Bull.Chem.Soc.Ethiop.,3(2), 115-120 (1989).

SOLVENT EFFECTS IN THE HYDROXIDE AND ALKOXIDE PROMOTED DECOMPOSITION OF 3-BROMOPROPYLTRIPHENYLPHOSPHONIUM BROMIDE

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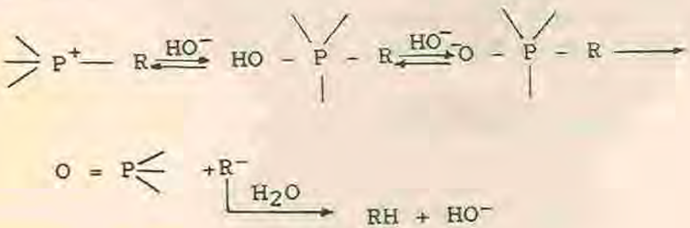
(Received December 12, 1988; revised March 3, 1989)

ABSTRACT. The work reports a kinetic study of the hydroxide and alkoxide promoted decomposition of 3-bromopropyltriphenylphosphonium bromide in purely aqueous medium, methanol and ethanol; and in a series of dioxane-methanol mixtures. The α scale of solvent HBD (hydrogen bond donor) acidities is used to rationalize solvent effects on rates of the reaction in pure water and alcohol solvents. The reaction rate in the mixed solvent increases as the medium is enriched in dioxane, where the nucleophile is either hydroxide or methoxide anions. The rate of the alkoxide promoted decomposition is smaller than that of the hydroxide promoted one due to a difference in the operating reaction mechanism. The effects of solvent or intermediate changes are best reflected on the activation energy and the thermodynamic parameters.

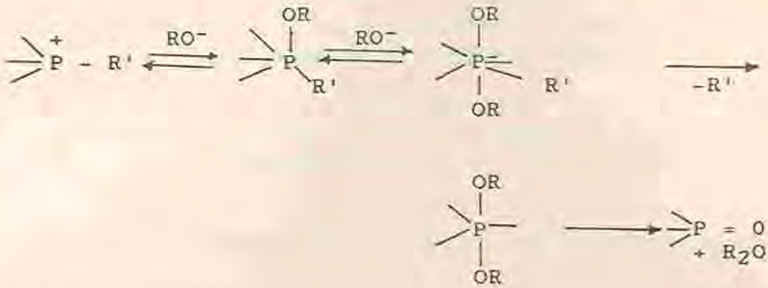
INTRODUCTION

Taft and his coworkers (1) have described the formulation and some applications of three new scales of intrinsic solvent properties: an α scale of solvent HBD (hydrogen bond donor) acidities (2,3), a β scale of HBA (hydrogen bond acceptor) basicities (4,5), and a π* scale of solvent polarity-polarizabilities (1-6). These indices were intended to serve, singly or in linear combinations with one another, in the rationalization or correlation of solvent effects on reaction rates and activation parameters. The objective of the present investigation was to examine the effect of these solvent parameters on the rates of the alkaline decomposition of phosphonium salts, being an example of one of the best known nucleophilic displacement reactions at phosphorous, which is the subject of our interest in recent years (7,8). The hydroxyl decompostion of phosphonium compounds proceeds through a pentacovalent phosphorus intermediate (9) (scheme 1), except when alkoxide ion is the attacking nucleophile, where the formation of a hexacovalent intermediate takes place (10) (scheme 2).

Scheme 1



Scheme 2



This difference in the path of the reaction made it of interest to undertake a systematic investigation of the alkaline decompostion of a member of this group of compounds, namely, 3-bromopropyltriphenylphosphonium bromide, in the pure solvents water, methanol, and ethanol to test the above new scales. The study is extended also in a series of the binary solvent sysytem methanol-dioxane with different ratios, in which the nucleophile is either, HO^- of MeO^- anions, to determine what factors control the rate of the reaction apart from the change in the skeleton of the probable intermediate. These solvent systems allow a continuous change from the polar, hydrogen-bond character of methanol to the solvent chartacteristics of the non-polar dioxane. The base-nucleophiles may be expected to become highly reactive in non-polar dioxane owing to the lack of hydrogen bond stabilization (11). Methoxide ion, however, being a strong hydrogen bond acceptor, compared to HO^- ions, becomes considerably less solvated and, therefore, a stronger mucleophile in non-polar dioxane than in protic methanol. The present system appears to be a useful one for examining such kinetic solvation effects on rates and mechanism.

EXPERIMENTAL

Pure 3-bromopropyltriphenylphosphonium bromide (Fluka) was used. Methanol (Merck) was purified and dried by the method of Lund and Bjerrum (12). The ethanol was dried by refluxing over freshly obtained quicklime, and then fractionated in a 40 plate column. A middle fraction was collected over less than 0.05°C. Dioxane was carefully purified using standard methods (13,14). The water used in kinetic experiments was freshly distilled from alkaline potassium permanganate. Sodium methylate solutions were prepared from sodium metal (BDH) and methanol, the concentrations were determined by titration with hydrochloric acid and adjusted to the desired value by dilution with pure methanol. A kinetic procedure involving analysis of the unreacted hydroxide or alkoxide ions during the course of the reaction was followed as described before (7). In all measurements at temperatures higher than 30°C allowance was made for the volume change of the solvent with temperature.

RESULTS AND CALCULATIONS

The rates of the reaction were determined in the pure solvents water, methanol and ethanol and in the binary solvent mixtures methanol-dioxane using HO^-

as the attacking anion. To ensure the HO^- reaction 1% of water was added to the CH_3O^- containing reaction solution (10). The temperature at which the reaction was studied depended on the rates in different media and varied from 20° to 45°C. Rate measurements were also made in methanol-dioxane mixtures in which the nucleophile was the methoxide anion. In all cases the reaction was found to obey third-order kinetics, i.e. first-order in phosphonium ions, and second order in HO^- or MeO^- anions. A statistical least squares treatment (15) of the Arrhenius equation was used to calculate the activation energies based on the rate constants. The correlation coefficients (r) of the linear plots of the Arrhenius equation are almost equal to unity. The results are set forth in Tables 1 and 2.

Table 1. Observed rate constants and activation energies of the HO^- promoted reaction in pure solvents with different solvatochromic parameters.

Solvents	Types of solvents	π^*	β	α	σ^* of R	k' 1^2 mol^{-2} min^{-1}						E KJ mol^{-1}	$\Delta S^{\#}$, J mol^{-1} deg^{-1} at 30°C
						20	25	30	35	40	45		
Water	HBA-D*	1.09	0.18	1.17	+0.49	-	-	0.17	0.33	0.63	1.20	104.28	42.01
Methanol $R = CH_3$	HBA-D	0.60	0.62	0.93	0.00	-	-	14.5	25	50	98	103.49	76.37
Ethanol $R = C_2H_5$	HBA-D	0.54	0.77	0.83	-0.10	525	950	2100	-	-	-	102.23	113.58

* HBA = hydrogen bond acceptor , HBD = hydrogen bond donor.

Table 2. Rate constants and activation energies for the HO^- and MeO^- promoted Reaction in MeOH-Dioxane mixtures.

a) HO^- reaction

Dioxane content			k' . 1^2 mol^{-2} min^{-1}				E,
Vol %	Wt %	mol %	30°	35°	40°	45°	K J mol^{-1}
10	12.60	4.98	28	37	155	220	106.9
20	24.40	15.51	95	190	358	563	95.8
30	35.61	16.74	375	871	1150	2089	87.1
40	46.19	23.79	1380	2399	3890	6310	80.1

b) MeO^- reaction

Dioxane content			k' . 1^2 mol^{-2} min^{-1}				E,
Vol %	Wt %	mol %	30°	35°	40°	45°	K J mol^{-1}
10	12.60	4.98	21	55	104	-	134.7
20	24.40	10.51	63	162	313	-	120.0
30	35.61	16.74	200	390	900	1550	111.9
40	46.19	23.79	692	1300	2500	3850	93.1

DISCUSSION

Examination of Table 1 shows that the rate constant increases considerably with decrease of HBD acidity (α), i.e., with decreasing electron-donating ability of R in R-OH, the effect being closely parallel to the decrease in σ^* values (16,17) of the alkyl group. Comparing the rates in water and ethanol shows that rate in the latter solvent is about 1.2×10^4 times higher at 30°C than in the former. This is caused by the large difference in the hydrogen-bonding ability in the two solvents. It is well known that water has an extensive tendency to solvate ions strongly and to form hydrogen bonds with hydroxide anions (11, 18). This appears in the high α value of water than methanol or ethanol, which, in turn, is due to the polar nature of this solvent and to the fact that the dimensions of the water molecule favour a tetrahedrally coordinated structure (18). Consequently, solvation of the reactants, through hydrogen bonding, will decrease from water ($\alpha = 1.17$) to ethanol ($\alpha = 0.83$) and hence the increase in the reaction rate. In other words, the retarding effect of the solvation sheath around the anion will drop causing a large enhancement in the reaction rate. More evidence can be gathered from calculation of the entropy of activation. The large increase of $\Delta S^{\#}$ from water (42.01, J $mol^{-1} deg^{-1}$) to ethanol (113.58, J $mol^{-1} deg^{-1}$), indicates an increase in the extent of expulsion of solvent molecules in the transition state as the medium changes from water to enthanol. The more positive values of $\Delta S^{\#}$ in ethanol presumably show a considerable decrease in order as ethanol molecules bounded to HO^- ions are partially released in attaining the transition-state structure.

Fig. 1 shows a plot of log k' against the mol % of dioxane in dioxane-methanol mixtures in the presence of hydroxide and methoxide anions. The rate increases as the medium is enriched in the dioxane cosolvent. Thus, at 30°C in 40% dioxane-methanol, the rate is 49 times faster than in 10% dioxane-methanol in the hydroxide reaction. In methoxide solution in 40% dioxane-methanol, it is 25 times faster than in 10% dioxane-methanol. The rate increase in the two cases is caused mainly by a decrease in E. The latter effect is also accompained by a corresponding decrease in $\Delta S^{\#}$ (Table 3) which confirms the involvement of many methanol molecules in the solvation shells of HO^- or MeO^- reactants. The phosphonium cation solvation is not of any contribution in causing rate enhancement (19,20). The main contribution to the decrease in E is believed to be due to the first step of the reaction, involving the formation of a neutral pentacovalent or hexacovalent intermediates from the HO^- or MeO^- reactions, respectively (10). The increase in solvation of the phosphorane intermediate in the two cases as well as the decrease in solvation of hydroxide or methoxide anions with increasing dioxane content of the medium will both help in the decrease of the activation energy. The fact that the rate of the hydroxide-promoted reaction is always higher than that in the methoxide-promoted one in the same solvent mixture must be due to the change of mechanism from the pentacovalent intermediate in the former reaction to the hexacovalent one in the latter. This rate change is, however, solvent-dependent, being lowest when the solvent becomes very poor in dioxane as a result of different solvation effects.

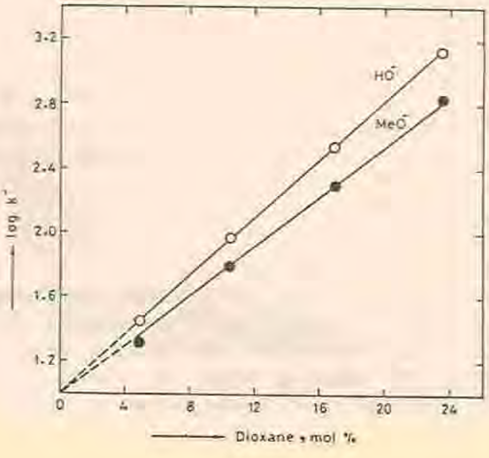


Fig. 1. Comparative polts of log k' against mol % at 30°C for the HO^- and MeO^- reactions.

The thermodynamic parameters of activation, namely, the free energies $\Delta G^{\#}$, the enthalpies $\Delta H^{\#}$, and the entropies $\Delta S^{\#}$ for the two reactions are listed in Table 3 where all parameters show considerable dependence on solvent composition.

Table 3. Thermodynamic activation parameters at 30°C for the reaction in MeOH-Dioxane mixtures.

Dioxane, Vol %	$\Delta G^{\#}$, kJ mol^{-1}		$\Delta H^{\#}$, kJ mol^{-1}		ΔS , J mol^{-1}deg^{-1}	
	HO^-	MeO^-	HO^-	MeO^-	HO^-	MeO^-
10	76.21	76.94	104.39	132.15	93.19	182.13
20	73.09	74.17	93.26	117.51	66.55	142.97
30	69.64	71.25	84.60	109.34	49.39	125.63
40	66.35	68.13	78.30	90.53	39.43	73.89

The increase in reaction rate is associated with a decrease in activation enthalpy by about 26 kJ mol^{-1} in the HO^- reaction and 41 kJ mol^{-1} in the MeO^- reaction, respectively. This is partially compensated (21-23) through the decrease of $\Delta S^{\#}$ by about 54 and 109 J mol^{-1} deg^{-1} respectively, over the whole range of medium composition studied, thus causing $\Delta G^{\#}$ to decrease only by 10 kJ mol^{-1}. The considerable changes in these functions imply that the contributions from relative changes in solvation shells of reactants and transition states during the course of the reaction are very important factors in the rate enhancement. The $\Delta H^{\#}$ is, however, higher in the OMe^- than the HO^- reactions (Table 3), and the difference in their values (about 13 kJ mol^{-1}) follows the same trend as activation energies. This indicates that in the region of high dioxane contents, in which anion desolvation is significant, the desolvation in the hydroxide reaction is larger than in the methoxide one.

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