A Mechanistic Study of the Termination Reactions of 2,4,6-Trialkylphenoxy Radicals

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Abstract: The phenoxy radicals, II and III, were generated in an esr cavity by photolysis of an α diketone in a solution containing 2,6-di-*tert*-butyl-4-methylphenol and 2,4,6-trimethylphenol, respectively. The decays of the phenoxy radical were found to be first order over a tenfold range of initial radical concentration and independent of the phenol concentration, the solvent, and the choice of ketone. These rates were measured from 10–60°. The activation energies were 18 and 14 kcal/mol in benzene solution for radicals II and III, respectively. When phenoxy radical II was generated in isooctane at temperatures below −5°, it was found that the radical did not decay. In the range from −5 to −45°, the amount of radical observed increased with increasing temperature. These results are consistent with a scheme in which two radicals are in rapid equilibrium with a dimer whose heat of formation is 17 kcal/mol. The nonradical products arise *via* a slow unimolecular decomposition of dimer and/or a bimolecular radical disproportionation.

From the results of a recent study[1] a mechanism has been proposed for the termination reaction of substituted phenoxy radicals. The mechanism involves the formation of metastable keto dimers in equilibrium with their precursor phenoxy radicals. These keto dimers then enolize to the final stable products in a subsequent and sometimes rate-controlling step. The interesting question now arises as to the nature of the mechanism for the termination of 2,4,6-trialkylphenoxy radicals, the dimers of which do not possess enolizable hydrogens and thus cannot be converted to stable products *via* an enolization reaction.

In the present work two such systems are examined: the phenoxy radicals derived from 2,6-di-*tert*-butyl-4-methylphenol and 2,4,6-trimethylphenol. Although a number of studies have been reported for the decay of the former radical and the initial products of the reaction have been established to be the parent phenol and quinone methide,[2] there is considerable disagreement concerning the kinetic order of the decay with respect to the phenoxy radical concentration. Several authors have reported a first-order decay[3,4] while recently the rate of the reaction has been reported to be second order in radical.[5] We noted that in these earlier studies the phenoxy radical was generated in heterogenous systems utilizing solid PbO_2 or aqueous $Fe(CN)_6{}^{3-}$ as oxidizing agents. With the hope of resolving the disagreement with respect to the kinetic order, we have utilized a technique by which phenoxy radicals are generated homogenously in an esr cavity by the photolysis of ketones in the presence of the parent phenols.[6]

Experimental Section

Materials. Benzene and isooctane were Matheson Coleman and Bell Spectrograde and were used as received. Biacetyl was distilled prior to use. *p*-Toluenesulfonic acid was from Aldrich and used as received. Camphorquinone, benzophenone, and the substituted phenols were recrystallized from hexane. All compounds had melting points in agreement with those in the literature.

Steady-State Irradiations. All samples were prepared and irradiated as previously described.[6]

Kinetic Measurements. The phenoxy radicals were generated by photolysis of a solution of phenol and either biacetyl, camphorquinone, or benzophenone. The radical concentration was on the order of 10^{-5} *M*. The light was filtered to allow only wavelengths greater than 330 nm to pass into the esr cavity. This guarantees that the light is absorbed only by the ketone. The initial phenoxy radical concentrations were varied by passing the light beam through neutral density filters. No radical from the ketone was ever observed, even though the spectrometer sensitivity was increased 100-fold. The light beam was then blocked and the radical decay monitored on an external Hewlett-Packard recorder. The response time of the esr spectrometer was set at 1, 0.3, or 0.01 sec depending on the rate of decay. As shown in Figure 1, plots of log of the radical concentration (peak height) *vs.* time were linear and the slopes of such plots were independent of the initial concentration of the radical.

The temperature was varied by means of a Varian temperature controller. The temperature was calibrated by placing the appropriate solvent in an esr tube and monitoring the temperature by means of a thermocouple. The results were reproducible to ±1°.

Equilibrium Measurements. Solutions of 2,6-di-*tert*-butyl-4-methylphenol in isooctane containing biacetyl were irradiated for approximately 10 min at temperatures below −5°. The light beam was then blocked and very little or no radical decay was observed. The temperature was then varied from −6 to −45°. The variation of radical concentration with temperature fits the van't Hoff equation. The relative radical concentration, as a function of temperature, was independent of the length of irradiation time. No signal other than that of the phenoxy radical was observable even when the sensitivity of the spectrometer was increased 100-fold.

Results and Discussion

Steady-State Irradiations. Irradiation of a solution containing the phenol and one of three ketones in either benzene or isooctane solution only yielded the spectrum of the phenoxy radical. The splitting constants are given in Table I.

Table I. Hyperfine Coupling Constants[a] of the Phenoxy Radicals

Radical	Position 2,6	Position 3,5	Position 4
2,4,6-Tri-*tert*-butylphenoxyl (I)		1.73	
2,6-Di-*tert*-butyl-4-methylphenoxyl (II)		1.68	11.20
2,4,6-Trimethylphenoxyl (III)	6.06	1.65	10.54

[a] The values are in gauss.

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(1) L. R. Mahoney and S. A. Weiner, *J. Amer. Chem. Soc.*, **94**, 585 (1972).

(2) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963).

(3) J. E. Bennett, *Nature (London)*, **186**, 385 (1960).

(4) A. I. Brodskii, V. D. Pokhodenko, and W. A. Kalibabchuck, *Dokl. Akad. Nauk SSSR*, **169**, 339 (1966).

(5) R. Stebbins and F. Sicilio, *Tetrahedron*, **26**, 291 (1970).

(6) S. A. Weiner, *J. Amer. Chem. Soc.*, **92**, 581 (1972).

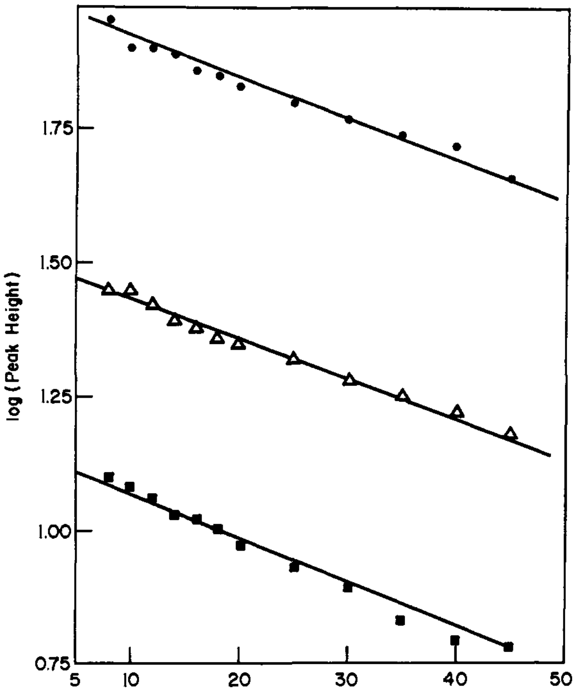


Figure 1. Plots of log of the radical concentration (peak height) *vs.* time for the decay of II in isooctane at 26° for three different initial radical concentrations.

The dependence of the steady-state radical concentration on the light intensity was determined by passing the light beam through a series of previously calibrated neutral density filters. The results are given in Table II. Plots of the log of the relative radical concentration *vs.* the optical density of the filter yield straight lines with slopes of 0.50 ± 0.02 and 0.53 ± 0.02 for 2,6-di-*tert*-butyl-4-methyl- (II) and 2,4,6-trimethylphenoxy radicals (III), respectively. These results are fully consistent with the same reaction sequence observed in the earlier work, *i.e.*[6]

Table II. Dependence of the Steady-State Radical[a] Concentration on Light Intensity

Optical density	2,4,6-Trimethylphenoxy[b]	2,6-Di-*tert*-butyl-4-methyl[c]
0	1.00	1.00
0.54	0.48	0.54
1.08	0.27	0.27
2.03	0.093	

[a] In the presence of biacetyl. [b] Relative radical concentration at 26° in benzene solution. [c] Relative radical concentration at 8° in isooctane solution.

$$\mathrm{K} \xrightarrow{h\nu} \mathrm{K}^* \qquad (1)$$

$$\mathrm{K}^* + \mathrm{ArOH} \longrightarrow \mathrm{KH}\cdot + \mathrm{ArO}\cdot \qquad (2)$$

$$\mathrm{KH}\cdot + \mathrm{ArO}\cdot \longrightarrow \mathrm{K} + \mathrm{ArOH} \qquad (3)$$

$$2\mathrm{KH}\cdot \longrightarrow \text{nonradical product} \qquad (4)$$

$$2\mathrm{ArO}\cdot \longrightarrow \text{nonradical product} \qquad (5)$$

where K, K*, and KH· are the ketone, excited states of the ketone, and ketyl radical derived from the ketone, respectively, and ArOH and ArO· represent the parent phenol and phenoxy radical. Under continuous irradiation a steady state is achieved and we may write

$$I\Phi = 2k_4(\mathrm{KH}\cdot)^2_{ss} + 2k_3(\mathrm{KH}\cdot)_{ss}(\mathrm{ArO}\cdot)_{ss} + 2k_5(\mathrm{ArO}\cdot)^2_{ss} \qquad (6)$$

where I and Φ are the intensity of irradiation and the quantum yield for reaction 2. Since the rates of formation of KH· and ArO· are equal

$$k_5(\mathrm{ArO}\cdot)^2_{ss} = k_4(\mathrm{KH}\cdot)^2_{ss} \qquad (7)$$

Since the ketyl radical is not observed, *i.e.*, the ratio of $[\mathrm{KH}\cdot]_{ss}/[\mathrm{ArO}\cdot]_{ss}$ is less than 0.01, the maximum value of k_5 is *ca.* $10^5\ M^{-1}\ \mathrm{sec}^{-1}$.[7] This estimate may be compared to a minimum value of *ca.* $1.5 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ obtained from a study of the generation of II by reaction of I with 2,6-di-*tert*-butyl-4-methylphenol in a stop flow experiment.[8] Combining eq 6 and 7

$$(\mathrm{ArO}\cdot)_{ss} = [I\Phi/(4k_5 + 2k_3(k_5/k_4)^{1/2})]^{1/2} \qquad (8)$$

and the photochemical steady-state concentration of the phenoxy radical is proportional to the square root of the light intensity, I, as is experimentally observed.

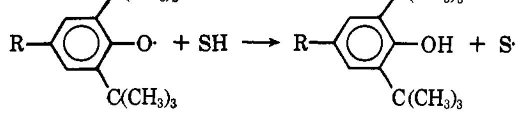
Kinetic Measurements. In order to assure that the first-order decays of radicals II and III were not dependent upon the initial radical concentrations, a systematic study of the decay constants as a function of initial steady-state concentration of the radicals was carried out. The results, summarized in Table III, demonstrate that the decay constants are indeed independent of the initial radical concentration in the range of 10^{-4} to 10^{-5} M.

Table III. First-Order Decay Constants as a Function of Relative Steady-State Radical Concentration

Radical	Relative concn	$k \times 10^2$, sec^{-1}[a]
2,6-Di-*tert*-butyl-4-methylphenoxy[b]	1.00	1.34 ± 0.04
	0.48	1.38 ± 0.05
	0.36	1.40 ± 0.04
	0.26	1.25 ± 0.04
	0.17	1.33 ± 0.06
2,4,6-Trimethylphenoxyl[c]	1.00	10.6 ± 0.7
	0.54	10.7 ± 0.7
	0.27	9.6 ± 0.7

[a] The error limits are ± the standard deviation of the regression coefficient. [b] At 26° in isooctane containing biacetyl. [c] At 8° in benzene containing biacetyl.

The possibility that the first-order decay for II is due to a transfer reaction with solvent and/or solvent impurity, *i.e.*, eq 9, was excluded by studies of the decay of the 2,4,6-tri-*tert*-butylphenoxy radical (I)



(9)

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[7] Based on a value of $2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ for k_4 for the biacetylsemidione radical in benzene at 30°.[6]

[8] L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967). In that work a lower limit for k_5 equal to 50 times the second-order rate constant for the transfer reaction of I with 2,6-di-*tert*-butyl-4-methylphenol was obtained. Utilizing the value of 300 M^{-1} sec^{-1} for the transfer reported by R. Krelick and S. Weissman, *ibid.*, **88**, 2645 (1966), leads to $k_5 \geq 1.5 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$.

generated by the photolysis of a benzene solution containing benzophenone and the parent phenol at 28°. The decay of that radical was extremely slow, manifesting a calculated first-order rate constant for decay smaller than or equal to 5×10^{-5} sec^{-1} or 400 times lower than that for radical II. Furthermore a systematic study of the first-order decay constants for radical II in isooctane at several temperatures revealed that the constants were independent of both the chemical nature of the ketone and the relative concentrations of the ketone and phenol utilized in the radical generation (see Table IV).

Table IV. First-Order Decay Constants of 2,6-Di-*tert*-butyl-4-methylphenoxyl in Isooctane

Ketone	Temp, °C	$k \times 10^2$, sec^{-1} [a]
A[b]	26	1.3 ± 0.1
A[b,c]	36	2.8 ± 0.2
A[b,d]	36	3.2 ± 0.2
A[b]	46	7.8 ± 0.2
A[b]	56	23 ± 1
B[e]	26	1.1 ± 0.1
B[e]	36	3.2 ± 0.2
C[f]	26	1.5 ± 0.1
C[f]	36	3.0 ± 0.2

[a] The error limits are ± the standard deviation of the regression coefficient. [b] Ketone A is biacetyl [c] The concentrations of A and phenol were 0.91 and 0.103 *M*, respectively. [d] The concentrations of A and phenol were 0.91 and 0.0103 *M*, respectively. [e] Ketone B is benzophenone. [f] Ketone C is camphorquinone.

In Figure 2 are presented the plots of the first-order rate constants *vs.* $1/T$ for radical II in benzene and isooctane and for radical III in benzene. The Arrhenius equations for these systems are

$$\log k_{\text{II}} = (11.4 \pm 0.6) - \frac{18{,}300 \pm 900}{2.3RT}(\text{isooctane}) \tag{10}$$

$$\log k_{\text{II}} = (11.5 \pm 0.8) - \frac{18{,}300 \pm 900}{2.3RT}(\text{benzene}) \tag{11}$$

and

$$\log k_{\text{III}} = (10.3 \pm 0.3) - \frac{14{,}600 \pm 500}{2.3RT}(\text{benzene}) \tag{12}$$

Equilibrium Measurements. When solutions of 2,6-di-*tert*-butyl-4-methylphenol and biacetyl in isooctane were irradiated at temperatures below 0° it was noted that little or no radical decay occurred when the irradiation was interrupted. Instead, it was found that in the absence of further irradiation the radical concentration could be varied by changing the temperature. The relative radical concentrations as a function of temperature are given in Table V. These values were not a function of irradiation time for irradiation periods greater than 10 min.

This observation is best accounted for by the formation and reversible disassociation of the dimer IV. This compound has previously been prepared and isolated from methanol solution at room temperature.[9]

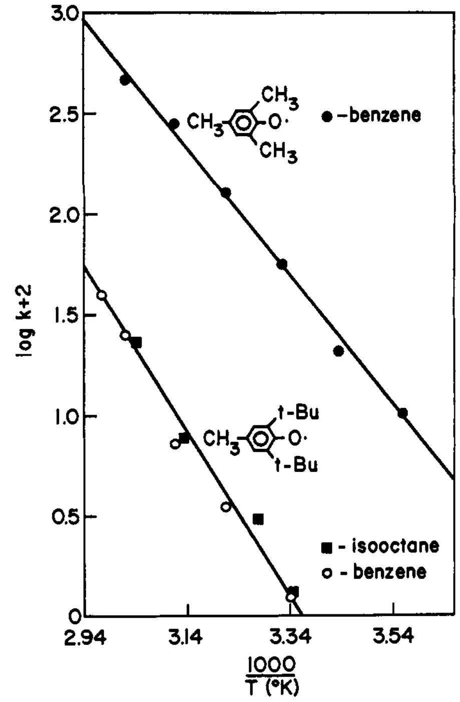
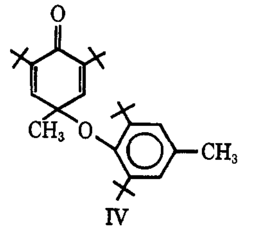


Figure 2. Plots of the first-order rate constants *vs.* $1/T$ (°K).

Table V. Steady-State Concentrations[a] of 2,6-Di-*tert*-butyl-4-methylphenoxyl in Isooctane as a Function of Temperature

Temp, °C	Relative radical concentration[b,c]
−45	0.39 ± 0.01
−35	1.00 ± 0.02
−25	1.86 ± 0.04
−15	3.84 ± 0.09
−6	6.8 ± 0.2

[a] Measured in the dark. [b] Relative to the radical concentration at −35° and corrected for the temperature dependent sensitivity of the esr spectrometer. [c] A van't Hoff plot yields Δ*H* equals 17.4 ± 0.5 kcal/mol.



IV

Combining our measured value of 17.4 ± 0.5 kcal/mol (*cf.* Table V) for the heat of formation of IV with a value for the equilibrium constant equal to 1.4×10^6 M^{-1} at room temperature reported by Land and Porter[10] from their flash photolysis experiments in carbon tetrachloride solution at room temperature leads to the following expression for the equilibrium constant as a function of temperature.

$$\log K_{\text{eq}} = \frac{17{,}400 \pm 500}{4.6T} - \frac{30}{4.6} \tag{13}$$

The value of the entropy charge for the dimerization is then equal to −30 eu. This value is a reasonable one for the dimerization since the reaction of substituted

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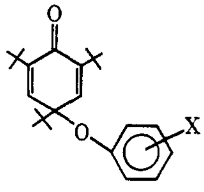
(9) H. D. Becker, *J. Org. Chem.*, 30, 982 (1965).

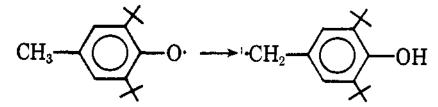
(10) E. J. Land and G. Porter, *Trans. Faraday Soc.*, 59, 2016 (1963).

phenoxy radicals with 2,4,6-tri-*tert*-butylphenoxy to form the analogous quinol ethers (V) manifests entropy changes of −28 to −33 eu.[11,12]



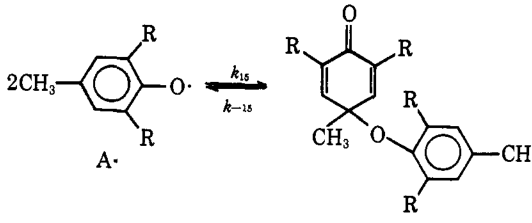
V

Possible Mechanisms. The results of the present study confirm the occurrence of the first-order decay of the 2,6-di-*tert*-butyl-4-methylphenoxy radical (II) as originally reported by Bennett.[3] Moreover we have shown that the 2,4,6-trimethylphenoxy radical (III) manifests the same unique decay kinetics. Bennett and several later workers[4,10] suggested that the mechanism for the reaction involved the unprecedented, unimolecular isomerization, shown in eq 14.



(14)

We now propose two alternatives, which in our view are much to be preferred mechanistic pathways which yield first-order decay kinetics. Both mechanisms involve as a key step the formation of a metastable dimer (eq 15).[13] The formation of products then arises either

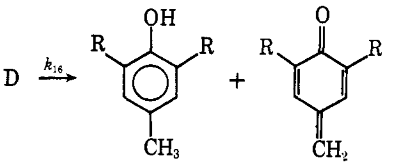


(15)

A·

D

via mechanism A, a unimolecular decomposition of dimer (eq 16), and/or mechanism B, a bimolecular di-



(16)

AH A(−H)

proportionation of the monomeric phenoxy radicals (eq 17).

$$2A\cdot \xrightarrow{k_{16}'} AH + A(-H) \qquad (17)$$

For mechanism A we may write

$$-\frac{d(D)}{dt} = -k_{15}(A\cdot)^2 + k_{-15}(D) + k_{16}(D) \qquad (18)$$

$$-\frac{1}{2}\frac{d(A\cdot)}{dt} = k_{15}(A\cdot)^2 - k_{-15}(D) \qquad (19)$$

and in general

$$-\left[\frac{d(D)}{dt} + \frac{1}{2}\frac{d(A\cdot)}{dt}\right] = k_{16}(D) \qquad (20)$$

At equilibrium and when $k_{15}(A\cdot) \gg k_{-15} \gg k_{16}$[14]

$$k_{-15}(D) = k_{15}(A\cdot)^2$$

differentiating (21)

$$\frac{d(D)}{dt} = \frac{2k_{15}}{k_{-15}}(A\cdot)\frac{d(A\cdot)}{dt}$$

Combining eq 20 and 21 yields the expression

$$-\frac{d(A\cdot)}{dt} = \frac{k_{15}}{k_{-15}}k_{16}(A\cdot)^2\Big/\left(\frac{2k_{15}}{k_{-15}}(A\cdot) + \frac{1}{2}\right) \qquad (22)$$

Under conditions such that $4k_{15}(A\cdot)/k_{-15} \gg 1$, *i.e.*, $(A\cdot) \gg 2 \times 10^{-7}$ *M* for the 2,6-di-*tert*-butyl-4-methylphenoxy system at 25°

$$-\frac{d(A\cdot)}{dt} = \frac{k_{16}}{2}(A\cdot) \qquad (23)$$

In a like manner for mechanism B

$$-\left[\frac{d(D)}{dt} + \frac{1}{2}\frac{d(A\cdot)}{dt}\right] = k'_{16}(A\cdot)^2 \qquad (24)$$

and when $k_{15} \gg k_{-15} \gg k'_{16}(A\cdot)$,[15]

$$-\frac{d(A\cdot)}{dt} = \frac{k'_{16}(A\cdot)^2}{\dfrac{2k_{15}}{k_{-15}}(A\cdot) + \dfrac{1}{2}} \qquad (25)$$

When $(A\cdot) \gg {}^1/_4\,(k_{-15}/k_{15})$ as above

$$-\frac{d(A\cdot)}{dt} = k'_{16}(A\cdot)/(2k_{15}/k_{-15}) \qquad (26)$$

Based upon the results of kinetic studies a clear choice between these two mechanistic pathways cannot be made. For mechanism A the observed rate constant is equal to $k_{16}/2$ and the values of log A_{16} are *ca.* 11.5 for II and 10.5 for III. A recent summary of activation parameters for molecular decomposition reactions reveals that log *A* factors for four-, five-, and six-centered transition states lie in the range of 11.0–15.0 units.[16] Although the present systems are too complex for an analysis of the type which Benson has carried out for simple molecules, we feel that the observed values of log *A* are not inconsistent with the occurrence of mechanism A.

If the reactions are occurring *via* mechanism B the observed rate constant is equal to k'_{16}/K_{15}. Combining eq 11 and 13 yields the following equation for k'_{16} as a function of temperature.

$$\log k'_{16} = 4.7 \pm 1.0 - \frac{900 \pm 1000}{4.6T} \qquad (27)$$

At 25° the value of *k* is equal to approximately $1.5 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. This result may be compared to the

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[11] L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 890 (1970).

[12] L. R. Mahoney and M. A. DaRooge, manuscript in preparation.

[13] The importance of the dimer IV in the reaction of II is also suggested by the results of Becker.[9] The half-life for the formation of quinone methide from the dimer IV is approximately 1 min at room temperature in ether solution. This value is in agreement with our own and Bennett's[3] half-life for the disappearance of II at room temperature.

[14] From Land and Porter's work[10] the rate constants k_{15} and k_{-15} are equal to $10^8\ M^{-1}\ \text{sec}^{-1}$ and $10^2\ \text{sec}^{-1}$ at 25°. If the mechanism is correct then k_{16} equals $2 \times 10^{-1}\ \text{sec}^{-1}$ at 25°.

[15] *Cf.* footnote 14 for value of k_{15} and k_{-15} at 25°. If this mechanism is correct then the inequalities are valid if A· lies between 0.1 *M* and 2×10^{-7} *M*.

[16] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 75 ff.

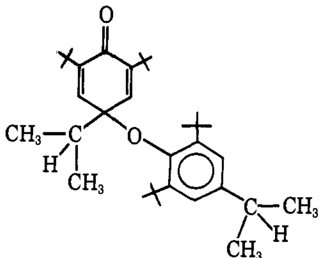
values of log $A = 4.8$ and $\Delta E^{\ddagger} = 6230 \pm 150$ cal/mol reported by Cook and Norcross[17] for the self reaction of 2,6-di-*tert*-butyl-4-isopropylphenoxyl which proceeds by an experimentally observed *second*-order process. The activation energies are strikingly different; one would anticipate that $\Delta E_{16}^{\ddagger}$ should be similar or perhaps somewhat smaller for the 4-isopropyl than the 4-methylphenoxy radical.[18]

This comparison then raises a question concerning the nature of the mechanistic pathway for the *4-isopropyl* derivative. From eq 22 we see that a reaction may manifest *second-order* decay kinetics and proceed *via* molecular decomposition of a dimer, *i.e.*, mechanism A, if $4k_{15}(\mathrm{A}\cdot)/k_{-15}$ is smaller than unity. In the experiments of Cook and Norcross[17] the concentration of A· was smaller than or equal to 10^{-3} *M* and thus if the reaction is proceeding *via* mechanism A the value of k_{15}/k_{-15} must be considerably smaller than 250 *M*.[1]

As the following analysis demonstrates, the isopropyl derivative may indeed be reacting *via* mechanism A. If mechanism A is operative the observed activation energy is given by the relation

$$\Delta E^{\ddagger}_{\mathrm{obsd}} = \Delta E^{\ddagger}_{16} + \Delta E_{\mathrm{dimerization}} \qquad (28)$$

If $\Delta E^{\ddagger}_{16}$ for the 4-isopropyl derivative is equal to that of II, *i.e.*, 18 kcal/mol, the value of $\Delta E_{\mathrm{dimerization}}$ is equal to -12 kcal/mol. This value is in the range one would anticipate for a dimer of the structure VI.[19]



VI

Utilizing values of $\Delta E_{\mathrm{dimerization}}$ equal to -12 kcal/mol and $T\Delta S_{\mathrm{dimerization}}$ at 25° equal to -10 kcal/mol, we calculate a value of $K_{\mathrm{dimerization}}$ equal to *ca.* 35 M^{-1} for the dimerization of the 2,6-di-*tert*-butyl-4-isopropylphenoxy radical at 25°. Since this value is nearly an order of magnitude smaller than the upper limit required for the observation of second-order kinetics from mechanism A, we conclude that the 4-isopropyl derivative may be reacting *via* molecular decomposition of its dimer.

From these considerations we would anticipate that a system in which the 4 substituent is intermediate in bulk, *i.e.*, ethyl, where $K_{\mathrm{dimerization}}(\mathrm{A}\cdot) \approx 1$, would manifest a mixed kinetic order for its decay by *either* mechanism A *or* B. Consistent with this view, Brodskii, *et al.*, report[4] that the 2,6-di-*tert*-butyl-4-ethylphenoxy radical decays by a first-order process at 21 and 26°, while at 35° a mixed order is observed, and at 47° a second-order decay predominates.

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(17) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **81**, 1176 (1959).

(18) Based on the idea that the C–H bond energy of isopropylbenzene is lower than that of toluene. S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," National Standard Reference Data Series, National Bureau of Standards 21, Washington, D. C., 1970, p 55.

(19) Substitution of *o*-dimethyl for hydrogen in the analogous quinol ethers derived from 2,4,6-tri-*tert*-butylphenoxy and phenoxy radicals lowers their heats of formation by 5 kcal/mol.[11] Similarly the substitution of an isopropyl for a methyl in IV would lower the heat of formation of the quinol ether by several kcal/mol.