Kinetics of Solvolysis of 2-Chloroquinoxaline

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Abstract

Pseudo-first-order rate constants and activation parameters have been measured for the solvolysis of 2-chloroquinoxaline in various aquo-organic mixtures using methanol, ethanol, and isopropanol as the organic solvent. Excellent linear correlations are found between lnk and the mol fraction of cosolvent and $\ln[H_2O]$. The medium effect on the rates of solvolysis is assessed by Grunwald–Winstein's *mY* correlationship. The estimated values of *m* (0.55–0.72) and the entropy of activation (148–212 J deg⁻¹ mol⁻¹) for the reactions are well in the range for a bimolecular aromatic substitution reactions. © 1994 John Wiley & Sons, Inc.

Introduction

Solvolyses of the alkyl halides [1-4], aryl halides [5], arylacyl halides [6,7], aryl alkyl halides [7,8], and aryl ethers [9] have been studied extensively using various organic solvent-water mixtures. Even though few articles are reported on the solvolysis of the halogeno-hetero-aromatic [10,11] compounds, no detailed and systematic efforts have been made to study the mechanistic aspects. With a view to studying the solvent effect on the solvolysis of 2-chloroquinoxaline in various aquo-organic mixtures, the present work was undertaken.

Experimental

Materials

2-Chloroquinoxaline (2CQ) was prepared following the method reported by Castle and Onda [12]. The organic cosolvents methanol, ethanol, and isopropanol were purified by the standard methods of purification [13]. Triple distilled water was used for preparing various solvent mixture of varying compositions.

Kinetic Measurements

All the binary solvent mixture were prepared from preequilibrated solution of substrate in organic solvent and required amount of water at a temperature of interest by calibrated pipetts and mixed uniformly in the conductance cell. Rates were followed by measuring conductance at regular intervals under thermostated $(\pm 0.1^{\circ}C)$ conditions. The pseudo-first-order rate constants were calculated within $\pm 4\%$ error.

Product Analysis

The reaction mixture of 2-chloroquinoxaline (0.05M, 100 ml) in 80:20 (W/W) ethanol-water was kept at 40° until near completion of the reaction. After concen-

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Scheme 1.

trating the mixture under reduced pressure to a small volume (ca. 20 ml), the solid obtained was filtered and dried. The major product obtained in ca. 80% yield (0.58 g) was the hydrolysis product, 2-hydroxyquinoxaline (m.p. 258°C). The other product obtained in a minor yield ca. 15% (0.13 g) was 2-ethoxyquinoxaline (Colorless needles from *n*-pentane, m.p. 58°). Analytical data and some spectral features are similar to those reported elsewhere [14].

However, it is worth mentioning here that the present report incorporates different alcohols and water system in different composition as reaction media. Each system mentioned here would have different dielectric constant and polarity. This polarity is the driving force for solvolysis as well as hydrolysis reactions taking place simultaneously (Reaction schematic). Each of these reactions provide different products. The separate experiments in dioxane-water and acetone-water media yielded only the hydrolysis product. These products naturally would be in different proportions in the different systems being utilized.

Results and Discussion

Included in the Table I are the values of rate constants at the specified temperatures and activation parameters for the reactions in various solvent mixtures utilized. The rate constants obtained under pseudo-first-order conditions represent the averages of at least three determinations in reported errors. For each solvent system dielectric constants, D was taken from the data [15] or calculated from the values by interpolation between different solvent mixtures. The selection of the range of solvent compositions was made on the basis of the consideration that in a mixture containing higher proportion of organic solvent the rate was very slow, while in a mixture containing too low proportion of organic solvent the problem of solubility of the reactant and product arised. The solutions (0.02M) of 2CQ in the pure organic solvents did not show any change in conductance when left at 40° for a period of about 8 h indicating the absence of solvolysis reaction in pure solvents under the experimental conditions. The rates of reactions of 2CQ in all the reaction media were free from autocatalysis as revealed by good linear plots of conductance vs. time upto ca. 70% conversion.

The rate data reported in Table I shows that the rate increases with increase in the concentration of water in an aquo-oraganic mixture indicating water as reactive species. The increase in k with the dielectric constant is ascribed to greater polarity of activated complex relative to the reactants. Though this type of trend is in confirmity

Reaction Medium	$K imes 10^7~{ m s}^{-1}$.+~ .	
	40°	35°	30°	$\Delta H^{+} \pm 2$ kJ mol ⁻¹	$\Delta S^* \pm 4$ J mol ⁻¹ k^{-1}	$\Delta^*G \pm 2$ kJ mol ⁻¹	m^*
Methanol (Wt %)							
60	1.2	0.9	0.5	62.3	148.8	116.2	
70	0.7	0.6	0.4	61.9	160.5	114.9	
80	0.6	0.4	0.3	66.5	182.7	117.5	0.55
90	0.4	0.3	0.2	71.0	195.6	121.1	
Ethanol (Wt %)							
60	4.0	2.1	1.9	54.3	113.7	154.7	
70	2.8	1.6	1.3	56.4	172.2	115.4	0.67
80	1.7	1.0	0.7	63.1	192.7	114.8	
90	1.1	0.7	0.5	66.9	204.8	116.2	
I-Propanol (Wt %)							
60	36.2	22.8	19.8	45.1	165.1	103.5	
70	28.7	17.5	14.5	46.4	189.3	103.7	0.72
80	17.6	10.6	7.3	41.8	199.8	105.7	
90	10.5	7.5	5.4	53.5	212.3	106.2	

TABLE I. Rate constants and activation parameters for the solvolysis of 2-chloroquinoxaline in various binary (organic solvent-water) mixture.

m = Grunwald-Winsteins parameter.

with Amis theory [16], the plots of lnk against the dielectric functions like 1/D and D - 1/2D + 1 were not perfectly linear. Very good linear plots of lnk vs. the mol fraction of the cosolvent (n_{cs}) and concentration of water were obtained.

The effect of reaction medium is also checked by the well known Grunwald-Winstein relation [1]. The values obtained for m (Table I) are lower than that for the solvolysis of *t*-butyl chloride indicating preferential solvation of halide ion by the solvent molecules [1,3,8]. The extent of solvation of the activated complex will be higher than that of the neutral reactant molecules. Extent of solvation will also depend upon the size of the solvent molecules, it will be the highest in the methanol and the lowest in isopropanol. The dissociation of activated complex to the products (Reaction Schematic) from a highly solvated intermediate complex, as in the case of methanol will be difficult than from the less solvated intermediate complex with isopropanol. This accounts for the increase in k from methanol-water medium to isopropanol-water medium.

The activation parameters calculated using the rate data of three different temperatures with the help of standard equations indicate that values of enthalpy of activation (ΔH^{\dagger}) are almost unchanged while the solvent medium affects the values of entropy of activation (Δs^{\ddagger}) , i.e., the reaction is entropy controlled. The values of (Δs^{\ddagger}) are all negative and becoming more negative as the polarity of the medium decreased showing the loss of entropy during the formation of activated complex. Near constancy in the values of free energy of activation (ΔG^{\ddagger}) indicates that the same mechanism is operative in all cases. Similarity in the mechanism for the reaction in all the solvent systems is also supported by very good linear plots [17] between the values of lnk₄₀ and lnk₃₀ (Correlation coefficient, = 0.99).

Reaction Mechanism

The experimental observations indicated that in more aqueous solvents the major product of solvolysis was 2-hydroxy-quinoxaline and the rate increased with increase in concentration of water. Therefore the nucleophilic solvent assistance may be described as of SN^2 character. The reaction involves a nucleophilically solvated intermediate. The experimental values obtained for m and the activation parameters favor a bimolecular aromatic nucleophilic substitution SN^2Ar process [8].

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