ACTA CHEMICA SCANDINAVICA 27 (1973) 3832–3838

Kinetics, Medium, and Deuterium Isotope Effects in the Alkaline Decomposition of Quaternary Phosphonium Salts I. Tetraphenylphosphonium Chloride in Dioxane-Water Mixtures

FAYEZ Y. KHALIL* and GUNNAR AKSNES

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

The alkaline decomposition of tetraphenylphosphonium chloride in 0 – 80 % dioxane-water mixtures was studied kinetically at 20 – 55°C. The reaction rate, which is first-order in phosphonium cation and second-order in hydroxide anion, is strongly accelerated by addition of dioxane, being 5×10^7 times as large in 80 % dioxane-water as in water at 35°C. The rate constant is expressed by $k' = 19.6\ e^{-33500}RT$ l^2 mol^{-2} sec^{-1} in water, and $k' = 10.7\ e^{-10630}RT$ l^2 mol^{-2} sec^{-1} in 80 % dioxane-water. The solvent deuterium isotope effect in 30 % D_2O-dioxane confirmed the current mechanistic views of the reaction. The termodynamic data are discussed as functions of solvent composition and solvation properties of the reaction medium.

The alkaline decomposition of quaternary phosphonium salts is known to yield phosphine oxide and hydrocarbon. It has long been assumed that the decomposition proceeds through a pentacovalent phosphorus intermediate whose formation is rate determining.[1–3] Although such reactions have been investigated from different points of view, systematic studies of solvent effects are lacking. The alkaline phosphonium decomposition is an example of an ion-ion interaction and is therefore expected to exhibit considerable medium effects. In the present rate study various dioxane-water mixtures are chosen as solvents, in which the dielectric constant can be varied over a wide range. The reaction is also studied in 70 % dioxane-D_2O mixture in order to provide additional mechanistic information.

* On leave of absence from Alexandria University. Permanent address: Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

EXPERIMENTAL

Materials. Tetraphenylphosphonium chloride (Fluka, Analytical Grade) was of sufficient purity to allow of its use without further purification. Fresh, UV spectroscopic grade, dioxane (Fluka) was used. The heavy water employed (Norsk Hydro) contained 99.8 % D_2O.

Kinetic Procedure. The reaction was followed by determining the decrease in concentration of the hydroxide or deuteroxide ion. The solvent composition covered the range 0 to 80 % (v/v) of dioxane. Experiments with NaOD were made in 70 % dioxane – 30 % D_2O. In a typical run an accurately measured volume of 0.02 M solution of NaOD or NaOH in the appropriate solvent mixture was placed in a thermostat adjusted to within ± 0.05°C of the required temperature. After thermal equilibrium, the solution was poured into an accurately weighed amount of the phosphonium salt to give a 0.02 M solution after mixing. The mixture was shaken vigorously and replaced in the thermostat. At various intervals, aliquots were withdrawn, poured into an excess of standard HCl solution and back titrated with standard NaOH. The reaction was investigated in the temperature range 20 – 55°C. The results were found to be reproducible within 2 %.

RESULTS

The third-order rate constants of the reaction were obtained from the slopes of the linear plots represented in Fig. 1. It was found, however, that in solvents containing less than 40 % dioxane, precipitation of phosphine oxide took place causing marked enhancement in rate due to surface adsorption of the phosphonium salt.[4,5] In such cases the reaction was followed only up to 30 % conversion. The rate constants and activation energies are tabulated in Table 1. The dielectric constants were interpolated from the findings of Åkerlöf and Short.[6] The data for the kinetic deuterium isotope effect are also reported in Table 1 (9th entry). Attempts to measure the rate in pure D_2O suffered from rapid precipitation of phosphine oxide due to its lower solubility in D_2O compared to H_2O, causing a very high catalytic effect after a short time of reaction. Tetraphenylphosphonium chloride undergoes no deuterium exchange when treated with deuteroxide anion in D_2O. The incorporation of deuterium necessitates the presence of α-hydrogen in the phosphonium salt.[7,8]

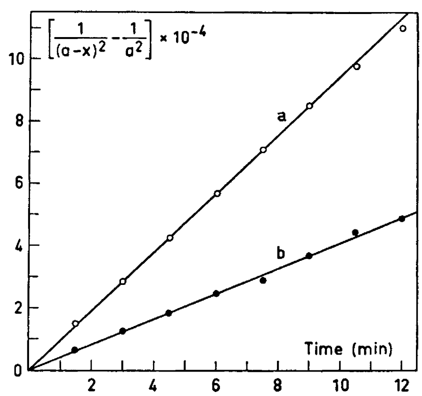


Fig. 1. Typical third-order plots for the alkaline decomposition of tetraphenylphosphonium chloride in dioxane-H_2O and dioxane-D_2O mixtures at 25°C. (a) 70 % dioxane-D_2O; (b) 70 % dioxane-H_2O.

Table 1. Third-order rate constants k' and activation energies E for the alkaline decomposition of tetraphenylphosphonium chroride in dioxane-water and dioxane-D_2O mixtures.[a,b]

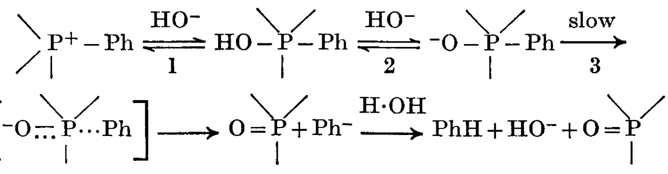
Dioxane, vol %	k', l^2 mol^{-2} min^{-1} 20°	25°	30°	35°	40°	45°	50°	55°	E, kcal/mol
0		0.00053[c]		0.0033	0.0079	0.018	0.043	0.096	33.50
10		0.00234[c]		0.013	0.030	0.066	0.149	0.303	32.24
20		0.00708[c]		0.037	0.081	0.175	0.379	0.741	30.71
30		0.02818[c]		0.141	0.309	0.660	1.318	2.639	29.61
40		0.2042[c]		0.933	1.950	3.981	7.943	15.49	28.34
50		3.516[c]		10.96	19.05	32.55	52.08	91.20	21.26
60	33.88	57.54	107.2	173.8	288.4	478.6[c]			17.54
70	1 324	2 046	3 333	4 786	7 188	10 230[c]			15.35
70–30 D_2O	3 125	4 737	6 313	8 636	11 100	15 850[c]			11.52
80	66 070	89 130	120 200	158 500	208 000	272 300[c]			10.63
k'_{DO^-}/k'_{HO^-}	2.36	2.32	1.90	1.81	1.55				
Ratio: k' 80 % dioxane/k' water				4.8×10^7	2.6×10^7				

[a] Equivalent concentrations of phosphonium and hydroxide or deuteroxide ions (0.02 M) were used throughout. [b] Total ionic strength amounts to 0.04. No corrections for zero ionic strength or thermal expansions were made. [c] Extrapolated.

DISCUSSION

Isotope effect and mechanism

The value of the kinetic isotope ratio k'_{DO^-}/k'_{HO^-}, given in Table 1, is the inverse of that expected for a primary isotope effect where an O–H or O–D bond is broken in the rate-determining step. This finding agrees with McEwen's elaboration [9] of Ingold's scheme.[2] The accepted mechanism may thus be illustrated as in Scheme 1.



Scheme 1.

Hence, the higher rate in dioxane–D_2O than in dioxane–H_2O mixture is to be ascribed to a secondary isotope effect. The greater base strength of DO^- compared to HO^- anions [10] may be the main explanation for this effect. Calculations by Bunton and Shiner [11] on the relative nucleophilicities of HO^- and DO^-, taking into account the differences in vibration forces of H-bonded or D-bonded ions, gave a 1.9 times rate increase in D_2O if covalent bond is formed with the oxyanion. Swain and Bader,[12] using a somewhat different approach, reported 3.2 times stronger basicity of DO^- than HO^-. Dahlgram and Long [13] came to a similar result based on kinetic data for proton removal. This leads one to conclude that the present secondary isotope effect is due to stronger solvation of HO^- in H_2O than DO^- in D_2O. The value obtained for k'_{DO^-}/k'_{HO^-} is of the magnitude expected for such an effect. Since two HO^- (or DO^-) ions are involved prior to the rate-determining step, the observed rates comprise the product of the rate constants of these two steps. In the second step, where a base of comparable basicity to HO^- is formed, the difference in the amount of solvation between reactants and products ought to be small, resulting in a minor solvent isotope effect. In the first step, however, where a covalent neutral intermediate is formed from two ions, the secondary isotope effect due to solvation differences will be strong. In the rate-determining step, where breaking of the P – C bond takes place, it is the difference in solvation of the transition state and the reacting anion which will contribute to the secondary isotope effect. Studies of the isotope content of the hydrocarbon in 50 % H_2O-D_2O mixture showed very little discrimination between hydrogen and deuterium uptake.[7] In line with the general view, Corfield and Trippett [7] concluded, therefore, that the P – C bond in the transition state suffers only very slight breaking. Applying this conclusion to the secondary isotope effect of the same step, the reactant-like transition state suggests also minor solvation effects and a correspondingly small secondary isotope effect in this step.

The temperature effect on the kinetic ratio k'_{DO^-}/k'_{HO^-} is rather high compared to those hitherto reported in secondary isotope rate studies. Thus, in the alkaline hydrolysis of alkyl halogenides [14] the ratio changes only by 5 % from 35 to 80°C. In the present reaction, however, the change is about 40 % in the range 20 to 40°C. As seen from Tables 1 and 2, the differences in E and ΔS^* in dioxane – D_2O and dioxane – H_2O are: $\Delta E = -3.8$ kcal/mol and $\Delta\Delta S^* = -11.2$ e.u. Such pronounced differences can only be understood if a considerable number of D_2O or H_2O solvent molecules, respectively, are involved, since the reactants, being charged species, have to get rid of their solvation shells prior to reaction.

Rate, activation energy, and solvent composition

The drastic influence of solvent composition is depicted in Table 1, where the rate at 35°C in 80 % dioxane-H_2O is 4.8×10^7 times faster than in water. The rate increase is caused mainly by a tremendous decrease in E (33.5 kcal/mol in H_2O and 10.6 kcal/mol in 80 % dioxane – H_2O). To a considerable extent, the decrease in E is, however, counteracted by a corresponding decrease in ΔS^* (Table 2), and confirms the involvement of many water molecules in the solvation shells of reactants. The main contribution to the decrease in E is, as already mentioned, believed to be due to the first step of reaction, involving the formation of a neutral pentacovalent phosphorane from the two ionic species Ph_4P^+ and HO^-. The increase in solvation of the phosphorane as well as the decrease in solvation of Ph_4P^+ and HO^- with increasing dioxane content of the medium will both decrease the activation energy.

Table 2. Thermodynamic parameters of activation and frequency factors at 25°C.

Dioxane, vol %	ΔF^*, kcal/mol	ΔH^*, kcal/mol	ΔS^*, cal/mol deg	log (A, l^2 mol^{-2} sec^{-1})
0	24.3[a]	32.9[a]	+29.1[a]	19.6[a]
10	23.4[a]	31.7[a]	+27.8[a]	19.3[a]
20	22.7[a]	30.1[a]	+25.1[a]	18.7[a]
30	21.9[a]	29.0[a]	+23.9[a]	18.5[a]
40	20.7[a]	27.8[a]	+23.6[a]	18.4[a]
50	19.1[a]	20.7[a]	+5.4[a]	14.4[a]
60	17.4	17.0	−1.5	12.9
70	15.3	14.8	−1.8	12.9
70−30 D_2O	14.8	10.9	−13.0	10.4
80	13.1	10.0	−10.2	10.7

[a] Based on extrapolated rate constants.

Effect of the dielectric constant

As a first approximation, the solvent effect can be expressed on the basis of Born's solvent model using the macroscopic dielectric constant,[15] D, as follows:

$$\ln k' = \ln k_0' - NZ_AZ_Be^2/DRTr^*$$

where $\ln k_0'$ is the rate at infinite dielectric constant, N is the Avogadro number, Z_A and Z_B the charges of reacting ions, e the electronic charge, R the gas constant, and r^* the average distance between the centers of reacting ions in the activated complex (closest distance of approach). The plot of $\ln k'$ against $1/D$ should be linear with a slope of $N\ e^2/RTr^*$ for a uni-univalent ionic reaction. In Fig. 2, deviations from linearity at low dielectric constants may be attributed to selective solvation or solvent sorting.[15] The average r^* value obtained from the linear portions of the plots in Fig. 2 is 1.3 Å which is much smaller than the value expected from the sum of radii of the unsolvated reacting ions Ph_4P^+ and OH^- (about 5−6 Å).[16] This reveals the inadequacy of the idealized Born model using the macroscopic dielectric constant in explaining the microscopic events of the present reaction.

Since E is proportional to $RT \ln k'$, it follows from the Born approximation that E ought to change linearly with $1/D$. Fig. 3 shows, however, a nonlinear behaviour and a rapid change through an inflection point around 40−50 % dioxane. This clearly illustrates the important role played by specific solvent effects which may suggest two underlying main types of mixtures: (a) "water-like", *i.e.*, water successively diluted with dioxane and (b) "dioxane-like", *i.e.*, dioxane successively diluted with water. Presumably water can be diluted with certain amounts of dioxane before its characteristic structure breaks down and, *vice versa,* that dioxane can be diluted with water, still keeping its "dioxane structure" up to a certain limit. Consequently, there will exist a transition region where the solvent mixture is neither water nor

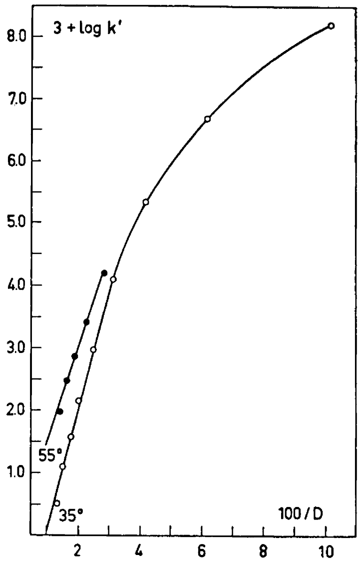


Fig. 2. Variation of log k' of reaction with $1/D$ of solvent mixture.

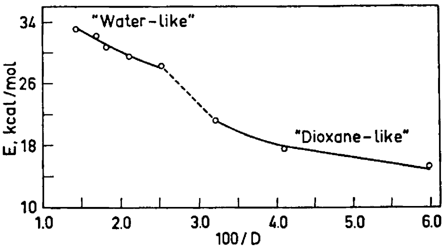


Fig. 3. Dependence of the activation energy of the reaction on $1/D$.

dioxane-like. It is a plausible assumption, therefore, that the characteristic features of Fig. 3 are caused by such structural changes of the solvent mixture, which appear as changes of E.

Thermodynamic parameters of activation

The activation parameters ΔF^*, ΔH^*, and ΔS^* and frequency factor log A (Table 2) show strong dependence on solvent composition. Thus, ΔF^* decreases at 25°C from 24.3 to 13.1 kcal/mol with increase of dioxane content from 0 to 80 %. The contributions to ΔS^* from relative changes in solvation sheaths of the reactants and transition states as the reaction proceeds are quite considerable. Progressive addition of water to dioxane will increase hydrogen bonding with reactants, which will add to ΔH^* the enthalpy associated with breaking such bonds, and hence ΔH^* increases. This increase is sharp first, until a sufficient amount of H_2O has been added to cause considerable solvation of all reactants, then further addition will have little effect on hydrogen bonding and hence on ΔH^*. The rate increase is due entirely to the decreased enthalpy since entropy changes oppose rate increase. The large changes in log A are also brought about mainly by changes in solvation of reactants and activated complexes. Nevertheless, the changes in E are much more pronounced since, according to the Arrhenius' equation, they outweigh the changes in A, causing rate changes. The relation between log A and E takes the form

$$\log A \ (\mathrm{l^2\ mol^{-2}\ sec^{-1}}) = 5.1 + 0.44\ E\ (\mathrm{kcal\ mol^{-1}})$$

The present thermodynamic parameters are, however, complicated by being resultants of components involving two fast preequilibria and a slow rate-determining step.

Acknowledgement. A post-doctoral fellowship from the *Royal Norwegian Council for Scientific and Industrial Research* (NTNF) granted to F.Y.K., during the tenure of which this work was accomplished, is gratefully acknowledged.

REFERENCES

1. Hey, L. and Ingold, C. K. *J. Chem. Soc.* **1933** 531.
2. Fenton, G. W. and Ingold, C. K. *J. Chem. Soc.* **1929** 2342.
3. Berlin, K. D. and Butler, J. B. *Chem. Rev.* **60** (1960) 243.
4. Aksnes, G. and Songstad, J. *Acta Chem. Scand.* **16** (1962) 1426.
5. Hoffman, H. *Ann.* **634** (1960) 1.
6. Åkerlöf, G. and Short, O. A. *J. Am. Chem. Soc.* **58** (1936) 1241.
7. Corfield, J. R. and Trippett, S. *Chem. Commun.* **1970** 1267.
8. Cremer, E. S. and Chorvat, R. J. *Tetrahedron Letters* **1966** 419.
9. McEwen, W. E., Kumli, K. F., Blade-Font, A., Zanger, M. and Vander Werf, C. A. *J. Am. Chem. Soc.* **86** (1964) 2378.
10. Wiberg, K. *Chem. Rev.* **55** (1955) 713.
11. Bunton, C. A. and Shiner, V. J., Jr. *J. Am. Chem. Soc.* **83** (1961) 42, 3207.
12. Swain, C. G. and Bader, R. F. W. *Tetrahedron* **10** (1960) 182.
13. Dahlgram, G. and Long, F. A. *J. Am. Chem. Soc.* **82** (1960) 1303.
14. Heppolette, R. L. and Robertson, R. E. *J. Am. Chem. Soc.* **83** (1961) 1834.
15. Amis, E. S. *Solvent Effects on Reaction Rates and Mechanism*, Academic, New York and London 1966.
16. Grunwald, E., Baughman, G. and Kohnstam, G. *J. Am. Chem. Soc.* **82** (1960) 5801.

Received May 28, 1973.