An Observation of the Effect of Ultrasonic Power on the Rates of Initiation and Polymerisation of *N*-Vinylcarbazole in Benzene

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Ultrasonic irradiation of *N*-vinylcarbazole in benzene, initiated by 2,2-azobis(isobutyronitrile), has revealed an optimum power for the rate of decomposition of both the solvent and the initiator, and also for the polymerisation of the monomer.

For many chemical reactions the application of high-power ultrasound has led to substantial improvements in both the reaction rate and yield. In general, the reactions may be divided into two groups. (*a*) Those which take place normally but are accelerated by ultrasound.[1-5] (*b*) Those which would not take place unless irradiated with ultrasound.[6-13]

Although the precise nature by which ultrasound enhances the rate of a reaction has not yet been fully resolved, the general conclusion is that it is the result of cavitation and as such must be the consequence of one, or more, of the following. (*a*) Reaction in the cavitation bubble within which there are high temperatures and pressures during collapse. (*b*)

Reaction at the gas–liquid interface between bubble and bulk liquid. (*c*) Reaction in the bulk liquid surrounding the bubble as a result of the enormous shear forces generated by bubble collapse.

Estimates[14–16] of the maximum temperature (T_{max}) and pressure (P_{max}) within a bubble, just prior to collapse, have been made using eqns. 1 and 2.

$$T_{max} = \frac{T_0 P_m(\gamma - 1)}{P_{vg}} \qquad (1)$$

$$P_{max} = P_{vg}\left[\frac{P_m(\gamma - 1)}{P_{vg}}\right]^{\gamma/(\gamma - 1)} \qquad (2)$$

Where T_0 is the ambient (experimental) temperature, γ is the ratio of specific heats of the gas–vapour mixture, P_{vg} is the pressure in the bubble at its maximum size, usually assumed to be equal to the vapour pressure of the liquid and P_m is the pressure in the liquid at the start of collapse. For a bubble containing nitrogen, in water at 20 °C and ambient pressure, the maximum temperature and pressure can be deduced to be 4200 K and 975 bar (1 bar = 10^5 Pa), respectively.

Of the many investigations into the effect of ultrasound on reacting systems, very few have reported any detailed kinetic study on the effect of irradiation intensity. Most have considered the effect of solvent vapour pressure, P_v. In this communication we report the effect of ultrasonic intensity on the free radical solution polymerisation of *N*-vinylcarbazole (NVC) initiated by 2,2-azobis(isobutyronitrile) (AIBN). We have chosen this particular monomer–initiator combination since both components have melting points above the experimental temperatures employed. This means that there will be very little chance of vapour from either material entering into the cavitation bubbles. Although it would have possible to use more conventional monomers, *e.g.* styrene or methyl methacrylate, both have the following properties: (*a*) Both monomers possess sufficiently high vapour pressures (40 and 179 kPa respectively at 60 °C) to allow entry into the cavitation bubble, where as with benzene (P_v = 308 kPa) they will be subject to pyrolysis temperatures. (*b*) The monomers are reported[17] to undergo thermal polymerisation even in the absence of an initiator.

In an attempt to assess the contribution of each component to the overall rate, we have also studied separately the ultrasonically induced decomposition of the solvent (benzene) and the initiator dissolved in benzene (Fig. 1).

The decomposition of the solvent (25 cm^3) was monitored by irradiating in the presence of the radical scavenger diphenyl picrylhydracyl (DPPH, ~1 × 10^{-4} mol dm^{-3}) and periodically determining the residual DPPH by UV spectroscopy (Shimadzu UV-240, λ_{max} = 525 nm). The decomposition of the initiator (0.1 mol dm^{-3}) was monitored by HPLC (LKB 2140) with UV detection (λ = 340 nm). The variation in monomer (and polymer) concentration was monitored by GPC analysis. For all investigations the sonic energy was supplied by a Heat Systems generator (W375) operating at 20 kHz, and introduced to the system using a titanium horn (end diameter 3.34 mm). All reactions were conducted at constant temperature in a rosette cell immersed in a thermostatted bath.† The reaction temperatures were monitored using a chrome–alumel thermocouple placed in the rosett cell. All input powers were determined calorimetrically.

Fig. 1 shows the effect of increased intensity on the breakdown of the solvent (*a*) and the initiator (*b*), together with the variation in the initial rate of polymerisation of the monomer (*c*). For all three systems there exists a maximum with respect to the ultrasonic intensity. The explanation offered for the observation of similar power maxima in other sonochemically enhanced systems has invoked the formation of a 'bubble-shield' which reduces the power input to the reaction. According to this rationale the increase in concentration of cavitation bubbles, and consequent increase in sonochemical effect, will rise with power input up to a point where the number of bubbles is so great that they act as a sound deadening shield around the sonic source thus leading to a decrease in the net sonic effect with increased energy input.

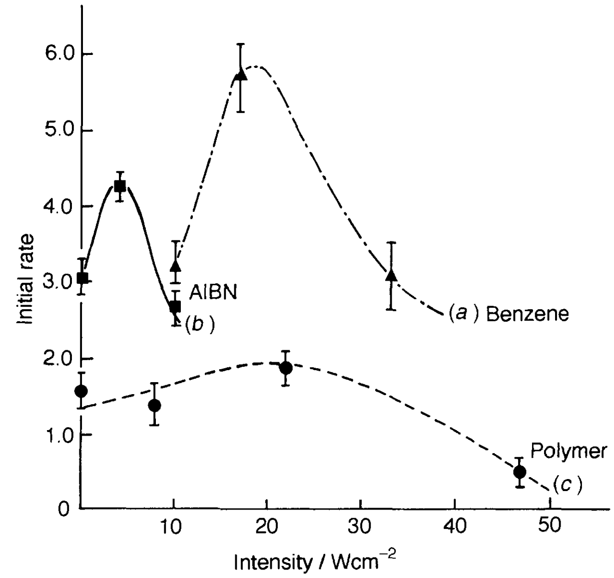

Fig. 1 The effect of ultrasonic intensity on the initial rates at 60 °C of: (*a*) decomposition of benzene (▲) – rate/10^{-6} mol dm^{-3} h^{-1}; (*b*) decomposition of AIBN (■) – rate/10^{-3} mol dm^{-3} h^{-1}; (*c*) polymerisation of NVC (●) – rate/mol dm^{-3} h^{-1}

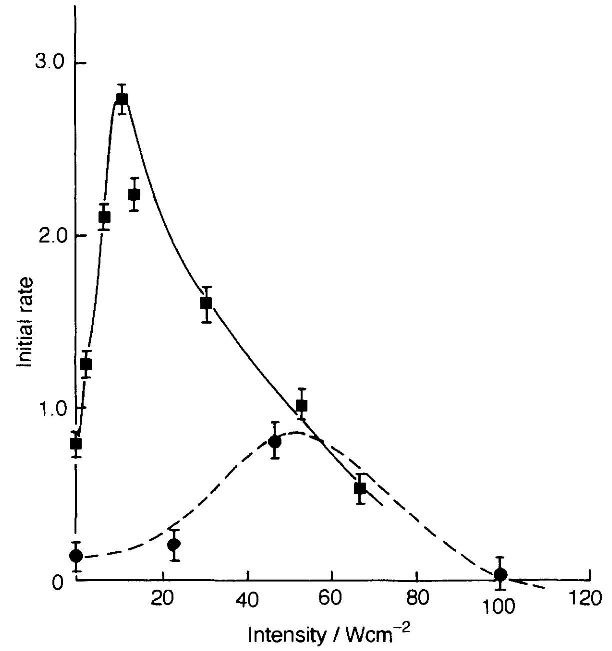

Fig. 2 The effect of ultrasonic intensity on the initial rates at 50 °C of: (*a*) decomposition of AIBN (■) – rate/10^{-3} mol dm^{-3} h^{-1}; (*b*) polymerisation of NVC (●) – rate/mol dm^{-3} h^{-1}

Whilst acknowledging that the above hypothesis has the advantage of simplicity, we report here an alternative explanation for the non-linear dependence of rate with applied

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† The thermostat bath was held at 2–6 °C below the required reaction temperature to compensate for the temperature rises resulting from sonication.

intensity. The explanation is based upon the following experimental observations.

First, in all experimental runs we have determined calorimetrically the energy inputs to the system at the various instrument settings. It is difficult, therefore, to envisage a reduction in power as a result of bubble formation with an increase in instrument setting.

Secondly, both the rate of polymerisation and the rate of initiator breakdown were found to be lower at the highest experimental intensity than they were *in the absence of ultrasound, i.e.* ultrasound slowed the reactions. This observation was also confirmed at 50 °C (Fig. 2). In fact at the lower temperature it proved impossible to produce any detectable polymer over a 2 h period, at the highest sonic intensity (100 $\mathrm{W cm^{-2}}$). On switching off the ultrasound, the polymerisation proceeded at the normal thermal rate. Again, it is difficult to rationalise these observations in terms of 'bubble-shielding' since at best it would be expected that the rate in the presence of high intensity ultrasouned would be similar to that observed conventionally, *i.e.* in the complete absence of ultrasound.

Most sonochemists would argue that the initial increases in reactivity with increased intensity (I) are as a result of the increase in P_m [eqn. (3)], which in turn increases the temperature and pressure associated with a bubble and its immediate environment [eqns. (1 and 2)]

$$P_m = \text{Hydrostatic pressure} + (2\rho c I)^{1/2} \tag{3}$$

where ρ is the density of the medium and c is the velocity of sound in the medium.

Whilst acknowledging that an increase in the temperature of the bubble will lead to an increase in both the rate of solvent and initiator breakdown (conventional Arrhenius behaviour), it is important to recognise that both systems should possess positive volumes of activation ($\Delta V^{\ddagger} \sim 10\ \mathrm{cm^3\ mol^{-1}}$) since they require bond extension[18] and subsequent bond breakage to produce radical species. This will result in a decrease in the reaction rate with an increase in acoustic pressure (*i.e.* ultrasonic intensity). The observed variation in rate with intensity will be a subtle balance of the two effects.

Since the rate of any free radical polymerisation reaction (R_p) depends upon the concentration of radical species present, the above variations in the rates of radical production ought to be reflected in the R_p *vs.* I curves (Figs. 1 and 2). The variation in rate with intensity however will be more complex than that observed for either the solvent, or the initiator and solvent. For example, propagation is a process which involves bond formation and as such will possess a negative value for the volume of activation[18] ($\Delta V^{\ddagger} \sim -20\ \mathrm{cm^3\ mol^{-1}}$). Hence, it is expected that the rate of polymerisation will increase with increasing acoustic intensity. However, such a conclusion is only valid if the reactant concentrations (here monomer and radical) remain constant. The shape of the R_p *vs.* I curve, and the position of the maximum, reflect the contributions from radical production and the enhancement of the polymerisation rate as functions of the ultrasonic intensity.

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