

Selectivity of solvolysis of acetic anhydride in the water—alcohol system

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The rate of solvolysis of acetic anhydride in water—alcohol mixtures was measured. The concentrations of products of the solvolytic reaction in neutral as well as alkaline medium were determined chromatographically.

Измерена скорость сольволиза уксусного ангидрида в водно-спиртовых смесях. Проведено хроматографическое определение концентраций продуктов реакции сольволиза в нейтральной и щелочной средах.

The relationship between reactivity and selectivity is frequently used as a tool for studying the mechanisms of solvolytic reactions [1, 2]. It results from the definition of selectivity given by eqn (1) that the calculation of selectivity necessitates not only the knowledge of the concentration ratio of the reaction products AX and AY but also the knowledge of the concentration of the competing reactants X and Y.

$$S = \log (k_x/k_y) = \log ([AX][Y]/[AY][X]) \quad (1)$$

For the reaction in which both protogenic components of the binary solvent take part as nucleophiles we need the data easily available for neutral region that are, however, obtainable only in a few cases for alkaline region [3—5]. It results from this fact that the selectivity of the competing hydrolysis and alcoholysis in alkaline region of the water—alcohol mixture escapes attention though it concerns one of the fundamental reactions. This communication points out the possibilities of using the known activities of the lyate ions in this or other problems. There is little experience with the equilibrium of the lyate ions governed by eqn (A)



where R is alkyl. For this reason, it is advisable to use such substrate the solvolytic mechanism of which is known. Thus we have chosen acetic anhydride the solvolysis of which is bimolecular in the rate-determining step in neutral as well as alkaline medium [6, 7].

Experimental

Acetic anhydride, the methyl and ethyl ester of acetic acid, methanol and ethanol (anal. grade chemicals, Lachema, Brno) were distilled before use. The alcohols were dehydrated in the usual way [8]. NaOH used was also a commercial preparation (anal. grade chemical, Lachema, Brno).

The solution of acetic anhydride of 0.1 mol dm^{-3} concentration in the water—alcohol mixture warmed beforehand to 25°C , 35°C , and 45°C was prepared for kinetic measurements. The temperature was held constant accurate to $\pm 0.1^\circ\text{C}$. The rate of solvolysis was investigated conductometrically (Conductivity Meter OK-102/1) and the rate constant was calculated from the relationship $\ln(G_\infty - G_0)/(G_\infty - G_t) = kt$ where G_0 and G_t are conductivities at the start of the reaction and in time t , respectively, and G_∞ is conductivity in time exceeding ten half-lives of the reaction. The method enabled us to measure the rate constant in neutral region while the rate of solvolysis of acetic anhydride in alkaline medium was too high for this method. After completion of the reaction, the reaction mixture was analyzed with a gas chromatograph Chrom 4 (Laboratorní přístroje, Prague). In these measurements a column of 2.5 m length packed with Chromaton N-AW and polyethylene glycol (Carbowax) as liquid phase were used. The esters of acetic acid served for test substances. Because of the known difficulties due to the tail formation, we did not succeed in measuring reliably the concentration of acetic acid. Therefore we preferred to calculate it from the difference between the known concentration of anhydride and the found concentration of ester.

Results and discussion

The rate constants determined in neutral medium, activation parameters, and concentration ratios of the used ester to anhydride obtained in the reaction in neutral and alkaline medium at 25°C are given in Table 1. These data as well as the ratios of molar concentrations of water to alcohol or hydroxide to alkoxide ions [3, 5] were used for calculating the selectivities of the solvolytic reaction defined by eqn (1) where k_x and k_y are rate constants of the alcoholic and hydrolytic reaction, respectively. The determined activation entropies, dependence of rate constants on the change in medium as compared with literature [9, 10] and the found selectivity of the reaction are in line with the S_N2 mechanism of the solvolytic reaction [6, 7]. The known selectivity and the known overall reaction rate enable us to calculate the rate constants of hydrolytic and alcoholic reaction k_{hydr} and k_{alc} . The dependence of logarithms of these rate constants on the Kirkwood function $(\epsilon_r - 1)/(2\epsilon_r + 1)$ (ϵ_r was taken from Ref. [11]) is represented in Fig. 1. The obtained relationships are unambiguous-

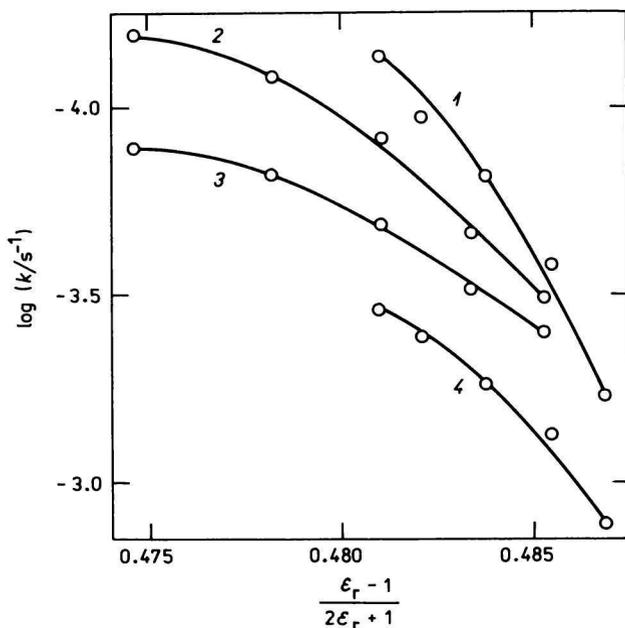
Fig. 1. Variation of logarithms of the rate constants with $(\epsilon_r - 1)/(2\epsilon_r + 1)$. 1. $\log(k_{\text{hydr}}/\text{s}^{-1})$ in the water—methanol system; 2. $\log(k_{\text{alc}}/\text{s}^{-1})$ in the water—ethanol system; 3. $\log(k_{\text{hydr}}/\text{s}^{-1})$ in the water—ethanol system; 4. $\log(k_{\text{alc}}/\text{s}^{-1})$ in the water—methanol system.

Table 1

Rate constants, activation parameters, concentration ratios of ester to acetic anhydride and selectivities of reactions at 25 °C

Medium	Measured quantity	$w(\text{alcohol})/\%$				
		50	60	70	80	90
Water— —methanol	$k \cdot 10^4/\text{s}^{-1}$	18.9	9.92	7.00	5.17	4.20
	$c_{\text{ester}}/c_{\text{anhydride}}^{a,b}$	0.55	0.68	0.82	0.89	0.96
	S^b	0.34	0.40	0.56	0.58	0.68
	$c_{\text{ester}}/c_{\text{anhydride}}^{a,c}$	0.46	0.58	0.72	0.84	0.94
	S^c	-0.10	-0.07	0.00	0.05	0.07
	$\Delta H^\ddagger/(\text{kJ mol}^{-1})$	22.9	—	—	—	31.0
	$-\Delta S^\ddagger/(\text{J mol}^{-1} \text{K}^{-1})$	220	—	—	—	204
Water— —ethanol	$k \cdot 10^4/\text{s}^{-1}$	7.20	5.18	3.25	2.35	1.92
	$c_{\text{ester}}/c_{\text{anhydride}}^{a,b}$	0.24	0.29	0.35	0.46	0.64
	S^b	-0.09	-0.15	-0.23	-0.26	-0.30
	$c_{\text{ester}}/c_{\text{anhydride}}^{a,c}$	0.29	0.37	0.53	0.67	0.64
	S^c	-1.02	-1.12	-1.23	-1.52	-1.62
	$\Delta H^\ddagger/(\text{kJ mol}^{-1})$	25.8	—	—	—	35.1
	$-\Delta S^\ddagger/(\text{J mol}^{-1} \text{K}^{-1})$	216	—	—	—	196

a) Concentration in mol dm^{-3} ; b) neutral medium; c) alkaline medium.



ly nonlinear, but the rate constant is frequently a complicated function of medium [12]. It results from the comparison of these relations that methanol is stronger nucleophile in the water—methanol system while water is stronger nucleophile in the water—ethanol system. The rate constants decrease with decreasing polarity of the system but the rate constant of reaction of the stronger nucleophile always decreases less than the rate constant of the weaker nucleophile. This fact manifests itself in the relationship between reactivity and selectivity in Fig. 2. The overall rate of solvolysis always decreases with increasing content of alcohol, but the selectivity defined by the difference of logarithms of the rate constants of alcoholic and hydrolytic reaction increases in the water—methanol system whereas it decreases in the water—ethanol system. Similar effects were occasionally observed in the solvolyses of alkyl halides [13]. The reactivity—selectivity relationship is most frequently used for studying S_N1 — S_N2 reactions [1, 2, 13] but there are only few experiences with typical S_N2 reactions including solvolysis of the anhydrides of acids. For this reason, we cannot at present use the experimental material for reasoning in reference to mechanism of the reaction.

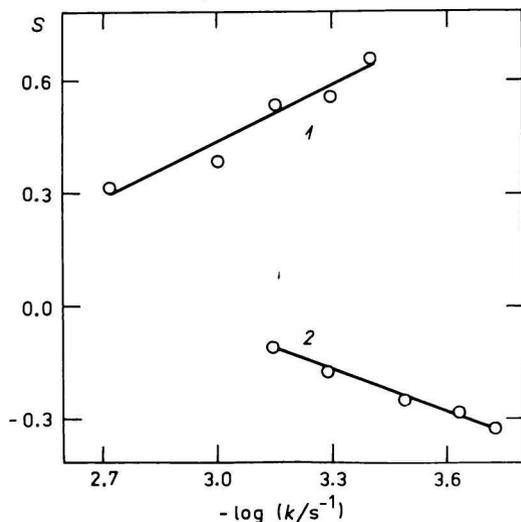


Fig. 2. Reactivity—selectivity relationship for neutral solvolysis: 1. in the water—methanol system, 2. in the water—ethanol system.

The selectivity—selectivity relationship does not usually bring more information than the reactivity—selectivity relationship [14], but it becomes useful if the reactivity—selectivity relationship cannot be measured. That most frequently occurs if the system contains slowly soluble substrates which are rapidly solvolyzed in alkaline medium, for instance the anhydrides of acids in alkaline region in a solvent containing great content of water. Then we may deduce that

the increasing selectivity in neutral region is accompanied by increasing selectivity in alkaline region and *vice versa* provided the reaction mechanism does not change because of the exchange of nucleophile (e.g. replacement of the water molecule by the OH^- ion) and the order of reactivities of the lyate ions is equal to that of neutral molecules. It is obvious from Fig. 3 that the solvolysis of acetic anhydride satisfies both postulates. Thus it results that the mechanism of the alkaline solvolysis of acetic anhydride is equal or similar to the mechanism of solvolysis in neutral region, *i.e.* the reaction under discussion is a $\text{S}_{\text{N}}2$ reaction. In this way, the presented experiment is in agreement with literature [6, 7] and suggests the possibility of using the selectivity—selectivity relationship.

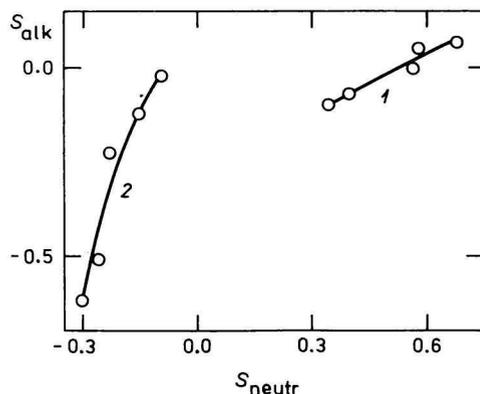


Fig. 3. Selectivity—selectivity relationship. 1. For the water—methanol system; 2. for the water—ethanol system (plotted $S + 1$).

This study is the first attempt to use the ratio of activities of the lyate ions for studying the solvolytic reactions and for this reason, it is confined only to a comparison of the results obtained by means of the lyate ions with the results obtained by other methods used for investigating the mechanism of the solvolytic reactions. The advantage of the applied method consists not only in the above-mentioned possibility of replacing the reactivity—selectivity relationship by the selectivity—selectivity relationship but also in the fact that a convenient choice of alcohol makes possible to change the steric relations in the reaction and thus the reactivity—selectivity and selectivity—selectivity relationships enable us to obtain information about steric relations for the reaction in alkaline region which is otherwise obtainable only with difficulty.

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