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The Pivotal Role of Ponderal Effect on the Energetics of Tertiary Amine/quaternary Ammonium Systems in Aliphatic Alcohols

J.M. JESSY
Department of Chemistry, University of Calicut, Calicut-673 635, India

A comparative study has been made of the reactivities of five closely related reactions, involving tertiary amines and/or quaternary ammonium salts in aliphatic alcohols. The qualitative and quantitative effects of changing alkyl substitution in the alcohols (along the series) on the transition or activation energies of the reactions were compared, for the sake of mechanistic details of solvation which could be obtained therefrom. The results demonstrate the surprising significance of ponderal hindrance in solvation—which is shown, in one of the reactions, to have reversed the direction of the relative reaction rates anticipated on the basis of polar factors alone.

Key words: Ponderal effect, energetics, tertiary amine, quaternary ammonium, aliphatic alcohols.

INTRODUCTION

Sovent effects on tertiary amine systems subjected to photochemical excitation are familiar in connection with solvent polarity parameters—Z-value, $E_T(30)$ value, Dimroth parameter and others[1–3]. These parameters are recognized as relative measures of solvent "polarity", which represents the solvent molecules' role as dipoles in the dipole-dipole interaction between solute and solvent. In the case of alcohols this will be the O—H dipole, whose strength may vary due to alkyl or other substituents, such variations being expected to be represented by changes in the parameter values.

A related reaction, thermal quaternization of pyridine by ethyl iodide has been used (along with a number of other reactions) to demonstrate the ponderal (mass) substituent effect on solvation due to changing alkyl substitution in aliphatic alcohols[4]. The linear correlation of the reactivity parameter, log k (k being second order rate constant) with the ponderal parameter, log $(1/\mu)$, has been given as a confirmation of this effect which, however, is admitted as weaker than the polar effect consequent of O—H dipole of the solvent, but shown to be significant as substituent effect.

In the present work a comparative study of solvent effects of aliphatic alcohols of α- and normal series on these reactions and on an additional related reaction, the quaternization of triethylamine by benzyl bromide, is carried out. The different aspects of the interaction between the reactant solutes and the solvent alcohols are considered from the view-point of *mechanistic details of solvation* on the following basis:

(i) The *differential* solvation of ground state *vs.* excited state or initial state *vs.* transition state, of the substrate—referred to as 'primary solvation'—are considered separately from the *differential* solvations in different alcohols due to the differences of their alkyl substitutions—referred to as 'secondary solvation'.

(ii) In addition to dipole-dipole interaction (between solute and solvent) interactions through H-bonding and orbital overlap at the two ends of the dipole are also taken account of.

(iii) Possibility of steric effect on solvation is ignored, on the basis that whenever the size of the alkyl substitution seemed to affect the reactivity of solvation-based reactions, the reactivity parameters did not show the expected quantitative correlation with steric substituent constant, E_s, and yet did give good quantitative correlations with ponderal parameter[4, 5] [The explanation could be that the solvation bonds are too long for hindrances due to bulk to be of significance[5].]

(iv) In addition to these electrical (dipole-dipole) and electronic (H-bonding and orbital overlap) effects on solvation, the mechanical (ponderal) effect is also included as a factor in determining the degree of solvation on the different species.

EXPERIMENTAL

Alcohols of analytical grade were purchased and further purified following standard methods[6], special care being taken with ethanol in view of its hygroscopic properties. Analytical grade triethylamine was further purified by slow distillation. The second order rate constants (k) of the triethylamine-benzyl bromide reaction in the different alcohols were determined following the procedure described in literature.[7] The kinetic runs were done in triplicate which showed variations of 1% or less. Results are given in Table-3.

TABLE-1
LINEAR CORRELATION BETWEEN ENERGY PARAMETERS OF ELECTRONIC TRANSITIONS AND POLAR SUBSTITUENT CONSTANTS (σ*) OF ALKYL SUBSTITUENTS IN SOLVENT ALCOHOL

Sl. No.	Reaction	Energy* parameters	Values of the parameter in alcohols				Correlation coefficient
			MeOH	EtOH	i-PrOH	t-BuOH	
I.	Energy changes due to solvation of 1-ethyl-4-carbomethoxy pyridinium iodide	Z-value (kcal/mole)[13]	83.6	79.6	76.3	71.3	0.999
IIa.	Transition energies for the intramolecular charge transfer of the pyridinium phenol betaine	$E_T(30)$ values (kcal/mole)[13]	55.5	51.9	48.6	43.9	0.999
IIb.	Transition energies associated with the electronic absorption maximum of 1,3,5-triphenyl pyridium-1,5-diphenyl phenol betaine	Dimroth parameter (ΔE/kJ mol^{-1})[14]	103	87.9	74.1	54.4	0.999
		σ* values of alkyl[12] groups of the alcohols	0.00	–1.00	–0.190	–0.300	

TABLE 2
LINEAR CORRELATION BETWEEN log k_{rel} OF THE QUATERNIZATION REACTION OF PYRIDINE WITH ETHYL IODIDE AND THE PONDERAL PARAMETER log (1/μ), FOR THE REACTION, IN ALCOHOLS OF THE α-SERIES[4]

Alcohol	log (k_{rel}) + 1	log (1/μ) + 2	Correlation coefficient
Methanol	1.3979	0.5499	0.988
Ethanol	1.1461	0.4141	
i-Propanol	1.0294	0.3200	
t-Butanol	0.9685	0.2492	

TABLE-3
SECOND ORDER RATE-CONSTANTS, k, OF THE QUATERNIZATION REACTION OF TRIETHYLAMINE WITH BENZYL BROMIDE IN ALIPHATIC ALCOHOLS OF THE α- AND n-SERIES

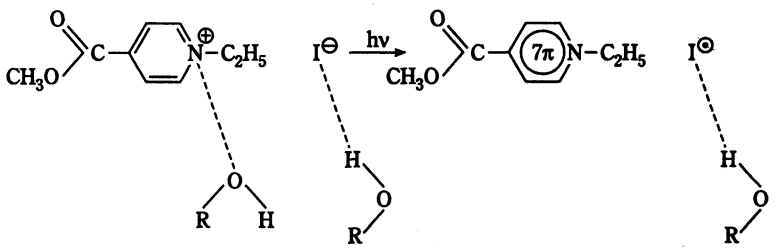
Temp. = 39.5°C

Alcohol	$k \times 10^3$	log k + 3
α-series		
MeOH	3.052	0.4846
EtOH	3.238	0.5102
i-PrOH	4.064	0.6090
t-BuOH	4.239	0.6270
Normal series		
EtOH	3.238	0.5102
1-PrOH	3.451	0.5379
1-BuOH	3.637	0.5607
1-PentOH	3.961	0.5978
1-HexOH	4.223	0.6253
1-HeptOH	4.495	0.6513
1-OctOH	4.862	0.6875
1-NonOH	5.389	0.7315
1-DecOH	5.966	0.7757

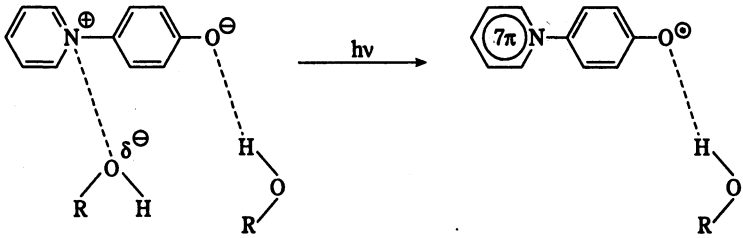
RESULTS AND DISCUSSION

The structural representations of the reactions compared are given below (choosing only the most relevant resonance structure in each case and) including solvation bonds at the most likely points of the given structures, with only one solvent molecule at each such point.

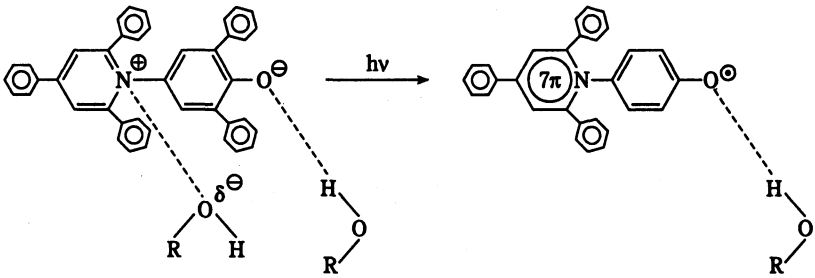
Reaction I



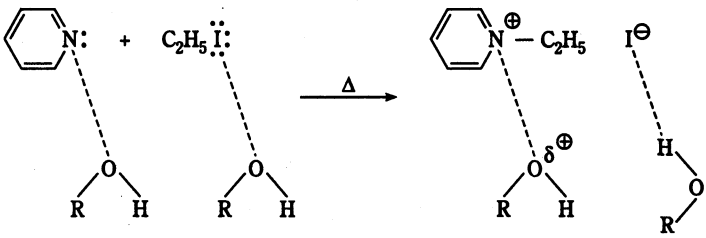
Reaction II (a)



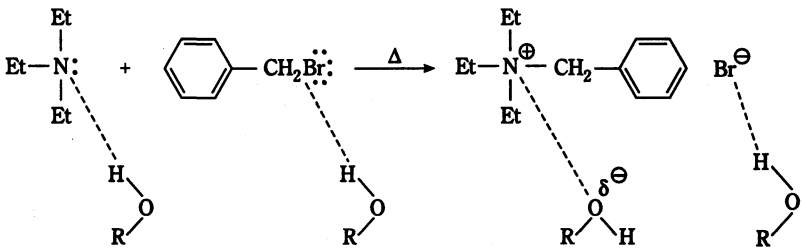
Reaction II (b)



Reaction III



Reaction IV



Reactions I and II

In these reactions, the primary solvation—ground state *vs.* excited state—is accepted to be strongly in favour of the ground state on the basis of strong dipole-dipole interaction between the dipolar substrates and the polar alcohol, any significant solvation of excited state being ruled out on the basis of its neutrality and Frank-Condon effect.[2, 8] As the molecular mass of excited state is same as that of the ground state there is no role for ponderal effect in the primary differential solvation (of ground state *vs.* excited state) in these cases.

Changing the solvent alcohol can however create changes in the solvation of ground state and of excited state separately due to the secondary differential solvation. When the ground state is more solvated than the excited state, any increase in solvation increases transition energy (E_T) consequent of the net secondary effect on the primary differential solvation (Fig. 1)[9].

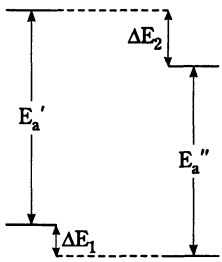
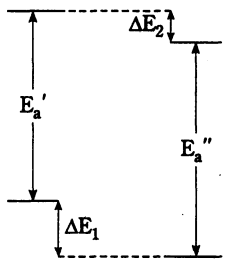
Primary differential solvation	(a) T.S./Exc.S. more solvated	(b) I.S./G.S. more solvated
T.S./Exc.S. I.S./G.S.		
Secondary differential solvation [under (a) and (b)]	(i) Less solvating solvent (ii) More solvating solvent $\Delta E_1 < \Delta E_2$ $E_a' > E_a''$	(i) Less solvating solvent (ii) More solvating solvent $\Delta E_1 > \Delta E_2$ $E_a' < E_a''$

Fig. 1. Changes in activation energy (E_a) on changing of solvent (a) when transition state/excited state is more solvated and (b) when initial state/ground state is more solvated [due to the differences in the solvation energies (ΔE)]. In photochemical changes, Activation energy = Transition energy ($E_a = E_T$).

The observed order of transition energy in all the three reactions is, for alcohols of α series:

$$E_T = \text{MeOH} > \text{EtOH} > \text{i-PrOH} > \text{t-BuOH}$$

Since solvation increases in the same order as does E_T, the order of solvation (of the ground state) in these alcohols must be

$$\text{Solvation} = \text{MeOH} > \text{EtOH} > \text{i-PrOH} > \text{t-BuOH}$$

This order of solvation is possible under two circumstances: (a) The predominant substituent effect is polar and the solvation is through the protic hydrogen of the alcohol. Increased substitution by electron-releasing alkyl groups reduces the protic character of the hydrogen and hence solvation through it. [Solvation through (hydroxy) oxygen will only be strengthened by the increased electron release of alkyl substituents.] (b) The predominant substituent effect is ponderal (so that the increase in alkyl mass due to increased alkyl substitution causes greater hindrance to solvation and solvation is reduced).

The quantitative correlation of the experimental energy parameters with the polar and ponderal substituent parameters can help us to choose between the two possibilities: Transition energies in all the three reactions give good linear correlation with the polar substituent parameter σ* as shown by the very good

correlation coefficient value in Table-1. No such correlation is obtained with the ponderal parameter.* Therefore, solvation is predominantly through protic hydrogen. Since this is possible only at anionic centres, the solvation is predominantly at iodide in reaction I and at O^- in reactions II.

Thus we have, for these reactions, the primary differential solvation in favour of T.S. is on the basis of solute- and solvent-polarity, selectively at the negative end of the solute dipole, and the secondary differential solvation is on the basis of the polar substituent effect (of the alkyl groups in the solvent).

[The reason for preferential solvation of I^- or O^- over the pyridinium centre could be either that the positive charge is dispersed relative to the negative charge concentrated on the single atom, which would be the polar reason; or, it could be the greater ponderal hindrance to solvation at the much more massive pyridinium ion; or it could be both.†]

Reaction III

In this reaction, the reactivity parameter is the second order rate constant, k, which is a function of the activation energy, E_a, which in turn, changes with the differential solvation of initial (I.S.) and transition (T.S.) states.[9] The products being ionic, T.S. must be much more polar than the neutral I.S. The T.S. is also much more ponderous (molecular mass larger) at the pyridinium ion, but less so at the iodide ion than the I.S. It is not therefore very simple to predict whether the I.S. or the T.S. must be more solvated. Under this circumstance of uncertainty we consider both possibilities separately in going to the next step of secondary solvation.

(1) *If the T.S. is more solvated (on the basis of polarity of solute and solvent):* Whenever T.S. is more solvated than I.S., the E_a decreases with increasing solvation (Fig. 1). The experimental value of k is seen to be highest for methanol and lowest for t-butanol in the α-series (Table-2) denoting that the activation energy is in the (opposite) order, as below:

$$E_a = \text{MeOH} < \text{EtOH} < \text{i-PrOH} < \text{t-BuOH}$$

Since activation energy decreases with increasing solvation, the order of solvation must be

$$\text{Solvation} = \text{MeOH} > \text{EtOH} > \text{i-PrOH} > \text{t-BuOH}$$

This order of solvation is expected if (a) the predominant substituent effect is ponderal (solvation decreasing with increasing alkyl mass) or (b) the prominent centre of solvation is the iodide ion solvated through protic hydrogen and the predominant substituent effect is polar (as for Reaction I) increasing alkyl substitution and decreasing acidity of protic H. As before, we look for quantitative correlation of secondary differential solvation to make the choice between the two possibilities.

*Nor is linear correlation obtained with steric substituent constant, E_s.

†Note that it cannot be steric as the bulk of pyridinium ion, in each case is confined to a single plane, and also the +ve charge can be dispersed to many peripheral non-hindered, points by resonance.

The quantitative correlation obtained for the experimental parameter of activation energy, log k, is with the ponderal substituent parameter, log $(1/\mu)$ (correlation coefficient in Table-2) and not with the polar substituent constant, σ^*. Therefore, of the two, ponderal substituent effect is the determining factor for solvation, if T.S. is more solvated than I.S.

(2) *If the I.S. is more solvated (on the basis of the ponderal character of solute and solvent):* When initial state is more solvated, the activation energry (E_a) should increase with increased solvation (Fig. 1). From the observed order of E_a, above, the order of solvation under this condition must be

$$\text{Solvation} = \text{MeOH} < \text{EtOH} < \text{i-PrOH} < \text{t-BuOH}$$

This order is possible only if the solvation is through hydroxy oxygen and the substituent effect is predominantly polar (increased alkyl substitution increasing electron density at oxygen). However, from the structural representation, it can be seen that in the I.S., solvation by alcohol is possible, both at nitrogen and iodine only through protic hydrogen. Therefore this possibility can be ruled out.

Thus in this reaction the primary differential solvation is in favour of T.S. on the basis of the polarities of the solute and the solvent whereas the secondary differential solvation is on the basis of ponderal substituent effect (due to alkyl substitution in the solvent). [One possible reason for this last—the predominant ponderal substituent effect—can be that polar substituent effect, opposite in direction on the two species in T.S. (see structure) being comparable in magnitude, could be self-cancelling.

Reaction IV

From the equation, this reaction is very similar to reaction III. The T.S. is more polar than the I.S. and also more ponderous at the pyridinium ion, but less so at bromide, than the I.S. Therefore one would expect the picture of solvation to be as in the case of reaction III, the parameter k changing in value in the same direction along the solvent alcohol series as in III. But, suprisingly, the direction shown by experimental values of rate constant (k) is the opposite one. The rate constants increase in value with increasing alkyl substitution in alcohols of both the α- and the normal series (Table-3) denoting the order of activation energy to be

$$E_a = \text{MeOH} > \text{EtOH} > \text{i-PrOH} > \text{t-BuOH}$$
$$= \text{EtOH} > \text{1-PrOH} > \text{1-BuOH} > \ldots > \text{1-DecOH}$$

Applying the same methods as above—of looking for a combination of primary and secondary differential solvations possible such that it agrees with experimental results—we can arrive at the following qualitative inferences.:

(a) One possibility is that the primary differential solvation is in favour of T.S. on the basis of solute-solvent polarity. If so, E_a must decrease with increasing solvation (Fig. 1), so that the order of solvation must be (from the above experimental order of E_a):

$$\text{Solvation} = \text{MeOH} < \text{EtOH} < \text{i-PrOH} < \text{t-BuOH}$$

= EtOH < 1-PrOH < 1-BuOH < . . . < 1-DecOH

This order of solvation indicates that the solvation must be through hydroxy oxygen and the predominant substituent effect polar (electron-releasing alkyl groups strengthening the solvation bond).

To confirm this, however, a quantitative correlation between log k and the polar substituent constant (σ^*) is not obtained. If the substituent effect is distinctly polar, there is no reason why such a correlation could not be obtained as in the reactions I and II. It is, however, possible that the two effects, polar and ponderal, are really comparable and that the order represents the net, polar effect over the opposing ponderal effect and hence the lack of correlation.

In order to test this, a semi-quantitative correlation was attempted between the activation energy and the degree of alkyl substitution in the normal series, by way of a plot of log k *vs.* the number of carbon atoms in the alcohol. The plot obtained is a curve (Fig. 2) with a smaller slope in the region of lower alcohols and a larger one, at higher alcohols. Now, the polar substituent effect is known to decrease with increasing distance (through intervening sigma bonds), whereas the ponderal substituent effect is expected to increase with distance.[11] Therefore if the observed order is due to a combination of polar and ponderal substituent effects on T.S. with polar effect dominating, the slope should be larger at lower alcohols (where the stronger, positive polar effect is compensated less by the weaker, negative ponderal effect), and smaller at higher alcohols (where the polar effect should be getting weaker steadily and fast and compensated more by the opposing ponderal effect which is getting stronger). Therefore the observed shape of the curve does not agree with this possibility.

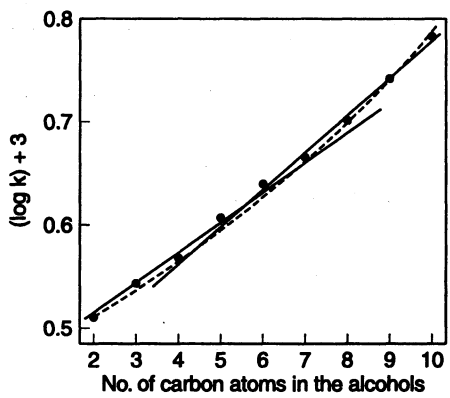


Fig. 2. Plot of log k vs. no. of carbon atoms in the alcohols of n-series

(b) The other possibility is that the primary differential solvation is in favour of the I.S., which is possible on the basis of the ponderal characters of the solute and the solvent (each of the solvated species being less massive than T.S.). In that case, activation energy should increase with increasing solvation (Fig. 1), so that the order of solvation will be (the same as the order of E_a) as follows:

$$E_a = \text{MeOH} > \text{EtOH} > \text{i-PrOH} > \text{t-BuOH}$$
$$= \text{EtOH} > \text{1-PrOH} > \text{1-BuOH} > \ldots > \text{1-DecOH}$$

This order is indicative of either (a) solvation through protic hydrogen of the alcohol with the dominant substituent effect being polar or (b) that the substituent effect is ponderal, irrespective of whether the solvation is through hydrogen or oxygen (see structure). To confirm one way or the other through quantitative correlation, however, no correlation was obtained between log k and either the polar substituent parameter, σ^*, or the ponderal substituent parameter, log $(1/\mu)$. It can be seen however that, in this case, both the (polar and ponderal) substituent effects are in the same direction. The I.S. solvation can be only through protic hydrogen of the alcohol at both points of solvation (see structural representation). And solvation at both points should decrease with increasing alkyl substitution due to (a) their electron releasing polar effect making the hydrogen less protic, and (b) the increasing substituent mass creating greater ponderal hindrance. Thus the effects are cumulative. If they are also in comparable magnitude, a quantitative correlation exclusively with either parameter cannot be expected.

Therefore, for a better understanding of the two effects on I.S. solvation we go back to the semi-quantitative plot (Fig. 3). The shape of the curve for normal series now becomes explicable with the two effects cumulative. The smaller slope at the lower alcohols can be due to the stronger polar substituent effect (alkyl substitution closer), supplemented by the weaker ponderal effect (alkyl mass smaller and closer); the larger slope at the higher alcohols can be due to the stronger ponderal effect (alkyl mass larger and increasing at greater distance) supplemented by the weaker polar effect (alkyl substitution farther). The slopes will then also imply that ponderal effect at larger distances, due to alkyl substituents, is greater than polar effect at shorter distances. The bend comes approximately at C_5, C_6 points where indeed one would expect the polar effect to peter out completely.

Coming to the α-series, one notes that all the four alcohols are lower alcohols. Both effects—polar and ponderal—increase at a higher rate than in the case of

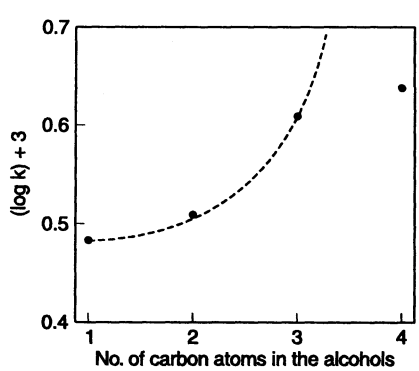


Fig. 3. Plot of log k vs. no. of carbon atoms in the alcohols of α-series

normal series which explains the sharper change in slope. This is as expected since σ^*-values have higher values at α-positions[12], and ponderal hindrance is also greater for α-distribution of mass[10]. Looking more closely at the values of the two parameters as they change along the series (Tables 1 and 2), whereas the σ^*-values are seen to change more steadily (a steady difference of about 0.1, numerically, between each pair of adjacent alcohols in the series), the change in values of log $(1/\mu)$ is telescoping (the numerical difference is about 0.1 at MeOH- EtOH gap, 0.08 at EtOH-i-PrOH gap and 0.05 at i-PrOH-t-BuOH gap). Therefore when the two effects get added up, the curve is no longer steady. The stronger polar component of substituent effect seems to be maximum at iso- propanol, the next alkyl group in tert-butanol decreasing solvation only slightly. This could be because of the cumulative effects being so large that the primary solvation itself is considerably weakened.* The shape of the curve for the normal series, thus, supports the second possibility and the curve for α-series is also explicable under the same possibility.

Therefore, in reaction IV, the primary differential solvation must be in favour of initial state on ponderal basis (due to solute and solvent molecular masses) and in secondary differential solvation, polar and ponderal substituent effects must be cumulatively overlapping. In this reaction it is seen, for the first time, that ponderal effect can play a determining role in the primary solvation of initial state *vs.* transition state in a reaction and thereby reverse the direction of its kinetics.

Summary

A study of mechanistic details of solvation is attempted—*albeit* indirectly—by comparing some related reactions involving tertiary amine/quaternary ammonium systems in the same set of alcohols. The basis of comparison is (1) their qualitative changes in reactivity due to changing alkyl substitution in solvent alcohol, and (2) differences in the quantitative correlations of their (activation) energy parameters with the (alkyl) substituent parameters of the solvent alcohols.

First, solvation is classified as primary and secondary: primary solvation being the differential solvation of the initial and transition states of the substrate if the reaction is thermal and of ground and excited states if it is photochemical; and the secondary solvation being the differential solvation between different alcoholic solvents differing in their alkyl substitution. The polar and ponderal effects of substrate and/or solvent responsible for these differential solvations at each point of solvation in each state are compared. The steric effect is ruled out as of any significance in the process of solvation.

The inferences which have been arrived at, for all the alcoholic solvents, are:

1. In the first and second reactions, the ground state is favoured over excited state in the primary differential solvation on the basis of polar characteristics of solute and solvent. The alkyl substituent effect on secondary solvation is also polar.
2. In the third reaction the T.S. is favoured over the I.S. for the primary

*Such a situation has not risen in the other reactions studied[4, 5] in all of which rate-determining solvation has been through alcoholic oxygen so that the substituents are closer and hence less ponderal effect has been observed.

solvation on the basis, again, of polar character of the solute and the solvent. The (alkyl) substituent effect on secondary solvation is ponderal.

3. In the fourth reaction the primary solvation is in favour of I.S. on the basis of ponderal characters of the solute and the solvent. The (alkyl) substituent effect on secondary solvation is polar.

Conclusion

The above inferences suggest that:

1. Ponderal effect plays a significant role, not only in secondary differential solvation as has hitherto been shown in the earlier works[4–6] but also on primary differential solvation. In other words, solvation is not always "essentially an electrostatic phenomenon"[11], but does have a mechanical aspect to it.
2. "Mechanism of solvation" can be worked out and hopefully predicted if more work is carried out with that aim, on the basis of polar and ponderal effects. Solvation being responsible for "differences in free-energy differences", it is perhaps necessary for the importance of "solvation mechanisms", to be better recognized.

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