

Effect of Ultrasound on the Base-Catalyzed Hydrolysis of 4-Nitrophenyl Acetate in Aqueous Ethanol

Siim Salmar,^{*,†} Giancarlo Cravotto,[‡] Ants Tuulmets,[†] and Hannes Hagu[†]

Institute of Organic and Bioorganic Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia, and Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, I-10125 Torino, Italy

Received: December 20, 2005; In Final Form: February 4, 2006

The kinetics of base-catalyzed hydrolysis of 4-nitrophenyl acetate was studied in water and water–ethanol mixtures under ultrasound (21.1 kHz) using a probe equipped with a quartz horn and, by comparison, without sonication. The ethanol concentration was varied from 0 to 50 wt % and pH from 7.5 to 9. The increase of reaction rate was inversely proportional to the strength of substrate interactions with the solvent structure. It was found that the effect of ultrasound could be related to the perturbation of solute–solvent interactions. This conclusion seems to apply to both acid-catalyzed and base-catalyzed hydrolysis reactions. Parallel experiments with a titanium horn revealed the catalytic action of undetermined chemical species formed from dispersed titanium metal.

1. Introduction

Because it can promote or speed up a wide range of chemical and physical processes,^{1–4} ultrasound has been used by chemists and chemical engineers for a variety of purposes in areas as diverse as electrochemistry, food technology, synthesis of fine chemicals, materials extraction, nanotechnology, and sewage treatment.

In heterogeneous systems the mechanical effects of ultrasonic irradiation are responsible for mass transfer, surface activation of solid reagents or catalysts, the dispersion of particles, and so forth. Many homogeneous and heterogeneous reactions can be initiated or accelerated by ultrasound through the generation of free radicals that give rise to chain reactions. The relevant mechanisms have not been sufficiently clarified for a number of basic reactions, particularly for homogeneous ionic reactions such as hydrolysis and solvolysis in water and in aqueous binary solutions. This is possibly because these reactions profit but slightly from the use of sonication in comparison with synthetically important ones. However, sonication studies on solvolysis and hydrolysis reactions in aqueous organic binary solvents have recently brought to light specific solute–solvent interactions and hydrophobic effects that are not manifested in conventional reaction kinetics.^{5–9} In this regard, ultrasound may become a useful tool for physicochemical, particularly mechanistic, investigations.

Recently we reported the effects of ultrasound on acid-catalyzed hydrolysis of alkyl esters in ethanol–water and 1,4-dioxane–water binary mixtures.^{8,9} We speculated that the observed sonochemical acceleration might be related with changes in the molecular structure of the binary solvent, essentially a perturbation of hydrophobic solute–solvent interactions.⁹

To gain a better insight into the matter, we extended our kinetic investigation to a mechanistically complementary reac-

tion, viz. the base-catalyzed hydrolysis of esters. An acceleration (14–15%) by ultrasound had previously been reported for the alkaline hydrolysis of 4-nitrophenyl esters of several aliphatic carboxylic acids in a water–acetonitrile mixture¹⁰ and for that of phthalic acid esters in water.¹¹ In contrast to these findings, an ultrasonic acceleration by 2 orders of magnitude was found by Hua et al.¹² for the hydrolysis of 4-nitrophenyl acetate (4-NPA) in water.

The present work also used 4-NPA as the model ester and ethanol–water as reaction medium. Unlike aliphatic esters studied in our previous work,^{8,9} 4-NPA is ideally suitable for spectrophotometric kinetic measurements using reagent concentrations several orders of magnitude lower than those required for GLC determinations (cf. ref 9). The complications that may arise from the well-studied sonolytic degradation of 4-nitrophenol (4-NP)^{12–16} or the radical-induced decomposition of 4-NPA¹⁶ will be discussed below.

The effect of ultrasound on our model reaction was investigated over the 0–50 wt % range of ethanol concentration and over the 7.5–9 pH range.

A specific feature of the present work consisted of the comparative use of two different immersion horns for sonication. A quartz probe avoided the well-known problems arising from the erosion of titanium horns and made it unnecessary to filter the samples. The titanium probe was still used to reproduce the experiments published by Hua et al.¹² A comparison of results obtained with the quartz and titanium horns enabled us to rationalize the sonication effects reported by those authors.¹²

2. Experimental Section

2.1. Reagents and Solutions. 4-NPA and 4-NP were purchased from commercial sources and were used without further purification. Commercially available EtOH (analytical grade) and doubly distilled water were used to prepare solvent mixtures.

Ethanol–water mixtures in the 0–50 wt % concentration range and pH values ranging from 7.5 to 9 were prepared with phosphate and Borax buffers by weighing calculated amounts

* Corresponding author. E-mail: siim.salmar@ut.ee.

[†] University of Tartu.

[‡] Università di Torino.

of reagents according to standard procedures.¹⁷ Density data were taken from ref 18. The ionic strength of all solutions was made up to $\mu = 0.045$ M with NaCl. The pH of the reaction mixtures, measured before and after each run, did not vary by more than 0.01 units (Orion Model 420A).

4-NPA was first dissolved in ethanol and then diluted to a 0.1 mM concentration with thermostated ethanol–water buffer immediately before starting the reaction. When no ethanol was present in the buffer, 4-NPA was dissolved in water by stirring overnight at room temperature.

2.2. Apparatus. Sonication was performed with two different direct immersion probe systems. One sonicator was an UZDN-2T 400 W cell disrupter operating at 22 kHz, equipped with a titanium sonication horn with a 14.5-mm tip diameter. Its energy output, estimated calorimetrically,⁹ was 55 W in water. Another apparatus was a handmade probe operating at 21.1 kHz, equipped with a quartz sonication horn (tip diameter 15 mm). Its average power delivery to water, estimated calorimetrically, was 9.4 W. The sonication horns were always immersed 2.5 cm below the liquid surface.

The ultrasonic experiments were performed under argon atmosphere in a 100-mL glass cell sealed with an elastomeric septum. The cell, equipped with an electronic thermometer and a magnetic stirrer, was cooled in a water–ice bath so that the temperature in the reaction vessel was maintained at 20 ± 0.5 °C during all measurements.

2.3. Kinetic Measurements. The kinetics of the base-catalyzed hydrolysis of 4-NPA was followed spectrophotometrically with a Varian Cary 50 Scan UV–visible spectrophotometer. Spectrophotometric calibrations were preliminarily carried out to determine in the 230–550 nm range the molar absorptivities of 4-NPA and 4-NP in buffered ethanol–water mixtures at pH 7.5, 8.0, and 9.0.

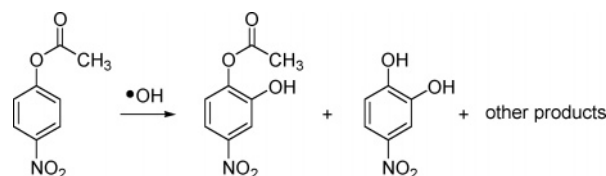
All hydrolysis reactions were performed without sonication and under ultrasound. Aliquots of 0.5–1 mL were withdrawn from the reacting mixtures at appropriate time intervals and the formation of the 4-nitrophenolate ion or the consumption of 4-NPA was monitored at 400 and 272 nm, respectively.

The hydrolysis of 4-NPA with a titanium probe was carried out in aqueous phosphate buffer ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$, $\mu = 0.045$ M) at pH 7.5. Aliquots were withdrawn with a syringe equipped with 0.2 μm HPLC filter to remove Ti particles released from erosion of the sonication horn. Spectra were recorded immediately, while some samples were analyzed by HPLC (Waters 6000 HPLC pump and 440 UV detector at 254 nm) on a reversed-phase column to detect products of OH-radical-induced reactions. Water/methanol/acetic acid (60:40:1) was used as eluent.

The sonolytic degradation of 4-NP was monitored in identical fashion and under the same conditions as the hydrolysis of 4-NPA. 4-NP (100 mL, 0.1 mM) in aqueous phosphate buffer was sonicated and the absorbance of the 4-nitrophenolate ion was measured at 400 nm.

In a similar way the kinetic measurements of 4-NP degradation and of base-catalyzed 4-NPA hydrolysis were carried out with the probe equipped with a quartz horn in 0–50 wt % aqueous ethanol buffered with phosphate salts at pH 8.0 and with Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}/\text{HCl}$) at pH 9.0. At appropriate time intervals, 0.5–1 mL aliquots were withdrawn with a syringe and their spectra were recorded immediately at 230–550 nm; preliminary filtration was found to be unnecessary. Rate constants for the reactions were likewise determined from the decrease of 4-NPA absorption at 272 nm and the increase of the 4-nitrophenolate absorption at 400 nm. In standard

SCHEME 1



experiments these absorbances were registered simultaneously and rate constants were calculated from both sets of data; averages of the resulting values are presented in the following tables and figures. All runs were carried out at least in triplicate. The standard deviations of mean values did not exceed 5% for experiments with the Ti horn and 0.8% for experiments with the quartz horn.

3. Results and Discussion

Ester hydrolysis under ultrasound in aqueous media can be accompanied by side reactions, mainly because of the activity of hydroxyl radicals generated from the decomposition of water. In such systems, cavitation bubbles are filled with water vapor, dissolved gas, and other volatile materials. As bubble collapse creates extreme physical conditions (several thousand degrees and several hundred atmospheres), water vapor undergoes thermal decomposition to yield an OH radical and an H atom.^{1–4} 4-NPA is liable to undergo OH-radical-induced reactions like the one shown in Scheme 1.¹⁶

The production of radicals depends primarily on the frequency of the ultrasound.^{19–21} Tauber et al.¹⁶ studied at 321 kHz the sonolysis of 4-NPA in an argon-saturated aqueous solution (pH 6.5, 25 °C, the reaction vessel being immersed in a water-filled sonicator, 85 W). Under these conditions, OH-radical-induced products (e.g. 2-hydroxy-4-nitrophenyl acetate, Scheme 1) and pyrolytic products were found exclusively; hydrolysis, however, was extremely slow at this pH.

Yim et al.¹¹ studied the degradation of phthalic acid esters in aqueous solution under ultrasound at 200 kHz. Compared to hydrolysis, attack by OH radicals was found to predominate in the degradation of diethyl phthalate in the pH range 4–11. However, the contribution of hydrolysis increased appreciably with increasing pH.

Ando et al.²² studied the decarboxylation of 6-nitrobenzoxazole-3-carboxylic acid under ultrasound with a horn-type sonicator (20 kHz) in phosphate-buffered solutions, pH 7.0, under argon. The rate was unaffected by sonication, and no products of free-radical reactions were detected. However, this substrate might be less prone to enter a radical pathway.

Hua et al.¹² reported that ultrasound increased by 2 orders of magnitude the rate constant of 4-NPA hydrolysis in aqueous solution over the pH range 3–8. In the presence of ultrasound, the observed first-order rate constant was independent of both pH and ionic strength and was equal to $4.6 \times 10^{-4} \text{ s}^{-1}$ at 25 °C with Ar as cavitating gas (a direct-immersion Ti probe was used at 20 kHz and 115 W). The authors found that OH radical reactions were not contributing significantly to the sonolytic hydrolysis.

The generation of OH radicals is obviously much more intense at 321 or 200 kHz than it is at 20 kHz. Besides, above pH 6.5 the hydrolysis of 4-NPA is base-catalyzed and its rate is strongly pH-dependent. The reaction is very slow at pH 6.5 with a specific rate of $1 \times 10^{-6} \text{ s}^{-1}$, but it becomes 10-fold faster at pH 7.5.¹² To observe the real effect of ultrasound on the base-catalyzed hydrolysis of 4-NPA, it was essential to find

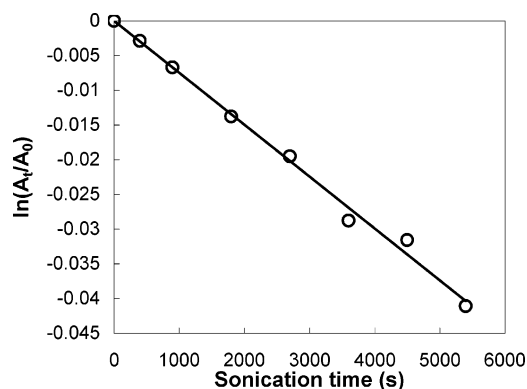


Figure 1. First-order plot of the sonolytic degradation of 4-NP in argon-saturated phosphate buffer, pH 7.5, at 20 °C. A is the absorbance of 4-NP measured at 400 nm.

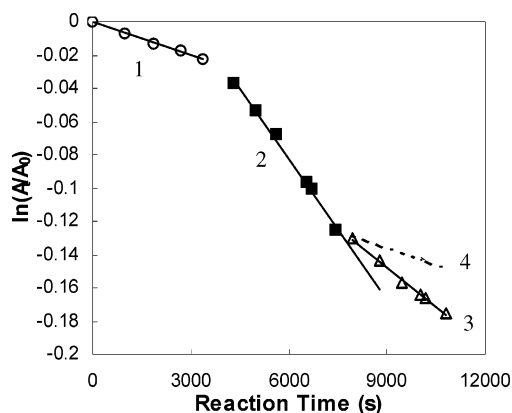


Figure 2. First-order plots for base-catalyzed hydrolysis of 4-NPA in argon-saturated phosphate buffer, pH 7.5: (1) without ultrasound, (2) under ultrasound, (3) successively without ultrasonic irradiation, and (4) (dashed line) calculated according to the rate of the reaction before sonication. A is the absorbance of 4-NPA measured at 272 nm.

reaction conditions under which pyrolytic degradation and free-radical processes would be relatively slow or entirely suppressed.

3.1. Experiments with a Ti Probe. Our aim was to reproduce in the first place the results published by Hua et al.¹² and then to extend our measurements to water–ethanol systems. To begin with, the sonolytic hydrolysis of 4-NPA was investigated in an aqueous solution at pH 7.5 with a direct-immersion Ti probe system. Furthermore, the sonolytic degradation of 4-NP was studied under these conditions. In accordance with former findings^{12–16} we found it to be first-order as shown in Figure 1. The slope of this plot gave a first-order rate constant of $7.5 \times 10^{-6} \text{ s}^{-1}$. This was almost 2 orders of magnitude smaller than the value of $5.2 \times 10^{-4} \text{ s}^{-1}$ reported by Hua et al.,¹² evidently because of the lower ultrasound power used by us. However, because the sonolytic degradation of 4-NP could not be ignored, for our kinetic calculations we quantitated 4-NPA at 272 nm rather than the formation of 4-nitrophenolate ion. The contribution to the absorbance at 272 nm made by 4-NP present in the solution was calculated from simultaneous measurements at 400 nm and subtracted from the total absorbance.

An additional feature of our experiment was to carry out kinetic measurements of base-catalyzed hydrolysis of 4-NPA with sonication and without ultrasound successively in the same reaction system. In Figure 2 the disappearance of 4-NPA is plotted vs time throughout a single experiment. The first-order rate constants presented in Table 1 were respectively determined from the plots for the silent reaction, for the reaction under

TABLE 1: Results of Kinetic Measurements for Base-Catalyzed Hydrolysis of 4-Nitrophenyl Acetate in Water at pH 7.5

rate constant $k \times 10^5 \text{ s}^{-1}$ ^a		
nonsonic 1	sonic 2	nonsonic 3
0.66 ± 0.01	2.85 ± 0.11	1.57 ± 0.07

^a Values are averages from three parallel runs.

ultrasound, and for the reaction after ultrasound was switched off.

Segments 2 and 3 in Figure 2 represent the kinetics of hydrolysis under irradiation and after ultrasound was switched off, respectively. The first-order rate constants from segments 1 and 2 reveal a considerable sonolytic acceleration, the ratio $k_{\text{ult}}/k_{\text{non}}$ being 4.3. This effect was not due to a loss of 4-NPA through OH-induced radical reactions,¹⁶ because after 1-h irradiation we could not detect by HPLC the products of such reactions at a level exceeding 2%.

The rate constant for silent hydrolysis after previous sonication (segment 3 in Figure 2) was distinctly greater than that determined before irradiation (segment 1 in Figure 2), their ratio equaling 2.3, a result that clearly indicates a catalytic build-up during sonication. Although kinetic curves obtained under sonication do not show the expected autocatalytic shapes, data recorded within about 1 h might not necessarily reflect this pattern. Identification of the catalyst must await a separate investigation; a decisive role in its formation is most probably played by the metal traces from the immersed titanium horn in conjunction with sonolytic products deriving from the phenyl ester and the phenol. As a matter of fact, the kinetic anomaly was not present when a quartz horn was used, nor did our former sonication experiments on alkyl esters with a titanium horn^{8,9} exhibit any catalytic phenomena.

We surmise that the entity of catalytic effects must depend on irradiation intensity. Judging from the relative rates of sonolytic degradation of 4-NP, the ultrasound power applied by Hua et al.¹² was almost 9 times greater than that emitted in the present experiments. Therefore, we suppose that the large sonication accelerations observed by Hua et al. were not only caused by direct effects of ultrasound but also involved a considerable contribution from catalytic effects.

As a conclusive caveat, it is clear that an immersion titanium probe is not suitable for kinetic experiments with 4-nitrophenyl esters under ultrasound. In the following kinetic measurements we always used a quartz horn.

3.2. Experiments with a Quartz Probe. The experiments were carried out in water at pH 7.5, 8.0, and 9.0 and in aqueous ethanol over the range of 0.8–50 wt % at pH 8.0 and 9.0. Remarkably, no catalytic effect was observed (cf. 3.1, Figure 2) and no degradation of the 4-NP could be detected during 2 h irradiation in any of the solvent mixtures. Rate constants for the hydrolysis reaction could equally be determined, with coinciding results within the experimental error, from the disappearance of 4-NPA or from the formation of 4-NP.

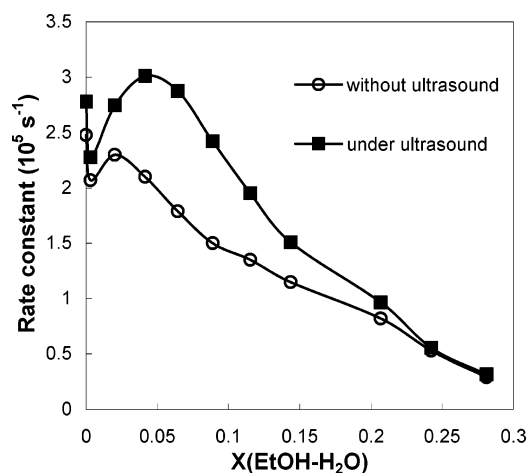
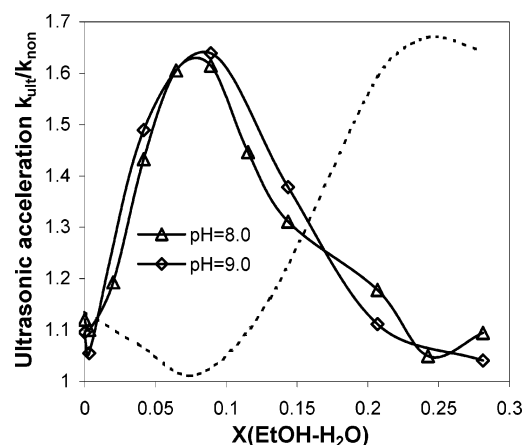
Results are presented in Table 2 and Figures 3 and 4. It is noteworthy that the sonication effect was virtually independent of pH, while the reaction rate increased 12 times with the pH change from 7.5 to 9.0.

In water or in the presence of minor additions of about 1 wt % ethanol, the sonication effect did not exceed 10%. With a further increase in the alcohol content, the ultrasonic acceleration increased rapidly, reaching a maximum at $X_{\text{EtOH}} \approx 0.08$; thereafter, it dwindled gradually and became almost negligible at $X_{\text{EtOH}} \approx 0.25$.

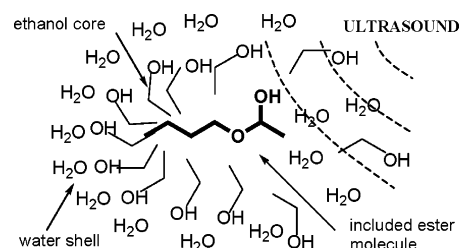
TABLE 2: Results of Kinetic Measurements for Base-Catalyzed Hydrolysis of 4-Nitrophenyl Acetate in Ethanol–Water Binary Mixtures with the Quartz Horn

% w/w (X) ^a ethanol in water	rate constant $k \times 10^5 \text{ s}^{-1}$								
	pH 7.5 ^b		pH 8.0 ^b		pH 9.0 ^c		ultrasonic acceleration		
	nonsonic	sonic	nonsonic	sonic	nonsonic	sonic	pH 7.5 ^b	pH 8.0 ^b	pH 9.0 ^c
0 (0)	0.66	0.73	2.48	2.78	8.12	8.90	1.10	1.12	1.10
0.8 (0.003)			2.07	2.28	8.02	8.46		1.10	1.06
5 (0.020)			2.30	2.74				1.19	
10 (0.042)			2.10	3.01	8.10	12.07		1.43	1.49
15 (0.065)			1.79	2.87				1.61	
20 (0.089)			1.50	2.42	6.75	11.06		1.61	1.64
25 (0.115)			1.35	1.95				1.45	
30 (0.144)			1.15	1.51	4.48	6.17		1.31	1.38
40 (0.207)			0.82	0.97	3.03	3.36		1.18	1.11
45 (0.243)			0.53	0.56				1.05	
50 (0.281)			0.29	0.32	1.30	1.36		1.09	1.04

^a Molar fraction of ethanol. ^b Phosphate buffer. ^c Borax buffer.

**Figure 3.** Rate constants for the hydrolysis of 4-NPA in ethanol–water binary mixtures at pH 8.0: (○) without ultrasound and (■) under ultrasound.**Figure 4.** Ultrasound-induced rate enhancements of the hydrolysis of 4-NPA in ethanol–water binary mixtures at pH 8.0 (○) and 9.0 (□). For comparison, the dashed line presents the rate enhancement for acid-catalyzed hydrolysis of ethyl acetate (in arbitrary units) (from ref 8).

Surprisingly, the plots for 4-NPA in Figure 4 are mirror images of the one found for acid-catalyzed hydrolysis of ethyl acetate,⁸ and their extremes lie at the same alcohol mole fractions. At $X_{\text{EtOH}} \approx 0.08$, ultrasound exerts a most pronounced effect on the hydrolysis of 4-NPA but has almost no influence on the rate of hydrolysis of ethyl acetate. At the same time in the region $0.2 < X_{\text{EtOH}} < 0.3$, the sonication effect of the hydrolysis of ethyl acetate is a maximum while it is nearly negligible for the hydrolysis of 4-NPA.

**Figure 5.** Schematic representation of the impact of ultrasound on ethanol–water clusters.

Our previous paper interpreted the results for ethyl acetate hydrolysis following the current conception for the structure of ethanol–water solutions. According to it,^{23–25} small additions of ethanol ($0 < X_{\text{EtOH}} < 0.08$) exert a strong structure-making effect accompanied by an increase in the self-association of water molecules. Further alcohol additions prevent water from organizing into 3D structures. A breakdown of the bulk structure of water and a parallel evolution of an ethanol polymer structure is found at $X_{\text{EtOH}} > 0.1$. In the region $X_{\text{EtOH}} > 0.2$, a large number of ethanol–water bonds are formed and water–water bonds are broken. These results have led to a cluster model featuring a stacked ethanol core and a thin water shell.^{23–25} For suggested structures of ethanol clusters in water, see ref 25.

The application of ultrasound, disrupting the binary solvent structure, would alter substrate solvation and result in higher reaction rates. Our previous papers found a negligible effect of ultrasound on the hydrolysis of ethyl acetate at $X_{\text{EtOH}} = 0.08$ and attributed it to the rigidity of the solvent structure.^{8,9}

Taking stock of cluster formation in ethanol–water mixtures, we wished to study the effect on the hydrolysis rate of the inclusion of a substrate in the hydrophobic interior of clusters, and to this end, we experimented with propyl and butyl acetates. In fact, sonication effects in the region $0.2 < X_{\text{EtOH}} < 0.3$ agreed well with the order of hydrophobicity of these esters.⁹ Butyl acetate should be the most powerfully held by clusters, and sonication was actually the least efficient in this case (cf. Figure 5).

With the hydrophobic propyl and butyl esters the hydrolysis reaction exhibited considerable sonication effects in the region $0.05 < X_{\text{EtOH}} < 0.15$, where 4-NPA hydrolysis had a distinct maximum of ultrasonic acceleration. In that study,⁹ because we resorted to a GLC method for kinetic measurements, large concentrations of the esters, close to solubility limits, had to be used. Experiments in water could not be carried out and results in the region up to $X_{\text{EtOH}} \sim 0.05$ might have been influenced by the presence of *sec*-butyl alcohol as an internal standard (X

= 0.002). Nevertheless, although no maxima were detected, hydrolyses of propyl and butyl esters, like that of the more hydrophobic 4-NPA, showed enhanced susceptibilities to ultrasound irradiation in the region of $X_{\text{EtOH}} \leq 0.1$, where water structure-making occurs.

We tend to interpret these experimental data as evidence for the inclusion of ester molecules in the solvent framework, which would make them less reactive. Sonication can increase the translational energy of molecules in the liquid phase, thus leading to a breakdown of solvent structure and/or a shift of solvation equilibria.

The more hydrophobic a substrate, the more weakly it should be held by the solvent structure and the greater should be the sonication effect, except the region of cluster formation (vide supra). In fact, Figure 4 shows a relatively fast decrease of the silent reaction rate in the region up to $X_{\text{EtOH}} \sim 0.09$, at which value the sonication effect is most pronounced. This fall is followed by a slower decrease up to the region of cluster formation where the drop becomes faster again and the sonication effect negligible, evidencing the remarkable hydrophobicity of the ester.

These findings lead us to attribute the observed differences in the reaction rate to the changes of solvent structure and confirm our earlier suggestion that sonication effects on polar homogeneous reactions primarily arise from a perturbation of weak solute–solvent interactions.^{7–9}

While an interrelation between sonication effects and reaction mechanism cannot be entirely ruled out, it is, however, self-evident that low-frequency ultrasound is not able to interact with a transition state or to interfere with the solvation process of the transition state. Moreover, in the present case, sonication effects were unrelated to pH while reaction rates changed considerably with small changes in pH. On the other hand, sonication effects were similarly interconnected with solvent structure changes for both acid-catalyzed and base-catalyzed hydrolysis of esters.

4. Conclusions

The present results, together with our previous data, led us to relate ultrasonic acceleration of ester hydrolysis in water and in ethanol–water mixtures to a perturbation of solute–solvent interactions by power ultrasound. In fact, the sonication effect varied inversely with the strength of substrate interactions with the solvent structure. This conclusion, which apparently applies to both acid-catalyzed and base-catalyzed hydrolysis, can be helpful in rationalizing the influence of solvent–solute interactions on these reactions.

Experiments with an immersed titanium horn revealed a catalytic action of materials formed from dispersed titanium metal and degradation products of 4-NPA.

Acknowledgment. This work has been carried out under the auspices of the European Union COST Action D32 (Working Group D32/006/04: Microwave and high-intensity ultrasound in the synthesis of fine chemicals). The financial support of CEBIOVEM (University of Turin) and the technical assistance of Dr. Ing. C. Buffa and Mr. G. Omiccioli deserve acknowledgments.

References and Notes

- (1) *Ultrasound: Its Chemical, Physical, and Biological Effects*; Suslick, K. S. Ed.; VCH: New York, 1988.
- (2) Mason, T. J.; Lorimer, J. P. *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*; Ellis Horwood: Chichester, England, 1988.
- (3) Cravotto, G.; Cintas, P. *Chem. Soc. Rev.* **2006**, 35, 180.
- (4) Petrier C., Luche, J. L. In *Synthetic Organic Sonochemistry*; Luche, J. L. Ed.; Plenum Press: New York, 1998; Chapter 2.
- (5) Mason, T. J.; Lorimer, J. P.; Mistry, B. P. *Tetrahedron* **1985**, 41, 5201.
- (6) Lorimer, J. P.; Mason, T. J.; Mistry, B. P. *Ultrasonics* **1987**, 25, 23.
- (7) Tuulmets, A. *Ultrason. Sonochem.* **1997**, 4, 189.
- (8) Tuulmets, A.; Salmar, S. *Ultrason. Sonochem.* **2001**, 8, 209.
- (9) Tuulmets, A.; Salmar, S.; Hagu, H. *J. Phys. Chem. B* **2003**, 107, 12891.
- (10) Kristol, D. S.; Klotz, H.; Parker, R. C. *Tetrahedron Lett.* **1981**, 22, 907.
- (11) Yim, B.; Nagata, Y.; Maeda, Y. *J. Phys. Chem. A* **2002**, 106, 104.
- (12) Hua, I.; Höchemer, R. H.; Hoffmann, M. R. *J. Phys. Chem.* **1995**, 99, 2335.
- (13) Kotronarou, A.; Mills, G.; Hoffmann, M. R. *J. Phys. Chem.* **1991**, 95, 3630.
- (14) Hoffmann, M. R.; Hua, I.; Höchemer, R. *Ultrason. Sonochem.* **1996**, 3, 165.
- (15) Tauber, A.; Schuchmann, H.-P.; von Sonntag, C. *Ultrason. Sonochem.* **2000**, 7, 45.
- (16) Tauber, A.; Schuchmann, H.-P.; von Sonntag, C. *Chem. Eur. J.* **1999**, 5, 2198.
- (17) *Determination of pH Theory and Practice*, 2nd ed.; Bates, R. G., Ed.; J. Wiley & Sons: New York, 1973.
- (18) *Handbook of Chemistry*, 2nd ed.; Nikol'skiy, B. P., Ed.; Khimiya: Moscow, 1965; Vol. 3 (in Russian).
- (19) Mark, G.; Tauber, A.; Rüdiger, L.; Schuchmann, H.-P.; Schultz, D.; Mues, A.; von Sonntag, C. *Ultrason. Sonochem.* **1998**, 5, 41.
- (20) Petrier, C.; Jeunet, A.; Luche, J.-L.; Reverdy, G. *J. Am. Chem. Soc.* **1992**, 114, 3148.
- (21) Entezari, M., H.; Kruus, P. *Ultrason. Sonochem.* **1992**, 1, S165.
- (22) Ando, T.; Fujita, M.; Kimura, T.; Kondo, Y. *J. Org. Chem.* **1998**, 63, 6048.
- (23) Nishi, N.; Takahashi, S.; Matsumoto, M.; Tanaka, A.; Muraya, K.; Takamuku, T.; Yamaguchi, T. *J. Phys. Chem.* **1995**, 99, 462.
- (24) Matsumoto, M.; Nishi, N.; Furusawa, T.; Saita, M.; Takamuku, T.; Yamagami, M.; Yamaguchi, T. *Bull. Chem. Soc. Jpn.* **1995**, 68, 1775.
- (25) Egashira, K.; Nishi, N. *J. Phys. Chem. B* **1998**, 102, 4054.