

SOLVENT STERIC EFFECT DUE TO ALKYL SUBSTITUTION

J. M. JESSY

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

ABSTRACT

Rate retardation is demonstrated for a few solvolytic reactions in a set of solvents which are structurally similar and of very nearly the same polarity but have gradually increasing bulk. This is suggested to be due to the solvent steric effect. The same effect is also demonstrated in selective solvation.

INTRODUCTION

ALTHOUGH structural effects of organic solvents on reactivity are widely studied and multiple parameter correlations have been derived on the basis of such structure-based characteristics of solvents as polarity, polarizability, acidity and hydrogen bonding capacity¹⁻⁸, mention is very seldom made⁹ of the steric effect possible due to the bulk of the solvent and that too, not in the context of its direct effect on the solvating capacity of solvents and consequently on reactivity. The present work is the beginning of an attempt in this direction.

EXPERIMENTAL METHODS

The solvolytic reaction of *tert*-butyl chloride by different alcohols, is chosen for the study since, the reaction is definitely known to follow S_N1 mechanism and is one in which solvation (by solvent) plays a very significant role in determining reactivity. The mechanism has recently been described as S_N2 (intermediate)¹⁰, according to which, the rate-determining step is one in which a weakly solvated ion pair is formed. The ion pair is then supposed to go on to solvated ions in a fast step, followed by another fast step in which the final products—ether and hydrochloric acid—are formed. The earlier picture¹¹ is different only in that the products of the slow step were believed to be solvated ions rather than a solvated ion pair. In either case, the rate-determining step and its transition state are the same; and this step involves solvation, giving solvated intermediate, be it ion pair or separated ions.

It is in this rate-determining solvation step, that the effect of solvent bulk is seen as explained below. The rate constant should therefore be a suitable criterion to measure the solvent steric effect in this reaction. Therefore the reactivity is measured in terms of the first order rate constants.

The alcohols selected as solvents are methanol,

ethanol, *iso*-propanol and *tert*-butanol, whose alkyl parts, sterically, constitute Ingold's α -series¹². All of them have very nearly the same polarity (dipole moments having values within the range of 1.63 to 1.81 Debye units in benzene at 25°C)¹³. The reactivity is also determined using aqueous solutions of the above alcohols as solvents, in order to observe solvent steric effect, if any, in selective solvation. In this mixed solvent series the molar ratio of water to alcohol was kept constant at 2:3.

For purification of solvents and for rate determination, experimental methods described in literature¹⁴ are followed.

The first order rate constants are given in table 1. Data for a few substrates other than *tert*-butyl chloride are also included for comparison.

Table 1. Changes in values of rate constants with solvent bulk

Substrate	Solvent	$k \times 10^6$
<i>t</i> -Butyl chloride (50°C)	Methanol	42.55
	Ethanol	4.605
	<i>i</i> -propanol	0.8465
	<i>t</i> -Butanol	0.3343
<i>t</i> -Butyl Chloride (50°C)	aq. Methanol	1151
	aq. Ethanol	151.2
	aq. <i>i</i> -Propanol	33.87
	aq. <i>t</i> -Butanol	15.67
<i>t</i> -Butyl Bromide* (25°C)	Methanol	34.67
	Ethanol	4.467
	<i>i</i> -propanol	1.000
	<i>t</i> -Butanol	0.3162
<i>t</i> -Butyl Iodide* (25°C)	Methanol	125.9
	Ethanol	17.38
	<i>i</i> -Propanol	4.365
	<i>t</i> -Butanol	1.445
Benzhydryl Chloride (25°C)‡	Methanol	833.0
	Ethanol	54.11
	<i>i</i> -Propanol	5.701

* Logarithmic values of rate constants taken from ref. 5.

‡ Rate constant values taken from ref. 15.

DISCUSSION

Table I shows a significant and steady decrease in rate corresponding to the increase in alkyl substitution in the solvent, in the case of all the substrates. This cannot be due to polar effects since (i) the alcohols have all the same polarity and (ii) any polar effect is expected to act in the opposite direction¹⁶. In the case of *aq.* alcohols, the constancy of the molar ratio of water to alcohol—and hence the constancy of the relative numbers of water dipoles and alcohol dipoles—assures that polarity of all *aq.* alcohols is also very nearly the same, though this will be higher than that for the dry alcohols. Therefore, the rate decrease within each series is to be taken as due to steric hindrance to solvation caused by the increasing alkyl substitution in the solvent molecules.

Secondly, in the *aq.* alcohols the rates are all higher, clearly due to increased solvent polarity. However as the molar ratio of water remains the same, the increase in polarity should also be the same; it follows that selective solvation consequent of the higher polarity of water and the rate increase caused thereby must be the same. Then, in the absence of any other effect, while the rate constants are expected to be higher in this series, the range of the rate constants—between *aq.* methanol and *aq. tert.* butanol—ought to remain the same as that of the dry alcohols—between dry methanol and dry *tert*—butanol. It is found, however, that change in *k* values is 130 times across the dry alcohol series, but only 70 times in the *aq.* alcohol series.

This can be explained as due to selective solvation by water consequent of its smaller bulk. This effect will be maximum in *tert*-butanol-water mixture and minimum in methanol-water mixture as the bulk difference between the alcohol and water molecules is most in the former and least in the latter. Such an order of variation in selective solvation can lead to the observed decrease in the range of solvolysis rates in the *aqueous* series; a smaller increase in rate in *aq.* methanol compared to dry methanol and a larger increase in *aq. tert*-butanol compared to dry *tert*-butanol giving

smaller range between the two *aqueous* alcohols than between the dry ones.

Further work is being done towards determining the solvent steric effect in more solvents and for other reactions.

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