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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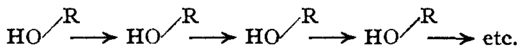
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Molecular Refractivity and Association of Liquids Containing the Hydroxyl Group

BY R. P. ALLARD AND H. H. WENZKE

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



$$HO\overset{R}{/}\longrightarrow HO\overset{R}{/}\longrightarrow HO\overset{R}{/}\longrightarrow HO\overset{R}{/}\longrightarrow \text{etc.}$$

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).

in heptane varied about the same amount with concentration as did an alcohol in the same solvent. As there can be no coördination between the molecules of an alkyl halide the data on refractivity were regarded as evidence against the association suggested by Sidgwick.

In order to determine whether molecular refractivity can be used as a simple test for the association of hydroxyl compounds the authors investigated the rather interesting case of acetic acid. Acetic acid, like the other lower fatty acids, at room temperature and even at its boiling point exists to a considerable extent as double molecules in the gaseous state and therefore may safely be assumed to exist to at least as great if not greater degree of association in the liquid state. When diluted with an oxygenated solvent such as dioxane these double molecules are broken up into single ones. If the formation of a coördinate valence bond results in an appreciable change in molecular refractivity, this change should be evident upon investigating a series of acetic acid and dioxane solutions. Acetic acid and dioxane do not associate with each other, there being no complications due to coördination between these two substances. This point has been proved by showing that acetic acid has the same electric moment in dioxane as the single molecules have in the gaseous state. Hydrocarbons like benzene do not have the property of breaking up the double molecules of fatty acids, freezing point measurements giving double the molecular weight even in quite dilute solutions. If molecular refractivity is a simple test of association there should be a marked difference in the behavior of acetic acid when diluted with the two solvents dioxane and benzene the values of the molecular refractivity of the acid being much higher in dioxane. As is shown in Table I the molecular refractivity of the solute is remarkably constant in both series of solutions. The variation in both cases is a little greater than experimental error but the molecular refractivity for the double molecules in benzene is, contrary to expectation, as large as that for the single molecules in dioxane. While there can be little doubt that the formation of a coördinate valence bond affects the molecular refractivity it is apparent that there are other factors that exert an appreciable influence. In calculating the molecular refractivity for the solute it was of course necessary to assume that that for the solvent dioxane or benzene was constant. A change in the molecular refractivity of the solvent may be opposite in sign from that taking place in the solute and thus mask an increase due to the breaking up of coördinate links.

TABLE I

MOLECULAR REFRACTIVITIES OF ACETIC ACID

Dioxane–acetic acid (solute)		Benzene–acetic acid (solute)	
c_2	MR_2	c_2	MR_2
0.00000	12.93	0.000000	13.03
.02992	13.00	.050476	13.07
.04997	12.91	.07613	13.00
.10101	12.98	.13790	12.99
.16885	12.934	.17538	12.980
.20932	12.923	.38701	12.997
.26940	12.921	.50061	12.992
.31192	12.913	.85239	12.988
.50695	12.951	.90361	12.980
.60660	12.952	.95629	12.991
.70266	12.968	1.00000	13.002
.84221	12.991		
.89763	12.991		
.94271	12.999		
.96622	12.996		
.98207	12.997		
1.00000	12.997		

In the table c_2 is the mole fraction of the solute while MR_2 is the molal refractivity of acetic acid for the sodium D line. The values of MR_2 reported for zero concentration were calculated from the slopes at infinite dilution of the refractive index *versus* concentration and the density *versus* concentration curves. To save space the authors have omitted the experimental values of the densities and refractive indices of the solutions in the article. It might be mentioned in passing that the density curve for acetic acid in dioxane passes through a maximum at about 93.5% acid. Obviously the values of the molecular refractivity calculated for the solute must be less accurate in dilute solution and this fact must be kept in mind in making comparisons. In the table the values for the dilute solutions are recorded to one less significant figure.

Summary

It has been shown that the changes in molecular refractivity of a solute with dilution do not constitute a simple test of association of hydroxyl compounds. There is no evidence from this source to disprove the type of coördination suggested by Sidgwick.[1]

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