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THE KINETICS OF DISPROPORTIONATION OF THE 2,6-DI-T-BUTYL-4-METHYL PHENOXY RADICAL

R. STEBBINS and F. SICILIO
Department of Chemistry, Texas A & M University, College Station, Texas 77843

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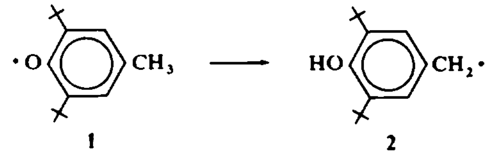
Abstract—The reaction between 2,6-di-t-butyl-*p*-cresol (BHT) and lead dioxide produces the 2,6-di-t-butyl-4-methyl phenoxy radical. Decay of this radical in THF and benzene has been studied by optical and ESR methods. Decay is second order with respect to the radical, with a specific rate constant $k_d = 3{\cdot}33 \times 10^2\ M^{-1}\,sec^{-1}$ in THF and $k_d = 4{\cdot}59 \times 10^2\ M^{-1}\,sec^{-1}$ in benzene at $24{\cdot}0 \pm 1{\cdot}0°$. The specific rate constant is independent of [BHT] and [PbO_2], but is extremely sensitive to oxygen. Isolation of dimeric products 1,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)ethane and 3,3′, 5,5′-tetra-t-butyl-4,4′-stilbenequinone and observation of the quinone methide intermediate in both solvent systems suggest that disproportionation of phenoxy radicals to yield quinone methide and the parent phenol is the mechanism for phenoxy decay.

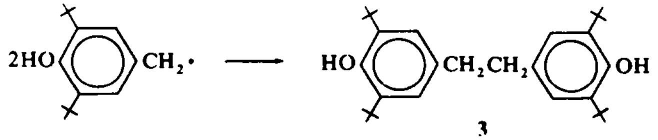
INTRODUCTION

OXIDATION of 2,6-di-t-butyl-*p*-cresol (**5**) by various reagents has been studied extensively.[1–16] The phenoxy radical, **1**, resulting from oxidation by alkaline ferricyanide,[7] lead dioxide in anhydrous acetone or benzene,[9] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[12] has been observed by ESR.

Although a general mechanism of hindered phenoxy decay has been postulated by both Cook[14] and Müller,[15] the decay mechanism of **1** has been subject to debate over the past 15 years. Bennett[7] and Brodskii, *et al.*[13] advocate first order kinetics, supporting rearrangement of **1** to the hydroxybenzyl free radical, **2**. Dimerization of **2** and subsequent oxidation of the dimeric products leads to the final products, 1,2-bis (3,5-di-t-butyl-4-hydroxyphenylethane, **3**, and 3,3′, 5,5′-tetra-t-butyl-4,-4′-stilbenequinone,**4**.


1 **2**

(a)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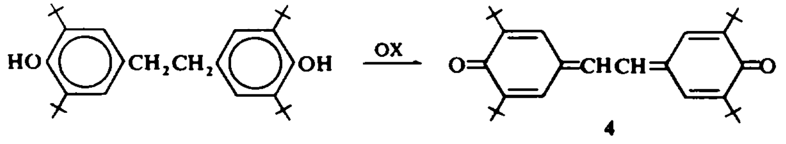
(b)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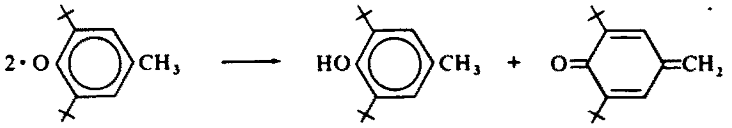
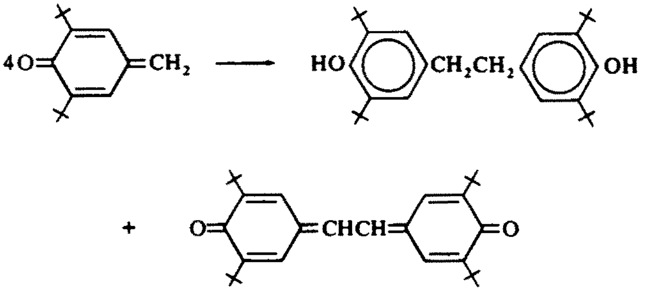
(c)

However, Bauer and Coppinger[16] obtained second order kinetics, supporting the disproportionation of **1** to the parent phenol, **5**, and the quinone methide, **6**. Further reaction of **6**, stoichiometrically represented by Eq. (e), results in the end products, **3** and **4**



5 **6**

(d)

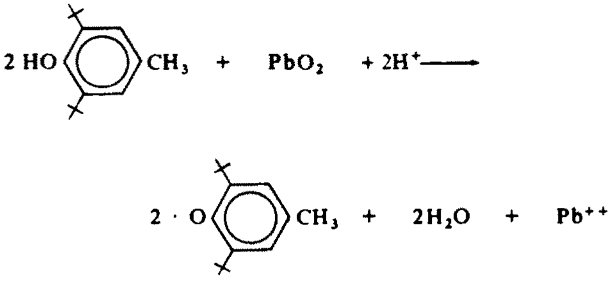


(e)

The rapid decay of the phenoxy radical, coupled with its small concentrations at other than very short times, are the main experimental reasons for disagreement as to reaction order.

Since the dimeric end products are the same for each mechanism, settlement of the debate hinges on the detection of intermediates (**2** or **6**), and determination of the correct reaction order.

Oxidation of **5** with lead dioxide in THF and benzene has been carried out in this laboratory, and can be represented by the following reaction



(f)

Reaction (f) and the subsequent decomposition of **1** has been followed by observing the characteristic ESR spectrum of **1**. Plots of [**1**] *vs* time have shown the decay to be second order in both solvents. In THF, the specific rate constant is $k_d = 3{\cdot}33 \times 10^2\ M^{-1}\ sec^{-1}$ with a relative standard deviation of 10·9%. In benzene, $k_d = 4{\cdot}59 \times 10^2\ M^{-1}\ sec^{-1}$ with a relative standard deviation of 9·62%. Intermediate **6** has been observed in both solvent systems, while intermediate **2** has not been observed. Thus our findings are in agreement with those of Bauer and Coppinger.[16]

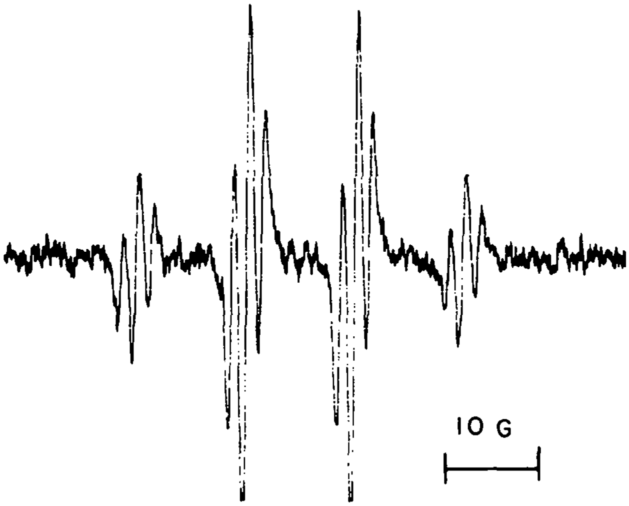


FIG. 1. ESR spectrum of 2,6-di-t-butyl-4-methyl phenoxy radical in THF at 24·0°. Magnetic field increases to right. Initial moles: 1·20 × 10^{-4} (5), 3·21 × 10^{-3} PbO_2.

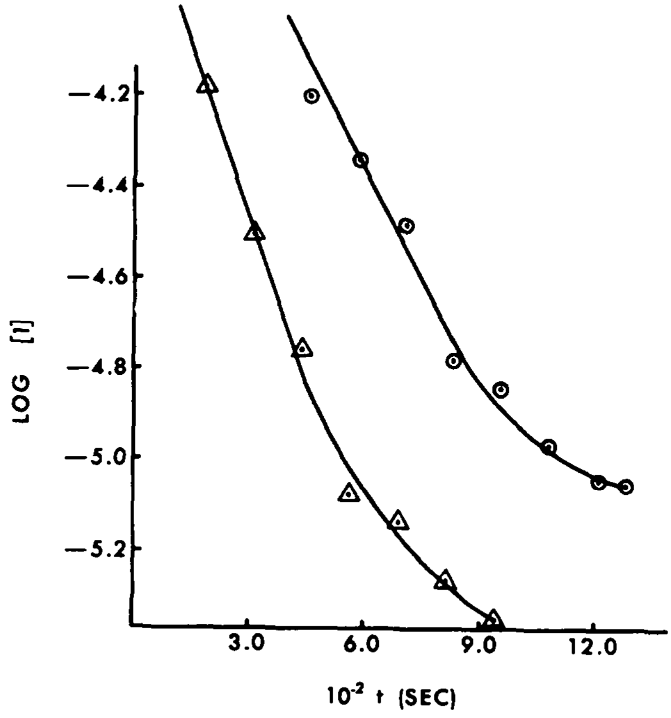


FIG. 2. Log [1] vs time at 24°. ⊙ in THF. Initial moles: 1·09 × 10^{-3} (5), 4·74 × 10^{-4} PbO_2. Δ in benzene. Initial moles: 3·45 × 10^{-3} (5), 3·74 × 10^{-4} PbO_2.

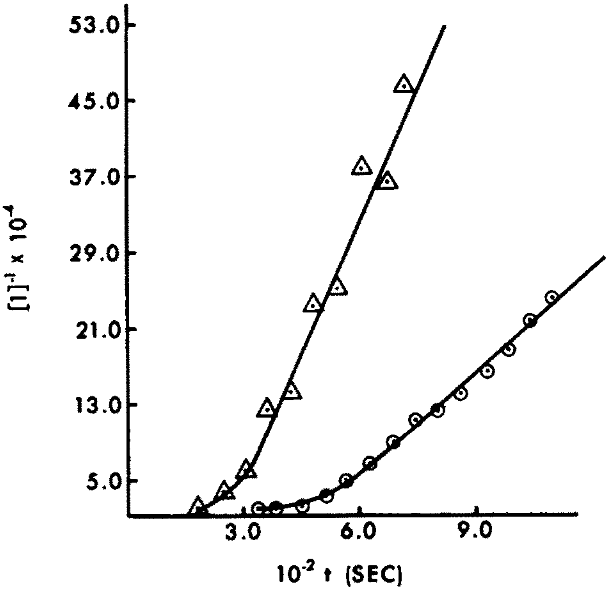


FIG. 3. Reciprocal phenoxy concentration, $[1]_t^{-1}$ vs time at 24°. O in THF. Initial moles: $1{\cdot}09 \times 10^{-3}$ (5), $4{\cdot}74 \times 10^{-4}$ PbO_2. Δ in benzene. Initial moles: $3{\cdot}45 \times 10^{-3}$ (5), $3{\cdot}74 \times 10^{-4}$ PbO_2.

RESULTS AND DISCUSSION

The phenoxy radical 1 was generated in THF and benzene under N_2 according to reaction (f), and the characteristic ESR spectrum of 1, a quartet of triplets ($g = 2{\cdot}0028 \pm 0{\cdot}0002$), was observed, Fig. 1. Splitting from the Me hydrogens is 10·8 ± 0·1 G, and splitting from the meta hydrogens is 1·8 ± 0·1 G. Signal intensity decreases with time; plots of various orders of phenoxy decay were graphed.

Comparison of the first and second order phenoxy decay plots of Brodskii, *et al.*[13] seems to indicate that the decay is first order. However, the time range for their plots extends up to 300 sec. Figures 2 and 3 are representative of first and second order plots for data obtained in this laboratory, with the time scale extended to 1200 sec. The range of observable phenoxy concentration is thus extended by an order of magnitude. Up to 300 sec, the first order decay plots are indeed linear, but beyond this deviation from linearity is observed. Alternatively, the second order decay plots are linear from 500 to 1200 sec. Therefore, a decay mechanism combining a first and second order phenoxy term, with the second order term predominating at higher concentrations, is ruled out.

At $t < 500$ sec, deviation of the second order plot from linearity is caused by the formation of 1, from reaction of unfiltered particles of lead dioxide with 5. Whatman #42 filter paper proved to be the most efficient filtration system for lead dioxide, but complete removal of the oxidizing agent from the solvent proved impossible even by this method. Using the method of Sandell,[20] it was found that approximately $2{\cdot}0 \times 10^{-7}$ moles of PbO_2 remained in 10·0 ml of solvent after filtration. Since the maximum observable concentration of phenoxy radicals for any given run is in the order of $1{\cdot}0 \times 10^{-4}$ M, and the stoichiometry of reaction (f) shows that

2 moles of 1 are generated by 1 mole of PbO_2, the observed magnitude of deviation from linearity at the shorter times is reasonable. Further, examination of all second order plots reveals that as [5] is increased, the magnitude of deviation becomes more predominant at shorter times. Since the formation term for 1 may be written as $k_f[PbO_2]^m[5]^n$, where m and n are unknown, and since the number of moles of unfiltered PbO_2 has been found to remain constant, one would expect that an increase in [5] would lead to the above result.

In Table 1, the rate constant for disproportionation of 1 is given for different initial concentrations of starting reactants in THF and benzene. Although the initial concentrations and ratios of starting reactants are varied by more than an order of magnitude, there are no obvious effects on the value of the rate constants. The average value for all runs in THF is $k_d = 3{\cdot}33 \times 10^2\ M^{-1}\ sec^{-1}$, with a relative standard deviation of 10·9%. In benzene, $k_d = 4{\cdot}59 \times 10^2\ M^{-1}\ sec^{-1}$, and the relative standard deviation is 9·62%. Due to the magnitude of the rate constant, experimental difficulties, and the limits of reproducability of signal intensity of the ESR spectrometer, it is doubtful that significant improvement of this figure can be obtained by the present method.

Disproportionation was further confirmed by observation of the intermediate quinone methode, 6, and the two dimeric end products (3 and 4) in both THF and benzene. The quinone methide buildup was followed in the UV region at 285 mμ, with 85% reaction occurring in the first 90 min. The end products, (3 and 4), were isolated according to the procedure of Yohe, *et al.*[4] White needles, m.p. 170·0–170·5° were obtained for 3, while red rodlets, m.p. 312·0–315·0°, were obtained for 4.

TABLE 1. VALUES OF k_d FOR DIFFERENT RATIOS OF STARTING REACTANTS AT 24°

Run[a]	Moles (5) × 10^3	Moles PbO_2 × 10^3	Moles (5)/Moles PbO_2	$k_d \times 10^2\ (M^{-1}\ sec^{-1})$[b]
1	3·500	0·408	8·59	3·97 ± 0·21
2	1·199	0·4912	2·441	2·88 ± 0·11
3	1·109	1·371	0·8090	2·09 ± 0·05
4	1·089	0·4740	2·296	2·43 ± 0·13
5	0·9957	0·4418	2·254	2·46 ± 0·85
6	0·9712	4·568	0·2126	1·90 ± 0·03
7	0·8750	0·357	2·45	4·80 ± 0·15
8	0·6757	0·167	4·05	3·78 ± 0·15
9	0·6716	0·124	5·42	4·50 ± 0·21
10	0·5650	0·1112	5·081	4·47 ± 0·14
11	1·743	0·022	79	4·17 ± 0·23
12	1·467	0·366	4·01	4·80 ± 0·35
13	1·029	0·411	2·50	3·84 ± 0·23
14	0·345	0·922	0·374	5·56 ± 0·23
15	2·248	0·361	6·23	6·06 ± 0·36
16	0·309	0·6071	0·509	9·13 ± 0·42

[a] Runs 1–10 in distilled THF, runs 11–14 in benzene, and runs 15 and 16 in oxygenated THF.

[b] Limits calculated as the square of the standard deviation, σ, using the equation $\sigma^2 = \sum_i (y_i - \varepsilon_i)^2 / N \sum_i x_i^2 - (\sum x_i)^2$ where x_i is the time after mixing, ε_i is the least squares computed value of reciprocal concentration, y_i is the observed value of reciprocal concentration, and N is the number of points.

Runs 15 and 16 of Table 1 show that the presence of oxygen produces an increase in the rate constant. It has been reported[4] that in neutral solutions **5** takes up negligible amounts of oxygen. This was further confirmed by Coppinger,[17] who found that reaction of **5** with oxygen yielded no peroxycyclohexadienones, characteristic of oxygen reaction with other 4-substituted analogs of **5**. Although no peroxidic products were observed by the above authors or in this laboratory, formation of trace amounts of peryoxycyclohexadienones could significantly change the value of the rate constant, due to the low concentration of phenoxy radicals. Alternatively, reaction of oxygen with the solvent and reaction of the resulting peroxide with **1** could also form peroxycyclohexadienones. Thus, failure to exclude oxygen may lead to erroneous results.

We have thus concluded that Brodskii, *et al.*[13] failed to remove all of the lead dioxide from their system. The decay of **1**, as suggested by Bauer and Coppinger,[16] is second order. Further, the rate constant is two orders of magnitude greater than that for disproportionation of the 2,6-di-t-butyl-4-isopropyl phenoxy, the 2,6-di-t-butyl-4-s-butyl phenoxy and the 2,6-di-t-butyl-4-cyclohexyl phenoxy radicals.[14] This seems reasonable in light of the decreased stability of **1** due to absence of branching on the 4-substituent.

EXPERIMENTAL

Starting materials. 2,6-di-t-butyl-*p*-cresol (Eastman practical grade) was recrystallized from a 9:1 acetone–water mixture and dried overnight in a vacuum oven at 30°; m.p. 69·5–70·0° agrees with the lit value.[8] THF (Baker analyzed reagent grade) was dried over Na wire, refluxed under N_2 until dry and free of peroxides, and distilled under N_2. Benzene (Fisher spectroanalyzed thiophene free) was refluxed over Na wire for 3 hr, and then distilled under N_2. Purity of both the THF and benzene was checked and confirmed with a Hewlett–Packard 5750 gas chromatograph and a Beckman DK-1 spectrophotometer. CCl_4 (Baker analyzed reagent grade) was dried over $CaCl_2$ for 24 hr and then distilled. PbO_2, $Pb(NO_3)_2$ (both Mallinckrodt analytical grade) and sodium oxalate (Baker analyzed primary standard) were used without further purification.

Procedure. For the reaction of PbO_2 with **5**, both PbO_2 and 2,6-di-t-butyl-*p*-cresol were weighed directly into 10-ml volumetric flasks. Along with freshly distilled solvent, they were transferred to a dry bag. After several alternate fillings and deflations with dry N_2, air was expelled and **5** was dissolved in solvent and diluted to 10 ml. The soln was added to the PbO_2 and a timer started simultaneously. The soln was then swirled, filtered through two pieces of Whatman #42 filter paper, and transferred to a Varian static quartz cell. The cell was stoppered, removed from the dry bag, and placed in the resonant cavity of a Varian 4502-15 ESR spectrometer equipped with V-4560 100-kHz field modulation and Fieldial units. All kinetic and spectral measurements were made in the X-band region with about 30 mW microwave power and 0·8 G modulation amplitude. At these settings, no saturation or modulation broadening was observed. Magnetic field intervals were calibrated with the nitrosodisulfonate anion ($a = 13{\cdot}0 \pm 0{\cdot}1$ G).[18] To measure g-values, 2,2,-diphenyl-1-picrylhydrazyl, (DPPH), with $g = 2{\cdot}0036 \pm 0{\cdot}0002$,[19] was introduced into the flat cell after obtaining the first low field peak of the quartet, without interruption of scan.

All work in the visible and UV regions was performed on a Beckman DK-1 double beam spectrophotometer at 24·0 ± 0·5° using 1·0-cm matched cells. The characteristic peak of **6**, was observable in the UV region at 285 mμ. Solns of $1{\cdot}0 \times 10^{-3}$ M (**5**) in THF and benzene were reacted with excess PbO_2, and the growth of the UV peak observed as a function of time. Each growth point was obtained by diluting a 1·0-ml aliquot of filtered reaction mixture 1:100, transferring a portion to a 1·0-cm matched cell, and obtaining the spectrum using pure solvent as a reference. Since λ_{max} for **5** occurs at 275 mμ, a standard curve for **5** in each solvent was obtained, and its extinction coefficient at 285 mμ calculated.

The analysis of unfiltered PbO_2 was accomplished by the dithizone method as described by Sandell.[20] A soln of dithizone in CCl_4 extracts Pb^{++} from an aqueous phase at a pH of approximately 9·5 according to the following scheme, where w and o represent the water and organic layers respectively.

$$Pb^{++}(w) + 2H_2Dz(o) \rightarrow Pb(HDz)_2(o) + 2H^+(w) \qquad (g)$$

All solns and all glassware used in the analysis were treated with dithizone in CCl_4 to preclude extraneous Pb contamination. Standard solns of $Pb(NO_3)_2$ in dil HNO_3 were prepared, aliquots placed in a separatory funnel, adjusted to pH ≈ 9·5 with dil NH_4OH, and extracted with aliquots of dithizone in CCl_4. The organic layer was then transferred directly into a UV cell, and a working curve for the Pb complex established by observation of its characteristic absorption curve at 510 mμ.

Samples of PbO_2 were then weighed into 100-ml flasks and reacted with excess sodium oxalate according to the reaction

$$PbO_2 + C_2O_4^{=} + 4H^+ \rightleftharpoons 2CO_2(g) + Pb^{++} + 2H_2O \qquad \text{(h)}$$

After heating to 50° for 1 hr to remove the CO_2 and shift the equilibrium to the right, the soln was diluted so that $[Pb^{++}]$ was within the range of working curve concentrations. Extraction by the same method employed above gave values of $[Pb^{++}]$ some 20% lower than expected.

Two samples of PbO_2 were weighed into 10·0-ml volumetric flasks for each solvent to be studied. The flasks were filled to the mark, shaken for 15 min, and filtered as in the ESR runs. The solvent was evaporated to dryness, and excess oxalate was added to the beaker in HNO_3 soln. Each sample was then treated as above to determine the Pb^{++} in 10 ml of solvent after filtration.

Kinetic measurements. Decay of the phenoxy radical signal was noted as a function of time at 24·0 ± 1·0°. Plots of reciprocal area *vs* time gave a straight line after $t = 500$ sec. The area, A, under the absorption curve was calculated by the relation $A\alpha\Delta H^2 \times I_p$ where ΔH is the peak to peak width of the first derivative curve and I_p is the peak to peak intensity.[21] This method was found to be more reliable than double integration, especially at small peak heights. The area to peak height ratio was found to be constant within the limits of experimental error, allowing one to plot reciprocal peak height *vs* time.

Absolute radical concentrations were calculated using DPPH as a standard. The DPPH was analyzed for purity by the method of Nazaki,[22] and was found to be 98·7 ± 0·1% pure. Before and after each set of runs, DPPH was dissolved in freshly distilled solvent and injected into the clean ESR cell with a syringe. The area under this absorption was then measured and related to the area of the phenoxy radical spectrum.

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