# CARBONATE FORMATION DURING THE ISOMERIZA-TION OF AMMONIUM CYANATE IN UNBUFFERED AQUEOUS SOLUTION

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In unbuffered aqueous solution at 70°, the reaction NH<sub>4</sub>OCN  $\rightarrow$  urea is accompanied by the formation of larger amounts of carbonate than was formerly supposed. This leads to a modification of the rate constants for the urea reaction, but the new constants still show the expected primary salt effect. For initial concentrations of 0.01, 0.02, 0.05 and 0.10 M HCO<sub>3</sub><sup>-</sup>, OCN<sup>-</sup>, urea and, in some cases, ammonia have been estimated manometrically, and the constitution of the solutions at all stages in the reaction has been calculated. The rate constants at infinite dilution become 7.3 × 10<sup>-3</sup> (mole/l.)<sup>-1</sup> sec<sup>-1</sup> for NH<sub>4</sub><sup>+</sup> + OCN<sup>-</sup>  $\rightarrow$  CON<sub>2</sub>H<sub>4</sub> and (2.3 - 4) × 10<sup>2</sup> (mole/l.)<sup>-1</sup> sec<sup>-1</sup> for H<sub>3</sub>O<sup>+</sup> + OCN<sup>-</sup>  $\rightarrow$  NH<sub>2</sub>COOH (the NH<sub>2</sub>COOH changing rapidly to HCO<sub>3</sub><sup>-</sup> and NH<sub>3</sub> at 70°); but neither mechanism can be distinguished from the corresponding non-ionic one (NH<sub>3</sub> + HOCN  $\rightarrow$  CON<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>O + HOCN  $\rightarrow$  NH<sub>2</sub>COOH respectively). Former methods are discussed in the light of these results.

The isomerization of ammonium cyanate  $(NH_4OCN \rightarrow CON_2H_4)$  is a reaction of two-fold interest; for not only is its mechanism still a matter for discussion, but through its possible relationship to urea metabolism in the body it has also attracted the attention of biochemists. It is therefore desirable that accurate information should be available on the course of this reaction in aqueous solutions.

In the important work of Walker and Hambly 1 and Warner and Stitt,2 in which the kinetics and the primary salt effect were established, the side-reaction leading to the formation of carbonate (viz.,  $OCN^- + 2H_2O \rightarrow HCO_3^- + NH_3$ ) was assumed to interfere only to a slight extent : in fact, Warner and Stitt claimed that no detectable carbonate was formed up to 70 % conversion at 70°. However, the method used by these authors for the detection of carbonate, viz. the formation of a precipitate on adding  $Ca(NO_3)_2$  solution, is not free from objection; for the solutions during the reaction have a pH low enough ( $\sim 8$ ) to render this test unreliable, since almost all the carbonate is present as  $HCO_3^{-}$ . Moreover, in attempts to determine the influence of polyvalent cations on this reaction, we have found that the presence of heavy metals always leads to the precipitation of much larger amounts of carbonate during the reaction than would be expected from the earlier work. These observations could have serious consequences; for the rate constants for urea formation have in the past been based upon the rate of disappearance of cyanate, and a false estimate of the extent of carbonate formation might affect these constants considerably. An investigation has therefore been undertaken to re-assess the importance of this side-reaction.

With the aid of the convenient techniques of biochemistry, it has been possible to estimate cyanate, carbonate, urea and (in some cases) ammonia at several stages of the reaction. ("Carbonate" is used throughout this paper to denote the quantity measured by the total  $CO_2$  produced on acidification other than that produced from cyanate: it is shown below that the "carbonate" is mostly in the  $HCO_3^-$  form). The fuller account thus obtained of all the changes taking place shows clearly that carbonate formation is considerably more important

than was formerly supposed. This has led to a reduction in the rate constants for urea formation of about 40 %.

# EXPERIMENTAL

MATERIALS.—The pure sodium cyanate of Genatosan Ltd. was used throughout. It gave satisfactory analyses for cyanate and contained no detectable carbonate. Ammonium chloride was of A.R. quality and standard reagents were used in the biochemical analyses. Conductivity water (produced from a mixed-bed resin column) was used in all reaction solutions.

PROCEDURE.—Solutions of NH<sub>4</sub>Cl and NaOCN of 10·2 times the strength required in the reaction were prepared, the factor 10·2 including a 2 % correction for expansion to 70°. Of the NH<sub>4</sub>Cl solution 40 ml were pipetted into a 500 ml stoppered bottle containing 320 ml of water and the bottle was immersed in a thermostat at  $70\cdot0 \pm 0.05^{\circ}$  and equilibrated for 40 min. At a noted time, 40 ml of the NaOCN solution was added and the bottle thoroughly shaken for a few seconds. A 20 ml sample was immediately pipetted out to check the initial concentrations. Thereafter, other samples were withdrawn at convenient intervals, rapidly frozen (in closed tubes) in a solid CO<sub>2</sub> + acetone mixture, and stored at  $-12^{\circ}$  for analysis.

Since doubts have been cast upon the purity of the starting materials of former workers,<sup>3</sup> the uncertainties involved in attempting to prepare solutions of pure NH<sub>4</sub>OCN have been avoided by using mixtures of NaOCN and NH<sub>4</sub>Cl. It was assumed that the only effect of the NaCl thus introduced was to increase the ionic strength.<sup>2</sup>

ESTIMATION OF CARBONATE AND CYANATE.—Use was made of the manometric method described by Dirnhuber and Schutz.<sup>4</sup> This depends upon the fact that almost all the  $CO_2$  evolved at pH 5 comes from the carbonate alone; subsequent further acidification to pH 1 then liberates  $CO_2$  equivalent to the cyanate. The figures were corrected for the slight decomposition of cyanate at pH 5, determined from the small steady  $CO_2$  output at this pH after the complete decomposition of the carbonate.

ESTIMATION OF UREA.—The method of Krebs and Henseleit <sup>5, 6</sup> was used. In this method the volume of the  $CO_2$  produced during the enzymatic breakdown of urea by jack bean urease is measured.

Molarities were calculated from the CO<sub>2</sub> output using the conversion factor  $22 \cdot 26 \times 10^6 \mu$  μl./mole at s.t.p. and were all corrected to the reaction temperature.

ESTIMATION OF AMMONIA.—Ammonia was estimated by the method of Conway.<sup>7</sup>

#### RESULTS

The results of the determinations for initially equimolar NaOCN + NH<sub>4</sub>Cl mixtures are collected in table 1. The initial concentrations, 0·01, 0·02, 0·05 and 0·10 M, refer to the initial molarity of ammonium cyanate; i.e. initial NaOCN molarity = initial NH<sub>4</sub>Cl molarity (= initial NH<sub>4</sub>OCN molarity) = 0·01, 0·02, 0·05 or 0·10 M. These numbers are later used for brevity to characterize particular experiments, as, for instance, "the 0·01 M run".

These results show that: (i) carbonate formation is not negligible even at 0.10 M, whilst at 0.01 M it is almost half that of urea; and (ii) in those cases in which ammonia has been measured, the rate of its disappearance is considerably less than that of cyanate. Since both ammonia and carbonate are formed in the side-reaction, each of these observations provides independent evidence of the importance of this effect.

No special precautions were taken to prevent loss or gain of  $CO_2$  or  $NH_3$  other than keeping vessels well stoppered during reactions and storage, but the number of constituents estimated provides a means of cross-checking that errors of this kind were not large. Three such methods of checking are illustrated in the last three columns of table 1, which give an idea of the reliability of the data. Thus the total carbon estimated, as given by [carbonate] + [urea] + [cyanate], generally agrees with the initial [ $NH_4OCN$ ] to within 3 %, and the occasional deviations outside this limit can usually be ascribed to definite errors in one or other of the measurements. In the 0.10 M run, for example, the figure 106 is certainly due to an overestimate of urea in this sample, since the 76.4 figure lies well off the smooth curve defined by the other urea figures in this experiment. Similarly, the last two figures in the 0.01 M run, 10.5 and 10.7, probably indicate an overestimate of carbonate. The stoichiometry also requires that the total ammonia should be represented by both initial [ $OCN^{-}$ ]-[urea]+[carbonate] and [cyanate]+2 [carbonate].

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Inspection of the seventh and eighth columns of table 1 again shows agreement to about 3 %. Where the total ammonia estimated is also available there is also fair agreement with columns 7 and 8, except towards the end of the 0.01 M run; but the ammonia figures quoted in brackets were not regarded as very reliable because of a delay in estimation and are only included to give an idea of the general trend. In spite of these obvious discrepancies, however, the overall impression is that the several estimations do provide a consistent account of the concentrations of the important constituents, which are probably reliable in most cases to about 1 % of the initial [NH<sub>4</sub>OCN].

Table	1.—Results	OF ANA	LYSES C	OF REA	CTION	MIXTURES
All	concentration	ns (exce	pt colui	mn 1)	in mm	oles/1.

initial [NH4OCN]	time (min)	[carbonate]	[urea]	[cyanate]	[ammonia]	initial [OCN-] [urea] + [carbon- ate]	[cyanate] + 2[car- bonate]	[carbonate] + [urea] + [cyanate]
0·01 M	40	$0.5_{2}$	0·78	8·6 <sub>2</sub>	9·7 <sub>0</sub>	9.7	9.7	9.9
(70° C)	80	0·7 <sub>9</sub>	1.94	7·35	8.91	8.9	8.9	10.1
	120	1·1 <sub>0</sub>	2.55	6.87	9·0 <sub>0</sub>	8∙6	9.1	10.5
	160	$1.2_{8}$	3·1 <sub>3</sub>	5·95	8·3 <sub>0</sub>	8.2	8.5	10.4
	200	$1.2_{8}$	3·4 <sub>8</sub>	5·34	7·80	7.8	7.9	10.1
	240	1·4 <sub>2</sub>	3·78	4.93	(6·7 <sub>6</sub> )	7.6	7.8	10.1
	300	1·4 <sub>6</sub>	4·27	4·35	(6.66)	7.2	7.3	10.1
	1440	$2.6_0(?)$	6·82	1·0 <sub>6</sub>	4·31	5.8	6.3	10.5
	2880	2·8 <sub>2</sub> (?)	7·2 <sub>3</sub>	0·6 <sub>6</sub>	4·3 <sub>9</sub>	5.6	6.3	10.7
0·02 M	20	0.59	1·7 <sub>6</sub>	17.1	_	18.8	19-3	19.5
(70° C)	40	1.34	3·35	15.1		18.0	17.8	19.8
	60	2.60	4·7 <sub>5</sub>	13.4	_	17.9	18.6	20.8
	80	2·60	5·8 <sub>5</sub>	11.9		16.8	17.1	20.4
	100	2·77	6.87	11.0		15.9	16.5	20.6
	120	2.24	7·6 <sub>0</sub>	10.2		14.6	14.7	20.0
0∙05 M	10	0.02	5.5	43·1	43·0	45	43	48·7
(70° C)	20	2.5	12.5	35.5	41·6	40	39	50.2
	30	3.3	14.7	32.7	36.8	39	39	50.7
	46	4·4	18.7	25.7	33.8	36	35	48·8
	60	3·2 (?)	21.3	22.1	30.7	32	29	46.6
0·10 M	10	4.9	21.2	76.7		84	87	103
(70° C)	20	5.5	32.7	66.1		73	77	104
	30	6.0	40·2	54.6		66	67	101
	45	7.5	49.6	41.7		58	57	99
	60	8.6	55.3	34.4		53	52	98
	120	8·2	76.4(?)	20.9		32	37	106
	180	8.0	81.4	14.2		27	30	104
	1240	9.0	88.4	1.8	_	21	20	99
0·02 M	120	0.6	2.7	16.4	_	17.9	17.6	19.7
(50° C)	176	0.8	3.5	15.8		17.3	17•4	20.1
	271	0.8	4.1	14.8	—	16.7	16.4	19.7
	392	1.1	5.2	13.1	<u> </u>	15-9	15.3	19.4

Results are included for 0.02 M at  $50^{\circ}$  C, and these show that the side reaction is important even at this lower temperature. The proportion of carbonate is not as high as in the corresponding experiment at  $70^{\circ}$ , but its concentration is still more than 20 % of that of urea.

#### CALCULATIONS

CONSTITUTION OF SOLUTIONS.—The effect of the side-reaction is more profound than the mere reduction of the effective cyanate concentration: the other reactant is also affected in two ways. For not only is extra ammonia formed, but its distribution between the forms  $NH_4^+$  and  $NH_3$  varies with the accompanying change in pH.

A further complication would arise if any of the probable intermediate, carbamate, persisted in solution. From a consideration of the results of Faurholt and others,<sup>8</sup> however, this seems very unlikely; for the equilibrium concentration of carbamate in such dilute solutions must be extremely small, and equilibrium would be established in a few seconds at 70°. (Times for the attainment of equilibrium from pure NH<sub>2</sub>CO<sub>2</sub>NH<sub>4</sub> are about 1 day at 0° and the rate is 20 times as great at 18°: a continuation of this increase with temperature would lead to rates about 10<sup>5</sup> as great at 70° as at 0°.) It is therefore assumed that the carbamate concentration can be ignored.

Although the mechanism of carbamate formation probably involves  $OCN^-$  and  $H_3O^+$  (or HOCN and  $H_2O$ ), no equivalent increase in [OH<sup>-</sup>] would be expected in the presence of the buffering  $NH_4^+$  and  $HCO_3^-$ ; and a consideration of the acid strengths of these latter ions leads to the following equation as the best approximation to the stoichiometry :

$$OCN^- + 2H_2O \rightarrow HCO_3^- + NH_3$$
(1)  

$$y \qquad y \qquad y$$

where the total estimated carbonate at any time is represented by y. (This stoichiometric equation does not conflict with the mechanisms implied in eqn. (iv) below.) In the presence of excess  $NH_{+}^{*}$ , the  $HCO_{3}^{-}$  will show some tendency to behave as a base, giving as a refinement to our calculations:

$$\begin{array}{l} \text{HCO}_3 + \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}_2\text{CO}_3 \\ y - z \quad b - z \quad y + z \quad z \end{array}$$

where b = initial [OCN-]-[urea] (i.e. all ammonia other than that formed in the carbonate reaction) and  $z = [H_2CO_3]$ . All the quantities are now defined for the calculation of z by the application of the relevant dissociation constants; for it must be emphasized that reactions (1) and (2) are not arbitrary choices but are confirmed by the dissociation equilibria. To simplify the calculations, the (verifiable) assumption is made that  $[CO_3^{-1}]$ is negligible, an assumption which is more readily justified at 70° than at room temperature, by reason of the much greater increase in  $K_w$  than in  $K_{2a}$  (defined as below):

The following dissociation constants at 70° are required :

$$K_b = [NH_4^+][OH^-]f_{12}/[NH_3] = 1.80 \times 10^{-5}$$
 (interpolated 9);

- $K_{1a} = [\text{HCO}_{3}^{-}][\text{H}_{3}\text{O}^{+}]f_{1}^{2}/[\text{H}_{2}\text{CO}_{3}] = 5.00 \times 10^{-7}$  (extrapolated from the 0°-38° data of Shedlovsky and MacInnes with their formula <sup>10</sup>);
- $K_{2a} = [H_3O^+][CO_3^-]f_2/[HCO_3^-] = 9.43 \times 10^{-11}$  (extrapolated from the 0°-50° data of Harned and Scholes with their formula <sup>11</sup>);
- $K_w = [H_3O^+][OH^-]f_1^2 = 1.60 \times 10^{-13}$  (extrapolated from the 0°-60° data quoted by Harned and Owen, using their formulae <sup>12</sup>);
- $K_{\text{HOCN}} = [H_3O^+][OCN^-]f_1^2/[HOCN] = 2 \times 10^{-4}$  (an approximation based on the value at 0° quoted by Beilstein,<sup>13</sup> viz. 1.86 × 10^{-4}, but sufficiently accurate for the present purpose).

In these equations,  $f_1$  and  $f_2$  represent activity coefficients for 1- and 2-valent ions respectively. For all the calculations in this work, these activity coefficients are always assumed to be represented with sufficient accuracy by Davies' extension <sup>14</sup> of the Debye-Hückel equation:

$$\log_{10} f_i = -\alpha z_i^2 \left\{ \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.2I \right\},$$
 (i)

where  $z_i$  is the valency of the ion, *I* the ionic strength, and  $\alpha$  has the value 0.5619 at 70°. With the concentrations defined above,  $K_b$ ,  $K_{1a}$  and  $K_w$  give

$$\frac{[\mathrm{NH}_4^+]}{[\mathrm{NH}_3]}\frac{[\mathrm{HCO}_3^-]}{[\mathrm{H}_2\mathrm{CO}_3]} = \frac{(b-z)(y-z)}{(y+z)z} = \frac{K_b K_{1a}}{K_w f_{1}^2} = \frac{56\cdot 25}{f_{1}^2},$$

whence

$$\left\{\frac{56\cdot 25}{f_1^2} - 1\right\}z^2 + \left\{\frac{56\cdot 25y}{f_1^2} + y + b\right\}z - yb = 0,$$
 (ii)

from which z can be calculated for any given time since y is then a constant. The ionic strength required for  $f_1^2$  can, with sufficient accuracy, be regarded as  $[NaCl] + [OCN^-] + [carbonate]$ , these values being the unmodified experimental figures.

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The solution of (ii) leads directly to  $[H_2CO_3]$ ,  $[HCO_3^-]$ ,  $[NH_4^+]$  and  $[NH_3]$ .  $[H_3O^+]$  is next obtained by applying  $K_{1a}$  (or  $K_b$  and  $K_w$ ) and thence an approximate value for [HOCN]. Thus a complete account of the constitution of the solutions at every stage of the reaction can be made.

This has been done for all the solutions, and a specimen of the results is shown in table 2, which gives the figures for the 0.01 M run. It appears that z is always small compared with y, so that no great error would be involved by taking  $[NH_4^+]$  to be the initial  $[OCN^-]-[urea]$ , and assuming that all the ammonia produced by the side reaction is unionized, as represented by (1).

The last column of table 2 shows the marked change in  $[H_3O^+]$  to be expected during the reactions. It was not easy to check this at 70°, but the drift in pH was readily demonstrated on the samples cooled to room temperature, which showed a change of 1-2 pH units in the 8-9 region (corresponding to the 7-8 region at 70°). The pH of a 0.05 M NaOCN solution was also measured and found to be 8.72. The figure calculated from  $K_{\text{HOCN}}$  is 8.11. The difference probably represents some stabilizing free alkali, but in such minute quantities this would not affect the calculations since buffers of concentration at least 10<sup>-3</sup> M are produced during the reactions.

THE RATE CONSTANT FOR UREA FORMATION  $(k_u)$ .—Because of the interfering side reaction, no simple integration is available for establishing the constant of the urea reaction and the simplest course is to use the differential form:

$$d [urea]/dt = k_u [OCN^-][NH_4^+]$$
(iii)

(or  $k_u$  [HOCN][NH<sub>3</sub>]).

The graphical method was adopted: [urea] was plotted against time, a smooth curve was drawn through the points and the slope was measured for various t values.  $k_u$  was then calculated directly from (iii), using the corresponding  $[NH_4^+]$  and  $[OCN^-]$  from table 2. Values obtained in this way are recorded in the second column of table 3, where the *second* is taken as the unit of time.

TABLE 2.—CONSTITUTION OF SOLUTION DURING REACTION WITH INITIAL  $[NH_4OCN] = 0.01 \text{ M}$ : All concentrations in mmoles/L.

time (min)	[NH4]	[NH <sub>3</sub> ]	[OCN"]	[HOCN] × 10 <sup>3</sup>	[HCO_3]	[H <sub>2</sub> CO <sub>3</sub> ]	[H <sub>3</sub> O+] × 10 <sup>4</sup>
40	9.13	0.61	8.62	4.25	0.43	0.086	1.34
80	7.98	0.88	7.35	2.18	0.71	0.084	0.80
120	7.36	1.19	6.87	1.44	1.02	0.085	0.57
160	6.79	1.36	5.95	0.99	1.20	0.080	0.44
200	6.44	1.36	5.34	0.85	1.20	0.077	0.43
1440	3.13	2.65	1.06	0.05	2.55	0.047	0.12
2880	2.74	2.85	0.66	0.02	2.79	0.035	0.08

TABLE 3.--THE UNITS OF ALL RATE CONSTANTS ARE (MOLE/L.)-1 SEC-1.

initial [NH₄OCN]	$k_u \times 10^3$ (ionic)	$k_{\mu_0}  imes 10^3$	$k_{u'} \times 10^{-2}$ (non-ionic)	mean I	$k^{*} \times 10^{3}$
0·01 M	$5.0 \pm 0.3$	6.8	1·5 <sub>2</sub>	0.018	$7.1 \pm 0.6$
0·02 M	4.9 + 0.5	7.2	1.62	0.035	$6.9 \pm 0.2$
0·05 M	4.5 + 0.4	7.6	$1.7_{2}^{-}$	0.084	$6.4 \pm 0.8$
0·10 M	$3.9 \pm 0.5$	7.4	1.67	0.161	$5.1 \pm 0.7$

No very great precision emerges in the values of  $k_u$  obtained from several points in the same run, the limits of error being  $ca. \pm 10\%$ ; but even so there is a clear trend of  $k_u$  with ionic strength of the magnitude demanded by Brønsted's theory for this reaction. The significance of this is discussed below.

THE RATE CONSTANT FOR CARBONATE FORMATION  $(k_c)$ .—If the rate of the side reaction is assumed to be represented by the equation

d [carbonate]/dt = 
$$k_c$$
[OCN<sup>-</sup>][H<sub>3</sub>O<sup>+</sup>] (iv)  
(or  $k_c$ '[HOCN][H<sub>2</sub>O]),

the analogy with (iii) suggests a similar method for calculating  $k_c$ . Because of the smaller and less accurately known [carbonate], however, it is difficult to make convincing estimates of d [carbonate]/dt from the graph, and it is better to proceed as follows. Let [urea] = x, [carbonate] = y, initial [OCN<sup>-</sup>] = initial [HN<sub>4</sub><sup>+</sup>] = a. At time t, [OCN<sup>-</sup>] = a - x - y, [NH<sub>4</sub><sup>+</sup>] = a - x, (replacing the b of a former section, where the x would have been confusing), [NH<sub>3</sub>] = y. (These last two estimates are accurate enough for present purposes: see above.)

Then

 $dx/dt = k_u [OCN^-][NH_4^+]$ =  $k_{u_0} f_1^2 [OCN^-][NH_4^+].$  (v)

(where  $k_{u_0}$  is the rate constant at infinite dilution).

Similarly  $dy/dt = k_c[OCN^-][H_3O^+]$ 

$$= k_{c_0} f_1^2 [OCN^-] [H_3O^+],$$

(where  $k_{c_0}$  is the rate constant at infinite dilution).

But 
$$[H_3O^+] = K_w/[OH^-]f_1^2 = K_w[NH_4^+]/K_b[NH_3] = 8.9 \times 10^{-9}[NH_4^+]/[NH_3].$$
  
 $\therefore dy/dt = (k_{c_0}f_1^2 \times 8.9 \times 10^{-9}) [OCN^-][NH_4^+]/[NH_3].$  (vi)

Then dividing (v) by (vi),

$$dx/dy = (10^9 k_{u_0}/8.9 k_{c_0})$$
 [NH<sub>3</sub>] = ky.

Integrating, and remembering that when t = 0, x = y = 0,

$$x = \frac{1}{2}ky^2 = (10^9 k_{\mu_0}/17 \cdot 8k_{c_0})y^2.$$
 (vii)

Thus a plot of [urea] against [carbonate]<sup>2</sup> should give a straight line from the gradient of which  $k_{c_0}$  should be calculable once  $k_{u_0}$  is known.

Fig. 1 shows the results so plotted for the 0.01 M run. Considering the very wide range of  $[H_3O^+]$  involved (see table 3), the form of the graph satisfactorily confirms (vii),



and hence also (iv). (A more accurate form of (vii),  $x = \frac{1}{2}k(y^2 + 2yz)$ , makes no significant difference to the plot.) From the slope and  $k_{u_0}$  deduced below (7.3 × 10<sup>-3</sup>),  $k_{c_0}$  is obtained as 2.3 × 10<sup>2</sup> (mole/l.)<sup>-1</sup> sec<sup>-1</sup>.

When the data for all the runs were plotted in this way on the same graph (a procedure rather overweighting the 0.1 M data), the best value of  $k_{c_0}$  derived was  $4 \times 10^2$  (mole/l.)<sup>-1</sup> sec<sup>-1</sup>. A value in the range (2.3-4) × 10<sup>2</sup> (mole/l.)<sup>-1</sup> sec<sup>-1</sup> is therefore suggested for  $k_{c_0}$  at 70°.

THE EQUILIBRIUM BETWEEN UREA AND CYANATE.—Two of the reactions (0.01 M and 0.1 M) have been carried to a stage advanced enough to make possible a re-estimate of Walker's equilibrium constant,<sup>2</sup>

$$K = [NH_4^+][OCN^-]f_1^2/[urea].$$
(viii)

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From the concentrations in the final samples given in table 2 (and its analogue for 0.1 M), K was found to be  $1.9 \times 10^{-4}$  at 0.01 M and  $1.3 \times 10^{-4}$  at 0.1 M. (Table 2 is derived from corrections based on the carbonate estimation. Little difference in K is made, however, if calculations are based on the total ammonia : it becomes  $1.8 \times 10^{-4}$  at 0.01 M.) The mean K as defined by (viii) thus becomes  $1.6 \times 10^{-4}$  at 70°, a value in good agreement with that obtained from Walker's data by the method of Lewis,15 which yields

$$K = 1.62 \times 10^{-4}$$
 at 70°.

It is also possible to write

$$K' = [NH_3][HOCN]/[urea], \qquad (ix)$$

where K' is related to K in (viii) by the factor  $K_w/K_bK_{HOCN}$ . Thus  $K' = 7 \times 10^{-9}$ .

## DISCUSSION

Although the new data reported here invalidate former rate constants, they do not conflict with the two main conclusions of former workers: (i) that the rate of the conversion of NH4OCN into urea depends upon the product of the concentrations of  $NH_4^+$  and  $OCN^-$  ions; <sup>1</sup> and (ii) that the rate constant depends upon the ionic strength as expected for an ionic reaction between NH<sup>+</sup><sub>4</sub> and OCN<sup>-</sup> according to Brønsted's theory.<sup>2</sup> It is, however, a mistake to suppose that these conclusions demand the ionic mechanism: 16, 17

$$OCN^- + NH_4^+ \to CO(NH_2)_2. \tag{3}$$

Weil and Morris have shown that identical results are expected from

HOCN + NH<sub>3</sub>  $\rightarrow$  CO(NH<sub>2</sub>)<sub>2</sub>; (4)

in fact they prefer this mechanism on other grounds.

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An interesting feature of this reaction is that it is difficult to find any mechanism which does not demand a primary salt effect. For instance, Moelwyn-Hughes quoted Doyle <sup>18</sup> as having found  $k_u$  to be independent of the ionic strength, and suggested a mechanism involving collisions between undissociated NH4OCN molecules; i.e. rate of reaction  $\propto$  [NH<sub>4</sub>OCN]<sup>2</sup>. But the conductivity suggests that NH4OCN is extensively dissociated (even according to the Arrhemius theory used by Walker), so that the molarity approximates to  $[NH_4^+]$  and  $[OCN^-]$ . The unknown [NH<sub>4</sub>OCN] must therefore be expressed in terms of the concentrations of these two ions:

$$[NH_4OCN] = [NH_4^+][OCN^-]f_1^2/K.$$

Hence

rate of reaction 
$$\propto$$
 [NH<sub>4</sub>OCN]<sup>2</sup>  $\propto$  [NH<sup>+</sup>]<sup>2</sup>[OCN<sup>-</sup>]<sup>2</sup>f<sub>1</sub><sup>4</sup>

a result which does not agree with the established kinetics; and, far from giving no salt effect, this mechanism would lead to one of much greater magnitude than (3) and (4). Unimolecular conversion of NH4OCN would give results indistinguishable from (3) and (4).

Since the choice of mechanism cannot be regarded as settled, the constants for both (3) and (4) are recorded in columns 2 and 4 of table 3: they are simply related by the factor  $K_{HOCN}K_b/K_w f_1^2$ . For the ionic mechanism, values calculated for  $k_{\mu_0}$  (the rate constant at infinite dilution : see eqn. (v)) are also included (column 3): they are obtained by dividing  $k_u$  by the mean  $f_{1^2}$  over the time range for which  $k_u$  was calculated. A further advantage of using NaOCN and NH<sub>4</sub>Cl as reactants appears at this stage, for the ionic strength varies much less during a reaction than with pure NH4OCN, and mean ionic strengths can therefore be regarded with more confidence.

The mean values for  $k_{\mu_0}$  and  $k_{\mu'}$  are:

$$k_{u_0} = 7.3 \times 10^{-3} \text{ (mole/l.)}^{-1} \text{ sec}^{-1},$$
  
 $k'_u = 1.6 \times 10^2 \text{ (mole/l.)}^{-1} \text{ sec}^{-1}.$ 

Eqn. (iv) is the exact analogue of (iii) and the mechanism of carbonate formation is therefore subject to the same uncertainty. The cases are slightly different, however, for the relationship between  $k_c$  and  $k_c'$  involves [H<sub>2</sub>O] which could be omitted to arrive at a practical pseudo-unimolecular constant instead of  $k_c'$ .

The rate constants quoted in this paper are not claimed to be of great accuracy; the experimental data and the graphical methods involved preclude this. The carbonate rate constants are also unreliable for the additional reason that they depend upon dissociation constants which have been arrived at by extrapolations. But it is claimed that the urea reaction constants are much more reliable than those obtained by cyanate disappearance methods. In this respect, a striking confirmation of the general trend of our data is demonstrated by calculating apparent rate constants using only the cyanate concentrations in table 1: the resulting values (quoted in the last column of table 3 as k'') are 40 % higher than those calculated correctly (table 3, column 2), but when plotted on the log k against  $I^{\frac{1}{2}}$ graph of Warner and Stitt they lie well amongst the experimental points of those authors. (It is, of course, necessary for such a comparison to show that the silver precipitation technique used by Warner and Stitt did measure [OCN-] correctly even in the presence of considerable concentrations of HCO<sub>3</sub><sup>-</sup>. That this was the case was shown by parallel experiments at  $70^{\circ}$  in which [OCN<sup>-</sup>] was measured both by this method and by the manometric technique: the results agreed well up to about 40 % conversion.)

Since both the general kinetics of the isomerization of NH<sub>4</sub>OCN and the salt effect were established by measurements of the rate of disappearance of cyanate only, it is necessary to show why it was that the large carbonate error did not interfere with these conclusions. This is readily understood from a consideration of eqn. (v) and (vi), from which

$$- d[OCN^{-}]/dt = dx/dt + dy/dt = (k_{u_0} + k_{c_0} \times 8.9 \times 10^{-9}/[NH_3])f_1^2[NH_4^{+}][OCN^{-}]$$

or, in the symbols used previously,

 $\begin{array}{l} -- \ d[OCN^{-}]/dt \\ = (k_{u_0} + k_{c_0} \times 8.9 \times 10^{-9}/y)f_1^2(a - x - y)(a - x) \\ = [f_1^2(k_{u_0} + k_{c_0} \times 8.9 \times 10^{-9}/y)(a - x)/(a - x - y)](a - x - y)^2 \\ = k''[OCN^{-}]^2 \ (\text{the form used in the silver method}). \end{array}$ 

The quantity k'' tends to remain constant since the factor (a - x)/(a - x - y) increases with time whilst  $k_{c_0} \times 8.9 \times 10^{-9}/y$  decreases: it also incorporates  $f_1^2$  and so explains why Warner and Stitt demonstrated the correct salt effect.

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