516. *The Decomposition of Ionised Cyanates in Aqueous Solution. Part II.* Kinetic Studies on the Isomerisation of Alkylammonium Cyanates.*

By P. Johncock, G. Kohnstam, and D. Speight.

The formation of alkylureas from aqueous alkylammonium cyanates is considered to occur by nucleophilic addition of the conjugate amine to cyanic acid. There is no relation between the base strength and the rate, and the results suggest that C–H bonds attached to the nitrogen atom of the amine stabilise the transition state by hyperconjugative electron-release which is relayed to the reaction centre by the inductive mechanism.

Ionised cyanates decompose in water to give *carbonate* † and urea; when alkylammonium ions are present, substituted ureas are also formed. Bearing in mind that the reactants and products will participate in the usual acid–base equilibria, these processes can be represented by the stoicheiometric equations:

$$NCO^- + 2H_2O \rightleftharpoons CO_3^{2-} + NH_4^+ \quad \text{(i)}$$

$$NCO^- + NH_4^+ \rightleftharpoons (NH_2)_2CO \quad \text{(ii)}$$

$$NCO^- + NRR'H_2^+ \longrightarrow NRR'{\cdot}CO{\cdot}NH_2 \quad \text{(iia)}$$

where R and R′ are alkyl or H. The kinetics of reactions (i) and (ii) were discussed in Part I where it was proposed that a molecule of cyanic acid, and not a cyanate ion, is concerned in each of the various rate-determining steps. There is no reason for supposing that this does not also apply in reaction (*iia*), and we now report a kinetic study of the isomerisation of some alkylammonium cyanates in water. Some of the present systems

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* The paper, *J.*, 1956, 900, by Kemp and Kohnstam, is to be regarded as Part I of this series.

† Throughout this paper the italicised terms *carbonate, cyanate, ammonium,* and *alkylammonium* are used collectively and refer to the total amounts in which these substances can be shown to be present.

were investigated many years ago by Walker and Appleyard,[1] but a repetition of their work seemed desirable since several of their assumptions can no longer be justified. A few of the reactions have also been studied in 98% ethanol,[2] but an interpretation of the results is difficult as we do not know the proportions of the reactants which are in the form of their conjugate acids and bases.*

Rate measurements were carried out at 60·10° on *ca.* 0·05M-aqueous alkylammonium cyanate which had been made slightly alkaline ($[OH^-]$ varied in the range 3×10^{-5} to 5×10^{-4}). The initial ionic strength was adjusted to 0·25 by the addition of potassium nitrate; changes in ionic strength during any one kinetic run were then small enough to permit the use of concentration units in the rate equations. Rate coefficients were obtained from equation 1 which had already been found to predict the rate of formation of urea over a wide range of pH (Part I):

$$d[NRR'{\cdot}CO{\cdot}NH_2]/dt = k_1'[NRR'H_2^+][NCO^-] - k_2[NRR'{\cdot}CO{\cdot}NH_2] \quad . \ . \ . \ . \ . \ . \quad (1)$$

The second term gives the rate of the retrograde step, but it was only necessary to determine this for the reactions of the dimethyl and diethyl compounds (see p. 2550) where k_2 was obtained from independent measurements on the alkyl-ureas.

Walker and Appleyard [1] studied the reactions in 0·1M-solutions, no other substances being added. Their data at *ca.* 60° are compared below with the present results, the earlier figures in parentheses (k_1' in sec.$^{-1}$ mole^{-1} l., k_2 in sec.$^{-1}$):

$NRR'H_2^+$	NH_4^+	$NMeH_3^+$	$NMe_2H_2^+$	$NEtH_3^+$	$NEt_2H_2^+$
$10^3k_1'$	1·250 (2·40)	1·695 (2·23)	3·202 (4·22)	1·116 (1·35)	1·052 (1·50)
10^6k_2	0·262 (0·63)	—	1·15 (12·2)	—	3·65 (24·7)

The smaller values now observed for k_1' are consistent with the neglect of *carbonate* formation by reaction (i) in the previous work (cf. Part I and ref. 3), and with the lower and variable ionic strength of the solutions then employed. It is noteworthy that the discrepancy is greatest for ammonium cyanate, where we would also expect the most *carbonate* formation since the ammonium ion is a considerably stronger acid than its alkyl-substituted derivatives and therefore yields solutions of lower pH.† The other four cations have roughly the same acid strengths, and the earlier values differ from ours by an almost constant factor. It was therefore assumed that the same factor applies to *iso*- and *tert.*-amylammonium ions (which were not studied in the present work) and the corrected data for these species have been included in Table 1 where our main results are summarised. The large discrepancies in the k_2's probably result from the fact that the earlier values were obtained from k_1 at 60° and the equilibrium constant at 100°.

Equation 1 can also be written in the form

$$d[NRR'{\cdot}CO{\cdot}NH_2]/dt = k_1[NRR'H][HNCO] - k_2[NRR'{\cdot}CO{\cdot}NH_2] \quad . \ . \ . \ . \ . \ . \quad (2)$$

where $k_1 = k_1'K_{iv}/K_{iii}$, $K_{iii} = [HNCO][OH^-]/[NCO^-]$ and $K_{iv} = [NRR'H_2^+][OR^-]/NRR'H$. The values of these equilibrium constants at ionic strength 0·25 are given in the Experimental section (p. 2550). K_{iii}, and K_{iv} for the amines containing branched alkyl groups, are not accurately known at our reaction temperature, and each k_1' is therefore more reliable than the corresponding k_1. However, any error in K_{iii} does not affect a

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* A change from water to 98% ethanol, a poorer ionising solvent, will greatly decrease the dissociation constant of cyanic acid, but will have a very much smaller effect on the dissociation constant of ammonium ions. The equilibrium $NH_4^+ + NCO^- \rightleftharpoons NH_3 + HNCO$ will therefore move to the right, and appreciable amounts of cyanic acid may be present. Unfortunately the dissociation constant of this acid in 98% ethanol is not known.

† The rate law for *carbonate* formation contains a kinetic term involving the hydrogen-ion concentration (see equation 3 of Part I).

[1] Walker and Appleyard, *J.*, 1896, **69**, 193.

[2] Miller and Nicholson, *Proc. Roy. Soc.*, 1938, **168**, *A*, 206.

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

comparison of the k_1's for the various compounds. Errors in K_{iv} also influence the value of k_1' ($[NRR'H_2^+]$ depends on this constant), but the effect is only small since nearly all the ***alkylammonium*** is in the acid form under our experimental conditions.

TABLE 1. *Specific rates* (*in* $sec.^{-1}$ $mole^{-1}$ *l.*) *for the formation of carbamides in water at* 60·10°.

NRR'H	$10^{-9}/K_a$ *	n_β †	$10^3k_1'$ ‡	$10^{-2}k_1$	k_1/k_1 (calc.) §
NH_3	0·182	0	1·250 ϕ	0·915	1·9
NBu^tH_2	3·76	0	0·140	2·12	1·5
NAm^tH_2	3·76	0	0·165 □	2·50	1·7
NPr^iH_2	3·76	1	0·618	9·37	6·5
$NEtH_2$	3·76	2	1·116	16·9	11·8
NAm^iH_2	3·76	2	1·12 □	17·0	11·9
$NMeH_2$	3·43	3	1·695	23·4	16·8
NEt_2H	8·93	4	1·052	37·8	19·0
NMe_2H	5·78	6	3·202	77·8	46·2

* The base strength; K_a is the thermodynamic dissociation constant of $NRR'H_2^+$. † The number of C–H bonds directly attached to the central nitrogen atom. ‡ At ionic strength 0·25. § k_1 (calc.) from equation 3. ϕ Part I. □ From Walker and Appleyard's data [1] (see p. 2545).

The two alternative rate coefficients, k_1' and k_1, are given in Table 1 for the compounds now investigated. It can be seen that the base strength of the amine is certainly not the principal factor controlling the rate. The values of k_1' follow no simple sequence, but k_1 seems to depend mainly on the number of C–H bonds attached to the nitrogen atom of the amine, n_β; within the limits of experimental error, amines having the same n_β also have the same k_1.

In Part I we assumed that urea and carbonate formation proceed by the addition of bases to cyanic acid. The appropriate rate coefficients for the four reactions involved are then predicted to within a factor of two by the Brönsted equation for base catalysis [4] in the form:

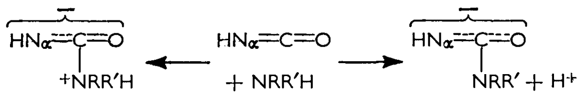
$$\log_{10}(k^\circ/q) = -1{\cdot}447 + 0{\cdot}3764 \log_{10}(p/qK_a) \quad . \quad . \quad . \quad . \quad (3)$$

where k° is the rate coefficient at zero ionic strength for reaction with 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. For the addition of amines to cyanic acid $k^\circ = k_1$, and the present values of k_1 are compared with those calculated from equation 3 in the last column of Table 1. It can be seen that this equation predicts the rates for *tert.*-amylamine and *tert.*-butylamine as well as can be expected, but the calculated values for the other amines are much too small; k_1/k_1 (calc.) increases with increasing n_β.

DISCUSSION

By analogy with the mechanism proposed in Part I for the formation of urea, the present reactions can be considered to involve nucleophilic addition of the amine to cyanic acid by one of the following two processes:

(I)



(II)

Rapid proton-transfer [prototropic change in (I) or proton addition to (II)] then yields

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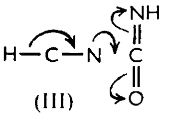
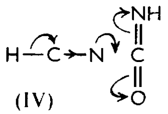
[4] Brönsted and Pedersen, *Z. phys. Chem.*, 1924, **108**, 185; Brönsted, *Chem. Rev.*, 1928, **5**, 332; Bell, "Acid–Base Catalysis," Clarendon Press, Oxford, 1941, p. 85.

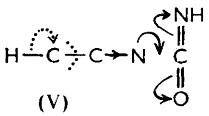
the alkyl-urea, and k_1 therefore represents the specific rate of the slow reaction stage.* A detailed discussion of our results is given below, but it is worth noting now that we have been unable to visualise any other acceptable scheme which is consistent with the figures in Table 1 and with the observation that the kinetics of urea formation are accurately predicted by equation 1 over wide ranges of pH and concentration (Part I).

It has been suggested that the base strength of an amine may control its rate of reaction with cyanic acid, apart from complications caused by steric effects.[5] Our results do not confirm this view; the values of k_1 show no relation with the base strength (see Table 1), and an examination of scale-models with $\angle N_\alpha CO = 120°$, and calculations assuming $\angle N_\alpha CO = 180°$,[6] reveal no significant steric compressions in either (I) or (II). There are, however, considerable similarities with other reactions involving nucleophilic attack by amines. In ethereal solution, alkylamines with $n_\beta = 2$ react with phenyl *iso*cyanate at the same rate, and about ten times more rapidly than ammonia; [7] the corresponding factor in the present reactions is eighteen. The attack of amines on 1-chloro-2 : 4-dinitrobenzene follows the rate sequence dimethylamine > piperidine > methylamine,[8] but the base strength decreases in the order piperidine > dimethylamine > methylamine. Steric hindrance is not envisaged in these reactions,[8] and the rates decrease with decreasing n_β, as in the present systems.

Passage into the transition state of amine addition to cyanic acid requires a displacement of the lone-pair electrons on the central nitrogen atom in the direction further away from the rest of the molecule, and thus results in a demand for electrons at the reaction centre. All the amines now considered have roughly the same base strength, steric effects have already been excluded, and it therefore seems reasonable to assume that the different reactivities arise from differences in the constitutional ability to stabilise the transition


(III)


(IV)


(V)

state by electron-release. Such a release of electrons is quite feasible in view of the polarisability of C–H bonds by the hyperconjugative mechanism † when linked to a suitably situated electron-demanding centre. Full hyperconjugation with the reaction centre (III) is considered unlikely as this would offend the principle of octet preservation,‡ but

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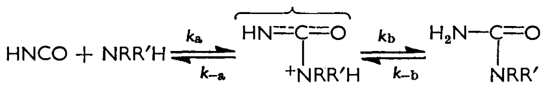
* The validity of this statement can be readily demonstrated. The proposed reaction scheme is:



$$\mathrm{HNCO} + \mathrm{NRR'H} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \underset{{}^{+}\mathrm{NRR'H}}{\mathrm{HN{=}\overset{|}{C}{=}O}} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} \underset{\mathrm{NRR'}}{\mathrm{H_2N{-}\overset{|}{C}{=}O}}$$

There is no evidence that the intermediate addition complex ever reaches detectable concentrations, and the stationary-state principle will therefore apply to this species. If we assume that the equilibrium between cyanic acid and cyanate ions is not upset by the reactions a comparison of the theoretical rate law with equation 2 shows that

$$k_1 = \frac{k_b k_a}{k_{-a}(1 + k_b/k_{-a})} \text{ and } k_2 = \frac{k_{-b}}{1 + k_b/k_{-a}}$$

Now k_{-b} refers to the transfer of a proton from one nitrogen atom to another and is therefore most unlikely to be less than 10^{-2} sec.$^{-1}$. Since $k_2 \sim 10^{-6}$, $k_b/k_{-a} > 10^4$ and hence $k_1 = k_a$ with negligible error. The same conclusion is obtained if the cyanic acid concentration is calculated from the stationary-state approximation.

† Ingold's nomenclature [9] is employed throughout this discussion.

‡ It has, however, been postulated that quinquevalent nitrogen may exist under some conditions.[10]

[5] Frost and Pearson, " Kinetics and Mechanism," Chapman and Hall, London, 1952, p. 263.

[6] Baker and Holdsworth, *J.*, 1947, 713.

[7] Davies and Ebersole, *J. Amer. Chem. Soc.*, 1934, **56**, 885.

[8] Brady and Cropper, *J.*, 1950, 507.

[9] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, ch. II.

[10] Gillespie, *J.*, 1952, 1002.

it has been pointed out that hyperconjugation must also involve participation by the valence-bond structure corresponding to the simple ionisation of C–H.[11] A part of this type of electron-displacement can be relayed to an adjacent atom by the inductive mechanism. Thus, a C–H bond in (IV) can respond to electron-demand at the reaction centre and therefore stabilises the transition state, but the poor relay of inductive effects along saturated carbon–carbon systems makes the stabilising effect of such a bond in (V) extremely small, if not negligible. On this view, the number of C–H bonds attached to the central nitrogen atom of the amine should control its rate of reaction with cyanic acid, *i.e.*, k_1 should increase with increasing n_β, as observed. The similar observations in those reactions of amines with 1-chloro-2 : 4-dinitrobenzene which are not sterically hindered can be explained in the same manner.

tert.-Butylamine and *tert.*-amylamine react at rates which are predicted as well as can be expected by the Brönsted equation for base catalysis (equation 3). None of the groups in these two bases or the four which were employed in Part I to set up this equation (water, ammonia, hydroxide ions, and carbonate ions) is polarisable with respect to electron-demand at the reaction centre, and it is then reasonable to expect a linear relation between the free-energy of activation for addition to cyanic acid and the standard free-energy change for protonation, as observed. It has, however, been noted before (cf. ref. 12) that the Brönsted equation may not apply when polarisable groups are present—the electron displacements in the conjugate acid need not now parallel those in the transition state of another reaction—and the observation (Table I) that k_1/k_1 (calc.) increases with increasing n_β suggests that polarisable groups in an amine stabilise the transition state of the addition reaction more than they stabilise the corresponding alkylammonium ion. This conclusion is to be expected if this transition state is associated with the greater electron-demand at the central nitrogen atom.

The present results are fully consistent with the view that the formation of urea and its substituted derivatives involves addition to cyanic acid in the rate-determining step. Further work is, however, required before it can be established whether the activation process requires proton loss by the amine (process II), or not (process I). The former process would be retarded by electron-releasing substituents, but the observed accelerating effect of such groups merely indicates that the formation of the N–C bond is more important than the fission of the N–H bond.

EXPERIMENTAL

Materials and Rate Measurements.—Alkylammonium chlorides were obtained in a sufficient state of purity by the recrystallisation of commercial products, or by the action of dry hydrogen chloride on the ethereal solution of the amines; the final products never contained more than 0·3% of amine or hydrochloric acid. Alkylammonium cyanates were prepared in 0·5M-solution by shaking the chlorides with a slight excess of silver cyanate; for details, see Part I.

NN-Dimethylurea was prepared by treating pure sodium cyanate with dimethylammonium chloride in water, removing the solvent under reduced pressure, and recrystallising the product from methanol. *NN*-Diethylurea was obtained by analogous methods and recrystallised from ether.

Acetone was purified by Conant and Kirner's method,[13] and all distilled water used in the experiments was passed through a mixed-resin exchange column and equilibrated with respect to atmospheric carbon dioxide.

Rates were measured at 60·10° (±0·02°) by the sealed-tube technique. Reaction mixtures were made up by volume at 0° to contain *ca.* 0·05M-cyanate, 0·002—0·004M-sodium hydroxide, and sufficient potassium nitrate to bring the initial ionic strength to 0·25 at the reaction temperature. All the cyanates were studied at two or more different sodium hydroxide concentrations. The reactions were followed by determining the total basicity,

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[11] Hine, " Physical Organic Chemistry," McGraw-Hill, New York, 1956, p. 22.

[12] de la Mare and Vernon, *J.*, 1956, 41.

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

$X = Cy + 2C + [\mathrm{OH^-}]_i$ (g.-equiv. l.$^{-1}$), and the basicity after all the cyanate had been removed, $Y = 2C + [\mathrm{OH^-}]_i$, where Cy and C are the *cyanate* and *carbonate* [*] concentrations, respectively, and $[\mathrm{OH^-}]_i$ represents the concentration of the added hydroxide ions before any reaction with the acids present. For details, see Part I.

Calculations.—The stoicheiometric equations (i), (ii),[†] and (ii*a*) show that at any stage of the reaction

$$\left.\begin{aligned} N_0 - N = U - U_0 = (Cy)_0 - Cy + C_0 - C + U_0' - U' \\ \text{and} \qquad N' - N_0' = C - C_0 + U_0' - U' \end{aligned}\right\} \quad . \quad . \quad . \quad (4)$$

where N, N', U, and U' are the concentrations of alkylammonium, ammonium, substituted urea, and urea, respectively, and the subscript o refers to " zero time " (*i.e.*, the time of the first reading which was usually taken two or three minutes after immersion in the thermostat). N_0 and U_0 were obtained by analysing the reaction mixture before its introduction in the thermostat, and assuming that no reaction had taken place at this stage.

Our analytical procedure allows calculation of all the stoicheiometric concentrations provided $U' - U_0'$ is known. Unfortunately accurate determination of small amounts of urea in the presence of a considerable excess of its substituted derivatives is difficult, but urea formation is slow under the existing experimental conditions,[‡] and the term $U' - U_0'$ in equation (4) was therefore neglected in our calculations. In most cases this procedure has a negligibly small effect on the rate coefficients for the formation of the substituted ureas. The data in Table 2 show that in the decomposition of diethylammonium cyanate the urea concentration is always less than 0·3% of the diethylurea concentration, and even this figure represents an overestimate since it was obtained by assuming that $N' - N_0' = C - C_0$ at all stages of the reaction; the corresponding figures for methyl-, ethyl-, and dimethyl-ammonium cyanate are lower still. In the slower decompositions of *iso*propyl- and *tert.*-butyl-ammonium cyanate, however, urea formation makes a greater contribution to the overall reaction and its neglect leads to rate coefficients (for the formation of the substituted ureas) which are initially constant but decrease as the reaction proceeds. This effect is more pronounced for the *tert.*-butyl compound which reacts more slowly under our experimental conditions than any of the other compounds investigated. Rate coefficients for these two systems were obtained by extrapolation to " zero time."

The actual concentrations of the various species present in a reaction mixture can be obtained from the analytical results and the appropriate dissociation constants, provided the concentration of the hydroxide ions is known. Using methods analogous to those already described in Part I, and omitting terms which are negligible under the present experimental conditions, we have

$$[\mathrm{OH^-}]_i - [\mathrm{OH^-}] = \frac{[\mathrm{OH^-}]}{[\mathrm{OH^-}] + K_{iv}} \cdot N - \frac{K_v}{[\mathrm{OH^-}] + K_v} \cdot C + \frac{[\mathrm{OH^-}]}{[\mathrm{OH^-}] + K_{iv}'} \cdot N' \qquad (5)$$

where $K_{iv} = [\mathrm{NRR'H_2^+}][\mathrm{OH^-}]/[\mathrm{NRR'H}]$, $K_{iv}' = [\mathrm{NH_4^+}][\mathrm{OH^-}]/[\mathrm{NH_3}]$, and $K_v = [\mathrm{HCO_3^-}][\mathrm{OH^-}]/[\mathrm{CO_3^{2-}}]$. This equation can be solved graphically by assuming that $N' = C$. Under our experimental conditions, however, the last two terms then only make a very small contribution. If they are neglected, the resulting quadratic equation readily yields $[\mathrm{OH^-}] = [\mathrm{OH^-}]_i K_{iv}/(N + K_{iv} - [\mathrm{OH^-}]_i)$, since $(N + K_{iv} - [\mathrm{OH^-}]_i)^2 \gg [\mathrm{OH^-}]_i K_{iv}$, and hence $[\mathrm{NRR'H_2^+}] = N\{1 - [\mathrm{OH^-}]_i/(N + K)\}$. Errors resulting from this procedure increase as the reaction proceeds, but they are usually too small to have any significant effect on the integrated rate coefficients. For example, the data in Table 2 lead to the conclusion that $[\mathrm{NRR'H_2^+}]$ calculated directly from equation (5) is only 1% greater at 45% reaction than the value obtained by the approximate method, and only 2% greater at 60% reaction. Larger errors are to be expected in the slower reactions (*iso*propyl and *tert.*-butyl compounds) where $N' < C$ since significant urea formation now occurs. This accounts for the decreasing rate

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[*] See footnote, p. 2544.

[†] It is necessary to consider reaction (ii) since *carbonate* formation by reaction (i) also produces ammonium.

[‡] In alkaline solution only a small fraction of the *ammonium* is present as ammonium ions ($\mathrm{d}U'/\mathrm{d}t = k_1'[\mathrm{NCO^-}][\mathrm{NH_4^+}]$), and the *ammonium* concentration does not reach large values since $\mathrm{d}N'/\mathrm{d}t \leqslant \mathrm{d}C/\mathrm{d}t = k_3'[\mathrm{NCO^-}] + k_4'[\mathrm{H_3O^+}][\mathrm{NCO^-}] + k_5'[\mathrm{HCO_3^-}][\mathrm{NCO^-}]$ (Part I, equation 3).

coefficients observed in these systems since [OH⁻] calculated by the approximate method is now too small, resulting in too large a value for $[\mathrm{NRR'H_2^+}]$.*

Values for K_{iv} and K_{iv}' at 60° and ionic strength 0·25 were obtained from the thermodynamic dissociation constants of the conjugate acids,[14] the ionic product of water,[15] and the ionic activity coefficients given by Davies's equation; [16] the values are given below. Accurate data for the amines containing branched alkyl groups were not available at our reaction temperature and it was therefore assumed that K_{iv} had the same value as for ethylamine. This may represent a slight overestimate,[17] but errors in this direction do not affect the conclusions regarding the variation of k_1 with amine structure. The values for K_{iii} (see p. 2545) and K_{v} were the same as in Part I.

NRR'H	NH_3	$NMeH_2$	$NEtH_2$	NMe_2H	NEt_2H
10^4K_{iv}	0·352	6·63	7·28	11·2	17·3

$$10^{10}K_{\mathrm{iii}} = 4{\cdot}81,\ 10^4K_{\mathrm{v}} = 6{\cdot}41$$

Reaction Rates.—The rate coefficients k_1' were obtained from the integrated form of equation (1):

$$k_1' = \frac{U - U_0 + k_2\int_0^t U\,.\,\mathrm{d}t}{\int_0^t [\mathrm{NRR'H_2^+}][\mathrm{NCO^-}]\,.\,\mathrm{d}t}$$

The integrals were evaluated graphically. Neglect of the term in k_2 gave constant values of k_1' for methyl- and ethyl-ammonium cyanate and it was therefore assumed that here the decomposition of the substituted urea was too slow to affect the observed rate. For dimethyl and diethyl compounds, however, the neglect of this term led to decreasing values of k_1', but these became constant when this term was included; k_2 was determined from measurements on the substituted urea by the methods already described in Part I. Rate coefficients k_1 were obtained from the corresponding k_1' and the appropriate equilibrium constants.

TABLE 2. *Illustrating the decomposition of ethylammonium cyanate.*

Temp. = 60·10°; initial ionic strength = 0·25; $[\mathrm{OH^-}]_i = 0{\cdot}00384$; $10^4U_0 = 2{\cdot}5$; $C_0 = 0$. t in sec., k_1' in sec.⁻¹ mole⁻¹ l.

		10^4C				
$10^{-3}t$	10^2Cy	obs.*	calc.†	$10^2(U - U_0)$	$10^5U'$ ‡	$10^3k_1'$
0	$4{\cdot}46_5$	—	—	—	—	—
13·80	$4{\cdot}20_8$	0·6	0·7	$0{\cdot}25_1$	0·03	$1{\cdot}06_6$
18·00	$4{\cdot}11_3$	0·7	0·8	$0{\cdot}34_5$	0·06	$(1{\cdot}14_3)$
34·20	$3{\cdot}86_5$	1·5	1·5	$0{\cdot}58_5$	0·2	$1{\cdot}09_7$
63·60	$3{\cdot}49_9$	2·7	2·8	$0{\cdot}93_9$	0·6	$1{\cdot}05_9$
82·20	$3{\cdot}29_0$	3·5	3·5	$1{\cdot}14_0$	1·0	$1{\cdot}06_2$
109·2	$3{\cdot}05_3$	4·6	4·5	$1{\cdot}36_6$	1·5	$1{\cdot}04_7$
153·6	$2{\cdot}68_2$	6·1	6·0	$1{\cdot}72_2$	2·6	$1{\cdot}07_3$
180·6	$2{\cdot}52_0$	6·8	6·7	$1{\cdot}87_7$	3·2	$1{\cdot}07_3$
208·2	$2{\cdot}39_1$	7·7	7·6	$1{\cdot}99_7$	3·9	$1{\cdot}06_3$
238·8	$2{\cdot}25_1$	8·7	8·5	$2{\cdot}12_6$	4·6	$1{\cdot}06_2$
277·2	$2{\cdot}11_1$	9·7	9·6	$2{\cdot}25_7$	5·5	$1{\cdot}05_8$
327·0	$1{\cdot}95_2$	11·0	10·9	$2{\cdot}40_3$	6·7	$1{\cdot}05_6$
358·2	$1{\cdot}87_1$	11·6	11·7	$2{\cdot}47_8$	7·4	$1{\cdot}05_6$

$10^3k_1'$ (mean) = 1·064, a duplicate run ($[\mathrm{OH^-}]_i = 0{\cdot}00192$) gave 1·039.

* From the smoothed curve, C against t. † Part I, equation (3). ‡ Calculated from equation (1) by assuming $N' = C$.

Details of a typical run are given in Table 2 where it is also shown that *carbonate* formation follows the rate law proposed in Part I.

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* The decomposition of the substituted urea, which was not investigated for these systems, may also contribute to the decreasing rate coefficients.

[14] Everett and Wynne-Jones, *Proc. Roy. Soc.*, 1941, **177**, *A*, 499; Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 34.

[15] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, equation 15-3-6a.

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

[17] Personal communication from Dr. H. K. Hall, jun.

Errors in k_1 and k_1' resulting from the use of the Davies equation [16] in calculating the ionic activity coefficients have already been discussed in Part I. Any such errors will, however, have a negligible effect on the present comparison of the reactivities of a series of amines.

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