An Electron Spin Resonance Study of the Second-order Decay of 4-Alkyl-2,6-di-t-butylphenoxyl Radicals in Solution

By **Robert D. Parnell** and **Kenneth E. Russell,*** Department of Chemistry, Queen's University, Kingston, Ontario, Canada

The decay of 4-methyl- and 4-ethyl-2,6-di-t-butylphenoxyl radicals in benzene solution is first-order at high radical concentrations and second-order at low radical concentrations. The concentration range in which the changeover from first- to second-order reaction occurs is determined by the equilibrium constant for quinol ether dimer formation from the phenoxyl radicals. Observed second-order rate constants at 22 °C for the loss of 4-methyl-, 4-ethyl-, and 4-isopropyl-2,6-di-t-butylphenoxyl radicals are, respectively, 2200, 500, and 2 l $\mathrm{mol^{-1}\,s^{-1}}$. The activation energy for the decay of 4-methyl-2,6-di-t-butylphenoxyl in benzene solution is 3·2 ± 0·3 kcal $\mathrm{mol^{-1}}$.

A PREVIOUS e.s.r. investigation of the decay of 4-methyl-2,6-di-t-butylphenoxyl (4-methyl-DTBP) in benzene solution indicated that the reaction is first-order with a rate constant of $1{\cdot}3 \times 10^{-2}\,\mathrm{s^{-1}}$ at 25 °C.[1] A later flash photolysis study showed that the first-order decay is preceded by a rapid second-order reaction to give a high yield of phenoxyl dimer.[2] At concentrations of phenoxyl in the range 10^{-4} to 2×10^{-6}M the reaction again appears to be essentially second-order, the rate constant at 24 °C being estimated to be $4{\cdot}59 \times 10^{2}$ l $\mathrm{mol^{-1}\,s^{-1}}$.[3] The decay of 4-ethyl-2,6-di-t-butylphenoxyl (4-ethyl-DTBP) was found under given reaction conditions to be first-order at 21—26 °C but second-order at 47 °C.[4]

Weiner and Mahoney[5] have recently proposed a mechanism which accounts for the observed e.s.r. and flash photolysis results for the decay of 4-methyl-DTBP at high concentrations. The rapid initial decay observed by Land and Porter[2] yields a quinol ether dimer and a low ' equilibrium ' concentration of phenoxyl radical. The observed first-order decay of phenoxyl involves either the direct conversion of 4-methyl-DTBP into phenol and quinone methide or the breakdown of the quinol ether dimer to the same products. In terms of either mechanism, the reaction order should change from one to two at sufficiently low concentrations of phenoxyl radical. E.s.r. measurements of the disappearance of 4-methyl-, 4-ethyl-, and 4-isopropyl-DTBP at relatively low concentrations in benzene and vinyl acetate solutions confirm the general predictions of the proposed mechanisms and allow direct estimates of kinetic parameters to be made. It has also been shown that 4-methyl-DTBP produced by flash photolysis of the corresponding phenol undergoes second-order decay at concentrations less than 10^{-6}M.

EXPERIMENTAL

Benzene (Fisher Scientific Company spectroanalysed grade) was used as supplied. Vinyl acetate was successively fractionally distilled, partially polymerised, and redistilled according to a procedure generally used in the preparation of monomer for free radical polymerisation.[6]

4-Ethyl- and 4-isopropyl-2,6-di-t-butylphenol were subjected to chromatography on neutral alumina with benzene as solvent, followed by recrystallisation from methanol in a nitrogen atmosphere. Their m.p.s were, respectively, 44—44·5 and 43·5—44 °C. 4-Methyl-2,6-di-t-butylphenol was recrystallised from methanol under nitrogen (m.p. 70—70·5 °C). The phenoxyl radicals were prepared by oxidising the corresponding phenols with (*a*) lead dioxide, (*b*) 2,2-diphenyl-1-picrylhydrazyl (DPPH),[7] or (*c*) galvinoxyl. Lead dioxide, in the form of a compressed smooth pellet, was placed in the side-arm of an e.s.r. tube. A weighed amount of hindered phenol was added, the apparatus was evacuated, and degassed solvent was distilled into the side-arm. The mixture was warmed to 22 °C and gently shaken, and a portion of the solution was isolated in the e.s.r. tube. When DPPH or galvinoxyl was used as oxidant, it was placed directly in the e.s.r. tube. Sufficient phenol was added to give a high concentration (*ca.* 0·1M) in the final reaction mixture; solvent was distilled into the tube and a rapid and essentially complete conversion of DPPH or galvinoxyl into phenoxyl was effected when the mixture was warmed to 22 °C.

E.s.r. measurements were carried out by means of a Varian V-4502 spectrometer fitted with a Varian-4540 variable temperature control unit. Saturation occurs readily with phenoxyl radicals in the absence of air, and low microwave power (*ca.* 1 mW) was essential. A detailed separate study showed that slight saturation occurs even at low microwave power and appropriate corrections were applied to the experimental peak heights. The modulation amplitude was 0·1 G. The standards for concentration measurements were solutions of DPPH in benzene and in vinyl acetate and comparisons were made by double integration of first-derivative spectra obtained under similar conditions. Minor variations in sensitivity were monitored by means of a manganese standard;[8] this standard also undergoes saturation but the effect is small at the low microwave power used in this experiment. Hyperfine splitting constants and g values for the phenoxyl radicals were obtained from double-cavity studies with Fremy's salt as standard (g 2·0055, a_{N} 13·0 G).

In flash photolysis studies, a 10^{-3}M-solution of 4-methyl-2,6-di-t-butylphenol was degassed and subjected to a 500 J flash; the e.s.r. tube was then transferred from the flash apparatus to the e.s.r. cavity in order to follow the slow decay of the radical intermediate.

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[2] E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2016.

[3] R. Stebbins and F. Sicilio, *Tetrahedron*, 1970, **26**, 291.

[4] A. I. Brodskii, V. D. Pokhodenko, V. A. Khizhnyi, and N. N. Kalibabchuk, *Doklady Akad. Nauk S.S.S.R.*, 1966, **169**, 339.

[5] S. A. Weiner and L. R. Mahoney, *J. Amer. Chem. Soc.*, 1972, **94**, 5029.

[6] H. Lilles, R. D. Parnell, and K. E. Russell, *Canad. J. Chem.*, 1972, **50**, 3304.

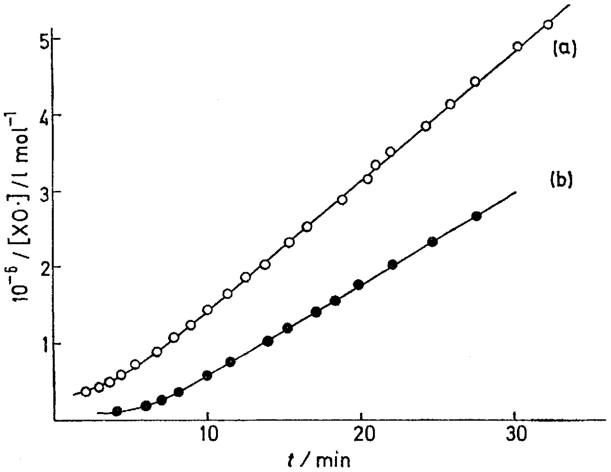
[7] P. B. Ayscough and K. E. Russell, *Canad. J. Chem.*, 1965, **43**, 3039.

[8] D. R. Gee, K. E. Russell, and J. K. S. Wan, *Canad. J. Chem.*, 1970, **48**, 2740.

RESULTS

E.s.r. Studies of 4-Methyl-DTBP.—4-Methyl-DTBP was prepared in benzene or vinyl acetate solution by oxidation of the phenol with lead dioxide or by addition of a large excess of the phenol to low concentrations of DPPH or galvinoxyl. The e.s.r. spectrum consists of a quartet of triplets, the main splitting being 11·15 ± 0·1 G and the secondary splitting, 1·70 ± 0·05 G; the *g*-factor is estimated as 2·0045 ± 0·0001.

The observed decay behaviour of the 4-methyl-DTBP radicals was independent of the method of preparation. Typical decay curves for the concentration range 5×10^{-6} to 2×10^{-7}M are shown in the Figure. At concentrations less than 10^{-6}M, the reaction follows second-order kinetics but at concentrations greater than 10^{-6}M the order is less than 2. Rate constants, k_{obs}, for the second-order reaction are given in Table 1. Similar results are obtained in the two solvents at 22 °C. There appears however to be a slight dependence of rate constant on the initial concentration of 4-methyl-DTBP, the latter being estimated by extrapolation of the decay curve to the time of mixing. A minimum value of k_{obs} of $1{\cdot}1 \times 10^3$ l mol^{-1} s^{-1} is observed with benzene as solvent and an initial phenoxyl concentration of 7×10^{-4}M, but k_{obs} increases to $2{\cdot}4 \times 10^3$ l mol^{-1} s^{-1} for an initial radical concentration of 2×10^{-6}M. This is in part due to slight overlap with a reaction of lower order, but the trend is probably real because the rate constants are based on linear plots which extend over a 5—10-fold concentration range in individual experiments. The second-order decay was studied over the temperature range 7—56 °C for reactions in which the initial phenoxyl concentration was 2×10^{-5}M. The activation energies are, respectively, 3·2 ± 0·3 and 3·3 ± 0·3 kcal mol^{-1} in benzene and vinyl acetate.



Decay curves for 4-methyl-DTBP (a) in benzene and (b) in vinyl acetate at 22 °C

Table 1

Rate constants for decay of 4-methyl-DTBP in benzene and in vinyl acetate at 22 °C

Solvent	Initial [4-Methyl-DTBP]/M	10^{-3} k_{obs}/ l mol^{-1} s^{-1}
Benzene	7×10^{-4}	1·1
Vinyl acetate	8×10^{-5}	1·1
Vinyl acetate	7×10^{-5}	2·0
Vinyl acetate	3×10^{-5}	1·6
Benzene	6×10^{-5}	2·6
Benzene	3×10^{-5}	1·9
Vinyl acetate	7×10^{-6}	2·7
Benzene	6×10^{-6}	2·7
Benzene	5×10^{-6}	2·3
Vinyl acetate	3×10^{-6}	2·9
Benzene	2×10^{-6}	2·4

The disappearance of 4-methyl-DTBP is first-order at high radical concentrations.[1,5] Analysis of the present data at the highest concentrations studied yields first-order rate constants of 9×10^{-3} in benzene and 5×10^{-3} s^{-1} in vinyl acetate at 22 °C; *cf.* 9×10^{-3} s^{-1} in iso-octane at 22 °C, estimated from the data of Weiner and Mahoney.[5]

E.s.r. studies of benzene solutions of 4-methyl-2,6-di-t-butylphenol subjected to flash photolysis confirm Land and Porter's conclusion[2] that a slow decay of 4-methyl-DTBP occurs over an extended period. The reaction becomes second-order in the concentration range 10^{-6} to 10^{-7}M and the observed rate constant at 22 °C is 4×10^3 l mol^{-1} s^{-1}.

E.s.r. Studies of 4-Ethyl- and 4-Isopropyl-DTBP.—4-Ethyl-DTBP and 4-isopropyl-DTBP were the only radicals observed on oxidation of the corresponding phenols under the experimental conditions of this work. The main splittings, arising from the α-hydrogen atoms of the 4-alkyl groups, are respectively 8·60 ± 0·10 G (*cf.*[1] 8·65 ± 0·10) and 4·68 ± 0·02 G (*cf.*[9] 4·6). The *g*-factor for 4-isopropyl-DTBP is estimated to be 2·0045 ± 0·0001 (*cf.*[10] 2·0047 ± 0·0002).

The decay of 4-ethyl-DTBP follows the same pattern as that of 4-methyl-DTBP. At high concentrations (3×10^{-5}M down to 5×10^{-6}M) the reaction is close to first-order and the rate constant in benzene solution at 22 °C is 7×10^{-3} s^{-1} (*cf.*[4] $7{\cdot}8 \times 10^{-3}$ at 26 °C). At lower concentrations of 4-ethyl-DTBP the reaction becomes second-order; rate constants for the decay at 22 °C are given in Table 2. The results for initial phenoxyl concentrations from 2×10^{-6} to 3×10^{-4}M are all in the range $3{\cdot}7 \times 10^2$ to $5{\cdot}7 \times 10^2$ l mol^{-1} s^{-1}.

Table 2

Rate constants for decay of 4-ethyl- and 4-isopropyl-DTBP in benzene at 22 °C

	(M)	l mol^{-1} s^{-1}
4-Ethyl-DTBP	3×10^{-4}	$3{\cdot}7 \times 10^2$
	2×10^{-4}	$4{\cdot}3 \times 10^2$
	4×10^{-5}	$5{\cdot}1 \times 10^2$
	2×10^{-5}	$4{\cdot}6 \times 10^2$
	1×10^{-5}	$5{\cdot}7 \times 10^2$
	5×10^{-6}	$5{\cdot}6 \times 10^2$
	2×10^{-6}	$5{\cdot}4 \times 10^2$
4-Isopropyl-DTBP	$1{\cdot}6 \times 10^{-3}$	1·6
	9×10^{-4}	1·7
	5×10^{-4}	1·8
	8×10^{-5}	1·9
	6×10^{-5}	2·1
	4×10^{-5}	2·5
	6×10^{-6}	3·6

The decay results for 4-isopropyl-DTBP are also given in Table 2. There is no curvature in the plots of reciprocal phenoxyl concentration *versus* time at initial concentrations up to $1{\cdot}6 \times 10^{-3}$M. In some instances the decay was followed for periods of 24 h; the derived rate constants remained the same within experimental error. The rate constants are generally close to 2 l mol^{-1} s^{-1} at 22 °C, in agreement with the estimate of 2·2 l mol^{-1} s^{-1} at 25 °C for

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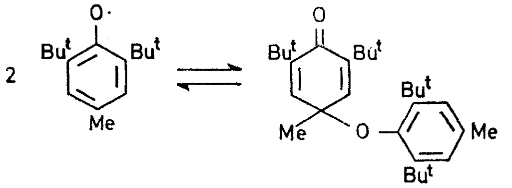
[9] K. Scheffler, *Z. Electrochem.*, 1961, **65**, 439.

[10] P. B. Ayscough and K. E. Russell, *Canad. J. Chem.*, 1967, **45**, 3019.

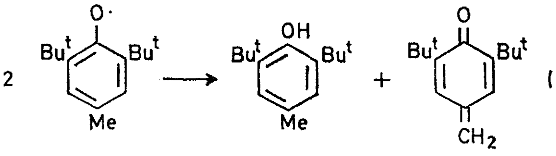
the reaction followed spectrophotometrically in benzene.[11] They increase slightly as the initial phenoxyl concentration decreases, a value of 3·6 l mol^{-1} s^{-1} being observed for an initial radical concentration of 5×10^{-6}M. An increase in apparent rate constant with decreasing 4-isopropyl-DTBP concentration was also observed by Huberle *et al.*[12]

DISCUSSION

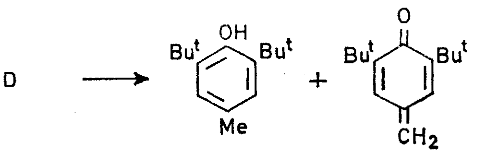
The initial product of oxidation of 4-methyl-2,6-di-t-butylphenol is the dimer, 4-(2,6-di-t-butyl-4-methylphenoxy)-4-methyl-2,6-di-t-butylcyclohexa-2,5-dienone (D).[13] Land and Porter[2] showed by flash photolysis of the phenol in benzene solution that the dimerisation is very rapid with a rate constant of $1{\cdot}5 \times 10^{8}$ l mol^{-1} s^{-1} in carbon tetrachloride solution at 20 °C. The reaction is reversible and the equilibrium constant K_1 is *ca.* $1{\cdot}4 \times 10^{6}$ mol l^{-1} in carbon tetrachloride at 20 °C.[2] The dimer is not stable[13] and in dilute solution the products are identified as the phenol and 3,5-di-t-butyl-1,4-benzoquinone methide.[14] Further reaction of the quinone methide is very slow.[15] The quinone methide is formed either by the reaction of two 4-methyl-DTBP radicals (ii) or by decomposition (iii) of the dimer, D, formed reversibly in reaction (i).



(i)



(ii)



(iii)

Weiner and Mahoney have analysed their results for the concentration range 10^{-4} to 10^{-5}M in terms of both mechanisms. If 4-methyl-DTBP is converted into quinone methide only by reaction (ii), the observed rate of disappearance of radical is given by the expression $2k_2[XO\cdot]^2/(4K_1[XO\cdot] + 1)$, where $2k_2$ is the second-order rate constant for loss of phenoxyl in reaction (ii). If the radical is converted into quinone methide only *via* the dimer and reaction (iii), the observed rate of disappearance of radical is given by the expression $2k_3K_1[XO\cdot]^2/(4K_1[XO\cdot] + 1)$, where k_3 is the rate constant for loss of dimer in reaction (iii). The two expressions are of the same form and imply that at high concentrations of phenoxyl ($4K_1[XO\cdot] \gg 1$) the reaction is first-order, whereas at low concentrations ($4K_1[XO\cdot] \ll 1$) it becomes second-order.

If the first mechanism is operative, the rate constant, k_2, is obtained from the disappearance of 4-alkyl-DTBP at low concentrations where the reaction is observed to be second-order; the value of $2k_2$ for 4-methyl-DTBP is thus 2200 l mol^{-1} s^{-1} at 22 °C. At high concentrations of phenoxyl the reaction is first-order and the rate constant, $k_2/2K_1$, is $9{\cdot}0 \times 10^{-3}$ s^{-1} in benzene at 22 °C. The equilibrium constant K_1 is thus estimated to be *ca.* 6×10^{4} l mol^{-1} in benzene at 22 °C. The changeover from first-order to second-order reaction actually occurs when $4K_1[XO\cdot] \simeq 1$, as anticipated on the basis of this mechanism.

If the second mechanism is operative, the rate constant, k_3, is obtained from the disappearance of 4-methyl-DTBP at high concentrations where the reaction is observed to be first-order; the value of $k_3/2$ is 9×10^{-3} s^{-1} at 22 °C. At low concentrations of phenoxyl, the reaction is second-order and the rate constant, $2k_3K_1$, is 2200 l mol^{-1} s^{-1} at 22 °C. The equilibrium constant, K_1, is again estimated to be 6×10^{4} l mol^{-1}.

Values of k_2, k_3, and K_1 for the decay of 4-methyl-DTPB in benzene and in vinyl acetate and of 4-ethyl- and 4-isopropyl-DTBP in benzene are summarised in Table 3. The rate constant, k_2, derived on the assumption that reaction (ii) is important, decreases by a factor of 4 in going from 4-methyl- to 4-ethyl-DTBP and by a factor of 250 with 4-isopropyl-DTBP. The activation energies for the 4-methyl- and 4-isopropyl-DTBP reactions are 3·2 and 6·2 kcal mol^{-1},[10,11] respectively, so that the decrease in the second-order rate constant is almost entirely associated with the increase in activation energy. On the basis of this mechanism, the increased steric hindrance for the attack of a hindered phenoxyl on an isopropyl group leads to a 3 kcal mol^{-1} increase in activation energy and a slight decrease in *A* factor.

TABLE 3

Rate constants k_2 and k_3 and equilibrium constants K_1 for 4-alkyl-DTBP reactions at 22 °C

4-Alkyl	Solvent	k_2/ l mol^{-1} s^{-1}	k_3/s^{-1}	K_1/ l mol^{-1}
Me	Benzene	$1{\cdot}1 \times 10^{3}$	$1{\cdot}8 \times 10^{-2}$	6×10^{4}
Me	Vinyl acetate	$1{\cdot}1 \times 10^{3}$	$1{\cdot}0 \times 10^{-2}$	6×10^{4}
Et	Benzene	$2{\cdot}5 \times 10^{2}$	$1{\cdot}4 \times 10^{-2}$	1×10^{4}
Pr^i	Benzene	1·0		$<2 \times 10^{2}$

Weiner and Mahoney estimated the activation energy for reaction (ii) to be $0{\cdot}9 \pm 1{\cdot}0$ kcal mol^{-1} for 4-methyl-DTBP, utilising their experimental values of the activation energy for the reaction in the first-order high-concentration region ($18{\cdot}3 \pm 0{\cdot}9$ kcal mol^{-1}) and the enthalpy change in reaction (i) ($-17{\cdot}4 \pm 0{\cdot}5$ kcal mol^{-1}). They found the increase in activation energy from 0·9 for 4-methyl-DTBP to 6·2 kcal mol^{-1} for 4-isopropyl-DTBP to be so surprising that they ' concluded that the 4-isopropyl derivative may be reacting *via*

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[11] C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, 1959, **81**, 1176.

[12] H. Huberle, H. Suhr, and U. Heilmann, *Chem. Ber.*, 1962, **95**, 639.

[13] H. D. Becker, *J. Org. Chem.*, 1965, **30**, 982.

[14] R. H. Bauer and G. M. Coppinger, *Tetrahedron*, 1963, **19**, 1201.

[15] L. J. Filar and S. Winstein, *Tetrahedron Letters*, 1960, 9.

molecular decomposition of its dimer.' We believe the route *via* reaction (ii) is more probable, particularly since the activation energies for hydrogen abstraction from 4-isopropyl-DTBP by the radicals DPPH [10] and 4-isopropyl-DTBP are almost the same.

The equilibrium constant, K_1, for dimerisation of 4-methyl-DTBP in benzene is estimated from these kinetic studies to be 6×10^4 l mol^{-1} at 22 °C. An approximate but more direct estimate from flash photolysis studies of 4-methyl-2,6-di-t-butylphenol in carbon tetrachloride [2] is $1{\cdot}4 \times 10^6$ l mol^{-1} at 20 °C. The lower value in the present work may be partly explained by the change in solvent. Substitution of 4-ethyl for 4-methyl leads to a lower value of K_1; there is no evidence for dimer formation of 4-isopropyl-DTBP even at concentrations of *ca.* 2×10^{-3}M, and K_1 for this radical must be less than 200 l mol^{-1} at 22 °C.

The present results confirm the main prediction of the mechanism of Weiner and Mahoney concerning the transition to an overall second-order reaction at low concentration of 4-methyl-DTBP. The changeover from first-order to second-order kinetics occurs at 4-methyl-DTBP concentrations in the range 10^{-5}—10^{-6}M as would be expected if the equilibrium constant for dimer formation is about 6×10^4 l mol^{-1}. The change from first-order to second-order kinetics in the 4-ethyl-DTBP decay as the temperature was raised from 21—26 to 47 °C (ref. 4) can be rationalised if the equilibrium constant for dimerisation decreases rapidly with temperature. If we assume that $\Delta H = -17{\cdot}4 \pm 0{\cdot}5$ kcal mol^{-1} for the dimerisation of 4-ethyl-DTBP (as observed by Weiner and Mahoney for 4-methyl-DTBP), an increase of 20° could lead to a six-fold increase in the concentration range in which the order changes from 2 to 1.

The rate constants, k_{obs}, given in Tables 1 and 2 show a trend towards higher values as the estimated initial concentration of phenoxyl decreases. Further increases in the so-called 'rate constants' occur as the initial concentrations of phenoxyl drop below 10^{-6}M and the decay is observed for radical concentrations down to 10^{-7}M. One possible reason for this behaviour is retardation of the reaction by the quinone methide product. However, addition of the corresponding quinone methide to decaying 4-isopropyl-DTBP (10^{-3} to 10^{-5}M) had no effect on the rate of disappearance of the radical. Product retardation is thus not a general explanation for the variation in rate constant. A second possible reason is suggested by the results of Huberle *et al.*; [12] they recorded a three-fold increase in apparent rate constant and a change in product when they decreased the initial concentration of 4-isopropyl-DTBP from $2{\cdot}8 \times 10^{-2}$ to 2×10^{-3}M. Their reaction mixtures were prepared in an atmosphere of nitrogen but oxygen was not rigorously excluded and the higher rate constants can probably be ascribed to a side reaction with oxygen. The benzene and vinyl acetate used in the present work were carefully degassed and any side reactions of the phenoxyl radicals, particularly with oxygen, should not seriously compete with the main reactions at relatively high phenoxyl concentrations. At very low initial concentrations of phenoxyl ($<10^{-6}$M), it is possible that a side reaction becomes important and the trend in observed rate constants is tentatively ascribed to this source.

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