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THE EFFECT OF TEMPERATURE ON THE ULTRASONICALLY ENHANCED REACTION RATES OF 2-CHLORO-2-METHYLPROPANE IN AQUEOUS ETHANOL MIXTURES

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Abstract The effect of ultrasound on the solvolysis of tert-butyl chloride in aqueous ethanol is to lower the activation energy for the reaction as the alcohol content is increased.

Ultrasonic irradiation has been shown to increase the solvolysis rate constant (at 25°C) of tert-butyl chloride in various aqueous ethanol mixtures[2]. The relationship between the observed rate enhancement and solvent composition is similar to trends found in other solvent dependent physical parameters (eg. ΔH_m[3], $\Delta V^{\ddagger}$[4], η[5] and low frequency ultrasound absorption[6]).

In each case a maximum is observed at around 0.3 mole fraction of ethanol. This is taken to be the region of maximum solvent structuredness. It is the close parallel between ultrasonic acceleration and $\Delta V^{\ddagger}$ measurements in particular, which indicate that the rate enhancements induced by ultrasound are linked to a concomitant disruption of the solvent hydrogen bonded structure. Although the pressures used in $\Delta V^{\ddagger}$ measurements are much lower than the instantaneous pressures developed following an ultrasound wave[7], it is thought that they are large enough to bring about a diminution of hydrogen bonding[8]. Since Arnett[9] has shown that the effect on reaction rate of changes in the solvent composition can be mainly attributed to changes in the solvation of the transition state, we have investigated the effect of ultrasonic excitation on the solvolysis of tert-butyl chloride at different temperatures and at different aqueous ethanol compositions.

Mol.Fraction of Alcohol	T °C (a)	Rate Constants/s^{-1} $10^5 k_{NON}$ (b)	Rate Constants/s^{-1} $10^5 k_{ULT}$ (c)	k_{ULT}/k_{NON}	E_a/kJ mol^{-1} ULT	E_a/kJ mol^{-1} NON (d)
0.089	6.0	63.0	153.0	2.4	69	92
	15.9	238.0	358.0	1.5		
	23.4	645.0	787.0	1.2		
0.144	6.3	25.0	121.0	4.8	30	87
	14.5	74.0	168.0	2.3		
	23.3	217.0	250.0	1.2		
0.207	7.7	7.1	55.6	7.9	19	91
	14.4	17.5	70.4	4.0		
	25.0	68.0	89.6	1.3		
0.281	9.1	2.5	29.8	12.2	approx. zero	93
	15.0	5.5	30.1	5.5		
	24.3	18.6	26.5	1.4		

(a) Temperatures quoted are within ±0.3°C; (b) Interpolated results - Ref.11,12;
(c) Mean of 3 runs reproducibility ±4% ; (d) Value at 25°C - Ref.11,12.

For this study an ultrasonic source developing 120 watts and 20KHz was used. The results at higher temperatures (approx. 25°C) show lower rate enhancements (TABLE) than those previously reported where a different ultrasonic source and method of power input was used[2]. Other workers have also noted variations in rate enhancement with different input powers[10].

Although the results at 25°C show only a small rate enhancement as the solvent composition is varied a remarkable increase in rate enhancement is found for all solvent compositions as the reaction temperature is lowered. This effect is reflected in the calculated E_a values for these solvolyses. The striking feature is the trend in E_a values which fall as the ethanol content of the solvent increases. At 50% ethanol, a composition near to that which yields a maximum in ultrasonic absorption, E_a is close to zero. These results suggest that the energy input via ultrasonic irradiation is sufficient to lower the inherent activation energy for the reaction and further, that the amount by which it is lowered depends upon the solvent composition.

A possible explanation for the observed dependence of E_a values on solvent composition is that ultrasonic disruption of the solvent hydrogen bonded structure allows more solvation of the dipolar transition state with consequent lowering of E_a. Since the degree of solvent disruption (induced by ultrasound) is greatest[6] for the most structured solvent composition ($x_E = 0.3$) the predicted trend for E_a will be that reported (TABLE), with the lowest value for E_a occurring at 50% w/w.

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