

Ponderal Effect due to Changing Alkyl Substitution in a Solvent and its Quantitative Correlation

J.M. JESSY

Department of Chemistry, University of Calicut
Calicut, Kerala-673 635, India

Effect of changing alkyl substitution in a solvent which has been reported as steric is demonstrated to be ponderal (mass) effect. The quantitative correlation between reactivity parameters and reduced molecular weights (of solute and solvent) in different reactions, indicated earlier as empirical, is shown to have theoretical basis as a relationship between solvation-dependent reactivity and ponderal substituent effect of alkyl groups (in solvent) on solvation.

INTRODUCTION

The term '*ponderal*' is due to Ingold¹ according to whom it is a structural effect which depends on "the distribution of mass independently of bulk or charge" and which must have "frequently passed unnoticed in the admixtures of steric and polar effects". The present communication is to demonstrate that, while it passes unnoticed on covalent bonds, the ponderal effect is observable on solvation bonds and that it is also subject to theoretically justifiable quantitative correlation.

In earlier works in this laboratory it has been shown that with increasing alkyl substitution in solvent alcohol, there is (i) steady decrease in the rate constant (*k*)s of solvolyses of tertiary butyl chloride², (ii) steady shift of the equilibrium constant (*K*)s of the keto-enol equilibria of methyl and ethyl acetoacetates in favour of (less solvated) enols³, and (iii) steady decrease in the solubilizing number (*N*)s* of benzoic acid in alcohols. In all these cases alcohols of the α -series (methanol, ethanol, *iso*-propanol and *tert*-butanol) and of the normal series (ethanol, *n*-propanol, *n*-butanol, . . . *n*-decanol) were used. And, in all these cases, very good linear correlations were demonstrated between logarithms of the reactivity (experimental) parameters $\log k$, $\log K$ and $\log N$, and the mass function $\log (1/\mu)$, where μ is the reduced molecular weight of the solute and the solvent (given by $\mu = M_a M_b / (M_a + M_b)$, M_a and M_b representing molecular weights of the solute and of the solvent respectively). The changes in the reactivity parameters in all these cases were attributed to the increasing steric hindrance to solvation of the substrate caused by the increasing alkyl substitution in the solvent, though no explanation could be offered as to why the increase in *bulk* should produce effects which correlate with a function of *mass*. Indeed no correlation was obtained, as was looked for, with the steric substituent constant, E_s . Relevant data for showing the correlations in the above cases are listed in Table-1 (items 7 to 10).

*The solubilizing number (*N*) is defined as the number of solvent molecules per solute molecule, given by the solvent-to-solute molar ratio in saturated solution.

More instances in which ponderal effect due to alkyl groups seems to be the determining factor for reactivity changes are listed in Table-1 (items 1 to 6).*

TABLE-1
LINEAR CORRELATIONS BETWEEN EXPERIMENTAL PARAMETERS OF
SOLVATION AND THE PONDERAL PARAMETER ($1/\mu$)
IN ALCOHOLIC SOLUTIONS

Reaction	Alcohol	Logarithm of solvation parameter	$\log(1/\mu)$	Correlation coefficient	Slope	Ref. for data in I, II and III
		$\log k_{rel}^*$				
1. Reaction of Pyridine and ethyl iodide in alcohol $N + C_2H_5I \rightarrow N^+ - C_2H_5I^-$	MeOH	0.3979	-1.4501	0.992	1.48	5
	EtOH	0.1461	-1.5858			
	<i>i</i> -PrOH	0.0294	-1.6800			
	<i>t</i> -BuOH	-0.9315	-1.7508			
		$\log \delta^*$				
2. Solution of <i>m</i> -fluoro-nitrobenzene in alcohol	MeOH	-0.5289	-1.3939	1.000	0.17	6
	EtOH	-0.5478	-1.5104			
	<i>t</i> -BuOH	-0.5717	-1.6448			
		$\log k^*$				
3. Solvolysis of <i>t</i> -butyl bromide	MeOH	-4.46	-1.4145	1.000	7.63	7
	EtOH	-5.35	-1.5376			
	<i>i</i> -PrOH	-6.00	-1.6210			
	<i>t</i> -BuOH	-6.50	-1.6821			
		$\log k^*$				
4. Solvolysis of <i>t</i> -butyl iodide	MeOH	-3.90	-1.4360	0.999	6.76	7
	EtOH	-4.76	-1.5664			
	<i>i</i> -PrOH	-5.36	-1.6562			
	<i>t</i> -BuOH	-5.84	-1.7231			
		$\log k^*$				
5. Solvolysis of benzhydryl chloride	MeOH	-3.0794	-1.4078	0.998	10.64	7
	EtOH	-4.2668	-1.5286			
	<i>i</i> -PrOH	-5.2441	-1.6103			
		$\log K^*$				
6. Solubility of HCl in alcohols	MeOH	0.0670	-1.2320	0.998	0.44	8
	EtOH	0.0223	-1.3090			
	<i>i</i> -PrOH	0.0128	-1.3560			

*The data for these were collected from literature where they have been reported under different contexts; the references are provided in the Table.

Reaction	Alcohol	Logarithm of solvation parameter	log (1/μ)	Correlation coefficient	Slope	Ref. for data in I, II and III
		log N*				
7. Solubility of benzoic acid in alcohols at 35°C	MeOH	0.6531	-1.404	1.00	0.64	4
	EtOH	0.5908	-1.524			
	<i>i</i> -PrOH	0.5417	-1.605			
	<i>t</i> -BuOH	0.5097	-1.664			
		log K*				
8a. Solvolysis of <i>t</i> -butyl chloride in alcohols of α -series	MeOH	Values in reference	Values in reference	1.00	9.31	2a
	EtOH					
	<i>i</i> -PrOH					
	<i>t</i> -BuOH					
		log K*				
8b. Solvolysis of <i>t</i> -butyl chloride in alcohols of α -series	EtOH	Values in reference	Values in reference	0.998	4.69	2b
	<i>n</i> -PrOH					
	...					
	<i>n</i> -HeptOH					
		log K*				
9a. Keto-enol equilibrium of methylacetoacetate in alcohols of α -series	MeOH	Values in reference	Values in reference	0.997	1.40	3
	EtOH					
	<i>i</i> -PrOH					
	<i>t</i> -BuOH					
		log K*				
9b. Keto-enol equilibrium of methylacetoacetate in alcohols of <i>normal</i> series	EtOH	Values in reference	Values in reference	0.996	2.46	3
	<i>n</i> -PrOH					
	...					
	<i>n</i> -DecOH					
		log K*				
10a. Keto-enol equilibrium of ethylacetoacetate in alcohols of α -series	MeOH	Values in reference	Values in reference	1.00	1.49	3
	EtOH					
	<i>i</i> -PrOH					
	<i>t</i> -BuOH					
		log K*				
10b. Keto-enol equilibrium of ethylacetoacetate in alcohols of <i>normal</i> series	EtOH	Values in reference	Values in reference	0.998	1.79	3
	<i>n</i> -PrOH					
	...					
	<i>n</i> -DecOH					

k = rate constant

N = solubilizing number

K = equilibrium constant

 δ = NMR shift

RESULTS AND DISCUSSION

It is the first purpose here to point out that the changes in reactivity in all these cases (measured in terms of the different reactivity parameters) are caused by changes in the mass of the alkyl groups and not as effect of their changing bulk. This inference is drawn from the fact that the correlations are all obtained with a function of the alkyl mass and not obtained with the bulk parameter (E_s) of the alkyl groups, in spite of the fact that mass could be (?) proportional to bulk in the case of alkyl substituents. *This effect of mass on reactivity is referred to here as the ponderal effect.*

Secondly, a theoretical basis for the observed linear correlation between the logarithms of the linear parameters and the function $\log(1/\mu)$ is suggested in the following paragraphs:

(i) A covalent bond in a diatomic molecule is generally approximated to a spring, and Hooke's law applied to it, such that work required for the vibration of the bond through distance Δr is given by $[(1/2)f(\Delta r)^2]$ where 'f' is the force constant of the bond⁵. If we apply this to solvation bond, which has two masses—of the solute and the solvent—attached to its two ends, 'f' will be the force constant of the solvation bond. Just as the force constant of the spring represents its strength against the forces of vibration, *the force constant of the solvation bond* represents the strength of this bond against which the solute and solvent molecules vibrate. For the solvation bonds in the polar alcoholic solvents, the vibration and therefore the force constant can be taken as a function of the dipole-dipole interaction between the solute and the solvent, which is the major and macroscopic solute-solvent interaction to be expected. *For each of the reactions listed, since the solute (or substrate) is constant and all the solvent alcohols used have almost same dipole moment, the force constant remains very nearly constant in all the solvent alcohols.*

(ii) A covalent bond is also generally treated as harmonic oscillator⁵. If we consider solvation bond also as a harmonic oscillator, the vibrational frequency, ν , of the bond is given by:

$$\nu \text{ (cm}^{-1}\text{)} = (1/c)(f/4\pi^2\mu)^{1/2}$$

where 'c' is the velocity of light, 'f' the force constant of the bond and ' μ ' the reduced mass of the solvated system given by $\mu = (M_a M_b)/(M_a + M_b)$, M_a and M_b being the molecular weights of the solute and solvent molecules respectively⁵. For each of the reactions in the table we can rewrite the equation as below, incorporating the fact that the force constant, f , is a constant:

$$\nu = Z(1/\mu)^{1/2} \text{ where } Z (= (1/c)(f/4\pi^2)^{1/2}) \text{ is a constant.} \quad (I)$$

(iii) It may be noted that in each of the reactions listed, the mechanism is such that the reactivity depends on the degree of solvation. Let us suppose that what we mean by '*the degree of solvation*' is *actually the vibrational frequency of the solvation bond or a function of the same*. It is reasonable since the greater the

*Note that the degree of solvation at the macroscopic level due to OH group is constant for each reaction in all solvents.

vibrational frequency of the solvation bond, the greater the solute–solvent interaction at the molecular (microscopic) level*, which is indeed the degree of solvation. And, greater this interaction, greater the reactivity of any process which depends on solvation. In that case, *the reactivity parameter of a solvation-dependent chemical reaction (or physical process) will be proportional to the vibrational frequency of the solvation bond.* This is just the quantitative way of presenting the qualitative statement that reactivity depends on degree of solvation.

Therefore, if 'X' stands for any of the reaction parameters used for reactions in Table-1,

$$X \propto \nu$$

Substituting for 'ν' from equation (I),

$$X \propto Z(1/\mu)^{1/2}$$

or

$$Z = z \cdot X \cdot (1/\mu)^{1/2}$$

where 'z' is the proportionality constant.

Combining the constants,

$$X = \rho_{\text{solvn.}} \cdot (1/\mu)^{1/2} \quad (\text{II})$$

where $\rho_{\text{solvn.}} = z \cdot Z$

$\rho_{\text{solvn.}}$ may be called 'solvation constant', characteristic of the reaction and of the solvent series (such as the two series of alcohols). The equation (II) thus relates the reactivity parameter of a solvation-dependent reaction (or physical process) to the reduced molecular weight of the solute and the solvent. When an alkyl substituent in the alcohol molecule is changed, the reduced molecular mass, μ , gets changed, which in turn changes the degree of solvation and thereby the reactivity of the process which depends on solvation. *It is this effect of alkyl mass on reactivity which was observed empirically and which, it is being suggested, is the ponderal effect of alkyl substitution.*

(iv) In the comparison of the solvation bond to the covalent bond of a diatomic molecule, it has been ignored that while such a covalent bond has two *point* masses (by way of the two atomic masses) at its ends, the solvation bond has two groups of atomic masses—those of the solute and solvent molecules—at its ends. Unlike the point masses, these groups of masses can each have different modes of distribution for the atomic masses in them. And ponderal effect can change with the change in mode of distribution of the masses. To accommodate the possibility of such variations in ponderal effect causing changes in reactivity, another variable needs to be introduced in equation (II). This is done in equation (III), given below, by way of introduction of the variable 'x' such that:

$$X = \rho_{\text{solvn.}} \cdot (1/\mu)^{x/2} \quad (\text{III})$$

where 'x' is characteristic of the mode of distribution of mass in the solvent molecule, provided the solute molecule remains unchanged.

(v) Equation (III) represents the theoretically derived quantitative relationship between reactivity parameter, X, and the mass function $(1/\mu)$. Direct verification

of this relationship is however difficult since ' $\rho_{\text{solvn.}}$ ' and ' x ' are difficult to be determined for each reaction and for each solvent series. But the relationship can be indirectly validated by taking logarithms of both sides of the equation (III), which gives equation (IV):

$$\log X = \log \rho_{\text{solvn.}} + (x/2) \log (1/\mu) \quad (\text{IV})$$

This is an equation for straight line-plot so that, for a particular reaction in a particular solvent series, $\rho_{\text{solvn.}}$ and ' x ' being constants, the linearity of the plot of ' $\log X$ vs. $\log (1/\mu)$ ', can be tested. And, indeed, this is the linearity which has been obtained—*albeit* as an empirical correlation—for all the processes listed in Table-1, with very good values for correlation coefficients. The fact that for reactions in alcohols of α -series there are only four points to determine the linearity of the plot, needs to be recognized as a theoretical limitation (carbon having valency of four). The difference in ponderal effect on reactivity due to difference in *the distribution* of mass shows up in the plot as difference in *slope of the straight line* (*cf.*, items 8, 9 and 10 in Table-1) as is expected from the equation (IV) in which ' x ' is the variable characteristic of the distribution factor.

Changing alkyl substitution on the solute side of the solvation bond would be expected to produce overpowering polar and steric effects, possibly affecting mechanism also, so that detection of any ponderal effect is likely to be hard. Nevertheless, it is perhaps worth trying with carefully chosen substrates.

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