

# Sonochemistry in non-aqueous liquids

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The chemical effects of high-intensity ultrasound on organic liquids are reported. In order to probe the factors which affect sonochemistry in non-aqueous solvents, two very different chemical dosimeters have been used: radical trapping by diphenylpicrylhydrazyl and decomposition of  $\text{Fe}(\text{CO})_5$ . In both cases, good correlation is found between the logarithm of the sonochemical rate and the solvent vapour pressure. This result is justifiable in terms of the cavitation 'hot-spot' mechanism of sonochemistry. Thus, decreasing solvent vapour pressure increases the intensity of cavitation collapse, the peak temperature reached during such collapse, and, consequently, the rates of sonochemical reactions.

**KEYWORDS:** ultrasonics, cavitation, vapour pressure, organic liquids, dosimetry

## Introduction

The chemical effects of high-intensity ultrasound have been extensively studied only in aqueous solutions<sup>1-5</sup>. The origin of such sonochemistry is acoustic cavitation: the creation, growth and implosive collapse of gas vacuoles in solution by the sound field. This collapse generates transient hot-spots with local temperatures and pressures of several thousand K and hundreds of atmospheres<sup>6-8</sup>. Although the first observation of sonochemistry dates back 50 years<sup>1-4</sup>, very few reports of the effects of ultrasound on non-aqueous liquids exist<sup>9-13</sup>. A resurgence of interest in the chemical uses of ultrasound in homogeneous<sup>14-28</sup> and heterogeneous<sup>29-43</sup> systems may be noted. Much of this recent work involves non-aqueous solvents, but no systematic study of the *chemical* effects of ultrasound on these has been made. The only surveys of cavitation in non-aqueous solvents have monitored either white noise emission<sup>11</sup> or sonoluminescence<sup>12</sup>. Neither of these techniques, however, is a direct probe of the chemistry occurring during acoustic cavitation.

We wish to report here the first studies of the sonochemistry of and in non-aqueous solvents. We find that organic liquids do support acoustic cavitation and associated sonochemistry and that the peak temperatures reached in such cavities are controlled by the vapour pressure of the solvent.

## Experimental section

All ultrasonic irradiations were made with a collimated 20 kHz beam from a titanium amplifying horn (1 cm in diameter at its radiating surface) driven by a lead zirconate titanate transducer (Heat-Systems Ultrasonics, model W-375P), with total acoustic power 40 to 300 W and acoustic intensities 40 to 300  $\text{W cm}^{-2}$  at the horn's surface. Reactions were performed in a glass sonication cell under an Ar atmosphere, as

described in detail elsewhere<sup>14,16</sup>. With direct immersion of the horn in the solution, the effects of solvent height in the sonication vessel were negligible.

The reaction zone can be defined by dosimetry studies as a function of vessel shape and solvent volume. It is a cylindrical volume of 1 cm diameter extending from the horn's surface for  $\sim 3$  cm, and is independent of vessel shape. Erosion of the horn was negligible in these experiments and good reproducibility was found from three different transducers and power supplies.

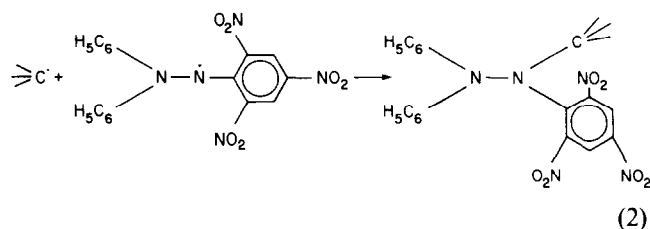
Two different dosimeters were utilized in these studies. The bleaching of 2,2-diphenyl-1-picrylhydrazyl (DPPH) was monitored on a Hitachi 100-80 UV-vis spectrophotometer (2 nm resolution,  $\pm 0.001$  OD photometric repeatability) for the absorption band at 512 nm. The extinction coefficient of this band is slightly solvent-dependent<sup>44,45</sup> (total range  $1.00 \times 10^4$  to  $1.70 \times 10^4$   $\text{M}^{-1} \text{cm}^{-1}$ ) and was determined with an accuracy of 2%. The DPPH, from Aldrich Chemicals, was multiply recrystallized, vacuum dried, and stored under Ar, in the dark, at  $-20^\circ$ . Solutions were prepared immediately before use from solvents of the highest available purity (99+%, gold label, spectrophotometric grade). Care was taken to thoroughly filter the DPPH solutions to remove small amounts of undissolved solid which upon sonication would give erroneous dosimetry results. The second dosimeter, the sonochemical decomposition of  $\text{Fe}(\text{CO})_5$ , was monitored by Fourier transform infra-red spectrophotometry (Nicolet 7199 or MX-5), as described in detail elsewhere<sup>14-16</sup>. Iron pentacarbonyl was purchased from Alpha Chemicals, filtered or distilled immediately prior to use, and protected from light.

## Results and discussion

Two chemical dosimeters were examined in non-aqueous solvents in order to gain further insight into the factors affecting acoustic cavitation: the bleaching of diphenylpicrylhydrazyl (DPPH) and the decomposition of  $\text{Fe}(\text{CO})_5$ . DPPH is a well studied stable free radical and has been extensively used as a radical trap

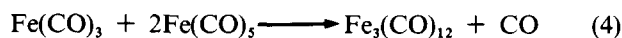
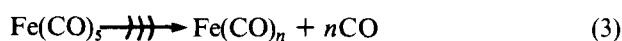
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even in sonochemical reactions<sup>15,26,45</sup>. This dosimeter functions as a measure of the radical species produced from sonolysis of the solvent:



As such, the trapping of radicals by DPPH, as in (2) has some dependence on the specific chemical reactivity of the solvent (its susceptibility to form radicals and their subsequent stability). Within a single class of solvents (for example alkanes, arenes, alcohols, etc) such variation should be small, but one might expect to see larger differences between one solvent class and the next. The observed data are shown in Table 1.

The second dosimeter, the sonochemical decomposition of  $\text{Fe}(\text{CO})_5$ , has been studied in some detail<sup>14,15</sup>. Its general mechanism is shown in equations (3)–(5), with the observed products of  $\text{Fe}_3(\text{CO})_{12}$  and iron metal.



In this dosimeter, the sonochemistry being monitored is that directly associated with the volatile  $\text{Fe}(\text{CO})_5$  in the cavitation event, and is not a secondary trapping of solvent sonolysis products. The rate of sonochemical

**Table 1. Rate of DPPH trapping in non-aqueous solvents**

Solvent	Vapour pressure <sup>a</sup> [torr]	$-\frac{d[\text{DPPH}]}{dt}$ [ $\mu\text{M min}^{-1}$ ] <sup>b</sup>
Isooctane	16.4	3.37
Decane	0.25	7.75
Decalin	0.20	11.8
Toluene	8.7	2.17
1,3-dimethylbenzene	2.2	7.25
1,3,5-trimethylbenzene	0.53	11.4
1-propanol	4.6	5.43
1-butanol	1.1	6.20
1-pentanol	0.35	6.66
1-hexanol	0.12	7.74
2-butanone	33.1	0.88
2-pentanone	11.3	4.13
2-hexanone	10.1	5.44
Cyclohexanone	1.3	8.91
Di-n-propylether	22.8	1.61
Di-n-butylether	1.9	10.4

<sup>a</sup>vapour pressure calculated from data in Ref. 47

<sup>b</sup>Rates determined after 10 min irradiation at 50 W cm<sup>-2</sup> under Ar at 4°; initial [DPPH] = 2 x 10<sup>-4</sup> M; error limits ±0.08  $\mu\text{M min}^{-1}$

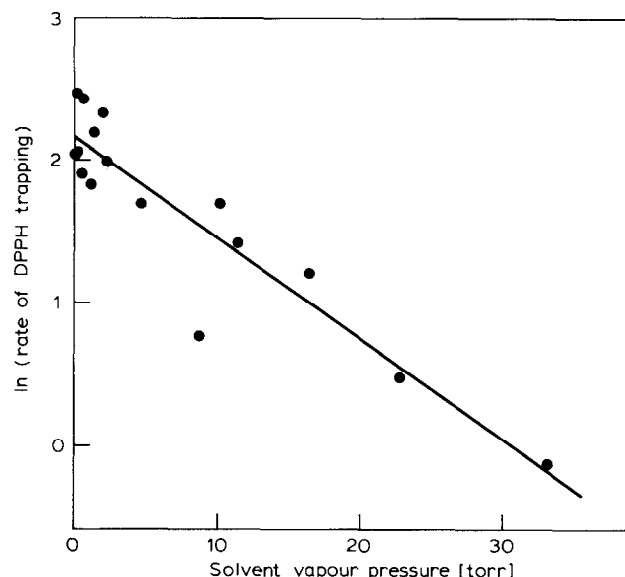


Fig. 1  $\ln(\text{rate of DPPH trapping})$  against solvent vapour pressure. Data given in Table 1

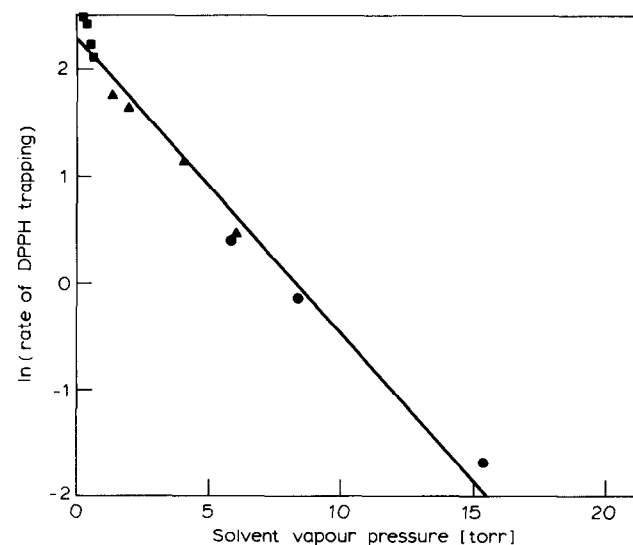


Fig. 2  $\ln(\text{rate of DPPH trapping})$  against alkane solvent system vapour pressure. In order of increasing vapour pressure, ■: decane at 8°, 11°, 13°, 15°; ▲: octane at -10°, -5°, 5°, 11°; ●: heptane at -10°, -5°, 5°. Vapour pressures calculated from data in Ref. 47. Rate in units of  $\mu\text{M min}^{-1}$ , determined after 15 min irradiation at 100 W cm<sup>-2</sup>, under Ar

decomposition of  $\text{Fe}(\text{CO})_5$  is well behaved and first order in  $[\text{Fe}(\text{CO})_5]$  over >3.5 half-lives.

In studying the physical parameters which influence acoustic cavitation in non-aqueous liquids, we find that the vapour pressure dominates the observed rates of sonochemical reactions. We have systematically varied the vapour pressure of these solvent systems in three different ways: by choice of pure solvent, by varying solvent mixtures, or by changing the ambient temperature. With any of these methods and with either of our two dosimeters, we always observe a good linear correlation between the log of the reaction rate with the vapour pressure of the solvent system, as shown in Figs 1, 2, and 3.

This correlation can be predicted from simple hydrodynamic models of the cavitation process. Neppiras<sup>6</sup>, for example, derives the peak temperature generated during collapse of a gas-filled cavity as

$$T_{\max} \approx \frac{T_0 P_a (\gamma - 1)}{Q} \quad (6)$$

where  $T_0$  is the ambient temperature;  $P_a$  the acoustic pressure at initiation of collapse;  $\gamma$  the ratio of specific heats, and  $Q$  the gas pressure in the bubble at initiation of collapse. In the case of vapour filled cavities, we may take  $Q = P_v$ , the vapour pressure of the solvent<sup>6</sup>. If we assume that the sonochemical reactions follow Arrhenius behaviour, as in (7), then the simple relationship between the log of the sonochemical rate with solvent system vapour pressure (8) can be derived

$$\ln k = \ln(A) - E_a/RT_{\max} \quad (7)$$

$$\ln k = \ln(A) - \frac{E_a}{RT_0 P_a (\gamma - 1)} P_v \quad (8)$$

This should be taken as only a rough approximation since it neglects the effects of both the thermal conductivity and the condensation of the vapour during cavitation collapse. Figs 1, 2 and 3 do demonstrate, however, a reasonable correlation of  $\ln k$  with  $P_v$  for very different sonochemical reactions in a wide range of solvent classes and vapour pressures. Considering the variations in bond energies, reactivities, ambient temperature, and colligative properties (surface tension, viscosity, etc), the scatter observed in our data is surprisingly small. In fact, only one solvent in Fig. 1 deviates significantly from (8): toluene. This low rate of DPPH trapping may reflect the facile sonochemical polymerization to which aromatic solvents are prone<sup>10</sup>.

An alternative model of the cavitation collapse has been presented by Sehgal et al,<sup>26</sup> who have shown that the total free energy of cavity formation ( $\Delta\tilde{A}$ ) is related to the vapour pressure ( $P_v$ ) and the ambient pressure ( $P_0$ ) as

$$\Delta\tilde{A} = RT \ln(P_v/P_0) \quad (9)$$

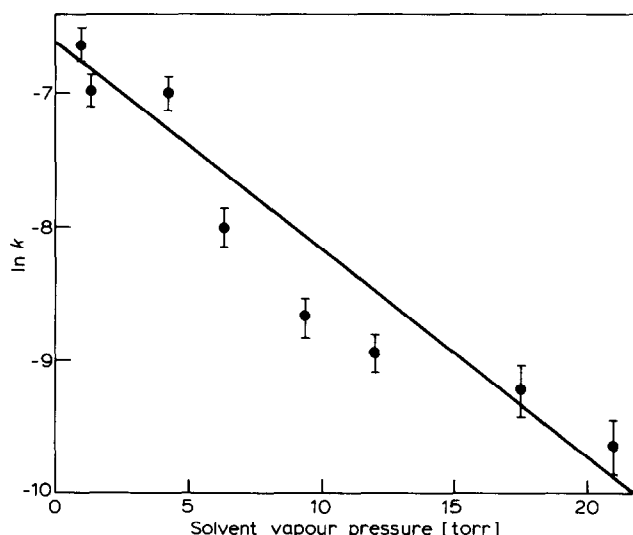


Fig. 3  $\ln(\text{rate of Fe}(\text{CO})_5 \text{ decomposition})$  against solvent vapour pressure at 25°, under Ar. In order of increasing vapour pressure: decalin, decane, nonane, 0.22 mole fraction octane in nonane, 0.52 mole fraction octane in nonane, octane, 0.11 mole fraction heptane in octane, and 0.22 mole fraction heptane in octane. Vapour pressures calculated from data in Ref. 47, assuming ideal solution behaviour.  $d[\text{Fe}(\text{CO})_5]/dt = -k[\text{Fe}(\text{CO})_5]$ , with  $k$  in units of  $\text{s}^{-1}$ . Acoustic intensity was  $80 \text{ W cm}^{-2}$

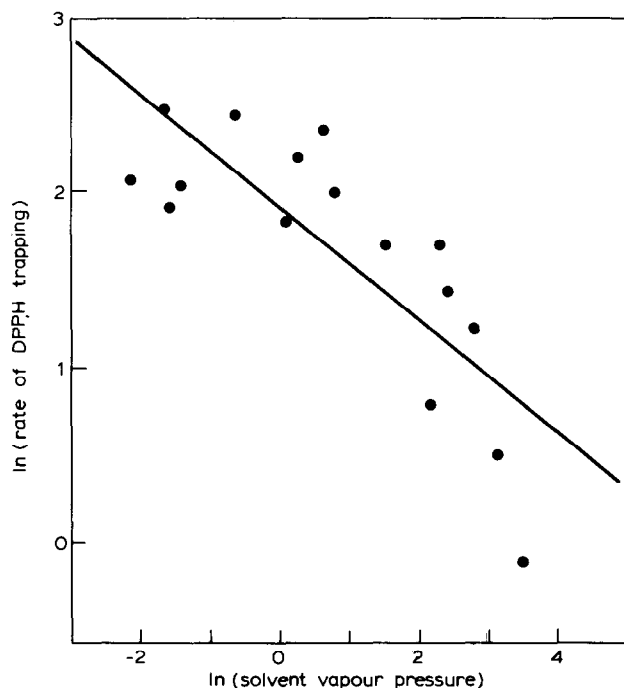


Fig. 4  $\ln(\text{rate of DPPH trapping})$  against  $\ln(\text{solvent vapour pressure})$ . Data given in Table 1

If one assumes that the free energy released during cavitation collapse is related to the free energy of cavity formation, then a correlation between  $\ln k$  and  $\Delta\tilde{A}$  should be found. Qualitatively we find this to be the case over a limited range of vapour pressures. As clearly shown in Fig. 4, however, the correlation of the  $\ln(\text{sonochemical rate})$  with  $\Delta\tilde{A}$  or  $\ln P_v$  does not hold over an extended range.

Other correlations which have been suggested are difficult to justify as more than *ad hoc* empirical fittings. Jarman for example, did fit sonoluminescent intensities to  $\alpha^2/P_v$ , where  $\alpha$  is the surface tension<sup>13</sup>. This relationship does not hold for our chemical dosimeters. Golubnichii, using semiquantitative sonoluminescent data, suggested<sup>12</sup> a correlation of intensities with a 'free molecular interaction energy', which went as  $RT \ln(RT/P_v V_m) - RT$  where  $V_m$  is the molar volume. The authors note, however, that their solvent purities are dubious, which makes this data of limited quantitative value. Furthermore, this correlation does not fit our present data. Niemczewski's white noise studies showed no discernible correlation with any chemical or physical property<sup>11</sup>; clearly, white noise is not a good measure of the chemical effects of cavitation.

## Conclusion

Thus we have demonstrated a facile means to control the conditions generated during acoustic cavitation: solvent vapour pressure. As one diminishes the solvent volatility, the intensity of cavitation collapse, the maximum temperature reached, and the rate of reaction all increase. The sonochemical reactions examined here, then, have the curious property of *decreasing* rates with increasing ambient temperature, due to the increased solvent vapour pressure. Good correlations are found between  $\log(\text{reaction rate})$  and solvent system vapour pressure. As we have noted elsewhere,<sup>14</sup> the solvent control exerted on sonochemical pathways can be extreme: the change in

vapour pressure from decane to heptane can change relative product yields by a hundredfold for reaction pathways which differ significantly in their activation energies.

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