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THE EFFECT OF ULTRASOUND ON THE SOLVOLYSIS OF 2-CHLORO-2-METHYLPROPANE IN AQUEOUS ALCOHOLIC MEDIA[1]

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Abstract. The effect of ultrasonic irradiation (45KHz at 25°C) on the solvolysis of *t*-butyl chloride in aqueous ethanol, *i*-propanol and *t*-butanol is (1) to increase the rate constants in the more alcoholic media and (2) to reduce the m values of these reactions.

In the last two years a number of papers have been published dealing with the effect of ultrasound on chemical reactivity. Some have used ultrasonic irradiation as an energy source for the promotion of reactions useful in organic synthesis[3,4] while others have been concerned with ultrasonically induced enhancements of reaction rates for homogeneous hydrolysis reactions[5,6]. Such rate enhancements have been ascribed to cavitation (the formation and collapse of microbubbles)[7]. It has been estimated that the temperature at the centre of these collapsing bubbles rise to 10^4 to 10^6K with pressures up to several thousand atmospheres[8].

We wish to report the effects of ultrasonic irradiation on the rate constants for the homogeneous solvolyses of *t*-butyl chloride in mixed aqueous alcoholic solvents.

The rate enhancements induced by ultrasound are shown (TABLE) from which it is apparent that the large increases in the rate constants occur in the more alcoholic region of the solvent ranges studied. For aqueous ethanol a maximum in rate enhancement occurs at approximately 0.3 mol fraction, a concentration generally accepted to be the most structured region for this binary mixture[9]. In the highly aqueous regions the solvolysis

TABLE Effect of Ultrasound on the Rates of Solvolysis of t-Butyl Chloride at 25°C

Solvent	Mol Fraction of Alcohol	Rate Constants/s^{-1}		k_{ULT}/k_{NON}
		$10^5 k_{NON}$	10^5 ULT	
Aqueous Ethanol	0.089	835 ± 19	1020 ± 45	1.22 ± 0.09
	0.144	279 ± 5	320 ± 15	1.15 ± 0.07
	0.207	64.9 ± 1.8	95.6 ± 8	1.47 ± 0.17
	0.281	19.0 ± 0.6	40.5 ± 0.8	2.13 ± 0.11
	0.307	6.5 ± 0.12	12.3 ± 0.4	1.89 ± 0.10
Aqueous *i*-Propanol	0.070	718 ± 14	663 ± 3	0.93 ± 0.02
	0.114	142 ± 5	127 ± 5	0.89 ± 0.07
	0.167	30.4 ± 1	43.8 ± 1.6	1.44 ± 0.10
	0.231	10.5 ± 0.1	20.2 ± 2.3	1.92 ± 0.22
Aqueous *t*-Butanol	0.057	506 ± 17	450 ± 10	0.89 ± 0.05
	0.094	76.3 ± 1.2	79.3 ± 3	1.04 ± 0.06
	0.139	24.2 ± 0.5	25.8 ± 1.8	1.07 ± 0.09
	0.196	8.7 ± 0.1	11.6 ± 0.6	1.33 ± 0.09

reactions are little effected by ultrasound. In the case of the aqueous t-butanol system this is a surprising result in view of low intensity ultrasound absorption measurements which show a pronounced maxima for excess sound absorption occurring at about 0.1 mol fraction of the alcohol. This maximum is much larger than the corresponding maximum for ethanol water which is found at 0.3 mol fraction[10].

The solvolysis of t-butyl chloride has for many years been regarded as a 'model' for S_N1 type reactions[11] though recent studies have cast doubt on this and suggested that these reactions proceed via an S_N2 (intermediate) mechanism[12]. Such a mechanism involves weak nucleophilic solvation of the ion pair in the rate determining step.

If nucleophilic solvation is a factor in these reactions then any change in such participation induced by ultrasound might be reflected in a change in their Grunwald Winstein m values. The m values of 1.00, 1.04 and 1.00 (S.D.'s 0.022, 0.026 and 0.026 respectively) obtained for the normal solvolyses in aqueous ethanol, i-propanol and t-butanol are reduced to 0.88, 0.93 and 0.91 (S.D.'s 0.027, 0.033 and 0.007 respectively) on application of ultrasound. In all cases the correlation coefficients were better than 0.998. Such a reduction could be interpreted in terms of increased S_N2 character for all three reactions under ultrasonic irradiation.

This conclusion can be rationalised in the case of reaction in aqueous ethanol in terms of the disruption of solvent structure produced by ultrasound. The breaking down of ordered structure would facilitate the reorganisation of the binary solvent to provide more effective nucleophilic solvation. The effect of ultrasound would thus be expected to be greatest at the point of maximum solvent structuredness (0.3 mol fraction ethanol) and to be small in the more highly aqueous (less ordered) region. A similar explanation would apply to the aqueous i-propanol results but those obtained in t-butanol appear anomalous.

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