The Critical Increment of Ionic Reactions. V. The Influence of Dielectric Constant and Ionic Strength[1]

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The investigation of the conversion of ammonium cyanate to urea in isodielectric mixtures of various solvent–water media has been continued in this research using isodielectric mixtures of dioxane–water. The reaction has been studied over a temperature range of 30 to 60° in isodielectric media having a dielectric constant range of 63.5 to 5. The critical increments obtained from the experimental data are compared with those calculated from theoretical equations previously given.[2] Comparison is also made with other existing solution kinetics theories.

Experimental and Discussion

The dioxane was refluxed over calcium oxide and over sodium for about twenty-four hours. It was then distilled twice, the middle portions of each run being collected. The final fraction had a freezing point of 11.72°. The preparation of other materials, purification, experimental procedure, etc., have already been described.[2] Dielectric constants for the dioxane–water media were taken from the work of Åkerlöf and Short.[3] In the preceding paper[2] of this series, these equations were given

$$k_0 t = \left(\frac{1 + 4A\sqrt{C}}{C} \right) - \left(\frac{1 + 4A\sqrt{C^0}}{C^0} \right) \quad (1)$$

$$k_1 = \frac{k_0}{1 + 2A\sqrt{\mu}} \quad (2)$$

$$\log k = \log K - \frac{E}{4.58T} \quad (3)$$

$$(E^0)_{\text{fixed comp.}} = (E_D^{0*}) + \frac{2.3RT^2}{} \left(\frac{\partial \log k_0}{\partial D} \right) \frac{dD}{dT} \quad (4)$$

$$E = E^0 + \frac{12.5 \times 10^8 \sqrt{\mu} RT}{(TD)^{3/2} + 8.36 \times 10^8 \sqrt{\mu}} \left(1 + \frac{d \ln D}{d \ln T} \right) \quad (5)$$

From equation (4) one obtains in dioxane–water media with water as the solvent of fixed composition the relation

$$(E^0)_{\text{H}_2\text{O}} - (E_D^{0*}) = 587T/D \quad (6)$$

Equation (6) leads to a difference of 2720 cal. between the two critical increments at 50°. The experimental differences using 23,580 cal.[2] for $(E^0)_{\text{H}_2\text{O}}$ and using the values of the E_D^{0*}'s given

in Table I vary from 3570 cal. at $D = 63.5$ to 4810 cal. at $D = 20$ and then they decrease again.

TABLE I

SUMMARY OF DATA AT ZERO IONIC STRENGTH IN CONSTANT DIELECTRIC CONSTANT MEDIA

Temp. °C.	Wt. % Diox.	k_0 Eq. 1	Eq. 3	Wt. % Diox.	k_0 Eq. 1	Eq. 3
		At 63.5			At 60	
30	15.0	0.0111	0.0113	19.0	0.0140	0.0138
40	11.50	.0327	.0327	15.65	.0393	.0400
50	7.70	.0896	.0884	12.05	.1075	.108
60	3.85	.223	.225	8.30	.266	.274
log K_0 (eq. 3)		12.46			12.54	
E (eq. 3)		20,010			20,000	
E (eq. 9)		(20,010)			19,850	
		At 55			At 50	
30	24.8	0.0181	0.0187	30.5	0.0262	0.0259
40	21.65	.0524	.0537	27.65	.0734	.0737
50	18.06	.140	.144	24.26	.196	.196
60	14.75	.370	.367	21.20	.488	.492
log K_0 (eq. 3)		12.64			12.61	
E (eq. 3)		19,960			19,720	
E (eq. 9)		19,610			19,310	
		At 45			At 40	
30	36.2	0.0381	0.0378	42.0	0.0567	0.0561
40	33.75	.1071	.107	39.70	.160	.156
50	30.55	.279	.282	36.8	.421	.407
60	27.60	.708	.704	34.0	.997	1.002
log K_0 (eq. 3)		12.68			12.65	
E (eq. 3)		19,590			19,310	
E (eq. 9)		18,930			18,480	
		At 35			At 30	
30	47.8	0.0769	0.0771	53.80	0.163	0.160
40	45.75	.224	.215	51.80	.438	.440
50	42.95	.555	.561	49.50	1.145	1.14
60	40.45	1.490	1.38	47.25	2.79	2.77
log K_0 (eq. 3)		12.81			12.94	
E (eq. 3)		19,340			19,080	
E (eq. 9)		17,880			17,090	
		At 25			At 20	
30	59.80	0.324	0.323	66.10	0.671	0.673
40	58.30	.874	.874	64.90	1.83	1.82
50	56.30	2.19	2.22	63.30	4.57	4.61
60	54.50	5.38	5.35	61.60	11.00	11.08
log K_0 (eq. 3)		13.05			13.34	
E (eq. 3)		18,810			18,770	
E (eq. 9)		15,990				
		At 15			At 10	
30	72.75	1.62	1.61	80.70	5.26	5.25
40	71.80	4.47	4.48	79.90	14.5	14.70
50	70.5	11.30	11.30	79.10	38.50	38.50
log K_0 (eq. 3)		13.85			14.70	
E (eq. 3)		18,940			19,420	
		At 5				
30	91.20	37.2	37.0			
35	90.95	62.4	63.3			
40	90.70	106.0	106.7			
log K_0 (eq. 3)		15.98				
E (eq. 3)		20,000				

(1) Presented at the Baltimore meeting of the A. C. S. April, 1939.

(2) Rampino and Svirbely, THIS JOURNAL, 61, 3534 (1939), was the previous paper of the series.

(3) Åkerlöf and Short, ibid., 58, 1241 (1936).

Reference to Table I shows that E^0_D is apparently constant over part of the higher dielectic range, then it decreases until a minimum value around $D = 20$ is reached and after that a rapid increase occurs. We shall show later that even if we use a more extended equation for calculating the k_0's and consequently should get more reliable E_0's at the lower dielectrics, nevertheless the minimum still exists.
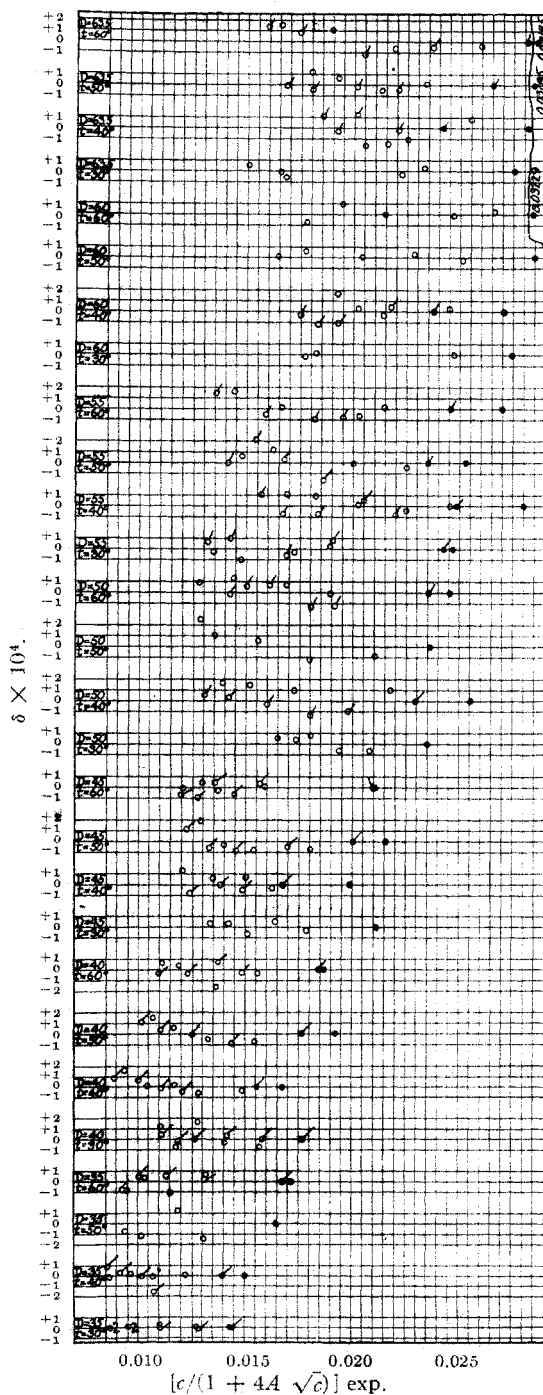

$\delta \times 10^4$

$[c/(1 + 4A \sqrt{c})]$ exp.

Fig. 1.—Dioxane–water mixtures.

$\delta \times 10^4$

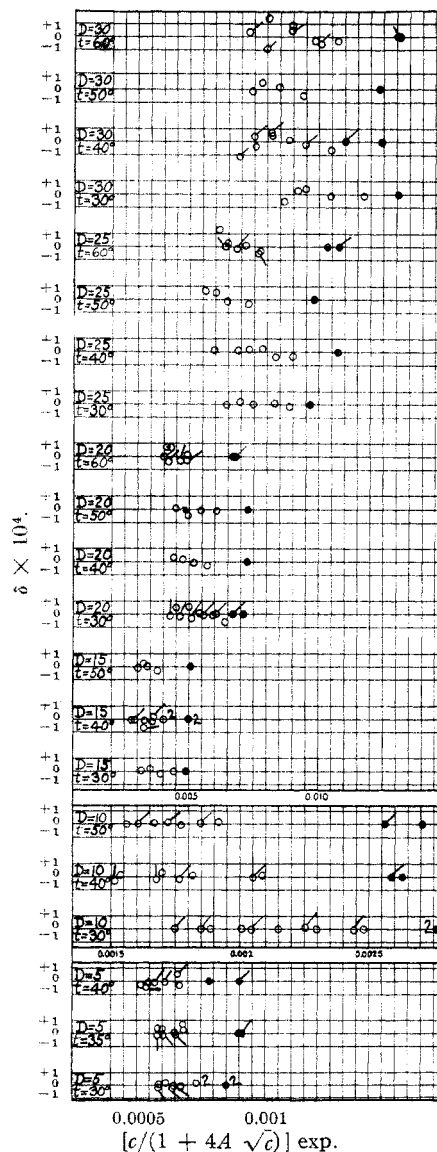0.0005   0.001

$[c/(1 + 4A \sqrt{c})]$ exp.

Fig. 2.—Dioxane–water mixtures.

Using equation 5, the values of E at $\sqrt{\mu} = 0.194$ have been calculated and collected in Table II. These results are in good agreement with the experimental E's.

Similarly to the results in the other solvent–water mixtures, we find in this case deviations from the linearity predicted by Scatchard's equation[4]

$$\log k_0 - \log k_0{}^* = \frac{e^2 Z_A Z_B}{2.3 K T r}\left(\frac{1}{D^0} - \frac{1}{D}\right) \qquad (7)$$

when $(\log k_0 - \log k_0{}^*)$ is plotted against $(1/D^0 - 1/D)$. These plots are shown in Fig. 3 at the

(4) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

TABLE II

SUMMARY OF DATA AT $\sqrt{\mu} = 0.194$ FOR CONSTANT DIELECTRIC CONSTANT MEDIA

| Temp. °C.	k_1 Eq. 2	Eq. 3	k_1 Eq. 2	Eq. 3	k_1 Eq. 2	Eq. 3
	At 63.5		At 60		At 55	
30	0.00691	0.00699	0.00843	0.00827	0.01032	0.0106
40	.0207	.0206	.0241	.0243	.0305	.0311
50	.0577	.0567	.0672	.0667	.0831	.0853
60	.146	.147	.169	.172	.224	.220
log K (eq. 3)	12.53		12.56		12.64	
E (eq. 3)	20,400		20,340		20,300	
E (eq. 5 at 50°)	20,350		20,410		20,350	
	At 50		At 45		At 40	
30	0.0140	0.0140	0.0189	0.0187	0.0255	0.0258
40	.0402	.0405	.0544	.0540	.0743	.0737
50	.110	.109	.145	.146	.200	.197
60	.278	.279	.376	.371	.486	.498
log K (eq. 3)	12.58		12.67		12.68	
E (eq. 3)	20,050		20,000		19,820	
E (eq. 5 at 50°)	20,150		20,050		19,820	
	At 35		At 30		At 25	
30	0.0310	0.0318	0.0568	0.0568	0.0938	0.0938
40	.0929	.0907	.158	.161	.262	.263
50	.236	.242	.424	.426	.678	.694
60	.612	.612	1.064	1.067	1.720	1.720
log K (eq. 3)	12.77		12.90		13.01	
E (eq. 3)	19,820		19,650		19,500	
E (eq. 5 at 50°)	19,890		19,690		19,480	
	At 20		At 15		At 10	
30	0.151	0.152	0.258	0.263	0.494	0.491
40	.428	.427	.744	.745	1.417	1.43
50	1.111	1.113	1.954	1.980	3.93	3.91
60	2.77	2.80				
log K (eq. 3)	13.22		13.58		14.24	
E (eq. 3)	19,500		19,670		20,210	
E (eq. 5 at 50°)	19,500		19,740		20,290	
			At 5			
30			1.31	1.30		
40			3.92	3.94		
log K (eq. 3)			15.21			
E (eq. 3)			20,970			
E (eq. 5 at 50°)			20,950			
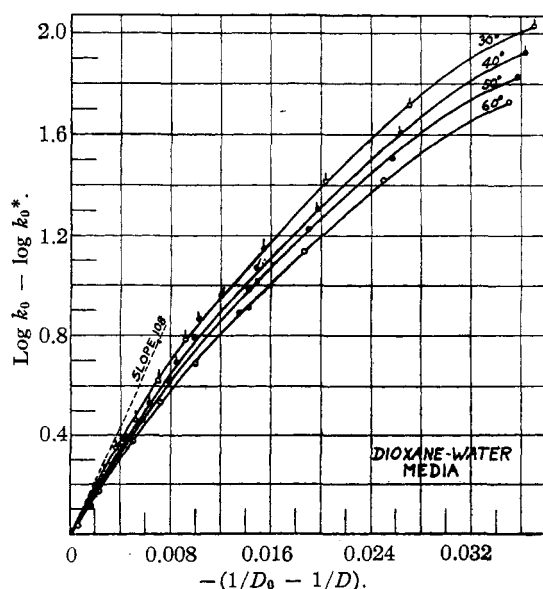
Fig. 3.

various temperatures. The limiting slopes of the curves are in good agreement with the predicted values assuming $r = 2 \times 10^{-8}$ cm. In Fig. 3 we have not shown all of the data obtained. The complete curves tend to flatten out although the slopes are still finite.

The effect of dielectric change and of temperature change on the limiting velocity constant can be expressed by the empirical relation[2]

$$\left(\frac{\Delta k_0}{\Delta D}\right)_T = -C\left(\frac{\Delta k_0}{\Delta T}\right)_D \qquad (8)$$

Using the values of k_0 listed in Table I, it can be shown that C has an average value of 0.61 from $D = 60$ to $D = 35$. On going to lower dielectrics the value of C increases, reaching a value of 14 at $D = 5$.

La Mer's[5] thermodynamic treatment of reactions predicts constancy for the log K's shown in Tables I and II. It is observed that the agreement between the log K's in the two tables in the same isodielectric mixture down to $D = 25$ is good. There is however a tendency toward increased values of the log K's as the dielectric constant is decreased. The increase is not as large however as in the isopropanol–water mixtures.[2]

In calculating critical increments La Mer[5] developed an equation which in isodielectric media and at zero ionic strength becomes

$$(\Delta E^0_D{}^*)_{\sqrt{\mu}=0} = \Delta E_0^* + \frac{Z_A Z_B N e^2}{D}\left(\frac{1}{r_A + r_B}\right) \qquad (9)$$

ΔE_0^*, the energy contribution for the reactants as uncharged molecules can be calculated from the value of $(\Delta E^0_D{}^*)$ at $D = 63.5$ and is 22,620 cal. Using this value of ΔE_0^*, values of $\Delta E^0_D{}^*$ have been determined by means of equation (9) assuming $(r_A + r_B) = 2 \times 10^{-8}$ cm. and are given in Table I. Here again, as in the previous investigation, the agreement between ΔE^*_D calculated and ΔE^*_D by experiment is as good at the higher dielectric constants as could reasonably be expected.

Using La Mer's method[5] for testing the collision theory in terms of the thermodynamic theory, one can calculate σ_{12}, the distance of nearest approach between the centers of the reactants for an effective collision, by means of the equation[2]

$$\log \sigma_{12} = \log K_0/2 - 13.791 \qquad (10)$$

Using the values of log K_0 in Table I, one obtains $\sigma_{12} = 2.75$ Å. at $D = 63.5$. The values then increase to $\sigma_{12} = 5.42$ Å. at $D = 25$. It is interest-

(5) Amis and La Mer, THIS JOURNAL, 61, 905 (1939).

ing to observe that using equation (10) at the higher dielectrics where it should hold best one obtains a variety of σ_{12} values for the reactants in the various solvent–water mixtures in which this reaction has been studied. For example, at $D = 63.5$, σ_{12} equals 1.24 Å., 3.54 Å., 4.83 Å., 2.75 Å. in methanol, glycol, isopropanol and dioxane mixtures, respectively. It is possible that specific solvent influences may be responsible for these variations.

One may compare the percentages by weight of the non-aqueous solvents in the solvent–water mixtures just mentioned at each temperature and at each dielectric value with the values of the limiting velocity constant obtained in order to observe whether the variation in the k_0's seems to depend on the amount of non-aqueous solvent added. No correlation is observed. Plots of log k_0 versus $1/D$ are shown in Fig. 4. It is seen that the dioxane, isopropanol, and glycol curves are fairly close to each other at each temperature although the order of the curves is not the same at all of the temperatures. However, placing each solvent in the order of increasing percentage of non-aqueous solvent, we have dioxane, isopropanol, methanol and glycol, respectively.

It was considered worth while to develop a more accurate method of calculating the limiting velocity constant and observe whether or not the new results would influence the conclusions previously drawn. Starting with the equation[4]

$$\ln k = \ln k_0 + \frac{2.3e^2 Z_A Z_B \kappa}{DKT\,(1 + \kappa b)} \tag{11}$$

substituting in the various terms and using the well-known relation

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_x} \tag{12}$$

one obtains

$$\frac{\gamma_A \gamma_B}{\gamma_x} = e - a\sqrt{\mu}/(b + d\sqrt{\mu}) \tag{13}$$

where

$$a = 8.35 \times 10^6$$
$$b = (DT)^{3/2}$$
$$d = 100\,DT$$

Following Scatchard's[6] method equation (13) becomes

$$\frac{\gamma_A \gamma_B}{\gamma_x} = \frac{b + d\sqrt{\mu}}{b + \mathrm{d}\sqrt{\mu} + a\sqrt{\mu}} \tag{14}$$

Applying Scatchard's[6] treatment of the rate of reaction in a changing environment, the Brönsted rate equation on using equation 14 becomes

$$\frac{dx}{dt} = \frac{k_0 C_0 (1 - x)^2 (b + d\sqrt{C_0}\sqrt{1 - x})}{b + (a + d)\sqrt{C_0}\sqrt{1 - x}} \tag{15}$$
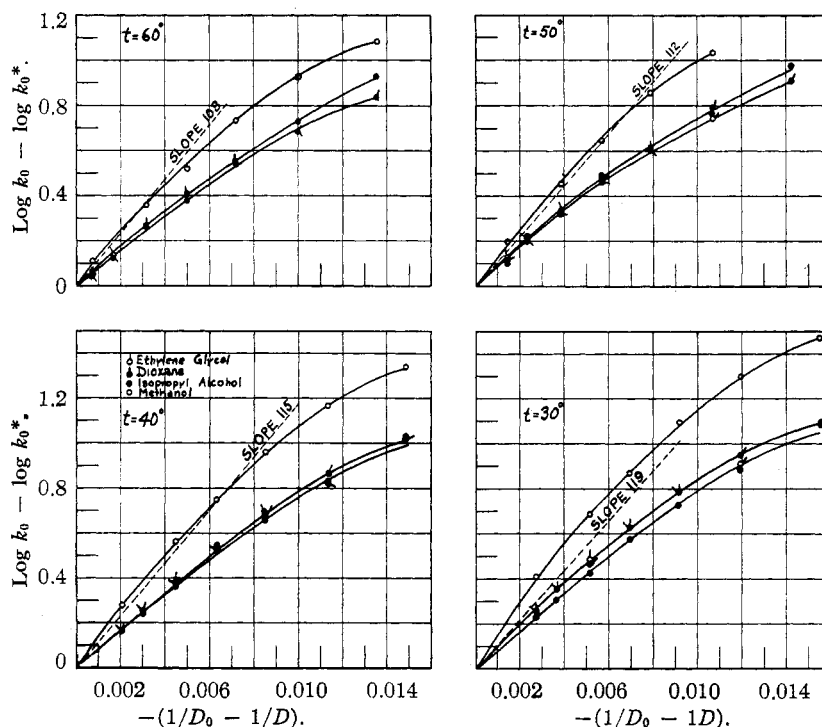

Fig. 4.

where $x = (C_0 - C)/C_0$. Clearing and integrating by parts equation (15) becomes

$$\left(\frac{2A\sqrt{C_0}}{b} + 1\right)\left(\frac{1}{C} - \frac{1}{C_0}\right) +$$
$$\frac{2ad}{b^2}\ln\frac{\sqrt{C}\,(b + d\sqrt{C_0})}{\sqrt{C_0}\,(b + d\sqrt{C})} = k_0 t \tag{16}$$

Using equation (16) values of k_0 were calculated for some of the isodielectric media and are given in Table III. Comparison of the values of k_0 in Tables I and III shows that with equation (16) one obtains higher values of k_0 than with equation (1). However, the values of ΔE are not affected down to $D = 25$. The increase in log K_0

(6) Scatchard, THIS JOURNAL, 52, 52 (1930).

TABLE III

k_0 VALUES USING EQ. 16 IN ISODIELECTRIC MEDIA

Temp., °C.	63.5	60	55	25	5
30	0.0167	0.0211	0.0283	0.58	71
40	.0470	.0574	.0813	1.63	221
50	.131	.158	.211	4.14	
60	.330	.401	.561	10.1	
E (eq. 3)	20,000	19,950	19,950	18,750	21,700
log K_0 (eq. 3)	12.63	12.67	12.82	13.29	17.47

is still obtained. The minimum in ΔE is emphasized more than before due to the large increase in ΔE at $D = 5$. This increase may only be an apparent one due to the method of calculation and it may be necessary for an entirely new treatment in low dielectrics to allow for association effects.

TABLE IV

RATE OF CONVERSION OF AMMONIUM CYANATE INTO UREA AT 40°

D	t, min.	C, moles/liter	Range of concn.	$\sqrt{\mu}$	Bimolecular, k (graphical)
25	0	0.08648	0.07 –0.06	0.255	0.218
	20	.06348	.06 – .05	.2343	.225
	30	.05550			
	40	.04971	.05 – .045	.218	.227
	50	.04434	.045– .04	.206	.247
	60	.03994	.04 – .035	.194	.255
	87	.03102	.035– .030	.180	.269
20	0	.07294	.07 – .06	.255	.335
			.06 – .05	.2343	.370
	20	.04740	.05 – .045	.218	.383
	30	.03995	.045– .04	.206	.402
	40	.03426	.04 – .035	.194	.425
	50	.02992	.035– .030	.180	.434
15	0	.07170	.07 – .06	.255	.627
			.06 – .05	.2343	.640
	10	.04966	.05 – .045	.218	.660
	16	.04093	.045– .04	.206	.692
	21	.03570	.04 – .035	.194	.700
	34	.02587	.035– .030	.180	.768
10	0	.06782	.06 – .05	.2343	1.15
			.05 – .045	.218	1.28
	7	.04356	.045– .04	.206	1.32
	12	.03333	.04 – .035	.194	1.43
	15	.02937	.035– .030	.180	1.53
	19	.02436	.030– .025	.166	1.59
5	0	.06003	.06 – .05	.2343	2.77
			.05 – .045	.218	3.03
			.045– .04	.206	3.65
			.04 – .035	.194	4.02
	4	.03263	.035– .030	.180	4.62
	5	.02794			
	6	.02467	.030– .025	.166	5.04
	7	.02210			

In solvents of $D \geqq 25$, calculations by equation (1) and by (16) lead to essentially the same values for E and log K_0 and we therefore could see no advantage in recalculating all of our results by the use of equation (16). Equation (16) apparently represents only a slight improvement over equation (1) and neither equation is adequate for calculating true k_0 values in the solvents of lower dielectric constant. We, therefore, are giving the actual time–concentration data for typical experiments at 40° in solvents of dielectric constants 25, 20, 15, 10 and 5 in Table IV. The ordinary bimolecular constants over finite ranges of concentration are also given in the table.

Summary

1. The rate of conversion of ammonium cyanate to urea has been studied over the temperature range 30 to 60° in isodielectric mixtures of dioxane with water over a dielectric range 63.5 to 5.

2. The influence of ionic strength upon the observed critical increments at zero ionic strength is in good agreement with the theory. It is observed that the critical increment first decreases somewhat with the dielectric constant and then increases, with a minimum appearing at about $D = 20$.

3. From $D = 63.5$ to $D = 35$, the following empirical relation holds

$$\left(\frac{\Delta k_0}{\Delta D}\right)_T = -0.61\left(\frac{\Delta k_0}{\Delta T}\right)_D$$

4. The influence of the dielectric constant upon the rate constants is in reasonably good agreement with the Scatchard–Christiansen theory at the higher dielectric constants.

5. The value of the collision factor Z varies somewhat with the dielectric constant, especially at the lower dielectric constants.

6. The collision theory is shown to be in satisfactory agreement with the thermodynamic treatment in the higher isodielectric mixtures.

7. The new method of calculating the limiting velocity constants leads to higher values but does not influence the conclusions previously drawn.