Ultrasonic acceleration of ester hydrolysis in ethanol–water and 1,4-dioxane–water binary solvents

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Abstract. Kinetics of the acid-catalysed hydrolysis of butyl acetate in ethanol–water and 1,4-dioxane–water binary solutions was investigated without sonication and under ultrasound at 22 kHz. Rate enhancements by 2.42 times or less were found to decrease with an increase in the content of the hydrophobic co-solvent in the binary solvent. The results suggest that ultrasonic acceleration of the reaction may be interrelated to the perturbation of hydrophobic solute–solvent interactions.

Key words: binary solvent mixtures, ester hydrolysis, ultrasound.

INTRODUCTION

The nature of the sonication effect on heterogeneous processes and free radical reactions is well understood by now [1, 2]. However, the acceleration of homogeneous polar reactions has not been investigated sufficiently, and the background of this phenomenon is not entirely clear.

Known examples of homogeneous polar reactions accelerated by ultrasound are solvolyses of organic halides and hydrolyses of esters. Moderate rate enhancements of 14–60% induced by irradiating the reacting solution with ultrasound have been reported for acid-catalysed or alkaline hydrolyses of esters [3–8]. Under conditions affording more pronounced sonication effects a many-fold acceleration of the acid-catalysed hydrolysis of ethyl acetate was attained in water [7] and ethanol–water mixtures [8]. Larger sonication effects were observed for the solvolysis reaction of *tert*-butyl chloride in ethanol–water and

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tert-butanol–water mixtures [9, 10], and also for the solvolysis of 1-bromo-1-phenylethane in ethanol–water mixtures [11].

It is generally accepted that ultrasonic irradiation affects chemical reactions through acoustic cavitation in the reaction medium [1, 2]. The collapse of cavitation bubbles generates transient hot spots with extremely high local temperature and pressure. It is hardly possible to conceive of a neat heterolytic reaction in a hot-spot region. Also, the effect of a possible temperature gradient after the cavitation collapse proves to be insignificant [12].

For polar reactions the solvation of reactants is one of the most important factors governing the rates of the reactions. In binary solvents the situation is complicated by the selective solvation of species. This means that the composition of the solvation shell around a species is different from the bulk solvent composition. In solvents capable of hydrogen bonding the structuredness of the medium is of great importance [13]. Explanations of the sonochemical effect dealing with the perturbation of the molecular organization of or the solvation in the reaction system have been suggested [10, 12]. In this connection, polar reactions in composite solvents must be the most sensitive to sonication. For this reason we are investigating sonochemistry in binary solvent systems.

Mason et al. [9, 10] studied the effect of ultrasound on the kinetics of *tert*-butyl chloride solvolysis in various alcohol–water mixtures. Acceleration increasing nonlinearly with an increase in the ethanol or *tert*-butanol content was found for the reaction. We are investigating a mechanistically different reaction, viz. the acid-catalysed hydrolysis of esters in organic–water mixtures, to elucidate some more details of the sonication effect on polar reactions. In this report we present the results for the acid-catalysed hydrolysis of butyl acetate in water–ethanol and water–1,4-dioxane binary solvents.

EXPERIMENTAL

The kinetics of the acid-catalysed hydrolysis of butyl acetate was followed by the gas-liquid chromatography (GLC) determination of the ester concentration in 1 M HCl solutions. The binary aqueous mixtures were prepared by weighing the calculated amounts of 1,4-dioxane or ethanol, water, and HCl solution. The experimental apparatus for ultrasonic measurements consisted of a stainless-steel cell reaction vessel provided with a cooling jacket and equipped with an electronic thermometer and a titanium sonication horn immersed reproducibly into the reaction solution. Ultrasound was generated by an UZDN-2T probe disrupter operating at 22 kHz. Its energy output was 34 W in water estimated calorimetrically in the same reaction vessel.

For kinetic measurements 80 mL of the solution was transferred into the reaction vessel, 1.5 mL of *sec*-butyl alcohol was added as the internal standard for GLC analyses, and ultrasound was switched on. The reaction temperature was maintained at $18.3 \pm 0.3\,°C$ by regulating water circulation in the cooling jacket of

the apparatus. After the temperature was equilibrated in the whole system, 0.5 mL of butyl acetate was injected into the solution to start the reaction. Aliquots of 0.5 mL were taken at appropriate time intervals and treated three times with 0.2 mL of hexane. The joint hexane extracts were analysed by using GLC. The ratios of the peak areas for the ester and the internal standard were plotted against time, and first-order kinetic constants were calculated from the obtained kinetic curves by means of a differential method.

Measurements without sonication were performed similarly in a reaction cell thermostatted at 18.3 °C and equipped with a magnetic stirrer.
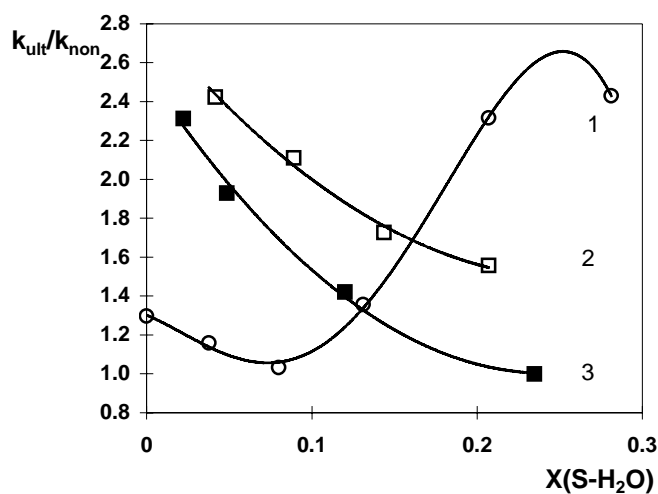
RESULTS AND DISCUSSION

Nonsonic and ultrasonic rate constants for the reaction in water–ethanol and water–1,4-dioxane binary mixtures are presented in Table 1. Figure 1 shows the ultrasonic enhancement of the reaction rate as a function of solvent concentration expressed in molar ratios. In Fig. 1 the data from Ref. [8] for the hydrolysis of ethyl acetate at 18.3 °C are also shown.

As Fig. 1 demonstrates the dependence of the ultrasonic effect on solvent composition for ethyl acetate has a complicated shape involving minimum and maximum points. In our previous study [8] it was concluded that these phenomena should be related to the molecular structure of the binary solvent rather than to the reaction mechanism. However, replacement of ethyl acetate by more hydrophobic butyl acetate changed beyond recognition the dependence of the sonication effect on the solvent composition. Moreover, a very similar dependence was obtained in the 1,4-dioxane–water system for the same ester.

Engberts and co-workers (see [14] and references therein) have developed a versatile approach to reactions in binary solvent systems, ester hydrolyses included, basing on an idea about equilibrium formation of encounter complexes between reactants and hydrophobic co-solvents. The more hydrophobic are the reagents and the co-solvents, e.g. alcohols, the more extensively the reagents are included in the encounter complexes, being thus rendered unreactive.

Table 1. Results of kinetic measurements at 18.3 °C

| % w/w | Rate constants $k \times 10^4$ s^{-1} | | | | Ultrasonic acceleration | |
| | 1,4-Dioxane–water | | EtOH–water | | | |
	Nonsonic	Sonic	Nonsonic	Sonic	1,4-Dioxane	EtOH
10	0.89 ± 0.069	2.07 ± 0.042	0.92 ± 0.0029	2.24 ± 0.0038	2.31	2.42
20	–	–	0.79 ± 0.015	1.66 ± 0.013	–	2.11
30	0.78 ± 0.031	1.41 ± 0.028	0.55 ± 0.0016	0.95 ± 0.0019	1.81	1.73
40	0.59 ± 0.0016	0.84 ± 0.0018	0.48 ± 0.0013	0.74 ± 0.001	1.42	1.56
60	0.37 ± 0.0019	0.34 ± 0.0014	–	–	0.94	–

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Fig. 1. Rate enhancements induced by ultrasonic irradiation for various solvent compositions (k_{ult} – sonic, k_{non} – nonsonic). 1 – hydrolysis of ethyl acetate (S = EtOH) from Ref. [8]; 2 – hydrolysis of butyl acetate (S = EtOH); and 3 – hydrolysis of butyl acetate (S = dioxane).

As a provisional explanation of our results we suggest an effect of ultrasound on solute–solvent interactions. In the case of ethyl acetate the hydrophobic interaction with ethanol systems seems to be relatively weak and the disturbing effect of ultrasound on the solvent structure is more pronounced. More hydrophobic butyl acetate forms stronger encounter complexes with ethanol and particularly with 1,4-dioxane. In this case the sonication effect consists mainly in the destruction of the encounter complexes. The efficiency of this decreases with increasing content of the hydrophobic co-solvent in the binary solvent mixture.

Further sonochemical investigations of ester reactions in binary solvents are in progress.

ACKNOWLEDGEMENT

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Estri hüdrolüüsi kiirendamine ultraheliga binaarsetes solventides etanool ja vesi ning 1,4-dioksaan ja vesi

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Butüülatsetaadi happekatalüütilise hüdrolüüsi kineetikat uuriti binaarsetes lahustes etanool ja vesi ning 1,4-dioksaan ja vesi ultrahelita ning ultraheliga kiiritades 22 kHz sagedusel. Reaktsiooni kiiruse kasv (kuni 2,42 korda) vähenes hüdrofoobse kaassolvendi sisalduse suurenemisega binaarses solventsüsteemis. Tulemused võimaldavad järeldada, et ultrahelist tingitud reaktsiooni kiirenemine võib olla seotud lahustatud aine ja lahusti hüdrofoobse vastastikmõju häiritusega.