The Conversion of Ammonium Cyanate into Urea. Mechanism and Kinetic Salt Effect

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Studies of the rate of conversion of ammonium cyanate into urea have been the subject of a number of investigations.[1] In these investigations there is agreement upon the following points. (a) The reaction is bimolecular in character. (b) The reaction is not complete in aqueous solution, some unchanged NH_4OCN remaining at equilibrium. (c) There is a slight side reaction leading to the formation of carbonate. (d) The bimolecular rate constant increases with a decrease in the concentration of NH_4OCN. (e) The rate constant is higher in mixtures of water with alcohols, sugars, acetone, etc., than it is in pure water.

Concerning the exact nature of the bimolecular mechanism, there has been considerable controversy. J. Walker and Hambly, J. Walker and Kay, and Ross[1] supported the assumption that the rate depends upon collisions between ammonium ions and cyanate ions (ionic mechanism). Chattaway[2] argued against the ionic mechanism and assumed the rate to depend upon collisions between molecules of ammonia and isocyanic acid. This view, in a modified form, was supported by Werner,[3] and E. E. Walker[1] favored a non-ionic mechanism. Recently, Moelwyn-Hughes[4] has assumed the rate to depend upon collisions between unionized molecules of ammonium cyanate. Contrary to the results of earlier investigators, Doyle[5] reported the rate constants at 35 and 55° to be practically independent of the ammonium cyanate concentration. Since the magnitude of the kinetic salt effect can be used to decide the mechanism of the reaction, a systematic investigation of the effect of the concentration of NH_4OCN and added salts upon the velocity of the conversion was undertaken.

According to the Brönsted theory,[6] if the rate depends upon collisions between NH_3 and HOCN molecules or between two molecules of undissociated NH_4OCN, there should be only a small positive or negative primary salt effect and the effect should be a linear function of the ionic strength. If, however, the rate depends upon collisions between ammonium and cyanate ions, the primary salt effect should be negative and a function of the square root of the ionic strength. This was the type of salt effect indicated in the preliminary results obtained by Mr. J. S. Peake.[7]

(1) J. Walker and Hambly, J. Chem. Soc., 67, 746 (1895); J. Walker and Kay, ibid., 71, 489 (1897); Ross, ibid., 105, 690 (1914); E. E. Walker, Proc. Roy. Soc. (London), A87, 539 (1912).

(2) Chattaway, J. Chem. Soc., 101, 170 (1912).

(3) Werner, ibid., 103, 1010 (1913).

(4) Moelwyn-Hughes, Chem. Rev., 10, 244 (1932).

(5) Doyle, Thesis, Liverpool, 1922; reviewed by Moelwyn-Hughes, Ref. 4.

(6) Brönsted, Chem. Rev., 5, 231 (1928); La Mer, ibid., 10, 179 (1932).

(7) J. S. Peake, Thesis, Carnegie Institute of Technology, 1932.

Materials and Experimental Procedure.—Silver cyanate was prepared by heating a solution containing c. p. silver nitrate and about five equivalents of Eastman "Highest Purity" urea. The silver cyanate was filtered off from time to time, carefully washed and then dried in a vacuum desiccator. Solutions of c. p. ammonium chloride and potassium thiocyanate were standardized by precipitating the silver salts and weighing. All experiments were carried out at 70 ± 0.05°. The ammonium cyanate solutions were prepared by agitating standard ammonium chloride solution with a slight excess of silver cyanate until the solution was free of chloride ion. The precipitated silver chloride was filtered off and the solution, in the reaction flask, heated in an open flame to approximately the thermostat temperature. As soon as the solution reached the thermostat temperature, an initial sample was pipetted from the reaction flask into an excess of standard silver nitrate solution. The precipitated silver cyanate was filtered off and an aliquot portion of the filtrate, made acid with nitric acid, was titrated with standard potassium thiocyanate, using concentrated ferric nitrate as an indicator. As the reaction proceeded other samples were treated in a similar manner. In experiments with added salts, a weighed amount of the c. p. salt was dissolved in the freshly prepared ammonium cyanate solution.

The titration of an aliquot portion of the filtrate eliminates washing the silver cyanate (which is appreciably soluble) and allows a convenient volume to be used in all titrations. In all runs, concentrations of silver nitrate and potassium thiocyanate solutions were chosen so that (a) a considerable excess of silver nitrate was present to ensure more complete precipitation of the silver cyanate, (b) the back titrations changed considerably during the course of a run, (c) errors in titration and pipetting were relatively unimportant.

Experimental Results.

—In the calculation of velocity constants from our data, we have considered the effect of the back reaction, the side reaction leading to carbonate formation, and the changing ionic strength during the course of the reaction. The effect of the back reaction is easily less than our experimental error up to 70% conversion. This is evident from an examination of the data in columns 6 and 7 in Table II. The effect of carbonate formation is also less than the experimental error. Not enough carbonate has formed at 70% conversion to give a precipitate with calcium nitrate even when the initial concentration of ammonium cyanate is 0.5 mole per liter. If the reaction were strictly bimolecular, the reciprocal of the ammonium cyanate concentration should be a linear function of the time. We have therefore plotted $1/(NH_4OCN)$ against t (min.) and assumed a linear relationship over such a range as seemed justified by the experimental points. In this way the second-order constant for the mean ionic strength of the range was calculated. The results obtained in this manner are listed in Table I.

In Fig. 1, log k is plotted against the square root of the ionic strength. It was very difficult to obtain reliable experimental results in the range $\sqrt{\bar{\mu}} = 0$ to 0.1 due to the difficulty of simultaneously meeting all three conditions noted under procedure. When much excess silver nitrate is used, the titrations become inaccurate, whereas for small excesses, appreciable amounts of AgOCN remain in solution. The effect of dissolved AgOCN is to give values of the velocity constant which are too high.

Table I

Run	Initial molality NH₄OCN	Range μ used in calcns.	Midpoint of range (μ)	$\sqrt{\mu}$	Bimolecular k (min.)	Minus log k	Molality added salt
		Pure NH₄OCN (no added salt)					
36	0.01	0.0077–0.0065	0.00709	0.0843	0.505	0.297	
15	.025	.020– .013	.0165	.1285	.427	.369	
30	.05	.028– .0078	.0182	.135	.465	.332	
31	.05	.023– .0135	.0183	.135	.433	.367	
35	.025	.023– .017	.0200	.141	.447	.350	
33	.20	.029– .019	.0243	.156	.428	.368	
37	.10	.026– .022	.0244	.156	.415	.388	
17	.05	.038– .023	.0306	.175	.379	.421	
31	.05	.046– .023	.0346	.186	.394	.404	
33	.20	.044– .029	.0366	.191	.392	.406	
30	.05	.046– .029	.0370	.192	.376	.424	
22	.10	.070– .043	.0567	.238	.357	.447	
21	.10	.069– .051	.0597	.244	.345	.462	
28	.10	.084– .041	.0628	.251	.354	.451	
37	.10	.089– .060	.0745	.272	.341	.467	
33	.20	.170– .078	.124	.352	.301	.521	
34	.35	.281– .108	.196	.443	.283	.548	
32	.50	.407– .097	.252	.502	.262	.582	
		KNO₃ as added salt					
20	0.05	0.063–0.044	0.0533	0.231	0.380	0.420	0.025
46	.05	.095– .076	.0857	.293	.345	.462	.05
19	.05	.094– .084	.089	.298	.338	.471	.05
18	.05	.138– .119	.129	.359	.319	.496	.10
13	.10	.194– .138	.164	.405	.295	.530	.10
45	.10	.190– .144	.167	.409	.294	.532	.10
16	.05	.245– .231	.238	.488	.288	.540	.20
44	.10	.265– .245	.255	.505	.267	.573	.20
43	.10	.385– .344	.365	.604	.247	.607	.30
42	.10	.488– .434	.461	.659	.241	.618	.40
		NaF as added salt					
24	0.05	0.144–0.115	0.129	0.359	0.309	0.510	0.10
49	.10	.169– .131	.150	.387	.297	.527	.10
23	.04	.209– .195	.202	.449	.272	.565	.17
48	.10	.388– .341	.365	.604	.234	.630	.30
47	.10	.489– .456	.473	.679	.223	.651	.40

Discussion of Results

From Fig. 1 it is evident that the velocity constants at various ionic strengths, with or without added salts, determine a fairly smooth curve. In general, the velocity constants, at equal ionic strengths, are somewhat smaller in the presence of sodium fluoride and somewhat higher with potassium nitrate, than they are for pure ammonium cyanate. By extrapolation to $\sqrt{\mu} = 0$, a value $k_0 = 0.615$ is obtained. This value represents the velocity constant at 70°, free from all salt effects. Due to the difficulty

in obtaining reliable results at low ionic strengths, we have been guided in our extrapolation by the theoretical limiting slope indicated by the Brönsted theory

$$\log k = \log k_0 + \log (\gamma_{NH_4^+}\gamma_{OCN-}/\gamma_X^0)$$
$$= \log k_0 - (2 \times 1.816 \times 10^6 \sqrt{\mu})/(DT)^{3/2}$$

Using Wyman's[8] value of 63.5 for the dielectric constant of water at 70°, we obtain

$$\log k = \log k_0 - 1.13\sqrt{\mu}$$
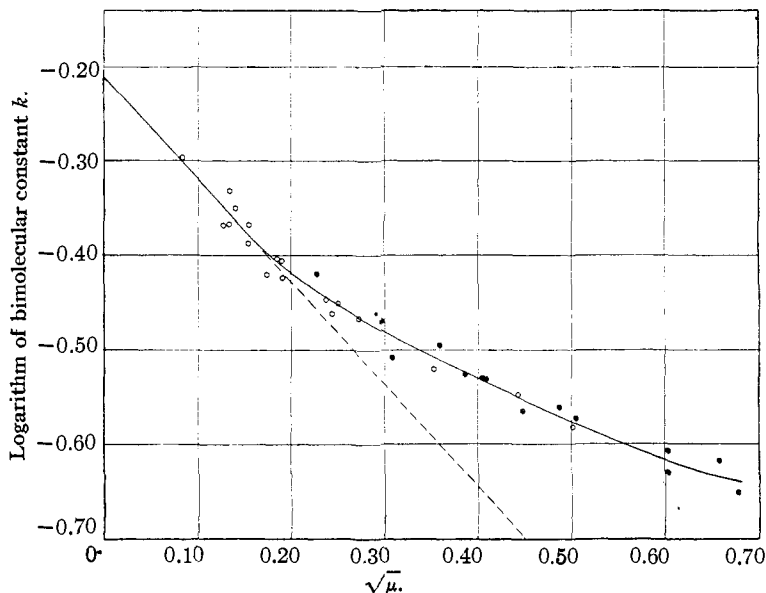
This limiting slope is shown by the dotted line in Fig. 1.

Fig. 1.—⊙, No added salt; ●, KNO$_3$ as added salt; ⊗, NaF as added salt.

The Limiting Velocity Constant.—We have considered the possibility of calculating the limiting velocity constant (k_0) directly from experimental data by taking into account the effect of the changing ionic strength during the course of the reaction. According to the Brönsted theory, the rate of formation of urea is given by the expression

$$dx/dt = k_1 C_{NH^+} C_{OCN-} (\gamma_{NH_4^+}\gamma_{OCN-}/\gamma_X^0) - k_2 C_{urea}$$

Let a = initial concentration of ammonium cyanate, b = initial concentration of urea and assume $\gamma_{NH_4^+} = \gamma_{OCN-}$ and that $\gamma_X^0 = 1$. Substitute $k_2 = k_1 K_e$, where $K_e = 1.62 \times 10^{-4}$ is the thermodynamic equilibrium constant at 70°.[9] Our velocity equation then becomes

$$\int k \, dt = \int \frac{dx}{(a-x)^2 \gamma_{\pm}^2 - K_e(b+x)}$$

(8) Wyman, Phys. Rev., **35**, 623 (1930).

(9) Lewis and Randall. "Thermodynamics." McGraw-Hill Book Co.. Inc.. New York, 1923, p. 587.

When γ is expressed as a function of the ionic strength, an expression is obtained which we have been unable to integrate analytically. It may, however, be integrated graphically if $\gamma_{\pm}$ is known as a function of the ionic strength. No data are available on the activity coefficients of NH_4-OCN, but we have applied this method to the data obtained in a number of our experiments, using the activity coefficients of ammonium nitrate at $0°$.[10] The results of a typical calculation are given in Table II. A summary of the results for a number of runs is given in Table III. Since the combined effect, on the activity coefficients, of an increase in temperature and a decrease in dielectric constant in going from 0 to $70°$ is probably smaller than the error involved in the assumption of equal activity coefficients for NH_4OCN and NH_4NO_3, no correction was thought necessary for our purpose.

TABLE II

Run 31. Initial molality of NH_4OCN, 0.05. No added salt

Time, min.	Molality NH_4OCN	Molality urea	Δ(Urea)	$\gamma_{NH_4NO_3}$	$\gamma^2(NH_4OCN)^2$	K_e(Urea)	$1/[\gamma^2(NH_4OCN)^2 - K_e(Urea)]$	Area from $t=0$	Limiting k
0	0.04575	0.00425		0.789	130.3×10^{-5}	0.1×10^{-5}	767		
			0.00725						
10	.03850	.01150		.803	95.6	.2	1048	6.56	0.656
			.00462						
20	.03388	.01612		.810	75.3	.3	1332	12.04	.602
			.00601						
35	.02782	.02213		.825	52.7	.4	1911	21.68	.620
			.00489						
55	.02298	.02702		.836	36.9	.4	2740	32.98	.600
			.00526						
85	.01772	.03228		.853	22.85	.52	4480	51.9	.611
			.00417						
125	.01355	.03645		.868	13.85	.59	7540	76.7	.614
			.00335						
175	.01020	.03980		.883	8.11	.65	11820	108.5	.620

TABLE III

Run	Initial molality NH_4OCN	Initial molality added salt	Salt added	Mean limiting k	Run	Initial molality NH_4OCN	Initial molality added salt	Salt added	Mean limiting k
30	0.05		None	0.60	49	0.10	0.10	NaF	0.61
31	.05		None	.61	48	.10	.30	NaF	.66
17	.05		None	.61	47	.10	.40	NaF	.70
11	.05		None	.61	19	.05	.05	KNO_3	.59
28	.10		None	.62	20	.05	.025	KNO_3	.62
37	.10		None	.60	18	.05	.10	KNO_3	.66
7	.10		None	.61	16	.05	.20	KNO_3	.69
12	.10		None	.60	13	.10	.10	KNO_3	.66
33	.20		None	.60	45	.10	.10	KNO_3	.65
34	.35		None	.74 down	44	.10	.20	KNO_3	.68
32	.50		None	.77 down	43	.10	.30	KNO_3	.72
23	.043	0.17	NaF	.63	42	.10	.40	KNO_3	.77

The values of the limiting k thus found show little variation over the range of ionic strength at which the assumption of equal activity coefficients for NH_4OCN and NH_4NO_3 seems valid. The close agreement between the mean velocity constant calculated by this method and the extrapolated value from Fig. 1 should be noted. Above $\mu = 0.1$, the value of the limiting constant increases with increasing ionic strength showing that the activity coefficient of NH_4OCN decreases less rapidly than that of

(10) Scatchard and Prentiss, THIS JOURNAL, 54, 2702 (1932).

NH_4NO_3 with increase of ionic strength. In those runs with no added salt in which the initial concentration of NH_4OCN was high, the limiting constant drops from a high value toward the extrapolated value as the reaction proceeds. The results obtained by this method suggest the important possibility of determining activity coefficients from velocity measurements when the reaction can be followed with extreme accuracy. This method should be particularly useful in solvent mixtures where the usual methods are less applicable. One should, however, take into account La Mer's[11] suggestion that the activity coefficients entering into rate equations are probably not always the true thermodynamic coefficients.

Inasmuch as we have observed a marked negative primary salt effect of the magnitude predicted by the Brönsted theory for a reaction between univalent ions of opposite charge, our data strongly support the assumption of Walker and Hambly that the rate of conversion of ammonium cyanate into urea depends upon collisions between ammonium and cyanate ions. Investigations now in progress in this Laboratory on the effect of the dielectric constant of the solvent upon the rate of this reaction also strongly support the ionic mechanism.

Summary

1. The dependence of the rate of conversion of ammonium cyanate into urea upon ionic strength has been determined in the presence and absence of added salts.

2. A negative primary salt effect of the magnitude predicted by the Brönsted theory has been observed.

3. The observed salt effects support the assumption that the rate of conversion of ammonium cyanate into urea depends upon collisions between ammonium and cyanate ions, and not upon collisions between undissociated molecules of ammonium cyanate as has been suggested recently.

4. A method is presented for evaluating the limiting velocity constant (free from salt effects) directly from the experimental data when activity coefficients are known. The constant calculated by this method is in good agreement with that obtained by extrapolating the ordinary bimolecular constant to zero ionic strength.

5. The possibility of determining activity coefficients from velocity measurements is suggested.

(11) La Mer, J. Chem. Phys., 1, 289 (1933).