As described by Johns,[3] PuH_2 will take considerable hydrogen into solid solution to form a solid of composition approaching PuH_3. We have also observed this behavior and, in addition, it appears that as the composition of the solid solution of hydrogen in PuH_2 approaches PuH_3, the cubic PuH_2 lattice transforms to a hexagonal structure. This will be treated in detail in a subsequent report.

Debye powder patterns of many samples of PuH_2 have been examined by F. H. Ellinger of this Laboratory, and the authors are indebted to him for permission to include the following unpublished information for reference purposes: The structure of PuH_2 is face-centered cubic (fluorite type) with cell dimension 5.359 ± 0.002 Å. The calculated X-ray density is 10.40 g./cc.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

The Acid Hydrolysis of Ethyl Dichloroacetate in Acetone–Water Solvent[1]

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The acid hydrolyses of ethyl dichloroacetate were investigated in acetone–water media at 25, 35 and 45°. The neutral hydrolyses of the ester in the same solvent media were studied at 35 and 45°.

Introduction

An investigation of the rates of hydrolysis of substituted halogen esters in mixed solvents might be expected to throw light on the influence of substitution on the various factors involved in the solvent effect upon reactions in solution. The results of a study of the acid-catalyzed and neutral hydrolysis of ethyl dichloroacetate are reported in this communication.

Experimental

Acetone was purified as described previously.[2] Ethyl dichloroacetate was shaken up with 3% sodium bicarbonate solution to remove free acid, washed with distilled water, dried over anhydrous $CaSO_4$ for three days and distilled under reduced pressure. The fraction boiling between 131.0 and 131.5° under 401 mm. pressure was collected for use.

All water was double distilled, a little potassium permanganate being added before the second distillation.

Procedure.—Stock solutions of $Ba(OH)_2$ and HCl of strengths 0.0250 and 0.6000 N, respectively, were prepared from analytical reagent grade materials and these were standardized using potassium acid phthalate, phenolphthalein serving as indicator. The strengths of the stock solutions were checked periodically.

All glassware was standardized. The thermostats employed controlled temperature within ±0.02° at 25° and 35° and within ±0.03° at 65°.

The procedure for preparing solutions for kinetic runs was the same as reported in previous studies on ester hydrolysis.[2,3] The required volume of acetone, kept at the temperature of the experiment, was pipetted into a 100-ml. volumetric flask, the required amount of the standard acid to make a 0.0500 N solution was added and the contents made up approximately to the neck of the flask with water. The solution was then left in the bath for 1.5 to 2 hours to attain temperature equilibrium. Each run was started by adding the required volume of the ester from a micropipet to make a 0.0500 N solution and making up with water at the temperature of the bath. The flask was withdrawn, well shaken and quickly returned to the bath. The time of shaking was taken as starting time since in most cases the ester does not go into solution until it is shaken; 10-ml. samples were withdrawn at convenient intervals and run into crushed ice prepared from the purified water and titrated against standard calcium hydroxide (approximately 0.025 N, actual standardization being to four significant figures) using brom phenol blue as indicator.

The procedure for neutral hydrolysis was the same except no acid was added to the run.

The unimolecular rate constants k' for the acid catalyzed and k_n for neutral runs were obtained from plots of log $(a - x)$ against t, where $(a - x)$ is the concentration of unreacted ester at time t. The true rate constant k_a for the acid-catalyzed reaction was calculated from the expression

$$k' = k_a(\mathrm{H}) + k_n$$

Activation energies in the case of acid hydrolyses were calculated from plots of log k' vs. $1/T$. Since neutral hydrolysis was done at two temperatures only, the values were calculated straight from the velocity constants.

The low solubility of $Cl_2CHCOOEt$ in water-rich solvent mixtures limited the range of investigation. An ester concentration of 0.05 M was desirable for reasonable accuracy in the measurements by the procedure employed and it is impossible to prepare a solution of that strength even in 40% acetone. The solvent compositions employed in the study were 50, 60, 70 and 80% by volumes of acetone.

The specific reaction rate constants were in general reproducible to within ±3–5%. The greatest variation (5%) was found in the solutions containing the larger percentages of acetone.

Discussion

The velocity constants for both acid and neutral hydrolysis in the various media are given in Tables I and II and indicate that the changes of the rate constants with solvent composition are roughly the same as obtained by Nair and Anantakrishnan[3] and Hockersmith and Amis[2] for acid hydrolysis of ethyl acetate and methyl propionate, respectively, in acetone–water systems. The activation energies and frequency factors for acid-catalyzed and neutral hydrolysis are shown in Tables III and IV. There was no noticeable drift of the constants for the neutral hydrolyses since the acid formed was weak and at low concentrations.

The changes in activation energy and PZ factor are in the expected direction for halogen substitution at the α-position. The decrease in activation energy is more than compensated by the decrease in the PZ factor and hence the hydrolysis is very slow compared to that of ethyl acetate.

The specific velocity constant for the neutral hy-

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[1] This work was done on a contract made by the Institute of Science and Technology of the University of Arkansas with the Office of Naval Research.

[2] J. L. Hockersmith and E. S. Amis, *Anal. Chim. Acta*, **9**, 101 (1953).

[3] P. M. Nair and S. V. Anantakrishnan, *Proc. Ind. Acad. Sci.*, **32**, 85 (1950).

TABLE I

ACID HYDROLYSIS, k' IN LITERS MOLE^{-1} HOUR^{-1}

Temp. →	25°		35°		45°	
Vol. % of acetone	Dielectric constant	$k' \times 10^2$	Dielectric constant	$k' \times 10^2$	Dielectric constant	$k' \times 10^2$
50	52.09	8.27	49.79	16.10	47.87	33.83
60	45.59	6.28	43.49	12.05	41.80	26.15
70	39.60	3.95	37.78	8.02	35.55	16.91
80	32.10	2.62	30.56	6.35	29.25	13.58

TABLE II

NEUTRAL HYDROLYSIS, k_n IN LITERS MOLE^{-1} HOUR^{-1}

Temp. →	35°		45°	
Vol. % acetone	Dielectric constant	$k_n \times 10^4$	Dielectric constant	$k_n \times 10^4$
50	49.79	17.56	47.87	37.04
60	43.49	7.01	41.80	15.61
70	37.78	2.27	35.55	5.47
80	30.56	0.885?	29.25	1.60

TABLE III

ACID HYDROLYSIS

Acetone, %	$\log_{10}$ PZ	E, cal.
50	8.59	13,200
60	8.68	13,500
70	8.71	13,800
80	9.68	15,300

TABLE IV

Acetone, %	$\log_{10}$ PZ	E, cal.
50	7.53	14,500
60	7.91	15,600
70	8.49	17,100
80	4.10 ?	11,500 ?

drolysis in 80% acetone solvent at the lower temperature (35°) seems to be in error. This is because of the extremely small value of the constant at this high acetone concentration and at this lower temperature. The activation energies and PZ values which result from calculations using this value of the rate constant are consequently in error and have therefore been neglected in this discussion. The questionable values of these quantities have, however, been inserted in Tables II and IV.

In order to compare the effect of variation of dielectric constant on reaction rate for the substituted ester with that for unsubstituted ester a plot of log k'/C_{H_2O} against $1/D$ was made (Fig. 1). The division by C_{H_2O}, the concentration of water in solution, takes care of the molecularity with respect to water. The plots indicate linear variations of log k'/C_{H_2O} with $1/D$ within the range 50–75% acetone. A sharp upward curvature somewhere around 25% acetone is indicated. The interesting feature about these curves is that they have a negative slope for the straight line portion while those for ethyl acetate show a positive slope. Decrease of dielectric constant here results in decrease of k'/C_{H_2O}.

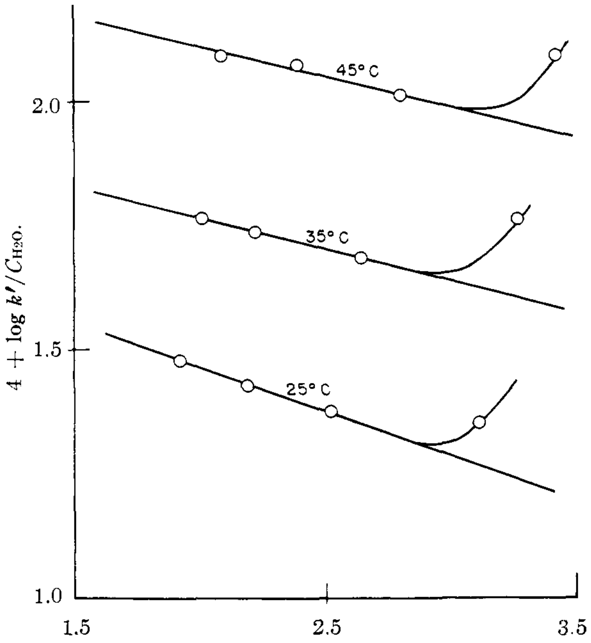

Fig. 1.

The linear correlation between log PZ and $1/E$ which Fairclough and Hinshelwood[4] had observed in a large number of cases and which had been accounted for on the basis of some statistical considerations is found to hold good for the data presented here (Fig. 2).

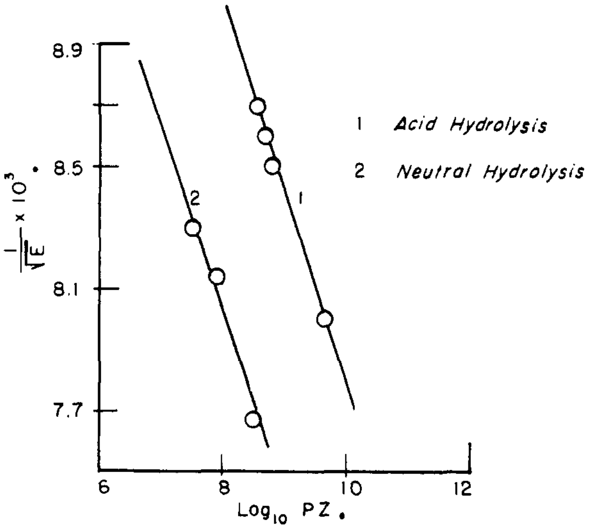

Fig. 2.

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[4] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 1573 (1937).