Intermediates in the Pulse Radiolysis of Solutions of Phenothiazine and its Derivatives: Reactions of Cycloalkylperoxyl Radicals with Phenothiazines

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Aerated cycloalkane solutions of phenothiazine (PTH) undergo pulse radiolysis to yield a transient species (λ_{max} 590 nm) building up after the pulse with $k = 3{\cdot}42 \times 10^6$ l mol^{-1} s^{-1} (for C_5H_{10}). A comparison of the spectrum with spectra of ^{3}PTH, PTH$^{\cdot+}$, and PTH$^{\cdot-}$ (or of its conjugate acid) prepared by unambiguous routes, and with literature spectra (where known) of these species, suggests that the transient is not any of these, but is more probably the neutral radical species PT•, formed by attack of cycloalkylperoxyl radicals upon the substrate. Further evidence for this is supplied by the presence of a primary deuterium kinetic isotope effect upon the rate of formation of the transient, and alternative preparations of the neutral radical are discussed. Pulse radiolysis of an aerated solution of *N*-methylphenothiazine (PTMe) in cyclohexane gives a different type of spectrum ($\lambda_{max.}$ *ca.* 520 nm) which is formed very rapidly even after 25 ns pulses and which is characterised by comparison with spectra of species generated by known routes as the radical cation PTMe$^{\cdot+}$, possibly formed by electron transfer between PTMe and $RO_2\cdot$. *N*-Benzyl-3,7-dioctylphenothiazine (dioctyl-PTCH$_2$Ph) again reacts with $RO_2\cdot$ on a ns time scale at mM solute concentrations; the species formed in this case has not been identified unambiguously, but may be dioctyl-PT• formed by the loss of the benzyl group.

THE autoxidation of liquid hydrocarbons takes place by a chain mechanism involving alkylperoxyl radicals as chain carriers [1-3] and the action of antioxidants mainly involves scavenging of these species. The reactions of alkylperoxyl radicals have recently been reviewed [4] and the kinetics of their reactions discussed.[5]

Pulse radiolysis (p.r.) of aerated alkanes has been shown to be a useful technique for generating optically detectable concentrations of alkylperoxyl radicals, and studying their reactions,[6] and more recently an extension of this technique incorporating e.s.r. detection of intermediates has been achieved.[7]

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[1] L. Bateman, *Quart. Rev.*, 1954, **8**, 147.

[2] N. M. Emanuel, 'The Oxidation of Hydrocarbons in the Liquid Phase,' Pergamon, Oxford, 1965.

[3] D. M. Brown and A. Fish, *Proc. Roy. Soc.*, 1969, *A*, **308**, 547.

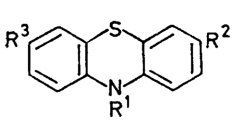
[4] K. U. Ingold, *Accounts Chem. Res.*, 1969, **2**, 1.

[5] J. A. Howard, *Adv. Free Radical Chem.*, 1971, **4**, 75.

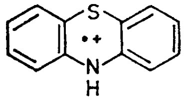
[6] A. MacLachlan, *J. Amer. Chem. Soc.*, 1965, **87**, 960 and references therein.

[7] B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, 1968, **48**, 5174.

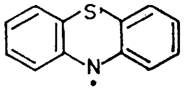
We have been interested in the initial mode of action of phenothiazine (I) (PTH) and of some substituted phenothiazines (II)—(IV) in the inhibition of hydrocarbon autoxidation. The ready oxidation of PTH



(I) $R^1 = R^2 = R^3 = H$
(II) $R^1 = H, R^2 = R^3 = n\text{-}C_8H_{17}$
(III) $R^1 = CH_2Ph, R^2 = R^3 = n\text{-}C_8H_{17}$
(IV) $R = Me, R^2 = R^3 = H$



(V)



(VI)

has resulted in the accumulation of a substantial and complex compilation of optical spectra of free radical derivatives both of (I) and its semi-oxidised forms (V) and (VI). Michaelis and his co-workers [8] have shown that (I) readily undergoes a one-electron oxidation in acidic media to yield either (V) or (VI). Shine and Mach [9] have elucidated the situation as regards the inter-relation of the semi-oxidised forms (V) and (VI), and even higher oxidation levels of (I). Lewis and Bigeleisen [10] have shown that PTH can be photo-oxidised in an ether–isopentane–alcohol glass at 90 K to yield a species absorbing at *ca.* 520 nm which they have suggested to be the cation radical $\text{PTH}^{\cdot+}$ (V). On leaving at a temperature of *ca.* 100 K this absorption disappeared, and a new band at *ca.* 530 nm was formed which they attributed to the neutral species PT· (VI). Irradiation of solutions of (I) in aqueous acetic acid gives optical and e.s.r. spectra assigned to $\text{PTH}^{\cdot+}$, whilst irradiation in ethanol gives a different e.s.r. spectrum assigned to PT·.[9] E.s.r. spectra of $\text{PTH}^{\cdot+}$ and PT· have also been obtained in acetonitrile [11] and dimethyl sulphoxide–acetic anhydride [12] media. Flash photolysis of (I) in degassed ethanol solution [13] yields a strongly absorbing, short-lived transient ($\lambda_{\text{max.}}$ 465 nm) assigned to the triplet state ^{3}PTH, in agreement with the spectrum of this species recorded in low temperature glasses; [14] in contrast, oxygenation of the ethanol solution results in the absence of ^{3}PTH on flashing, and instead a weaker absorption appears ($\lambda_{\text{max.}}$ 385 nm) attributed to a complex of the type $\text{PTH} \cdots \text{O}_2$, which dissociates to give PT· and HO_2· [13] An assignment of the spectrum of the species $\lambda_{\text{max.}}$ 385 nm to the neutral radical PT·, which then reacts with oxygen to give the 5-oxide has been discounted on the basis of solvent effects, and a comparison of u.v. and e.s.r. data.[15]

In the present work, we describe the kinetic and spectroscopic results of µs and ns pulse radiolysis of (I)—(IV) in aerated cycloalkane solutions and assign the spectra of the transients observed by comparison with spectra of intermediates obtained by pulse radiolysis, flash photolysis, and chemical oxidation.

EXPERIMENTAL

Materials.—Phenothiazine, 3,7-dioctylphenothiazine, and *N*-benzyl-3,7-dioctylphenothiazine were supplied by Shell Research Ltd. and were purified by two recrystallisations from ethanol or 10% benzene–ethanol. Purity was confirmed by t.l.c. (eluant chloroform). *N*-methylphenothiazine (Eastman) was purified in the same way. Cyclopentane (Aldrich spectrophotometric grade) and cyclohexane (Hopkin and Williams spectrograde) were purified by passing down a neutral alumina column impregnated with silver nitrate. Carbon tetrachloride and chloroform were purified as described previously.[16] Benzene, ethanol, toluene, iso-octane, and acetonitrile were of spectroscopic grade and were used without further purification. Triethylamine was purified by the method of Swift.[17] Other materials were of the highest grade available.

Pulse Radiolysis.—This was performed using 25 or 600 ns or 1·2 µs pulses of 3 MeV electrons of between 4 and 8 krad dose delivered by a Van de Graaff accelerator at the Cookridge High Energy Radiation Research Centre of Leeds University at Cookridge Hospital, Leeds. The general experimental arrangement has been described before, as also have the methods of dosimetry, degassing of solutions, and remote control of the flow system.[18,19] Samples were normally protected from photolysis by the monitoring light by insertion of a filter cutting off just below the relevant transient absorption. Spectral absorptions at wavelengths longer than 650 nm were studied using a Mullard BPY 13 photodiode. Spectra were obtained on a point-to-point basis using a Biomation 610 transient recorder. $G\varepsilon$ Values are given throughout in units of molecules $100\ \text{eV}^{-1}\ \text{M}^{-1}\ \text{cm}^{-1}$.

Flash Photolysis.—A Northern Precision FP-1D apparatus capable of operation in both spectrographic and photoelectric modes was used. In the spectrographic mode, spectra were recorded on Ilford HP3 plates, and were converted to graphical traces using a Joyce MK IIIC recording microdensitometer.

Analysis of Kinetic Data.—Rate constants were obtained from the normal first- and second-order plots. In cases where it was not possible to obtain infinity readings, kinetic traces were analysed by using a non-linear, least-squares programme devised in these laboratories.[20]

RESULTS

Aerated and Oxygenated Cycloalkanes.—P.r. of argon-flushed cyclohexane gave a broad spectrum with $\lambda_{\text{max.}}$

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[8] L. Michaelis, S. Granick, and M. P. Schubert, *J. Amer. Chem. Soc.*, 1941, **63**, 351.

[9] H. J. Shine and E. E. Mach, *J. Org. Chem.*, 1965, **30**, 2130.

[10] G. N. Lewis and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2419.

[11] B. C. Gilbert, P. Hanson, R. O. C. Norman, and B. T. Sutcliffe, *Chem. Comm.*, 1966, 161.

[12] Y. Tsujino, *Tetrahedron Letters*, 1968, 4111.

[13] T. Iwaoka, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1971, **44**, 341.

[14] B. R. Henry and M. Kasha, *J. Chem. Phys.*, 1967, **47**, 3319.

[15] T. Iwaoka, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1971, **44**, 3466.

[16] H. D. Burrows, D. Greatorex, and T. J. Kemp, *J. Phys. Chem.*, 1972, **76**, 20.

[17] E. Swift, *J. Amer. Chem. Soc.*, 1942, **64**, 115.

[18] T. J. Kemp, J. P. Roberts, G. A. Salmon, and G. F. Thompson, *J. Phys. Chem.*, 1968, **72**, 1464.

[19] D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. Roy. Soc.*, 1972, *A*, **328**, 23.

[20] P. Moore, *J.C.S. Faraday I*, 1972, **68**, 1890.

245 nm due to $C_6H_{11}\cdot$, but on aeration or oxygenation the absorption was intensified with $\lambda_{max.}$ 260 nm, with the same value of $G\varepsilon$ in the two cases: the latter absorption is

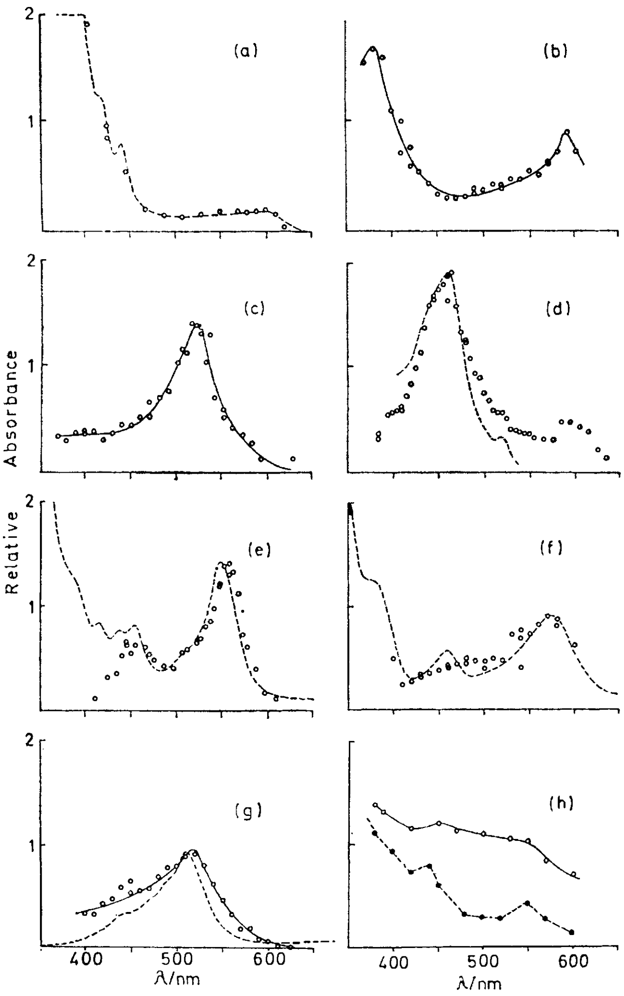

FIGURE 1 (a) Circles; spectrum recorded *ca.* 100 μs after p.r. of 2×10^{-2}M-dioctyl-PTH (II) in aerated cyclohexane; broken line, spectrum obtained on adding triethylamine to a solution of dioctyl-PTH and ceric ammonium nitrate in CCl_4; (b) p.r. spectrum of 4×10^{-3}M-dioctyl-$PTCH_2Ph$ (III) in aerated cyclohexane; (c) p.r. spectrum of 2×10^{-3}M-PTMe (IV) in aerated cyclohexane; (d) circles, p.r. spectrum of 10^{-2}M-PTH (I) in argon saturated benzene; broken line, spectrum obtained 10 μs after flash photolysis of 7×10^{-4}M-PTH in degassed ethanol; (e) circles, p.r. spectrum of 10^{-2}M-dioctyl-PTH in argon saturated $CHCl_3$; broken line, spectrum obtained on chemical oxidation of dioctyl-PTH in CCl_4; (f) circles, p.r. spectrum of 10^{-2}M-dioctyl-$PTCH_2Ph$ in argon saturated $CHCl_3$; broken line, spectrum obtained on chemical oxidation of dioctyl-$PTCH_2Ph$ in CCl_4; (g) circles and full lines, p.r. spectrum of 10^{-2}M-PTMe in argon saturated $CHCl_3$; broken line, spectrum of PTMe in concentrated H_2SO_4; (h) circles and full line, p.r. spectrum of 10^{-2}M-dioctyl-PTH in argon saturated ethanol; filled circles and broken line, p.r. spectrum of same solution saturated with N_2O

attributed to $C_6H_{11}O_2\cdot$ in agreement with McCarthy and MacLachlan.[21] In view of the equivalent production of $C_6H_{11}O_2\cdot$ in the two solutions, aerated solutions were employed throughout the remainder of this work and oxygen concentrations are taken as *ca.* 2mM. Holroyd [22] quotes *G*(cycloalkyl) *ca.* 4 for both cyclohexane and cyclopentane, with only trivial (*G ca.* 0·1) contributions from other radicals.

Aerated Cycloalkanes (C_nH_{2n}) *Solutions* (n = 5 *or* 6). P.r. of solutions (10^{-4}—2×10^{-2}M) of PTH (I) or 3,7-dioctyl-PTH (II) in aerated cyclohexane or cyclopentane resulted in the observation of closely similar transient spectra, exemplified in Figure 1(a) for (II) in aerated cyclohexane, which grew-in after the electron pulse on a time scale of several μs. The spectra display an absorption increasing strongly below 420 nm, weak maxima ($G\varepsilon$ *ca.* 5×10^3 for 10^{-2}M solution) near 590 nm, and little absorption at wavelengths longer than 640 nm. The build-up of the absorption followed good pseudo-first-order kinetics, in most cases to at least two half-lives, and had the same rate at both 380 and 590 nm. Plots of pseudo-first-order rate constant against phenothiazine or dioctylphenothiazine concentration gave good straight lines (Figure 2), indicating that the build-up was a second-order process. For the dioctylphenothiazine solutions these lines passed through the origin, whilst with the phenothiazine solutions they both showed a small positive intercept, for no obvious reason.

A $0·91 \times 10^{-3}$M solution of PTH in aerated C_5H_{10} was pulsed, and the build-up of absorption at 370 and 590 nm was followed, and was found to obey good pseudo-first-order kinetics with $k_{obs} = 8·6 \times 10^3$ s^{-1}. The solution (25 cm^3) was shaken with deuterium oxide (2 cm^3) for 1 h and was pulsed under identical conditions. The growing-in of the absorption was again found to follow pseudo-first-order kinetics with $k_{obs} = 5·2 \times 10^3$ s^{-1}, indicating the presence of a primary deuterium isotope effect on the build-up process with $k_H/k_D = 1·7$. An identical isotope effect was observed on p.r. of an aerated cyclopentane solution of PTH which had previously been deuteriated at the nitrogen atom (as demonstrated by n.m.r. and mass spectrometry) by two recrystallisations from deuterium oxide–dioxide solution.

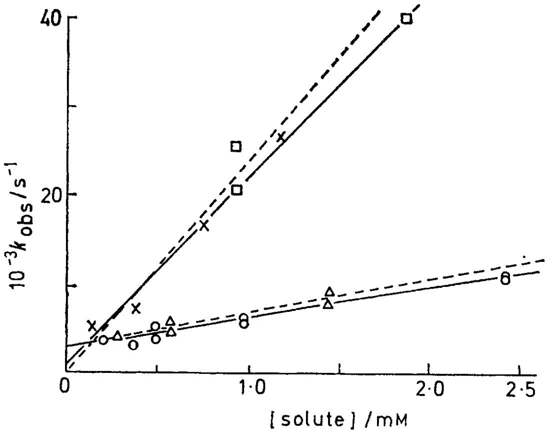

FIGURE 2 Typical plots of rate of build up of absorption (k_{obs}) on p.r. of aerated cycloalkane solutions of phenothiazines against solute concentration: full line and ○, PTH in aerated cyclopentane; broken line and △ PTH in aerated cyclohexane; full line and ×, dioctyl-PTH in aerated cyclopentane; broken line and □, dioctyl-PTH in aerated cyclohexane. For the dioctyl-PTH solutions, only the points at the lowest concentrations studied are shown. Straight lines were obtained by the least squares method

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[21] R. L. McCarthy and A. MacLachlan, *J. Chem. Phys.*, 1961, **35**, 1625.

[22] R. A. Holroyd, 'Fundamental Processes in Radiation Chemistry,' ed. P. Ausloos, Interscience, New York, 1968, ch. 7.

P.r. of 3,7-dioctyl-PTCH$_2$Ph (III) in aerated cyclohexane yielded a weak absorption $\lambda_{max.}$ 390 and 590 nm, $G\varepsilon_{590}$ *ca.* 2·2 × 10^3 for 5 × 10^{-3}M solution [Figure 1(b)], which, even at the lowest concentration studied with the μs pulse radiolysis set-up (*ca.* 2·5 × 10^{-5}M), was completely formed < 1 μs. Attempts to follow the build-up of this absorption using ns p.r. (25 ns pulses) were similarly unsuccessful, formation being complete for a 10^{-3}M solution within the shortest time which could be realised (50 ns). The weakness of the absorptions prevented examination on this time scale at lower concentrations of (III).

With PTMe (IV) in aerated cyclohexane, a weaker transient absorption of different type [Figure 1(c)], $\lambda_{max.}$ 520, $G\varepsilon$ *ca.* 1·4 × 10^3 for a 2 × 10^{-3}M solution, was observed directly after the pulse. P.r. of a 0·96 × 10^{-3}M solution using 25 ns pulses indicated that the build-up of this absorption was complete in less than 50 ns.

TABLE 1

Values for $\lambda_{max.}$ and $k_{formation}$ for p.r. of solutions of phenothiazines in aerated alkanes

	PTH		Dioctyl-PTH		Dioctyl-PTCH$_2$Ph		PTMe	
	$\lambda_{max.}$/nm	$10^{-6}k$/ l mol^{-1} s^{-1}	$\lambda_{max.}$/nm	$10^{-6}k$/ l mol^{-1} s^{-1}	$\lambda_{max.}$/nm	k/ l mol s^{-1} [a]	λ/nm$_{max.}$	k/ l mol^{-1} s^{-1} [a]
C_5H_{10}	600 < 370	3·4	585 < 400	21·4				
C_6H_{12}	600 < 380	3·9	590 < 380	24·4	590 380	> 10^{10}	520	> 10^{10}
Iso-octane	380	*b*						
Toluene	395	*c*						

[a] Calculated assuming reaction is second order. [b] $k_1 = 6{\cdot}2 \times 10^5$ s^{-1} at 0·77mM-solute. [c] $t_{\frac{1}{2}}$ *ca.* 1μs at 1·0mM-solute.

TABLE 2

Values of $\lambda_{max.}$, $G\varepsilon_{max.}$, and k_{decay} for triplet–triplet absorptions of substituted phenothiazines

	PTH			Dioctyl-PTH			Dioctyl-PTCH$_2$Ph		
	$\lambda_{max.}$/nm	$10^{-3}G\varepsilon_{max.}$	$10^{-5}k$/s^{-1}	$\lambda_{max.}$/nm	$10^{-3}G\varepsilon_{max.}$	$10^{-5}k$/s^{-1}	$\lambda_{max.}$/nm	$10^{-3}G\varepsilon_{max.}$	$10^{-5}k$/s^{-1}
Argon saturated benzene, pulse radiolysis [a]	460	21·7	1·73 [c]	480	29·3	0·82	490	29·6	0·79 [c]
Argon saturated C_6H_{12}, pulse radiolysis [b]				475	13·2	1·03 [c]			
Degassed ethanol flash photolysis	460								

[a] 10^{-2}M Solutions. [b] 5 × 10^{-3}M Solution. [c] Strictly first-order only to one half-life.

All kinetic and spectral data for these systems are summarised in Table 1. P.r. of PTH in aerated toluene and iso-octane gave absorptions similar to those observed for this system in aerated cycloalkanes, and data for these systems are also recorded.

Deoxygenated Benzene and Cyclohexane Solutions.—P.r. of argon saturated solutions of PTH, 3,7-dioctyl-PTH, and 3,7-dioctyl-PTCH$_2$Ph in benzene all gave strongly absorbing transient species. A typical spectrum is shown in Figure 1(d) for PTH, which decayed with good first-order kinetics (to two half-lives) with $k_1 = 1{\cdot}73 \times 10^5$ s^{-1}. This spectrum was found to be closely similar to that obtained 10 μs after flash photolysis of a degassed solution of PTH (7 × 10^{-4}M) in ethanol. P.r. of an argon saturated solution of dioctyl-PTH in cyclohexane gave an absorption comparable to that obtained in benzene. Data for these systems are summarised in Table 2. Comparison with literature spectra,[13,14] the similarity of the p.r. spectrum of PTH in benzene with the flash photolysis spectrum in degassed ethanol, the first-order decay of the species, and the general observation of solute triplet state spectra in the p.r. of aromatic solutes in benzene and cyclohexane[23] strongly suggest that all the transients listed in Table 2 can be assigned to solute triplet states.

Deoxygenated Chloroform Solutions.—Strongly absorbing transients were obtained on p.r. of argon saturated solutions of all of the phenothiazines in chloroform, a solvent affording large yields of solute radical-cations following p.r.[16] The similarity of the spectra from (i) PTH ($\lambda_{max.}$ 435 and 520 nm) and that of Shine and Mach[9] for PTH$^{\cdot+}$ ($\lambda_{max.}$ 437 and 515 nm), (ii) dioctyl PTH or dioctyl-PTCH$_2$Ph and the same solute oxidised by ceric ammonium nitrate in carbon tetrachloride (containing 1% acetonitrile) [Figures 1(e) and (f)], and (iii) PTMe and the spectrum obtained on dissolving this solute in concentrated sulphuric acid [Figure 1(g)] make it clear that we are observing solute radical-cations in all cases, in conformity with the general behaviour of radiation-excited chlorinated hydrocarbon solvents towards aromatic solutes.[16,24] A summary of spectral data for these solutions is given in Table 3.

TABLE 3

Values of $\lambda_{max.}$ and $G\varepsilon_{max.}$ for p.r. of 10^{-2}M solutions of phenothiazines in argon saturated chloroform

PTH		Dioctyl-PTH		Dioctyl-PTCH$_2$Ph		PTMe	
$\lambda_{max.}$/ nm	$10^{-3}G\varepsilon$	$\lambda_{max.}$/ nm	$10^{-3}G\varepsilon$	$\lambda_{max.}$/ nm	$10^{-3}G\varepsilon$	$\lambda_{max.}$/ nm	$10^{-3}G\varepsilon$
520	4·1	555	8·4	560	9·8	515	4·2
436	3·6	455	3·8	485	5·2	450	3·0

Ethanolic Solutions.—P.r. of deaerated ethanolic solutions of PTH and 3,7-dioctyl-PTH gave similar spectra, which were significantly reduced in intensity upon saturation with N_2O. The spectrum for 3,7-dioctyl-PTH is shown in

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[23] See for example J. W. Hunt and J. K. Thomas, *J. Chem. Phys.*, 1967, **46**, 2954.

[24] T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 2369, 2375, 4372.

Figure 1(h). These spectra are assigned on the basis of the N_2O quenching, and the general behaviour of alcohols on radiolysis,[25] to the anion radicals $PTH^{\cdot -}$, or their conjugate acids $PTH_2\cdot$. Spectroscopic data for these solutions are given in Table 4.

TABLE 4

Values of $\lambda_{max.}$ and $G\varepsilon_{max.}$ for p.r. of 10^{-2}M solutions of PTH and dioctyl-PTH in argon saturated ethanol

PTH		Dioctyl-PTH	
$\lambda_{max.}$/nm	$10^{-3}G\varepsilon_{max.}$	$\lambda_{max.}$/nm	$10^{-3}G\varepsilon_{max.}$
380	15·3	380	14·0
450	6·7	450	12·2
610	1·6	550	10·3

Chemical Oxidation Spectra of Radical Cations and Neutral Radicals of Phenothiazines.—The most successful literature methods for producing radical cation spectra of the phenothiazines were found to be oxidation by concentrated H_2SO_4,[9] and oxidation of a carbon tetrachloride solution of the phenothiazine by addition of a small volume of a concentrated solution of ceric ammonium nitrate in acetonitrile.[16]

Neutral radical spectra could be obtained from these by ionisation with a suitable base. Attempts to obtain neutral radical spectra in the concentrated H_2SO_4 solutions by addition of acetone or sodium sulphate as base[26] were unsuccessful. However, in the carbon tetrachloride solutions, triethylamine was found to act as a good base, and spectra were obtained by addition of NEt_3 (*ca.* 50 μl) to a cuvette containing *ca.* 3 ml of an oxidised solution of the phenothiazine in carbon tetrachloride. The resulting spectra were recorded immediately after mixing.

The literature methods for obtaining the neutral radical species[9-13] all gave complex optical spectra, suggesting complicated mixtures of species. The assignment by Lewis and Bigeleisen[10] of the absorption at *ca.* 530 nm produced on warming an EPA glass containing photolysed PTH to the neutral species PT· is thought by us to be in error. These workers also observed absorption bands at 605 and 655 nm, and it appears likely that these absorptions were due to PT·, whilst the 530 nm absorption arose from some product derived from this.

DISCUSSION

The aim of this work has been to investigate the kinetics and primary reactions of several phenothiazine derivatives with cycloalkylperoxyl radicals, $RO_2\cdot$, derived from pulse radiolysis of aerated cycloalkanes, *viz.* the simplified scheme (1)—(3).

$$RH \rightsquigarrow RH^{\cdot +} + e^- \longrightarrow RH^* \longrightarrow R\cdot + H\cdot \qquad (1)$$

$$H\cdot + RH \longrightarrow H_2 + R\cdot \qquad (2)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (3)$$

Under conditions of aeration, (3) represents the principal fate of R· and (2) that of H·. Although solute positive[27] and negative[28] ions have been detected during μs p.r. experiments on deaerated cyclohexane solutions as a result of reaction with $C_6H_{12}^{\cdot +}$ and e^- respectively, *G*(ion) is only *ca.* 0·2 and capture of free ions is probably insignificant in the present work. MacLachlan[6] has demonstrated the applicability of the p.r. technique to the elucidation of the kinetics and mechanisms of the reactions of cycloalkylperoxyl radicals with aromatic amines of low ionisation potential such as diphenylamine, *N*-methylaniline, and *NN'*-diphenyl-*p*-phenylenediamine. The principal mechanism of inhibitor action of these amines is considered[5] to be (4).

$$RO_2\cdot + Ar_2NH \xrightarrow{k_4} RO_2H + Ar_2N\cdot \qquad (4)$$

The reaction of $RO_2\cdot$ ($R = C_5H_9$ or C_6H_{11}) with PTH (I) or 3,7-dioctyl-PTH (II) yields a transient absorbing rather weakly in the visible region ($\lambda_{max.}$ *ca.* 600 nm) which is formed in a second-order process. Comparisons of the spectrum with the spectra of the appropriate triplet state, radical-cation, and radical-anion (or its conjugate acid) demonstrated that this short lived species is none of these. We assign this transient to the species PT·, formed by hydrogen abstraction from the N–H bond by $RO_2\cdot$ on the basis of (i) a comparison of the p.r. spectrum with that obtained by oxidation by Ce^{VI}, followed by neutralisation with NEt_3 and (ii) the observation of a primary kinetic deuterium isotope effect of $k_H/k_D = 1{\cdot}7$ upon p.r. of an aerated solution of phenothiazine in cyclopentane.

The presence of this isotope effect rules out the presence of any complex of the type $PTH \cdots O_2$ such as those proposed by Koizumi and his co-workers[13] in the flash photolysis of PTH in aerated ethanol.

The rates of hydrogen abstraction from a given phenothiazine are similar for cyclohexylperoxyl and cyclopentylperoxyl radicals, suggesting similar steric and electronic interactions in these two secondary peroxyl radicals. However, hydrogen abstraction appears to occur more than six times faster from 3,7-dioctylphenothiazine than from phenothiazine itself. Such a rate enhancement must arise from some electronic effect of the two octyl groups. Brownlie and Ingold[29] found that whilst poly(peroxystyryl)peroxyl radicals abstract the amino-hydrogen atom from *N*-methyl- and 3,*N*-dimethyl-aniline at similar rates, abstraction from 4,*N*-dimethylaniline occurs three times faster. This fairly small rate factor in both the phenothiazine and *N*-methylaniline systems probably results from either an inductive or, more probably, a hyperconjugative substituent effect of the alkyl group in the position para to the nitrogen atom. The much higher values of k_4 found in the present work compared with those reported by Brownlie and Ingold[29] for reaction of diarylamines with polymeric peroxyl radicals reflects both the lower reactivity of the latter species and the great effectiveness of PTH as a peroxyl radical scavenger.

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[25] S. Arai and L. M. Dorfman, *J. Chem. Phys.*, 1964, **41**, 2190.

[26] These are both known to be strong bases in this solvent (see R. J. Gillespie and E. A. Robinson, 'Non-aqueous Solvent-Systems,' ed. T. C. Waddington, Academic Press, London, 1965, ch. 4).

[27] C. Capellos and A. O. Allen, *J. Phys. Chem.*, 1968, **72**, 4265

[28] J. P. Keene, E. J. Land, and A. J. Swallow, *J. Amer. Chem. Soc.*, 1965, **87**, 5284.

[29] I. T. Brownlie and K. U. Ingold, *Canad. J. Chem.*, 1967, **45**, 2419.

P.r. of aerated cyclohexane solutions of 3,7-dioctyl-$PTCH_2Ph$ (III) and PTMe (IV) showed very different behaviour from that of PTH. In both of these cases a transient species from the solute is formed within the shortest time observable in our experiments (50 ns; concentration 10^{-3}M), suggesting reaction at a rate approaching diffusion control. In the case of PTMe, the transient absorption obtained [Figure 1(c)] is assigned to the radical cation $PTMe^{\cdot +}$ on the basis of comparison of the spectrum with that of $PTMe^{\cdot +}$ obtained by sulphuric acid oxidation of (IV), and by p.r. of (IV) in chloroform [Figure 1(g)]. Two mechanisms are possible for the formation of this species, electron transfer to $RO_2\cdot$ [equation (5)] or electron transfer to the primary species R· [equation (6)].[3]

$$RO_2\cdot + PTMe \rightleftharpoons RO_2^- + PTMe^{\cdot +} \quad (5)$$

$$R\cdot + PTMe \longrightarrow R^- + PTMe^{\cdot +} \quad (6)$$

We, at present, are not able to distinguish between these competing processes although (5) is intrinsically the more probable. If the electron transfer is to the alkylperoxyl radical, then this process will have to be an equilibrium, to account for the low $G\varepsilon$ observed in this case ($G\varepsilon$ *ca.* $1{\cdot}3 \times 10^3$ at 520 nm) assuming the extinction coefficient of the radical cation is comparable to, or greater than, that of the neutral radical at 590 nm, and also to account for the fact that electron transfer (though a fast reaction) is not the predominant pathway for reaction of $RO_2\cdot$ with PTH [assuming that the ionisation potentials of (I) and (IV) are similar]. However, such electron transfers to alkylperoxyl radicals are known.[4]

With 3,7-dioctyl-$PTCH_2Ph$, assignment of the transient absorption formed at the end of the pulse [Figure 1(b)] is more difficult. The spectrum shows certain similarities to the spectrum obtained on p.r. of 3,7-dioctyl-PTH in aerated C_6H_{12} [Figure 1(a)], so that this species could be the neutral radical, 3,7-dioctyl-PT·. If this is so, then it would represent an extremely rapid cleavage of the nitrogen–carbon bond in (III) possibly following an electron-transfer step. Other possible assignments of this absorption include a complex of the type 3,7-dioctyl-$PTCH_2Ph \cdots O_2$, similar to that suggested by Koizumi *et al.*[13] for PTH, and products formed on opening of the phenothiazine rings.

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