THE EFFECT OF ULTRASOUND ON THE SOLVOLYSIS OF 2-CHLORO-2-METHYLPROPANE IN AQUEOUS ETHANOL

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Abstract—Ultrasonic irradiation has been found to accelerate the solvolysis of 2-chloro-2-methylpropane in aqueous ethanol mixtures from 20 to 60% w/w in ethanol at temperatures between 10° and 25°. The effects are more marked at lower temperatures and higher alcohol compositions with a 20 fold rate acceleration occurring at 10° and 60% w/w. The results also lend independent support to two previous observations that (a) the position of maximum in solvent structuredness is 50% w/w and (b) a logarithmic relationship exists between solvent vapour pressure and ultrasonically enhanced rate constant. At solvent compositions of 50 and 60% w/w ethanol the absolute rate of reaction under irradiation increases with decreasing reaction temperature below 20°.

Ultrasonics is the name given to the study of the effects of sound waves having frequencies higher than those to which the human ear can respond (normally greater than 16 kHz). Over the years a wide spectrum of scientific fields have developed uses for ultrasound which range from the medical applications of ultrasonic imaging and physiotherapy to non-destructive testing of metals and echo-ranging. Up to a few years ago the uses of ultrasound in chemistry (sonochemistry) was mainly the domain of the physical and polymer chemist.[1,2] This situation has now changed as chemists of all disciplines have discovered that ultrasound can be used not only for the enhancement of reaction rates but also to optimise yields and even to direct reactions along particular pathways.[3]

The effects of ultrasound on a liquid phase reaction can be ascribed to the phenomenon known as cavitation. As an ultrasonic wave passes through a fluid rapidly fluctuating pressures are set up as a result of the alternate period of compression and rarefaction associated with the wave. During rarefaction provided that the negative pressure is strong enough to overcome the intermolecular forces bonding the fluid, the fluid is literally torn apart producing small cavities. In the succeeding compression cycle the cavities collapse almost instantaneously with the release of large amounts of energy. It has been estimated that temperatures up to several thousand Kelvin and pressures of several hundred atmospheres may exist in the vicinity of the collapsing "bubble". The applications of sonochemistry rely broadly on three physical consequences of this cavitation:

(a) The well-known cleaning action can be used to activate the surfaces of metal catalysts or reagents.

(b) The contact area between immiscible liquids can be greatly increased by emulsification leading to enhanced reactivity, particularly where phase transfer catalysis is involved.

(c) The energy can be used to aid in the breaking of chemical bonds.

These effects have been exploited mostly in the field of organometallic chemistry under mainly heterogeneous conditions. Improved reactivities have been reported in Wurtz,[4] Bouveault[5] and Barbier[6] type reactions. Much

of this research has been achieved using simple ultrasonic cleaning baths as a source of irradiation but more intense power can be introduced into a system using a sonic probe. This latter method has been adopted in the study of the sonically induced ligand dissociation reactions of metal carbonyls.[7]

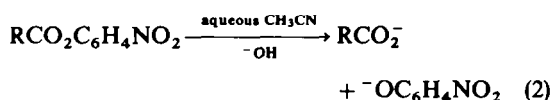## THE EFFECT OF ULTRASOUND ON REACTION RATE

If a chemist wants to alter the reactivity of a system he will normally look to the traditional external physical variables such as heat, light or pressure. By experience he will know the type of change these parameters might induce in his reaction. The effect of ultrasound however is not so well established. One of the fundamental questions in sonochemistry is to what extent is the effect of ultrasound controllable, i.e. is there a relationship between power and frequency input, reaction temperature and solvent composition? There are of course several variables in any relationship of this type but few research groups have applied themselves to the problem.

In 1974 Couppis and Klinzing reported the effects of ultrasonic irradiation on the rates of hydrolysis of methyl ethanoate as a function of reaction temperature (Eq. 1).[8] The rate enhancements induced by irradiating the system at 540 kHz over a range of temperatures were found to fall from 28% (at 20°) to 20% (at 30°). The inverse relationship between ultrasonically induced rate acceleration and reaction temperature which they reported has been related to solvent vapour pressure in that as the solvent volatility is reduced, the intensity of cavitational collapse, the maximum temperature reached and the rate of reaction all increase.[7]

$$CH_3CO_2Me \xrightarrow[\text{acetone}]{\text{aqueous}} CH_3CO_2H + CH_3OH \quad (1)$$
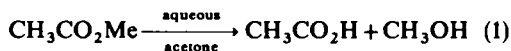
More recently Kristol has reported the ultrasonically induced rate enhancements for the hydrolysis of 4-nitrophenyl esters of a number of aliphatic carboxylic acids (Eq. 2).[9] The rate enhancements at 35° were all in the range of 14–15% and were independent of the alkyl substituent (R) on the carboxylic acid. The authors concluded that the rate enhancements were not due

simply to an increase in the macro reaction temperatures (due to an ultrasonic heating effect) since there are large differences in E_A for the hydrolyses of these substrates and thus considerable variation in rate enhancements would be anticipated from simple heating effects.

$$RCO_2C_6H_4NO_2 \xrightarrow[-OH]{\text{aqueous } CH_3CN} RCO_2^-$$

$$+ \ ^-OC_6H_4NO_2 \quad (2)$$

Our own studies have been centred on the effect of ultrasound on the hydrolysis of 2-chloro-2-methylpropane in aqueous alcohol. The system was chosen since for many years this reaction has been taken to be a classic example of a reaction proceeding through an S_N1 pathway[10,11] and, in addition, the structure of binary aqueous alcohol mixtures has been the subject of a number of studies.[12]

$$R-X \underset{\text{slow}}{\overset{}{\rightleftharpoons}} R^+ + X^- \xrightarrow{\text{fast}} \text{products} \quad (3)$$
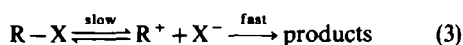
The rate determining step for an S_N1 solvolysis reaction is ionisation of the covalent starting material to the free carbocation (or ion-pair) intermediate (Eq. 3). The energy requirement for this step of the reaction will be dependent upon the degree of solvation (stabilisation) of the transition state leading to ionisation. Since solvation involves the restructuring of solvent around this transition state it might be expected that ultrasonic disruption of structure within the bulk solvent would greatly influence the reaction rate and perhaps give more information on this type of reaction.

RESULTS AND DISCUSSION

The initial results of this work were most encouraging,[13,14] in that not only did ultrasonic irradiation enhance the rate of solvolysis, but the enhancement became larger as the mole fraction of ethanol was increased. These first results were obtained using an ultrasonic cleaning bath at constant temperature and the rate enhancements observed were not very large (~ 2). However, in subsequent studies we have used a cup-horn device (see below) which provides more efficient power transmissions and temperature control and has resulted in much larger rate enhancements.[15,16]

The results in Table 1 show the effect of ultrasonic irradiation on the solvolysis reaction with respect to variations in the solvent composition and reaction temperature.

Although the reaction temperatures for individual ultrasonically irradiated kinetic runs could be held to within $\pm 0.2°$ it proved impossible to reproduce precise temperatures for each. As a result of this the results quoted in Table 1 represent interpolations of the rate constant based upon a number of results obtained close to that temperature.

(a) *The effect of solvent composition.* Whilst crossing the composition range from pure water to pure ethanol, the structural order passes from that of a three dimensional system to that of a two dimensional system. Although a continuous breakdown of structure might have been expected, a careful consideration of a number of properties of the binary liquid mixture, for example, the viscosity or the excess enthalpy of mixing,[12] has shown the existence of a structurally critical region.

As ethanol is added to water, the water acts as host to the alcohol molecules and the structural order of the water increases until a critical region of maximum structure is reached (0.3 mol fraction of alcohol). According to Franke and Ives[12] there is little doubt that this structural enhancement derives from the replacement of some water–water H-bonds by strong hydrogen bonding between water and the hydroxyl groups of the alcohol. With increasing concentration of ethanol, the water can no longer accommodate the alcohol molecules and depolymerisation of the three dimensional structure of water occurs.

Although a sound wave is not electromagnetic it is attenuated when it passes through a fluid since some of the sound energy is absorbed. It is possible to estimate a

Table 1. Ultrasonic (k_{ULT}) and non-ultrasonic (k_{NON}) rate constants for the solvolysis of 2-chloro-2-methylpropane in aqueous ethanolic solvents at different temperatures

% w/w ethanol in water	Rate constant $\times 10^5$	Temp (°)			
		10	15	20	25
20	k_{ULT}	220.0 ± 10.0	338.0 ± 4.0	570.0 ± 15.0	995.0 ± 5.0
	k_{NON}	128.0 ± 3.0	248.0 ± 1.5	469.0 ± 5.0	839.0 ± 4.0
	ratio	1.72 ± 0.12	1.36 ± 0.02	1.22 ± 0.05	1.19 ± 0.01
30	k_{ULT}	135.0 ± 10.0	157.0 ± 5.0	211.0 ± 5.0	340.0 ± 10.0
	k_{NON}	44.7 ± 1.0	88.0 ± 2.0	160.0 ± 3.8	280.0 ± 8.0
	ratio	3.02 ± 0.30	1.78 ± 0.10	1.32 ± 0.06	1.21 ± 0.07
40	k_{ULT}	57.4 ± 0.5	65.3 ± 0.4	70.9 ± 1.0	74.3 ± 0.5
	k_{NON}	10.4 ± 0.3	19.8 ± 0.3	38.8 ± 1.4	64.7 ± 1.1
	ratio	5.52 ± 0.21	3.30 ± 0.07	1.83 ± 0.10	1.15 ± 0.03
50	k_{ULT}	38.8 ± 2.0	32.0 ± 2.0	27.5 ± 2.0	31.6 ± 2.0
	k_{NON}	3.08 ± 0.07	5.86 ± 0.10	10.8 ± 0.2	20.0 ± 0.4
	ratio	12.60 ± 0.96	5.46 ± 0.44	2.55 ± 0.24	1.58 ± 0.14
60	k_{ULT}	17.2 ± 0.2	12.2 ± 0.4	8.2 ± 0.5	11.4 ± 0.2
	k_{NON}	0.86 ± 0.03	1.79 ± 0.01	3.50 ± 0.03	6.78 ± 0.07
	ratio	20.0 ± 0.96	6.82 ± 0.26	2.34 ± 0.16	1.68 ± 0.03

factor known as the excess sound absorption for the fluid as the difference between the measured and calculated attenuation of the ultrasound wave. When the excess sound absorption for a series of aqueous mixtures are plotted against the mole fraction of ethanol, the plot passes through a maximum at approximately 0.30 ($\sim 50\%$ w/w).[17] It has been argued that this maximum may be taken to be the point of maximum rigidity of structuredness of the solvent mixture.

For the solvolysis of 2-chloro-2-methylpropane the relationship between ultrasonic acceleration (k_{ULT}/k_{NON}) and solvent composition is shown in Fig. 1 from which it is immediately apparent that at 20° there is a maximum in rate acceleration at about 50% w/w. While no actual maximum is present at lower temperatures there is nevertheless a point of inflexion on each curve at around 50% w/w. At 25° the ultrasonic enhancement is not large enough to allow any corresponding observation to be made.

Ultrasonic irradiation can be thought of as a structure breaker by virtue of its ability to disrupt H-bonding. The application of ultrasonic irradiation to the reaction would, by disrupting the binary solvent structure, permit easier solvation and result in enhanced rates of reaction. The rate enhancement would be expected to increase with increase in solvent structure and this appears to be borne out by the experimental results—particularly those at 20°.

These results are also consistent with a more recent proposal that the solvolysis of 2-chloro-2-methylpropane may not follow a pure S_N1 mechanism but rather an S_N2 (intermediate) mechanism.[18] Such a mechanism entails the formation of a weakly

nucleophilic solvated ion-pair in the rate determining step. If the solvolysis is assisted by weak nucleophilic solvation of the ion-pair then this assistance must depend to some extent on the ability of the solvent to re-organize its bulk structure and solvate the incipient carbocation. Such solvation could thus be considered to be inversely related to the structuredness of the binary solvent in the same way as in the classical S_N1 process. It is because of this similarity however that our results cannot be used to distinguish between these two mechanisms.

(b) *The effect of solvent vapour pressure.* From Table 1 it can be seen that the acceleration in rate induced by ultrasonic irradiation increases as the reaction temperature is reduced and further that this effect is more marked in the more alcoholic media. For both 50 and 60% compositions the sonicated rate constants actually increase as the temperature is reduced below 20°. This observation is similar to that reported by Suslick in his study of the sonochemistry of alkanes, these reactions also had the curious property of increasing rates with decreasing ambient temperature.[19] This he ascribed to differences in the solvent vapour pressures of the systems under investigation. Assuming that sonochemical reactions follow Arrhenius behaviour, a relationship between reaction rate constant (k) and solvent vapour pressure (P_v) was derived from simple hydrodynamic models (Eq. 4) in which T_0 is the ambient temperature, P_a is the acoustic pressure at initiation of bubble collapse and γ is the ratio of specific heats.

$$\ln k = \ln A - \frac{E_a}{R T_0 P_a (\gamma - 1)} \cdot P_v \qquad (4)$$

Suslick found that even though this equation can be taken as only a rough approximation nevertheless a reasonable correlation of $\ln k$ with P_v was found for a number of different alkanes.

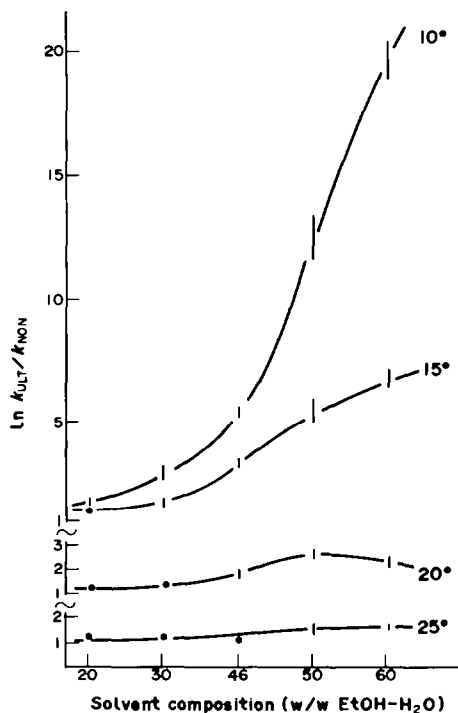The results for the present system have been presented in a similar manner (Fig. 2). As may be seen,

Fig. 1. Rate enhancements induced by ultrasonic irradiation (k_{ULT}/k_{NON}) for various solvent compositions at different temperatures.

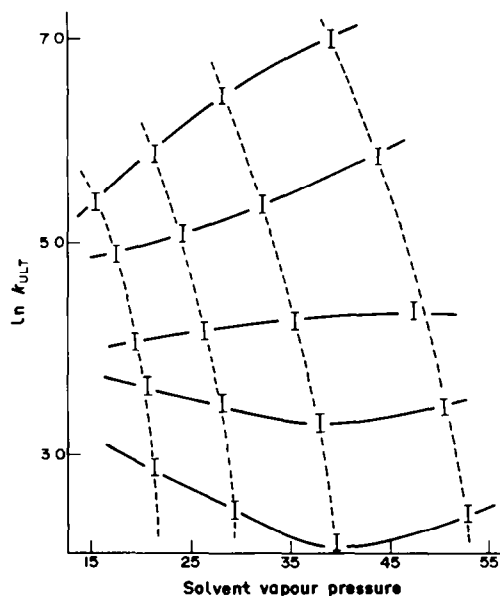Fig. 2. The relationship between ultrasonically enhanced rate constant and solvent vapour pressure.
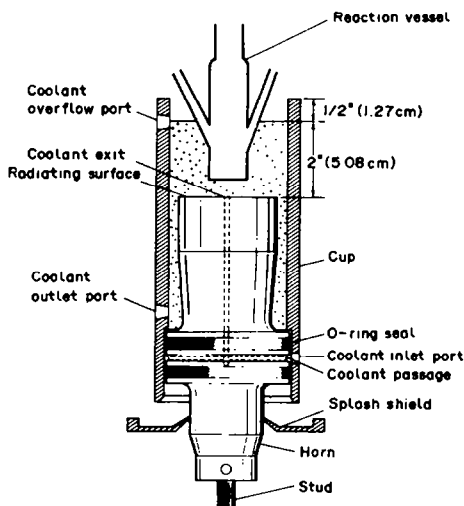
Fig. 3. Cup-horn.

Each solvolysis was followed conductometrically employing bright Pt electrodes (cell constant *ca* 1.0). The conductance cell (capacity *ca* 20 cm^3) was fitted with two side arms, one to allow rapid injection of 15 μl of a 10% solution of the chloroalkane in EtOH, the other to allow insertion of a chrome–alumel thermocouple. The cell contents were agitated continuously using a mechanically driven polypropene stirrer. For the irradiated samples the conductance cell was immersed in a cup-horn device (Fig. 3) attached to a Heat-Systems Ultrasonic, Inc., Model W-225R generator, operating at 60% of maximum power (max ~200 W) at 20 kHz. The reaction temperature was maintained at $\pm 0.2°$ by circulating water, from a thermostatted reservoir, through the cup-horn.

The solvolyses followed first order kinetics to at least 70% reaction.

two correlations are apparent. The more vertical lines (----) represent the relationship ln k_{ULT} vs P_v at constant temperature[20] (variable composition), whilst the more horizontal lines (——) represent the relationship at constant composition (variable temperature).

(1) *Constant temperature—variable composition.* The plots of ln k_{ULT} vs P_v yield approximately parallel lines at all four temperatures. Provided P_a and γ (Eq. 4) can be assumed to be constant over the temperature range employed (15°), the slope of the lines will be proportional to E_a/T_0. Further since T_0 is effectively constant (273 to 298, 5% change), E_a can be taken to be independent of the temperature; the fundamental assumption of the Arrhenius equation.

(2) *Constant composition—variable temperature.* Assuming, as above, that P_a, γ and T_0 are effectively constant, the slopes of the lines are again proportional to E_a. In this case, however, the lines are not parallel, their slopes decrease in magnitude with increase in ethanol content. This suggests the effect of ultrasound increases (lowering of E_a) as the alcohol content of the mixture increases, and corroborates the evidence shown in Fig. 1. The initial lines for both 50 and 60% composition follow the same trend as above with each of the slopes being negative. At about 20° however there is a change to a positive slope in each case.

The minimum obtained suggest that for both of these compositions the maximum effect of ultrasonic irradiation can only be achieved at temperatures below 20°.

EXPERIMENTAL

2-Chloro-2-methylpropane was freshly distilled before use. The binary aqueous mixtures were prepared by mass from absolute alcohol and conductance water.

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