	0.0133
4106	0.0153	0.02890	0.0080	0.0136

k_U = 0.074

Run 21 continued

Time	t	$C - C_o$ (observed)	$C - C_o$ (calculated)
162	0		
355	193	0.00134	0.00135
537	375	0.00283	0.00204
851	689	0.00548	0.00494
1072	910	0.00719	0.00667
1349	1187	0.00940	0.00898
1778	1616	0.0130	0.0127
2344	2182	0.0178	0.0171
2951	2789	0.0218	0.0213
3548	3386	0.0250	0.0242
4266	4104	0.0274	0.0269

Run 22

Sodium Cyanate with 0.01122 M. Boric Acid added

A duplicate run led to similar agreement between $(C - C_o)$ observed and $(C - C_o)$ calculated.

Run 23 Temp. = 80.13°C.

0.0569 M. Sodium Cyanate

Time	N	$[CNO^-]$	C	[Urea]
0	0.0004	0.0569	0.00039	
30	0.0010	0.0555	0.00100	
60	0.0021	0.0549	0.00227	0.0001
120	0.0038	0.0518	0.00467	0.0009
180	0.0054	0.0486	0.00711	0.0016
230	0.0072	0.0455	0.00951	0.0023
291	0.0093	0.0421	0.0123	0.0030
355	0.0115	0.0378	0.0155	0.0040
420	0.0139	0.0334	0.0189	0.0050
525	0.0173	0.0268	0.0239	0.0066
600	0.0198	0.0227	0.0272	0.0074
683	0.0219	0.0183	0.0304	0.0084
803	0.0250	0.0137	0.0343	0.0093
921	0.0273	0.0100	0.0373	0.0100
1049	0.0290	0.0079	0.0392	0.0102

$k_C = 6.96 \times 10^{-2}$

$k_W = 5.15 \times 10^{-4}$ (mins^{-1})

Run 24 Temp. = 60.12°C.

0.1990 M. Urea

Time HOURS	N	[CNO$^-$]	C	x/at * 10^{-4}
0				
2.67	0.00060	0.0004	(0.0001)	9.4
4.92	0.00093	0.0007	(0.00013)	8.5
7.42	0.00154	0.0012	(0.00017)	9.3
15.37	0.00280	0.0022	0.00030	(8.2)
22.17	0.00388	0.0029	0.00049	
25.09	0.00428	0.0034	0.00046	
39.40	0.00601	0.0045	0.00077	
47.92	0.00682	0.0048	0.00101	
64.1	0.00810	0.0050	0.00156	
71.3	0.00846	0.0048	0.00183	
86.46	0.00946	0.0048	0.00233	
95.3	0.00990	0.0047	0.00262	
118.7	0.01143	0.0043	0.00356	

Mean $k_R = 8.9 \times 10^{-4}$ (hr.$^{-1}$)

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* Approximate first order rate constants for the urea decomposition, see p. 118.

Run 24 continued

Time HOURS	t	$C - C_o$ (observed) (extrapolated)	$C - C_o$ (calculated)
4.92	0		
14.8	9.9	0.0002	0.0002
24.6	19.7	0.00041	0.0005
38.9	34.0	0.00071	0.0012
49.0	44.1	0.00105	0.0016
64.6	59.7	0.00151	0.0024
85.1	80.2	0.0025	0.0042
118.0	113.1	0.0035	0.0042

Run 25 Temp. = 60.13°C.

0.0987 M. Urea

Time HOURS	N	[CNO^-]	C	x/at (10^{-4})	[H^+] (10^{-8})
0	0.0001	0.00008			
1.92	0.00029	0.00029	-	(11.1)	
2.63	0.00036	0.00036		(10.8)	
4.83	0.00054	0.00054		9.7	
7.84	0.00081	0.00081		9.5	
12.2	0.00120	0.00120		9.3	
16.4	0.00161	0.00161		9.5	
21.9	0.00204	0.00196	(0.00003)		
25.0	0.00231	0.00209	0.00011		8.1
29.75	0.00274	0.00244	0.00020		5.9
31.83	0.00285	0.00244	0.00021		5.4
48.1	0.00419	0.00321	0.00049		3.4
58.0	0.00462	0.00340	0.00062		2.9
70.5	0.00520	0.00352	0.00084		2.5
78.2	0.0055	0.00372	0.00095		2.3
95.7	0.0063	0.00362	0.00136		1.8
119.7	0.0072	0.00342	0.00191		1.4

Mean k_R 9.76×10^{-4} ($hrs.^{-1}$)

Run 26

0.0991 M. Urea at 60.11°C.

$k_R = 9.7 \times 10^{-4}$ ($hrs.^{-1}$)

Run 27 Temp. = 60.12°C.

0.0979 M. Urea with 0.00351 M. Sodium Carbonate added

Time HOURS	N	[CNO⁻]	C	x/at (10^{-4})
0	0.0001	0.0001	0.00351	
2.65	0.0004	0.00038	0.00351	(10.8)
5.5	0.0006	0.00058	"	8.9
8.5	0.0009	0.00092	"	9.8
11.5	0.0012	0.00115	"	9.3
14.6	0.0013	0.00133	"	8.6
17.9	0.0016	0.00162	"	8.7
25.2	0.0024	0.00238	"	
29.0	0.0027	0.00273	"	
41.9	0.0038	0.00375	0.00356	
49.4	0.0046	0.00380	0.00389	
51.1	0.0047	0.00400	0.00386	
60.1	0.0056	0.00416	0.00420	
71.5	0.0063	0.00433	0.00450	
80.5	0.0069	0.00434	0.00480	
95.5	0.0079	0.00434	0.00533	
105.0	0.0084	0.00416	0.00561	
120.2	0.0093	0.00395	0.00622	
150.3	0.0110	0.00342	0.00732	
167.9	0.0119	0.00331	0.00781	
191.8	0.0132	0.00248	0.00886	

Mean k_R = 9.30×10^{-4} (hrs.^{-1})

Run 27 continued

Time HOURS	t	$C - C_o$ (observed) (extrapolated)	$C - C_o$ (calculated)
41.9	0		
51.5	9.6	0.00030	0.00029
71.52	29.6	0.00100	0.00097
112.0	70.1	0.00229	0.00217
149.6	107.7	0.00381	0.00420
188.4	146.5	0.00530	0.00563

Run 28 Temp. = 60.11°C.

0.1029 M. Urea with 0.00138 M. Sodium Carbonate added

$$k_R = 9.60 \times 10^{-4} \quad (\text{hrs.}^{-1})$$

APPENDIX I

The effect of ionic strength on the rate of reaction (see p.31)

Values of $k_U^{\ddagger}$, calculated from the equation:

$$\frac{d[\text{Urea}]}{dt} = -\frac{d[\text{CNO}^-]}{dt} = k_U^{\ddagger}[\text{CNO}^-]^2$$

are found, at constant ionic strength, to be virtually constant, over the reaction range considered (~ 70%). The American authors (30-39) observed the correct salt effects for the reaction, i.e., the predicted variation of $k_U^{\ddagger}$ with ionic strength agreed well with that observed experimentally. For this to be so, $k_U^{\ddagger}$ must be dependent only on ionic strength, under the conditions of an ammonium cyanate run.

We have in a pure ammonium cyanate run:

$$-\frac{d[\text{CNO}^-]}{dt} = k_U[\text{NH}_4^+][\text{CNO}^-] + k_H[\text{H}^+][\text{CNO}^-] \quad ..\underline{\text{A.I, 1}}$$

since, under these conditions, the second term of eqn. II, 2, is responsible for the majority of the carbonate formed.

If the assumption is made that all carbonate is present as HCO_3^- (very nearly correct at this pH), then:

$$[\text{NH}_4^+] = [\text{CNO}^-] + C$$

and $$[\text{NH}_3] = C$$

and since

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_1 \quad (K_1 = 5 \times 10^{-7} \text{ at } 60^{\circ}C. \quad I = 0.25)$$

$$[H^+] = \frac{K_1([CNO^-] + C)}{C} \qquad .. \quad .. \quad .. \qquad \underline{A.I,\ 2}$$

Substituting in eqn. AI, 1 above

$$-\frac{d[CNO^-]}{dt} = [CNO^-]\left[k_U\left\{[CNO^-] + C\right\} + \frac{K_1k_H}{C}\left\{[CNO^-] + C\right\}\right]$$

$$-\frac{d[CNO^-]}{dt} = [CNO^-]^2 \left\{1 + \frac{C}{[CNO^-]}\right\}\left\{k_U + \frac{K_1k_H}{C}\right\} \qquad ..\underline{A.I,\ 3}$$

$$= [CNO^-]^2\, k_U^{\ddagger}$$

In practice, $k_U^{\ddagger}$ was calculated from the integrated rate equation so that:

$$k_U^{\ddagger}t = \int_0^t \left\{1 + \frac{C}{[CNO^-]}\right\}\left\{k_U + \frac{K_1k_H}{C}\right\} dt$$

Values calculated from Run 1 are listed below.

Run 1 60°C. $I = 0.25$

Time (mins)	t	$\left(1 + \frac{C}{[CNO^-]}\right)$	$\left(k_U + \frac{K_1 k_H}{C}\right)$	$k_U^{\ddagger}$
16	0	1.02	0.093	
40	24	1.04	0.087	0.092
73	57	1.07	0.083	0.091
140	124	1.10	0.082	0.090
196	180	1.13	0.081	0.091
437	421	1.28	0.079	0.095
525	509	1.33	0.079	0.098

It will be noted that the values of $\left\{1 + \frac{C}{[CNO^-]}\right\}$ tend to increase and that of $\left\{k_U + \frac{K_1 k_H}{C}\right\}$ to decrease during the run, with the result that $k_U^{\ddagger}$ remains virtually constant. The variation in the values of $k_U^{\ddagger}$ would be small compared with variations due to salt effects.

APPENDIX II

Apparent Quasi-stationary State for Ammonium Ions in the presence of Ba^{++} Ions at 60°C., I = 0.25. (Comparison with the work of I. & O. Masson (48)).

It has already been pointed out that during the decomposition of cyanate ions in the presence of Ba^{++} ions, N, the total ammonium content, apparently reaches a constant value throughout the run, within the limits of experimental error: if it is assumed (incorrectly) that all carbonate is precipitated as barium carbonate (cf. p. 44):

i.e., $$\frac{dN}{dt} = \frac{dC}{dt} - \frac{dU}{dt} = 0 \qquad \text{(From eqns. II, 1 and II,2)}$$

A. II, 1

Now, for such a system, it has already been pointed out (p. 42) that eqn. II, 2 reduces to

$$\frac{dC}{dt} = k_H[H^+][CNO^-] + k_W[CNO^-]$$

and $$\frac{dU}{dt} = k_U[NH_4^+][CNO^-] \qquad \text{(the reverse reaction is ignored)}$$

Hence, eqn. A.II, 1 becomes:

$$\frac{dN}{dt} = k_H[H^+][CNO^-] + k_W[CNO^-] - k_U[NH_4^+][CNO^-] = 0$$

or $$k_H[H^+] + k_W - k_U[NH_4^+] = 0 \quad .. \quad .. \qquad \text{A. II, 2}$$

Now $$[H^+] = \frac{[NH_4^+]}{[NH_3]}\,\frac{K_W}{K_1} \qquad \text{A.II, 3}$$ [*]

From eqn. V, 25, we have

$$[H^+] = [HCO_3^-][Ba^{++}]\,\frac{K_2K_W}{K_7}$$

$$= [NH_3][Ba^{++}]\,\frac{K_2K_W}{K_7} \qquad \text{A.II, 4}$$

as $[NH_3] = [HCO_3^-]$ at the pH prevailing in the system considered. From the eqns. AII, 3 and AII, 4, we have

$$[H^+] = \sqrt{[NH_4^+][Ba^{++}]\,\frac{K_2K_W^2}{K_1K_7}}$$

Substituting for $[H^+]$ in AII, 2, we have

$$k_W + \left[k_H\,K_W[Ba^{++}]^{\frac{1}{2}}\left(\frac{K_2}{K_1K_7}\right)^{\frac{1}{2}}\right][NH_4^+]^{\frac{1}{2}} - k_U[NH_4^+] = 0 \qquad \text{A.II, 5}$$

The values of the equilibrium constants K_1, K_2, K_5 and K_W are given on p. 101 , k_W, k_H, and k_U in Table II, 2. The values of $[NH_4^+]$ may be obtained by solving eqn. AII, 5 for given values of $[Ba^{++}]$.

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[*] For definition of constants, see Table V, 2.

Run 19 $60^{\circ}C$. I = 0.25

% reaction	$[Ba^{++}]$	$[H^+]$	$[NH_4^+]$ calc.	$[NH_4^+]$* found
36	0.02	1.99×10^{-8}	0.0017	0.0017
80	0.01	1.20×10^{-8}	0.0015	0.0015

It can be seen that observed and calculated values are in excellent agreement. (The extent of the agreement is probably somewhat fortuitous!).

---

* $[NH_4^+]$ found = N, when N = 0.0021, the average experimental value from Run 19; see p. 159.

APPENDIX III

Calculation of N, C and $[H^+]$ in the early stages of Urea Decomposition

The calculation of N and C over the first 1,000 minutes of the decomposition of 0.1 M. urea is given below. It is assumed that urea decomposes to give cyanate according to eqn. I, 2 and that carbonate is formed only from cyanate in accordance with the rate eqn. II, 1.

A number of further reasonable assumptions must be made.

(a) In such systems, $N > 10\ C$ over the first 1,000 minutes. It can, therefore, be assumed as a first approximation that:

(i) all carbonate is present as HCO_3^-, i.e., $[HCO_3^-] = C$ A.III, 1

hence

(ii) $[NH_3] = [HCO_3^-] = C$ .. .. .. A.III, 2

and

(iii) $[CNO^-] = N - 2C = [NH_4^+] - C$ .. A.III, 3

(b) The first order rate constant for urea decomposition, k_R, is $1.6 = 10^{-5}$ (min.$^{-1}$). This means that in 1,000 minutes, only 1.6% of the urea will have decomposed: i.e.,

$[Urea] = [Urea]_0$, the initial concentration, $= 0.1M.$

(c) The formation of urea can be neglected. This is seen to be justified from Table VI, 3; the amount of urea formed over the initial 1,000 minutes is less than 5% of that decomposed.

Thus:

$$[NH_4^+] = \text{reduction in } U \quad \text{(writing U for urea concentration)}$$

$$= - \frac{dU}{dt}$$

$$= \int_o^t k_R \; U \; dt$$

$$= k_R \; U_o \; t$$

([illegible] A.III, [illegible]) .. <u>A.III, 5</u>

The rate of carbonate formation is given by:

$$\frac{dC}{dt} = k_H[H^+][CNO^-] + k_W[CNO^-] + k_C[HCO_3^-][CNO^-]$$

Now $$[H^+] = \frac{[NH_4^+]}{[NH_3]} \; \frac{K_W}{K_1} = \frac{k_R \; U_o \; t}{C} \; \frac{K_W}{K_1}$$ .. <u>A.III, 6</u>

from 2 and 5.

Substituting for $[CNO^-]$ from 3 and 5, and $[HCO_3^-]$ from 1, [illegible]

[illegible]:

$$\frac{dC}{dt} = \frac{K_W}{K_1} \; \frac{k_H(k_R \; U_o \; t)^2}{C} - \frac{K_W}{K_1} \; k_H \; k_R \; U_o \; t + k_W(kU_o \; t - C)$$

$$+ k_C \; C(k_R \; U_o \; t - C)$$

This equation cannot be integrated directly unless the last three terms are ignored. The contribution of these three terms increases with time, and after 1.000 minutes, their value is only 16% of the first term for $U_o = 0.1$ and $C = 1.8 \times 10^{-4}$, reasonable values under these conditions. In the integration from $t = 0$ to some value up to 1,000 minutes, the neglect of these terms cannot depress the value of C below 90% of the value obtained by rigorous integration. The effect of this on $[H^+]$ will be of the same magnitude (cf. eqn. A.III, 6) i.e., the pH value thus calculated may be too high by 0.04 pH units. Such error is quite acceptable, especially as it will only have this magnitude at 1,000 minutes.

Equation A.III, 7, thus becomes:

$$\frac{dC}{dt} = \frac{K_W\ k_H\ (k_R\ U_o t)^2}{K_1 C}$$

which gives on integration:

$$C^2 = \frac{2}{3}\frac{K_W}{K_1}\ k_H \left(k_R\ U_o\right)^2 t^3 \qquad \text{.. .. ..} \ \underline{\text{A.III, 8}}$$

From this C may be obtained.

Substituting for k_H and k_R (see Table II, 1) and K_W, K_1 (cf. Table V, 2) and putting $U_o = 0.100$ M., eqn. A.III, 8 becomes:

$$C^2 = 3.1 \times 10^{-17}\ t^3$$

and from A.III, 6 and 8:

$$[H^+] = \frac{k_R\, U_o\, t\, \frac{K_W}{K_1}}{\left[\frac{2}{3}\, \frac{K_W}{K_1}\, k_H (k_R\, U_o)^2\right]^{\frac{1}{2}} t^{3/2}} \quad \ldots \quad \underline{\text{A.III, 9}}$$

$$\text{or} \qquad [H^+] = \frac{1.35 \times 10^{-6}}{\sqrt{t}} \quad \ldots \quad \ldots \quad \ldots \underline{\text{A.III, 10}}$$

Values of C, [CNO$^-$] and [H$^+$] from equations A.III, 9 and 10 are listed below:

Table A.III, 1

Time	C	[CNO$^-$]	[H$^+$] (recorded in Fig. 6 as ⊙)
10	1.2×10^{-7}	1.5×10^{-5}	4.3×10^{-7}
300	2.8×10^{-5}	4.2×10^{-4}	7.8×10^{-8}
600	8.1×10^{-5}	8.2×10^{-4}	5.5×10^{-8}
1000	1.8×10^{-4}	1.3×10^{-3}	4.3×10^{-8}

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