LXX.—*The Rate of Transformation of Ammonium Cyanate in Absolute Alcohol.*

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It has been shown by Walker and Hambly (T., 1895, **67**, 746) that the transformation of ammonium cyanate into carbamide follows the course of a bimolecular reaction, and they considered the active substances to be ammonium ions and cyanate ions. Walker and Kay (T., 1897, **71**, 489) have studied the transformation in aqueous-alcoholic solutions. They found that ethyl alcohol produced a marked accelerating effect on the speed of the transformation, which was supposed to be due to the increased rate at which the ions, produced by the dissociation of ammonium cyanate, react in alcohol. The greatest concentration of alcohol used in their experiments was 90 per cent. At Professor Walker's suggestion, I undertook the investigation of this transformation in more concentrated alcoholic solutions. This appeared to be of special interest in view of recent discussion of the previous results by E. E. Walker (*Proc. Roy. Soc.*, 1912, *A*, **87**, 539) and by Chattaway (T., 1912, **101**, 170).

In dealing with alcoholic solutions of 95 per cent. and upwards, the formula, used by Walker and Kay to represent the course of the reaction, was subject to considerable simplification, since in such solutions the transformation was complete, no measurable quantity of cyanate being left.

If a = the initial concentration of cyanate, x = the amount transformed, p = the degree of dissociation of cyanate, then the velocity-equation becomes

$$\frac{dx}{dt} = kp^2(a-x)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1).$$

The investigation is further simplified by the fact that in solutions containing more than 90 per cent. of alcohol no ammonium carbonate is formed.

It is to be noted that p does not remain constant, but varies continuously with x. This is specially true in concentrated alcoholic solutions. When, for purposes of calculation, the integral, obtained from equation (1) on the assumption that p is constant, is used, the total range has to be subdivided, and the average value of p throughout the interval considered must be taken. We thus deduce the equation

$$kp^2 = \frac{1}{ta}\cdot\frac{x}{a-x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2).$$

EXPERIMENTAL.

The method of preparing a solution of ammonium cyanate by shaking silver cyanate with ammonium chloride solution, used by previous workers, was not in this case available, owing to the sparing solubility of ammonium chloride in concentrated alcohol. For the purpose in hand, it was necessary to prepare pure dry ammonium cyanate. This was done by mixing cooled ethereal solutions of cyanic acid and ammonia (Walker and Wood, T., 1900, **77**, 21). The solid substance so prepared could easily be kept, without undergoing decomposition, in a vacuum desiccator until required for experiments.

In the preparation of the alcohol used in the following experiments, the starting material was Kahlbaum's "absolute" alcohol. It was first distilled twice from freshly prepared quicklime, obtained by heating marble in a muffle furnace. The alcohol so obtained was then heated, for at least one day, to about 70° over dry calcium turnings, which had previously been washed with ether, whilst it was protected from the air by calcium chloride tubes. It was then distilled, only the middle fraction of the distillate being used. During the distillations contact with moist air was avoided. Experiments were made in order to find out how much water this absolute alcohol would contain under the conditions at which the velocity experiments were carried out. The method adopted was that of measuring the conductivity of a decinormal solution of picric acid in alcohol (Goldschmidt, *Zeitsch. Elektrochem.*, 1909, **15**, 6). It was found that the "absolute alcohol" throughout the experiments did not contain more than 0·8 gram of water in 1 litre. The value of the specific gravity of the alcohol agreed with that of Wade and Merriman (T., 1912, **101**, 2432) to within one part in eight thousand. This would correspond with a liquid containing 0·5 gram of water per litre.

Solutions containing varying amounts of alcohol were all prepared by diluting this absolute alcohol with water. The velocity of the transformation was measured at 32°.

The requisite amount of ammonium cyanate to give a decinormal solution was weighed into a measured volume of alcohol contained in a stoppered flask, which had been placed in the thermostat. It was found that the cyanate, although finely powdered, did not dissolve at all readily in the more concentrated alcoholic solutions. When the cyanate had nearly all dissolved, the solution was decanted into another stoppered flask, which had already been heated to the temperature of the thermostat. The first measurement was made about five minutes afterwards. At measured intervals samples of the solution were transferred, by means of a 5 c.c. pipette, to a weighed flask containing a measured quantity of a $N/50$-solution of silver nitrate diluted with water in small and approximately constant excess of that required to precipitate the cyanate. The flask was then weighed again, cooled in running water, and the silver cyanate collected, the excess of silver nitrate being estimated by titration with a $N/50$-solution of ammonium thiocyanate. The specific gravities of the solutions were also determined. From these data the concentration of the cyanate in the solution could be calculated.

Data for the Degree of Dissociation.

In order to estimate the degree of dissociation of ammonium cyanate in solutions containing more than 90 per cent. of alcohol, measurements of the conductivity of such solutions were made at 32°. Part of a solution of ammonium cyanate, prepared as before, was placed in a stoppered cell, and values of the conductivity were taken at definite times, a galvanometer and rotating commutator being used. At other definite times the amount of cyanate in the solution was estimated by titration as before. Since the course of the reaction in the various alcoholic solutions had already been determined, the amount of cyanate in the solution at the times corresponding with the electrical measurements could be found. The molecular conductivity of the solution with different concentrations of cyanate was then calculated. By using the value of the molecular conductivity at infinite dilution for potassium cyanate in water, and considering the effect of alcohol, at least as regards infinite dilution, to be the same for potassium cyanate and for ammonium cyanate as for diethylammonium chloride (Walker and Hambly, T., 1897, **71**, 61), the molecular conductivity at infinite dilution for ammonium cyanate was calculated in 95 per cent., 99 per cent., and 100 per cent. alcoholic solutions. From these numbers the degree of dissociation of ammonium cyanate at various dilutions was obtained. The specific conductivity of the absolute alcohol used in the experiments was found to be about $5{\cdot}8 \times 10^{-6}$ at 32°.

Ninety per cent. Alcohol.

In order to effect connexion with the results of Walker and Kay obtained by conductivity measurements, and not by direct titration, a set of velocity experiments in 90 per cent. alcohol was made. In this case the simplified formula cannot be applied. Instead of "*a*," the initial concentration of cyanate, we must substitute "*E*," the total change in the concentration of cyanate, 1 per cent. of the cyanate remaining untransformed. The value of *p* used in the calculation is the mean between the initial and final values in each section considered.

I.

$a = 0{\cdot}05088$, $p = 0{\cdot}516$; $a - x = 0{\cdot}04810$, $p = 0{\cdot}520$.

t.	E.	$E-x$.	$\frac{1}{tE} \cdot \frac{x}{E-x}$.	kp^2.
8	0·04988	0·04710	0·148	0·142

II.

$a = 0{\cdot}04810$, $p = 0{\cdot}520$; $a - x = 0{\cdot}03646$, $p = 0{\cdot}540$.

t.	E.	$E-x$.	$\frac{1}{tE} \cdot \frac{x}{E-x}$.	kp^2.
40	0·04710	0·03546	0·174	0·167

III.

$a = 0{\cdot}03646$, $p = 0{\cdot}540$; $a - x = 0{\cdot}03326$, $p = 0{\cdot}547$.

t.	E.	$E-x$.	$\frac{1}{tE} \cdot \frac{x}{E-x}$.	kp^2.
15	0·03546	0·03226	0·186	0·176

IV.

$a = 0{\cdot}03326$, $p = 0{\cdot}547$; $a - x = 0{\cdot}02960$, $p = 0{\cdot}555$.

t.	E.	$E-x$.	$\frac{1}{tE} \cdot \frac{x}{E-x}$.	kp^2.
21	0·03226	0·02860	0·189	0·178

V.

$a = 0{\cdot}02960,\ p = 0{\cdot}555;\ a - x = 0{\cdot}02184,\ p = 0{\cdot}600.$

t.	*E.*	*E* − *x*.	$\frac{1}{tE} \cdot \frac{x}{E-x}$.	kp^2.
61	0·02860	0·02084	0·213	0·200

VI.

$a = 0{\cdot}02184,\ p = 0{\cdot}600;\ a - x = 0{\cdot}01867,\ p = 0{\cdot}630.$

t.	*E.*	*E* − *x*.	$\frac{1}{tE} \cdot \frac{x}{E-x}$.	kp^2.
40	0·02084	0·01767	0·220	0·203

Combining these results, we get the following table:

a.	kp^2.	*p.*	*k.*
0·05088	0·142	0·518	0·530
0·04810	0·167	0·530	0·594
0·03646	0·176	0·544	0·597
0·03326	0·178	0·551	0·582
0·02960	0·200	0·578	0·598
0·02184	0·203	0·615	0·537
			Average = 0·573

The mean value of *k* is in accordance with the average value 0·575 obtained by Walker and Kay.

Ninety-five per cent. Alcohol.

In this and the following cases the simple formula can be applied, since the transformation is complete, so that

$$\frac{1}{ta} \cdot \frac{x}{a-x} = kp^2.$$

t.	*a*	*a* − *x*.	kp^2.	*p.*	*k.*
18	0·06122	0·05036	0·196	0·480	0·85
15	0·05036	0·04274	0·236	0·497	0·96
50	0·04274	0·02828	0·239	0·529	0·86
15	0·02828	0·02536	0·272	0·562	0·86
15	0·02536	0·02272	0·306	0·578	0·92
					Average = 0·89

The values of *p* in column five of this and similar tables do not correspond with the concentration *a*, but are mean values for the interval considered.

Ninety-nine per cent. Alcohol.

t.	*a.*	*a* − *x*.	kp^2.	*p.*	*k.*
16	0·05072	0·04198	0·257	0·420	1·45
9	0·04198	0·03830	0·254	0·438	1·33
20	0·03830	0·03114	0·300	0·457	1·44
15	0·03114	0·02714	0·316	0·480	1·37
30	0·02714	0·02108	0·353	0·508	1·37
31	0·02108	0·01642	0·435	0·548	1·44
					Average = 1·40

Absolute Alcohol.

t.	*a.*	*a−x.*	*kp*².	*p.*	*k.*
10	0·06476	0·05580	0·248	0·383	1·69
15	0·05580	0·04628	0·246	0·402	1·53
15	0·04628	0·03868	0·283	0·427	1·56
15	0·03868	0·03286	0·305	0·446	1·54
20	0·03286	0·02716	0·319	0·465	1·48
25	0·02716	0·02152	0·386	0·495	1·60
25	0·02152	0·01740	0·440	0·526	1·59
					Average = 1·57

If, now, we calculate the value kp^2 for the last three alcoholic solutions when the concentration $a = 0·08$, we obtain the values 0·176, 0·187, and 0·200 respectively, and may now complete the table given by Walker and Kay, thus:

TABLE I.

Volume-percentage of alcohol.	*kp*².	*k.*	$kp^2 \times W$.
0	0·00434	0·00595	0·00434
10	0·00550	0·00774	0·00499
30	0·00918	0·0129	0·00666
49	0·0184	0·0295	0·0101
72	0·0428	0·093	0·0133
90	0·131	0·575	0·0156
95	0·176	0·89	0·0109
99	0·187	1·40	0·0023
100	0·200	1·57	0·00016

We see from this table that there is a continual increase in the rate at which ammonium cyanate is converted into carbamide as we pass from pure water to nearly pure alcohol. The increase is most marked when the solution contains more than 90 per cent. of alcohol. On the assumption that the action is between the ions, the alcohol must exercise a very great accelerating influence, which more than counterbalances the effect due to the decrease in the number of ions present in the solution. By considering the action as due to the ions, perfectly definite results are obtained, which are compatible with each other over the entire range from pure water to absolute alcohol. E. E. Walker (*Proc. Roy. Soc.*, 1912, *A*, **87**, 539) has suggested that, in order to obtain numbers which shall properly represent the rate of the reaction, the values of kp^2 must be multiplied by W, the weight of water in 1 c.c. of the solution. E. E. Walker proceeds: "Whereas Walker and Kay were led to assume that the rate of change is increased 30 times in 90 per cent. alcohol, the values obtained by the method of reducing the results I have adopted indicate that the rate in such a solution is not more than about three times as great as when no alcohol is present." A column giving the values of $kp^2 \times W$ has been added in table I. The rise of $kp^2 \times W$ is steady up to 90 per cent. alcohol, but afterwards falls off slowly from 0·0156 at 90 per cent. to 0·0109 at 95 per cent., and rapidly to 0·0023 at 99 per cent. and 0·00016 in 99·94 per cent. by volume. Adopting E. E. Walker's interpretation, these values indicate that the rate in solutions above 90 per cent. falls to values below that for pure water, and, necessarily from his mode of calculation, to zero in alcohol absolutely free from water. This interpretation is in direct contradiction of the plain fact that the rate of transformation of ammonium cyanate not only increases with increasing concentration of alcohol, but increases the more rapidly as the alcohol approaches absolute purity. In calculating the rate of the transformation by the method of Walker and Kay, the only assumptions made are that the reaction may be regarded as bimolecular, and the active substances ammonium ions and cyanate ions. The latter assumption has already been shown to be very probable, since on calculating k, the velocity-coefficient, on this assumption, it is found that an approximately constant number is obtained.

It has been pointed out by Wegscheider, however (compare J. Walker, *Brit. Assoc. Reports*, 1911, 354), that, provided ionisation takes place at a rate immeasurably greater than the transformation studied, it is impossible to ascertain from the reaction-velocity alone whether the ions or the non-ionised substance is primarily responsible for the transformation. It is of interest, therefore, to calculate the accelerating influence of alcohol if we refer the transformation to the non-ionised substance instead of to the ions. This may be done as follows:

If i = the concentration of the ionised cyanate, and u = the concentration of the non-ionised cyanate, then, if the non-ionised part acts abnormally, as is usual for a strong electrolyte, we have

$$\frac{i^2}{u^n} = c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

n has, in accordance with van't Hoff's dilution law, a value about 1·33. The general equation, representing the transformation of ammonium cyanate into carbamide, when referred to the ions is

$$\frac{dx}{dt} = ki^2 - k'(B+x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

where B = the initial concentration of carbamide, and x = the amount of carbamide formed.

If the non-ionised cyanate be the active substance, the general velocity-equation is

$$\frac{dx}{dt} = k_1u^n - k'(B+x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

where k_1 represents the velocity-constant of the direct transformation. Combining equations (4) and (5), we get

$$k_1 u^n = ki^2,$$

and using equation (3) we get

$$k_1 = ck.$$

By calculating the mean values of c for the various solutions we may obtain values of k_1. Values of c, and corresponding values of k_1, are given in the following table.

TABLE II.

Volume-percentage of alcohol.	c.	k_1.
0	1·91	0·011
10	1·71	0·013
30	1·26	0·016
49	0·82	0·024
72	0·38	0·035
90	0·098	0·056
95	0·075	0·067
99	0·052	0·073
100	0·047	0·074

A continuous increase in the value of k_1, the velocity-constant when the action is referred to the non-ionised substance, is apparent as we proceed from aqueous solutions to those containing a large percentage of alcohol. The change in the value of k_1 with increasing amounts of alcohol is not so great as in the case of the constant k. This is to be expected, as the supposed active substance, the non-ionised cyanate, increases with the amount of alcohol in the solution. Alcohol therefore is found to produce an accelerating effect on the transformation of ammonium cyanate into carbamide, whether we consider the active substance to be ionised or non-ionised cyanate, although in the second case the effect is considerably smaller.

To sum up, if the crude bimolecular constant kp^2 is considered, the velocity in "absolute" alcohol (99·94 per cent. by volume) is 46 times that in water; if the action is referred to the ions of ammonium cyanate, it is 264 times; if the action is referred to the non-ionised cyanate it is 6·7 times. Even the greatest of these numbers is not unusual for complete change of solvent, since, for example, the formation of tetraethylammonium iodide from triethylamine and ethyl iodide proceeds 700 times as fast in benzyl alcohol as it does in hexane.

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