presence of charcoal. The triple point of deuterium is 18.66°K., and the boiling point is found by extrapolation to be 23.6°K.

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The Racemization of *l*-Bromosuccinic Acid by Bromide Ion in Non-Aqueous Solvents. The Mechanism of Organic Reactions

BY A. R. OLSON AND H. H. VOGE

The various attempts which have been made to explain mechanisms of organic reactions such as substitutions and molecular rearrangements, can be divided into two groups: (a) those in which primary dissociations into radicals or ions are assumed in the mechanism, and (b) those in which additions or simultaneous additions and dissociations occur. A detailed exposition of this latter view-point can be found in papers by Meer and Polanyi[1] and by Olson,[2] and an experimental proof of the mechanism for a particular case in an article by Olson and Long.[3] It is to be noted that not only has it been demonstrated that the latter theory is capable of explaining the experimental facts, but also that the former theory must meet objections of the following type.

The average strength of a carbon–bromine bond for a substance in the gaseous state is 65,400 calories per mole.[4] This presupposes a dissociation into neutral particles. Since the ionizing potential of carbon is very much greater than the electron affinity of bromine, a dissociation into ions would require much more energy than this. Even if we assume that it requires only 65,400 calories per mole to separate the molecule into a bromide ion and a positive residue, we can easily calculate by means of the Arrhenius equation, rate $= Se^{-E/RT}$, that, at room temperature, under the most favorable conditions, it would require millions of years to produce enough bromide ion to be detected by silver nitrate. Actually if bromosuccinic acid is dissolved in water a detectable amount of bromide ion will be formed in a few minutes. Furthermore Olson and Long[5] have shown that in aqueous solutions the heat of activation of the reaction *l*-bromosuccinic acid + Br^- = *d*-bromosuccinic acid + Br^- is 22,300 calories per mole. Obviously, either the mechanism does not involve such a simple bond rupture, or the physical properties of the solvent operate to reduce greatly the bond strength. This latter alternative appears, *a priori*, to be unreasonable when we remember that most of the work of separation is done at distances which are small compared to intermolecular distances.

The widespread use of simple dissociations in the explanation of reaction mechanisms caused us to investigate this possibility more fully by studying the reaction *l*-bromosuccinic acid + Br^- = *d*-bromosuccinic acid + Br^- in methyl alcohol, acetone and acetic acid, as well as in acetone containing various amounts of water.[6]

Experimental Method and Preparation of Materials

The reaction rates were studied polarimetrically using the equipment described by Olson and Long.[3]

Methyl Alcohol.—Commercial methyl alcohol was fractionally distilled in a 60-cm. bead-filled column. The center fraction which was retained had a constant boiling point. It was treated with magnesium after the method of Lund and Bjerrum[7] to ensure removal of all water, and was subsequently fractionated in a small column to yield the alcohol used as a solvent.

Acetone.—Acetone was purified in the manner recommended by Conant and Kirner.[8] The alkaline permanganate solution was fractionated in a 60-cm. bead-filled column. The central fraction had a constant boiling point of 56.2° (corr.). To this fraction was added sodium hydroxide, and it was again fractionated in the 60-cm. column to give the acetone used in the experiments.

Acetic Acid.—A high grade of glacial acetic acid was twice fractionated in a 25-cm. column with retention of

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[1] Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

[2] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[3] Olson and Long, THIS JOURNAL, **56**, 1294 (1934).

[4] Pauling, *ibid.*, **54**, 3570 (1932).

[5] Olson and Long, unpublished work in this Laboratory.

[6] For references on investigations of the effect of solvent on reaction velocity see: Soper and Williams, *Proc. Roy. Soc.* (London), **A140**, 59 (1933); Thompson and Blandon, *J. Chem. Soc.*, 1237 (1933); Walden, "Electrochemie nichtwassriger Lösungen," Barth, Leipzig, 1924, pp. 370–426; Christiansen, Landolt-Börnstein, "Tabellen," Zweiter Erg. bd., Verlag Julius von Springer, Berlin, 1931, pp. 1621–1632.

[7] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

[8] Conant and Kirner, THIS JOURNAL, **46** 232 (1924).

only the last half of the distillate. This acid had a melting point of 16.64°.

Lithium Bromide.—The C. P. salt was recrystallized from water and fused in an atmosphere of hydrogen bromide.

Sodium Bromide.—The C. P. salt was recrystallized from water and dried by heating in a vacuum.

***l*-Bromosuccinic Acid.**—*l*-Bromosuccinic acid was prepared from *l*-aspartic acid according to the directions of Holmberg.[9] The purified product contained no free bromide ion. A solution of 5 g. in 100 cc. of water showed a specific rotation of 50.6° at 25° with the 5461 Å. line. This compares favorably with the rotation given by Clough.[10] The equivalent weight as determined by titration with alkali was the correct value for bromosuccinic acid.

Results

Methyl Alcohol Solutions.—When *l*-bromosuccinic acid (*l*-Brs) is dissolved in methyl alcohol containing bromide ion, reactions which may conceivably occur are the following

(1) *l*-Brs + Br^- = *d*-Brs + Br^-
(2) *l*-Brs = Fumaric Acid + HBr
(3) *l*-Brs + CH_3OH = Methyl Esters of Brs + H_2O
(4) *l*-Brs + CH_3OH = Methoxysuccinic Acid + HBr

Experiments showed that the rates of reactions (2), (3) and (4) are negligible compared to that of reaction (1). This fact was also evident from the absence of any change of the velocity constant for (1) over the entire course of the reaction.

Constants for the racemization of *l*-Brs by lithium bromide and sodium bromide in methyl alcohol are shown in Table I. They have been calculated from the formula $k = \frac{1}{2t(\text{Br}^-)} \ln \frac{\alpha_0}{\alpha}$, where t is the time in minutes, (Br^-) the concentration of LiBr or NaBr in moles per liter at the temperature of the experiment, and α is the observed rotation. The activation energy E and the collision number S have been calculated from the Arrhenius equation; for S the unit of time is the second.

TABLE I

VELOCITY CONSTANTS FOR THE REACTION *l*-Brs + Br^- = *d*-Brs + Br^- IN METHYL ALCOHOL. CONCENTRATION OF *l*-Brs = 0.2 *M*

Concn. NaBr, *M*	$k_{50} \times 10^3$	Concn. LiBr, *M*	$k_{25} \times 10^3$	$k_{50} \times 10^3$
0.2	0.930	2.0	0.0722	1.260
.3	.940	2.0	.0719	1.270
.4	.982	2.0	.0722	1.265
.6	1.09			
.7	1.17	Average	.0721	1.265
.8	1.23			
.9	1.28			

$E = 21{,}950 \quad S = 0.14 \times 10^{11}$

In addition to the experiments listed in Table I, rates were determined in methyl alcohol with *l*-Brs concentrations of 0.05, 0.1 and 0.15 *M*, and constant sodium bromide concentration. All three runs gave the same constant within the experimental error. This shows the activity of *l*-Brs to be directly proportional to its concentration over this range.

Acetone Solutions.—When *l*-Brs is dissolved in acetone and kept at 50° the rotation remains constant for a time which is long compared to that required for racemization by bromide ion. All side reactions can therefore be neglected. Constants for the racemization of *l*-Brs by lithium bromide in acetone were determined at 25 and 50°. The results are summarized in Table II.

TABLE II

VELOCITY CONSTANTS FOR THE REACTION OF 0.2 *M* *l*-Brs WITH LITHIUM BROMIDE IN ACETONE

Concn. LiBr	$k_{25} \times 10^2$	$k_{50} \times 10^2$	E
0.1235	2.88	27.0	17,090
.248	3.38	31.2	16,990
.2504	3.34	31.4	17,100
			17,060

$S = 0.0188 \times 10^{11}$

Acetic Acid Solutions.—In acetic acid, as in the other solvents, no trends in the constants with time were evident. It is thus apparent that reactions other than the direct racemization are so slow as to have no effect. The results obtained in acetic acid are shown in Table III.

TABLE III

VELOCITY CONSTANTS FOR THE REACTION OF 0.2 *M* *l*-Brs WITH 1.480 *M* LITHIUM BROMIDE IN ACETIC ACID

$k_{25} \times 10^3$	$k_{50} \times 10^3$	E	S
0.0898	1.246		
.0901	1.232		
.0899	1.239	20,080	0.0078×10^{11}

Acetone–Water Solutions.—Preliminary experiments showed that whereas the rates of racemization in methyl alcohol and acetic acid were almost unaffected by the addition of small amounts of water, in acetone the rate was greatly reduced. Reactions were carried out in a series of acetone–water mixtures with the results shown in Table IV. The values for pure water are from Olson and Long.[5]

Discussion

In attempting to compare the rate of a reaction in different solvents we are immediately con-

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[9] Holmberg, *Ber.*, **60**, 2194 (1927).

[10] Clough, *J. Chem. Soc.*, 1674 (1926).

TABLE IV

VELOCITY CONSTANTS FOR THE REACTION OF 0.2 *M* *l*-Brs WITH 0.25 *M* LITHIUM BROMIDE IN ACETONE CONTAINING WATER

Moles H_2O per liter	Ratio H_2O/LiBr	$k_{25} \times 10$	$k_{50} \times 10$	E	$S \times 10^{-11}$
0.000	0.000	0.336	3.13	17,060	0.0188
.358	1.43		2.13		
.454	1.81	.162	1.752	18,200	.058
.628	2.51		1.57		
1.138	4.55	.0807	0.930	18,690	.063
1.580	6.31		.657		
2.20	8.88	.0368	.446	19,070	.056
4.25	16.96	.0152	.196	19,510	.049
11.05	44.2	.0050	.0660	19,700	.022
Pure water	(27.8)	.00089	.0164	22,300	.31

TABLE V

DATA ON THE REACTION OF *l*-Brs WITH Br^- IN VARIOUS SOLVENTS

Solvent	D. C.	$u \times 10^{18}$	t	k	E	$S \times 10^{-11}$
Water	78	1.85	25	0.000089	22,300	0.31
			50	.00164		
Methyl alcohol	31	1.68	25	.0000721	21,950	.14
			50	.00126		
Acetone	19	2.80	25	.0336	17,060	.019
			50	.3131		
Acetic acid	6.2	0.4	25	.0000899	20,080	.0078
			50	.00124		

fronted with troublesome questions of standard states and activities. In the absence of information which would permit corrections to be made, we have assumed that Henry's law is obeyed in all solutions over the range of concentration with which we have worked, and have performed various subsidiary experiments to show that our conclusions are not invalidated by this assumption. Thus, using acetone as a solvent, we have shown that the heat of activation is independent of the concentration of lithium bromide within the experimental error; and using alcohol as a solvent we have shown that the specific rate of racemization of *l*-bromosuccinic acid is independent of the concentration of *l*-bromosuccinic acid, and that a four-fold change in the concentration of sodium bromide at 50° changes the specific rate by only 30%. Even if this change in the rate were entirely due to a change in the heat of activation, which is improbable, it would mean a difference of only 170 calories per mole.

Having thus established the validity of comparing activation energies for a given reaction in different solvents, we must conclude that the solvent cannot alter greatly the strength of the bond. Thus in Table V where we have collected the pertinent facts from the section on experimental work, we see that the heat of activation in aqueous solutions is not greatly different from that in acetic acid, though the dielectric constants of these solvents are 80 and 6, respectively.

Changes in the heat of activation of the order of 5000 calories are indeed produced by the different solvents, but in this connection it is to be noted that in the solvents which can form hydrogen bonds[11] with the bromide ion the reaction has about the same heat of activation, whereas in acetone, which cannot form such bonds, it exhibits a lower heat of activation. This is strikingly corroborated in the acetone–water mixtures. The addition of small amounts of water to dry acetone solutions at first produces changes in the heat of activation of the order of 1000 calories per mole; the further additions of similar amounts of water have much less effect. This leads to the conclusion that on the addition of water a statistical distribution of water molecules between the bromide ions and the acetone molecules, which is largely in favor of the bromide ions, occurs. Similar conclusions were reached by Hughes and Hartley,[12] in explaining their work on the conductivity of salts in acetone solutions to which varying amounts of water had been added. Eastman[13] in his work on the Soret effect also concluded that negative ions formed hydrogen bonds with water. The differences in the energy of activation which occur even in the hydroxylic solvents are probably due to variations in the number and strength of the hydrogen bonds; at any rate, these differences are small compared to the differences between this group as a whole and the solvent acetone, in which the bromide ions can be solvated only by dipole forces.

While it is not to be denied that in compounds such as hexaphenylethane, bonds even as strong as the carbon–carbon bond may break due to the phenomenon of resonance, nevertheless, it appears quite certain that at ordinary temperatures most of the mechanisms of organic reactions in which bond ruptures have been assumed must be fallacious. For we have shown above that such a reaction must be extremely slow and that the presence of the solvent does not remedy matters. Reactions in which the solvent is one of the reactants are not to be classed with this group in

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(11) Rodebush and Latimer, THIS JOURNAL, **42**, 1419 (1920).

(12) Hughes and Hartley, *Phil. Mag.*, [7] **15**, 610 (1933).

(13) Eastman, THIS JOURNAL, **50**, 283 (1928).

which simple bond ruptures occur. Thus in the reactions between chlorine and water to form hydronium ion, chloride ion and hypochlorous acid, and between bromosuccinic acid and water to form malic acid, bromide ion and hydronium ion, the mechanism must be explained by additions or simultaneous additions and dissociations.

The S factor in the acetone–water solutions exhibits a curious and interesting change as the amount of water is increased. Since this factor is usually interpreted as the number of favorable collisions, and since the addition of water results in a heavier particle, we might expect to observe a decrease in S not only due to the slower speed of the particle, but also due to an increased protection of the hydrated bromide ion by the bound water molecules. Actually the reverse is the case for the first small additions of water. The further addition of water causes the S factor to decrease, yet it rises again to a much higher value for pure water. Any explanation of this behavior must, at the present time, remain speculative. The increase in steric hindrance which is certainly produced by the attachment of water must be more than compensated for by an increase in the effective collision radius. Such an increased radius might be accounted for in a number of different ways. Thus we might think of the size of the bromide ion as that of the hydrated particle. Or we might consider the increased effective radius of the bromide ion as being due to an increased probability of interaction because of a lower velocity, in analogy with the increased ionizing power of alpha particles toward the end of their range. Perhaps the most enticing explanation that occurs to us is the following. The unsolvated bromide ion is spherically symmetrical. The addition of water would destroy such symmetry. If the characteristic functions occupied by the uncombined electron pairs of the partially hydrated ion consist largely of *p*-electronic functions, we could expect an increased radius. The completely hydrated bromide ion would again be in a spherically symmetrical state. While this explanation is concordant with the initial rise in S, and with its subsequent drop, it does not account for the higher value observed in pure water.

Summary

The heat of activation for the reaction *l*-bromosuccinic acid + Br^- = *d*-bromosuccinic acid + Br^- has been determined in solvents of widely varying physical properties. It has been shown that the heat of activation depends only to a negligible degree on the dielectric constant or other physical properties of the solvent. The chemical properties of the solvent change the heat of activation by as much as 5000 calories, probably because of hydrogen bond formation with the bromide ion in the case of hydroxylic solvents.

We therefore conclude that in the absence of large resonance effects any reaction mechanism which involves primary breaking of strong bonds at ordinary temperatures is erroneous.

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Molecular Refractivity and Association of Liquids Containing the Hydroxyl Group

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It is a well-known fact that liquids containing a hydroxyl group behave as substances having a much higher molecular weight than is indicated by their simplest formulas. They are said to be associated and this association according to Sidgwick[1] takes place by the oxygen of one hydroxyl group acting as a donor of electrons to the hydrogen of another hydroxyl group. Alcohols would associate as follows

According to Smyth, Engel and Wilson[2] such a coördination should be accompanied by an appreciable lowering of the molecular refraction of the alcohol. These authors estimated a reduction of 0.2 to 0.5 in the molecular refraction due to such a linkage. This estimate was based upon a comparison of the following refractions: O^{--}, 7; OH^-, 5.10; OH_2, 3.75; OH_3^+, 3.04. These same authors investigated the molecular refractions of a number of binary solutions and found that the molecular refraction of an alkyl halide dissolved

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[1] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, Oxford, England, 1927, p. 134.

[2] Smyth, Engel and Wilson, THIS JOURNAL, 51, 1736 (1929).