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

$$\begin{aligned} -\mathrm{d}[NCO^-]/\mathrm{d}t &= [NCO^-](k_1'[NH_4^+] + k_3' + k_4'[H_3O^+] + k_5'[HCO_3^-]) \\ &= [HNCO](k_1[NH_3] + k_3[OH^-] + k_4 + k_5[CO_3^{2-}]) \end{aligned}$$

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

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

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

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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.

[1] Walker and Hambly, *J.*, 1895, **67**, 746; Walker and Kay, *J.*, 1897, **71**, 489; Janelli, *Gazzetta*, 1953, **83**, 983.

[2] Miller, *Proc. Roy. Soc.*, 1934, **145**, *A*, 288; 1935, **151**, *A*, 188; Warner and Stitt, *J. Amer. Chem. Soc.*, 1933, **55**, 4807; Warner and Warrick, *ibid.*, 1935, **57**, 1491; Svirbely and Warner, *ibid.*, p. 1883; Svirbely and Schramm, *ibid.*, 1938, **60**, 330; Svirbely and Lander, *ibid.*, p. 1613; 1939, **61**, 3538; Svirbely and Rampino, *ibid.*, p. 3534.

[3] Wyatt and Kornberg, *Trans. Faraday Soc.*, 1952, **48**, 454.

[4] Amis, " Kinetics of Chemical Change in Solution," Macmillan, New York, 1949, Chapters 4, 5, 6, and 9.

[5] Chapman and Chattaway, *J.*, 1912, **101**, 170.

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.

The kinetics of *carbonate* formation have been studied on only a few occasions,[3, 8, 9, 10] and the observations of different workers are not always consistent. It is generally assumed that carbamic acid or the carbamate ion is an intermediate in this reaction, and there is some experimental evidence in favour of this hypothesis.[11] The acid can be expected to be converted into *carbonate* as soon as it is formed, and this also applies to carbamate ions at the high temperatures employed in these experiments.[12]

The present investigation aimed to establish general rate equations for urea and *carbonate* formation in water over a wide range of pH, and to obtain further information about the mechanism of these reactions. The decomposition of ammonium, sodium, and barium cyanates was examined at 60° and, in some cases, at 80°. Sealed containers were employed to avoid any possible loss of carbon dioxide, bases or weak acids being added to some of the reaction mixtures to alter $[OH^-]$ (which ranged from 4×10^{-7} to 2×10^{-3} mole $l.^{-1}$), and also to determine whether they specifically affected the reactions. The decomposition of urea was also studied, though in less detail. $[NCO^-]$ was never greater than 0·055 mole $l.^{-1}$ and the initial ionic strength in all reaction mixtures was adjusted to 0·25 by the addition of potassium nitrate. This value did not change unduly during the course of any one run and concentration units were therefore used when setting up the rate equations. The reactions were followed by analysis for *cyanate* * and *carbonate*; *ammonium* * and urea concentrations were then obtained from the stoicheiometry of the processes and the initial concentrations. Control experiments showed that the urea concentration so calculated was within the experimental error of its value determined by the xanthhydrol method.[13] The concentrations of the various species present at any stage of a kinetic run were calculated from the analytical results, the appropriate thermodynamic equilibrium constants, and the ionic activity coefficients which were taken as 0·705 and 0·686 for univalent ions at 60° and 80°, respectively, and as 0·240 and 0·222 for bivalent ions. Details are given in the Experimental section.

RESULTS

Reaction Products.—The results of this investigation fully confirm Wyatt and Kornberg's observations [3] that *carbonate* formation is not negligible in the decomposition of ammonium cyanate (cf. Run 1, Table 4); the probable reason for the failure of previous workers to observe this has already been discussed by them. In the decomposition of sodium and barium cyanates at 60° the ratio of urea to *carbonate* was substantially the same as found by Masson and Masson.[8] Their observation of a stationary *ammonium* concentration in the decomposition of barium cyanate was based on the assumption that the precipitated barium carbonate represents the total *carbonate* formed. In the present work this assumption leads to a stationary concentration of the same magnitude, but an allowance for the *carbonate* in solution results in *ammonium* concentrations which increase as the reaction proceeds.

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* Cf. footnote, p. 900.

[6] Weil and Morris, *J. Amer. Chem. Soc.*, 1949, **71**, 1664.
[7] Frost and Pearson, " Kinetics and Mechanism," Chapman and Hall, London, 1953, pp. 257 *et seq.*
[8] Masson and Masson, *Z. phys. Chem.*, 1910, **70**, 290.
[9] Täufel, Wagner, and Dünwald, *Z. Elektrochem.*, 1928, **34**, 115.
[10] Lister, *Canad. J. Chem.*, 1955, **33**, 426.
[11] Fearon and Dockeray, *Biochem. J.*, 1926, **20**, 13.
[12] Faurhoult, *Z. anorg. Chem.*, 1922, **120**, 85.
[13] Fosse, *Compt. rend.*, 1914, **158**, 1076.

Kinetics of Urea Formation.—In all our experiments the rate of urea formation was given by

$$dU/dt = k_1'[NH_4^+][NCO^-] - k_2U \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$= k_1[NH_3][HNCO] - k_2U \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

where U is the urea concentration, and $k_1 = k_1'/K_{iii}K_{iv}$ with $K_{iii} = [HNCO][OH^-]/[NCO^-]$ and $K_{iv} = [NH_3]/[NH_4^+][OH^-]$. The values of the equilibrium constants at ionic strength 0·25 are given on p. 910.

All former workers in this field have reported that the rate of urea formation is given by one or other of these equations, usually (1). The present results show that they apply up to higher pH values than previously examined, and also when no ammonium ions are present initially (cf. Run 18). The second term has often been omitted; its effect on the overall rate is only significant in the later stages of the reaction, or if urea has been added to the reaction mixture.

The rate coefficients, and the appropriate energies and entropies of activation (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. 911), 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. 903).

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.

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[14] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 199.

[15] Naumann, *Z. Elektrochem.*, 1910, **16**, 773.

[16] Warner and Stitt, ref. 2; Warner and Warrick, ref. 2.

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 $E = 24{\cdot}0$ 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
$10^4 Cy$	22	29	45	48	50	48	48	47	42
$10^5 C$	30	49	77	101	156	183	233	262	356

As *carbonate* is formed from the *cyanate*, and not directly from urea (cf. p. 904), the urea–*cyanate* equilibrium could not be observed at this temperature. From the rates of the forward and back reactions we find $K' = [NH_4^+][NCO^-]/U = 1{\cdot}04 \times 10^{-4}$ and $K = [NH_3][HNCO]/U = 2{\cdot}64 \times 10^{-9}$, at 60·10° and zero ionic strength. Lewis and Randall's data,[17] which are based on Walker and Kay's[1] direct observation of the equilibrium at 100° and the enthalpy change of the reaction,[18] lead to $K' = 1{\cdot}20 \times 10^{-4}$ under these conditions; presumably equilibrium at 100° is established before any *carbonate* has been formed.

Kinetics of Carbonate *Formation.—Carbonate* was always formed according to the equations

$$dC/dt = k_3'[NCO^-] + k_4'[H_3O^+][NCO^-] + k_5'[HCO_3^-][NCO^-] \quad . \quad . \quad . \quad . \quad (3)$$

$$= k_3[OH^-][HNCO] + k_4[HNCO] + k_5[CO_3^{2-}][HNCO] \quad . \quad . \quad . \quad . \quad (4)$$

where $k_3 = k_3'/K_{iii}$, $k_4 = k_4'K_{viii}/K_{iii}$, and $k_5 = k_5'K_v/K_{iii}$, with $K_{viii} = [H_3O^+][OH^-]$, and $K_v = [HCO_3^-][OH^+]/[CO_3^{2-}]$. The values of these equilibrium constants at ionic strength 0·25 are given on p. 910.

TABLE 2. *Instantaneous rates of carbonate formation at* 60·10° *and ionic strength* 0·25.

[Initial reactants: NH_4NCO in Runs 1, 2, 3, and 7; $Ba(NCO)_2$ in 19; NaNCO in all others. Small amounts of the following substances were added to reaction mixtures: NH_3 in Runs 7 and 17; Na_2CO_3 in 2 and 3; $NaHCO_3$ in 12 and 12*a*; NEt_3 in 20; H_3BO_3 in 21.]

Run	1	3	12*a*	2	7	12	21	20	19	14	17	16
$\frac{10^7}{[NCO^-]} \cdot \frac{dC}{dt}$ (sec.$^{-1}$)	240	48	37	36	33	33	33	32	20	11	11	10
$10^4[NCO^-]$	519	530	518	211	507	506	396	355	477	489	496	260
$10^{10}[H_3O^+]$	5000	320	100	120	370	30	40	3	120	10	4	10
$10^4[HCO_3^-]$	2	55	68	73	5	74	67	70	3	2	1	1
$10^4[CO_3^{2-}]$	—	—	—	—	—	6	5	59	—	—	—	—
$10^4[NH_4^+]$	520	469	1	199	514	3	16	7	7	1	5	—
$10^4[NH_3]$	5	64	1	80	70	4	20	106	2	4	61	2
$10^4[NEt_3H^+]$	—	—	—	—	—	—	—	50	—	—	—	—
$10^4[NEt_3]$	—	—	—	—	—	—	—	25	—	—	—	—
$10^4[H_3BO_3]$	—	—	—	—	—	—	104	—	—	—	—	—
$10^4[H_2BO_3^-]$	—	—	—	—	—	—	49	—	—	—	—	—

None of the other species which were present in the various reaction mixtures had any effect on the rate. This is illustrated in Table 2, where instantaneous rates of *carbonate* formation at $[NCO^-] = 1$ are compared for a variety of conditions. These rates were

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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."

[17] Lewis and Randall, " Chemical Thermodynamics," McGraw-Hill, New York, 1923, p. 587.

[18] Walker, *Z. phys. Chem.*, 1902, **42**, 207.

obtained from the reaction–time curve, sometimes by extrapolation, and are therefore not very accurate. They do, however, show clearly that the rate is not significantly affected by ammonium ions or ammonia (Runs 12*a* and 2, 14, and 17), triethylammonium ions or triethylamine (Runs 12 and 20), borate ions or boric acid (Runs 12 and 21), or carbonate ions (Runs 12 and 20). It is also apparent that the reaction is of the first order in cyanate ions (Runs 12*a* and 2, 14 and 16), and accelerated by hydroxonium ions (Runs 1, 7, 19, and 14) and hydrogen carbonate ions (Runs 7 and 3, 12*a* and 19).

The rate coefficients, and the appropriate energies and entropies of activation, are given in Table 1. For the reasons already mentioned, each k' is regarded as more reliable than the corresponding k. As before, the other possible errors do not appear to be important; C, when calculated from the mean rate coefficients did not, on the average, differ by more than 3% from the observed value in any one run (illustrated for Run 18). This did not, however, apply in the decomposition of urea solutions. Here C (calc.) was always too high, particularly in the early stages of the reaction. A check of the analytical methods revealed no systematic error, and the observation of a similar, though smaller, discrepancy when carbonate ions were added suggests that the urea may have contained a small amount of some basic impurity or that biuret is formed in the reaction. This substance was present at less than 0·0005M * in our systems, but the neglect of, say, 0·0003M has an appreciable effect on the calculated pH. Further work is necessary before 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 $[\mathrm{NCO}^-] \simeq [\mathrm{OH}^-]$, 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

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

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* The biuret test will not detect smaller quantities

[19] Fawsitt, *Z. phys. Chem.*, 1902, **41**, 61; Burrows and Fawsitt, *J.*, 1914, **105**, 609; Krasil'shchikov, *Zhur. fiz. Khim.*, 1939, **13**, 767; Dirnhuber and Schültz, *Biochem. J.*, 1948, **42**, 628.

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

$$-\,\mathrm{d}Cy/\mathrm{d}t = \{\mathrm{NCO^-}\}[(k_1')^\circ\{\mathrm{NH_4^+}\} + (k_3')^\circ + (k_4')^\circ\{\mathrm{H_3O^+}\} + (k_5')^\circ\{\mathrm{HCO_3^-}\}] \quad . \quad . \quad (5)$$

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

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 equal ease, and p the number of equivalent, dissociable protons attached to different atoms in the conjugate acid. The rate coefficients calculated from this equation are between three-quarters and twice those observed (see Table 3); this agreement is as good as can be expected from the application of the Brönsted relation to such widely different bases.†

In the reactions of cyanic acid general base catalysis can only apply to *carbonate* formation (ammonia is not a catalyst in urea formation), and would require a kinetic term, k_B° {B}{HNCO}, to contribute to the rate for each base B present in the reaction mixture. The Brönsted relation derived from k_3°, k_4°, and k_5° does not differ sensibly from equation (7), and leads to the values of k_B° given in Table 3 (for ammonia the rate coefficient for *carbonate* formation should equal k_1°). The expected contribution to C from catalysis by B, *viz.*, C(B), is compared in Table 4 with the difference between the observed value of C and that calculated from equation (4), ΔC, for a number of bases which are present in

TABLE 3. *Base strength and rate coefficients for reaction with cyanic acid, at* 60·10°.

Base	p	q	K_a	k° (obs.)	k° (calc.) *
$\mathrm{OH^-}$	1	1	$9{\cdot}62 \times 10^{-14}$	2200	2840
$\mathrm{CO_3^{2-}}$	1	3	$7{\cdot}24 \times 10^{-11}$	389	466
$\mathrm{NH_3}$	1	1	$5{\cdot}07 \times 10^{-9}$	99·2	47·4
$\mathrm{H_2O}$	1	1	1·00	0·0270	0·0357
$\mathrm{NEt_3}$	1	1	$1{\cdot}50 \times 10^{-10}$	—	178
$\mathrm{H_2BO_3^-}$	3	1	$9{\cdot}24 \times 10^{-10}$	—	136
$\mathrm{NCO^-}$	1	1	$2{\cdot}00 \times 10^{-4}$	—	0·88
$\mathrm{HCO_3^-}$	2	2	$5{\cdot}19 \times 10^{-4}$ †	—	1·24

* From equation (7). † This is 1000 times the generally accepted value of the first dissociation constant of carbonic acid.[23]

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

† This agreement was obtained by taking $\{\mathrm{H_2O}\} = 1$, a reasonable procedure in view of the suggestion [21] that the " effective " concentration of water molecules is between 0·13 and 55·5. The more general procedure of taking $\{\mathrm{H_2O}\} = [\mathrm{H_2O}]$ leads to the prediction of too high a catalytic constant for hydroxide ions, in agreement with other observations.[22]

[20] Brönsted and Pedersen, *Z. phys. Chem.*, 1924, **108**, 185; Brönsted, *Chem. Rev.*, 1928, **5**, 332; Bell, " Acid-Base Catalysis," Clarendon Press, Oxford, 1941, p. 85.

[21] Bell, *Trans. Faraday Soc.*, 1943, **39**, 253; Bell and Higginson, *Proc. Roy. Soc.*, 1949. **197**, *A*, 141.

[22] *Idem, op. cit.*, ref. 20, p. 93.

[23] Roughton and Booth, *Biochem. J.*, 1938, **32**, 2049; Olson and Youle, *J. Amer. Chem. Soc.*, 1940, **62**, 1027.

reaction mixtures but do not appear in this equation : $C(HCO_3^-)$ is not quoted, but it is always very small. It can be seen that the catalytic constants employed in the calculation of C(B) are considerably too large when B = NH_3, NEt_3, $H_2BO_3^-$, or NCO^-. Admittedly k_B° calculated from equation (7) may be subject to error but this error should not be as large as a factor of 100, and an error in the same direction for four such widely different bases would be highly fortuitous. It seems much more likely that this relation between base strength and the rate coefficients is a specific one which does not apply to all bases.

TABLE 4. *Base catalysis in carbonate formation at* 60·10°.

(Ionic strength 0·25, concentrations in 10^{-4} mole $l.^{-1}$, t in sec.)

Run 1 : initially 0·0521M-NH_4NCO.

$10^{-1}t$	0	166	242	319	437	630	846	1008	1176	1686	2622	3150
Cy	521	454	427	411	380	340	321	285	265	213	165	147
C (obs.)	3	16	17	21	25	28	31	33	35	44	47	49
ΔC	—	+2	−1	+1	+1	+1	0	−1	0	+3	0	−1
$C(NH_3)$	—	52	71	89	113	146	178	198	216	256	306	326
$C(NCO^-)$	—	23	26	29	32	35	38	39	40	43	45	46

Run 20 : initially 0·0499M-NaNCO + 0·0075M-NEt_3.

$10^{-2}t$	0	97	221	434	551	702	823	1020	1297	1529	1702	2160
Cy	494	487	481	469	461	447	436	417	390	367	344	278
C (obs.)	5	12	18	30	38	50	59	74	98	119	138	185
ΔC	—	+2	+1	0	0	+2	+2	+1	+2	−1	0	−1
$C(NEt_3)$	—	2	4	8	11	15	18	22	29	34	38	49

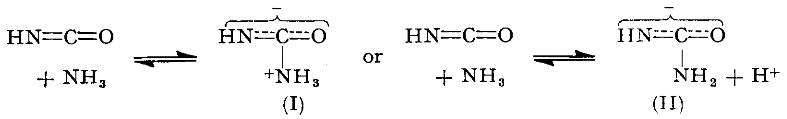
Run 21 : initially 0·0504M-NaNCO + 0·0153M-H_3BO_3.

$10^{-2}t$	0	115	238	415	549	718	984	1283	1506	1625	1837	2147	2366
Cy	485	463	439	396	369	335	282	215	178	161	134	96	80
C (obs.)	18	31	45	73	90	114	151	193	219	231	251	276	289
ΔC	—	−2	−2	+3	−3	+4	+4	+6	−3	+5	+5	+4	+3
$C(H_2BO_3^-)$ ...	—	45	88	140	172	207	250	283	302	309	321	334	340

Alternatively, equation (5) can be considered to imply reactions of cyanate ions with acids. The " best " Brönsted relation for acid catalysis predicts the rate coefficients $(k')^\circ$ 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]



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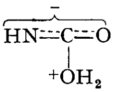
[24] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 201.

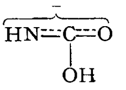
[25] Lowry, *Trans. Faraday Soc.*, 1934, **30**, 375; Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.

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.



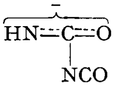
$\overset{-}{\overbrace{HN{=}C{=}O}}$ with $^{+}OH_2$ on C

(III)



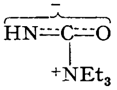
$\overset{-}{\overbrace{HN{=}C{=}O}}$ with OH on C

(IV)



$\overset{-}{\overbrace{HN{=}C{=}O}}$ with NCO on C

(V)

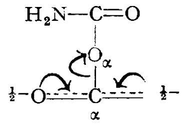


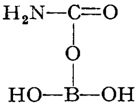
$\overset{-}{\overbrace{HN{=}C{=}O}}$ with $^{+}NEt_3$ on C

(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 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 protonated addition complex (VII), the amide group repels electrons less strong than the carboxylate-ion group. Electron shift thus favours the heterolysis of the C_α–O_α linkage, and leads to a carbamate ion and carbon dioxide. In (VIII), however, the corresponding process is much less likely; the hydroxy-groups are less powerful electron donors and the products of the bond-rupture now carry opposite charges. These considerations apply even more strongly to an addition complex of cyanic acid with a metaborate ion.

(VII)





$H_2N—C({=}O)—O—B(OH)—OH$

(VIII)

The proposed reaction mechanism shows many analogies with other carbonyl addition reactions, but it appears that the hydration of cyanic acid (which would lead to carbamic acid by rapid proton transfer) is not subject to general acid–base catalysis, unlike the hydration of acetaldehyde.[29] A reaction similar to *carbonate* formation, the conversion of aryl *iso*cyanates into urethanes, is catalysed by tertiary bases, and it has been proposed that here an addition complex analogous to (VI) reacts with an alcohol molecule.[28] This conclusion is not necessarily incompatible with our view that such a reaction is extremely rare in the present systems. The earlier work was carried out in poorly ionising solvents containing small quantities of alcohol, and the more highly associated solvent and less stable addition complex of the present study are likely to favour the return of the complex to the initial reactants, rather than its solvolysis.

EXPERIMENTAL

Materials and Rate Measurements.—Sodium cyanate (B.D.H., Commercial) was purified by recrystallisation from water at 0°, a large first fraction being discarded; the dried product

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[26] Davis and Ebersole, *ibid.*, 1934, **56**, 885.

[27] Naegeli, Tyabji, and Conrad, *Helv. Chim. Acta*, 1938, **21**, 1127.

[28] Baker and Holdsworth, *J.*, 1947, 713; Baker and Gaunt, *J.*, 1949, 9, 19, 27.

[29] Bell and Darwent, *Trans. Faraday Soc.*, 1950, **46**, 34.

contained less than 0·5% of *carbonate,* and no detectable cyanide. Ammonium cyanate was prepared in 0·5M-solution by shaking ammonium chloride (" AnalaR ") with a slight excess of silver cyanate (from urea and silver nitrate) till the supernatant liquid gave only a very faint reaction for chloride; the *carbonate* content of the solution was never greater than 1% of the ammonium cyanate. Barium cyanate was prepared in solution by adding the nitrate to sodium cyanate. Urea (" AnalaR ") was recrystallised twice from ethanol; m. p. 132° (no detectable biuret). Commercial acetone was purified by Conant and Kirner's method.[30] All other materials were commercial products of good purity. " Equilibrium " water was employed in all the solutions, and also as the solvent in the kinetic experiments.

Rates were measured at 60·10° and 80·10° in conventional thermostats (±0·02°). Reaction mixtures were made up at 0°. Ammonia, boric acid, triethylamine, sodium carbonate, sodium hydrogen carbonate, or sodium hydroxide were added (in the form of standard solutions) to some of the reaction mixtures. The ionic strength was adjusted by addition of potassium nitrate to be 0·25 at the reaction temperature, and the cyanate concentration was never greater than 0·055M. 3·75 ml. samples, at 0°, were pipetted into glass tubes which were sealed off so that the free space occupied the same volume as the liquid. The tubes were introduced, with shaking, into the thermostat and removed from time to time, rapidly cooled to −80°, and their contents analysed. The first tubes, which were considered to refer to " zero time," were removed when the solution had attained thermostat temperature (after 2—3 min.), or when enough *carbonate* had been formed to allow of the calculation of [OH⁻] with some certainty (cf. p. 909).

Analytical.—The reactions were followed by analysing for $2C + Cy$, and Cy or C, where C and Cy are the *carbonate* and *cyanate* concentrations, respectively. The stoicheiometric equation (i) and (ii) (p. 900) then show that at any stage of the reaction

$$\mathrm{U} - \mathrm{U}_0 = -(Cy - Cy_0) - (C - C_0)$$

$$N - N_0 = (Cy - Cy_0) + 2(C - C_0)$$

where U and N are the urea and *ammonium* concentrations, respectively, and the subscript refers to " zero time." U_0 was obtained by analysing the reaction mixture before its immersion in the thermostat, and assuming that this contained no urea. Similarly, when no *ammonium* had been added, N_0 was obtained by assuming that all *carbonate,* other than any added, initially, resulted from reaction (i).

(a) *Determination of* 2C + Cy. In the presence of a large excess of acetone, substances which are weak acids in water do not interfere in the titration of hydrochloric acid with alkali. Thus the addition of excess of this acid, followed by back-titration, gave the total basicity of the solution, X (in g.-equiv. l.$^{-1}$). This quantity is independent of any acid–base equilibria which are set up in the reaction mixture, as these merely result in the formation of equivalent amounts of one base from another. Allowing for all the added substances employed, we can therefore write

$$X = 2C + Cy + [\mathrm{NH_3}]_\mathrm{i} + [\mathrm{NEt_3}]_\mathrm{i} + [\mathrm{OH^-}]_\mathrm{i} - [\mathrm{HCO_3^-}]_\mathrm{i}$$

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:

$$Y = 2C + [\mathrm{NH_3}]_\mathrm{i} + [\mathrm{NEt_3}]_\mathrm{i} + [\mathrm{OH^-}]_\mathrm{i} - [\mathrm{HCO_3^-}]_\mathrm{i}$$

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*

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[30] Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 245.

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. 910. 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 :

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

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

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

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

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

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

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

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

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

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

Allowing for all the substances which were added to reaction mixtures, we then have

$$\begin{aligned}[OH^-] = [HCO_3^-] + 2([H_2CO_3] + [CO_2(g)]) - [NH_3] + [HNCO] + [H_3O^+] - [H_3O^+]_i \\ + [OH^-]_i + [Et_3NH^+] - [H_2BO_3^-] - [HCO_3^-]_i + [NH_3]_i \quad . \quad (9)\end{aligned}$$

where, in the absence of added hydroxide ions, $[OH^-]_i$ and $[H_3O^+]_i$ are the values corresponding to " equilibrium " water.

When no barium ions are present, this equation takes the form

$$\begin{aligned}N = \frac{1 + K_{iv}[OH^-]}{K_{iv}[OH^-]}\Bigg\{\frac{[OH^-]K_v + 2(1 + K_{vii})K_{vi}}{[OH^-]^2 + [OH^-]K_v + (1 + K_{vii})K_{vi}}C - [OH^-] + \frac{K_{iii}}{K_{iii} + [OH^-]}Cy + \frac{K_{viii}}{[OH^-]} \\ - \frac{K_{viii}}{[OH^-]_i} + [OH^-]_i + \frac{K_{ix}}{K_{ix} + [OH^-]}[NEt_3]_i - \frac{K_x[OH^-]}{1 + K_x[OH^-]}[H_3BO_3]_i - [HCO_3^-]_i + [NH_3]_i\Bigg\}\end{aligned}$$

where K_{iii}, K_{iv}, etc., are the equilibrium constants (in concentration units) of processes (iii), (iv), etc., respectively, with terms in $[H_2O]$ included in the constants. Graphical methods were employed to solve this equation for $[OH^-]$, the only unknown parameter. This was less tedious

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[31] Werner, *J.*, 1923, **123**, 2577.

than might appear, for several of the terms only enter when the appropriate additions have been made, and some of the others could be neglected without error under the experimental conditions.

In the decomposition of barium cyanate the concentration of *carbonate* in the solution is controlled by the solubility of its barium compound. No acids or bases were added in these experiments, and equation (9) can be written in the form

$$N = \frac{(1 + K_{\text{iv}}[\text{OH}^-])K_{\text{v}}K_{\text{xi}}}{K_{\text{iv}}[\text{OH}^-]^2[\text{Ba}^{++}]}$$

where all negligible terms have been omitted. A correction was, however, necessary before the concentrations of the various species could be calculated. The analytical methods assumed that carbonate precipitation was complete, and the " observed " values of N and C are therefore too small, and those of Cy too large, by an amount $[\text{HCO}_3^-]$, as virtually all the *carbonate* in solution is in the form of bicarbonate ions under the existing experimental conditions. The " observed " value of N was employed to obtain a preliminary value of $[\text{OH}^-]$ and hence a preliminary value of $[\text{HCO}_3^-]$. The resulting " improved " N led to " improved " $[\text{OH}^-]$ and $[\text{HCO}_3^-]$ values, and the process was repeated till constant values were obtained.

The constants K_{iii}, K_{iv}, etc., were obtained from published thermodynamic equilibrium constants (extrapolated to our reaction temperatures where necessary) and the ionic activity coefficients at ionic strength 0·25. Their values are given below; f_1 and f_2 are the activity coefficients of uni- and bi-valent ions, respectively.

Temp.	f_1	f_2	$10^{10}K_{\text{iii}}$	$10^{-4}K_{\text{iv}}$	10^4K_{v}	$10^{10}K_{\text{vi}}$	K_{vii}	$10^{13}K_{\text{viii}}$	10^3K_{ix}	$10^{-3}K_{\text{x}}$	10^7K_{xi}
60·10°	0·705	0·240	4·81	2·62	6·41	1·19	3·0	1·936	1·29	9·62	1·87
80·10°	0·686	0·222	12·6	2·80	15·7	8·27	3·5	5·357	—	—	—

Rate Coefficients.—k_2 was obtained from studies of the decomposition of urea solutions; the first-order rate law applies over the first 10—12 hr., as the reactions of the cyanate produced do not contribute significantly to the overall rate during this period. Details of a typical run are given below :

t (hr.)	0	1·92	2·63	4·83	7·84	12·2
10^4Cy	0	1·9	2·6	4·4	7·1	11·0
10^7k_2 (sec.$^{-1}$)	—	2·79	2·78	2·56	2·55	2·54

The lack of precision of k_2 does not have a corresponding effect on the reliability of the other rate coefficients. These were obtained from the results observed in the decomposition of cyanates where the term in k_2 is responsible for only a small part of the rate of urea formation.

Once k_2 has been determined, k_1' is the only unknown parameter in equation (1) and can be obtained from its integrated form :

$$k_1' = \frac{\text{U} - \text{U}_0 + k_2\int_0^t U\,.\,\text{d}t}{\int_0^t [\text{NH}_4^+][\text{NCO}^-]\,.\,\text{d}t}$$

The integrals were evaluated graphically.

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 $\beta = \int_0^t [\text{H}_3\text{O}^+][\text{NCO}^-].\text{d}t$, $\gamma = \int_0^t [\text{NCO}^-].\text{d}t$, and $\delta = \int_0^t [\text{HCO}_3^-][\text{NCO}^-].\text{d}t.[\text{H}_3\text{O}^+]$ 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 $[\text{H}_3\text{O}^+]$ 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,[32] 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%.

[32] Davies, *J.*, 1938, 2093.