# The Equilibrium Reaction of 2,4,6-Tri-*t*-butylphenol and Organic Peroxy Radicals[1]

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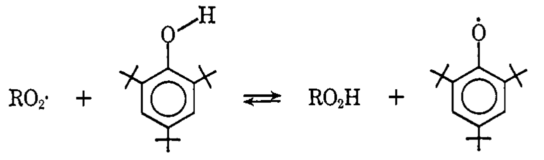
**Abstract:** An experimentally determined value for the difference in the heats of formation in solution of an organic hydroperoxide and its peroxy radical has been obtained for the first time. The equilibrium constants for the reaction $RO_2\cdot + AH \rightleftarrows RO_2H + A\cdot$ where A· and AH are the 2,4,6-tri-*t*-butylphenoxy radical and phenol and ROOH and $RO_2\cdot$ are organic hydroperoxides and peroxy radicals, respectively, are determined by kinetic studies of (1) the inhibition by AH of the liquid phase oxidation of hydrocarbons and (2) the reaction of A· with hydroperoxides. For the system where R is the tetralyl moiety in the mixed solvent tetralin (0.335 mol fraction)-chlorobenzene the equilibrium constant in the temperature range 30–60° is given by the expression $\log (k_1/k_{-1}) = [0 \pm 1.2] + (7000 \pm 1700)/2.3\,RT$. A value of $+35.9 \pm 1.7$ kcal/mol is then obtained for the difference in the heats of formation of the tetralylperoxy radical and tetralin hydroperoxide by combining this result with the previously determined difference in the heats of formation of AH and A· in the same solvent. The significance of the results of the present study with regard both to the analysis by Benson of the thermochemistry of peroxy radical reactions and to the mechanism of the phenolic inhibition of the liquid phase oxidation of hydrocarbons is then discussed.

In recent work from our laboratory the differences in the heats of formation in solution of 2,4,6-tri-*t*-butylphenol and 2,4,6-tri-*t*-butylphenoxy were determined by direct calorimetric techniques.[2] That work provided a starting point for the determination of the differences in heats of formation in solution of a variety of free radicals and their hydrogenated precursors. Estimates of the differences in the heat of formation in solution of a number of substituted phenols and their phenoxy radicals were subsequently obtained by means of a detailed kinetic and thermochemical study of the reactions of 2,4,6-tri-*t*-butylphenoxy with the phenolic compounds.[3]

Organic peroxy radicals are the primary chain carrying species in the free radical initiated reaction of hydrocarbons and oxygen in both the liquid and gaseous phases at moderate temperatures. Benson has presented a very complete analysis of the thermochemistry of hydrocarbon oxidation[4] based upon the assumption that the differences in the heats of formation of organic peroxy radicals and their hydroperoxides are equal to the previously experimentally determined difference in the heat of formation of the hydroperoxy radical and hydrogen peroxide in the gas phase.[5]

The goal of the present work is to provide an experimentally determined value for the differences in the heat of formation in solution of an organic peroxy radical and its hydroperoxide. The values of the absolute rate constants for the forward and the reverse hydrogen atom transfer reaction at several temperatures are determined by kinetic studies of the inhibition of hydrocarbon oxidation by the hindered phenol and by a stop-flow study of the reaction of the hindered phenoxy radical with hydroperoxide. From the derived heat of the reaction and the previously determined differences in the heat of formation in solution of the hindered phenol and phenoxy radical, the difference in the heats of formation of the peroxy radical and hydroperoxide is obtained.



## Results and Discussion

**Reaction of Peroxy Radicals with 2,4,6-Tri-*t*-butylphenol.** A reaction scheme which quantitatively accounts for the free radical initiated oxygen absorption of a liquid hydrocarbon, RH, strongly inhibited by a hindered phenol or hydroquinone, AH, is given in Scheme I, where $R'O_2\cdot$ and $RO_2\cdot$ represent the peroxy radicals derived from the initiator; R′R′, and RH, respectively, and AH represents the inhibitor molecule. Under conditions such that $k_3' = k_3$ and $k_1' = k_1$, *i.e.*, the reactivities of the peroxy radicals derived from the initiator and the hydrocarbon are the same, the rate of oxygen absorption is accurately described by the expression

**Scheme I**

$$\begin{array}{lr}
R' - R' \xrightarrow{k_d} 2R\cdot' & 2k_d[R'R'] \\
R\cdot' + O_2 \xrightarrow{k_0'} R'O_2\cdot & \text{(fast)} \\
R'O_2\cdot + AH \xrightarrow{k_1'} RO_2H + A\cdot & k_1'(R'O_2\cdot)(AH) \\
R'O_2\cdot + A\cdot \xrightarrow{k_2'} R'O_2A & \text{(fast)} \\
R'O_2\cdot + RH \xrightarrow{k_3'} R'O_2H + R\cdot & k_3'(R'O_2\cdot)(RH) \\
R\cdot + O_2 \xrightarrow{k_0} RO_2\cdot & \text{(fast)} \\
RO_2\cdot + AH \xrightarrow{k_1} RO_2H + A\cdot & k_1(RO_2\cdot)(AH) \\
RO_2\cdot + RH \xrightarrow{k_3} RO_2H + R\cdot & k_3(RO_2\cdot)(RH) \\
RO_2\cdot + A\cdot \xrightarrow{k_2} RO_2A & \text{(fast)}
\end{array}$$

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[1] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, PETR-1.

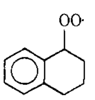
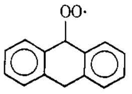
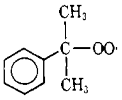
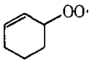
[2] L. R. Mahoney, F. C. Ferris, and M. A. DaRooge, *J. Amer. Chem. Soc.*, **91**, 3883 (1969).

[3] L. R. Mahoney and M. A. DaRooge, *ibid.*, **92**, 890 (1970).

[4] S. W. Benson, *J. Amer. Chem. Soc.*, 87, 972 (1965).

[5] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962).

Table I. Summary of Data of Peroxy Radical-Hindered Phenol Transfer Reaction

| Peroxy radical | Hindered phenol | Solvent | Temp, °C | $(k_1/k_3) \times 10^{-3}$ | $k_1 \times 10^{-4}$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|---|
|  | (AH) | Tetralin[a]–$C_6H_5Cl$ | 30.0 | 4.43 ± 0.14 | 2.86 ± 0.07[b] |
| | | | 45.0 | 2.29 ± 0.08 | 2.82 ± 0.10[b] |
| | | | 60.0 | 1.29 ± 0.10 | 2.86 ± 0.23[b] |
| | (DBPC) | Tetralin | 40.0 | 3.0[c] | 2.75 |
|  | (AH) | $C_6H_5Cl$ | 30.0 | 0.037 ± 0.002 | 1.28 ± 0.07[a] |
| | (DBPC) | $C_6H_5Cl$ | 30.0 | 0.032 ± 0.002 | 1.10 ± 0.06[d] |
|  | (DBPC) | Cumene | 40.0 | 28.6[c] | 1.20[c] |
|  | (DBPC) | Cyclohexene | 30.0 | 4.55[c] | 3.05[c] |

[a] Mole fraction of tetralin equal to 0.3350. [b] Calculated from values of $k_3$ reported by J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **44**, 1119 (1966). [c] Data of H. Berger, *et al.*[9] [d] Calculated from value of $k_3$ reported by J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **46**, 2661 (1968).

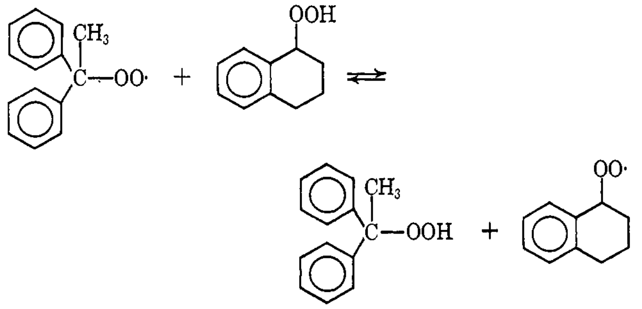
$$-\frac{dO_2}{dt} = 2k_d(R'R') + \frac{k_3[2k_d(R'R')](RH)}{2k_1(AH)} \qquad (1)$$

Provided the absolute values of $k_3$ for a given hydrocarbon system are known this technique represents a method for the determination of the values of $k_1$.

For the system 9,10-dihydroanthracene as the hydrocarbon, 2,2′,3,3′-tetraphenylbutane, TPB, as the initiator and a large number of 2,6-di-*t*-butylphenols and hydroquinones as the inhibitors in chlorobenzene at 60°, it has been shown that plots of $[1/2(RR)[d(O_2)/dt]$ *vs.* (RH)/(AH) are strictly linear over wide ranges of concentration and the values of the intercepts of these plots were independent of the structure of AH.[6] Moreover, the addition of the hydroperoxide of 9,10-dihydroanthracene did not alter the observed rates of oxygen adsorption.[6] Thus within small experimental uncertainties (±3%) the reactivity of the 1,1-diphenylethylperoxy radical derived from TPB and the peroxy radical derived from 9,10-dihydroanthracene are identical.

In contrast to the 9,10-dihydroanthracene system at low kinetic chain lengths, the initial rates of oxygen absorption of solutions of tetralin (mole fraction 0.335)–chlorobenzene containing 2,4,6-tri-*t*-butylphenol with TPB as the initiator do not obey eq 1 at 30, 45, and 60°. In Figure 1 is presented a plot of the values of $[d(O)_2/dt]/2(TPB)$ *vs.* (RH/AH) for the system at 30°. The source of the curvature in the plot is due to the *different values* of $k_1$ and/or $k_3$ for the diphenylethylperoxy radical derived from TPB and the peroxy radical derived from tetralin. Under such conditions the rate of oxygen absorption will be a complex function of the individual rate constants and of the concentrations of RH, AH, and RR.

This problem may be circumvented by employing the elegant technique of Howard, Schwalm, and Ingold,[7] first developed in their studies of the variation of the values of $k_3$ for the reaction of a given hydrocarbon with a variety of peroxy radicals. The technique involves the addition of a second hydroperoxide to an oxidizing hydrocarbon. Upon the addition of tetralin hydroperoxide to a system containing diphenylethylperoxy radical the rapid transfer equilibrium takes



place. At sufficiently high concentrations of tetralin hydroperoxide the equilibrium will lie far to the right and the system well be populated exclusively with tetralylperoxy radicals. Upon the addition of tetralin hydroperoxide (Figure 1), the rates decrease and at concentrations equal to or larger than $5 \times 10^{-3}$ $M$ the plot becomes linear and eq 3 is obeyed. This procedure, *i.e.*, addition of tetralin hydroperoxide, was also carried out at 45 and 60° and the values of $k_1/k_3$ for 2,4,6-tri-*t*-butylphenol calculated from eq 3 are summarized in Table I. Also included in the table are value of $k_1/k_3$ for 2,4,6-tri-*t*-butylphenol and for 2,6-di-*t*-butyl-4-methylphenol (DBPC) with 9,10-dihydroanthracene as the hydrocarbon at 30°. As in earlier work at 60°,[6,8] the values of $k_1/k_3$ for the two hindered phenols are equal.

Values of the ratios $k_1/k_3$ previously reported for hindered phenols utilizing different initiator and hydrocarbon systems are widely scattered and nearly all are lower than the values reported in the present work.[9] It is likely that the anomalies in the earlier data were due to the problems of the partitioning of the peroxy radicals derived from the initiator and from the hydrocarbon at low kinetic chain lengths and to the usual difficulties involved in the accurate determination of the rate of formation of free radicals from the initiator.

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(6) L. R. Mahoney, *J. Amer. Chem. Soc.*, **88**, 3035 (1966). From radical counting experiments and earlier product isolation studies, reactions 2 and 2′ are the sole termination events for hindered phenol systems

(7) J A. Howard, W. J. Schwalm, and K. U. Ingold, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 6.

(8) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).

(9) *Cf.* N. M. Emanuel, E. T. Denison, and Z. K. Maizus, "Liquid-Phase Oxidation of Hydrocarbons," Plenum Press, New York, N. Y., 1967, Chapter VII, pp 242-248.

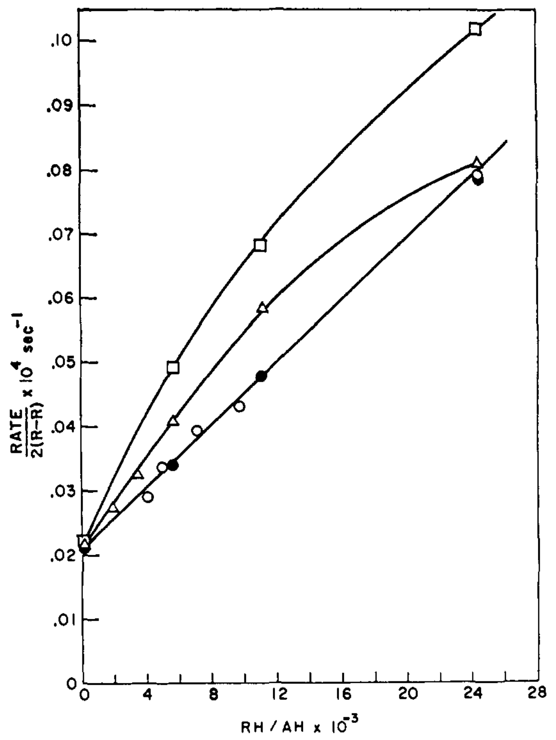

Figure 1. Plot of $(d(O_2)/dt)/2(R - R)$ *vs.* RH/AH at 30° in tetralin (0.3350 mol fraction)-$C_6H_5Cl$: □, concentration of ROOH equal to $0.1 \times 10^{-3}$ *M*; △, concentration of ROOH equal to $1.1 \times 10^{-3}$ *M*; ●, concentration of ROOH equal to $5.1 \times 10^{-3}$ *M*; ○, concentration of ROOH equal to $10.1 \times 10^{-3}$ *M*.

Values of $k_1/k_3$ reported recently by Berger, *et al.*,[10] for DBPC in a number of systems utilizing a technique where kinetic chain lengths are very long and the initiator–hydrocarbon radical problem will be minimized are given in Table I. Those workers reported a value of $k_1/k_3$ for DBPC in pure tetralin at 40° which is in excellent agreement with our results.

In the final column of Table I are presented the values of $k_1$ for a number of peroxy radicals calculated from $k_1/k_3$ and the literature values of $k_3$. At a given temperature the values of $k_1$ decrease in a regular manner with increasing size of the hydrocarbon moiety of the peroxy radical. For the tetraylperoxy radical where values at several temperatures are available the rate constant appears to be independent of temperature. Weissman and Kreilick[11] have reported a very low activation energy (1.0 ± 0.5 kcal/mol) for the identity reaction of A· and AH. The same activation energy is observed for the hydrogen atom abstraction reaction of A· with 2,6-di-*t*-butylphenol.[12] These extremely low temperature coefficients for the rates of hydrogen atom transfer between oxy radicals may have their source in the stabilization of the activated complex by hydrogen bonding of the oxy radical and the OH bond of the reactant molecule. Such an intermediate has been detected by Weissman and Kreilick in their study[11] and it has recently been shown that peroxy radicals strongly hydrogen bond to the OH of hydroxylic solvents.[13]

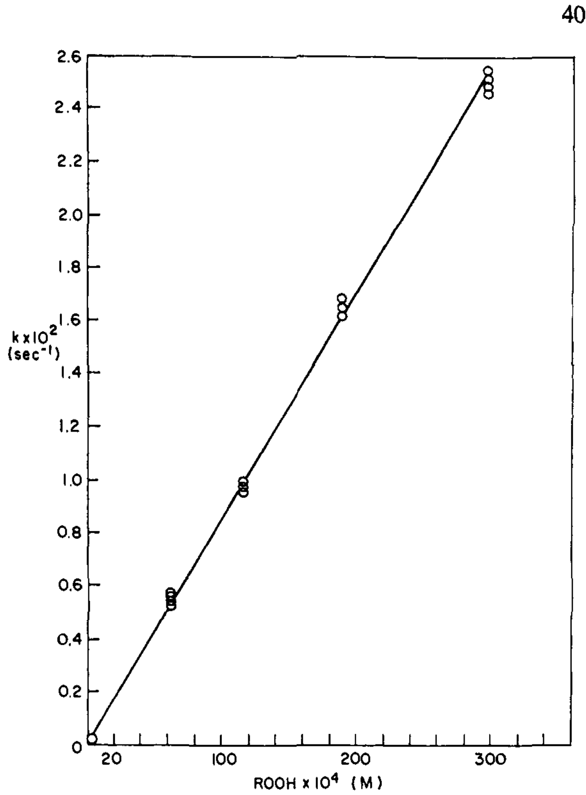

Figure 2. Plot of first-order decay constant for 2,4,6-tri-*t*-butylphenoxy *vs.* concentration of tetralin hydroperoxide in tetralin (0.3350 mol fraction)-chlorobenzene at 30°.

Formation of stabilized free radical–molecule complexes have recently been suggested by Golden and Benson[14] to account for the apparent very low activation energies (0 ± 1 kcal/mol) for the reaction of hydrocarbon radicals with $I_2$.

**Reaction of 2,4,6-Tri-*t*-butylphenoxy with Hydroperoxides.** A kinetic study of the reaction of 2,4,6-tri-*t*-butylphenoxy, A·, with several hydroperoxides derived from alkylaromatic hydrocarbons was carried out utilizing the stop-flow technique reported in earlier work from our laboratory.[15,16] Under the conditions of the stop-flow experiments the rate of disappearance of A· in the presence of a constant concentration of hydroperoxide is accurately first order in A·. The first-order decay constant is proportional to the concentration of the hydroperoxide. In Figure 2 is presented typical results obtained from the study of tetralin hydroperoxide. These results are consistent with the scheme

$$A\cdot + RO_2H \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} AH + RO_2\cdot$$

$$RO_2\cdot + A\cdot \xrightarrow{k_2} AO_2R$$

where $k_2(A\cdot) \gg k_1(AH)$. Under these conditions the rate of disappearance of A· is given by the expression

$$-\frac{d(A\cdot)}{dt} = 2k_{-1}(A\cdot)(RO_2H) \qquad (2)$$

In Table II are summarized the values of $k_{-1}$ for the hydroperoxides studied in the present work. The

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(10) H. Berger, A. M. W. Blaauw, M. M. Al, and P. Smael, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 346.

(11) R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, **88**, 2645 (1966).

(12) Unpublished work of L. R. Mahoney and M. A. DaRooge.

(13) L. M. Andronov, G. E. Zaikov, and Z. K. Maizus, *Russ. J. Phys. Chem.*, **41**, 590 (1967).

(14) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 126 (1969).

(15) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967).

(16) M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

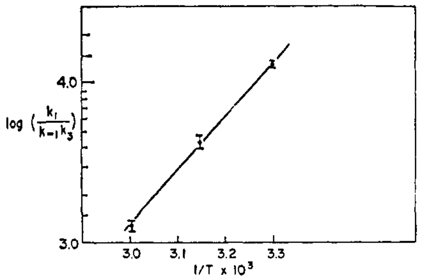
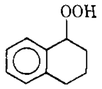
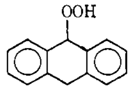
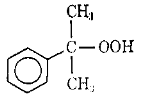


Figure 3. Plot of log $k_1/k_{-1}k_3$ *vs.* $1/T$ for the reaction of the tetralylperoxy radical–2,4,6-tri-*t*-butylphenol in tetralin (0.3350 mol fraction)–chlorobenzene.

values of $k_{-1}$ are dependent upon the size of the hydrocarbon moiety of the hydroperoxide; decreasing in the order tetralin > 9,10-dihydroanthracene ≈ cumene. This is the same order as that found for the value of $k_1$ (Table I). In addition it should be noted that the reaction of tetralin hydroperoxide manifests a small but measurable solvent effect at 30° and 45° when the solvent is changed from pure chlorobenzene to a mixture of tetralin (0.3350 mol fraction)–chlorobenzene.

Table II. Summary of Absolute Rate Constants, $k_{-1}$, for the Reaction of 2,4,6-Tri-*t*-butylphenoxy with Hydroperoxides

| Hydroperoxide | Solvent | Temp, °C | $k_{-1}$, $M^{-1}$ sec$^{-1}$ [a] |
|---|---|---|---|
|  | $C_6H_5Cl$ | 30.0 | 0.34 ± 0.02 |
| | $C_6H_5Cl$ | 45.0 | 0.55 ± 0.02 |
| | $C_6H_5Cl$ | 60.0 | 1.00 ± 0.07 |
| | Tetralin-$C_6H_5Cl$[b] | 30.0 | 0.43 ± 0.02 |
| | Tetralin-$C_6H_5Cl$[b] | 45.0 | 0.66 ± 0.02 |
| | Tetralin-$C_6H_5Cl$[b] | 60.0 | 0.97 ± 0.03 |
|  | $C_6H_5Cl$ | 30.0 | 0.153 ± 0.005 |
|  | Cumene | 40.0 | 0.365 ± 0.008 |

[a] Corrected for thermal expansion of solvent. [b] Mole fraction of tetralin equal to 0.3350.

**Lower Limit of the Ratio $k_2/k_{-1}$.** Under conditions such that the ratio of rate constant $k_1/k_2$ is larger than the ratio of concentrations, (A·)/(AH), the initial transfer reaction becomes reversible and the rate expression for the disappearance of (A·) is given by the expression

$$-\frac{d(A\cdot)}{dt} = \frac{2k_1k_2(A\cdot)^2(RO_2H)}{k_{-1}(AH)} \quad (3)$$

The rate of disappearance of (A·) in its reaction with a number of phenols under conditions where the concentration of AH exceeded 0.1 *M* and the concentration of A· was equal to or less than 5 × $10^{-4}$ *M* has been found to be accurately described by eq 5.[3] The values of $k_2/k_1$ for a number of phenoxy radicals determined by this technique were found to be in the range of 60–120.

We have systematically studied the effect of added AH on the rate of disappearance of A· in the stop flow experiments with tetralin hydroperoxide as the reactant at 30°. The value of the first-order decay constant was *unaffected* by the presence of added AH up to a concentration of 0.5 *M*. This result requires that the ratio of $k_2/k_1$ must greatly exceed $10^3$ and from Table I $k_2$ must be considerably larger than 2 × $10^7$ $M^{-1}$ sec$^{-1}$. This result is consistent with a lower limit value of 6 × $10^7$ $M^{-1}$ sec$^{-1}$ obtained by means of oxygen absorption studies on hydrocarbons inhibited by AH.[15]

**Equilibrium Constant and Heat of the Transfer Reaction.** In Figure 3 is presented a plot of the values of log ($k_1/k_{-1}k_3$) in the solvent mixture tetralin (0.335 mol fraction)–chlorobenzene *vs.* $1/T$. The equation for the least-squares line is

$$\log \frac{k_1}{k_{-1}k_3} = -[6.8 \pm 0.7] + \frac{15300 \pm 900}{2.3RT} (M\,\text{sec}) \quad (4)$$

The most extensive determinations of the absolute values of $k_3$ for the tetralylperoxy radical in tetralin–chlorobenzene solution have been those of Howard and Ingold.[17] In the temperature range 13–50° they report that

$$\log k_3 = +[6.76 \pm 0.3] - \frac{[8300 \pm 800]}{2.3RT} (M^{-1}\,\text{sec}^{-1}) \quad (5)$$

Combining the two expressions then yields the expression for the equilibrium constant

$$\log \frac{k_1}{k_{-1}} = [0 \pm 1.2] + \frac{7000 \pm 1700}{2.3RT} \quad (6)$$

for the reaction of tetralylperoxy radical with 2,4,6-tri-*t*-butylphenol to yield tetralin hydroperoxide and 2,4,6-tri-*t*-butylphenoxy radical in the solvent mixture tetralin (0.335 mole fraction)–chlorobenzene. Thus within our experimental error the entropy change accompanying the hydrogen atom transfer equilibrium is 0 ± 5.5 eu and the enthalpy change corresponds to −7000 ± 1700 cal/mol. These thermodynamic quantities do not appear to be sensitive to the structure of the peroxy radical since the values of $k_1/k_{-1}$ are equal to 8.4 × $10^4$ for the 9,10-dihydroanthracene system at 30° and 3.3 × $10^4$ for the cumene system at 40° compared to a value of [6.6 ± 0.3] × $10^4$ for the tetralin system at 30°.

**Difference in the Enthalpies of Formation of $RO_2\cdot$ and ROOH in Solution.** The difference in the enthalpies of formation of A· and AH in tetralin (0.335 mol fraction)–chlorobenzene solution at 25° by direct calorimetric determination is equal to 28.91 ± 0.05 kcal/mol.[2] Utilizing the value of that quantity and the enthalpy change for the equilibrium transfer reaction yields a value for the difference in the enthalpies of formation of the tetralylperoxy radical and tetralin hydroperoxide in the same solvent equal to +35.9 ± 1.7 kcal/mol.

This value is the first experimentally determined value for an organic peroxy radical–hydroperoxide system. It is similar to the value of +38.0 ± 2.0 kcal/mol reported for the difference in the enthalpies of formation in the *gas phase* for the hydroperoxy–hydrogen peroxide system.[5] Benson[4] based his elegant analysis of the thermochemistry of organic peroxy radicals upon the assumption that these two quantities were equal. That assumption has been experimentally verified by the results of the present work and his thermochemical analysis may be directly applied to oxidation reactions in the liquid phase.

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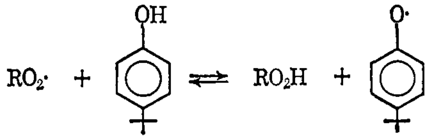
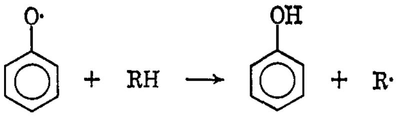
(17) See Table I, footnote *b*.

The results of the present work taken together with the results of our earlier studies[3] of the thermochemistry of phenoxy radicals establishes a thermochemical basis for the important steps in the mechanism of the inhibition of hydrocarbon oxidation by phenolic compounds. The heat of the reaction of the hydrogen atom transfer between peroxy radical and 4-*t*-butylphenol[3] is thermo-

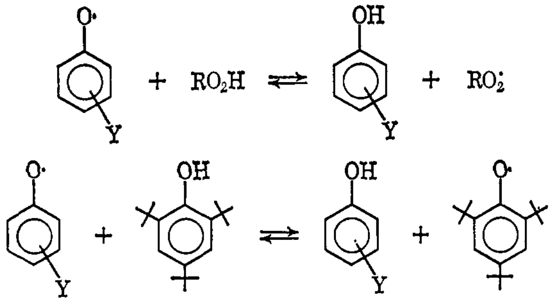


neutral or slightly endothermic and with groups more electron withdrawing the reaction becomes progressively more endothermic. Thus the facile reversibility of this step proposed by Thomas to account for the effect of hydroperoxide on the rates of hydrocarbon oxidation inhibited by phenol[18,19] is acceptable on thermochemical grounds. The corresponding chain transfer reaction with hydrocarbons,[20,21] where RH is a hydrocarbon



with $D$(RH) equal to or smaller than 85 kcal/mol is also thermochemically allowed.

A mechanism proposed from this laboratory to account for the synergistic behavior of mixtures of hindered and nonhindered phenols as antioxidants[16] is based upon the relative rate constants and/or equilibrium constants for the reactions



The mechanism requires that the second equilibrium constant and/or rate constant for the forward reaction be much larger than those for the hydroperoxide transfer. Again the thermochemistry is in full accord with this view since the second reaction is 7.0 ± 1.7 kcal/mol more exothermic than the first reaction.

## Experimental Section

**Materials.** Tetralin hydroperoxide was prepared and purified according to the procedure of Knight and Swern.[22] Cumyl hydroperoxide was purified by the threefold preparation and regeneration of its sodium salt. The hydroperoxide of 9,10-dihydroanthracene was prepared and purified by procedures previously described.[6]

**Rates of Oxygen Absorption.** The rates of oxygen absorption were determined by means of the automatic recording constant pressure gas apparatus previously described.[23]

**Reaction of 2,4,6-Tri-*t*-butylphenoxy with Hydroperoxides.** The rates of reaction of 2,4,6-tri-*t*-butylphenoxy with hydroperoxides were determined by means of the stop-flow apparatus described in earlier work from our laboratory.[15,16]

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