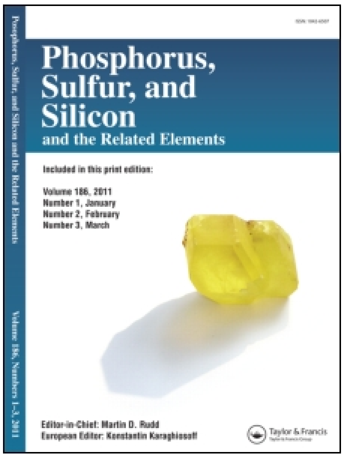

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# KINETICS OF ALKALINE HYDROLYSIS OF QUATERNARY PHOSPHONIUM SALTS. THE DEPENDENCE OF MEDIUM EFFECTS ON THE STRUCTURE OF THE SALTS

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# KINETICS OF ALKALINE HYDROLYSIS OF QUATERNARY PHOSPHONIUM SALTS. THE DEPENDENCE OF MEDIUM EFFECTS ON THE STRUCTURE OF THE SALTS

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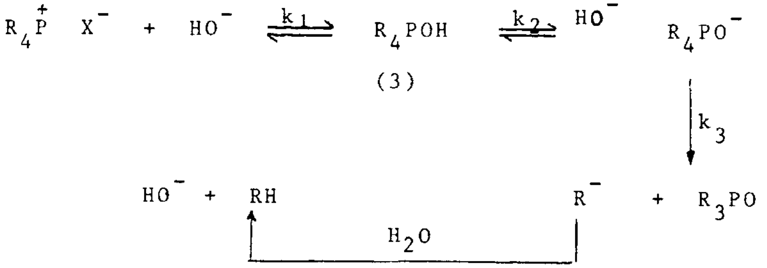
Third order rate constants have been determined for the alkaline hydrolysis of ethyl phenyl- and benzyl alkyl phenyl-phosphonium salts (**1**) and (**2**) in aqueous methanol and aqueous tetrahydrofuran. The hydrolyses in the low polarity medium containing tetrahydrofuran are faster than those performed in aqueous methanol of higher polarity. The differences in rate between the two solvent systems are very large when there are no, or few, ethyl groups bound to phosphorus but decreases markedly as ethyl groups replace phenyl groups. This trend is not dependent on the nature of the leaving group. The replacement of a phenyl group by a benzyl group not only increases the rates of hydrolysis in both solvent systems, but it also accentuates the difference in rates between the two media.

The influence of the nature of the solvent medium on the rates of alkaline hydrolysis of quaternary phosphonium salts has been studied by Aksnes and his coworkers in considerable detail.[1,2] In aqueous alcohol modest changes in the rates of hydrolysis may be induced by changes in solvent composition, the rate constants being inversely proportional to the dielectric of the medium.[1] Much larger changes in the rates of hydrolysis may be obtained by using mixtures of water and aprotic solvents such as dioxan, tetrahydrofuran and acetone.[2] The mechanism of hydrolysis is widely accepted to be, normally, that shown in the Scheme 1. In solvent mixtures containing an excess of water over that of cosolvent the reacting ions are highly

$Et_n\overset{+}{P}Ph_{4-n}\ I^-$ (1)

$Et_n\overset{+}{P}(CH_2Ph)Ph_{3-n}\ Br^-$ (2)



SCHEME 1

solvated. The increase in rates of hydrolysis which occurs upon introducing protic solvents is consistent with the desolvation of the reacting ions.

We have previously studied the alkaline hydrolysis of ethyl phenyl phosphonium salts (**1**) in homogeneous low and high dielectric solvent systems at one temperature.[3] It was hoped that by using a low polarity medium, the rate of hydrolysis of aliphatic salts could be sufficiently enhanced to be able to obtain more accurate kinetic and activation energy data. However, the huge increase in rate of hydrolysis induced by aprotic solvents for the aromatic salts, (a factor of $5 \times 10^7$ has been reported for the hydrolysis of tetraphenylphosphonium chloride in aqueous dioxan[2a]), falls almost to nothing for the aliphatic salts. By incorporating and extending several of the conclusions drawn by Aksnes, we suggested that the phenyl groups, possibly with the assistance of $d_\pi$–$p_\pi$ bonding, caused the positive charge to be localized on phosphorus, which in turn induced highly specific solvation of the phosphonium ion. We postulated that the effect of changing the solvating power of the medium will be felt most when there is least dispersion of the charge, as proposed for the aromatic salts, and conversely the effect minimal when there is most dispersion of charge which would be the case for the aliphatic salts. Further work was required in order to establish the generality of the structural influence within the reactant on medium effects and to test the above proposals.

## RESULTS

The rates of hydrolysis of the salts (**2**, $n = 0$–$3$) were measured using two solvent systems, one of high dielectric (70% v.v. methanol in water; $\epsilon \sim 40$)[4] and one of low dielectric (70% v.v. tetrahydrofuran in water; $\epsilon \sim 20$)[4]. The hydrolyses were carried out at 40° and 55°—the reactants and products remaining in solution throughout the whole of the reaction. At 55° the aqueous tetrahydrofuran was a two phase system. The rates of hydrolysis of the salts (**1**; $n = 0$–$4$) were measured in the two phase system at 55°.

Table I gives the third order rate constants, $k$, obtained from linear plots of $1/c_t^2 - 1/c_0^2$ against time. The reactions were normally followed to 80% completion.

TABLE I

Third order rate constants, $k/\text{dm}^6\ \text{mol}^{-2}\ \text{min}^{-1}$, for salts (**1**) and (**2**)

| Salt | $k^{55°}$ aq.THF | Salt | $k^{40°}$ aq.MeOH | $k^{55°}$ aq.MeOH |
|---|---|---|---|---|
| **1**; $n = 0$ | $1.45 \times 10^3$ | **2**; $n = 0$ | 4.0 | 7.52 |
| **1**; $n = 1$ | $1.86 \times 10^2$ | **2**; $n = 1$ | 1.87 | 2.77 |
| **1**; $n = 2$ | $4.88 \times 10$ | **2**; $n = 2$ | $8.0 \times 10^{-1}$ | 1.02 |
| **1**; $n = 3$ | 4.48 | **2**; $n = 3$ | $3.63 \times 10^{-1}$ | $3.77 \times 10^{-1}$ |
| **1**; $n = 4$ | $8.0 \times 10^{-1}$ | | | |

| Salt | $k^{40°}$ aq.THF | $k^{55°}$ aq.THF |
|---|---|---|
| **2**; $n = 0$ | $2.20 \times 10^4$ | $6.31 \times 10^4$ |
| **2**; $n = 1$ | $4.40 \times 10^2$ | $6.84 \times 10^2$ |
| **2**; $n = 2$ | $3.0 \times 10$ | $5.90 \times 10$ |
| **2**; $n = 3$ | $8.47 \times 10^{-1}$ | 1.27 |

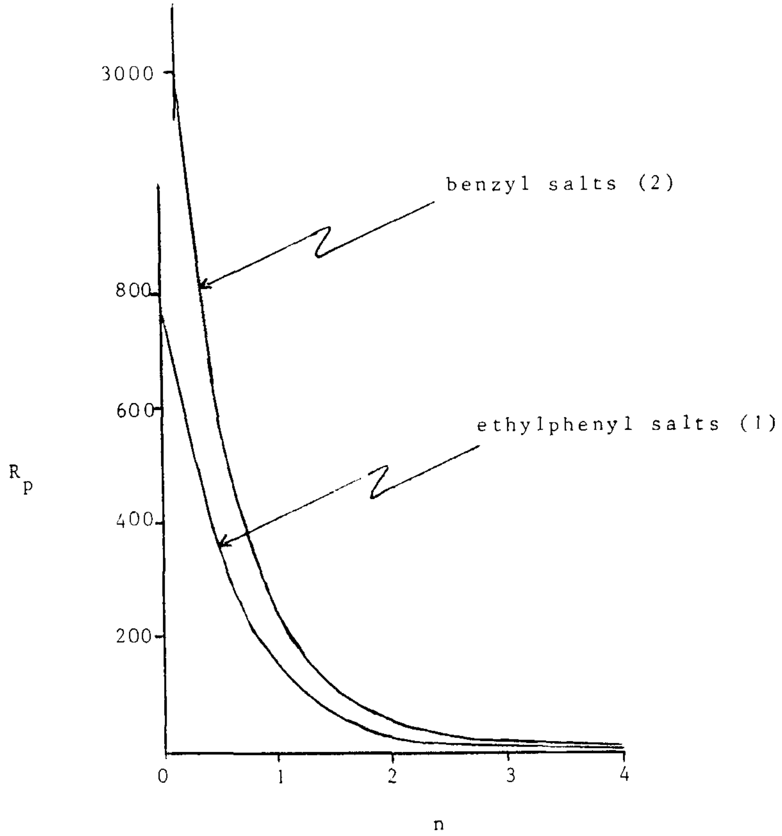


FIGURE 1 Plot of $R_p$ against number of ethyl groups $n$ for salts (**1**) and (**2**).

Figure 1 shows the change in the rate constants caused by the change in medium, where $R_p$ is the ratio of the rate constants for the two solvent systems (see Eq. 1).

$$R_p = \frac{k\ (\text{aqueous tetrahydrofuran at } 40°)}{k\ (\text{aqueous methanol at } 55°)} \tag{1}$$

The rate constants determined for the aqueous methanol solutions decrease fairly uniformly as the salts become more aliphatic, whereas the corresponding values for the aqueous tetrahydrofuran solutions do not. This is presented graphically in Figures 2 and 3, where $R_s$ is the ratio of the rate constants of adjacent benzyl salts (**2**) (i.e. those salts which differ in the number of ethyl groups by one) for a given medium and temperature.

## DISCUSSION

The replacement of an alkyl or aryl group in a quaternary phosphonium salt, by a benzyl group increases the rate of hydrolysis through its favourable influence on the final step of the reaction pathway, $k_3$ (see Scheme 1). The benzyl group is ejected in

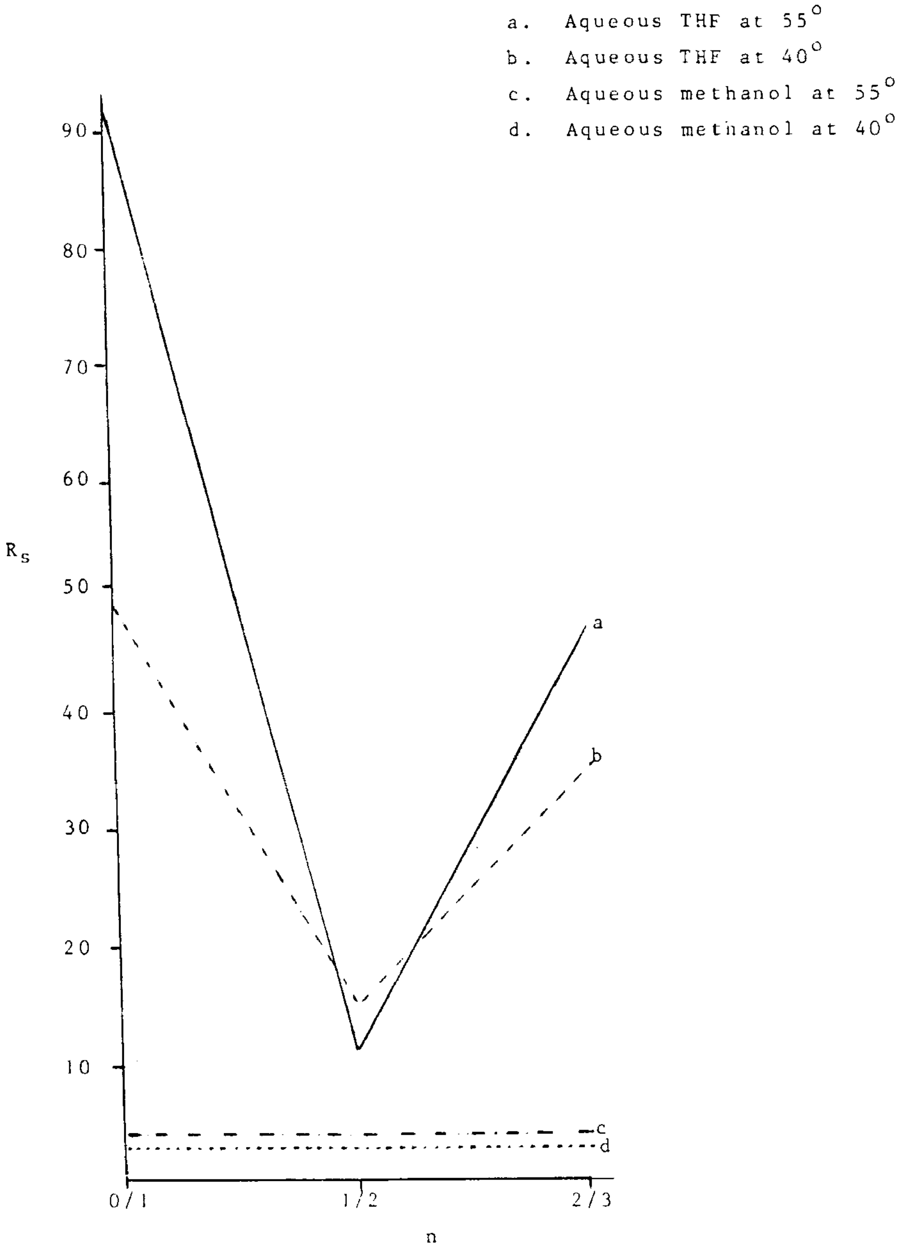


FIGURE 2 Plot of the ratio of rate constants of the benzyl salts (2) differing by one ethyl group ($R_s$) against the number of ethyl groups ($n$) in the compared salts.

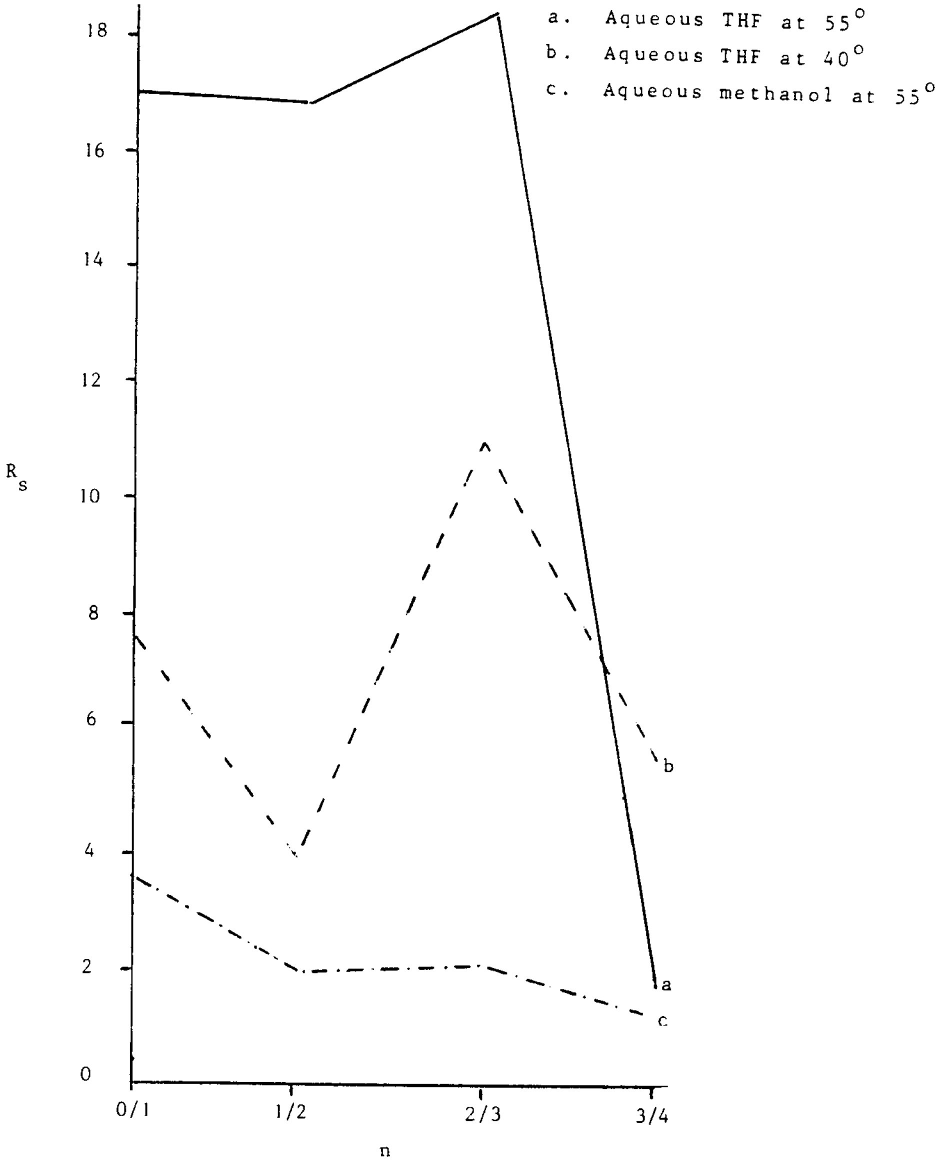


FIGURE 3 Plot of the ratio of the rate constants of the ethylphenyl salts (1) differing by one ethyl group, ($R_s$) against the number of ethyl groups ($n$) in the salts compared.

preference to alkyl or aryl groups. The extra stabilisation of the developing benzylic carbanion, during the third step of the mechanism, facilitates the cleavage of the phosphorus–carbon bond.[5] The resultant effect on the rate constants is clearly apparent for the benzyl salts (2) compared to the ethyl phenyl salts (1), see Table I and previously published data.[3]

Both series of salts show a dramatic fall in the value of $R_p$ (see Figure 1) as the phenyl groups are replaced by ethyl groups. Thus the structural dependence of the effect of the medium appears to be of general applicability and it is not dependent on the nature of the leaving group. This also supports the more general assumption that the main impact of changes in the medium is on the first step ($k_1$) of the reaction mechanism, i.e. on the relative position of the pre-equilibrium.[6]

When the effect of changing the medium is compared for the two series of salts (**1**) and (**2**), it is possible to pair either those salts with the same number of ethyl groups or those salts with the same number of phenyl groups. Figure 1 shows that the $R_p$ values are of a similar order only for the salts with the same number of ethyl groups. Thus the benzyl group has an effect more closely related to a phenyl group than an ethyl group. In fact the sensitising influence of the benzyl group on the salts responsiveness to medium changes is noticeably greater than the phenyl group. The mode of action of the two groups is probably similar since the ratio, $R_s$, of the rate constants of adjacent salts in aqueous tetrahydrofuran match up (see Figure 2) only if salts with a similar number of ethyl groups are compared.

The benzyl group has a weaker inductive ($+I$) effect than an ethyl group and therefore it would not delocalise the positive charge on phosphorus as effectively as an ethyl group, and yet it would not be expected to exhibit $d_\pi$–$p_\pi$ bonding. As a consequence, the present results do not support our previous suggestion that the origin of the changes in $R_p$ resides in the localisation of the positive charge on the phosphorus atom. The benzyl groups most striking resemblance to the phenyl group is the presence of a benzene ring, in which case the controlling factor may reside in the different effects of aliphatic groups and aromatic rings on the specific solvation of the phosphonium ion.

We noted with considerable interest the separation of the aqueous tetrahydrofuran reaction mixture into two phases when the temperature was raised above 50°C. Two phase reactions often show enhanced rates of reaction when phase transfer catalysts such as ammonium or phosphonium salts are present.[7] For both series of salts the rate constants were higher for the two phase system than those estimated from the rate constants of the homogeneous reaction at 40°. Furthermore the plots of the $R_s$ values for the heterogeneous reactions (see Figure 2) followed a similar but more accentuated pattern than the homogeneous reactions. Thus it appears possible that the reactions occurring at or near the phase boundary are magnifications of the processes occurring under homogeneous conditions.

Clearly further studies are required in order to clarify the role of solvation in the mechanism of hydrolysis especially with regard its dependence on the aliphatic/aromatic character of the salts.

## EXPERIMENTAL

*Benzyl Ethyl Phenyl Phosphonium Bromides* (**2**). The salts were prepared from benzyl bromide and the appropriate phosphine. They were purified by recrystallisation from water. The phosphines were prepared and purified by the method of Davies and Jones.[8] The purity of the salts was established by $^1$H and $^{31}$P n.m.r. spectroscopy and by comparison of their melting points with published data.

*Kinetics of Alkaline Hydrolysis.* The apparatus and methods used were the same as published previously.[3]

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