

Liquid Xenon as a Solvent for E.S.R. Studies

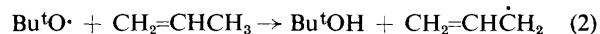
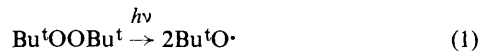
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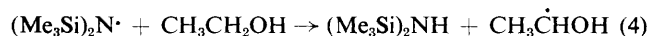
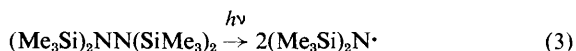
Liquid xenon is a useful inert solvent for e.s.r. studies of reactive free radicals; the *g*-factors of many types of radical are not the same in xenon as in normal solvents.

E.s.r. studies of transient free radicals in fluid solution are often hampered by the lack of a sufficiently unreactive solvent. Rentzepis and Douglass¹ have recently reported the i.r., u.v., and n.m.r. spectra of a number of organic compounds dissolved in liquid xenon and we were prompted to investigate the usefulness of this solvent in our e.s.r. studies. Indeed, many commonly used radical precursors turn out to be relatively soluble in liquid xenon, even at close to its freezing point (161.3 K, the critical temperature is 289.8 K).

For example, a xenon solution containing di-*t*-butyl peroxide (DTBP) and propene (each *ca.* 10% v/v) was homogeneous at 170 K.† When this solution was photolysed with light from a 500 W high-pressure mercury lamp whilst the sample was in the cavity of an e.s.r. spectrometer,² the spectrum of the allyl radical shown in Figure 1a was recorded [equations (1) and (2)].



The general utility of the liquid xenon solvent was established by monitoring a variety of radical reactions using e.s.r. spectroscopy and the systems examined are listed in Table 1. The spectrum of $\text{CH}_3\dot{\text{C}}\text{HOH}$ shown in Figure 1b was obtained during photolysis of a xenon solution containing tetrakis-(trimethylsilyl)hydrazine (TTMH; *ca.* 0.3 M)³ and ethanol [equations (3) and (4)], and the solubility of TTMH (m.p. 290 °C) in xenon is surprisingly high.



† Samples were prepared using a standard vacuum line and were sealed in Suprasil quartz tubes (4 mm o.d., 3 mm i.d.).

Table 1. E.s.r. parameters and sources of radicals studied in liquid xenon and in cyclopropane (Δ) solvents.

Radical	Source ^a	Solvent	T/K	<i>g</i> -Factor ^{b,c}	Hyperfine splittings/ <i>G</i> ^b
Me•	MeI + Bu ₃ SnSnBu ₃ + DTBP ^d	Xe	183	2.0011	22.90 (3H)
		Xe	252	2.0015	22.81 (3H)
		Δ	183	2.0027	22.76 (3H)
		Δ	246	2.0027	22.80 (3H)
Bu ⁿ •	Bu ⁿ Br + Me ₃ SiH + DTBP ^e	Xe	170	2.0026	22.08 (2H _{α}), 29.33 (2H _{β}), 0.74 (2H _{γ})
		Δ	169	2.0027	22.08 (2H _{α}), 29.38 (2H _{β}), 0.74 (2H _{γ})
Bu ^t •	Bu ^t H + DTBP	Xe	205	2.0027	22.74 (9H)
		Δ	205	2.0027	22.77 (9H)
CH ₂ =CH \dot{C} H ₂	CH ₂ =CHCH ₃ + DTBP	Xe	184	2.0032	14.95 (2H), 14.00 (2H), 4.15 (1H)
		Δ	181	2.0027	14.90 (2H), 14.00 (2H), 4.10 (1H)
Ph \dot{C} H ₂	PhCH ₃ + DTBP	Xe	175	2.0037	16.32 (2H _{α}), 5.15 (2H _{β}), 1.78 (2H _{m}), 6.20 (1H _{p})
		Δ	175	2.0027	16.30 (2H _{α}), 5.15 (2H _{β}), 1.78 (2H _{m}), 6.18 (1H _{p})
Me \dot{C} (H)OH	EtOH + TTMH	Xe	205	2.0039	15.72 (1H _{α}), 22.38 (3H _{β}), 1.06 (1H)
		Δ	205	2.0033	15.50 (1H _{α}), 22.29 (3H _{β}), 1.18 (1H)
Me ₂ \dot{C} CN	Me ₂ C(H)CN + DTBP	Xe	204	2.0036	20.55 (6H), 3.35 (1N)
		Δ	204	2.0029	20.63 (6H), 3.38 (1N)
F ₃ C•	CF ₃ I + Bu ₃ SnSnBu ₃ + DTBP	Xe	205	2.0027	143.49 (3F)
		Δ	205	2.0031	143.72 (3F)
Ph \dot{C} =O	PhCHO + DTBP	Xe	205	2.0002	1.18 (2H _{m})
		Δ	205	2.0007	1.20 (2H _{m})
Me ₃ Si•	Me ₃ SiH + DTBP	Xe	205	2.0016	6.33 (9H)
		Δ	205	2.0032	6.32 (9H)
(EtO) ₃ P \dot{O} Bu ^t	(EtO) ₃ P + DTBP	Xe	205	2.0019	891.7 (1P)
		Δ ^f	208	2.0021	889.9 (1P)
Bu ^t Me ₂ Si \dot{N} Bu ^t	Bu ^t Me ₂ Si(Bu ^t)NCl	Xe	194	2.0066	12.55 (1N)
		Δ ^g	194	2.0068	12.5 (1N)
Bu ^t ₂ NO•	Bu ^t ₂ NO ^h	Xe	205	2.0064	15.17 (1N)
		Δ	205	2.0062	15.25 (1N)
Bu ^t OO•	Bu ^t OOH	Xe	205	2.0154	
		Δ	205	2.0152	

^a Samples consisted of *ca.* 50 μ l of each reagent in xenon or cyclopropane (*ca.* 360 μ l). ^b When second-order effects were important [for F₃C•, (EtO)₃P \dot{O} Bu^t, Bu^t•, and Me₂ \dot{C} CN] the e.s.r. parameters were calculated using Preston's program ESRLSQ (see D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975). Hyperfine splittings are considered accurate to ± 0.05 G and *g*-factors to ± 0.00005 . ^c In xenon, the *g*-factors of some radicals were temperature dependent. ^d MeBr + Me₃SiH + DTBP gave similar results. ^e Bu₃P + DTBP gave similar results. ^f Data from B. P. Roberts and K. Singh, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1549. ^g Data from J. C. Brand, M. D. Cook, A. J. Price, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1982, 151. ^h Concentration *ca.* 1×10^{-4} M in xenon or in cyclopropane.

No spectra attributable to discrete xenon-containing radicals of the type [XeX] \dot{X} (*cf.* ref. 4 Xe⁻F) were obtained in this work.† The hyperfine splittings of all the radicals studied were very close to the values observed in hydrocarbon solvents (see Table 1); no additional splittings due to ^{129/131}Xe were observed and, generally, line widths were similar in xenon or cyclopropane. However, we note that small splittings⁵ from

neighbouring xenon molecules could well be lost as a result of rapid solvent exchange processes.

In contrast, the *g*-factors of many radicals were not the same in xenon as in cyclopropane (see Table 1). The effect is clearly evident in Figure 2, which shows the spectra of methyl and n-butyl radicals generated simultaneously in xenon, since the *g*-factors of these two alkyl radicals are almost identical in normal solvents. The *g*-shifts do not necessarily imply a much greater radical-solvent interaction energy in xenon than in cyclopropane, but are undoubtedly a consequence of the very large spin-orbit coupling constant (ζ) for Xe-5p electrons compared with ζ for p-electrons in the much lighter atoms of which 'normal' solvents are composed. Our preliminary qualitative explanation of this effect follows closely the analysis

† Poorly defined spectra centred at *g ca.* 2.003 were observed during photolysis of DTBP or TTMH alone in xenon. The radicals responsible probably arise from attack on the parent peroxide or hydrazine.

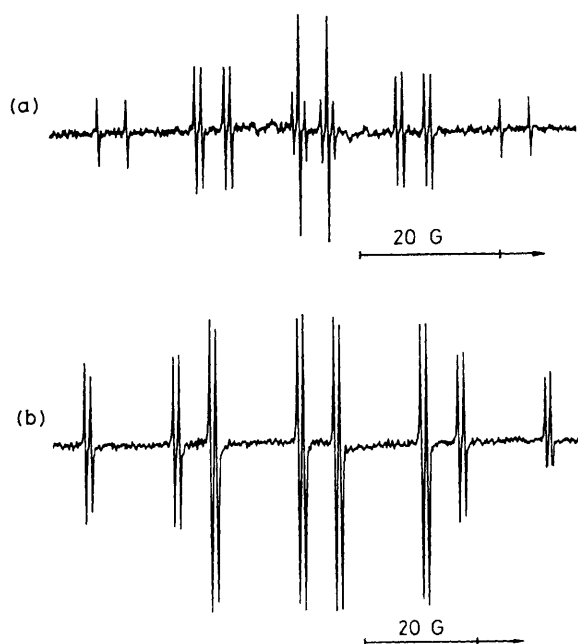


Figure 1. (a) E.s.r. spectrum of the allyl radical in xenon at 192 K. (b) E.s.r. spectrum of the 1-hydroxyethyl radical in xenon at 204 K.

given by Morton *et al.*⁶ of the g -shifts shown by hydrogen atoms in rigid krypton and xenon matrices at 10 K. The deviation from the free-spin value ($\Delta g = g - g_e$) was explained in terms of an 'overlap' interaction (resulting from violation of the Pauli exclusion principle) and a charge transfer interaction {represented by a contribution from the canonical structure $[\text{Xe}^{+\cdot}:\text{H}^-]$ which result in negative and positive contributions, respectively, to Δg .⁶

Within the van der Waals solvent matrix, a solute radical X^\cdot will be held in close proximity to xenon atoms, leading to admixture of Xe-5p character into the SOMO and into the unoccupied molecular orbitals of X^\cdot . The overlap contribution to the g -factor (g_{Xe}) of X^\cdot in xenon will depend upon the ease of excitation of the unpaired electron into unoccupied orbitals of X^\cdot and upon the extent of overlap between the SOMO and Xe-5p orbitals. The charge transfer contribution to g_{Xe} will depend upon the electron affinity of X^\cdot and the coulombic stabilisation of $[\text{Xe}^{+\cdot}:\text{X}^-]$. The difference between g_{Xe} and $g_{\text{cyclopropane}}$ would be expected to be a complex function of the structure and electronic configuration of X^\cdot but, nevertheless, some general patterns are discernible.

For the σ -radicals F_3C^\cdot , $\text{Me}_3\text{Si}^\cdot$, and $\text{Ph}\dot{\text{C}}=\text{O}$ the SOMO is relatively localised and spin-orbit interactions which mix the SOMO with excited unoccupied-orbital states are already important in determining $g_{\text{cyclopropane}}$. For these radicals SOMO-(Xe-5p) overlap is relatively large, electron excitation costs relatively little energy and, consequently, the overlap interaction is dominant, leading to $g_{\text{Xe}} < g_{\text{cyclopropane}}$.

Radicals of low electron affinity with more remote unoccupied orbitals, such as the simple alkyl radicals (except Me^\cdot) show $g_{\text{Xe}} = \text{ca. } g_{\text{cyclopropane}}$, since neither overlap nor charge-transfer interactions are significant. However, radicals with higher electron affinities, such as $\text{CH}_2=\dot{\text{C}}\text{H}_2$, $\text{Ph}\dot{\text{C}}\text{H}_2$, and $\text{Me}_2\dot{\text{C}}\text{CN}$, show $g_{\text{Xe}} > g_{\text{cyclopropane}}$. Now the charge-transfer interaction is dominant, because of the greater importance of contributions from $[\text{Xe}^{+\cdot}:\text{X}^-]$ and the rela-

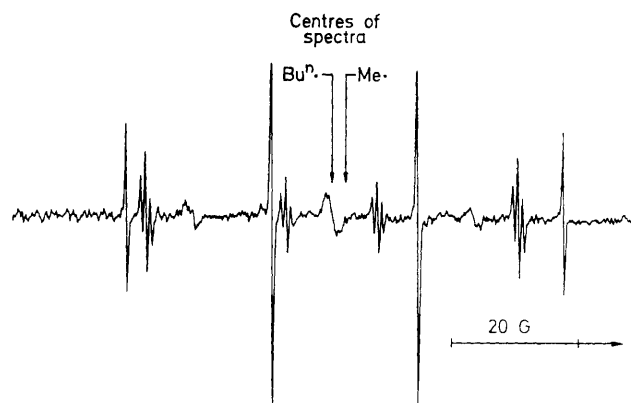


Figure 2. E.s.r. spectra of the methyl and n-butyl radicals in xenon at 169 K. The sample consisted of MeBr , Bu^nBr , Me_3SiH , Bu^tOOBu^t , and xenon (ca. 1:4:10:4:30 v/v).

tively poor overlap between the delocalised SOMOs and the Xe-5p orbitals. The charge-transfer contribution would also be expected to be important for F_3C^\cdot , because of the large electron affinity of this radical, but evidently the overlap contribution is even greater (see above).

The shape and size of Me^\cdot are probably such as to permit substantial overlap between the highly localised SOMO and the Xe-5p orbitals. The overlap contribution is larger than that for the bulkier alkyl radicals and is not compensated by a significant charge-transfer interaction,[¶] since the electron affinity of Me^\cdot is small.

Provided that the precursor reagents have adequate solubility, liquid xenon could often be the solvent of choice for studies of chemically reactive radicals. Although xenon is a relatively expensive solvent, its chemical inertness facilitates recovery and re-use.

Received, 3rd December 1982; Com. 1385

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[¶] With a mixture of xenon and cyclopropane (ca. 2:3 mol/mol, 1:2 v/v) as solvent, the g -factor of methyl was 2.0020 at 183 K, indicating the absence of selective radical-solvent molecule interactions.

[¶] Xenon is isoelectronic with I^- and a weak charge-transfer interaction is known to exist between caged methyl radicals and iodide ions in rigid matrices.⁷ The anisotropic g -factors of such alkyl radical-halide ion 'adducts' have not been discussed.