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THE EFFECT OF ULTRASOUND ON THE ALKALINE HYDROLYSIS OF NITROPHENYL ESTERS

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Summary: Ultrasound was found to increase the rate of hydrolysis of a series of esters by up to 15%. No effect of molecular structure upon this enhancement was observed.

Little work has been done on the effects of ultrasound on the rates of chemical reactions. It has been proposed that observed effects are due to cavitation, by which is meant the formation of cavities and their subsequent collapse accompanied by intense hydraulic shocks.[1]

Schumb and Rittner[2] found an enhancement of up to 9.5% in the hydrolysis of potassium persulfate produced by an audible signal of 8.7 kHz. Chen and Kalbach[3] found that the hydrolysis of methyl acetate catalyzed by HCl was enhanced by about 3.5% with a 23 kHz signal. Moon et al.[4] reported that the rate of the two-phase alkaline hydrolysis of esters of aromatic carboxylic acids was catalyzed by a 20 kHz signal as determined by isolation of the products. Of the possible mechanisms for the enhancement they suggested that the ultrasound facilitated emulsification.

We have investigated the ultrasonic enhancement of alkaline hydrolysis of the p-nitrophenyl esters of a series of substituted acetic acids (1-4) in order to determine whether the size of the alkyl group attached to the reactive center has any effect on this catalysis. We have previously shown that the rates of the alkaline hydrolysis of p-nitrophenyl esters are strongly affected by steric factors.[5]

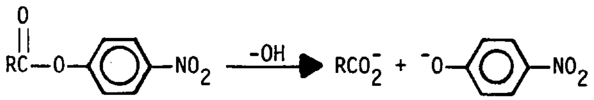
Reactions were conducted in a 60:40 (V/V) mixture of pH 8.0 THAM buffer and acetonitrile in an ethylene glycol jacketed cylindrical vessel with a 20 kHz transducer fitted at the base. They were followed spectrophotometerically at 35°C by periodically monitoring the formation of p-nitrophenolate at 400 nm. A control was run simultaneously with each ultrasonics reaction. Linear regression analyses were performed on the rate data. The results presented in the Table are averages of at least five runs.

Enhancements of 14-15% were observed for each of the esters (1-4) in the series. These percentages are the largest increases in rate due to application of sound yet observed for a one-phase hydrolytic reaction.

These enhancements were virtually identical for all four esters in spite of a large 17-fold range in their rates of hydrolysis. Therefore the replacement of hydrogens with methyls in the acyl portions of the esters has no effect on the ability of the sound wave to increase the rate of hydrolysis.

Several explanations have been offered to account for the rate enhancement due to the application of sound. They include macroscopic heating and cavitation-related phenomena such as large temperature and pressure changes in the collapsing bubbles and emulsification. No temperature difference was observed between the sound and control reactions because of the rapidly circulating ethylene glycol.

TABLE 1. HYDROLYSIS RESULTS



Compound	R	control x 10^{10},Ms^{-1}	ultrasound x 10^{10},Ms^{-1}	enhancement
1	CH_3-	79.7	91.2	14%
2	CH_3CH_2-	42.4	48.8	15%
3	$(CH_3)_2CH$-	24.7	28.5	15%
4	$(CH_3)_3C$-	4.84	5.53	14%

We have thus ruled out macroscopic heating effects by conducting the reactions at constant temperature. Clearly, emulsification has no bearing on these one-phase reactions. The activation energies for the control reactions are 11.9, 12.5, 13.0, and 13.7 kcal/mole for 1, 2, 3, and 4, respectively[5]. If the enhancement in the ultrasound hydrolysis were due to a localized temperature effect, we would expect a range of enhancements whereby 4 would be most accelerated and 1 least accelerated. Therefore, the major effect of ultrasound in our experiments is most probably due to the intense localized pressure increase in the collapsing bubbles.

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