

[JOINT CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF CANISIUS COLLEGE AND OF THE UNIVERSITY OF MARYLAND]

The Critical Increment of Ionic Reactions. IV. The Influence of Dielectric Constant and Ionic Strength¹BY LOUIS RAMPINO² AND W. J. SVIRBELY

In this investigation the conversion of ammonium cyanate to urea has been carried out over a temperature range of 30 to 60° in isodielectric mixtures of water with isopropanol over a dielectric range of 63.5 to 20. The critical increments obtained from the corresponding rate constants are compared with those obtained from theoretical

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

Temp. °C.	Wt. % <i>i</i> -PrOH		k_0		Wt. % <i>i</i> -PrOH		k_0	
	Eq. 1	Eq. 3	Eq. 1	Eq. 3	Eq. 1	Eq. 3	Eq. 1	Eq. 3
	At 63.5				At 60			
30	18.70	0.0105	0.0103	23.50	0.0125	0.0128		
40	14.15	.0313	.0309	19.30	.0372	.0384		
50	9.65	.0852	.0865	14.8	.114 ^a	.108		
60	4.98	.228	.228	10.50	.279	.285		
log K_0 (eq. 3)		12.95			13.08			
<i>E</i> (eq. 3)		20,750			20,800			
<i>E</i> (eq. 9)		(20,750)			20,590			
	At 55				At 50			
30	30.65	0.0165	0.0168	37.75	0.0234	0.0234		
40	26.58	.0502	.0505	33.90	.0709	.0702		
50	22.60	.145 ^a	.142	30.20	.210 ^a	.197		
60	18.30	.378	.376	26.16	.516	.518		
log K_0 (eq. 3)		13.22			13.30			
<i>E</i> (eq. 3)		20,830			20,740			
<i>E</i> (eq. 9)		20,350			20,050			
	At 45				At 40			
30	44.85	0.0331	0.0332	51.90	0.0479	0.0493		
40	41.25	.0975	.0994	48.65	.147	.148		
50	37.80	.273 ^a	.278	45.40	.397 ^a	.414		
60	34.17	.725	.731	42.10	1.094	1.091		
log K_0 (eq. 3)		13.43			13.63			
<i>E</i> (eq. 3)		20,710			20,750			
<i>E</i> (eq. 9)		19,670			19,220			
	At 35				At 30			
30	59.05	0.0762	0.756	66.35	0.135	0.134		
40	56.10	.233	.229	63.90	.408	.406		
50	53.05	.642	.644	60.90	1.122	1.146		
60	50.10	1.71	1.71	58.15	3.030	3.038		
log K_0 (eq. 3)		13.91			14.16			
<i>E</i> (eq. 3)		20,880			20,880			
<i>E</i> (eq. 9)		18,620			17,830			
	At 25				At 20			
30	75.55	0.296	0.296	88.80	0.954	0.956		
40	72.40	.856	.853	84.20	2.470	2.45		
50	69.60	2.290	2.30	80.60	5.940	5.92		
60	66.82	5.840	5.880	77.60	13.51	13.59		
log K_0 (eq. 3)		13.89			12.75			
<i>E</i> (eq. 3)		20,030			17,780			
<i>E</i> (eq. 9)		16,730			15,070			

^a k_0 value from work of Warner and Warrick, ref. 6.

(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) From the thesis presented to the Graduate Committee of Canisius College by Louis Rampino in partial fulfillment of the requirements for the degree of Master of Science, June, 1939.

TABLE II

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

Temp. °C.	k_1		k_1	
	Eq. 2	Eq. 3	Eq. 2	Eq. 3
	At 63.5			
30	0.00654	0.00646	0.00753	0.00769
40	.0198	.0198	.0229	.0235
50	.0548	.0563	.0712	.0672
60	.146	.151	.177	.180
log K (eq. 3)	13.00		13.09	
<i>E</i> (eq. 3)	21,100		21,120	
<i>E</i> (eq. 6 at 50°)	21,090		21,160	
	At 55			
30	0.00941	0.00974	0.0125	0.0126
40	.0293	.0299	.0388	.0387
50	.0861	.0857	.118	.111
60	.229	.231	.294	.297
log K (eq. 3)	13.25		13.32	
<i>E</i> (eq. 3)	21,200		21,140	
<i>E</i> (eq. 6 at 50°)	21,220		21,170	
	At 45			
30	0.0164	0.0164	0.0215	0.0219
40	.0496	.0503	.0683	.0676
50	.142	.144	.188	.195
60	.385	.385	.533	.525
log K (eq. 3)	13.42		13.66	
<i>E</i> (eq. 3)	21,120		21,280	
<i>E</i> (eq. 6 at 50°)	21,180		21,260	
	At 35			
30	0.0307	0.0309	0.0471	0.0468
40	.0967	.0958	.147	.145
50	.274	.277	.416	.421
60	.749	.749	1.157	1.145
log K (eq. 3)	13.86		14.09	
<i>E</i> (eq. 3)	21,350		21,420	
<i>E</i> (eq. 6 at 50°)	21,430		21,490	
	At 25			
30	0.0857	0.0852	0.215	0.214
40	.256	.253	.578	.572
50	.710	.705	1.445	1.442
60	1.887	1.845	3.395	3.437
log K (eq. 3)	13.76		12.72	
<i>E</i> (eq. 3)	20,600		18,600	
<i>E</i> (eq. 6 at 50°)	20,700		18,510	

equations previously derived and used.³ Comparison is also made with other existing kinetics theories.

Experimental and Discussion

The isopropanol⁴ was refluxed over calcium oxide and anhydrous potassium carbonate for twenty hours and then fractionally distilled. The center portion was redistilled over a small amount

(3) Lander and Svirbely, THIS JOURNAL, 60, 1613 (1938), previous paper of the series.

(4) Grateful acknowledgment is made to the Union Carbide and Carbon Corp., N. Y. for providing the isopropanol used.

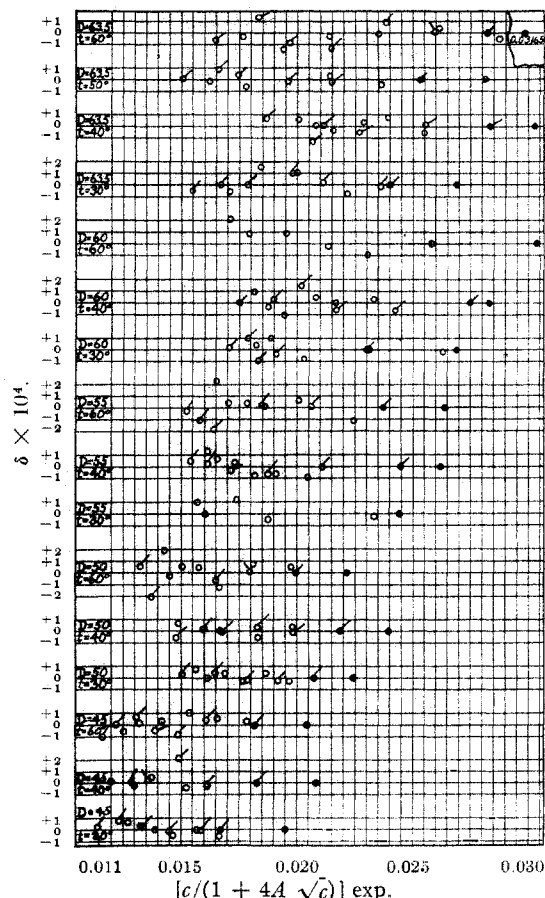


Fig. 1.—Isopropyl alcohol-water mixtures.

of sodium, the boiling point being 82° (uncorr.). All other materials were prepared or purified as described in previous papers,³ which also describe the procedure used in this investigation. Temperatures were checked against a thermometer calibrated by the Bureau of Standards. Thermostat temperatures were maintained constant within $\pm 0.01^\circ$. Dielectric constants for the isopropanol-water mixtures were taken from the work of Åkerlöf.⁵

Average values of the limiting velocity constant at $\mu = 0$ listed in Table I were obtained by means of the usual equation^{3,6}

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

Derivations (δ) of the experimental value of $C/(1 + 4A\sqrt{C})$ from the value calculated from the average k_0 are plotted^{3,6} against the experimental values of this function in Figs. 1 and 2. In Table II we give velocity constants (k_1) at $\sqrt{\mu} = 0.194$ obtained from k_0 by the relation^{3,6}

(5) Åkerlöf, *THIS JOURNAL*, **54**, 4125 (1932).

(6) Warner and Warrick, *ibid.*, **57**, 1491 (1935).

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

If $\log k_0$ is plotted against $1/T$ for the various isodielectric mixtures, then one may express the linear plots as well as those of $\log k_1$ against $1/T$ by means of the general equation

$$\log k = \log K - (E/4.58T) \quad (3)$$

Values of $\log K_0$ and E_0 and of $\log K_1$ and E_1 obtained by means of equation (3) are listed in Tables I and II, respectively. Values of k_0 and k_1 calculated by equation (3) using the tabulated values of $\log K$ and E are also shown in the tables.

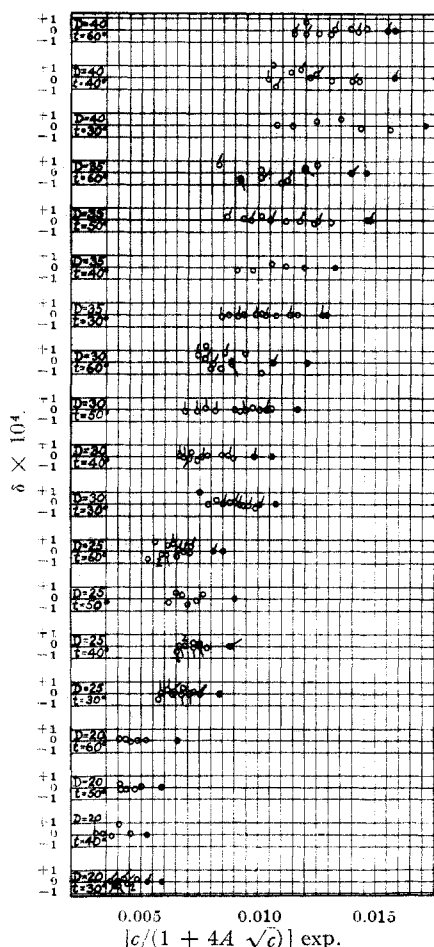


Fig. 2.—Isopropyl alcohol-water mixtures.

From the equation³

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

one obtains in this case using water as the solvent of fixed composition

$$(E^0)_{\text{H}_2\text{O}} - (E^0)_D = 620T/D \quad (5)$$

At 50° , using equation (5), one calculates the difference between the two critical increments to be

2860 cal. Using the experimental values of the E_0 's given in Table I and taking E_0 in water³ to be 23,580 cal., one observes that the difference between the two critical increments varies between 2830 to 2700 cal. in the isodielectric mixtures from 63.5 to 30. The difference becomes larger at the dielectric values of 25 and 20. Thus E_D^* apparently is independent of the dielectric constant over the major portion of the dielectric range covered.

One may calculate the critical increment at a fixed ionic strength by means of the equation³

$$E = E^0 + \frac{(12.5 \times 10^6 \sqrt{\mu} RT)}{(TD)^{3/2} + 8.36 \times 10^6 \sqrt{\mu}} \left(1 + \frac{d \ln D}{d \ln T} \right) \quad (6)$$

The values for E at $\sqrt{\mu} = 0.194$ have been obtained using equation (6) and are listed in Table II. These results are in good agreement with the E 's obtained by equation (3).

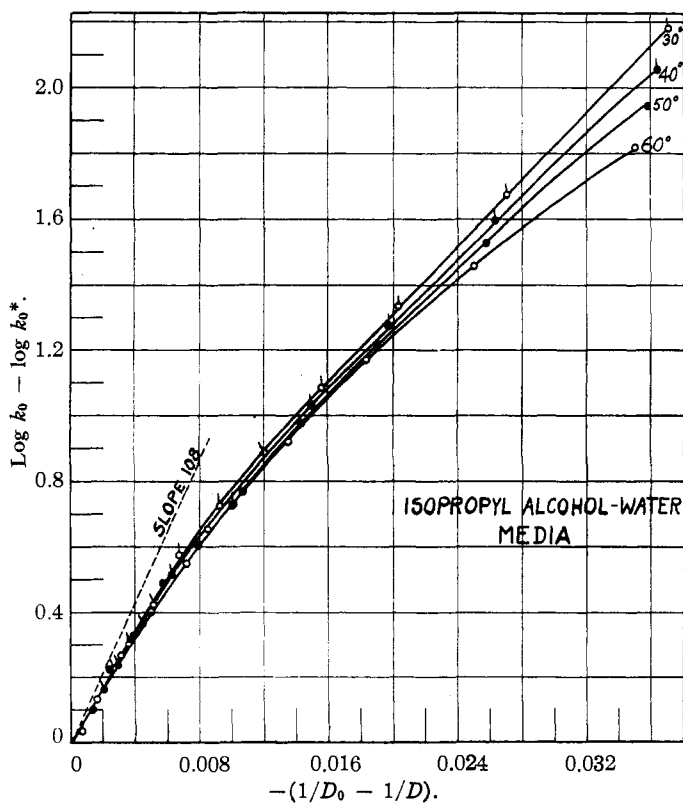


Fig. 3.

Deviations from the linearity predicted by Scatchard's⁷ equation

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

are obtained when $(\log k_0 - \log k_0^*)$ are plotted

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

against $(1/D^0 - 1/D)$. These plots are shown in Fig. 3 at the various temperatures. The limiting slopes of the curves are in fair agreement with the predicted values assuming $r = 2 \times 10^{-8}$ cm.

As pointed out before, an empirical relation can be obtained between the dielectric effect and the temperature effect on the value of the limiting velocity constant, namely

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

Using the values in Table I, one observes that C has an average value⁸ of 0.52 from $D = 60$ to $D = 40$. On going to lower dielectrics C increases reaching an average value of 2.80 at $D = 20$.

Referring to the values of $\log K_0$ and $\log K$ in Tables I and II, it is observed that for any isodielectric mixture the two values are fairly constant. However, as one goes to lower dielectrics ($D = 63.5$ to $D = 30$) a continual increase is obtained.

This behavior of $\log K_0$ is similar to that observed in the isodielectric glycol-water mixtures³ and also in isodielectric dioxane-water mixtures (forthcoming paper). La Mer's⁹ treatment for reactions predicts constancy¹⁰ for the $\log K$'s (B in his notation).

Taking into account the various factors which should influence the critical increment, La Mer⁹ developed an equation which in isodielectric media and at zero ionic strength becomes

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

where (ΔE_D^*) is the critical increment in isodielectric media, ΔE_0^* refers to the energy contribution for the reactants as uncharged molecules and the other terms have the usual meanings. Using the experimental values of ΔE_0^* at $D = 63.5$ one calculates ΔE_0^* to be 23,360 cal. Values of ΔE_D^* calculated from this value of ΔE_0^* by means of equation (9) assuming $(r_A + r_B) = 2 \times 10^{-8}$ cm. are given in Table I. The agreement at the

higher dielectric constants is as good as should be expected considering the limitations imposed

(8) We wish to point out an error in the paper using glycol-water mixtures, Ref. 3, where C should be 0.55.

(9) Amis and La Mer, *This Journal*, **61**, 905 (1939).

(10) It should be pointed out that this constancy is obeyed for this reaction in isodielectric methanol media.

on equation (9), especially due to the assumption of a constant value for $r_A + r_B$.¹¹

In testing the collision theory in terms of the thermodynamic theory as developed by La Mer⁹ the following equation is obtained when the P factor is assumed = 1

$$\frac{RT}{Nh} e^{\Delta S^*/R} = \frac{N}{1000} \sigma_{12}^2 \left[8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} \quad (10)$$

where N = Avogadro's number, h = Planck's constant, M_1 and M_2 are the molecular weights of the reactants and σ_{12} is the distance of the approach between centers of reactants for an effective collision. Substituting in the various values at $t = 60^\circ$ using $M_1 = 18$, $M_2 = 42$, and clearing one obtains

$$\log \sigma_{12} = 1/2(\Delta S^*/2.3R) - 6.7125 \quad (11)$$

which in turn⁹ leads to

$$\log \sigma_{12} = 1/2(\log K_0 - \log(RT/hN)) - 6.7125 \quad (12)$$

Since $\log RT/hN = 14.1520$ (min.⁻¹) at 60° then equation (12) becomes

$$\log \sigma_{12} = \frac{\log K_0}{2} - 13.791 \quad (13)$$

Using the values of $\log K_0$ given in Table I, σ_{12} can be determined in the various isodielectric media by means of equation (13). This method gives $\sigma_{12} = 4.83 \text{ \AA.}$ at $D = 63.5$, and then σ_{12} increases to a maximum value of 19.4 \AA. at $D = 30$. Thus

TABLE III

RATE OF CONVERSION OF AMMONIUM CYANATE INTO UREA AT 40°

D	t , min.	C , moles/liter	Range of concn.	$\sqrt{\mu}$	Bimolecular k_1 , (graphical)
30	0	0.05686			
	43	.04264	0.050-0.045	0.218	0.130
	60	.03885	.045-.040	.206	.147
	84	.03412	.040-.035	.194	.156
	101	.03100	.035-.030	.180	.169
	115	.02949			
25	0	.06032	.06-.05	.2343	.220
	16	.04938	.050-.045	.218	.229
	24	.04557			
	29	.04315	.045-.040	.206	.252
	37	.03962			
	45	.03622	.040-.035	.194	.295
20	0	.04035	.040-.035	.194	.526
	12	.03144	.035-.030	.180	.618
	21	.02571	.030-.025	.166	.661
	32	.02203	.025-.020	.150	.703
	44	.01863			
	54	.01625			

(11) In glycol-water media the agreement between ΔE^*_{D} calculated and ΔE^*_{D} by experiment is comparable to that found in this investigation. It is rather surprising that considerably better agreement is found in methanol-water media.

at the higher dielectrics the collision theory is in satisfactory agreement with the thermodynamic treatment although at the lower dielectrics the agreement is less satisfactory.

Finally as to the behavior of this reaction in $D = 25$ and $D = 20$ media as evidenced by the very marked drop in ΔE and in $\log K_0$, we can offer no definite answer. Undoubtedly association plays some part as the dielectric constant is decreased and probably the mechanism of the reaction itself changes. Due to this uncertainty concerning the mechanism and the inadequacy of equations (1) and (2) in the solvents of lower dielectric constant, we are presenting the actual time-concentration data in Table III on typical experiments at 40° in solvents of dielectric constants 30, 25 and 20, along with the second order constants calculated for a mean ionic strength at various concentration ranges by the graphical method.⁶

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 isopropanol with water over the dielectric range of 63.5 to 20 .

2. The influence of ionic strength upon the observed critical increments at zero ionic strength is in good agreement with equations previously derived. It is observed that the critical increment is apparently independent of the dielectric constant in isodielectric mixtures over the major portion of the range investigated.

3. From $D = 63.5$ to $D = 40$, the following empirical relation holds

$$\left(\frac{\Delta k_0}{\Delta D} \right)_T = -0.52 \left(\frac{\Delta k_0}{\Delta T} \right)_D$$

4. At the higher dielectric constants, the influence of the dielectric constant of the solvent upon the rate constants is in as good agreement with the Scatchard-Christiansen theory as can reasonably be expected.

5. The value of the collision factor Z in the Arrhenius theory varies with dielectric constant.

6. Comparisons are made between the observed critical increments and those calculated by the thermodynamic treatment of La Mer.

7. The collision theory is shown to be in satisfactory agreement with the thermodynamic treatment at the higher dielectrics used.

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