

Inhibition of Free-Radical Reactions. II.¹ Kinetic Study of the Reaction of Peroxy Radicals with Hydroquinones and Hindered Phenols

L. R. Mahoney

Contribution from the Scientific Laboratory, Ford Motor Company, Dearborn, Michigan. Received January 14, 1966

Abstract: The rate of dissociation of 2,2,3,3-tetraphenylbutane (TPB) in solution at 60.0° has been measured by the oxygen scavenging-antioxidant technique. The first-order rate constant is independent of oxygen pressure (above 200 mm) in chlorobenzene and has the value of $2.0 \pm 0.1 \times 10^{-4} \text{ sec}^{-1}$ in the three solvents chlorobenzene, nitrobenzene, and isopropylbenzene. In the three solvents the efficiency of radical production is essentially unity. Solutions of 9,10-dihydroanthracene (0.050 to 1.580 M) in chlorobenzene containing TPB absorb oxygen at a rate which is accurately first order in hydrocarbon and one-half order in TPB, indicating a lack of solvent effects due to variations in hydrocarbon concentration in the region examined. A series of hydroquinones and hindered phenols were then employed as inhibitors for the 9,10-dihydroanthracene-TPB system. Rate measurements conducted in the presence and in the absence of added hydroperoxide are consistent with the view that chain transfer reactions of the radicals derived from the inhibitor with hydrocarbon and with hydroperoxide are very inefficient processes for these compounds. Although the relative reactivities of these inhibitors vary among themselves by a factor of 2000, the results of this portion of the study also demonstrate that peroxy radicals derived from TPB and from the hydrocarbon are indistinguishable in their rates of reaction with each inhibitor.

Low concentrations of phenols and hydroquinones reduce the rates of oxygen absorption by solutions of hydrocarbons containing a source of free radicals. The complexities of the reactions occurring in these systems have been the subject of a number of recent reports.¹⁻⁵ Due to the theoretical and practical importance^{6,7} of the reactions of phenols and hydroquinones with peroxy radicals and of the species derived from such reactions, this laboratory has initiated an extensive kinetic and mechanistic investigation of such systems.

Many standard hydrocarbon-initiator systems have been used previously for such studies. Unfortunately most of them were designed originally for mechanistic studies of unretarded chain oxidations involving long kinetic chain lengths, and their use to obtain meaningful rate data under conditions of retardation where chain lengths are short is problematical. Bickel and Kooyman in their studies of trialkylphenols⁸ and aromatic amines⁹ introduced the use of 9,10-dihydroanthracene as a standard hydrocarbon and 2,2,3,3-tetraphenylbutane as an initiator for studies of strongly retarded oxidations. Although this system has not been used by other workers, it possesses a number of desirable characteristics for such studies.

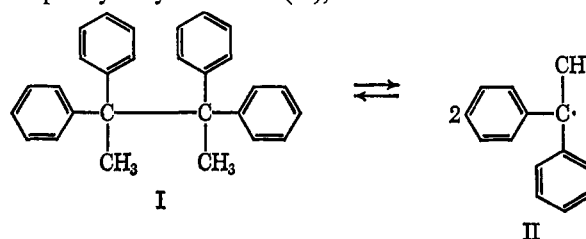
The present work has several goals, the first of which is to determine the effect of solvent on both the rate of decomposition of, and efficiency of radical production from, the initiator. Secondly the solvent effects due to variation of hydrocarbon concentrations are to be evaluated for the system of Bickel and Kooyman.

Finally, the effects of hydroperoxide,³ chain transfer by inhibitor radicals,^{1,8,9} and the relative reactivities of the peroxy radicals derived from the initiator and from the hydrocarbon⁴ are then to be determined for a number of hydroquinones and hindered phenols of widely varying structures and reactivities.

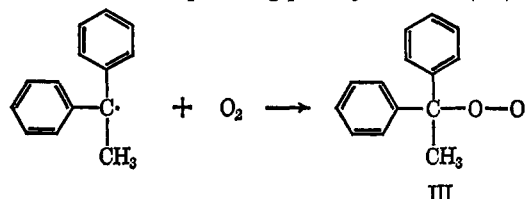
Results and Discussion

Source of Free Radicals. The choice of an initiator for a quantitative study of the inhibition of free-radical autoxidation of hydrocarbons is very important. The initiator must decompose by a well-understood and preferably first-order process. The wastage of radicals by solvent cage recombinations of geminate radicals should be independently measurable. Corrections due to the absorption of oxygen or evolution of gaseous products by the initiator must be known and/or measurable for each system studied.

The initiator adopted by Bickel and Kooyman, 2,2,3,3-tetraphenylbutane (I, TPB), meets most of these requirements. It dissociates in solution to form 1,1-diphenylethyl radicals (II),¹⁰ which react with oxy-



gen to form the corresponding peroxy radicals (III).



(10) K. Ziegler, *Ann.*, **551**, 150 (1942).

- (1) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2345 (1963), is considered paper I in this series.
- (2) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 2324 (1964).
- (3) J. R. Thomas, *J. Am. Chem. Soc.*, **85**, 2166 (1963).
- (4) W. G. Lloyd and C. E. Lange, *ibid.*, **86**, 1491 (1964).
- (5) J. R. Thomas, *ibid.*, **86**, 4807 (1964).
- (6) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).
- (7) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 192.
- (8) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).
- (9) A. F. Bickel and E. C. Kooyman, *ibid.*, 2217 (1957).

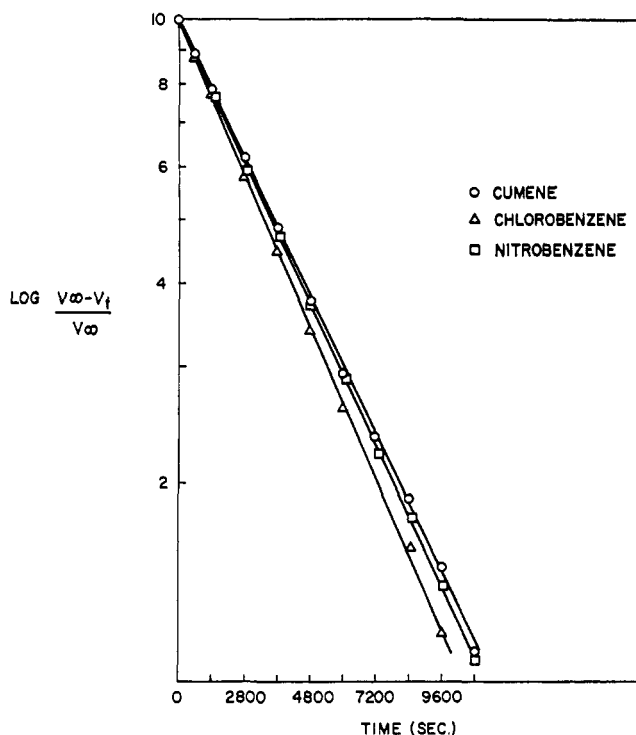
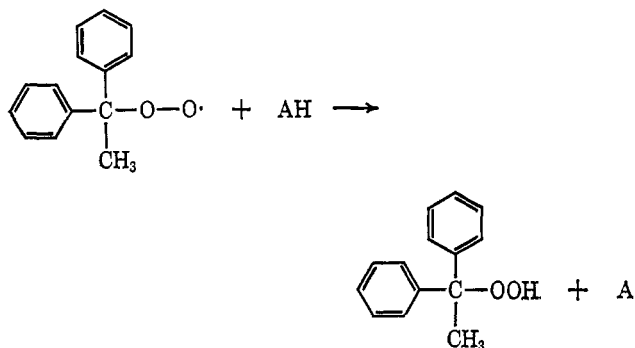


Figure 1. First-order plot for the absorption of oxygen by 2,2,3,3-tetraphenylbutane in the solvents cumene, chlorobenzene, and nitrobenzene at 60°.

In the presence of a hydrogen donor (AH) the peroxy radicals are converted to the hydroperoxide. Since



TPB does not evolve nitrogen or carbon dioxide, its rate of dissociation can be followed readily by measurement of the rates of oxygen absorption of its solutions in the presence of AH, provided that A· neither absorbs oxygen nor induces the decomposition of I and provided that the reaction of oxygen with II to form III is rapid compared to the rate of formation of II.

In this work, we have measured the initial rates of oxygen absorption of solutions of chlorobenzene containing I and 2,6-di-*t*-butyl-4-methylphenyl (2,6-TBPC) at different oxygen pressures. The data are presented in Table I. In contrast to hexaphenylethane¹⁰ the rates are independent of oxygen pressures; thus, reaction of II with O₂ is rapid. The rates are first order in I and are independent of the concentration of 2,6-TBPC; therefore, induced decomposition is negligible. The value for the first-order rate constant obtained in this study at 60.0° in chlorobenzene is $2.0 \times 10^{-4} \text{ sec}^{-1}$. This value compares to $2.057 \times 10^{-4} \text{ sec}^{-1}$ at 60.05° and $2.06 \times 10^{-4} \text{ sec}^{-1}$ at 60.0° in bromo-

benzene reported by earlier workers.^{8,10} The oxygen absorption of the compound was also determined as a function of time in two other solvents, cumene and nitrobenzene. For times corresponding to 16 half-lives, the stoichiometric amount ($\pm 4\%$) of oxygen was absorbed and excellent first-order plots were obtained in all cases (cf. Figure 1 and Table II). The decomposition rate is thus insensitive to solvent and the efficiency of radical production is also essentially unity under a variety of conditions.

Table I. Rate of Decomposition of 2,2,3,3-Tetraphenylbutane at 60° in Chlorobenzene

TPB $\times 10^3$ moles l. ⁻¹	p_{O_2} , mm	2,6-TBPC $\times 10^3$ moles l. ⁻¹	Rate $\times 10^7$ moles l. ⁻¹ sec ⁻¹	$k' \times 10^4$ sec ⁻¹ ^a
5.95	680	1.97	22.3	1.88
5.95	215	1.97	22.6	1.90
2.38	200	1.97	9.40	1.97
2.38	680	1.97	9.70	2.04
2.38	680	1.97	9.50	2.00
1.19	680	8.60	5.00	2.10
1.19	680	0.86	4.70	2.02

^a Rate was determined by absorption of 0.22×10^{-3} mole l.⁻¹ of O₂ or decomposition of 0.11×10^{-3} mole l.⁻¹ of TPB.

Table II. Decomposition of 2,2,3,3-Tetraphenylbutane at 60° in Various Solvents

Solvent	TPB, mmoles	Oxygen absorbed, mmoles ^a	2,6-TBPC $\times 10^3$ moles l. ⁻¹	$k' \times 10^4$ sec ⁻¹ ^b
Chlorobenzene	1.41	2.91	28.0	2.01
Chlorobenzene	2.84	5.48	28.3	2.06
Nitrobenzene	3.51	7.41	34.4	1.99
Cumene	3.50	6.70	417.0	1.94

^a At 6×10^4 sec (approximately 16 half-lives). ^b Rate determined from plot of $\log ((V_\infty - V_t)/V_t)$ vs. time.

Ideally, the structure of the initiator radical should be identical with that of the radical derived from the substrata although this can seldom be realized in practice. At the low kinetic chain lengths obtained in inhibited oxidations, reactivity differences between the initiator radical and the radical derived from the hydrocarbon can result in partitioning of the two species between the substrata and the inhibitor. Such partitioning leads to very complicated kinetic rate expressions,^{4,11,12} for the rate of oxygen absorption. Since the diphenylethylperoxy radical (III) possesses a hydrocarbon moiety, possible complications due to differences in its reactivity compared to the chain carrying arylalkylperoxy radicals are expected to be minimized. This expectation has been realized (*vide infra*).

The Standard Hydrocarbon and the Kinetics of the Unretarded Oxidation. The hydrocarbon used for the study of inhibited oxidations must be reactive enough so that measurable oxidation occurs in the presence of strongly retarding phenols. As a corollary of this requirement the concentration of the hydrocarbon should not exceed 2.0 M. Howard and Ingold¹³ have reported anomalous rate effects due to changes in

- (11) W. A. Waters and C. Wickham-Jones, *J. Chem. Soc.*, 812 (1951).
 (12) W. A. Waters and C. Wickham-Jones, *ibid.*, 2420, 2427, 2432 (1952).
 (13) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 42, 1044 (1964).

reaction media on increasing hydrocarbon concentration to higher levels.

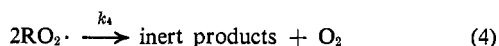
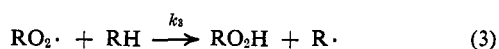
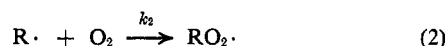
In order to ascertain the importance of this effect in the present system, the rates of oxygen absorption of solutions of 9,10-dihydroanthracene in chlorobenzene at 60° were determined as a function of the hydrocarbon and tetraphenylbutane concentrations. The results are summarized in Table III. The rate expression

Table III. Oxidation of 9-10 Dihydroanthracene in Chlorobenzene at 60°

[RH] × 10 ³ l. ⁻¹	TBP × 10 ³ moles l. ⁻¹	R _i × 10 ⁷ ^a moles l. ⁻¹ sec ⁻¹	$\frac{d[O_2]}{dt}$ × 10 ⁷ moles l. ⁻¹ sec ⁻¹	$\left(\frac{d[O_2]}{dt} - \frac{R_i}{2}\right) /$ [RH](R _i) ^{1/2} mole ^{-1/2} l. ^{1/2} sec ^{-3/2} ^b
50.0	1.24	4.96	39.4	0.105
242.3	1.20	4.80	163.0	0.095
243.3	0.12	0.48	51.4	0.096
242.3	0.03	0.12	26.3	0.099
334.0	1.18	4.72	224.0	0.095
1041.0	1.28	5.12	765.0	0.102
1565.0	0.33	1.32	588.0	0.103
1565.0 ^c	0.33	1.32	576.0	0.101

^a The quantity R_i was calculated from the relation, R_i = 2k₁[R—R]. ^b Assuming that one molecule of oxygen is produced in the termination of two radicals. ^c Pressure of oxygen is equal to 400 mm.

describing the oxidation is the well-known one-half-order dependence on initiator concentration and first-order dependence on hydrocarbon concentration. The kinetic mechanism consistent with the rate expression is the following



where R—R is 2,2,3,3-tetraphenylbutane, R· is the 1,1-diphenylethyl radical, RH is the hydrocarbon, and RO₂· is the chain-carrying peroxy radical. Utilizing the steady-state concentration assumption for radicals and since reaction 2 is not rate controlling, one may write

$$\frac{d[O_2]}{dt} - 0.5R_i = \frac{k_3}{(2k_4)^{1/2}} (R_i)^{1/2} [RH]$$

where R_i = 2k₁[R—R].

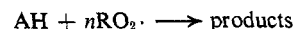
The value of k₃/(2k₄)^{1/2} is 100 × 10⁻³ mole^{-1/2} l.^{-1/2} sec^{-1/2}. The value of this ratio for tetralin is 5.5 × 10⁻³ mole^{-1/2} l.^{-1/2} sec^{-1/2} at the same temperature¹⁴ with AIBN as the free radical catalyst. If k₄'s for the secondary radicals are similar¹⁵ we see that 9,10-dihydroanthracene is 18 times more reactive than tetralin toward peroxy radicals.

Stoichiometric Factors, n. Since the rate of radical production from tetraphenylbutane is accurately known,

(14) L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 444 (1964).

(15) See, for example, (a) L. Bateman and G. Gee, *Trans. Faraday Soc.*, **47**, 155 (1951); L. Bateman, J. L. Bollard, and G. Gee, *ibid.*, **47**, 274 (1951); L. Bateman, G. Gee, S. L. Morris, and W. F. Watson, *Discussions Faraday Soc.*, **10**, 250 (1951).

it is possible to determine the stoichiometric factor *n* for each compound.¹⁶ The factor *n* is defined by the equation



and represents the total number of radical chains terminated by the phenolic compound and its products.

We have measured the inhibition period as a function of concentration of the strongly inhibiting phenolic compounds and the results are presented in Table IV. All of the inhibitors are capable of stopping at least two radical chains. The compound 1-hydroxyfluoranthene exhibits very complex stoichiometry suggesting the formation of products also capable of strong inhibition. A cobalt blue color is formed as this inhibitor is oxidized and the color reaches a maximum in intensity at an approximate stoichiometry of one radical per molecule of the starting phenol. The color is stable for several minutes at room temperature and is apparently not associated with a free radical since the solution does not yield an esr signal. As the oxidation progresses the solution becomes black and finally fades to a pale yellow at the end of the inhibition period.

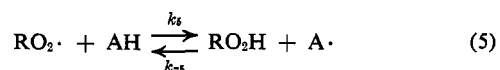
Table IV. Summary of Stoichiometric Factors

Compound	Original concn × 10 ⁴ moles l. ⁻¹	[Hydrocarbon] × 10 ³ moles l. ⁻¹	n ^a
1-Hydroxynaphthalene	1.52	148.0	2.09
	6.10	148.0	2.06
1-Hydroxyfluoranthene	1.01	148.0	3.35
	2.24	148.0	3.89
1,4-Dihydroxybenzene	2.24	148.0	1.76
	4.45	148.0	1.73
1,5-Dihydroxynaphthalene	1.56	148.0	1.95
	3.12	148.0	2.08
3,10-Dihydroxypyrene	2.04	1565.0	2.03
	3.06	1565.0	1.90
	4.08	1565.0	1.89
3,8-Dihydroxypyrene	1.28	1565.0	1.94
	2.13	1565.0	1.82
	2.99	1565.0	2.12

^a The value of *n* is defined by the expression

$$n = \frac{\text{moles of radicals produced during the inhibition period}}{\text{moles of compound originally present}}$$

Effect of Hydroperoxide. It has been demonstrated by Thomas that the measured rates of the phenol retarded oxidation of cumene³ and of tetralin⁵ are affected by the hydroperoxide formed in the reaction. The explanation offered for this observation is that a facile equilibrium exists between the peroxy radical and phenol, *i.e.*



In order to obtain reliable reactivity data, hydroperoxide should be absent from the system during the rate measurement or, equivalently, at a low enough concentration level so that the rate of reaction -5 is minimized. In this study the concentration of hydroperoxide initially present in the hydrocarbon was not

(16) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).

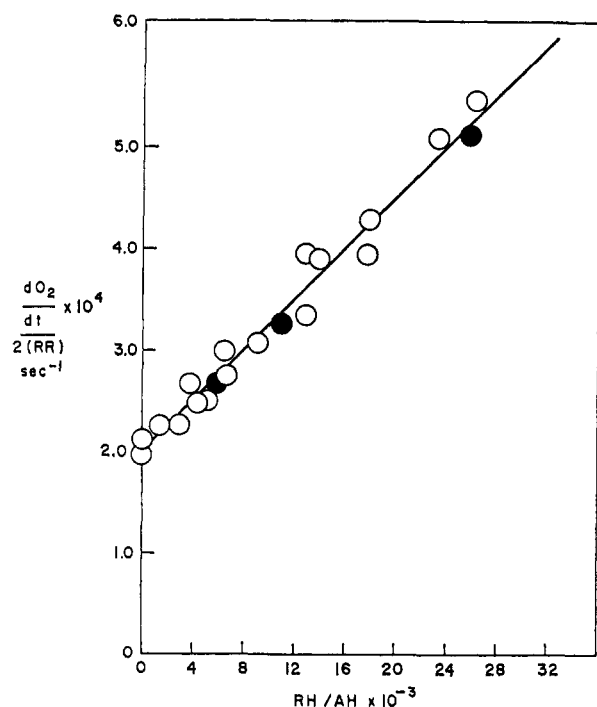


Figure 2. The rates of oxygen absorption of solutions of 9,10-dihydroanthracene and TPB in chlorobenzene inhibited by 3,8-dihydroxypyrene. The solid circles are the rates with $40 \times 10^{-4} M$ hydroperoxide added.

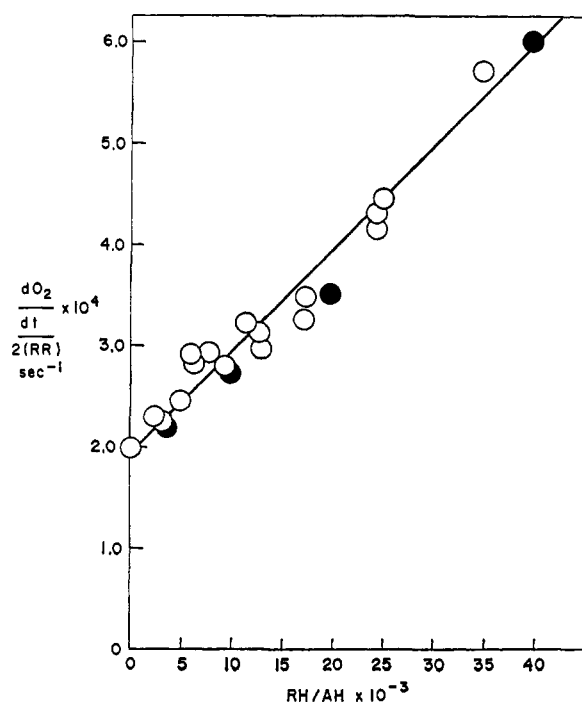


Figure 3. The rates of oxygen absorption of 9,10-dihydroanthracene and TPB in chlorobenzene inhibited by 3,10-dihydroxypyrene. The solid circles are the rates with $40 \times 10^{-4} M$ hydroperoxide added.

detectable, *i.e.*, less than $1 \times 10^{-4} M$, and the amount of hydroperoxide produced during the rate measurement corresponded to a maximum final concentration of $2.2 \times 10^{-4} M$. Neither autocatalysis nor auto-inhibition was observed during the course of the measurement. In Figures 2 and 3 are presented rate data

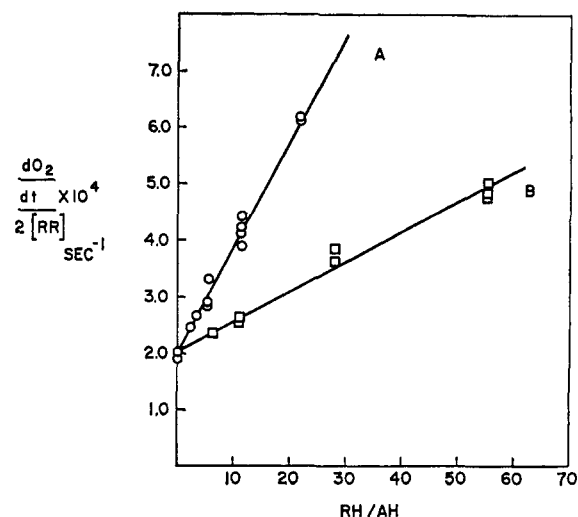


Figure 4. The rates of oxygen absorption of solutions of 9,10-dihydroanthracene and TPB in chlorobenzene inhibited by (A) 2,6-di-*t*-butylphenol and (B) 2,6-di-*t*-butyl-4-methylphenol.

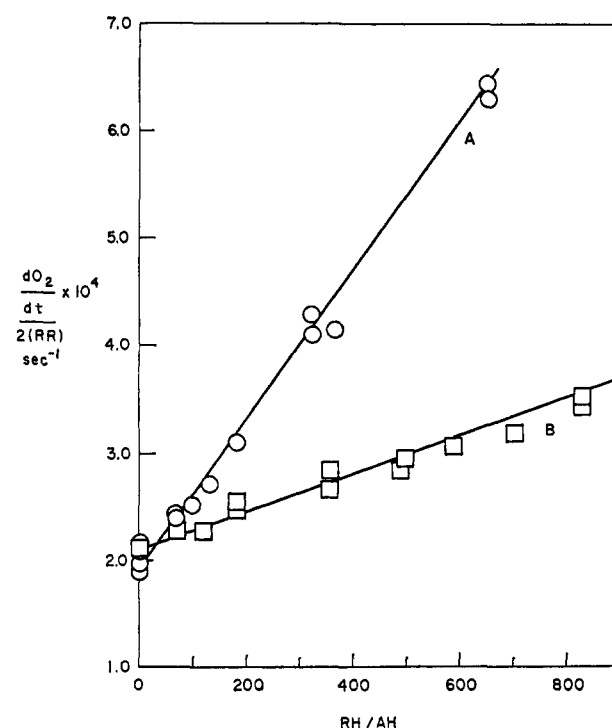


Figure 5. The rates of oxygen absorption of solutions of 9,10-dihydroanthracene and TPB in chlorobenzene inhibited by (A) 1,4-dihydroxybenzene and (B) 1,5-dihydroxynaphthalene.

obtained upon the addition of 9,10-dihydro-9-anthryl hydroperoxide at concentration levels up to 10 to 20 times higher than those encountered during the measurement. The change in the rate of oxygen absorption is small and the importance of the reaction -5 is negligible for the phenolic compounds reported in this work. Similar results have been reported for 2,6-di-*t*-butyl-4-methylphenol.^{2,3,5}

The Kinetics of the Inhibited Oxidation. The initial rates of oxygen absorption of solutions of 9,10-dihydroanthracene in chlorobenzene containing 2,2,3,3-tetraphenylbutane and sufficient phenols or hydroquinone to retard the oxygen absorption to less than 15% of its original rate were measured. The experimental data are presented in Figures 2-6 and the

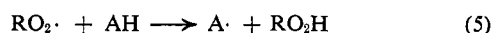
Table V. Rate of Oxidation of 9,10-Dihydroanthracene in Chlorobenzene at 60° Inhibited by 1,4-Dihydroxybenzene

[AH] × 10 ³ moles l. ⁻¹	[RH] × 10 ³ moles l. ⁻¹	[TPB] × 10 ³ moles l. ⁻¹	Rate × 10 ⁷ moles l. ⁻¹ sec ⁻¹
0.72	458	0.58	7.30
0.72	458	1.16	15.0
0.77	50	1.24	6.0
0.785	0	1.16	4.7
0.785	0	1.19	5.0
0.785	0	1.19	4.6
0.74	242	1.19	9.60
0.765	99	1.23	6.70
1.44	458	1.16	10.1
1.44	458	1.16	9.8
1.48	242	1.19	7.4
1.53	99	1.23	5.9
1.51	148	1.22	6.1
1.57	0	1.26	4.9

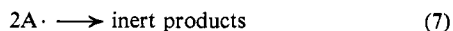
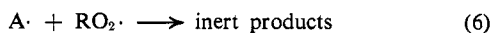
results obtained for 1,4-dihydroxybenzene are given in Table V. The rates are accurately described by the expression

$$\frac{1}{2[R-R]} \frac{d[O_2]}{dt} = a + b \frac{[RH]}{[AH]} \quad (A)$$

This expression is consistent with the mechanism in which there is a competition for the peroxy radical between the hydrocarbon (reaction 3) and the phenolic compound (reaction 5). Reaction 5 is then followed



by one or both of the rapid reactions (6 and 7)



At a steady-state concentration of radicals we may write

$$2k_1[R-R] = 2k_5[RO_2 \cdot][AH]$$

or

$$2k_1[R-R] = k_5[RO_2 \cdot][AH]$$

depending on whether reaction 6 or reaction 7 to form an inert dimer is predominant. In the first case

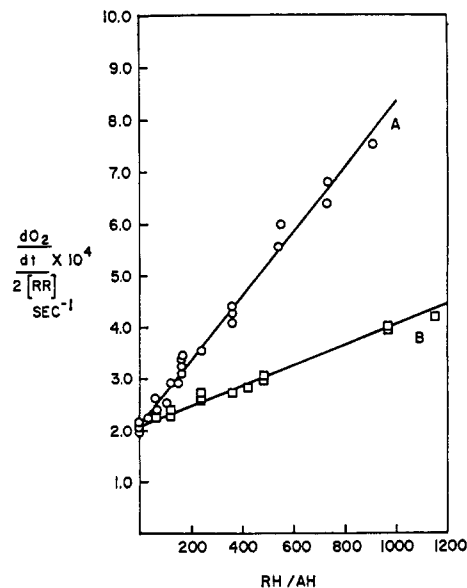
$$\frac{d[O_2]}{dt} = 2k_1[R-R] + 2k_1[R-R] \frac{k_3[RH]}{2k_5[AH]}$$

while

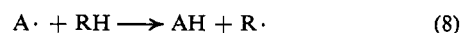
$$\frac{d[O_2]}{dt} = 2k_1[R-R] + 2k_1[R-R] \frac{k_3[RH]}{k_5[AH]}$$

in the case where reaction 7 is predominant.

There are two important features to be noted from Figures 2-6 and the data in Table VI. Although the slopes, and, therefore, k_3/k_5 (or $k_3/2k_5$) vary by a factor of 2000, the plots are linear in all cases to very low (less than 1) kinetic chain lengths. This observation demands that in the present system the phenolic compound does not partition the initiator and chain carrying peroxy radicals; *i.e.*, the reactivities of the two species are the same. The second feature concerns the value of the intercepts for the plots. The derived rate expression predicts that the intercept for all these inhibitors should be the same, *i.e.*, $2.0 \times 10^{-4} \text{ sec}^{-1}$, the first-order rate constant for the formation of radicals from tetraphenylbutane. The values of the intercept as calcu-

**Figure 6.** The rates of oxygen absorption of solutions of 9,10-dihydroanthracene and TPB in chlorobenzene inhibited by A, 1-hydroxynaphthalene and B, 1-hydroxyfluoranthene.

lated from the method of least squares confirms this prediction. As a consequence, the chain transfer (reaction 8) must have a very low efficiency for these compounds since even the highly reactive substrate,



9,10-dihydroanthracene, fails to yield an intercept in excess of theory.

Although expression A has been utilized by a number of investigators to treat oxygen absorption data, in only a few cases has the form of the equation been experimentally demonstrated. A direct proportional-

Table VI. Summary of Kinetic Rate Data

Compound	Slope × 10 ⁷ sec ⁻¹	Intercept × 10 ⁴ sec ⁻¹	Intercept/ slope
2,6-Di- <i>t</i> -butylphenol (I)	185.8	1.99	10.7
2,6-Di- <i>t</i> -butyl-4-methylphenol (II)	51.5	2.04	39.5
1,4-Dihydroxybenzene (III)	6.53	1.95	282.4
1-Hydroxynaphthalene (IV)	6.29	2.06	327.0
1-Hydroxyfluoranthene (V)	1.92	2.09	1090.0
1,5-Dihydroxynaphthalene (VI)	1.64	2.13	1299.0
3,10-Dihydroxypyrene (VII)	0.126	2.01	15980.0
3,8-Dihydroxypyrene (VIII)	0.098	1.96	20000.0

ity of the rate to RH at constant AH does not guarantee that reaction 8 is not occurring.¹⁷ Only the highly hindered phenols 2,6-di-*t*-butyl-4-methylphenol,^{2,8} 2,4,6-tri-*t*-butylphenol,⁸ and 2-*t*-butyl-4-methylphenol⁸ have been previously shown to fulfill all of the requirements demanded by eq A.

The ideality of behavior of these compounds would appear to depend on several factors. The first is a steric hindrance to reaction 8 by large groups *ortho* to the phenolic oxygen. Such an effect has been invoked to rationalize the results for the hindered phenols⁸

(17) See, for example, ref 8, p 2220.

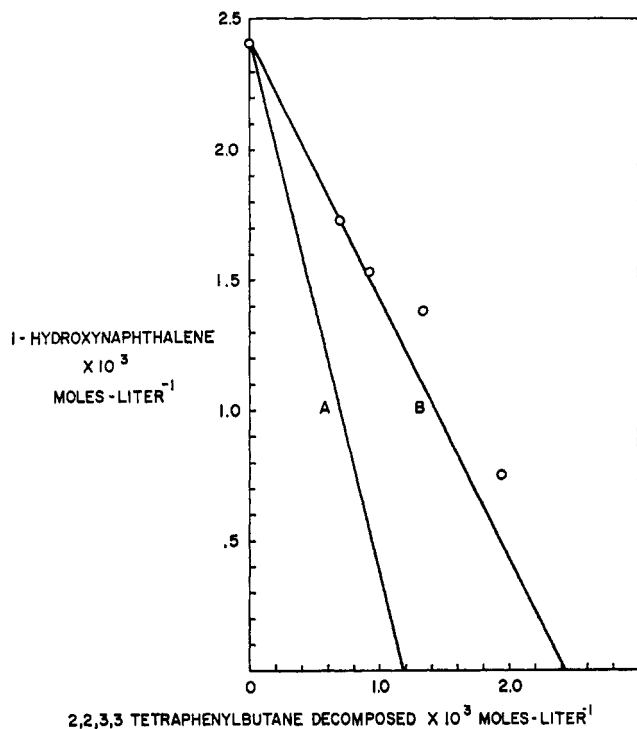
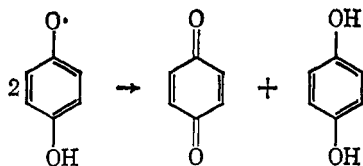


Figure 7. The concentration of 1-hydroxynaphthalene as a function of the moles l^{-1} of TPB decomposed. Curve A represents the case where the ratio of b/a is equal to k_5/k_3 . Curve B represents the case where the ratio of b/a is equal to $2(k_5/k_3)$.

and this explanation may suffice for 1-hydroxynaphthalene and 1-hydroxyfluoranthene since perihydrogens manifest a steric effect to numerous reagents substituting at the 1 position.¹⁸ The second is the facile disproportionation of the unhindered compounds, 1,4-dihydroxybenzene and the dihydroxypyrenes. As a



result the steady-state concentration of A \cdot radicals is maintained at a low level and the rates of reactions 8 and -5 are reduced. Additionally, a third factor which will be explored in future work from this laboratory is the reactivity of A \cdot in reactions 7, 8, and -5 as a function of structure.

True Reactivity for α -Naphthol. The determination of what multiple of k_5/k_3 is represented by the ratio of the intercept to the slope in eq A requires either a study of the products of an inhibition or a study of the concentration of the parent phenol as functions of the radicals produced in the system. In this work the concentration of 1-hydroxynaphthalene has been followed colorimetrically and the results shown in Figure 7 indicate that 1 mole of 1-hydroxynaphthalene is consumed by the radicals produced from 1 mole of 2,2,3,3-tetraphenylbutane. This result is consistent with the view that termination reaction 6 is predominant and $a/b = k_3/2k_5$ for this compound.

(18) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, p 487.

Experimental Section

Materials. The oxidizable hydrocarbon 9,10-dihydroanthracene was obtained from Henley and Co. (98% minimum). This material, after three recrystallizations from ethanol, had mp 109.5–110.0° cor (lit.⁸ mp 109–109.5°). Periodically during use the hydrocarbon was subjected to iodometric analysis and contained less than 0.02% (limit of detection) hydroperoxide. Spectrophotometric analysis revealed an impurity of 0.08% anthracene.

2,2,3,3-Tetraphenylbutane was synthesized by the method of Müller and Roscheisen,¹⁹ mp 122–123° (lit.¹⁹ mp 122–123°).

9,10-Dihydro-9-anthylhydroperoxide was prepared according to the procedure of Bickel and Kooyman.⁵ Two recrystallizations from toluene–pentane yielded a material, mp 109–110°; iodometric analysis gave a value of 95% peroxide. The material contained a 4.8% impurity of anthracene as determined by spectrophotometric analysis.

1-Hydroxyfluoranthene was prepared *via* the sulfonate and alkali fusion according to the method of Braun and Manz.²⁰ Multiple recrystallizations from chlorobenzene gave a material of melting point 188–189° (lit.²⁰ mp 190°).

Anal. Calcd: C, 88.08; H, 4.62. Found: C, 87.71; H, 4.64.

The 3,8-quinone of pyrene, mp 309° (lit.²¹ mp 309°), and the 3,10-quinone, mp 267–269° (lit.²¹ mp 270°) were obtained by the method of Vollman, *et al.* These quinones were reduced with sodium dithionite to yield the respective hydroquinones. The compounds were then acetylated *via* acetic anhydride–pyridine. The 3,8-diacetate was purified by recrystallization three times from acetic acid and finally chromatographed on neutral alumina and eluted with 1:1 benzene–ethyl acetate to yield pale yellow needles, mp 230–231°.

Anal. Calcd: C, 75.46; H, 4.42. Found: C, 75.42; H, 4.31.

The 3,10-diacetate was recrystallized three times from benzene to yield long, pale yellow needles, mp 195–196° (lit.²¹ mp 190°).

Anal. Calcd: C, 75.46; H, 4.42. Found: C, 75.42; H, 4.32.

The hydroquinones were then regenerated from the respective purified diacetates just before use by treatment with ethanolic sodium hydroxide under purified nitrogen to yield the 3,8-hydroquinone as a yellow powder, mp 266–268° (sealed capillary).

The 3,10-hydroquinone was obtained as fine, pale yellow needles whose surface becomes red on standing in air. The material had mp 258–260° (sealed capillary).

The other phenols used in this study were obtained from commercial sources and were purified by recrystallization to yield materials whose melting points agreed with values previously reported in the literature. The solvent chlorobenzene (Baker analyzed reagent) was passed through activated silica gel before use. Purification by methods previously described²² had no effect on the value obtained for the efficiency of the weak inhibitor 2,6-di-*t*-butyl-4-methylphenol.

Rate Measurements. All the rate measurements reported in this work were determined on the automatic constant pressure apparatus recently developed in this laboratory;²³ however, the precision of the instrument was doubled by the use of a constant-speed stirring motor. A weighed amount of the solid hydrocarbon was placed into the reaction vessel and a solution of the phenol in chlorobenzene was added. After 20 min of equilibration at 60.0°, the initiator (0.5 ml) in chlorobenzene was introduced *via* a syringe. The rate of gas absorption commenced in less than 1 min and was constant within 2 min after injection. The rate was determined from the graphic recording. In most cases the total oxygen absorbed for the rate determination corresponded to 2.2×10^{-4} mole l^{-1} . Rates were reproducible to within $\pm 3.0 \times 10^{-8}$ mole $\text{l}^{-1}\text{sec}^{-1}$ in all cases.

The densities of all the solutions were determined at 60.0° and the concentrations reported in this work are the molar concentrations at that temperature.

Concentration of 1-Hydroxynaphthalene. Standard solutions of 1-hydroxynaphthalene (2.41×10^{-3} M) in chlorobenzene were stirred in the presence of oxygen with varying amounts of tetraphenylbutane for 16 hr (*ca.* 16 half-lives). The solutions were then

(19) E. Müller and G. Roscheisen, *Ber.*, **90**, 543 (1957).

(20) J. von Braun and G. Manz, *Ann.*, **488**, 111 (1931); *ibid.*, **496**, 170 (1932).

(21) H. Vollman, H. Becker, M. Correll, and H. Streek, *ibid.*, **531**, 1 (1937).

(22) L. R. Mahoney, *J. Am. Chem. Soc.*, **87**, 1089 (1965).

(23) L. R. Mahoney, R. W. Bayma, A. Warnick, and C. H. Ruoff, *Anal. Chem.*, **36**, 2516 (1964).

analyzed for residual 1-hydroxynaphthalene by the method of Pearse.²⁴

Induction Periods. The induction periods were measured in the oxygen absorption apparatus previously described.²⁵ The end of the induction period was chosen as that point at which the rate of oxygen absorption was the same as the uninhibited rate,

(24) G. A. Pearse, *Anal. Chem.*, **35**, 1954 (1963).

(25) L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 444 (1964).

correcting for the consumption of initiator. The total number of radicals stopped by the phenol was calculated from the first-order rate constant for the decomposition of 2,2,3,3-tetraphenylbutane.

Acknowledgment. The author acknowledges the helpful advice in the preparation of the manuscript rendered by Dr. C. H. Ruof and the excellent technical assistance of Mrs. L. W. Skewes and Mr. F. C. Ferris, who carried out much of the experimental work.

Thermal Rearrangement of Phosphorodihalidothioites. A New Synthesis of Phosphonothioic Dihalides

Joseph W. Baker, Raymond E. Stenseth, and Leo C. D. Groenweghe

Contribution from the Research Departments of the Organic Chemicals Division and the Inorganic Chemicals Division, Monsanto Company, St. Louis, Missouri.

Received February 3, 1966

Abstract: The preparation of phosphonothioic dihalides, $RP(S)X_2$, by the thermal rearrangement of phosphorodihalidothioites, $RSPX_2$, in a sealed vessel is described. A second product of the reaction is the corresponding phosphinothioic halide, $R_2P(S)X$. The reaction has a wide scope and is promoted by catalysts, preferably iodine, methyl iodide, and iodide salts, and it can be carried out in the vapor phase at atmospheric pressure. It also has been found that a phosphonothioic dihalide can be prepared by the reaction of an alkyl sulfide or alkyl disulfide with phosphorus trichloride at elevated temperatures.

Phosphonothioic dihalides ($RP(S)X_2$) are important intermediates in the preparation of petroleum additives, agricultural chemicals, organophosphorus polymers, and other products of commercial interest. A number of procedures have been reported¹⁻⁸ for the preparation of these intermediates. With respect to yield, scope, and ease of reaction, the addition of sulfur to a dihalophosphine^{1,2} is the only satisfactory method. Unfortunately, this method is practically limited to the preparation of phenylphosphonothioic dichloride from the readily available dichlorophenylphosphine, since other dihalophosphines are relatively difficult to prepare.

As a result of our search for a new route to alkylphosphonothioic dihalides, we wish to report their preparation by the thermal rearrangement of alkyl phosphorodihalidothioites ($RSPX_2$) in a sealed vessel (reaction 1). The reaction was applied also to the synthesis



of the cycloalkyl, allyl, benzyl, and aromatic analogs. The scope of the reaction was demonstrated by the preparation of 21 phosphonothioic dihalides. Whereas a pure alkyl phosphorodichloridothioite was employed

initially in the rearrangement, it was found that the use of undistilled material, obtained by the reaction of equimolar quantities of a mercaptan and phosphorus trichloride, was equally satisfactory for the rearrangement reaction. The reaction is general, with yields varying from 40 to 70%. Thirteen known compounds have been prepared in this manner, as shown in Table I.

In addition, eight other higher homologs were treated at temperatures ranging from 265 to 300°. These were *t*-butyl, pentyl, hexyl, heptyl, octyl, dodecyl, *p*-(*t*-butyl)phenyl, and *p*-nonylphenyl. Nuclear magnetic resonance (nmr) spectra made from the reaction products showed P^{31} resonance peaks which were very similar in chemical shift and in intensity to the ones obtained with the lower homologs. Vapor phase chromatography (vpc) also indicated the formation of the corresponding phosphonothioic dihalides.

In general, the temperature required for the reaction varied from 135–165° for $R = CH_2CH=CH_2$ to 275–400° for $R = CH_3$. The duration of heating usually depended upon the temperature and could be reduced to less than 1 hr at the higher temperatures. The pressures which developed during the rearrangement varied according to the nature of the substituents and the reaction temperature. In a typical autoclave preparation of the low-boiling methylphosphonothioic dichloride at 300°, the maximum pressure measured was ca. 40 atm. In most of the experiments involving the alkyl analogs, small quantities of the corresponding hydrocarbons were formed. Samples of the gases were collected and analyzed by infrared spectroscopy. Methane was the main component in the gas collected after rearrangement of the methyl compound, propane from the propyl and isopropyl, butane from the butyl, isobutane from the isobutyl and *t*-butyl, pentane from

(1) H. Kohler and A. Michaelis, *Ber.*, **9**, 1053 (1876).

(2) Fr. Guichard, *ibid.*, **32**, 1572 (1899).

(3) A. Michaelis, *Ann.*, **315**, 43 (1901).

(4) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(5) K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 796 (1954); *Chem. Abstr.*, **49**, 13074 (1955).

(6) H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse, and T. H. Chao, *J. Am. Chem. Soc.*, **78**, 5018 (1956).

(7) M. I. Kabachnik and N. N. Godovikov, *Dokl. Akad. Nauk SSSR*, **110**, 217 (1956); *Chem. Abstr.*, **51**, 4982 (1957).

(8) I. R. Komkov, S. Z. Ivin, and K. V. Karavanov, *Zh. Obshch. Khim.*, **28**, 2960 (1958); *Chem. Abstr.*, **53**, 9035 (1959).