[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Influence of Non-Electrolytes upon the Kinetics of the Reaction between Bromoacetate and Thiosulfate Ions[1,2]

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Introduction

The literature contains few precise values of the energy of activation for non-ionic reactions and still fewer values in the case of ionic reactions. The problem of solvent influence upon the kinetics of ionic reactions has been approached only through the change in velocity constant and with one exception[4] the data are limited to a single temperature and usually to one concentration of reactants.[5] In this investigation, both the energy and the entropy of activation calculated from experimental data for reaction velocity constants are utilized as a means of approach to the problem of solvent effect upon reaction velocity. The purpose of this investigation was to compare the data in terms of E_{act} and B for the bromoacetate–thiosulfate reaction after addition of urea, sucrose, glycerol or dioxane with the corresponding data for aqueous solution.

Materials

The purification of reacting materials has been described previously.[6]

Urea.—Pure carbamide was recrystallized from distilled water. The solution was not warmed above room temperature as Wyman[7] found that urea solutions allowed to stand for several hours at a temperature of 30 or 35° undergo a change associated with a change in conductivity. The urea was thoroughly air-dried and kept in a calcium chloride desiccator overnight before use.

Sucrose.—Commercial packaged cane sugar was used.

Glycerol.—Kahlbaum twice-distilled glycerol, density 1.26, was employed.

Dioxane.—The commercial product was purified as described by Kraus and Fuoss.[8]

Experimental

The reacting solutions were prepared as follows. After a solution of bromoacetic acid had been neutralized with sodium hydroxide solution, a weighed quantity of non-electrolyte was added and the solution was made up to volume and weighed. Sodium thiosulfate solution was prepared so as to contain the same weight per cent. of non-electrolyte as the bromoacetate solution and its molarity was determined by titration against a primary iodine standard and adjusted to that of bromoacetate solution.

For the velocity measurements, the two types of technique described in the previous paper were employed. Analytical errors are not greater than one part per thousand.

Experiments were carried out at 25.00 ± 0.01° and at 0.00 ± 0.02°. The 25.00° point was determined on two Beckmann thermometers by means of a platinum resistance thermometer (kindness of Dr. Shedlovsky of The Rockefeller Institute for Medical Research); the readings agreed throughout the work. For zero degrees, two Beckmann thermometers were set at the ice-point of water and the settings were checked frequently. A refrigeration unit maintained the temperature of a water–ethylene glycol bath at zero degrees. Two or more hours were allowed for temperature equilibrium at 25° and at least three hours at 0° before mixing the reactants.

Concentrations of reactants are expressed in moles per liter of solution at 25°. Concentrations of non-electrolytes are in grams of non-electrolyte per 100 g. of solution.

Analytical Precision and Controls

Sodium thiosulfate solutions were freshly prepared for each experiment. Much has been written about the instability of dilute solutions of sodium thiosulfate but the possibility of decomposition in the solid state seems to have been disregarded. A sample of $Na_2S_2O_3 \cdot 5H_2O$ which had been recrystallized several years before and yielded excellent results at that time, gave drifting velocity constants. The cause may have been a slight decomposition to form sulfur and sulfite ion; then, in solution, thiosulfate ions and sulfite ions reacted with bromoacetate simultaneously during the early part of the reaction, accounting for the drift in velocity constants. This source of error does not enter into any of the data presented here.

Commercial dioxane gave an acid solution with water and contained an impurity which oxidized iodide to iodine. After treatment with sodium hydroxide, drying with barium oxide and refluxing over sodium, a non-oxidizing sample was obtained. From an aqueous solution of this dioxane, thiosulfate measured by iodine titration gave 100.2% recovery after twenty-four hours and 100.6% recovery after two weeks. However, the iodine end-point is yellow in the presence of starch and dioxane! Whether dioxane samples remained free of oxidizing impurity and for what period of time was unpredictable and seemingly without relation to their having been protected from light or stored with or without water. It appeared to be not merely a matter of sufficiently long treatment with sodium.

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(1) This paper is abstracted from the dissertation of Mildred E. Kamner presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at Columbia University, July, 1934. For details, the reader is referred to The Dissertation.

(2) Read at the New York meeting of the American Chemical Society, April, 1935.

(3) Fellow, American Association of University Women (Dorothy Bridgman Atkinson Fellowship of the Northwest Central Section) 1933–34.

(4) A. N. Kappanna, *J. Indian Chem. Soc.*, **6**, 419 (1929).

(5) M. Prasad, C. L. Mankodi and R. D. Godbole, *ibid.*, **7**, 59 (1930); C. V. King and O. F. Steinbach, THIS JOURNAL, **52**, 4779 (1930); A. v. Kiss, *Acta Chemica, Mineralogica, Physica*, **3**, 20 (1933); D. Straup and E. J. Cohn, Preliminary Note, *J. Biol. Chem.*, **105**, Scientific Proc. LXXXVII (1934).

(6) La Mer and Kamner, THIS JOURNAL, **57**, 2662 (1935).

(7) J. Wyman, Jr., *ibid.*, **55**, 4116 (1933).

(8) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933).

Malone and Ferguson[9] reported that different samples of dioxane showed different dielectric constants depending upon the length of time the dioxane was allowed to stand over sodium. The data for the experiment with a dioxane–water mixture are presented as being only semi-quantitative; the reaction mixture was of *p*H about 5.5 to 6, assuming the same indicator colors for dioxane–water as for water.

The starch–iodine end-point was more easily detected by placing the solutions in an ice-bath. Blanks were usually from 0.01 to 0.04 cc. of iodine solution. If the total blank were due to the added non-electrolyte or an impurity in it, a mole of urea, sucrose or glycerol would react with 10^{-5} to 10^{-6} equivalents of iodine.

Thiosulfate ion does not react with urea, sucrose or glycerol in aqueous solution as shown by iodine titration values which agreed to within less than a part per thousand with the values in the absence of non-electrolyte. The following data show no indication of appreciable side reactions of bromoacetate ion in the presence of these non-electrolytes either with them or with water.

TABLE I

Concn. of reactants, *M* $a = b$	Non-electrolyte, %	% Completion of reaction Obs.	Theoretical[a]	Moles of bromoacetate reacting with one mole of thiosulfate
0.02	21.2 Urea	98.6	99.6	0.989
.05	21.2 Urea	99.2	99.9	.993
.05	21.0 Urea	98.6	99.2	.994
.02	32.4 Sucrose	99.97	99.7	1.003
.05	32.3 Sucrose	99.5	99.7	0.998
.02	67.9 Glycerol	98.6	98.9	.997

[a] Calculated on basis of initial quantities of reactants.

Calculations

The precision of k is expressed as the average deviation of a single value from the mean. The reliability of E_{act} was calculated using the maximum k_{25} value and minimum k_0 value as indicated by the individual precisions of k less the E_{act} using the average k values. This estimate of the deviations of E_{act} is thus a maximum for this pair of experiments. $\Delta E_{\text{act}} = (E_{\text{act}}$, non-electrolyte $- E_{\text{act}}$, water). The precision measure of ΔE_{act}, $= [(\text{precision in } E_{\text{act}}, \text{ water})^2 + (\text{precision in } E_{\text{act}}, \text{ non-electrolyte})^2]^{1/2}$. An error of 25 calories in E_{act} produces an error of about 0.02 logarithmic unit in B.

The detailed data for the velocity constants of four representative experiments are in Table II; the solvent in each case is water and the non-electrolyte indicated. Table III contains values of E_{act} and B for the reaction in aqueous solution quoted from the previous paper.[10] The values of E_{act} and B for the reaction in solutions containing non-electrolytes and the deviations of E_{act}, B and k from the values for aqueous solutions appear in Table IV.

TABLE II

t, min.	$(a - x)$ in cc. iodine,	% Reactants converted	k
Urea = 21.2%. $a = b = 0.05$, $T = 0°$			
0	44.09	..	...
84.4	33.31	24.4	0.0767
139.4	28.65	35.0	.0773
213.9	24.19	45.1	.0769
274.2	21.40	51.5	.0773
Average			.0771 ± 0.0003
Corrected for volume change			.0765
Sucrose = 32.4%, $T = 25°$. $a = b = 0.005$			
0	40.74	..	...
137.5	31.58	22.5	0.4219
177.6	29.63	27.3	.4223
378.9	22.66	44.4	.4214
1129.2	12.06	70.4	.4212
		Average	.4217 ± 0.0005
Glycerol 67.9%, $T = 0°$. $a = b = 0.02$			
0	49.50	..	...
247.5	36.81	25.6	0.0696
248.5	36.70	25.9	.0702
1042	20.28	59.0	.0691
1042	20.30	59.0	.0690
1092	19.67	60.3	.0694
Average			.0695 ± 0.0004
Corrected for volume change			.0690
Dioxane 50.3%, $T = 25°$. $a = b = 0.005$			
0	46.50	..	...
76	38.17	17.9	0.574
285	25.79	44.5	.564
334	23.95	48.5	.564
1154	10.90	76.6	.566
		Average	.567 ± 0.004

TABLE III

Concn. of reactants $a = b$ in aqueous soln.	$E_{(0-25)}$	B
0.002	15,880 ± 70	11.19
.005	16,010 ± 30	11.35
.02	15,980 ± 10	11.48
.05	15,940 ± 40	11.55

Discussion

The addition of urea, sucrose, glycerol or dioxane increased the rate of the bromoacetate–thiosulfate reaction in water at 25 and 0°, the only exception being the 2% decrease in k at 25° when a 0.002 *M* solution of reactants is 1.08 *M* in sucrose. These results are shown in Fig. 1. The change in velocity constant is not determined by the ratio of sucrose to reactants.

An interpretation of the changes in velocity constant can be obtained through consideration

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[9] M. G. Malone and A. L. Ferguson, *J. Chem. Phys.*, **2**, 99 (1934).

[10] V. K. La Mer and M. E. Kamner, Paper read at the March, 1934, meeting of the American Chemical Society.

TABLE IV

Concn. $a = b$ M	t, °C.	Average k	Log k + 2	E	ΔE from water	ΔE accounted for by errors	B	ΔB from water	% Δk from water 25°	% Δk from water 0°
Urea = 21.2% = 3.73 M										
0.05	25	0.903								
.05	25	.897[a] ± 0.003	1.9542	15,970 ± 40	+ 30	60	11.65	+0.10	+21.1	+20.7
.05	0	.0765 ± .0003	0.8837							
.02	25	.726 ± .0003	1.8609	16,000 ± 10	+ 20	15	11.58	+ .10	+25.6	+25.2
.02	0	.0613 ± .00005	0.7880							
Sucrose = 32.4% = 1.08 M										
0.05	25	0.795 ± 0.003	1.9004	15,820 ± 50	− 120	65	11.49	−0.06	+ 7.0	+ 9.0
.05	0	.0691 ± .0003	0.8395							
.02	25	.605 ± .001	1.7818	15,750 ± 30	− 230	30	11.32	− .16	+ 4.7	+ 8.6
.02	0	.0532 ± .0002	0.7259							
.02	25	.602 ± .002	1.7796	15,740 ± 30	− 240	30	11.31	− .17	+ 4.2	+ 8.2
.02	0	.0530 ± .0001	0.7243							
.005	25	.4217 ± .0005	1.6250	15,730 ± 40	− 280	50	11.15	− .20	+ 1.0	+ 5.7
.005	0	.0372 ± .0002	0.5705							
.002	25	.352 ± .002	1.5465	15,650 ± 100	− 230	125	11.02	− .17	− 2.0	+ 1.3
.002	0	.0314 ± .0003	0.4969							
Sucrose = 1.47%										
0.002	25	0.358 ± 0.001	1.5539	15,930 ± 40	+ 50	80	11.22	+0.03	+ 0.3	− 1.3
.002	0	.0306 ± .0001	0.4857							
Glycerol 68.5% = 8.78 M; 69.7% (last two expts.)										
0.05	25	0.879 ± 0.007	1.9440	14,770 ± 120	−1170	125	10.76	−0.79	+18.3	+41.8
.05	0	.0899 ± .001	0.9538							
.02	25	.677 ± .002	1.8306	14,790 ± 60	−1190	60	10.67	− .81	+17.1	+40.8
.02	0	.0690 ± .0004	0.8389							
Dioxane 50.3% = 5.92 M										
0.005	25	0.567 ± 0.004	1.7536	14,820	−1190	..	10.61	−0.74	+36	+63
.005	0	.0575 ± .0004	0.7597							

[a] k = 0.896 with 21.0% urea ≈ 0.897 with 21.2% urea.

of other properties of the reaction system; namely, the energy of activation and its change with temperature. If the Arrhenius equation, $d \ln k = (E_{act}/RT^2)dT$ is integrated by assuming that E_{act} is a function of temperature, *i. e.*, $E_{act} = E^0_{act} + \int_0^T (\partial E_{act}/(\partial T)dT$, then

$$\int_0^T (E_{act}/RT^2)dT = \frac{-E^0_{act} + \int_0^T (\partial E_{act}/\partial T)dT}{RT} + \frac{1}{R}\int_0^T \left(\frac{\partial E_{act}}{\partial T}\right) d \ln T \quad (1)$$

La Mer[11] has defined the change in energy of activation with temperature as the heat capacity of activation and by analogy with thermodynamic heat capacities has designated the last term as the entropy of activation divided by R. Thus

$$\ln k = -E_{act}/RT + (S_{act} - S_{0\,act})/RT + \ln \text{const.} \quad (2)$$

the constant having the dimensions of a frequency (time^{-1}). If the reactants require no activation for reaction, E_{act} becomes zero, and every collision results in reaction. If the reactants are ideal gases the constant becomes the gas kinetic collision frequency at unit concentrations designated as Z^0

$$\log k = -E_{act}/2.3RT + \underbrace{(S_{act} - S_{0\,act})/2.3R + \log Z^0}_{B} \quad (3$$

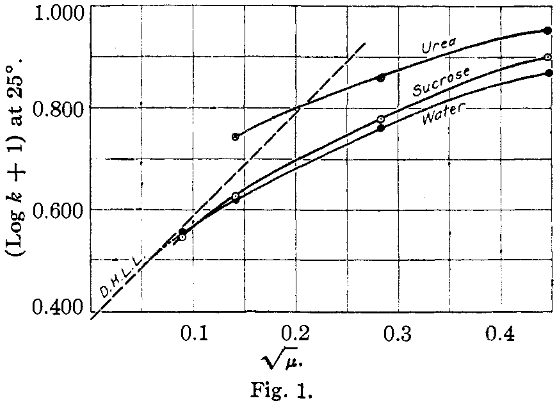

Fig. 1.

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(11) V. K. La Mer, *J. Chem. Phys.*, **1**, No. 5, 289 (1933).

B thus consists of two terms, one involving entropy of activation and the other a collision frequency. A change in the value of B may be attributed, in general, to a change in one or both of the quantities which determine its numerical magnitude, the collision frequency and the derivative of E_{act} with respect to temperature integrated with respect to ln T.

The experimental data show that when urea is added to the aqueous solvent for the bromoacetate–thiosulfate reaction, B is increased, E_{act} is unchanged and k is increased. The addition of sucrose, glycerol or dioxane to the aqueous solvent for the reaction causes a decrease in B, but this decrease in B in the cases of glycerol, dioxane and sucrose (at higher concentrations of reactants) is more than compensated for by the decrease in E_{act} and thus k is increased.

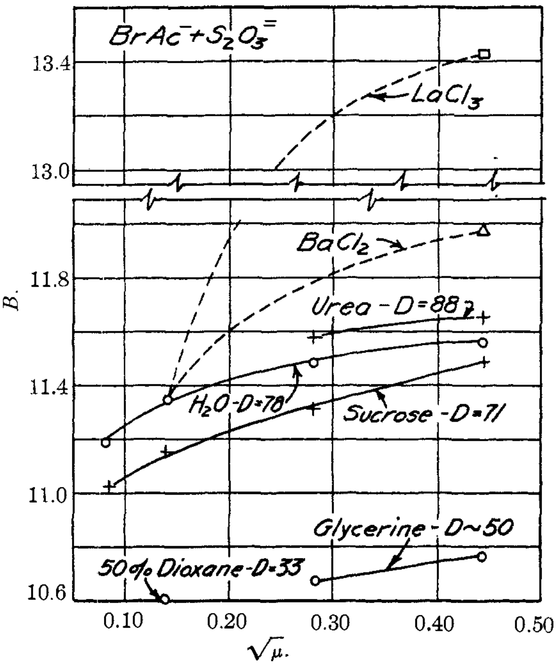

Fig. 2.

In the sucrose solutions as in the case of water (Table III and Fig. 2) B decreases significantly in passing from 0.05 to 0.002 M in reactants. The decrease in E_{act} over this same range may or may not be real; it exceeds but slightly the amount which can be accounted for by experimental errors. One cannot do more than suggest the possibility that the presence of 540 long chain sucrose molecules for a molecule of each reactant diminishes the velocity constant at $a = b = 0.002$ M by having decreased the number of collisions between reactants.

Kappanna[4] has studied the effect of sucrose addition to the bromoacetate–thiosulfate reaction; his data agree with those presented here in respect to the fact that sucrose increases the velocity constant at high concentrations of reactants and decreases it at low concentrations. Calculations made from his velocity constant data show that the addition of alcohol to the aqueous solvent decreases both E_{act} and B.

Influence of Dielectric Constant

For the case of reactions between an ion and a neutral molecule, Harned and Samaras[12] have shown that log k is frequently but not always proportional to D. For the reaction $NH_4^+ + CNO^- \longrightarrow$ urea which involves the collision of ions of opposite sign, Warner and Warrick[13] found that log k is roughly proportional to $1/D$ when the dielectric is decreased by addition of various alcohols or of dioxane to water.

However, no simple relation is revealed by plotting log k against D or $1/D$ either for our data or for those of Kappanna for the bromoacetate–thiosulfate reaction in aqueous alcohol solutions. Kappanna's data show a minimum k value at 40% ethyl alcohol for low concentrations of reactants. The minimum is displaced to lower alcohol concentrations as the ionic strength of the reactants is increased.

Although the dielectric constants of the solvents employed in this research range from urea, $D = 98.1$ (0°) $= 88.4$ (25°); water, $D = 88.2$ (0°) $= 78.5$ (25°); sucrose (32.4%) $D = 78.4$ (0°) $= 70$ (25°); glycerol $D = 63.2$ (0°) $= 55.7$ (25°); to dioxane $D = 33$ (25°), the velocity constants in the presence of non-electrolytes exceed those for water. Scatchard's theory[14] of the effect of D obviously does not hold for the present data. Straup-Cope and Cohn[15] report that amino acids which increase the dielectric constant increase the velocity of this reaction.

Since the magnitude of k is determined by the quantities E and B it is appropriate to attempt to correlate E and B rather than k with the dielectric constant of the solvent. In Fig. 3 ($E_{\text{act}} - 16{,}000$) and B are plotted against $1/D$. B decreases with decreasing dielectric constant of the

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(12) Harned and Samaras, THIS JOURNAL, **54**, 1 and 9 (1932).

(13) Warner and Warrick, *ibid.*, **57**, 1491 (1935); see also Piter Vass [*Magyar Chem. Folyoirat*, **37**, 217 (1931) through *C. A.*] who claims that the $Fe^{+++} + I^-$ reaction follows the Grube-Schmid law.

(14) Scatchard, *Chem. Rev.*, **10**, 229 (1932). See Eq. (9), p. 235.

(15) Straup-Cope and Cohn, *J. Biol. Chem.*, **105**, Proc. LXXXVII (1934); THIS JOURNAL, **57**, 1794 (1935).

solvent to a value of $D \simeq 55$; the lowering of D from 55 to $\simeq 33$ produces no further decrease. Except for the urea solutions, the E curve follows a parallel course to B but is distinctly less sensitive to changes in the concentration of reactants. The increasing value of B with increasing concentration of reactants in sucrose solutions would be interpreted as a result of the increased number of collisions arising from the interionic attraction effect. Our analysis thus supports the Christiansen[16] interpretation of the Brönsted–Debye effect. We suggest that the decrease in B values with decreasing values of D results from a decrease in the number of effective collisions as a result of the increased electrostatic repulsion between reacting ions of the same sign. Finally, with decrease of dielectric a point must be reached in which the reacting ions are no longer dissociated from the sodium ions. When the dielectric constant falls below about 50 the phenomenon of ion association of the sodium ions with the bromoacetate and the thiosulfate ions becomes very important. Fuoss and Kraus[17] claim that for uni-univalent electrolytes in solvents where D is less than 43.6 the behavior of ions of opposite sign is most easily accounted for in terms of a mass action dissociation constant of the salt. In the case of 50% dioxane–water where $D = 33$ the reactants will exist principally in the form of their neutral salt pairs. Somewhere in the neighborhood of $D = 50$, the repulsive effect of lowering the dielectric is exhausted and consequently no further decrease in B can be expected. The reaction now behaves substantially as a reaction between two uncharged molecules, though of course a considerable dipole interaction will still persist at close distances.

In solvents of extremely low dielectric constant the ternary and higher order ion-pairs become stable. It is conceivable that under such conditions the order of the reaction may change. In fact Brönsted and Bell[18] found that the diazoacetic ethyl ester reaction proceeds in benzene at a rate which is proportional to the square of the concentration of the catalyzing acid, whereas in water it is proportional to the first power of the hydrogen-ion concentration.

The kinetic data for the bromoacetate-thiosulfate reaction furnish examples of an increase in velocity constant with (1) an increase in E_{act}, (2) a decrease in E_{act}, (3) E_{act} remaining unchanged.

(1) The increase in E_{act} resulting from the addition of barium chloride or lanthanum chloride was more than compensated for by an increase in B, and k was increased.[10]

(2) In the present work, the addition of sucrose, glycerol or dioxane lowered E_{act} by such an amount that although B was also lowered, k was increased.

(3) E_{act} is unaffected by the addition of urea and the increase in velocity constant results entirely from an increase in B.

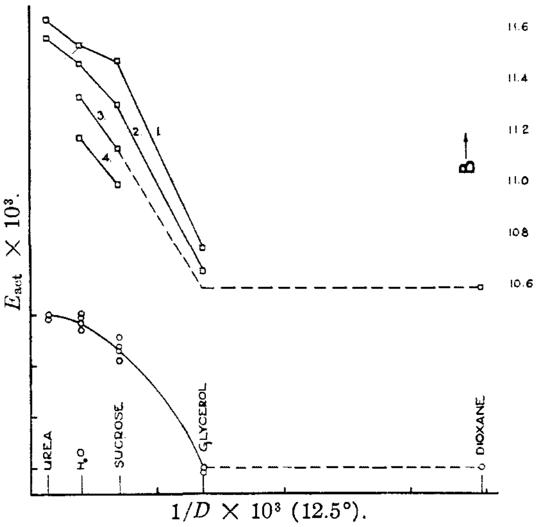

Fig. 3.—1, 0.05 M; 2, 0.02 M; 3, 0.005 M; 4, 0.002 M.

Summary

1. The kinetics of the reaction between bromoacetate ions and thiosulfate ions have been studied at 0 and at 25° in the presence of non-electrolytes; the precision of the experimental data is ±0.5%. The velocity constant is increased by addition of urea, sucrose, glycerol or dioxane to the aqueous solvent, in spite of the fact that urea raises the dielectric constant while the others lower it.

2. The energy of activation remains the same in the case of urea but is decreased by addition of each of the other non-electrolytes. The action constant B decreases almost linearly as a function of $1/D$ from $D = 88$ to 55.7.

3. In 32% sucrose solutions ($D = 70$ at 25°), as in water, the positive salt catalysis arises from an increase in the entropy of activation which more than compensates for the retarding influence of an increase in the energy of activation.

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[16] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

[17] Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933), and later papers of this series; Fuoss, *Chem. Rev.*, **17**, 27 (1935).

[18] Brönsted and Bell, *ibid.*, **53**, 2478 (1931).