XXI.—*Transformation of the Alkylammonium Cyanates into the corresponding Ureas.*

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IT has been shown by Walker and Hambly (Trans., 1895, **67**, 746) that the production of urea from an aqueous solution of ammonium cyanate is not a case of simple transformation of one molecule into another, but that the law regulating the transformation is the law of a bimolecular action, the active molecules being in all probability ammonium ions and cyanic acid ions. To use Ostwald's notation, the equation which expresses the action is

$$NH_4^{\cdot} + CNO' = CO(NH_2)_2.$$
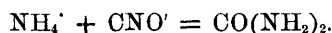
The velocity constant of the transformation is given by them for different temperatures, and in the present paper a comparison is effected between that constant and those obtained when the hydrogen atoms of the ammonium ion are replaced by alkyl radicles.

The experiments were all made with decinormal solutions, which were prepared in the manner described by Walker and Hambly. The alkylammonium chloride was agitated for an hour with excess of silver cyanate and the requisite quantity of water, after which the solution was filtered, and portions tested, with nitric acid and silver nitrate on the one hand, and with nitric acid and potassium chloride on the other, in order to prove the absence of soluble silver salt and soluble chloride respectively. By operating in this way, the solutions obtained were not always precisely decinormal, but in such cases the experimental numbers have been reduced to a uniform value by applying the very slight correction necessary, so that all the numbers given in the tables which follow are comparable with each other. Experiments were made at one temperature only, namely, at 59·6°, except when equilibrium points or reverse actions were being determined.

Ethylammonium Cyanate.

A decinormal solution of ethylammonium cyanate was heated at 59·6°, 5 c.c. of it being removed from time to time, and added to 5 c.c. of a decinormal solution of silver nitrate. After the mixture had cooled, the precipitated silver cyanate was filtered off, and the amount of silver in the filtrate determined by means of a N/50 solution of ammonium thiocyanate. In order to ascertain the point at which the action ceased, a decinormal solution of ethylurea was heated at 100°, and the amount of cyanate formed ascertained in the same way as in the direct action. The time which elapsed from the commence-

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ment of the heating is given in minutes under t, in the following table, the titres being given in the second column, and the actual concentration of the urea in the third.

t.	Titre.	Urea present.
0	25·0	0·1000
30	24·05	0·0962
80	23·6	0·0944
140	23·05	0·0922
200	22·95	0·0918
260	22·8	0·0912
320	22·9	0·0916

Ethylurea differs from urea in giving no perceptible quantity of carbonate when heated for a considerable time with water at 100°. After 260 minutes, the solution was found to possess a feeble ammoniacal smell, and a slight alkaline reaction, but it gave no precipitate with calcium nitrate. We are thus enabled to fix the end-point with accuracy, the concentrations for equilibrium being 0·0912 normal ethylurea, and 0·0088 normal ethylammonium cyanate.

Walker and Hambly found, for the direct transformation of ammonium cyanate, that the expression $\frac{1}{t} \cdot \frac{x}{E-x}$ remained constant, E being the end-point, and x the titre. This also holds good for ethylammonium cyanate, as may be seen from the following table.

Ethylammonium Cyanate. E $= 22·8$.

t.	x.	$E - x$.	$\frac{1}{t} \cdot \frac{x}{E-x}$.
30	4·95	17·85	0·0093
50	7·35	15·45	0·0096
70	9·1	13·7	0·0095
100	11·2	11·6	0·0097
130	12·6	10·2	0·0095
		Mean	0·0095

The value of the expression $\frac{1}{t} \cdot \frac{x}{E-x}$ for ammonium cyanate at 59·7° is 0·0144, the end-point being practically the same, namely, 22·9. It thus appears that the transformation of ethylammonium cyanate into ethylurea proceeds more slowly than the transformation of ammonium cyanate into ordinary urea, as a direct comparison of the titres at corresponding times will also show. The values of the constants in the above instance are nearly proportional to the rates at which the actions start, and this arises from the practical identity of the end-points. In the calculation, the progress of the reverse action

(transformation of urea into cyanate) has been neglected, but this neglect does not invalidate the comparison of the rates of the direct actions when the end-points have nearly the same value. When the end-points are widely apart, however, as they are in the case of other alkyl derivatives, the reverse action must be taken into account, if the comparison is to be of any value ; indeed, it is otherwise impossible to obtain a constant when the point of equilibrium is far removed from the urea end. This greatly complicates the calculation, but the expressions obtained give the true velocity constants.

If A is the original concentration of the cyanate expressed in terms of a normal solution, the active mass of the ammonium ions will be A, which is also the active mass of the cyanic ions, supposing the ammonium cyanate to be fully dissociated. This is not quite the case,* but as all the ammonium cyanates considered may be assumed to be equally dissociated in equivalent solutions, the comparison of the numbers obtained is not thereby affected. Let the quantity x have been transformed into urea at the time t; then the rate at which the direct reaction will proceed is

$$(1). \qquad \frac{dx}{dt} = k(A - x)^2.$$

But at the same time we have the reverse reaction proceeding according to the equation

$$(2). \qquad -\frac{dx}{dt} = k'x,$$

so that for the real progress of the action we have

$$(3). \qquad \frac{dx}{dt} = k(A - x)^2 - k'x.$$

At the equilibrium point, $\dfrac{dx}{dt} = 0$, therefore

$$k(A - \xi)^2 = k'\xi, \text{ or}$$
$$(4). \qquad K = \frac{k'}{k} = \frac{(A - \xi)^2}{\xi},$$

where ξ is the value of x at the point of equilibrium. K, the ratio of the velocity constants of the opposed reactions, is thus easily determined by means of the end-point experiment.

Substituting kK for k' in (3) we have

$$\frac{dx}{dt} = k\{(A - x)^2 - Kx\},$$

or
$$\frac{dx}{x^2 - (2A + K)x + A^2} = kdt.$$

* At the dilutions investigated, the degree of dissociation averages 90 per cent., with a variation from the mean of 4 per cent.

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Integrating the expression on the left hand side by partial fractions, and bearing in mind that for $t = 0$, $x = 0$, we obtain as the value of k,

$$\frac{1}{2t} \cdot \frac{1}{\sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}} \log_e \frac{A^2 - x\left(A + \frac{K}{2} - \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}{A^2 - x\left(A + \frac{K}{2} + \sqrt{\left(A + \frac{K}{2}\right)_2 - A^2}\right)}.$$

or, if we use decadic, instead of natural, logarithms,

$$(5).\ k = \frac{1 \cdot 15}{t\sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}} \log \frac{A^2 - x\left(A + \frac{K}{2} - \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}{A^2 - x\left(A + \frac{K}{2} + \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}.$$

The expression, although complicated, is sufficiently convenient for calculation in the form given. The value of k' is obtained from the equation $k' = Kk$.

In the case of ethylammonium cyanate, the value of A is 0.1, and of $\xi\ 0.0912$; so that from (4) we have

$$K = \frac{(0.1 - 0.0912)^2}{0.0912} = 0.00085.$$

If we now write the table for the transformation with the values of x in terms of a normal solution, and calculate the values of k by means of equation (5) we obtain it in the following form.

t.	Titre.	x.	k.
30	4·95	0·0198	0·081
50	7·35	0·0294	0·083
70	9·1	0·0364	0·082
100	11·2	0·0448	0·081
130	12·6	0·0504	0·079
		Mean........	0·081

The expression given in equation (5) is thus constant, the mean value of k being 0.081. For k' we have $0.081 \times 0.00085 = 0.000069$. These constants give the amounts transformed in one minute when the original concentration is normal, and is maintained at that value. Thus 8 per cent. of a normal solution of ethylammonium cyanate would be transformed into ethylurea in one minute at $59.6°$, if the concentration did not fall off as the action proceeded; whilst of a normal solution of ethylurea only 0.007 per cent. would be re-transformed into cyanate under the same conditions.

The value obtained for $\frac{1}{t} \cdot \frac{x}{E - x}$ in decinormal solution was 0.0095,

and this for a normal solution would become 0·095. It will be seen, therefore, that by neglecting the reverse action, the value of the simple constant is considerably greater than that of the real constant; and this divergence becomes more marked as the rate of the reverse action increases.

With ammonium cyanate itself, it is difficult to ascertain the actual constant k, because not only is there a reverse reaction, but a slow secondary transformation of cyanate into carbonate. Taking the "practical" end-point as the basis of calculation (Walker and Hambly, *loc. cit.*, 751), the values of the constant C is by the reverse action made greater than k, but by the subsidiary transformation it is made less than k. As these two disturbing influences nearly balance each other in amount, the observed value of C, namely $10 \times 0·0144 = 0·144$, must be very nearly equal to k, so that for the transformation of ammonium cyanate we may put $k = 0·144$. The real end-point (*loc. cit.*, 750) lies at 95 per cent., and so for ξ we have 0·095, and for K, $\dfrac{0·005^2}{0·095} = 0·000263$, giving us $k' = 0·144 \times 0·000263 = 0·000038$. These results show that whilst the transformation of the ethylammonium cyanate is more rapid than that of the ammonium cyanate, the reverse transformation of the ethylurea proceeds more slowly than is the case with urea itself.

Methylammonium Cyanate.

When a decinormal solution of methylurea is heated for half an hour at 100°, it gives on cooling only a faint turbidity with silver nitrate solution. The titre of the filtered solution (see p. 193) after heating for 120 minutes was found to be 23·9, and after 150 minutes, 24·0. The composition of the solution at the equilibrium point is thus 96 per cent. methylurea and 4 per cent. methylammonium cyanate, the value of ξ being, therefore, 0·096. For K, we have $\dfrac{0·004^2}{0·096} = 0·000166$.

Calculating the value of k from the formula given in equation (5) we obtain the following table from the experimental numbers for the direct transformation.

t.	Titre.	x.	k.
10	3·0	0·0120	0·141
20	5·3	0·0212	0·135
35	7·7	0·0308	0·129
50	9·9	0·0396	0·133
80	12·8	0·0512	0·132
110	14·9	0·0596	0·135
		Mean......	0·134

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The value of k' is $0.134 \times 0.000166 = 0.000022$. These numbers show that the direct transformation proceeds more rapidly in the case of methylammonium cyanate than in the case of the ethyl compound, the reverse being the fact for the retransformation of the corresponding ureas.

Diethylammonium] Cyanate.

Unsymmetrical diethylurea, $NH_2 \cdot CO \cdot NEt_2$, when heated at $100°$, gave the following numbers.

$t.$	Titre.	Urea present.
0	25·0	0·1000
60	19·15	0·0766
90	18·35	0·0734
170	17·7	0·0708
200	16·7	0·0668
260	16·7	0·0668

After three hours heating, the solution had acquired a faint ammoniacal smell and was alkaline to litmus paper. A very slight precipitate was obtained on the addition of calcium nitrate. The point of equilibrium in this case is much further removed from the urea end than in any of those previously considered, one-third of the urea having undergone transformation into diethylammonium cyanate. Calculating K from $\xi = 0.0668$ we obtain $K = \dfrac{0.0332^2}{0.0668} = 0.0165$.

For the direct transformation of decinormal diethylammonium cyanate at $59.6°$, the following values were obtained.

$t.$	Titre.	$x.$	$k.$
20	3·7	0·0148	0·088
35	5·8	0·0232	0·089
55	7·8	0·0312	0·087
80	9·8	0·0392	0·088
110	11·9	0·0476	0·097
		Mean........	0·090

The value of k' is $Kk = 0.0165 \times 0.090 = 0.00148$.

Whilst the constant for the direct transformation of the cyanate is not greatly different from the constant for the monethylammonium compound, namely 0.081, the constant of the reverse action is twenty times greater than the corresponding constant for monethyl urea, in consequence of the very different positions of the points of equilibrium in the two cases.

Dimethylammonium Cyanate.

A decinormal solution of unsymmetrical dimethylurea gave the following numbers on heating at 100°.

t.	Titre.	Urea present.
0	25·0	0·1000
30	23·8	0·0952
60	23·4	0·0936
90	22·8	0·0912
150	21·6	0·0864
210	21·1	0·0844
270	21·1	0·0844

After three hours heating, the solution had a feeble ammoniacal smell and gave no precipitate with calcium nitrate; after five hours the ammoniacal odour had greatly increased in intensity, and a slight turbidity with calcium nitrate was observed. The value of ξ is 0·0844, from which we obtain $K = \dfrac{0·0156^2}{0·0844} = 0·00288$.

The following table contains the results of the transformation of a decinormal solution of dimethylammonium cyanate at 59·6°.

t.	Titre.	x.	k.
20	8·2	0·0328	0·242
35	11·8	0·0472	0·260
45	13·0	0·0520	0·248
55	14·3	0·0572	0·253
75	16·2	0·0648	0·262
		Mean.........	0·253

For k' we have $Kk = 0·00288 \times 0·253 = 0·00073$.

Here the rate of the direct transformation is almost double that found for the monomethyl compound, and is indeed the greatest we have observed. The constant for the reverse action is no less than thirty times greater than that for the transformation of monomethylurea, but is still much less than the corresponding constant for unsymmetrical diethylurea.

Isoamylammonium Cyanate, $NH_3(CH_2 \cdot CH_2 \cdot CHMe_2)CNO$.

The urea prepared from this amylammonium cyanate melted at 88—89°, the melting point given by Custer (*Ber.*, 1879, **12**, 1330) being 89—91°. A decinormal solution yielded the following results at 100°.

t.	Titre.	Urea present.
0	25·0	0·1000
30	24·8	0·0992
90	24·3	0·0972
180	23·65	0·0946
270	23·6	0·0944

After five hours heating, the solution of the urea was slightly coloured, but had no ammoniacal smell, and gave no precipitate with calcium nitrate solution. The value of ξ being 0·0944, we have

$$K = \frac{0·0056^2}{0·0944} = 0·000334.$$

The results obtained for the transformation of the amylammonium cyanate at 59·6° were as follows.

t.	Titre.	x.	k.
40	7·2	0·0288	0·090
70	10·5	0·0420	0·100
100	12·1	0·0484	0·089
130	13·7	0·0548	0·090
175	15·6	0·0624	0·093
235	17·1	0·0684	0·090
		Mean........	0·092

For k' we obtain $Kk = 0·000334 \times 0·092 = 0·000031$.

The constants in this case resemble more closely those of the monethyl compounds than the constants of any of the other alkyl derivatives we have investigated.
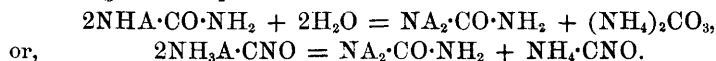
Tertiary Amylammonium Cyanate, $NH_3(CMe_2Et)\cdot CNO$.

Tertiary amylurea, melting at 155°, exhibited an abnormal behaviour when heated in decinormal aqueous solution at 100°. The titre, which at first diminished, after an interval of three hours reached a minimum, and then increased as the heating was prolonged.

t.	Titre.	Urea present.
30	21·1	0·0844
60	17·95	0·0718
90	16·2	0·0648
120	15·5	0·0620
150	14·8	0·0592
180	14·3	0·0572
200	15·1	0·0602?
230	15·5	0·0620?

The solution had acquired a pronounced ammoniacal smell after 90 minutes heating, and, after two hours, gave a very slight pre-

cipitate with calcium nitrate. When the minimum titre was reached, a light precipitate consisting of slender interlaced needles was observed to have separated from the solution, and this increased in bulk as the heating was continued. A small quantity of a white sublimate of similar appearance was also formed in the coldest part of the tube above the solution. Wurtz who first prepared tertiary amylurea (pseudo-amyleneurea) states that when tertiary amylammonium cyanate is treated with caustic potash it is converted into unsymmetrical tertiary diamylurea (pseudo-diamyleneurea; *Annalen*, 1866, **139**, 330). This substance he describes as being almost insoluble in water and extremely volatile, subliming to a network of light delicate needles. Its properties are, therefore, identical with those of the substance observed by us, which was probably formed according to the equations

$$2NHA \cdot CO \cdot NH_2 + 2H_2O = NA_2 \cdot CO \cdot NH_2 + (NH_4)_2CO_3,$$
or, $$2NH_3A \cdot CNO = NA_2 \cdot CO \cdot NH_2 + NH_4 \cdot CNO.$$

The ammonium cyanate, supposed to be produced in the second equation, might either appear as urea or as ammonium carbonate, more probably as the latter, as the rise in the titre would then be accounted for (compare Walker and Hambly, *loc. cit.*, 750). The abnormal course of the transformation renders the end-point uncertain, but the minimum value 0.0572 may be taken as an approximate value of ξ, an almost identical number having been obtained when the urea was transformed at $79.6°$.

Tertiary amylammonium chloride was prepared from the corresponding urea as follows. The urea was boiled with strong potash solution for several hours in a flask with condensing tube, so that the ammonia might escape, and the amylamine be returned to the flask. The contents were next distilled into hydrochloric acid solution, and the solution of chlorides thus obtained evaporated almost to dryness on the water bath; the evaporation was completed in an exhausted desiccator over solid potash. Very little ammonium chloride was present, for on the conversion of a portion of the chloride into cyanate in the usual way, by means of silver cyanate, and rapid evaporation to dryness of the cyanate solution, the urea obtained melted at $155°$, the melting point of the original substance.

A decinormal solution of the amylammonium cyanate, prepared in the manner above indicated, was heated at $59.6°$ with the following result.

t.	Titre.	x.	k.
100	3·0	0·0120	0·0137
160	4·1	0·0164	0·0127
220	4·4	0·0176	0·0101
404	6·1	0·0244	0·0085
584	7·6	0·0304	0·0082

The magnitude k was calculated with the end-point $\xi = 0\cdot0572$, whence $K = \dfrac{0\cdot0428^2}{0\cdot0572} = 0\cdot032$. It will be seen that the value does not remain constant, but continually diminishes as the action proceeds ; this is no doubt due to secondary decompositions of the same nature as those undergone by the urea. Wurtz remarks (*loc. cit.*, p. 329) that tertiary amylurea exhibits a marked tendency to break up, with the formation of amylene as one of the products of decomposition. At the beginning of the action, the values of k are probably nearest the true value, so that we may adopt $k = 0\cdot013$ as being approximately correct. A second set of experiments yielded almost identical results, the value of k for the first two determinations being $0\cdot0135$.

For k' we have $Kk = 0\cdot032 \times 0\cdot013 = 0\cdot0004$.

Although these values for k and k' are somewhat uncertain, they are sufficiently accurate to show that whilst the direct transformation proceeds much more slowly than is the case with any of the other compounds examined, the reverse transformation is only exceeded in velocity by the diethyl and dimethyl compounds.

Comparison of Constants.

In the following table the values of the constants for the various cyanates and ureas have been collected, in order to exhibit any regularities that might exist amongst them.

Cyanate.	$100k$.	$100k'$.
Ammonium.	14·4	0·0038
Methylammonium	13·4	0·0022
Dimethylammonium	25·3	0·073
Ethylammonium	8·1	0·007
Diethylammonium	9·0	0·148
Isoamylammonium	9·2	0·0031
Tertiary amylammonium	1·3	0·04

The values of the constants have all been multiplied by 100 to avoid unnecessary ciphers, and to give the results in percentages. Thus in the case of ammonium cyanate the numbers indicate that in a normal solution 14·4 per cent. would be transformed in the first minute if the concentration were maintained constant, the corresponding amount of retransformation in a normal solution of urea being only 0·0038 per cent. It must be borne in mind, however, that these values of k and k' would not agree exactly with those obtained by actual experiment in normal solutions, for in calculating them the change of dissociation effected by dilution has been neglected, and it has been shown by Walker and Hambly (*loc. cit.*, 763) that neglect

of this factor gives greater values for k in dilute solutions than it does in more concentrated solutions.

A glance at the table suffices to show that there is no pronounced regularity in the values of k. The introduction of a methyl group into ammonium cyanate leaves the velocity constant practically unaffected ; a second methyl group, however, raises it to almost double the original value. Ethyl groups diminish the value of the constant, the diminution being somewhat greater for the introduction of one group than for two. The increase in the constant effected by the second ethyl group is, however, very slight, and not at all comparable with the effect of a second methyl group. Both the amyl radicles lower the constant, the lowering in the case of tertiary amyl being very marked. The isomeric ethylammonium cyanate and dimethylammonium cyanate have very different constants. This might be attributed to the fact that one isomeride is the salt of a primary base whilst the other is a salt of a secondary base, but the widely divergent values of the amylammonium cyanates, where both bases are primary, show that isomerism within the alkyl group has as marked an influence on the constant as isomerism directly affecting the nitrogen atom.

The values of k' display as little regularity as the values of k. The introduction of one alkyl group into urea sometimes raises and sometimes lowers the constant ; the introduction of a second alkyl group increases the value greatly in both cases examined. Isomeric substances again have very different values of the constant.

Points of Equilibrium.

In calculating k and k' for $59.6°$, use was made of the end-point ξ, determined at $100°$. The calculation thus proceeds on the assumption that the end-point is not appreciably influenced by temperature. This has already been shown to be the case for ammonium cyanate (*loc. cit.*, 751), but there the circumstances were unfavourable for detecting any small variation. In the case of diethylurea and tertiary amylurea, the reverse action proceeds with considerable rapidity, and the equilibrium point is at a considerable distance from either end, so that the conditions are favourable for observing any displacement of this point by temperature. Experiments were therefore made at $80°$ with both of these substances, with the result that the end-points observed at that temperature were, within the experimental error, identical with those obtained at $100°$. Temperature, then, influences the position of the end-point to so small a degree that it is permissible to use the point of equilibrium determined at one temperature in calculating the velocity constants for another.

The point of equilibrium is greatly influenced by the concentration

of the solution, as the following consideration will show. The transformation of a cyanate into the corresponding urea is a bimolecular action; the reverse transformation of urea into cyanate is a unimolecular action. In the latter case, each molecule is transformed independently of the others, so that the proportion of the whole transformed in a given time is quite independent of the dilution. On the other hand, two ions must meet before a molecule of urea can be formed; consequently a smaller proportion of cyanate will be converted into urea as the dilution increases, for the chance of the ions meeting varies as the inverse square of the dilution. The result is that as the solutions are taken more and more dilute, the greater will be the proportion of ammonium cyanate present when equilibrium has been attained. It is easy to calculate the dilution at which half the cyanate has been converted into urea when equilibrium has been reached by means of the equation

$$K = \frac{(A - \xi)^2}{\xi}.$$

If we express A, the original concentration in terms of a normal solution, and ξ in terms of A, we have the following equation for the case of equilibrium in which the transformation has gone half way,

$$K = \frac{(A - 0\cdot5\,A)^2}{0\cdot5\,A} = 0\cdot5\,A.$$

That is, the original concentration of cyanate expressed in terms of a normal solution for which the transformation into urea will stop half way is numerically equal to twice the ratio of the velocity constants, K, as determined from any single end-point experiment. The values of the end-points and of 2K for the various cyanates are tabulated below.

Cyanate.	100ξ.	2K.
Ammonium..............	95·0	0·00052-normal.
Methylammonium	96·0	0·00033
Dimethylammonium	84·4	0·0057
Ethylammonium........	91·2	0·0017
Diethylammonium	66·8	0·033
Isoamylammonium	94·4	0·00067
Tertiary amylammonium.	57·0	0·064

In the first column the end-points are given in percentages for decinormal solutions; for example, the conversion of ammonium cyanate into urea ceases when 95 per cent. of the original amount has been transformed. The numbers in the second column give the concentrations of the solutions in which the transformation will come to an end, when half the cyanate (or half the urea) has disappeared. It

should again be remarked that owing to neglect of the influence of dilution on the degree of eletrolytic dissociation, these numbers are somewhat greater than the true values, the error being relatively larger the smaller the number is. The table, therefore, rather under-rates the differences between the various substances. A solution of methylurea has consequently to be diluted more than 200 times as far as a solution of tertiary amylurea in order to get the same amount of urea decomposed in both cases.

Trialkyl- and Tetralkyl-ammonium Cyanates.

Although trialkyl- and tetralkyl-ammonium cyanates are not supposed to be transformed into ureas by heating with water, a few experiments were made with them in decinormal aqueous solution, in order to ascertain their behaviour under conditions similar to those with the monalkyl- and dialkyl-ammonium cyanates.

Tetramethylammonium cyanate, prepared from the iodide and silver cyanate, did not change in titre after heating for 18 hours at $59 \cdot 6°$. Triethylammonium cyanate, on the other hand, exhibited distinct signs of change, even after one hour's heating, as may be seen from the following table.

t.	Titre.
30	0·1
90	0·2
150	0·25
1320	1·00
2700	1·85

When the experiment was interrupted, the solution was found to be strongly ammoniacal, and to give a copious precipitate with calcium nitrate. Five c.c. of the solution at $t = 2700$ were treated with excess of calcium nitrate, and the precipitate filtered off. To the filtrate 5 c.c. of decinormal silver nitrate solution were added, and the insoluble salt so obtained was then removed by filtration. The titre of the filtrate was now found to be 12·0 c.c. instead of 1·85, the number obtained without treatment with calcium nitrate. These figures would seem to indicate that the final product of the transformation in this case is mostly acid triethylammonium carbonate, produced from the normal carbonate by protracted heating.