Dielectric and Solvent Effects upon the Rate of Sucrose Inversion by Hydrochloric Acid

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A. Theoretical.—The experimental work for the application of kinetic theory to reactions in solution was for a long time confined to a study of reaction rates either in aqueous solution or in mixed solvents of fixed composition. Warner,[1] Svirbely,[2] and co-workers,[3] pioneered in the study of reaction rates in isodielectric media, and were struck by the contrast of the energies of activation in the two types of media. LaMer[4,5] and his students have emphasized the concept of entropies of activation, and have noted similar striking contrasts in these, as well as the energies, when measured in isodielectric and in isocomposition media.

In the few studies of reaction rates in isodielectric media so far published, the workers have been concerned only with charged types of reactants. Svirbely and Warner[1] have derived an equation relating the energies of activation in isocomposition and isodielectric media in infinitely dilute solution. Amis[6] has shown that the change in energies of activation with change in dielectric in isodielectric media is due to changes in coulombic energy. An equation relating the energies of activation in the two types of media may be derived from the Brönsted[7]–Christiansen[8]–Scatchard[9] equation which, in the limiting case of low concentration, is

$$\log k = \log k_\infty - \frac{Z_A Z_B e^2 N}{DRT} \frac{1}{r_A + r_B} + \frac{Z_A Z_B e^2 N}{DRT} \kappa \quad (1)$$

The difference in the expression obtained when this equation is differentiated with respect to T, T and D variable, and the one obtained when it is differentiated with respect to T, D constant, is when multiplied by RT^2:

$$\Delta E_C^* - \Delta E_D^* = \frac{RT}{D^2} \left(\frac{Z_A Z_B e^2}{kr} - \right.$$
$$\left. \frac{3\sqrt{2}\, Z_A Z_B e^3 \pi^{1/2} N^{1/2} \mu^{1/2}}{1000^{1/2} k^{3/2} D^{1/2} T^{1/2}} \right) \frac{dD}{dT} \quad (2)$$

where $r = r_A + r_B$, ΔE_C^* is the energy of activation in isocomposition media, ΔE_D^* is that in isodielectric media, and k is the Boltzmann gas constant. The derivation is based on the assumption that $\log k_\infty$ is independent of slight changes in dielectric constant. If we consider

$$\frac{d \log k}{d(1/D)} = - \frac{d \log k}{dD} D^2 \quad (3)$$

we can obtain

$$\frac{d \log k}{dD} = - \frac{1}{D^2} \frac{d \log k}{d(1/D)} \quad (4)$$

Our assumption implies, therefore, that for infinite dielectric constant d log k_∞/[d $1/D$] is zero or finite. Plots[10] of log k vs. $1/D$ indicate that log k is directly proportional to $1/D$, especially at high dielectric constant, the slope of the lines within the region studied being such as to indicate a finite value for d log k_∞/[d$(1/D)$]. For this reason we feel that our assumption is justified. For zero ionic strength, this equation reduces to the equation proposed by Svirbely and Warner[1] for the differences between these energies of activation. This equation should hold in any region of concentration where the Debye–Hückel limiting law is valid. Since the first term in the parentheses is generally large in comparison to the second term, and since the term dD/dT is negative, this equation would predict that the energy of activation would be less in isocomposition media than in isodielectric media for a reaction between ions possessing charges of like sign, and greater for those of opposite sign. The equation further predicts that for a reaction between an uncharged particle and an ion of either sign, the difference would be zero. Actually the energies may not be the same even when one or both of the reactants are not ionic, since there are small electrostatic forces between polar molecules and ions or between two polar molecules.

In order to test Eq. 2 together with the electrostatic theory of energies of activation, the authors investigated the acid inversion of sucrose in isocomposition and in isodielectric media. If the mechanism for the reaction is

$$S + H_3O^+ \rightleftharpoons SH_3O^+ \longrightarrow \text{Invert sugars} + H^+$$
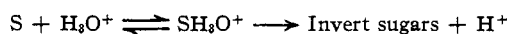
(1) Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935).
(2) Svirbely and Schramm, ibid., **60**, 330 (1938).
(3) Lander and Svirbely, ibid., **60**, 1613 (1938).
(4) LaMer and Kamner, ibid., **57**, 2662 (1935).
(5) LaMer and Amis, ibid., **61**, 905 (1939).
(6) Amis, ibid., **63**, 1606 (1941).
(7) Brönsted, Z. physik. Chem., **102**, 169 (1922); **115**, 137 (1925).
(8) Christiansen, ibid., **113**, 35 (1924).
(9) Scatchard, THIS JOURNAL, **52**, 52 (1930); Chem. Rev., **10**, 229 (1932).
(10) LaMer, J. Franklin Inst., **225**, 709 (1938).

to agree with Leininger and Kilpatrick,[11] the reaction is a dipole-ion type, and Eq. 2 would predict equal energies of activation in isocomposition and in isodielectric media.

For a dipole whose centers of charge are on a straight line with the center of charge on an ion, the equation for the change of electrostatic energy with changing dielectric constant in isodielectric media can be written

$$\Delta E_{Elec.} = \Delta(\Delta E^*) = \frac{69.1 Z_2 \mu_1}{D_1 D_2 r} \Delta D \text{ (kcal.)} \quad (5)$$

and indicates that the energy of activation should decrease with decrease in dielectric constant in the above reaction, which involves a positively charged ion and a dipole. This would be true in the case of the proposed mechanism, since the increase of electrostatic attraction at lower dielectric constants would increase the concentration of the complex and hence speed up the reaction rate.

If the effect of a solvent upon a reaction rate is not merely an electrostatic influence due to the change produced by the dielectric constant of the media, then Eq. 5 will not hold. Since it is known that alcohols form ROH_2^+ ions, their influence on the reaction involved in the inversion of sucrose would be other than electrostatic.

It was determined, therefore, in this investigation to use ethyl alcohol–water media to test the above phenomenon and to test what was hoped would be purely electrostatic effects by using dioxane–water media.

B. Purification of Materials and Experimental Details

The ethyl alcohol used was 95% alcohol. This was refluxed for five to eight hours over calcium oxide and distilled. The last trace of water was removed from this distillate by refluxing over metallic calcium until a precipitate of calcium alcoholate formed. The final fractionation was in an all-glass fractionating apparatus with a 48-inch Vigreux column and partial return still head. The alcohol was used immediately after final fractionation. The dioxane was purified according to the method described by Oxford,[12] and used immediately. The distilled water was of conductance quality. Dielectric data were taken from the findings of Akerlof[13] for alcohol–water and of Akerlof and Short[14] for dioxane–water. The sugar selected was Baker Analyzed, c. p. sucrose, and was always taken from freshly opened bottles. The hydrochloric acid was Merck c. p. grade made up to about 2 N and restandardized at frequent intervals with reagent quality sodium carbonate.

All volumetric apparatus was calibrated, and the weights were calibrated by the substitution method with weights

certified by the U. S. Bureau of Standards. The thermometers were calibrated at the temperatures used to 0.01° with Bureau of Standards certified thermometers. The saccharimeter was a Jos and Jan Fric split field polarimeter, and the light source was a General Electric Sodium Lab-Arc Lamp. The readings were taken in less than fifteen seconds, the average of readings taken from opposite directions of approach to the zero point being recorded.

The temperature was held to ±0.005° by a thermoregulator system described by Padgitt.[15] The reaction was studied in jacketed polarimeter tubes around which water from the bath was circulated at such a rate that no temperature gradient could be detected in the thermometer wells with a Beckmann thermometer.

The solution for study was prepared as follows: 1.2500 g. of sucrose was weighed out and transferred to a 25-ml. volumetric flask, taken up with the least possible amount of water, and the necessary volume of non-aqueous solvent added. The flask was next filled to about 5 ml. of the mark with water and carefully mixed. The flask was then placed in the bath and allowed to come to equilibrium. The required amount of acid to make the final solution exactly 0.1000 N was now added, the liquid adjusted to the mark with water, mixed and placed immediately in the tube. Time was taken at the midpoint of the time of introduction of the acid, which required about fifteen seconds. The first reading was taken as soon as possible after introduction into the tubes, and the time noted. Initial rotation was determined by extrapolation back to zero time. The reaction was followed until the reaction was about 75% complete. Final reading was taken after no change could be detected in eight hours for the slower runs and a proportionally shorter time for the faster ones.

The rate constant was calculated by the equation

$$k = \frac{2.3}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \quad (6)$$

where α_0 and α_∞ are the initial and final readings, and α_t is the reading at time t. Time t was taken in minutes and common logarithms were used. The mean of some 15 or 20 constants calculated from readings taken from 20 to 75% completion of a run was taken as the constant from the run.

C. Results and Discussion

In Table I are given the measured reaction rate constants and also the energies of activation and the quantity B (B is in min.$^{-1}$) from the Arrhenius equation, for the results of studies of reactions in isocomposition and in isodielectric alcohol–water media. Table II records the similar data for dioxane–water.

The B term was calculated from the expression

$$B = \frac{\Delta(T \log k)}{\Delta T} \quad (7)$$

where k is the unimolecular rate constant in min.$^{-1}$.

(11) Leininger and Kilpatrick, THIS JOURNAL, 60, 2891 (1938).

(12) Oxford, Biochem. J., 28, 1328 (1934).

(13) Akerlof, THIS JOURNAL, 54, 4125 (1932).

(14) Akerlof and Short, ibid., 58, 1242 (1936).

(15) Padgitt, Ind. Eng. Chem., Anal. Ed., 13, 60 (1941).

TABLE I

REACTION RATE CONSTANTS, AND ALSO THE ENERGIES OF ACTIVATION AND THE QUANTITY B IN MIN.$^{-1}$ CALCULATED BY THE ARRHENIUS EQUATION FROM THE RESULTS OF STUDIES OF THE ACID INVERSION OF SUCROSE IN ISOCOMPOSITION AND ISODIELECTRIC ALCOHOL–WATER MEDIA

	Constant composition, %					Constant dielectric constant			
	0 EtOH Pure water	12.65 EtOH	28.46 EtOH	45.43 EtOH	54.40 EtOH	D 68.15	D 60.00	D 50.00	D 45.00
$k_{21} \times 10^4$	4.42	4.28	3.73	3.22	3.13	4.10	3.62	3.04	...
$k_{31} \times 10^4$	19.16	18.83	17.09	14.83	14.51	18.72	17.09	14.83	14.42
$k_{41} \times 10^4$	73.5	71.9	65.7	59.6	58.5	72.1	66.8	61.0	60.3
$10^{-3} \Delta E^*$ (21–31°)	26.07	26.33	27.05	27.13	27.25	27.00	27.60	28.16	...
$10^{-3} \Delta E^*$ (31–41°)	25.51	25.42	25.62	26.42	26.47	25.57	26.14	26.86	27.18
B (21–31°)	20.02	20.20	20.68	20.68	20.67	20.67	21.06	21.41	...
B (31–41°)	19.62	19.55	19.60	19.60	20.15	19.67	19.83	20.47	20.67

TABLE II

REACTION RATE CONSTANTS, AND ALSO THE ENERGIES OF ACTIVATION AND THE QUANTITY B IN MIN.$^{-1}$ CALCULATED BY THE ARRHENIUS EQUATION, FROM THE RESULTS OF STUDIES OF THE ACID INVERSION OF SUCROSE IN ISOCOMPOSITION AND ISODIELECTRIC DIOXANE–WATER MEDIA

	Constant composition, %				Constant dielectric constant		
	Pure water	Dioxane 23.40	Dioxane 33.20	Dioxane 38.79	Dioxane D60	Dioxane D50	Dioxane D45
$k_{21} \times 10^4$	4.42	5.69	5.97	6.38	5.69	5.96	6.38
$k_{31} \times 10^4$	19.16	23.49	23.85	25.79	22.73	23.81	24.92
$k_{41} \times 10^4$	73.5	78.3	80.81	86.6	76.2	78.81	82.0
$10^{-3} \Delta E^*$ (21–31°)	26.07	25.21	24.68	24.63	24.68	24.54	24.23
$10^{-3} \Delta E^*$ (31–41°)	25.51	23.21	23.18	23.00	22.89	22.76	22.60
B (21–31°)	20.02	19.48	19.07	19.25	19.04	19.07	18.80
B (31–41°)	19.62	17.79	18.02	17.94	17.86	17.70	17.64

From the tables it can be observed that the energies of activation in isocomposition and in isodielectric media are sensibly the same, in agreement with predictions of Eq. 2. It is also evident that, in agreement with observations of Moelwyn-Hughes[16] and of Leininger and Kilpatrick[11] in studies in water, that the energy of activation decreases with increased temperature intervals. Furthermore, the values are in agreement with those observed by these authors. It is interesting to note that Leininger and Kilpatrick measured the inversion rate dilatometrically. The steady decrease of energy of activation with decreasing dielectric constant in isodielectric dioxane–water media can be accounted for according to the predictions of Eq. 5 as being purely electrostatic in nature. This is evident from Table III, which gives the calculated change of electrostatic energy with changing dielectric as compared with the

TABLE III

COMPARISON OF THE CHANGE OF ENERGY OF ACTIVATION IN ISODIELECTRIC DIOXANE–WATER MEDIA FROM 21 TO 41° WITH CHANGE IN ELECTROSTATIC ENERGY CALCULATED FROM EQ. 5

Dielectric range	$\Delta(\Delta E^*)$, calcd. from Eq. 5	$\Delta(\Delta E^*)$, obsd. from Table II
60–50	−200 cal.	−135 cal.
60–45	−330 cal.	−270 cal.

(16) Moelwyn-Hughes, Z. physik. Chem., **B26**, 281 (1934).

actually observed change. In these calculations the dipole moment of sucrose was taken as 3.4 Debye units[17] and r was taken as 2 Å.

It will be observed that the B term also decreases with increasing temperature intervals in all solvents,[18] and in general is less for dioxane–water than for water or alcohol–water solvents. These decreases are always in the right direction to compensate for decreased energy of activation. For isocomposition runs in mixed solvents the B terms are fairly constant, but in isodielectric media they show a gradual increase when alcohol is the non-aqueous solvent, and an opposite trend when it is dioxane. However, the change is not great in any case.

In the ethyl alcohol–water studies, the energy of activation gradually increases with increasing concentration of alcohol and with decreasing dielectric constant. From the standpoint of electrostatics, this could be interpreted as a reaction between a dipole and a *negative* ion. This, however, does not seem probable, in view of the fact that sucrose is not inverted by neutral chloride salts. A more probable explanation is that the alcohol unites with some of the hydrogen ion to form the $C_2H_5OH_2^+$ ion and thus reduce the concentration of one of the reactants, H_3O^+. The

(17) Landt, Naturwissenschaften, **22**, 809 (1934).
(18) See LaMer and Miller, THIS JOURNAL, **57**, 2679 (1935).

magnitude of this effect is such as to overcome the effect of lowered dielectric and to produce a slightly greater trend in the opposite direction. These trends are evident from Fig. 1, in which log k is plotted against $1/D$ for both mixed solvents at 31 and 41°.
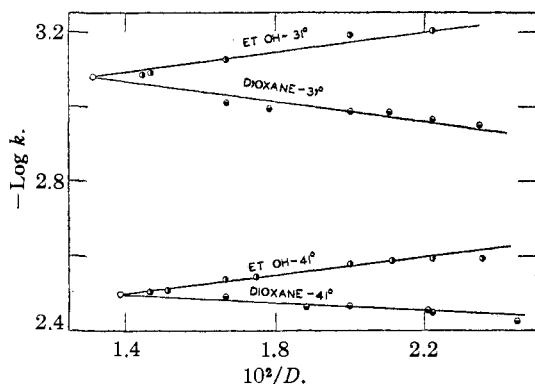

Fig. 1.— —Log k vs. $1/D$ for the acid inversion of sucrose in ethyl alcohol–water and dioxane–water at 31 and 41°. The unshaded circle is for pure water.

If the formation of the $C_2H_5OH_2^+$ ion is the explanation of the increases noted above, then the effect should be lessened at higher temperature intervals, since the hydrolysis of the ion increases with increasing temperature.[19]

TABLE IV

PERCENTAGE DEVIATION OF THE MEASURED RATE CONSTANT FROM THAT OF WATER FOR VARIOUS TEMPERATURES AND MOLE PERCENTAGES OF ETHYL ALCOHOL IN THE SOLVENT

Mole % EtOH	% decrease of rate const. from that of H_2O at 21°	% decrease of rate const. from that of H_2O at 31°	% decrease of rate const. from that of H_2O at 41°
5.36	3.22	1.71	2.24
13.5	18.5	12.1	11.8
24.6	37.1	29.2	23.2
32.0	41.2	32.1	25.6

Table IV contains the percentage deviations of the measured rate constant at the various temperatures and various dielectric constants in ethyl alcohol–water media from that of water at the same temperature. Except for the solvent which contains alcohol in the lowest concentration where the deviations are small, and subject to greatest error, the deviations become progressively less with increasing temperature, as would be the case if more hydrogen ion were freed by hydrolysis of the $C_2H_5OH_2^+$ ion. Hilton A. Smith[19] has given equations for the concentration of the $C_2H_5OH_2^+$ ion in solutions which contain only that amount

(19) Smith, THIS JOURNAL, **61**, 254 (1939).

of water released in acid catalyzed esterification reactions. His equations, however, are not likely to be applicable to solutions containing a high concentration of water. Hence a study of ROH_2^+ ions in such concentrations would have to be made before this theory could be tested quantitatively.

A further check of our Eq. 2 can be made by testing it against the results of Amis and LaMer[20] on the reaction between the negative bivalent brom phenol blue ion and the negative univalent hydroxyl ion, and also by the data reported by Warner,[1] Svirbely,[2] and students[3] for the reaction between the positive univalent ammonium ion and the negative univalent cyanate ion. Table V contains the calculated difference in energy of activation in the two types of media according to Eq. 2 as compared with observed values. In this table comparison between isocomposition and isodielectric media runs are made at equal dielectrics for the two types. The dielectric chosen was the intermediate value for the temperature range of the isocomposition run. The energy of activation of the isodielectric run used in comparison was corrected if necessary to this intermediate value by use of the ion-ion equation proposed by Amis[21] for change in electrostatic energy.

It will be observed from Table V that the differences calculated and observed between ΔE_C^* and ΔE_D^* are always of the same sign and order of magnitude. Observed and calculated values although agreeing within 200–400 cal. at higher dielectrics diverge almost 1000 cal. for the brom phenol blue reaction with hydroxyl ion. These runs, however, are for relatively high ionic strengths. The lack of agreement at low dielectric can be attributed to the fact that log k departs farther and farther from being proportional to $1/D$ as D is progressively lowered. The work of LaMer[10] is referred to for this fact.

In all cases where electrostatic corrections were made in order to compare the differences in the energies at equal dielectrics, much better agreement was obtained after these corrections were applied. Also in making the correction for electrostatic effects, much the best agreement was obtained by using the same value for the parameter r in the electrostatic correction equation as was used in Eq. 2. It is observed that the value for r in the brom phenol blue–hydroxyl ion reaction is

(20) Amis and LaMer, *ibid.*, **61**, 901 (1939).
(21) Amis, Ref. 6; the equation is

$$\Delta E_{\text{Elec.}} = \Delta(\Delta E^*) = -\frac{329.7 Z_1 Z_2}{D_1 D_2 r} \Delta D \text{ (kcal.)}$$

TABLE V

CALCULATED VALUES OF ΔE_C^* − ΔE_D^* ACCORDING TO EQ. 2 COMPARED WITH OBSERVED VALUES

Observer	Reaction	$\sqrt{\mu}$	Solvent	r in Å. for Eq. 2	Dielec. of const. dielec. run	Inter-mediate value of D	r in Å. used in electrostatic corr.	Electrostatic energy corr.	ΔE_C^* − ΔE_D^* Calcd.	ΔE_C^* − ΔE_D^* Obsd. − corr. for electrostatic energy
Amis–LaMer	BϕB⁻ + OH⁻	0.300	EtOH–H₂O	1.2	71.42	71.42	...	...	− 8931	−9915
Amis–LaMer	BϕB⁻ + OH⁻	.300	EtOH–H₂O	1.2	64.55	64.55	...	...	− 10303	−9835
Amis–LaMer	BϕB⁻ + OH⁻	.300	MeOH–H₂O	1.3	71.42	71.42	...	...	− 7888	−8835
Amis–LaMer	BϕB⁻ + OH⁻	.300	MeOH–H₂O	1.3	64.55	64.55	...	...	− 9580	−8835
Svirbely–Warner	NH₄⁺ + CNO⁻	.000	MeOH–H₂O	2.0	63.50	57.51	2.0	−271	4747	4489
Svirbely–Warner	NH₄⁺ + CNO⁻	.000	MeOH–H₂O	2.0	55.00	57.51	2.0	131	4747	4419
Svirbely–Warner	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	63.50	57.51	2.0	−271	3834	3941
Svirbely–Schramm	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	63.50	57.51	2.0	−271	3834	4160
Svirbely–Schramm	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	55.00	57.51	2.0	131	3834	4044
Svirbely–Schramm	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	50.00	57.51	2.0	430	3834	4064
Svirbely–Schramm	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	45.00	57.51	2.0	797	3834	3953
Svirbely–Schramm	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	40.00	57.51	2.0	1255	3834	3705
Svirbely–Schramm	NH₄⁺ + CNO⁻	.194	MeOH–H₂O	2.0	35.00	57.51	2.0	1844	3834	3291
Lander–Svirbely	NH₄⁺ + CNO⁻	.194	Glycol–H₂O	2.5	63.50	69.76	2.5	152	2270	2668
Lander–Svirbely	NH₄⁺ + CNO⁻	.194	Glycol–H₂O	2.5	60.00	69.76	2.5	308	2270	2589
Lander–Svirbely	NH₄⁺ + CNO⁻	.194	Glycol–H₂O	2.5	55.0	69.76	2.5	508	2270	2382
Lander–Svirbely	NH₄⁺ + CNO⁻	.194	Glycol–H₂O	2.5	50.00	69.76	2.5	746	2270	2234
Lander–Svirbely	NH₄⁺ + CNO⁻	.194	Glycol–H₂O	2.5	45.00	69.76	2.5	1040	2270	1930
Lander–Svirbely	NH₄⁺ + CNO⁻	.194	Glycol–H₂O	2.5	40.0	69.76	2.5	1410	2270	1620

higher for methyl alcohol–water than for ethyl alcohol–water media. This is in agreement with the findings of Amis and LaMer,[5] and the actual value is in very close agreement with the finding of Panepinto and Kilpatrick[22] for water media. It is observed that these parameters always have values that are reasonable in the light of kinetic theory.

Conclusions

1. In agreement with the predictions of our Eq. 2, the energies of activation are sensibly the same for isodielectric and for isocomposition media for the acid inversion of sucrose.

2. The influence of dielectric constant upon the rates and energies of activation for dioxane–water media can be accounted for on the basis of electrostatics.

(22) Panepinto and Kilpatrick, THIS JOURNAL, **59**, 1871 (1937).

3. The rate and energy phenomena in ethyl alcohol–water media can be explained qualitatively on the basis of formation of $C_2H_5OH_2^+$ ion.

4. Equation 2 has been shown to give fair agreement with the observed differences of energies of activation in isocomposition and isodielectric media for two types of ionic reactions in various mixed solvents.

5. Best agreement between observed and calculated values for this equation was obtained when electrostatic corrections were made to make the isodielectric energies correspond to the dielectric constant of the isocomposition energies.

6. The agreement between calculated and observed values was also best when the value of the parameter r in Eq. 2 and the r used in electrostatic corrections was made the same.