Chem. Rev. **1987**, *87*, 1313–1357

Mechanisms of Action and Reactivities of the Free Radicals of Inhibitors

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Received August 1, 1986 (Revised Manuscript Received July 7, 1987)

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I. Introduction

Autoxidation of organic compounds is a reaction of unique importance for mankind, who live in an atmosphere of the active chemical agent oxygen and heavily depend on organics for their existence. The enzyme-catalyzed oxidation of fats and carbohydrates is the source of energy in living organisms. In nature, spontaneous oxidation helps do away with enormous amounts of pollutants released into the environment by men and animals. Oxidation of organic compounds at moderate or elevated temperatures is one of the principal routes of organic synthesis of large-scale chemical processes.

At the same time autoxidation is obviously detrimental in some cases. Keeping or using various man-made products in air often results in their rapid dete-

0009-2665/87/0787-1313$06.50/0

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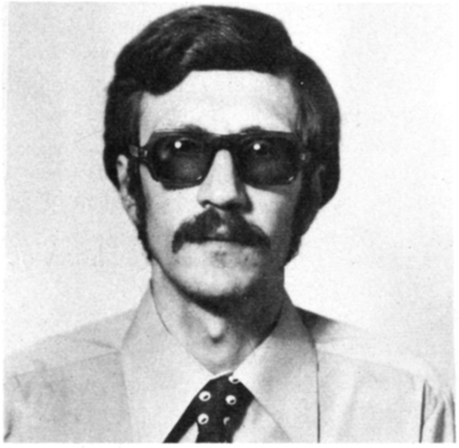


Igor V. Khudyakov was born in Moscow in 1949. He graduated from the Chemistry Department of Moscow State University in 1971 and in the same year joined the staff of the Institute of Chemical Physics, Academy of Sciences of the USSR. He won his Candidate Degree (Ph.D.) in 1975 and his Doctor Degree (D.Sc.) in 1984 (both in chemistry). He has received several awards for young scientists. During 1971–1985 he was Junior Research Fellow, and currently he is a Senior Research Fellow. His scientific interests include fast reactions of free radicals in solution, the kinetics of diffusion-controlled reactions, elementary acts of liquid-phase reactions, magnetic field effects in free radical reactions, and photogeneration of free radicals in solution. His research activities have led to 100 publications of original and review articles and to the presentation of many papers at conferences and symposia held within the country.

rioration or failure. There are many such products, including fuels, lubricant oils, rubber, polymers and articles made from them, medical preparations, chemicals, solvents, foodstuffs, paints, etc. For this reason much effort has been expended in finding appropriate inhibitors or antioxidants to stop or control such aging. The simplest solution to the problem seems to involve adding a small quantity of some inexpensive compound or mixture of compounds to obtain a maximum inhibiting effect on oxidation. Often, very small quantities of inhibitor produce a strong inhibition of autoxidation or initiated oxidation. This fact is not surprising when we remember that oxidation is more often than not a chain reaction.

The inhibiting activity is exhibited by materials of a most variegated nature: metal compounds, aromatic amines, hydroxy aromatic compounds, many natural compounds, and vitamins. Using mixtures, it is sometimes possible to obtain an unexpectedly high inhibiting effect.

A rational approach to selection of inhibitors and prediction of their lifetimes and effectiveness in compositions requires a knowledge of the mechanisms and kinetic parameters of oxidation of the chemical compound in question, as well as the effect of the added inhibitor on the mechanism and kinetics. Clearly, the ability to decelerate oxidation will depend on the nature of the oxidized compound, temperature, and other reaction conditions. It may be viable to have simple algorithms for estimating the appropriateness of an inhibitor for a given composition.

Widely used for inhibition of oxidation of hydrocarbons are substituted phenols, aromatic amines, and other valence-saturated compounds capable of reaction with the peroxyl radical to yield the inhibitor radical ($In^\bullet$). The inhibiting effect is determined by the reactivity of both the inhibitor (InH) itself and the radicals that it produces.

In this review we discuss the various mechanisms of the action of inhibitors. The reactivity of the free radicals of inhibitors is analyzed and related with the inhibition effectiveness.

There have been a number of books and reviews dealing with the problem of inhibition of oxidation.[1–11] Landmarks in the historical development of the field have been as follows.

Bäckström[12,13] was first to show that the inhibiting effect of inhibitors in liquid-phase oxidation of aldehydes and sodium sulfite was due to chain termination. Bolland and ten Haave[14,15] studied the kinetics of the oxidation of ethyl linoleate inhibited with phenols and aromatic amines and established that the chain growth is stopped due to inhibitor reactions with the peroxyl radical. The participation of aroxyls in chain propagation through reaction with hydrocarbon was kinetically observed by Bickel and Kooymen[16] and then thoroughly studied by Mahoney et al.[17,18] In the case of cumene it was demonstrated that the reaction of aroxyls with hydroperoxides affects the rate of inhibited oxidation of hydrocarbons.[19]

The boom in the study of liquid-phase reaction kinetics that began in the mid-1950s has led to the accumulation of a huge amount of rate constant data for individual fast radical reactions. Porter and co-workers[20–22] attracted attention to aromatic radicals (aroxyl, arylaminyl, ketyl, and semiquinone) as an important class of reactive intermediates, identified them by their absorption spectra, and began kinetic measurements.

An important body of kinetic data for aromatic radicals has been obtained by Mahoney, Ingold, Howard, Scaiano, and others. Their results are reviewed in ref 22–34 and are included in handbooks.[35,36]

There has been a considerable inflow of new data during the past decade that have allowed researchers to obtain a much deeper insight into the reactivity of the free radicals of inhibitors and kinetics of inhibited oxidation. Roginsky[37] carried out a systematic study of the reactions of sterically hindered aroxyl radicals with hydroperoxides and peroxyl radicals in solution and solid polymer. A wealth of material on the mechanism of the inhibiting action of phenols and reactivity of phenols and aroxyl radicals has been presented in a highly original kinetic–structural topology form in ref 38. Flash photolysis has been employed for investigation of a broad range of recombinations of aroxyl radicals, and a new class of reactions, the so-called pseudodiffusion bimolecular reactions, have been discovered as a result.[31] A number of reactions of the diphenylaminyl radical have been investigated, and its high activity in abstraction reactions has been demonstrated; a new mechanism of the reaction of this radical with hydroperoxide has been discovered.[39] All these results form the basis for the present review. But in order to outline the progress in the field and build a consistent and integral picture, we have also used the data mentioned or described in earlier reviews (for aroxyl and aminyl radicals).

This review deals with modern conceptions of the reactivity of inhibitors and their aromatic free radicals. The kinetics of the elementary reactions involving inhibitors and aromatic radicals is discussed, and a comprehensive list of the rate constants of these reactions is presented. The rate constants of the elementary reactions of radicals measured prior to the 1980s have been given in ref 36. We will take care to avoid duplicating the contents of ref 36 here and will report only the most representative constants for each class of inhibitors (radicals). The main emphasis will be on the most recent results of the mid-1980s. An attractive feature of this review is that Russian-language references have been drawn upon as comprehensively as possible, thereby providing to the English-speaking reader information not easily accessible.

We have attempted in this review to generalize some kinetic results in the form of diagrams or correlation equations.

The main purpose of this paper is to tie the elementary reaction rate data reported in various publications with modern conceptions of the kinetics and mechanisms of the action of inhibitors (InH).

II. Kinetics of Inhibited Oxidation of Hydrocarbons

A. Mechanisms of Inhibited Oxidation of Hydrocarbons

The oxidation kinetics and mechanisms of the simplest, though extremely important compounds, hydrocarbons (RH), have been studied in much detail; see, e.g., ref 1–4.

The early stage of oxidation of an organic compound at the C–H bond resulting in formation of the hydroperoxide consists of the following elementary steps:[3,6]

$$\text{I (initiator)} \xrightarrow{k_i} 2\text{r}^\bullet \qquad \text{(i)}$$

$$\text{R}^\bullet + \text{O}_2 \xrightarrow{k_1} \text{RO}_2^\bullet \qquad (1)$$

$$\text{RO}_2^\bullet + \text{RH} \xrightarrow{k_2} \text{ROOH} + \text{R}^\bullet \qquad (2)$$

$$\text{r}^\bullet + \text{RH} \xrightarrow{k_{2'}} \text{rH} + \text{R}^\bullet \qquad (2')$$

$$\text{ROOH} \xrightarrow{k_3} \text{RO}^\bullet + \text{HO}^\bullet \qquad (3)$$

or

$$\text{ROOH} + \text{RH} \xrightarrow{k_{3'}} \text{RO}^\bullet + \text{H}_2\text{O} + \text{R}^\bullet \qquad (3')$$

or

$$\text{ROOH} + \text{CH}_2{=}\text{CHX} \xrightarrow{k_{3''}} \text{RO}^\bullet + \text{HOCH}_2{}^\bullet\text{CHX} \qquad (3'')$$

or

$$2\text{ROOH} \xrightarrow{2k_{3'''}} \text{RO}_2^\bullet + \text{H}_2\text{O} + \text{RO}^\bullet \qquad (3''')$$

$$\text{R}^\bullet + \text{R}^\bullet \xrightarrow{2k_4} \text{RR (or RH + olefin)} \qquad (4)$$

$$\text{R}^\bullet + \text{RO}_2^\bullet \xrightarrow{k_5} \text{ROOR} \qquad (5)$$

$$\text{RO}_2^\bullet + \text{RO}_2^\bullet \xrightarrow{2k_6} \text{ROH} + \text{O}_2 + \text{R}'{=}\text{O or ROOR} + \text{O}_2 \qquad (6)$$

Oxidation is a chain process if chain propagation reactions 1 and 2 are faster than chain termination reactions 4–6. Radical $\text{R}^\bullet$ reacts violently with oxygen, $k_1 \simeq 10^7$–$10^9\ \text{M}^{-1}\cdot\text{s}^{-1}$; therefore, for oxygen concentrations above 10^{-4} M, $[\text{RO}_2^\bullet] \gg [\text{R}^\bullet]$ and the chains are terminated by reaction 6. Under these conditions oxidation rate $v = v_i + k_2(2k_6)^{-1/2}[\text{RH}]v_i^{1/2}$, and chain mechanism is realized when initiation rate $v_i < {}^1/_2 k_2^2 k_6^{-1}[\text{RH}]^2$.

The compounds that inhibit oxidation of organic compounds in the liquid phase may be broken up into four groups as regards the mechanism of such inhibition:[40] (1) inhibitors that terminate chains through reactions with peroxyl radicals, including phenols, aromatic amines, diamines, and aminophenols; (2) inhibitors that terminate chains through reactions with alkyl radicals, including stable radicals, quinones, quinone imines, methylenequinones, nitro compounds, and condensed aromatic hydrocarbons (these inhibitors are effective when dissolved oxygen concentration is low); (3) agents that decompose peroxides without generating free radicals, including sulfides, disulfides, phosphites, metal thiophosphates, and carbamates; (4) complexing agents that deactivate heavy metals capable of catalyzing hydroperoxide decomposition to free radicals and thereby promoting oxidation, including diamines, amino acids, hydroxy acids, and other bifunctional compounds.

The following reactions take place in the system upon introduction of InH, which reacts with $\text{RO}_2^\bullet$:

$$\text{r}^\bullet + \text{InH} \xrightarrow{k_{7'}} \text{rH} + \text{In}^\bullet \qquad (7')$$

$$\text{RO}_2^\bullet + \text{InH} \xrightarrow{k_7} \text{ROOH} + \text{In}^\bullet \qquad (7)$$

$$\mathrm{In^\bullet + ROOH \xrightarrow{k_{-7}} InH + RO_2^\bullet} \qquad (-7)$$

$$\mathrm{RO_2^\bullet + In^\bullet \xrightarrow{k_8} products\ (InOOR)} \qquad (8)$$

$$\mathrm{In^\bullet + In^\bullet \xrightarrow{2k_9} products} \qquad (9)$$

$$\mathrm{In^\bullet + RH \xrightarrow{k_{10}} InH + R^\bullet} \qquad (10)$$

$$\mathrm{InH + ROOH \xrightarrow{k_{11}} products} \qquad (11)$$

$$\mathrm{InH + O_2 \xrightarrow{k_{12}} In^\bullet + HO_2^\bullet} \qquad (12)$$

$$\mathrm{InOOR \xrightarrow{k_{13}} InO^\bullet + RO^\bullet} \qquad (13)$$

$$\mathrm{In^\bullet \xrightarrow{k_{14}} Q + r^\bullet} \qquad (14)$$

$$\mathrm{In_1^\bullet + In_2H \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} In_1H + In_2^\bullet} \qquad (15)$$

Reactions i, 1–15, including those marked by primes, make the principal kinetic scheme of inhibited hydrocarbon oxidation (IHO scheme). Each of these reactions will be discussed in detail.

In a given system these reactions take place with different intensities, so some are not as significant as others.

If InH is so active and its concentration so high that $RO_2^\bullet$ will react faster with InH than with RH, the oxidation will be a non chain radical reaction with rate $v = v_i + k_2[RH][RO_2^\bullet] \simeq v_i$. If the initiator radicals also react with InH, the reaction may proceed with a rate less than v_i. When, for example, reactions i, 2′, and 7′ occur, the oxidation rate is

$$v = k_{2'}[RH][r^\bullet] = v_i(1 + k_{7'}[InH]/k_{2'}[RH])^{-1} \qquad (2\text{-}1)$$

so that for $k_{7'}[InH] \gg k_{2'}[RH]$

$$v \simeq v_i k_{2'}[RH]/k_{7'}[InH] \qquad (2\text{-}2)$$

From eq 2-2 it follows that under certain conditions (type and concentration of RH and InH, temperature), the rate of inhibited oxidation may even drop below the initiation rate. The stoichiometric coefficient of inhibition, f, depends on the relation between the rates of reactions 8 and 9.

Often, one meets with a different situation: the oxidation is a chain reaction. If $In^\bullet$ takes no part in chain propagation but only reacts with $RO_2^\bullet$, the oxidation rate is

$$v = k_2[RH][RO_2^\bullet] = v_i + v_i k_2[RH]/fk_7[InH] \simeq v_i k_2[RH]/fk_7[InH] \qquad (2\text{-}3)$$

As more InH is consumed, the oxidation rate will increase and oxygen absorption kinetics will be given by (for current time $t < f[InH]_0/v_i$)[41]

$$\Delta[O_2] = -\frac{k_2[RH]}{k_7} \ln (1 - v_i t/f[InH]_0) \qquad (2\text{-}4)$$

$$\frac{1}{\Delta[O_2]} = \frac{fk_7[InH]}{k_2[RH]v_i} \Delta\left(\frac{1}{t}\right) \qquad (2\text{-}5)$$

Since $RO_2^\bullet$ is involved in the oxidation and InH-consuming reactions, the amount of absorbed oxygen and the amount of consumed InH in chain oxidation of RH are related by[42]

$$\Delta[O_2] = \frac{k_2[RH]}{k_7[InH]} \ln \frac{[InH]_0}{[InH]} \qquad (2\text{-}6)$$

The $ArO^\bullet$ formed from phenol (ArOH) or the $Am^\bullet$ formed from amine (AmH) may also participate in chain propagation. As we have already pointed out, this may happen via one of three reactions. The first route is reaction 10 (see IHO scheme). When its rate exceeds that of $In^\bullet$ decay, the kinetics of inhibited oxidation is changed. At $k_{10}[RH][In^\bullet] \gg k_8[RO_2^\bullet][In^\bullet] = {}^1/_2 v_i$, the quasi-steady concentration $[RO_2^\bullet] = (k_{10}[RH]v_i/fk_7k_8[InH])^{1/2}$ and the rate of chain oxidation is

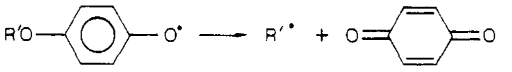
$$v = (k_2[RH] + k_7[InH])\left(\frac{k_{10}[RH]v_i}{fk_7[InH]}\right)^{1/2} \simeq k_2[RH]^{3/2}\left(\frac{k_{10}v_i}{fk_7[InH]}\right)^{1/2} \qquad (2\text{-}7)$$

The oxygen absorption kinetics during the early stages of oxidation is described by[41]

$$\Delta\left(\frac{1}{\Delta[O_2]}\right) = \frac{1}{k_2[RH]^{3/2}}\left(\frac{fk_7[InH]}{k_{10}v_i}\right)^{1/2} \Delta\left(\frac{1}{t}\right) \qquad (2\text{-}8)$$

The second route may be reaction with ROOH, reaction −7. In this reaction $Am^\bullet$ and $ArO^\bullet$, which have no *tert*-alkyl substituents in the ortho position (see earlier), actively participate. If this exchange is fast enough ($k_{-7}[ROOH][In^\bullet] > v_i$), it will affect the inhibited oxidation kinetics. The appropriate formulas for absorption kinetics are given in Table 1.

The third route of chain termination may be the breakdown of the inhibitor radical to a radical capable of participating in chain propagation. For example, the *n*-alkoxyphenoxyl radical decomposes to quinone and alkyl radical[43]



(14)

On reacting with oxygen the alkyl radical is converted to $RO_2^\bullet$, which propagates chains. As before, an intensive enough decomposition will give rise to a chain process with chains terminated through reaction 8 of the IHO scheme (cf. Table 1). As seen from Table 1, relationships of the type $v \sim v_i^{1/2}$ and $v \sim [InH]^{-1/2}$ are typical of all inhibited oxidation mechanisms with $In^\bullet$ participating in chain propagation. If $In^\bullet$ does not participate, $v \sim v_i$ and $v \sim [InH]^{-1}$.

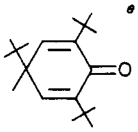
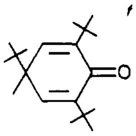
When trialkylphenols are used to inhibit RH oxidation via the reaction between $RO_2^\bullet$ and $ArO^\bullet$, *o*- and *p*-quinolide peroxides are formed.[3] The quinolide peroxides decompose unimolecularly in hydrocarbons (cf. Table 2).[43] *o*-Quinolide peroxides decompose much faster than their para counterparts, owing primarily to the lower activation energy for decomposition (Table 2). Investigation of cumene oxidation with quinolide peroxide as initiator has shown that these peroxides decompose to yield free radicals that initiate oxidation. The initiation rate constant $k_i = 2ek_{13}$, where e is the probability for radicals to escape from a solvent cage; in hydrocarbon solutions $e \simeq 1$, and in polymers $e \simeq 0.15$–0.20.[43] The degree of decomposition of the quinolide peroxide to radicals will determine the ArOH consumption rate in RH undergoing oxidation. At a temperature where the peroxide is stable, ArOH is

TABLE 1. Kinetics of Inhibited Oxidation of Hydrocarbons

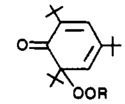
mechanism[a]	key reactions	v,[b] M·s^{-1}	$\Delta[O_2]$,[c] M
I	2′, 7′, 8	$v_i(1 + k_{7'}[InH]/k_{2'}[RH])^{-1}$	$fa^{-1} \ln \{(1 + a[InH]_0)(1 + a[InH]_0 - v_i a f^{-1} t)^{-1}\}^d$
II	7, 8	v_i	$v_i t$
III	2, 7, 8	$v_i k_2[RH]/fk_7[InH]$	$(k_2[RH]/k_7) \ln \{1/(1 - \alpha t)\}^e$
IV	2, 7, 8, 10	$k_2[RH]^{3/2}(k_{10}v_i/fk_7k_8[InH])^{1/2}$	$2v_0\alpha^{-1}[1 - (1 - \alpha t)^{1/2}]^e$
V	2, 7, 8, 13	$v_i k_2[RH]/fk_7[InH]$	$(k_2[RH]/k_7) \ln \{1/(1 - \alpha' t)\}^f$
VI	2, 7, 8, 12	$k_2k_{12}[RH][O_2]/fk_7$	$k_2k_{12}[RH][O_2]t/fk_7$
VII	2, 7, 8, −7	$k_2[RH](k_{-7}[ROOH]v_i/fk_7k_8[InH])^{1/2}$	$\{[ROOH]_0^{1/2} + b[[InH]_0^{1/2} - ([InH]_0 - \alpha t)^{1/2}]\}^2 - [ROOH]_0^{e,g,h}$
VIII	2, 7, 8, 14	$k_2[RH](k_{14}v_i/fk_7k_8[InH])^{1/2}$	$2v_0\alpha^{-1}[1 - (1 - \alpha t)^{1/2}]^{e,h}$
IX	2, 7, 8, 11	$k_2k_{11}[RH][ROOH]/fk_7$	$[ROOH]_0[1 - \exp(\beta t)]^i$

[a] A mechanism is defined by corresponding key reactions; see section IX.A also. [b] Formulas for rate of oxidation. [c] Formulas for consumed oxygen. [d] Here, $a = k_7' k_2'^{-1}[RH]^{-1}$. [e] Here, $\alpha = v_i f^{-1}[InH]_0^{-1}$. [f] Here, $\alpha' = (v_i + k_{13}[InOOR])[InH]_0^{-1} f^{-1}$. [g] $[ROOH]_0$ is the concentration of ROOH dissolved in solution before the start of inhibited oxidation (at $t = 0$). [h] Here, $b = (k_2[RH]/\alpha)(v_i k_{-7}/fk_7k_8)^{1/2}$. [i] Here, $\beta = 2k_2k_{11}[RH]/fk_7$.

TABLE 2. Rate Constants, Preexponential Factors, and Activation Energies of Reaction 13 for Quinolide Peroxides in Benzene at 363 K[a]

subst R in peroxide	$k_{13} \times 10^5$,[b] s^{-1}	log (A_{13}/s^{-1})[c]	E_{13},[d] kJ/mol
$C(CH_3)_3$[e]	6.6	14.0	127.5
$C(CH_3)_2CH_2C_2H_5$[e]	6.3	14.1	127.9
$C(CH_3)_2C_6H_5$[e]	19	15.5	134.6
 [e]	14	15.4	134.6
$C(CH_3)_3$[f]	0.18	14.0	137.9
$C(CH_3)_2CH_2C_2H_5$[f]	0.19	15.5	148.0
$C(CH_3)_2C_6H_5$[f]	0.68	15.7	146.3
 [f]	1.7	14.5	134.6
$C(CH_3)_3$[g]	0.66	13.6	137.9
$OC(CH_3)_3$[g]	2.5	12.8	121.2
C_6H_5[g]	3.7	14.4	131.7

[a] Reference 43. [b] Determination error is 2%. [c] Determination error of log (A_{13}/s^{-1}) is ±0.1. [d] Determination error of E_{13} is ±0.2 kJ/mol. [e] Peroxide has general formula i. [f] Peroxide has general formula ii. [g] Peroxide has general formula iii.



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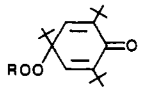

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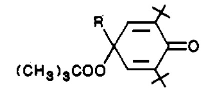


iii

consumed with a constant rate v_i = const, and $[InH] = [InH]_0 - v_i f^{-1} t$; at a higher temperature ArOH will be consumed with self-acceleration. For instance, in oxidation of *n*-decane (398 K, initiator = *tert*-butyl hydroperoxide at a concentration of 4.7×10^{-2} M), 2,4,6-tri-*tert*-butylphenol consumption is self-accelerated; if it were used up at the rate $v = 0.5v_i$, it would be half-consumed within 215 min, whereas in fact it took 170 min.[43] The authors of ref 43 attribute this difference to the extra initiation by the quinolide peroxide. Decomposition of the latter cuts the induction period τ. If the experimental termperature is high enough so that $k_{13}^{-1} \ll \tau$, the (RH–InH–initiator–O_2) system will within time $t \simeq k_{13}^{-1}$ relax to a quasi-steady regime with respect to the peroxide with the total initiation rate $v_{i\Sigma} = v_i + ek_{13}[InOOR] = 2v_i(2 - e)^{-1}$ if $f = 2$, as is usual for ArOH.[35] The induction period in such a system will be $\tau = {}^1/_2[InH]_0 v_i^{-1}(2 - e)$; that is, decomposition of quinolide peroxide shortens the induction period of phenol-inhibited oxidation.

TABLE 3. Rate Constants, Preexponential Factors, and Activation Energies of Reaction 11 for Cumyl Hydroperoxide and Phenols in Benzene at 413 K[a]

ArOH	k_{11},[b] M^{-1}·s^{-1}	log $(A_{11}/(M^{-1}·s^{-1}))$[c]	E_{11},[d] kJ/mol
2,6-dimethoxyphenol	6.5×10^{-3}	10	96
4-methoxyphenol	4.3×10^{-3}	10	97
2,3-dihydroxynaphthalene	4.5×10^{-3}	11	108
α-naphthol	6.7×10^{-4}	10	101
bis(5-methyl-3-*tert*-butyl-2-hydroxyphenyl)methane	4.2×10^{-4}	10	109
4-methylphenol	2.0×10^{-4}	10	110
2,4,6-tri-*tert*-butylphenol	7.8×10^{-5}	10	108

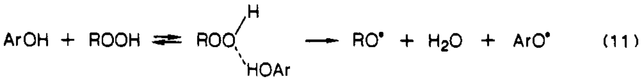
[a] Reference 47. [b] Determination error is 15%. [c] Determination error of log $(A_{11}/(M^{-1}·s^{-1}))$ is ±0.5. [d] Determination error of E_{11} is ±1 kJ/mol.

In hydrocarbon systems ArOH and AmH react not only with $RO_2^•$ but also with oxidants such as O_2 and ROOH. The reaction with oxygen[44,45]

$$InH + O_2 \xrightarrow{k_{12}} In^• + HO_2^• \qquad (12)$$

is endothermic since in most cases bond dissociation energy (D) $D_{In-H} > D_{H-O_2^•}$ and its activation energy is about equal to its endothermicity. The k_{12} values can be found in ref 35.

ArOH are oxidized with ROOH slowly (Table 3). The reaction apparently involves abstraction of H atom from ArOH by ROOH and scission of the O–O bond.[46] The reaction is preceded by H bonding between ArOH and ROOH:



As a result of reaction 11 free radicals are formed that initiate oxidation (RO•). This has been demonstrated in studies of 4-methoxyphenol-inhibited oxidation of cumene.[46,47] The probability for radicals to leave the cage in this reaction is $e = 0.27$ at 393 K in cumene.

Aromatic amines react faster with hydroperoxides than phenols. As with benzoyl peroxide, the reaction apparently involves electron transfer[3]

$$Ar\ddot{N}HAr + ROOH \rightarrow Ar\dot{N}^+HAr + ROOH^{•-} \rightarrow Ar_2N^• + H_2O + RO^• \qquad (11)$$

Both O_2 and ROOH are normally present in oxidizing RH, and InH is attacked by both these agents. Compare the rates of these reactions: $v_{11}/v_{12} = k_{11}[O_2]/k_{12}[ROOH]$. For *p*-cresol the k_{11}/k_{12} ratio (see ref 35 and Table 3) is 8.5×10^{-3} at 373 K, whereas $k_{11}/k_{12} =$

TABLE 4. Quantity of Consumed Oxygen in Inhibited Oxidation of Hydrocarbon under Nonsteady Conditions as a Function of the Quantity of Used Inhibitor[a]

mechanism	key reaction	$\Delta[O_2]$,[b] M	a[c]	τ, s
II	2, 7, 8	$[InH]_0(1 - x)$		$f[InH]_0/(v_{io} + {}^1/_2 k_3[InH]_0)$
III	2, 7, 8	$[InH]_0 a \ln (x - 1)$	$k_2[RH]/k_7[InH]_0$	$(1/k_3 a)\int_{x_{cr}}^{1}(A + \ln x)^{-1}\, dx$[d]
IV	2, 7, 10	$[InH]_0^{1/3}a(1 - x^{1/2})^{2/3}$	$(9fk_2^2k_{10}/k_3k_7k_8)^{1/3}[RH]$	$7.5f[InH]_0^{2/3}/k_3a$
VII	2, 7, −7	$[InH]_0^{1/2}a(1 - x^{1/2})$	$2k_2[RH](fk_{-7}/k_3k_7k_8)^{1/2}$	$(2f[InH]_0^{1/2}/k_3a) \ln \{k_3a[InH]^{1/2}/ev_{i0}\}$
VIII	2, 7, 14	$[InH]_0^{1/3}a(1 - x^{1/2})^{2/3}$	$(9fk_2^2k_{14}[RH]^2/k_3k_7k_8)^{1/3}$	$7.5f[InH]_0^{2/3}/k_3a$

[a] For definitions of most parameters in the table, see text. [b] Parameter x in this column is defined as $x = [InH]/[InH]_0$. [c] Dimensional or dimensionless parameter in corresponding equations presented in columns for $\Delta[O_2]$ and τ; all rate constants are expressed in s^{-1} or $M^{-1}\cdot s^{-1}$. [d] $x_{cr} = [InH]_{cr}/[InH]_0$, where $[InH]_{cr}$ is the critical concentration of InH (see text); $A = k_7v_{i0}/(fk_2k_3[RH])$.

0.02 at 423 K. Since normally $[ROOH] \gtrsim [O_2]$, it is clear that oxidation with ROOH is the main (next to reaction with $RO_2^{\bullet}$) route of ArOH consumption. For AmH the k_{11}/k_{12} ratio is even smaller.

B. Kinetics of Inhibited Autoxidation of Hydrocarbons

An important distinction of autoxidation of a hydrocarbon is that its product (hydroperoxide) is an initiator,[1,3,5] which causes a progressively increasing initiation rate in the course of the reaction. The rate of acceleration depends in turn on the rate of chain oxidation; i.e., there is a kind of a positive feedback between the autoinitiation and autoxidation reactions. A similar feedback exists in inhibited oxidation of other organic compounds, too.

First, the more effectively the inhibitor terminates the chains, the slower is its rate of consumption and the longer is the effective inhibition period τ, whereas in an initiated chain reaction, with v_i = const, τ is independent of InH effectiveness. Second, autoxidation of RH can be inhibited not only with compounds that act to terminate the chains but also with compounds that decompose ROOH.[1,3] Unless it involves buildup of free radicals, such decomposition will hamper accumulation of ROOH and thereby inhibit the autoinitiation. Good peroxide decomposers include sulfur and phosphorus compounds and various metal complexes, e.g., thiophosphates and thiocarbamates of zinc, nickel, and other metals.[48,49] Third, critical phenomena are often observed in inhibited autoxidation experiemnts,[50] which must be attributed to the above-mentioned feedback effect.

Since ROOH is decomposed during autoxidation, the oxidation may follow either of two regimes, a nonsteady-state or a quasi-steady-state one with respect to ROOH.

Under the non-steady-state process the ROOH is stable and almost no decomposition is perceptible during the induction period; that is, its decomposition rate constant $k_3 < \tau^{-1}$. Obviously, such a regime arises due to specific conditions of inhibited oxidation, which will depend on the structure and reactivity of RH, ROOH, and InH.

Since oxidation of RH and consumption of InH are interrelated processes, the O_2 absorption rate may be quantitatively expressed in terms of the rate of consumption of InH in the system by using the following equations (v_{InH} is the rate of consumption of InH):

$$v_i = v_{i0} + k_3[ROOH] \simeq k_3[ROOH]; \qquad v_{InH} = v_i/f \tag{2-9}$$

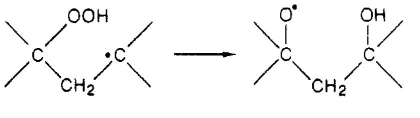
$$v = k_2[RH][RO_2^{\bullet}] + k_7[InH][RO_2^{\bullet}] \tag{2-10}$$

For every possible mechanism of inhibited oxidation one may correlate $[RO_2^{\bullet}]$ with [InH] and [ROOH], express the results mathematically and, after solving a set of two differential equations describing absorption of oxygen and consumption of InH, express the absorbed quantity of oxygen in terms of the consumed InH

$$\Delta[O_2] = [ROOH] = \int_0^t v\, dt$$

$$\tau = f \int_{[InH]_0}^{0} d[InH]/v_i \tag{2-11}$$

For each particular mechanism the correlation will have its special form. Table 4 contains formulas relating the degree of oxidation with consumed InH. The calculation was based on the following assumed conditions: (i) $\Delta[O_2]$ = [ROOH], (ii) rate of initial chain generation $v_{i0} \ll k_3$[ROOH], and (iii) the mechanism remains unchanged through the induction period. It should be noted that all oxygen is not always converted to hydroperoxide. For example, because isomerization occurs during solid-phase oxidation of polyolefins[51]



(2-12)

only a portion of the absorbed O_2 is converted to ROOH.[51] In this case the formulas for τ and O_2 are to be corrected accordingly.

Since the rate of inhibitor consumption $v_{InH} = v_i/f$ and v_i tends to increase during oxidation, the InH consumption kinetics is substantially nonlinear. During the early stages of oxidation $v_{InH} = v_{i0}/f$, but as more ROOH is accumulated v_{InH} increases and becomes maximum toward the end of the induction period. Calculation and experiment yield identical results; theoretically, this question has been treated in ref 3. Chain initiation via RH reaction with O_2 has been investigated in a number of works (cf. review 52) according to the early rate of InH consumption when $v_i \simeq v_{i0}$ and $k_3[ROOH] \ll v_{i0}$.

At a sufficiently high temperature or in the presence of a ROOH decomposer, ROOH will rapidly dissociate and therefore the oxidation regime will quickly become quasi-steady as regards the ROOH concentration, with the decomposition rate being equal to the rate of its formation. However, the ROOH concentration will tend to increase, since as more InH is consumed, the inhibition effect will decline and the ROOH formation rate will increase. A necessary condition for the quasi-steady process is the inequality $k_{\Sigma}\tau \gg 1$, where k_{Σ} is the total rate constant of ROOH consumption by all possible routes, including dissociation to radicals, decomposition

TABLE 5. Quasi-Steady Autoxidation of Hydrocarbon: Formulas for ν, $[\mathrm{InH}]_{\mathrm{cr}}$, $[\mathrm{ROOH}]_{\mathrm{s}}$, and τ[a]

mechanism	key reaction	ν	$[\mathrm{InH}]_{\mathrm{cr}}$, M	$[\mathrm{ROOH}]_{\mathrm{s}}$, M	τ/τ_0[b]	x
III	2, 7, 8	1		$\frac{v_{i0}\beta}{k_3(1-\beta)}$	$1-\beta$	
III	2, 7, 8	$\frac{k_2[\mathrm{RH}]}{fk_7[\mathrm{InH}]}$	$\frac{\beta k_2[\mathrm{RH}]}{fk_7}$	$\frac{\beta\nu v_{i0}}{k_3(1-\beta\nu)}$	$1-x^{-1}(1+\ln x)^c$	$\frac{fk_7[\mathrm{InH}]_0}{k_2[\mathrm{RH}]}$
IV	2, 7, 10	β^{-1}		$\beta^2k_2{}^2k_{10}[\mathrm{RH}]^3$	$1-x^{-1}\ln(1+x)^c$	$\frac{fk_7k_8[\mathrm{InH}]_0v_{i0}}{\beta^2k_2{}^2k_{10}[\mathrm{RH}]^3}$
VII	2, 7, −7	$k_2[\mathrm{RH}]\left(\frac{k_7}{fk_3k_7k_8[\mathrm{InH}]}\right)^{1/2}$	$\frac{\beta^2k_2{}^2k_{-7}[\mathrm{RH}]^2}{fk_3k_7k_8}$	$\frac{[\mathrm{InH}]_{\mathrm{cr}}v_{i0}}{fk_3([\mathrm{InH}]-[\mathrm{InH}]_{\mathrm{cr}})}$	$1-x^{-1}F(x)^{c,d}$	$\frac{fk_3k_7k_8[\mathrm{InH}]_0}{\beta^2k_2{}^2k_7[\mathrm{RH}]^2}$
VIII	2, 7, 14	β^{-1}		$\frac{\beta^2k_2{}^2k_{14}[\mathrm{RH}]^2}{fk_3k_7k_8[\mathrm{InH}]}$	$1-x^{-1}\ln(1+x)^c$	$\frac{fk_7k_8[\mathrm{InH}]_0v_{i0}}{\beta^2k_2{}^2k_{14}[\mathrm{RH}]^2}$

[a] For definitions of most parameters in the table, see text; $\beta = k_3/k_\Sigma$. [b] $\tau_0 = f[\mathrm{InH}]_0/v_{i0}$. [c] Corresponding expression for x is presented in the last column of the table. [d] $F(x) = 1 + \ln(2 - 2x^{1/2} + x) + \arctan(x^{1/2} - 1)$.

to molecular products, and decomposition under attack of free radicals. The change from a nonsteady to the quasi-steady condition is related to the induction period τ, which depends on the InH type and concentration. The transition from one inhibitor to another often manifests itself in transitions from one type of autoxidation process to another and various critical phenomena.[50]

What we mean by critical effects in inhibited autoxidation of RH is that under a certain critical InH concentration $[\mathrm{InH}]_{\mathrm{cr}}$ there takes place a sharp change in the τ vs. [InH] relationship; i.e., $d\tau/d[\mathrm{InH}]$ for [InH] $> [\mathrm{InH}]_{\mathrm{cr}}$ is much greater than $d\tau/d[\mathrm{InH}]$ for $[\mathrm{InH}] < [\mathrm{InH}]_{\mathrm{cr}}$. Critical effects may arise when inhibited oxidation proceeds via mechanisms III and VII (see Table 5) and $v_{i0} \ll k_3[\mathrm{ROOH}]$, so that decomposition of ROOH is sufficiently rapid and the condition $k_\Sigma\tau \gg 1$ for $[\mathrm{InH}] > [\mathrm{InH}]_{\mathrm{cr}}$ is satisfied. As we have said earlier the critical phenomena are due to the feedback effect in inhibited oxidation and occur when both the formation and decomposition rates are similarly dependent upon [ROOH], for example, when they are directly proportional to [ROOH], which is just the case in routes III and VII. If the oxidation rate $v \sim [\mathrm{ROOH}]^n$, with $n < 1$, and the decomposition rate is proportional to [ROOH], the critical effects will never take place. Table 5 contains formulas for chain lengths ν, $[\mathrm{InH}]_{\mathrm{cr}}$, and the quasi-steady hydroperoxide concentration $[\mathrm{ROOH}]_{\mathrm{s}}$ for different inhibited oxidation mechanisms. It is seen that the critical effects take place when the chain reaction proceeds via routes III and VII, whereas no critical effects can be possible with other mechanisms. The table also contains formulas for the induction periods of inhibited autoxidation. The induction period was calculated as the time of InH decrease from $[\mathrm{InH}]_0$ to $[\mathrm{InH}]_{\mathrm{cr}}$ (routes III and VII) or to zero (routes II, IV, and VIII).

One may obtain a synergistic effect in inhibition of autoxidation if two different InH, one of which acts to terminate the chains (ArOH, AmH) and the other of which decomposes by hydroperoxides (sulfide, zinc carbamate, etc.), are added to RH. In combination the two InH are operative for a longer period than either of them separately because one of them decelerates the buildup of ROOH by breaking the chains and the other, by decomposing ROOH, reduces v_i and thus slows down the consumption of the first InH. InH of complex function, containing groups reacting with both $\mathrm{RO_2^\bullet}$ and ROOH, may be expected to be highly effective.

C. Catalysis of Chain Termination in Oxidation

As it terminates the chains InH is consumed in the course of the oxidation process. If chain termination reactions 7 and 8 (see IHO scheme) dominate in the system and the products of reaction 8 are not active toward chain termination or initiation, $f = 2$. If $\mathrm{In^\bullet}$ decays by recombination 9, $f = 1$. If reaction 8 products take part in chain termination, then it may be that $f > 2$, but as experience shows, for oxidizing hydrocarbons $f \leq 4$ for hydroquinones, amines, and diamines of the *p*-phenylenediamine type.[35] At the same time there are InH that in a given system cause catalyzed termination of chains and $f \gg 2$.[7,29,54] Multiple chain termination was observed in oxidizing cyclohexanol with α-naphthylamine.[55] This was shown to be typical of a number of AmH in primary and secondary alcohol oxidation.[56] The range of compounds in oxidation of which the InH becomes involved in multiple chain terminations is rather broad and includes also cyclohexadiene,[57] primary, secondary, and tertiary aliphatic amines,[58,59] cyclohexanone containing hydrogen peroxide,[60] and 1,2-disubstituted ethylenes.[61] For these compounds $f \gg 2$ with AmH, nitroxyl radicals, certain ArOH, and quinones used as InH. The high nonstoichiometric values of f are due to the catalytic mechanism of chain termination occurring in such systems. The mechanism itself is due to the dual function of hydroxyperoxyl, aminoperoxyl, and hydroperoxyl radicals, which may either oxidize or reduce. The pure catalytic chain termination occurs on copper ions in oxidizing cyclohexanol[62]

$$\mathrm{{>}C(OH)OO^\bullet + Cu^+ \rightarrow {>}C(OH)OO^- + Cu^{2+}} \quad (2\text{-}13)$$

$$\mathrm{{>}C(OH)OO^\bullet + Cu^{2+} \rightarrow {>}C{=}O + O_2 + Cu^+ + H^+} \quad (2\text{-}14)$$

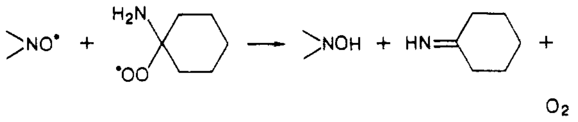
1,4-Benzoquinone (Q) multiply terminates the chains of oxidizing isopropyl alcohol[63]

$$\mathrm{Q + (CH_3)_2C(OH)OO^\bullet \rightarrow QH^\bullet + O_2 + (CH_3)_2C{=}O} \quad (2\text{-}15)$$

$$\mathrm{QH^\bullet + {}^\bullet OOC(OH)(CH_3)_2 \rightarrow Q + HOOC(OH)(CH_3)_2} \quad (2\text{-}16)$$

The data summarized in sections VIII.C and VIII.E favor the possibility of reactions 2-13 to 2-15: copper ions are highly reactive toward free radicals, and Q is a strong electron acceptor.

Nitroxyl radical is reduced to the corresponding hydroxylamine, and the latter is oxidized back to the nitroxyl radical with the peroxyl radicals of cyclohexylamine[64]



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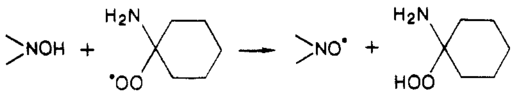

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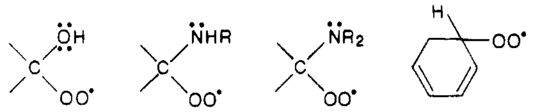
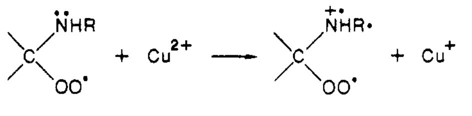
It is remarkable that oxidation–reduction activity is also exhibited by peroxyls that have next to their •OO group a heteroatom with a lone electron pair or a double bond:



Such peroxyls probably react with the inhibitor radical, quinone, or variable-valence metal ion by way of electron transfer, e.g.

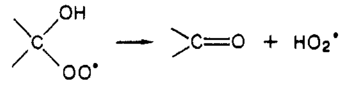


(2-19)

(cf. section VIII.C), followed by rapid elimination of the proton and oxygen molecule

$$>C(OO^\bullet)\dot{N}^+HR \rightarrow >C{=}NR + O_2 + H^+ \qquad (2\text{-}20)$$

All the peroxyls we have mentioned decompose, generating $HO_2^\bullet$



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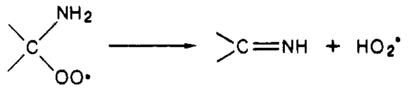

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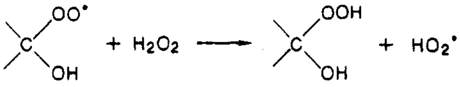


(2-22)

Thus, generated in the system and participating in catalyzed chain termination (if the corresponding InH has been added) are both hydroxyperoxides and hydroperoxides. Depending on the type of compound and oxidation conditions (temperature, degree of conversion), either $HO_2^\bullet$ or $>C(OH)OO^\bullet$ [$>C(NH_2)OO^\bullet$] radicals may preferentially take part in chain termination. Things are just the same with chain termination in oxidizing amines. Aliphatic and alkyl aromatic peroxyl radicals do not take part in reactions of this sort because they have no reducing activity. Since the hydroxyperoxyl (hydroperoxyl, aminoperoxyl) radical behaves as both an oxidant and a reductant, it will react with $In^\bullet$ by two parallel routes. In the case of AmH the following three mechanisms of chain termination appear to be probable (Ar = aryl)

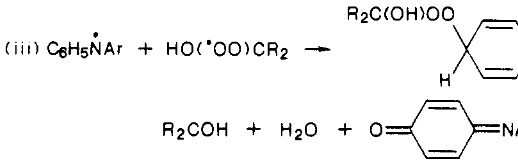
(i) $$Ar_2NH + HO(^\bullet OO)CR_2 \rightarrow Ar_2N^\bullet + R_2C(OH)OOH \qquad (2\text{-}23)$$

$$Ar_2N^\bullet + HO(^\bullet OO)CR_2 \rightarrow Ar_2NH + O_2 + R_2C{=}O \qquad (2\text{-}24)$$

(ii) $$Ar_2N^\bullet + HO(^\bullet OO)CR_2 \rightarrow Ar_2NO^\bullet + HO(^\bullet O)CR_2 \qquad (2\text{-}25)$$

$$Ar_2NO^\bullet + HO(^\bullet OO)CR_2 \rightarrow Ar_2NOH + O_2 + R_2C{=}O \qquad (2\text{-}26)$$

$$Ar_2NOH + HO(^\bullet OO)CR_2 \rightarrow Ar_2NO^\bullet + R_2C(OOH)OH \qquad (2\text{-}27)$$



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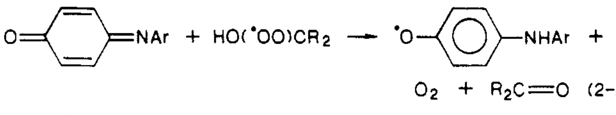

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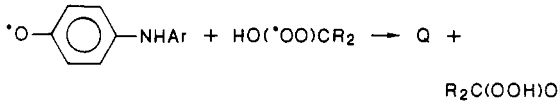


(2-30)

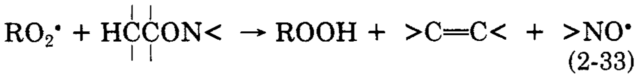
Multiple involvement in chain termination reactions has also been observed for the stable nitroxyl radicals 2,2,6,6-tetramethylpiperidin-*N*-oxyl and its derivatives.[65] Nitroxyl radicals ($>NO^\bullet$) break the chains in oxidizing hydrocarbons and polymers by reacting with alkyl radicals[65,66]

$$>NO^\bullet + R^\bullet \xrightarrow{k_{31}} >NOR \qquad (2\text{-}31)$$

If we accept this mechanism, the rate of inhibited polymer oxidation must be

$$v = k_1[O_2]v_i/k_{31}[>NO^\bullet] = k_1\gamma P_{O_2}v_i/k_{31}[>\dot{N}O^\bullet] \qquad (2\text{-}32)$$

where γ is the Henry coefficient for O_2. The k_{31}/k_1 ratio for 2,2,6,6-tetramethyl-4-benzoylpiperidinoxyl equals 0.09 in polypropylene at 387 K and 0.027 in polyethylene at 365 K.[66] Nitroxyl radicals react slower than oxygen with alkyl radicals, and their high inhibiting effect in polymers is due to the relatively low dissolved oxygen concentration in polymers. The multiple involvement of $>NO^\bullet$ in chain termination manifests itself in the fact that the rate of $>NO^\bullet$ consumption in a polymer is much smaller than the rate of initiation under conditions where all the chains are terminated via reaction 2-31.[65,66] Under the same conditions, but in the absence of oxygen, the nitroxyl radical is consumed at a rate equal to that of initiation. In an initiator-containing polymer all the $>NO^\bullet$ will be consumed within a time equal to $[>NO^\bullet]_0/v_i$ (as monitored by ESR). However, $>NO^\bullet$ reappears in the system to which oxygen has been admitted, under attack of $RO_2^\bullet$.[65,66] Regeneration has been proposed to be due to the following reaction:[65]



$$RO_2^\bullet + H\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}ON< \rightarrow ROOH + >C{=}C< + >NO^\bullet \qquad (2\text{-}33)$$

This supposition is consistent with the following data.

The >NO• are formed from the products of reaction between the alkyl macroradical with >NO• only in the presence of O_2 and initiator, that is, under attack of $RO_2^{\bullet}$. The product cannot be the corresponding hydroxylamine since it could not be extracted from the polymer with a solvent.

The following reaction has been demonstrated experimentally[67]

$$[(CH_3)_3C]_2NOC(CH_3)_3 + {}^{\bullet}OOC(CH_3)_3 \xrightarrow{k_{33}} [(CH_3)_3C]_2NO^{\bullet} + CH_2{=}C(CH_3)_2 + HOOC(CH_3)_3 \qquad (2\text{-}34)$$

The k_{33} value is rather high; it is 44 $M^{-1}{\cdot}s^{-1}$ at 403 K in *tert*-butylbenzene. The scission of the weaker secondary C–H bond should have been faster.

A different regeneration mechanism was proposed in ref 67, where it was noted that hydroxamic ester was thermally unstable and dissociated at the O–C bond, which was followed by cage disproportionation of radicals

$$R_2NOC(CH_3)_3 \xrightarrow{k_{35}} [R_2NO^{\bullet} + H{-}CH_2{-}\dot{C}(CH_3)_2] \rightarrow R_2NOH + CH_2{=}(CH_3)_2 \qquad (2\text{-}35)$$

By reacting with $RO_2^{\bullet}$ hydroxylamine was converted to >NO•. Below 400 K decomposition of hydroxamic esters is slow (at 403 K *N,N,O*-tri-*tert*-butylhydroxylamine decomposed with $k_{33} = 5.7 \times 10^{-4}$ s^{-1} [67]) and cannot be responsible for the experimentally observed regeneration rates. Besides, under the conditions that had been used in the polypropylene experiments[66] this mechanism runs contrary to some of the above factors. Yet at a higher temperature when hydroxamic ester decomposes faster, this mechanism might possibly become effective.

An increase of the stoichiometric coefficient f has also been observed for ArOH in polymers as the partial O_2 pressure was reduced. For example, $f = 1$ and 3.3 for α-naphthol in oxidizing polypropylene at 388 K at P_{O_2} = 100 and 0 kPa, respectively.[68] The reason is that the reduction of $[O_2]$ increases the fraction of ArO• reacting with alkyl radicals, which not only recombine but also disproportionate

$$ArO^{\bullet} + R_2CH\dot{C}R_2 \rightarrow ArOH + R_2C{=}CR_2 \qquad (2\text{-}36)$$

Thus the mechanisms by which the inhibitor radicals are regenerated in chain termination are quite variegated; cf. eq 2-23 to 2-30, 2-33, 2-35, and 2-36.

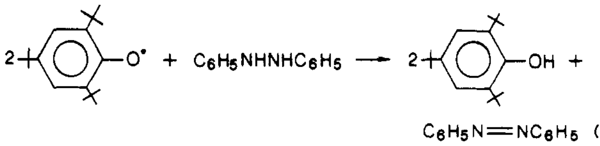
III. Radical Abstraction Reactions Involving Aroxyl Radicals

A. O–H Bond Dissociation Energies of Phenols

Reactions of In• with different substrates, RH in particular, have a strong effect on inhibition effectiveness. In this chapter we will discuss the kinetics of these reactions and factors affecting them.

The activity of the aroxyl radical (ArO•) in abstraction reactions is determined by two factors, viz., the O–H bond dissocation energy (D_{O-H}) of parent ArOH and availability of bulk substituents in the ortho position to create steric hindrances in the transition state of the abstraction reaction. It may therefore be helpful to discuss in brief the ways for and results of evaluation of D_{O-H} in ArOH.

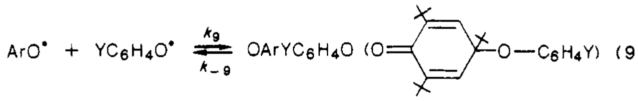
The authors of ref 69 investigated calorimetrically the following reaction in benzene solution:


(3-1)

From the heat of reaction of eq 3-1 the difference of formation enthalpies in benzene has been determined: $\Delta H^f{}_{ArO\bullet} - \Delta H^f{}_{ArOH} = 122$ kJ/mol. If we ignore the insignificant difference of the dissolution heats of ArOH and ArO•, then we obtain 339 kJ/mol for D_{O-H} of 2,4,6-tri-*tert*-butylphenol and 328 kJ/mol for D_{O-H} of galvinophenol.[69]

The authors of ref 70 investigated calorimetrically and kinetically in chlorobenzene at 303–333 K reactions of the type

$$ArO^{\bullet} + YC_6H_4OH \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} ArOH + YC_6H_4O^{\bullet}, \qquad K_{15} = k_{15}/k_{-15} \qquad (15)$$

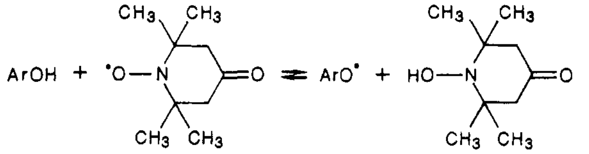

$ArO^{\bullet} + YC_6H_4O^{\bullet} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} OArYC_6H_4O$ (9)

ArO• = 2,4,6-tri-*tert*-butylphenoxyl

The stopped-flow method was used to investigate the kinetics and to evaluate the rate constants k_{15} and k_9/k_{-9} as well as the activation energies E_{15} and E_{-15} (assuming $E_9 \simeq 0$). In the presence of 2,5-di-*tert*-butylhydroquinone, an ArO• acceptor, the decomposition of the dimer $OArYC_6H_4O$ has been investigated and E_{-9} has been calculated. These data allow calculation of the difference $\Delta H^f{}_{YC_6H_4O\bullet} - \Delta H^f{}_{YC_6H_4OH}$ and estimation of the D_{O-H} in the investigated ArOH, relying on the D_{O-H} value for 2,4,6-tri-*tert*-butylphenol obtained earlier. The results are as follows:

Y in YC_6H_4OH	4-OCH_3	4-$C(CH_3)_3$	4-Br	3-$CO_2C_2H_5$
D_{O-H}, kJ/mol	339	361	367	373

The ESR technique was used in ref 71 and 72 to investigate in benzene and *n*-heptane the equilibrium (at 323–368 K)


(3-2)

The difference in the bond dissociation energies of ArOH and hydroxylamine was determined according to the temperature-dependent behavior of the reaction 3-2 equilibrium constant.[73]

For estimating the D_{O-H} for a series of 4-substituted 2,6-di-*tert*-butylphenols the authors of ref 74 used the ESR technique to investigate an equilibrium of the type

$$Ar_1O^{\bullet} + Ar_iOH \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} Ar_1OH + Ar_iO^{\bullet}, \qquad K_{15} = k_{15}/k_{-15} \qquad (15)$$

where $Ar_1O^{\bullet}$ is galvinoxyl and Ar_iOH is substituted 2,6-di-*tert*-butylphenol. The D_{O-H} values reported in ref 74 are based on D_{O-H} = 317 kJ/mol for galvinophenol. In the following table we give the values of K_{15} (298 K) measured in ref 74 and the D_{O-H} values calcu-

TABLE 6. O–H Bond Dissociation Energies (kJ/mol) in Substituted Phenols RC_6H_4OH Measured by Different Techniques

	reaction				
R	7,–7[a]	7,–7[b]	15,–15[c]	12[d]	calcd[e]
4-OCH_3	359	352	343	358	346
4-CH_3	362	365		364	364
4-$C(CH_3)_3$	362	364	365		
H	369	370		366	377
3-$C(O)OC_2H_5$	376		376		
3-OCH_3		369			
3-CH_3		366			368
4-Cl		370			
4-Br			372		
α-naphthol[f]				354	340
β-naphthol[f]	362			360	362

[a] Reference 18. [b] Reference 77. [c] Reference 70. [d] References 44 and 78. [e] Calculated according to eq 3-5 (see text). [f] Complete name of ArOH.

lated on the basis of D_{O-H} = 328 kJ/mol for galvinophenol (see above) for a number of 2,6-*tert*-butyl-4R-phenols:

R	OCH_3	$OC(CH_3)_3$	C_6H_5	
K_{15}	3.0	0.44	3.2×10^{-2}	
D_{O-H}, kJ/mol	318	329	336	
R	$C(CH_3)_3$	Cl	$COCH_3$	CN
K_{15}	1×10^{-2}	1.5×10^{-3}	6.8×10^{-5}	1.1×10^{-5}
D_{O-H}, kJ/mol	339	343	349	352

Another way to evaluate D_{O-H} consists in measuring the forward and back reaction rate constants of reaction 7

$$RO_2^\bullet + ArOH \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} ROOH + ArO^\bullet, \qquad K_7 = k_7/k_{-7} \qquad (7)$$

k_7 is calculated from the RH oxidation rate vs. ArOH concentration relationship: $v = k_2[RH]v_i/2k_7[ArOH]$. k_{-7} is determined either from the v vs. [ROOH] relationship when reaction –7 is sufficiently favored or from the rate of consumption of the stable $ArO^\bullet$ in the presence of the ROOH. In ref 75 the rate of consumption of 2,4,6-tri-*tert*-butylphenoxyl in the reaction with tetralyl hydroperoxide was investigated by the stopped-flow method; the kinetic parameters of inhibited oxidation of tetralin were also determined. It was found that $K_7 = \exp(29, \text{kJ·mol}^{-1}/RT)$ and therefore the D_{O-H} of the ROOH was 368 kJ/mol. The same result was reported in ref 76. Thus D_{O-H} of ArOH can be determined if we neglect the difference in the dissolution heats for ArOH and $ArO^\bullet$ by using the K_7 value in the formula

$$D_{O-H}, \text{kJ·mol}^{-1} = 368 - RT \ln K_7 \qquad (3\text{-}3)$$

Table 6 lists the D_{O-H} values obtained in this manner by the authors of ref 18 and calculated from the k_7 and k_{-7} values given in ref 77. The D_{O-H} values calculated in both ways are in close agreement and do not differ markedly from the data of ref 70 given above.

D_{O-H} may, alternatively, be calculated from the activation energy data for reaction 12

$$ArOH + O_2 \xrightarrow{k_{12}} ArO^\bullet + HO_2^\bullet \qquad (12)$$

This reaction is endothermal; its activation energy $E_{12} \simeq \Delta H^\circ_{12}$, and $\Delta H^\circ_{12} = D_{O-H} - D_{H-O_2^\bullet} + q_s$, where q_s is the difference in the dissolution heats of the reactants and products. Since k_{12} can be measured more accurately than E_{12} and the preexponential factor is constant ($A = 10^{10.5}$ $M^{-1}·s^{-1}$ [45]), the following formula may be obtained from data of ref 45 for calculation of D_{O-H}

$$D_{O-H}, \text{kJ·mol}^{-1} = 218 - RT \ln k_{12} \qquad (3\text{-}4)$$

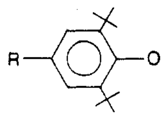
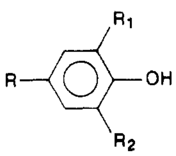
The D_{O-H} calculated in this manner on the basis of the data of ref 78 are presented in Table 6.

Finally, D_{O-H} may be estimated from the Fieser critical potential E_c[79] by using the formula[80]

$$D_{O-H}, \text{kJ·mol}^{-1} = 10^{-3} F E_c + 264 \qquad (3\text{-}5)$$

where F is the Faraday constant (96485 C/mol) and the constant 264 kJ·mol^{-1} may be estimated according to the D_{O-H} of *p*-cresol. The D_{O-H} calculated by eq 3-5 are given in Table 6. It is seen from Table 6 that the D_{O-H} estimated by different methods are in fairly good agreement with each other.

Linear correlations have been found between D_{O-H} and Hammet's substituent constants σ[74] as well as between D_{O-H} and k_7 and E_7 for reaction 7 between secondary $RO_2^\bullet$ and various ArOH.[81] The correlation equations are as follows (333 K) (substituents R_1 and R_2 are any primary or secondary alkyls, being constant through a reaction series):

ArOH type	RC_6H_4OH		
D, kJ/mol	$368 + 21.7\sigma$	$343 + 23.0\sigma$	$355 + 22.1\sigma$
E_7, kJ/mol	$0.32D_{O-H} -94$	$0.37D_{O-H} - 107$	
log (k_7/($M^{-1}·s^{-1}$))	$24.0 - 0.58D_{O-H}$	$22.0 - 0.050D_{O-H}$	

B. Reactions of Aroxyl Radicals with Hydrocarbons

Investigators of reaction 10 are faced with serious experimental difficulties due mainly to the fact that the reaction of $ArO^\bullet$ with most RH is slow whereas $ArO^\bullet$ (with the exception of several stable $ArO^\bullet$) recombine very rapidly. The authors of ref 18 investigated the kinetics of the oxidation of 9,10-dihydroanthracene inhibited with ArOH of different structures. Since this particular RH has weak C–H bonds in the CH_2 groups (D_{C-H} = 297 kJ/mol[6]), the $ArO^\bullet$ formed in the inhibited oxidation react as

$$ArO^\bullet + RH \xrightarrow{k_{10}} ArOH + R^\bullet \qquad (10)$$

This has an effect on the rate of inhibited oxidation (see later). From comparison of calculations with the experimental data in the form of relationships between the oxidation rate v and variable [ArOH], [RH], and v_i was calculated the ratio $k_{10}/(2k_9)^{1/2}$, where k_9 is the $ArO^\bullet$ recombination rate constant, which was measured in special experiments (for details, see section VI.C). Table 7 contains k_{10} and D_{O-H} for ArOH as well as the heats (q) of reaction 10. For reaction of $C_6H_5O^\bullet$ with tetralin the rate constant may be calculated on the basis of the data of ref 17. Comparison of k_{10} with the heats q (Table 7) shows that the higher the q, the higher the k_{10}. The following correlation holds with good accuracy (333 K):

$$\log (k_{10}/(M^{-1}·s^{-1})) = -1.7 + (0.056 \pm 0.009)q \qquad (3\text{-}6)$$

TABLE 7. Rate Constants of Reaction 10 Involving Aroxyl Radicals and Hydrocarbons, Dissociation Energies of O–H Bonds of Phenols, and Heats of Reaction 10 at 333 K

subst in phenoxyl	k_{10}, $M^{-1}\cdot s^{-1}$	D_{O-H}, kJ/mol	q, kJ/mol
$4-OCH_3$	37^a	359	62
$4-C_6H_5$	12^a	353	56
$4-CH_3$	99^a	362	65
$4-C(CH_3)_3$	87^a	362	65
$2-CH_3$, $6-CH_3$	78^a	354	57
$3-C(CH_3)_3$, $5-C(CH_3)_3$	176^a	363	66
4-H	110^a	369	72
$3-C(O)OC_2H_5$	1640^a	376	79
naphthalene-2-oxyl[b]	62^a	362	65
H	1.0^c	369	26

[a] Oxidation of 9,10-dihydroanthracene in chlorobenzene. k_{10} determination error is ca. 5%; after ref 18. [b] Complete name of $ArO^\cdot$. [c] Oxidation of neat tetralin; after ref 17. k_{10} calculated with literature data[18,35] on k_2, k_7, and k_8 for this RH. Determination error is ca. 15%.

For certain RH, e.g., 9,10-dihydroanthracene, relationship 3-6 takes the form

$$\log (k_{10}/(M^{-1}\cdot s^{-1})) = -18.3 + 0.056D_{O-H} \quad (3\text{-}7)$$

(In eq 3-6 and 3-7, q and D have units of kJ/mol.)

On the whole, available data on reactions of $ArO^\cdot$ with RH are scarce and are obtained by indirect methods. Further work in this direction may be desirable.

The kinetics of reactions of $ArO^\cdot$ with alcohols is discussed in section VIII.B.

C. Reactions of Aroxyl Radicals with Hydroperoxides

Aroxyls exhibit rapid reactions with ROOH, abstracting H from the O–H bond

$$ArO^\cdot + ROOH \xrightarrow{k_{-7}} ArOH + RO_2^\cdot \quad (-7)$$

For example, $C_6H_5O^\cdot$ abstracts the H atom from tetralyl hydroperoxide with $k_{-7} = 1.2 \times 10^4\ M^{-1}\cdot s^{-1}$ at 333 K in tetralin.[18] For $ArO^\cdot$ that do not have any *tert*-alkyl substituents in the ortho position the reaction involves the intermediate step of the radical–H-bond complex formation[18]

$$ArO^\cdot + HOOR \underset{}{\overset{K_H}{\rightleftharpoons}} ArO^\cdot\cdots HOOR \xrightarrow{k_8} ArOH + RO_2^\cdot \quad (-7)(3\text{-}8)$$

so that the effective rate constant $k_{-7} = K_H k_8$. The value of k_{-7} is estimated from the RH oxidation kinetic data in the presence of the corresponding ArOH and ROOH. Under specific conditions, the inhibited oxidation rate $v = v_i + k_2[RH](v_i k_{-7}[ROOH]/2k_7k_8[InH])^{1/2}$ and the v vs. v_i, [ROOH], and [InH] relationships are used to find the ratio $k_2(k_{-7}/2k_7k_8)^{1/2}$, from which k_{-7} can be calculated for known k_2, k_7, and k_8. Values of k_{-7} have been compiled.[36] Depending on the substituent, the reactivity of $ArO^\cdot$ varies over a range of 2 orders of magnitude. There is a linear correlation between $\log k_{-7}$ and σ[18]

$$\log k_{-7} = 4.0 + 1.56\sigma \quad (3\text{-}9)$$

as well as between $\log k_{-7}$ and D_{O-H} or q

$$\log k_{-7} = -29 + 0.09D_{O-H} \quad (3\text{-}10)$$

$$\log k_{-7} = 4.0 + 0.09q \quad (3\text{-}11)$$

(The constants in eq 3-9 to 3-11 correspond to 333 K. In these equations k_{-7} has units of $M^{-1}\cdot s^{-1}$ and D and q have units of kJ/mol.)

As we have stated above, $ArO^\cdot$ react much slower with RH; cf. eq 3–6. For a thermally neutral reaction, $\log (k_{-7}/k_{10}) = 5.7$ at 333 K; i.e., the reaction rate with ROOH is almost 6 orders of magnitude faster than with RH.

At least two reasons may be responsible for so large a discrepancy between the reactivities of RH and ROOH with respect to $ArO^\cdot$. The first inheres in the energetics of the transition state. In accordance with the bond energy–bond order method,[82] in the transition state of abstraction reactions of the type

$$X^\cdot + HY \rightarrow XH + Y^\cdot \quad (3\text{-}12)$$

two of the three electrons taking part in the rearrangement have parallel spins and repel each other. The repulsion energy depends on the antibonding orbital energy of the X–Y bond. The higher the energy of this bond, the stronger is the repulsion and the higher the activation enery. Since the C–O bond (334 kJ/mol) has a much higher dissociation energy than the O–O bond (142 kJ/mol), it follows that $E_{-7} < E_{10}$ for one and the same reaction heat. The second reason has already been mentioned and consists in that the reaction of $ArO^\cdot$ with ROOH is preceded by the formation of a complex, whereas with RH aroxyls react in bimolecular collisions. Since the concentration of the $ArO^\cdot\cdots HOOR$ complexes is higher than that of the $ArO^\cdot\cdots HR$ cage pairs, the reaction with ROOH will be faster for other conditions identical.

Sterically hindered aroxyl radicals (2,6-di-*tert*-butyl-substituted phenoxyls) react slower with ROOH. This enables one to monitor their consumption in the reaction with ROOH by ESR or spectrophotometric means. Since they do not recombine (provided there is a steric substitutent in the para position), the following reactions must take place in the $ArOH + ArO^\cdot + ROOH$ system:

$$ArO^\cdot + ROOH \underset{k_7}{\overset{k_{-7}}{\rightleftharpoons}} ArOH + RO_2^\cdot \quad (7)$$

$$ArO^\cdot + RO_2^\cdot \xrightarrow{k_8} ROOArO \text{ (quinolide peroxide)} \quad (8)$$

The $ArO^\cdot$ in such a system are consumed at a rate

$$v = k_{eff}[ArO^\cdot]^2$$

$$k_{eff} = 2k_{-7}k_8[ROOH]/k_7[ArOH] \quad (3\text{-}13)$$

if the conditions $k_7[ArOH] \gg k_8[ArO^\cdot]$ and $k_6[RO_2^\cdot] \ll k_8[ArO^\cdot]$ are satisfied. The rate constants are reported in ref 36 and are practically independent of the ROOH structure. However, the solvent does affect k_{-7}. In aromatic solvents k_{-7} is lower than in carbon tetrachloride, apparently due to formation of a hydrogen bond between ROOH and aromatic solvent. The value of k_{-7} depends on R in the series of 2,6-di-*tert*-butyl-4R-phenoxyl radicals: there is a linear correlation between $\log k_{-7}$ and σ of the substituent R.[83] At 333 K

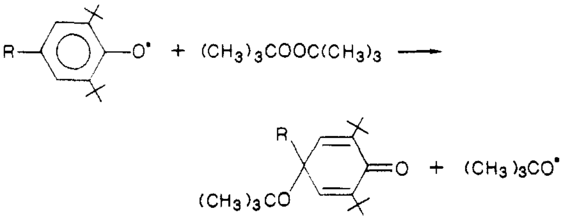
$$\log (k_{-7}/(M^{-1}\cdot s^{-1})) = 0.25 + 2.12\sigma \quad (3\text{-}14)$$

The stronger the O–H bond of ArOH, the more active the $ArO^\cdot$ and the higher the k_{-7}; there is also a fairly linear relationship between $\log k_{-7}$ and D_{O-H} or q. At 333 K

$$\log (k_{-7}/(\mathrm{M^{-1}{\cdot}s^{-1}})) = -27 + 0.08D_{\mathrm{O-H}} = 2.6 + 0.08q \qquad (3\text{-}15)$$

(In eq 3-15 D and q are in kJ/mol.) From comparison of these relationships for 4-$RC_6H_4O^\bullet$ and 2,6-di-*tert*-butyl-4R-phenoxyls it follows that when $q = 0$ the sterically unhindered $ArO^\bullet$ react 25 times as fast at 333 K.

It is known that in an $ArO^\bullet$ the unpaired electron density is distributed mainly among O, C_2, C_4, and C_6. Therefore, $ArO^\bullet$ can enter reactions typical of alkyl radicals. In particular, they enter substitution reactions with peroxides[84]

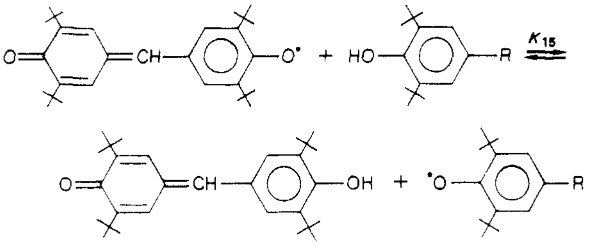


(3-16)

Reaction 3-16 is very slow as compared with reaction with hydroperoxides.

D. Reactions of Aroxyl Radicals with Phenols

Aroxyl radicals react with phenols rather fast. Provided the starting and the end $ArO^\bullet$ do not recombine, an equilibrium becomes established in the system. One example is the reaction of galvinoxyl with 2,6-di-*tert*-butyl-4R-phenols

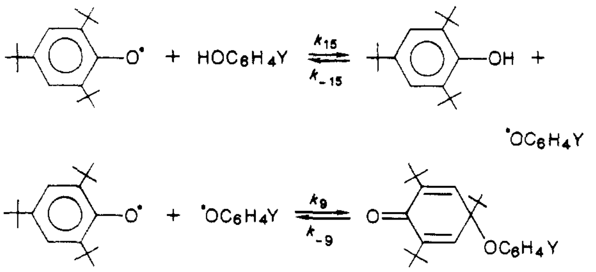


(15)

The equilibrium constant K_{15} is determined entirely by the difference in energies of the O–H bond formed and the one broken, so that $\Delta G° \simeq \Delta H° \simeq -RT \ln K_{15}$.[39] The K_{15} have been given in section III.A, where the energies of these bonds have been discussed. There is a linear correlation between $\log K_{15}$ and σ.[74] At 298 K

$$\log K_{15} = -2.0 - 3.66\sigma \qquad (3\text{-}17)$$

For ArOH whose $ArO^\bullet$ enter a recombination, reaction 15 is followed by recombination 9; e.g.



(15)

(9)

When the reaction is slow enough it may be studied by conventional kinetic methods, observing the concentration of the starting $ArO^\bullet$ by spectrophotometry or ESR. If it is fast, flow techniques have to be used.

Substitution of deuterium for hydrogen in the hydroxyl group decreases k_{15}. For example, in the reaction of 2,4,6-tri-*tert*-butylphenoxyl with 4-phenylphenol (297 K, benzene), $k_{15}^{\mathrm{H}}/k_{15}^{\mathrm{D}} = 7.6$.[85] A series of measurements of $k_{15}^{\mathrm{H}}/k_{15}^{\mathrm{D}}$ was undertaken in ref 86 for the reaction of galvinoxyl with a number of ArOH containing different substituents in the para position (298 K, benzene):

R	H	OH	CH_3O	$C(CH_3)_3$
$k_{15}^{\mathrm{H}}/k_{15}^{\mathrm{D}}$	1.2	4	3.5	2.1

The isotope effect is seen to vary tangibly (from 1.2 to 4). The low $k_{15}^{\mathrm{H}}/k_{15}^{\mathrm{D}}$ in such systems may alternatively be due to the reduced concentration of deuteriated ArOH through exchange with the uncontrolled admixtures of hydroxy-containing compounds. In the exchange reaction between indophenoxyl and indophenol (studied by the NMR technique) the isotope effect was 1.8 (300 K, carbon tetrachloride).[87] The k_{15} values are collected in ref 36.

The k_{15} values may vary over a range of 6 orders of magnitude: from 0.1 to 10^5 $\mathrm{M^{-1}{\cdot}s^{-1}}$ (333 K). Two factors control k_{15}, viz., reaction heat q, equal to the difference of dissociation energies of the formed and broken O–H bond, and the steric factor, which manifests itself when there are bulky substituents in the ortho position of the ArOH or $ArO^\bullet$. For reaction of 2,4,6-tri-*tert*-butylphenoxyl with ArOH of the type 4-RC_6H_4OH there is a linear correlation with Hammett σ constants of substituents R

$$\log (k_{15}/(\mathrm{M^{-1}{\cdot}s^{-1}})) = 1.21 - 3.41\sigma\ (333\ \mathrm{K})^{18} \qquad (3\text{-}18)$$

$$\log (k_{15}/(\mathrm{M^{-1}{\cdot}s^{-1}})) = 1.22 - 3.03\sigma\ (297\ \mathrm{K})^{88} \qquad (3\text{-}19)$$

The NMR technique allows one to measure the hydrogen transfer rate from ArOH to $ArO^\bullet$ of identical Ar when $q = 0$. The results of such measurements at 300 K are as follows: $k_{15} = 660$ for 2,4,6-tri-*tert*-butylphenol and $k_{15} = 1400$ $\mathrm{M^{-1}{\cdot}s^{-1}}$ for indophenol.[87] Another factor having an important effect on the rate of this reaction is the solvent—primarily the tendency of ArOH to form hydrogen bonds with it.

It was found[63] that k_{15} decreases in passing from carbon tetrachloride, which does not form hydrogen bonds, to benzene, acetonitrile, and dioxane. The reason lies with the fact that the H-bond-forming solvent screens the O–H bond of ArOH from attack by $ArO^\bullet$. Reaction 15 is therefore preceded by formation of the hydrogen-bonded complex[89]

$$Ar_1O^\bullet + HOAr_2 \underset{}{\overset{K_H}{\rightleftharpoons}} Ar_1O^\bullet{\cdots}HOAr_2 \xrightarrow{k_{20}} Ar_1OH + Ar_2O^\bullet \quad (15)(3\text{-}20)$$

and the experimentally measured $k_{15}^{\mathrm{obsd}} = k_{20}K_{\mathrm{H}}$. The estimates of ref 89 give for hydrogen transfer step 3-20 in such a complex preexponential $A_{20} \simeq 10^{13}$ $\mathrm{s^{-1}}$ and H-bond formation entropy $\Delta S_{\mathrm{H}} = -150$ J/(mol·K). This explains the relatively low observed A_{15} values for hydrogen abstraction reaction in such systems.

Thorough study of the reaction of 2,4,6-tri-*tert*-butylphenoxyl with ArOH in different solvents allows us to make the following conclusions.[89] The activity coefficients of the $Ar_1O^\bullet{\cdots}HOAr_2$ transition state are the same in carbon tetrachloride and benzene; that is, the transition state energy does not vary in passing from carbon tetrachloride to benzene. Therefore, the experimentally observed reduction of k_{15} from the former to the latter solvent is due only to formation of the hydrogen bond between ArOH and benzene. The transition state in polar solvents is weakly solvated in comparison with the starting reactants, which means that it is nonpolar. Thus the complex $Ar_1O^{\bullet}\cdots HOAr_2$ is nonpolar. From correlations for the H-bonded complex formation rate constant it is known that K_H depends little on the substituent(s) in the phenol molecule. Hence the effect of substituent at the para and meta positions on the k_{15} value is due to its effect on the transition state energy through the reaction heat. Correlation formulas like $\log k_{15} = B + bq$, composed on the basis of literature data with the help of the D_{O-H} values given in Table 6 or calculated from the σ-correlation equations (see above), are as follows:

$$\log k_{15} = 4.5 + 0.14q \qquad (3\text{-}21)$$

for 2,4,6-tri-*tert*-butylphenoxyl (benzene, 297 K, q is in $kJ{\cdot}mol^{-1}$) and

$$\log k_{15} = 7.6 + 0.18q \qquad (3\text{-}22)$$

for galvinoxyl (carbon tetrachloride, 300 K, q is in $kJ{\cdot}mol^{-1}$).

Both correlations are for reactions with $q < 0$. The exothermic reaction of any radical of structure $RC_6H_4O^{\bullet}$ with 2,4,6-tri-*tert*-butylphenol proceeds with $k_{15} = 3 \times 10^5$ to 6×10^5 $M^{-1}{\cdot}s^{-1}$ (333 K), whatever the substituent R.

E. Synergism of the Inhibiting Effect of Binary Mixtures of Sterically Hindered and Unhindered Phenols

tert-Alkyl groups in the ortho position decrease the reactivity of both the starting phenols and the aroxyls formed from them. The following table compares the rate constants of three reactions involving two phenols and aroxyls (333 K, aromatic solvent, data of ref 36).

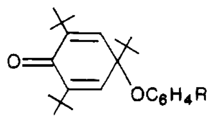
reaction (see IHO scheme)	k_7, $M^{-1}{\cdot}s^{-1}$	k_{-7}, $M^{-1}{\cdot}s^{-1}$	k_{10}, $M^{-1}{\cdot}s^{-1}$
4-methoxyphenol (4-methoxyphenoxyl)	2.5×10^5	650	37
2,4,6-tri-*tert*-butylphenol (2,4,6-tri-*tert*-butylphenoxyl)	1.4×10^4	0.87	$\sim 10^{-4}$

It is seen that tri-*tert*-butylphenol and the corresponding $ArO^{\bullet}$ are slower in all these reactions than 4-methoxyphenol and 4-methoxyphenoxyl. However, the actual reduction is widely different from one reaction to another: in reaction with $RO_2^{\bullet}$ the rate constants are only 1 order of magnitude different, whereas in reaction with ROOH the reactivity of these $ArO^{\bullet}$ differs by almost 3 orders of magnitude. This difference is the major principle behind the synergistic effect that is observed when hindered and unhindered phenols are added simultaneously to an RH mass.[88-92] Initiated oxidation of 9,10-dihydroanthracene remains almost unaffected in the presence of 10^{-4} M 2,4,6-tri-*tert*-butylphenol (Ar_2OH), but a similar quantity of 4-methoxyphenol (Ar_1OH) will hinder it to give rise to an induction period.[89] The induction period is almost doubled when both ArOH are added at 10^{-4} M concentration (333 K, [RH] = 0.15 M). The synergistic inhibition of the $Ar_1OH + Ar_2OH$ mixture, compared to no inhibiting effect at all of Ar_2OH, is due to the following reasons. Since $k_7^{(1)} < k_7^{(2)}$, the following conditions were satisfied in the above experiments: $k_7^{(1)}[Ar_1OH] > (2k_6v_i)^{1/2}$ and $k_7^{(2)}[Ar_2OH] < (2k_6v_i)^{1/2}$; therefore Ar_2OH inhibits oxidation to a small degree. When the mixture of phenols is added, the $Ar_1O^{\bullet}$ generated by Ar_1OH become involved in the exchange reaction

$$Ar_1O^{\bullet} + Ar_2OH \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} Ar_1OH + Ar_2O^{\bullet} \qquad (15)$$

Thereby, the less active Ar_2OH also becomes involved in the chain termination process. $k_{15} = 5 \times 10^5$ $M^{-1}{\cdot}s^{-1}$ and $K_{15} \simeq 50$;[36] i.e., the equilibrium is shifted to the right, thus creating the conditions necessary for chain termination via reactions 8 and 9 (see IHO scheme).

In oxidation of ethylbenzene with 4-methoxyphenol (Ar_1OH) (333 K, initiator = azobisisobutyronitrile, $[Ar_1OH] = 1.5 \times 10^{-4}$ M) Ar_1OH is consumed at a constant rate of $0.5v_i$. However, after addition of the *two* inhibitors Ar_1OH and ionol (Ar_2OH), one first observes a slow consumption of Ar_1OH for a time period close to $2[Ar_2OH]_0/v_i$, whereafter Ar_1OH disappears more rapidly at the rate $v_i/2$.[90] What this means is that first ionol is consumed in the system and then Ar_1OH. Since $RO_2^{\bullet}$ react with Ar_2OH 1 order of magnitude slower than with Ar_1OH, the fact must be due to the fast exchange reaction of $Ar_2O^{\bullet}$ for $Ar_1O^{\bullet}$. The fact that consumption of Ar_1OH follows in time the consumption of Ar_2OH is clear from comparison of the kinetic curves of chemiluminescence in ethylbenzene oxidation with Ar_1OH, Ar_2OH, and their mixture.[90] Similar results are observed in oxidation of ethylbenzene with 2-*tert*-butyl-4-methoxyphenol, ionol, and their mixture.[90] The latter composition displays a well-defined synergism under autoxidation of ethylbenzene. With ionol the induction period is 9 h, with 2-*tert*-butyl-4-methoxyphenol the induction time is 10 h, and with a mixture of 80% of the former and 20% of the latter the induction time is about 15 h (393 K, total concentration of phenols 10^{-5} M[91]). Judging by the kinetic curves of chemiluminescence, the rapid exchange of ionol radicals for semiquinone radicals also occurs in initiated oxidation of ethylbenzene with a mixture of hydroquinone and ionol (393 K[90]). A further reason for synergism in inhibition with a mixture of monosubstituted phenol and trialkylphenol is the reaction of $ArO^{\bullet}$ of a different structure which yields a thermally unstable quinol ether of the type



(See section VI.C for more details.) This ether slowly dissociates to the two starting $ArO^{\bullet}$ and, following their reaction with $RO_2^{\bullet}$, results in chain termination.[88] It has been shown for 9,10-dihydroanthracene that the quinol ether inhibits oxidation of RH.[88] The formation of the quinol ether is mentioned in ref 89 as the factor responsible for the synergism in inhibiting effects of 4-methoxyphenol and mesitol on oxidation of cumene at 333 and 393 K.

Returning now to the chief reason of synergism in such binary ArOH mixtures, namely, the substitution of one type of $ArO^{\bullet}$ with others, we note that the following conditions must be met for synergism to occur. First, for one of the phenols, Ar_1OH, the inhibition must follow the mechanism involving participation of $Ar_1O^{\bullet}$ in chain propagation via reactions with ROOH or RH, and $Ar_2O^{\bullet}$ (2,6-di-*tert*-alkylphenol) must be inactive in such reactions; i.e., the rate of such reactions must be lower than that of initiation. Second, the $ArO^{\bullet}$ exchange through reactions with ArOH must be fast (at a rate much greater than that of initiation) and equilibrium 15 must be shifted toward the low-active $ArO^{\bullet}$. The latter condition is possible when D_{O-H} is higher for Ar_1OH than for Ar_2OH. Third, since the reaction of trialkyl-substituted phenoxyl radical with $RO_2^{\bullet}$ yields quinolide peroxide,[44] then for synergism to manifest itself there must be an upper temperature limit owing to the thermal instability of quinolide peroxide.

IV. Radical Abstraction Reactions Involving Aminyl Radicals

A. N-H Bond Dissociation Energies of Aromatic Amines

The data from which one may calculate the N-H bond dissociation energies are much more scarce for aromatic amines (AmH) than for ArOH. Available data are summarized below.

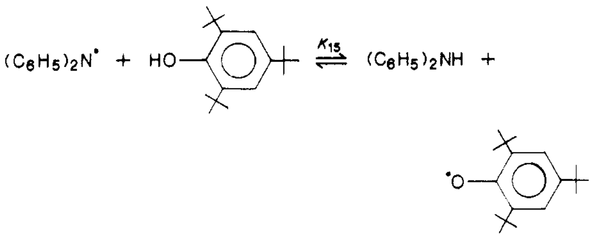
1. As for phenols, the D_{N-H} of aromatic amines may be estimated from the equilibrium constant

$$RO_2^{\bullet} + AmH \overset{K_7}{\rightleftharpoons} ROOH + Am^{\bullet} \qquad (7)$$

using the equality $\Delta H°_7 = -RT \ln K_7 + T\Delta S°_7$, where $\Delta S°_7 = \Delta S°_{ROOH} - \Delta S°_{RO_2^{\bullet}} = 11\ J{\cdot}mol^{-1}{\cdot}K^{-1}$[93] and $\Delta H°_7 = D_{N-H} - D_{ROO-H} = D_{N-H} - 368$ kJ/mol, whence

$$D_{N-H}\ (kJ/mol) = 368 - RT \ln K + 0.011\ T \qquad (4\text{-}1)$$

k_7 and k_{-7} have been measured for two AmH, viz., diphenylamine and *N*-phenyl-β-naphthylamine. Cumyl peroxyl radical reacts with diphenylamine with a rate constant $k_7 = 3.4 \times 10^5\ M^{-1}{\cdot}s^{-1}$, and the rate constant of the diphenylaminyl radical with ROOH is $k_{-7} = 1.1 \times 10^5\ M^{-1}{\cdot}s^{-1}$ at 348.5 K in benzene.[39] The constant $K_7 = 3$, $\Delta H°_7 \simeq 0.3$ kJ/mol, and $D_{N-H} = 368$ kJ/mol for diphenylamine. A close result is obtained from the kinetic data for the reaction



(15)

Measured by the flash photolysis technique,[94] $K_{15} = 1.4 \times 10^4$ (293 K), whence $\Delta H°_{15} = -RT \ln K_{15} + T\Delta S° = 28$ kJ/mol and $D_{N-H} \simeq 339 + 28 = 367$ kJ/mol.

Kinetic investigations of cumene oxidation inhibited with *N*-phenyl-β-naphthylamine revealed kinetic behavior typical of the mechanism where the $Am^{\bullet}$ reacts with the ROOH[95] (see below). From the kinetic data was calculated the ratio $k_{-7}/k_8 = 3.6 \times 10^{-4} \exp(-7.7\ kJ{\cdot}mol^{-1}/RT)$. Assuming that $k_8 = 6.8 \times 10^8\ M^{-1}{\cdot}s^{-1}$ (see section VI.I) for diphenylaminyl and *N*-phenyl-β-naphthylaminyl radicals, we find for the latter $k_{-7} = 2.2 \times 10^5 \exp(-7.7\ kJ{\cdot}mol^{-1}/RT) = 1.4 \times 10^4\ M^{-1}{\cdot}s^{-1}$ (333 K). Reaction 7 for *N*-phenyl-β-naphtylamine is characterized by $k_7 = 1.1 \times 10^7 (\exp(-14\ kJ{\cdot}mol^{-1}/RT) = 6.8 \times 10^4\ M^{-1}{\cdot}s^{-1}$ (333 K[95]). From these data it is easily obtained that $\Delta H°_7 = -1$ kJ/mol and $D_{N-H} = 367$ kJ/mol for *N*-phenyl-β-naphthylamine.

TABLE 8. N-H Bond Dissociation Energies (kJ/mol) in Aromatic Amines Measured by Different Techniques

AmH	reaction 7,−7[a]	reaction 12[b]	calcd[c]
$C_6H_5NH_2$			379
$4\text{-}CH_3C_6H_4NH_2$			374
$4\text{-}CH_3OC_6H_4NH_2$			356
$C_6H_5NHCH_3$			372
$4\text{-}(CH_3)_2NC_6H_4NH_2$			344
$(C_6H_5)_2NH$	367		367
$\alpha\text{-}C_{10}H_7NH_2$		364	351
$\beta\text{-}C_{10}H_7NH_2$			373
$\alpha\text{-}C_{10}H_7NHC_6H_5$		368	
$\beta\text{-}C_{10}H_7NHC_6H_5$	367	364	
$p\text{-}C_6H_5NHC_6H_4NHC_6H_5$			338
$\beta\text{-}C_{10}H_7NHC_6H_4NH\text{-}\beta\text{-}C_{10}H_7$		343	

[a] Calculated (see text). [b] Reference 45. [c] Calculated according to eq 4-5 (see text); after ref 80 and 81.

2. The D_{N-H} may be calculated from the activation energy or reaction rate constant data for

$$AmH + O_2 \xrightarrow{k_{12}} Am^{\bullet} + HO_2^{\bullet} \qquad (12)$$

This reaction is endothermal and its E_{12} is about equal to its endothermicity: $E_{12} \simeq \Delta H°_{12}$, whence

$$D_{N-H} = E_{12} + D_{H-O_2^{\bullet}} + \Delta \qquad (4\text{-}2)$$

where Δ is the difference of dissolution heats of the starting reagents and products. Since k_{12} have been measured with a higher precision than E_{12}, E_{12} may advantageously be replaced with the equivalent expression

$$E_{12} = RT(\ln A_{12} - \ln k_{12}) = D_{N-H} - D_{H-O_2^{\bullet}} - \Delta \qquad (4\text{-}3)$$

from which we obtain

$$D_{N-H}, kJ{\cdot}mol^{-1} = RT(\ln A_{12} - \ln k_{12}) + B_3 = RT(24 - \ln k_{12}) + 236 \qquad (4\text{-}4)$$

if we put, in accordance with ref 45, $\ln A_{12} = 24$ and calculate the constant B_3 using $k_{12} = 5.6 \times 10^{-5}\ M^{-1}{\cdot}s^{-1}$ for *N*-phenyl-β-naphthylamine (453 K, chlorobenzene[45]) and $D_{N-H} = 364$ kJ/mol. The D_{N-H} values calculated in this manner are listed in Table 8.

3. As for ArOH, one may estimate D_{N-H} in AmH using the potential E_c (cf. section IV.A), with which D_{N-H} is related as

$$D_{N-H}, kJ{\cdot}mol^{-1} = 10^{-3}\ FE_c + 270 \qquad (4\text{-}5)$$

The constant 270 kJ/mol in eq 4-5 is obtained if we take $D_{N-H} = 367$ kJ/mol for diphenylamine. The estimates are given in Table 8. Comparison of Tables 7 and 8 shows that the dissociation energies of the O-H bonds of ArOH and N-H bonds of AmH are close and lie within the range 340-380 kJ/mol.

B. Reactions of Aminyl Radicals with Hydrocarbon C-H Bonds

Few data are available for this important reaction (reaction 10). Recently, a new approach was inaugurated that permitted study of the reaction of diphenylaminyl radical with ethylbenzene.[97] In this approach tetraphenylhydrazine is used as the source of diphenylaminyl radicals. The generated diphenylaminyl radicals recombine (see section VI.F for a discussion of the recombination kinetics and products) or react with RH

$$(C_6H_5)_2N^\bullet + RH \xrightarrow{k_{10}} (C_6H_5)_2NH + R^\bullet \qquad (10)$$

The decomposition is carried out in the presence of O_2, with which the generated $R^\bullet$ radicals react rapidly. The resultant $RO_2^\bullet$ react with $(C_6H_5)_2N^\bullet$ ($Am^\bullet$), with the formation of brightly colored quinone imine and other colored products. It is thereby possible to monitor reaction 10 according to the rate of accumulation of the colored products of $RO_2^\bullet$ reaction with $Am^\bullet$. Experimental conditions are chosen to be such as to cause all $RO_2^\bullet$ to react with $Am^\bullet$. Under such conditions the reaction rate v_{10} is equal to the product buildup in the reaction of $Am^\bullet$ with $RO_2^\bullet$ (reaction 8). In addition, the conditions are so adjusted that the rates of $Am^\bullet$ recombination and its reaction with RH are commensurate. For such competing processes it was possible, using the dependences of the rate of reaction 8 for $RO_2^\bullet$ with ($Am^\bullet$) on concentration of RH and tetraphenylhydrazine, to calculate the ratio $k_{10}(2k_9)^{-1/2}$, where k_9 pertains to recombination of $Am^\bullet$. The rate constant of $Am^\bullet$ reaction 10 with ethylbenzene in chlorobenzene at 348.5 K was found to be 0.7 $M^{-1}{\cdot}s^{-1}$. Values of k_9 are listed in Table 19; cf. section VI. For comparison, the rate constant of the reaction of $RO_2^\bullet$ with ethylbenzene is $k_2 = 9.6 \times 10^5 \exp(-35,\ \text{kJ}{\cdot}\text{mol}^{-1}/RT) = 4.5\ M^{-1}{\cdot}s^{-1}$ at 348.5 K[35] in ethylbenzene. Thus $Am^\bullet$ are similar to $RO_2^\bullet$ in their activity as hydrogen acceptors. The reaction of *N*-phenyl-β-naphthylaminyl radical with ethylbenzene was studied in ref 98. Using the rate constant ratio $k_{10}/k_8 = 3.1 \times 10^{-9}$ (333 K, ethylbenzene) and assuming $k_8 = 6 \times 10^8\ M^{-1}{\cdot}s^{-1}$ as for the diphenylaminyl radical, we obtain $k_{10} = 19\ M^{-1}{\cdot}s^{-1}$. Since the value of k_{10} for $Am^\bullet$ reactions with RH depends on the N–H bond dissociation energy formed in the process and since D_{N-H} for *N*-phenyl-β-naphthylamine is less than D_{N-H} for diphenylamine, it may be expected that $k_{10} < 0.2\ M^{-1}{\cdot}s^{-1}$ for the *N*-phenyl-β-naphthylaminyl radical if we depart from $k_{10} = 0.7\ M^{-1}{\cdot}s^{-1}$ for reaction of diphenylaminyl radical at 348 K (see above). The large discrepancy may be due the rather fast reaction of $Am^\bullet$ with ROOH. Extra luminescence light due to reaction of $Am^\bullet$ with $RO_2^\bullet$ cannot be ruled out.

The reaction of diphenylaminyl radical with cumene was investigated by observing the diphenylamine buildup rate in the decomposition of tetraphenylhydrazine in *p*-xylene containing cumene.[99] The experiments were conducted for different cumene and tetraphenylhydrazine concentrations. $k_{10}k_9^{-1/2} = 3.8 \times 10^{-5}\ (M{\cdot}s)^{-1/2}$ (343 K) was calculated from experimental data. Using the known k_9 (Table 19), one obtains $k_{10} = 0.15\ M^{-1}{\cdot}s^{-1}$, which is similar to $k_{10} = 0.7\ M^{-1}{\cdot}s^{-1}$ for reaction of diphenylaminyl radical with ethylbenzene (see above). This value of k_{10} can only be considered to be tentative, because the above kinetic scheme disregarded the formation of diphenylamine through the reaction $Am^\bullet + Am^\bullet$ (reaction 9) (cf. section VI.F) and through disproportionation between $Am^\bullet$ and $R^\bullet$.

C. Reactions of Aminyl Radicals with Hydroperoxides

Reactions of diphenylaminyl radicals with hydroperoxides were investigated by different techniques in a number of works.

1. Decomposition of azobisisobutyronitrile (AIBN) was effected in benzene in the presence of diphenylamine and cumyl hydroperoxide under oxygen-bubbling conditions.[99] The cyanoisopropyl radicals formed from AIBN were converted to $RO_2^\bullet$ via reaction with O_2, which then reacted with AmH, and $Am^\bullet$ reacted with ROOH.

It was found from these data that $k_{-7} = 1.1 \times 10^5\ M^{-1}{\cdot}s^{-1}$ (348.5 K).

2. Another approach was used in the same work.[99] Tetraphenylhydrazine was decomposed in chlorobenzene in the presence of cumyl peroxide and diphenylamine. As in the previous case, the conditions were adjusted to ensure radical decay only through reactions 6 and 9. The rate of reaction 8 was measured according to the buildup of the colored products. The result, $k_{-7} = 1.1 \times 10^5\ M^{-1}{\cdot}s^{-1}$, is exactly the same as that of the previous case.

3. In ref 98 tetraphenylhydrazine was decomposed in the presence of cumyl hydroperoxide in *p*-xylene (343 K). The formation of diphenylamine was used as an indicator of the reaction rate. $k_{-7}/k_9^{1/2} = 3.8 \times 10^{-2}\ M^{-1/2}{\cdot}s^{-1/2}$ and hence $k_{-7} = 160\ M^{-1}{\cdot}s^{-1}$, which is 3 orders of magnitude below the values obtained in approaches 1, 2, and 4 (see below). The primary reason for such a large variance consists in that the authors of ref 98 failed to take into account the very fast reaction between $RO_2^\bullet$ and the generated AmH. What was actually measured was the difference of the rates of two fast reactions, reactions 7 and –7: $Am^\bullet$ with ROOH and the back reaction of $RO_2^\bullet$ with AmH.[99] Neither was the formation of AmH via reaction 9, $Am^\bullet + Am^\bullet$, accounted for (see below).

4. Reaction of diphenylaminyl radical with cumyl hydroperoxide in cyclohexane was studied by flash photolysis in ref 39. In the ROOH concentration range $(1.4\text{–}5.1) \times 10^{-3}$ M, $k_{-7} = 1.1 \times 10^5\ M^{-1}{\cdot}s^{-1}$ (293 K), which is coincident with the above values. If we use $A_{-7} = A_7 = 1.6 \times 10^7\ M^{-1}{\cdot}s^{-1}$, then we have $k_{-7} = 1.6 \times 10^7 \exp(-12,\ \text{kJ}{\cdot}\text{mol}^{-1}/RT)$. Analysis of the reaction of diphenylaminyl radical with ROOH over a broad ROOH concentration range (5×10^{-3} to 2.6×10^{-1} M) has shown that for [ROOH] > 0.02 M the reaction takes a more complicated route.[39] The $Am^\bullet$ acts like a base with respect to ROOH

$$Am^\bullet + HOOR \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} AmH^{\bullet+},ROO^- \qquad (4\text{-}6)$$

This is evidenced by the appearance of a new particle in solution, viz., the cation radical $(C_6H_5)_2NH^{\bullet+}$, displaying a typical absorption spectrum. The cation radical and aminyl radical are consumed through first-order reactions, obviously involving electron transfer:

$$AmH^{\bullet+},ROO^- \xrightarrow{k_7} AmH + RO_2^\bullet \qquad (4\text{-}7)$$

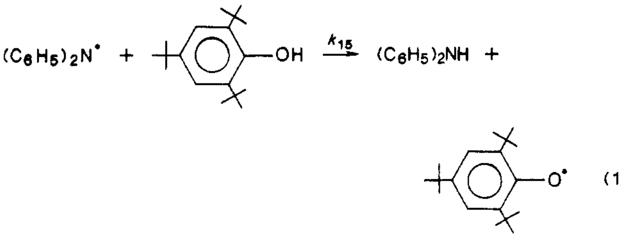
$\boldsymbol{K}_6 = 42\ M^{-1}$ and $\boldsymbol{k}_7 = 1.0 \times 10^3\ s^{-1}$ (393 K, cyclohexane) were calculated from the kinetic data.[39] The reaction involving consecutive proton transfer and then electron transfer is slower than the abstraction: $\boldsymbol{k}_7 \times \boldsymbol{K}_6 = 4 \times 10^4\ M^{-1}{\cdot}s^{-1}$ and $k_{-7} = 1.1 \times 10^5\ M^{-1}{\cdot}s^{-1}$. Investigation of the kinetics of cumene oxidation in the presence of *N*-phenyl-β-naphthylamine has shown that cumyl hydroperoxide promotes initiated oxidation of cumene by the mechanism where $Am^\bullet$ reacts violently with ROOH.[95] In this case the oxygen absorption kinetics is given by[95]

$$\frac{\Delta[O_2]}{[RH]} = 2k_2\left(\frac{k_{-7}}{k_7k_8}[ROOH]_0\right)^{1/2}[1-(1-t/\tau)] \quad (4\text{-}8)$$

where τ is the induction period, equal to $f[InH]_0/v_i$. From eq 4-8 we find $k_{-7}/k_8 = 4 \times 1.0^{-4}$ exp(−7.7, kJ·mol^{-1}/RT). Hence, $k_{-7} = 2.2 \times 10^5$ exp(−7.7, kJ·mol^{-1}/RT) = 1.4×10^4 M^{-1}·s^{-1} (333 K), if we assume that $k_8 = 6 \times 10^8$ M^{-1}·s^{-1}, as for diphenylaminyl radical.[100] (More details on reaction 8 are given in section VI.I.)

D. Reactions of Aminyl Radicals with Phenols

Aminyl radicals react rapidly with phenols. Reaction of diphenylaminyl radical with 2,4,6-tri-*tert*-butylphenol was studied by flash photolysis in cyclohexane at 293 K[94] with tetraphenylhydrazine as the source of diphenylaminyl radicals. The reaction



(15)

is bimolecular and occurs with $k_{15} \simeq 1.5 \times 10^7$ M^{-1}·s^{-1}.

E. Synergism in Inhibition of Oxidation with Mixtures of Amines and Phenols

The authors of ref 101, who investigated the inhibiting effect of mixtures of AmH and ArOH on initiated oxidation of ethylbenzene, discovered that ArOH disappears before any AmH is consumed. Such a sequence in the consumption of the inhibitor components was not due to the higher susceptibility of ArOH to attack by $RO_2^\bullet$. On the contrary, the InH used in ref 103 reacted with $RO_2^\bullet$ with the following rate constants: $k_7 \approx 10^4$ M^{-1}·s^{-1} for 2,6-di-*tert*-butylphenol and $k_7 = 1.3 \times 10^5$ M^{-1}·s^{-1} for *N*-phenyl-β-naphthylamine (ethylbenzene, 333 K).[35] AmH therefore reacts faster with $RO_2^\bullet$ than the ArOH, but still it is ArOH that is consumed first. The reason is the following fast exchange reaction

$$Am^\bullet + ArOH \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} AmH + ArO^\bullet \quad (15)$$

whereby $[Am^\bullet] \ll [ArO^\bullet]$ under the standard oxidation conditions, and hence the rate of reaction 8 between $ArO^\bullet$ and $RO_2^\bullet$ by which ArOH is actually consumed is greater than that of reaction 8 between $Am^\bullet$ and $RO_2^\bullet$ so long as there is any ArOH in the system. Synergism is observed in inhibition of autoxidation of ethylbenzene with a mixture of ArOH and AmH: the resultant induction period τ is longer than the mere sum of the induction periods due to inhibition with ArOH and AmH separately.[102] The synergistic effect resulted only with 2,6-di-*tert*-butyl-substituted phenols, on the one hand, and primary and secondary aromatic amines or substituted *p*-phenylenediamines on the other.[103] The mechanism of synergism in this case is as follows.[102,103] AmH rapidly reacts with $RO_2^\bullet$, but the active $Am^\bullet$ take part in the chain propagation process (it had previously been attributed to reaction with RH), which decreases the inhibiting effect of AmH. On the contrary, ArOH reacts with $RO_2^\bullet$ much slower, but its $ArO^\bullet$ (2,6-di-*tert*-butyl-substituted phenoxyls) do not take part in chain propagation, so that the reaction of $RO_2^\bullet$ with ArOH results in chain termination. When added together, the merits of the two InH combine. AmH rapidly reacts with $RO_2^\bullet$, $Am^\bullet$ exchanges for $ArO^\bullet$ with ArOH by reaction 15, and $ArO^\bullet$ does not participate in chain propagation but goes on to react with $RO_2^\bullet$. In ref 103–105 $Am^\bullet$ was assumed to participate in chain propagation only by reactions with RH. Since the rate constants of reactions of diphenylaminyl radical both with ROOH and with ethylbenzene have recently been reevaluated (see above), it may be worthwhile to reconsider the problem. We will exemplify it with ethylbenzene oxidation inhibited with diphenylamine. Suppose 10^{-4} M AmH has been added to ethylbenzene and the initiation rate $v_i = 10^{-7}$ M·s^{-1}. If $Am^\bullet$ react fast with RH, the inequality $k_8v_i < k_7k_{10}[RH][InH]$ must be valid (see below). At 348 K, $k_7 = 3.4 \times 10^5$, $k_8 = 6 \times 10^8$, and $k_{10} = 0.7$ M^{-1}·s^{-1}; thus $k_8v_i = 60$ s^{-2} and $k_7k_{10}[RH][InH] = 200$ s^{-2}—i.e., the inequality is valid. Therefore, chain termination occurs by reaction 8 between $RO_2^\bullet$ and $Am^\bullet$, and the ethylbenzene oxidation rate is

$$v = v_i + k_2[RH]^{3/2}\left(\frac{k_{10}v_i}{fk_7k_8[InH]}\right)^{1/2} = 2.1 \times 10^{-7}\ M\cdot s^{-1} \quad (4\text{-}9)$$

where $k_2 = 4.2$ M^{-1}·s^{-1},[35] $f = 2.8$,[35] and k_7, k_8, and k_{10} are as above. The induction period τ under such conditions is $f[AmH]_0/v_i = 2.8 \times 10^3$ s. Within a period of, say, 500 s a concentration of 1×10^{-4} M ROOH is produced. Already in the presence of such a small quantity of ROOH chain propagation through reaction of $Am^\bullet$ with ROOH is faster than through reaction of $Am^\bullet$ with RH, since $k_{-7}[ROOH] = (1.1 \times 10^5) \times (1 \times 10^{-4}) = 11$ s^{-1} and $k_{10}[RH] = 0.7 \times 8.2 = 5.7$ s^{-1}. As the reaction proceeds and more ROOH is formed, the role of the latter will increase. It may therefore be safe to conclude that the synergism in the inhibition of oxidation of RH with a mixture of AmH and sterically hindered ArOH is due to the following reactions. AmH rapidly react with $RO_2^\bullet$ but, in the absence of ArOH will also rapidly react with RH and ROOH, the latter being the main contributor. In the presence of ArOH, the $Am^\bullet$ will be rapidly substituted for with $ArO^\bullet$, which slowly react with ROOH and decay through reaction 8 with $RO_2^\bullet$.

However, as recently shown in ref 104 this presentation of the mechanism of synergistic effect of mixtures of AmH and ArOH is incomplete. For the *N*-phenyl-β-naphthylamine–α-naphthol pair in cholesteryl pelargonate undergoing oxidation (348 K, initiator = azoisooleic acid dinitryl) it was shown that the mixture of AmH and ArOH broke more chains than each of these separately. While for AmH $f = 2.5$ and for ArOH $f = 2$, for their mixture $f = v_i\tau/([AmH]_0 + [ArOH]_0) = 3.7$ ($[AmH] = 3 \times 10^{-5}$ M, $[ArOH] = 1.2 \times 10^{-4}$ M, $v_i = 6.6 \times 10^{-7}$ M·s^{-1}). This increase in the stoichiometry of chain termination is due to the reactions of the products of these ArOH and AmH.

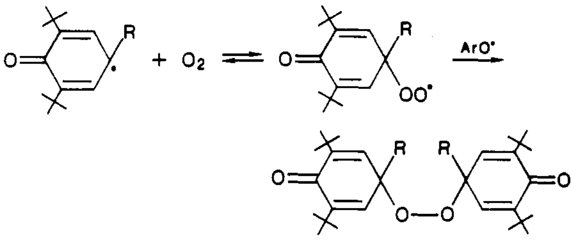
V. Reactions of Inhibitor Radicals with Oxygen

Important for inhibited oxidation is the reaction of inhibitor radicals with oxygen

$$\mathrm{In}^{\bullet} + O_2 \xrightarrow{k_1} \text{products} \qquad (5\text{-}1)$$

This reaction has been investigated by different techniques, including flash photolysis. Aromatic inhibitor radicals range broadly in their ability to react with oxygen.

$ArO^{\bullet}$ react with oxygen to form $RO_2^{\bullet}$, which, on reaction with a second $ArO^{\bullet}$, produce peroxide



(5-2)

The first reaction is reversible, so that the aroxyl radical consumption rate follows the equation[37,76]

$$v = k_2^{\mathrm{obsd}}[\mathrm{ArO}^{\bullet}]^2[O_2]$$

For 2,4,6-tri-*tert*-butylphenoxyl radical the observed rate constant is independent of temperature in the range 295–348 K, and $k_2^{\mathrm{obsd}} = 4.9 \times 10^3$ $M^{-2} \cdot s^{-1}$ in *n*-decane.[37] The oxidation of galvinoxyl is different. Its oxidation is self-accelerated, owing to the formation of peroxide.[37] ArOH inhibits oxidation of galvinoxyl. 2,6-Di-*tert*-butyl-1,4-benzoquinone and 4-formyl-2,6-di-*tert*-butylphenol, which are products of decomposition of the unstable quinolide peroxide, have been identified among the oxidation products.

The radicals of very effective polymer stabilizers, 2,6-diphenyl-4-alkoxyphenols, which feature a developed system of conjugation, do not react with oxygen-.[105,106] The short-lived $ArO^{\bullet}$ of *p*-cresol and thyrosine decay by a first-order reaction in air-saturated solution, which indicates that reaction 5-1 is taking place.[107] At the same time the attack of atmospheric oxygen leaves almost unaffected the decay rates of many short-lived $ArO^{\bullet}$ and neutral semiquinone radicals (see section VI.A), which allows us to estimate k_1 as $\ll 10^6$ $M^{-1} \cdot s^{-1}$.

1,3-Dioxo-2-arylindan-2-yl radicals (see section VI.A) do not react with oxygen.[108]

For quinone radical anions ($Q^{\bullet -}$) there is, generally, an equilibrium[33,109]

$$Q^{\bullet -} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Q + O_2^{\bullet -} \qquad (5\text{-}1)$$

The position of the equilibrium depends on the redox potential of the $Q/Q^{\bullet -}$ pair (cf. section VIII.E).

As monitored by pulsed radiolysis, the decay of the neutral *p*-benzosemiquinone radical was promoted by oxygen.[110] However, the authors of ref 110 preferred to attribute this acceleration not to reaction with oxygen but with the hydroperoxyl radical formed in the experiments.

Aniline radical cations decay in air-saturated solutions by a first-order reaction.[111] Ketyl radicals of benzophenone and acetophenone (see section VI.A) react with oxygen with diffusion rate constants.[112]

The rate constants of reaction 5-1 for different aromatic radicals are given in Table 9.

TABLE 9. Rate Constants of Reaction 5-1 between Inhibitor Free Radicals and Oxygen at Room Temperature

radical	solvent	k_1, $M^{-1} \cdot s^{-1}$	ref
$4\text{-}CH_3C_6H_4O^{\bullet}$	water	$\sim 1.0 \times 10^6$	107
$4\text{-}{}^{+}NH_3CH(COO^{-})CH_2C_6H_4O^{\bullet}$	water	$\sim 1.0 \times 10^6$	107
9,10-anthraquinone-2-sulfonate anion	water	1.8×10^{8} [a]	113
1,4-benzoquinone anion	water	$<1 \times 10^7$	109
duroquinone anion	water	2.0×10^{8} [a]	109
9,10-anthraquinone-2,6-disulfonate anion	water	5.0×10^{8} [a]	114
$(C_6H_5)_2\dot{C}OH$	benzene	2.3×10^{9} [a]	112
$(C_6H_5)\dot{C}(OH)CH_3$	benzene	$\sim 3.0 \times 10^9$	112

[a] Determination error is ca. 10–15%.

VI. Bimolecular Reactions between Radicals

A. General Comments

Most of the aromatic inhibitor free radicals ($In^{\bullet}$) are active short-lived particles and enter fast bimolecular reactions with each other. The rate constants are elementary reactions of $In^{\bullet}$ have in most cases been determined by fast-reaction techniques. Bimolecular radical decay involves recombination, disproportionation, or electron transfer (reaction 9) and plays an important part in inhibition (section IX). For brevity we will refer to reaction 9 simply as recombination here. In the absence in solution of other active reactants (free radicals, oxygen, oxidants, reductants) recombination of aromatic radicals

$$\mathrm{In}^{\bullet} + \mathrm{In}^{\bullet} \xrightarrow{2k_1\ (2k_9)} \text{products} \qquad (6\text{-}1)$$

is the dominant if not the only route of their decay. In order to choose the optimum conditions for promoting (or suppressing) reaction 9 in complex chemical systems, one must know the rates of this reaction and have a notion about the manner in which the radical structure and solvent affect these rates. This is the main topic of this chapter.

In this chapter we also consider ketyl radicals of benzophenone and other aromatic ketones. The antioxidant properties of the starting valence-saturated compounds are unknown. But these aromatic radicals have been thoroughly studied by fast-reaction techniques and may be advantageously considered alongside other aromatic radicals. Probably, benzopinacol, which dissociates to ketyl radicals, is an inhibitor. We are considering reaction 9 with participation of 1,3-dioxo-2-arylindan-2-yl radicals. The starting 2-arylindan-1,3-diones and radical dimers are effective inhibitors for hydrocarbon oxidation.[108]

Hydroquinone, catechol, and their derivatives are typical InH of the phenolic type, which generate neutral semiquinone radicals or radical anions. We discuss semiquinone radicals in this chapter, and we shall discuss their properties in sections VII and VIII.

In most cases the distribution of unpaired electrons in radicals is anisotropic, and therefore the reactivity of such radicals is also largely anisotropic. Bimolecular reactions of radicals are fast reactions and are characterized by high rate constants $k_7 \simeq 10^7$–10^9 $M^{-1} \cdot s^{-1}$ (nonviscous solvents, room temperature).

Before turning to analysis of the available kinetic data, it may be useful to recall the basic principles of the modern theory of diffusion-controlled reactions between chemically anisotropic reagents.

B. Diffusion-Controlled Reactions between Chemically Anisotropic Reagents

1. General Principles

Diffusion-controlled reactions are those which occur upon the very first contact of reactants in solution. An overwhelming majority of reactions of this type take place when the reactants approach each other to within a distance ρ close to the sum of the van der Waals radii of the radicals (molecules). The rate constant of a diffusion-controlled reaction between uncharged reagents is given by the well-known Smoluchowski formula[31,115]

$$k = k_{\text{diff}} = 4\pi\rho D \qquad (6\text{-}2)$$

where D is the coefficient of mutual diffusion.

For a diffusion-controlled reaction between two identical agents, $-\text{d}[\text{In}^{\bullet}]/\text{d}t = 2\boldsymbol{k}_1[\text{In}^{\bullet}]^2$ and $2\boldsymbol{k}_1 = k_{\text{diff}}$.

More general than the Smoluchowski boundary condition, which assumes an infinite rate of the chemical act, is the radiation boundary condition, implying a finite rate of the chemical act.[31,115] Under this condition[31,115]

$$\boldsymbol{k}_1 = \frac{k_{\text{diff}}k_{\text{chem}}}{k_{\text{diff}} + k_{\text{chem}}} \qquad (6\text{-}3\text{a})$$

$$\frac{1}{\boldsymbol{k}_1} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{chem}}} \qquad (6\text{-}3\text{b})$$

where k_{chem} is the rate constant of the bimolecular reaction between the reagents. The constant k_{chem} would have given the exact reaction rate had their been an equilibrium spatial distribution of reagents in the system. The rate constants of the pairwise encounters (k_{diff}) and the chemical act proper (k_{chem}) appear in formulas 6-3 as inverse resistivities, which is natural for consecutive reactions. The kinetic experiment for bimolecular reactions of radicals supports formula 6-3.

To calculate k_{diff} in eq 6-2 it is necessary to know ρ and D. In the simplest case the reactant diffusivity is expressed with the Stokes–Einstein formula. Substituting this D into eq 6-2 we obtain the Debye equation for reaction between identical reagents[31]

$$k_{\text{diff}} = 8RT/(3000\ \eta) \qquad (\text{M}^{-1}\text{·s}^{-1}) \qquad (6\text{-}4)$$

where η is the solvent viscosity. Equation 6-4 must be viewed as the lower estimate of the true k_{diff}. For more accurate evaluation of k_{diff}, the "microfriction" factor $\varphi < 1$ is entered in the denominator of eq 6-4 (for details, see ref 31).

The radical spin must also be taken into account. If the singlet–triplet transitions fail to occur in the radical pairs within their encounter time, eq 6-3 should be modified as follows for reactions between radicals:

$$k_1 = \frac{\sigma k_{\text{diff}}k_{\text{chem}}}{k_{\text{diff}} + k_{\text{chem}}} \qquad (6\text{-}5)$$

where $\sigma = {}^1/_4$ is the spin-statistical factor. If recombination is diffusion-limited ($k_{\text{chem}} \gg k_{\text{diff}}$), eq 6-5 will reduce to

$$k\ (2k) = \sigma k_{\text{diff}} = \sigma(4\pi\rho D) \qquad (6\text{-}6)$$

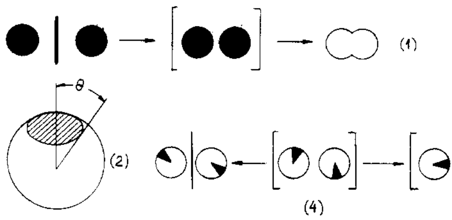


Figure 1. Diagram of reaction between black spheres (1) and between white spheres with black spots (3). Brackets indicate that the spheres are within the solvent cage; (2) the polar angle θ determines the relative size of the black spot; (4) mutual orientation of reagents in first contact.

If the spin-statistical factor is to be accounted for, the following formula should be used instead of eq 6-4:

$$k_{\text{diff}} = 2RT/(3000\ \eta) \qquad (\text{M}^{-1}\text{·s}^{-1}) \qquad (6\text{-}7)$$

If there are electrostatic interactions between the radicals participating in diffusion-controlled recombination, the following equation should replace eq 6-2 and 6-6:

$$k\ (2k) = \sigma(4\pi\rho D)\chi \qquad (6\text{-}8)$$

where $\chi > 1$ ($\chi < 1$) is the Coulombic term depending on the product of the reactants' charges and dielectric constant of solvent.[31]

It may be expected for a diffusion-controlled reaction that the activation enthalpy (activation volume) should be equal to the activation energy B (activation volume $\Delta V^{\ddagger}_{\text{diff}}$) for the viscous flow of solvent

$$\Delta H^{\ddagger} = B \qquad (6\text{-}9)$$

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{\text{diff}} \qquad (6\text{-}10)$$

2. Reactivity Anisotropy of Reagents

For convenience and brevity we will make use of the concepts of "black", "gray", and "white" spheres. Black spheres are exclusively reactive agents, reacting upon the very first contact. Equation 6-2 is valid for black spheres. Gray spheres are moderately active reagents and obey eq 6-3. For white spheres, $\boldsymbol{k}_1 = k_{\text{chem}} = 0$.

In deriving eq 6-2 it was assumed that the reactant molecules are spherical particles with isotropic reactivity (black spheres, Figure 1). However, as mentioned above, reactivity of free radicals is substantially anisotropic. The probability of a reaction upon encounter of radicals in solution depends on their mutual orientation. It is conventional in this case to use the concept of a "white sphere with a reactive spot"; see Figure 1. If upon contact the reaction will occur with a probability of unity, the spot will be referred to as "black". If the probability is between zero and unity, the spot will be "gray". Clearly, the requirement of specific mutual orientation of contacting reactants, like the requirement of a specific spin status of a radical pair, causes $\boldsymbol{k}_1$ to be lower than k_{diff} (eq 6-2).

The geometric steric factor f_{g} is equal to the statistical weight of orientations that are favorable for the reaction. The factor f_{g} equals the ratio of the product of the surface areas of the spots to the product of the surface areas of the spheres. In different theoretical models (see below) the reaction spots on the surface of the spherical reagent particle are normally assumed to be limited by a circle characterized by the polar angle θ (Figure 1). Then for reaction between two identical

TABLE 10. Rate, Equilibrium, and Thermodynamic Data for Reaction 6-1 Involving Aroxyl Radicals at 293 K[a]

subst in phenoxyl	solvent	$k_1 \times 10^{-8}$ $M^{-1} \cdot s^{-1}$	k_{-1}, s^{-1}	$K_1 \times 10^8$, M	$\Delta H^{\ddagger}_1$	$\Delta H^{\ddagger}_{-1}$	ΔH°	$-\Delta S^{\ddagger}_1$	$\Delta S^{\ddagger}_{-1}$	ΔS°	ref
2,6-diphenyl-4-methoxy	*n*-hexane	32	80	2.5	2	53.5	51.5	50	−21	30	106
4-phenyl	toluene	7.0	0.0070	0.0010	9	10	92	38	67	105	124
2,4-diphenyl	*n*-hexane	18	1.3	0.074	2	94	92	54	83	138	124
2,6-diphenyl	*n*-hexane	8			2			63			124
2-methoxy	*n*-hexane	17			2			54			124
2,6-dimethoxy	*n*-hexane	4.3	11	2.6	1	30	29	75	−121	−46	124
2,6-diphenyl-4-(diphenylmethyl)	*n*-hexane	7.5	3.0	0.40	2	75	73	63	25	88	125
2,4,6-triphenyl	*n*-hexane	5.4	1600	300							106
2,6-diphenyl-4-stearoxy	*n*-hexane	20	200	10	0	80	80	63	83	146	32
2,6-diphenyl-4-stearoxy	1-propanol	1.9	1000	500	17	58	40	25	17	34	106
2,6-diphenyl-4-methyl	*n*-hexane	11	0.23	0.020	6	113	105	46	142	188	32
2,6-diphenyl-4-(chloromethyl)	*n*-hexane	13	0.027	0.0020	2	119	117	55	155	209	32
2,6-diphenyl-4-(2,6-diphenylphenoxy)	*n*-hexane	0.5	30	60	4	69	65	84	25	109	32
2,6-dicyclohexyl-4-phenyl	1-propanol	0.27	1100	4000							106
4-(methoxycarbonyl)-2,6-di-*tert*-butylphenyloxyl[b]	deuterio-chloroform	0.05	210	8500	−7	42	48	138	−21	117	126
4-(ethoxycarbonyl)-2,6-di-*tert*-butylphenyloxyl[b]	carbon disulfide	0.133	120	1900	−12	34	46	155	−58	92	126
2,6-di-*tert*-butyl-4-methyl	toluene	0.45	112	250	−4	69	73	105	38	142	125
	di-*n*-butyl phthalate	0.075	6.75	90	12	81	69	63	54	117	125
	n-hexane	1.1	50	45	−6	90	96	105	100	205	32
2,6-diphenyl-4-ethoxy	*n*-hexane	22	315	14	2	73	71	58	58	117	32
2,6-dimethyl-4-(1,3-dioxo-2-indanyl)	toluene	2.0	0.21	0.43	6	63	57	54	−33	21	127
	di-*n*-butyl phthalate	0.05	0.16	0.008	13	72	60	71	−42	29	127

[a] ΔH is in kJ/mol; ΔS is in J/(mol·K). The mean errors are as follows: K_1, 20%; k_1, k_{-1}, 25%; ΔH, ±2 kJ/mol; ΔS, ±8 J/(mol·K). [b] Full name of radical; dimerization at 250 K.

spheres with spots $f_g = \sin^4(\theta/2)$, and for reaction between a sphere and the white sphere with a reaction spot, $f_g = \sin^2(\theta/2)$.

In the liquid phase, owing to the cage effect (the extended encounter time and repeated contacts), the anisotropy of reactivity may be partially, or even wholly, averaged. If in their first contact the spheres with black spots have approached each other in an unfavorable orientation, they will have a chance to change their orientation before they meet again and react; see Figure 1. It is also probable, however, that because of steric limitations the reagents do not react and part unreacted (Figure 1).

Thus the cage effect may raise f_g up to the effective steric factor f_{eff}.

For the molecular mobility limited reaction

$$k\ (2k) = \sigma(4\pi\rho D)f_{\text{eff}} \tag{6-11}$$

From the above it follows that $0 < f_g \lesssim f_{\text{eff}} \leq 1$.

In the general case the spot on the surface of the sphere is gray. Numerical and analytical calculations show that instead of eq 6-3 and 6-5, the following more general formula should be used:[31]

$$\frac{1}{k} = \frac{1}{\sigma k_{\text{chem}}} + \frac{1}{\sigma(4\pi\rho D)f_{\text{eff}}} \tag{6-12}$$

If k_{chem} is high enough, so that $k_{\text{chem}} \gg \sigma(4\pi\rho D)f_{\text{eff}}$, the reagents should be treated as white spheres with black spots and eq 6-12 reduces to eq 6-11.

The theory of reactions between chemically anisotropic reactants has been tempestuous development during the past decade or two and is now nearing completion. Choosing a certain model of chemical anisotropy and reactant motion patterns, the authors of theoretical treatments[116-122] established the relationships between f_g and f_{eff}. The theoretical treatments of anisotropy-averaging effects are reviewed in ref 31 and 123. It has been shown there that different theories gave relatively close values for degrees of anisotropy averaging for $f_{\text{eff}} \gtrsim 10^{-2}$, which in a sense simplifies for the experimenter the problem of selecting the proper model for data analysis. So far there is apparently no hope of assessing or refusing any particular model on the basis of experimental data. But the reverse problem, that of building the f_{eff} vs. f_g relationship from experimental results, is obviously more realistic.[122]

The molecular mobility limited bimolecular reactions between reactants, at least one of which features a substantial anisotropy of reactivity, have recently been termed pseudodiffusion reactions.[31] For a pseudodiffusion reaction eq 6-11 holds true, and $f_{\text{eff}} < 1$.

C. Recombination and Disproportionation of Aroxyl Radicals

1. Dimerization of Aroxyl Radicals and Dimer Structure

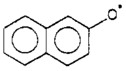
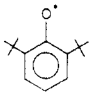
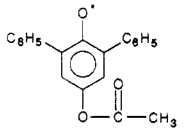
In the absence of scavengers, ArO• decays via dimerization (recombination) reactions

$$\text{ArO}^\bullet + \text{ArO}^\bullet \underset{2k_{-1}}{\overset{2k_1}{\rightleftharpoons}} \text{D}; \qquad K_1 = k_{-1}/k_1 \tag{6-1}$$

Aroxyl radical dimers are bonded with C–C or C–O bonds. The O–O dimers cannot be stable since the high energy of stabilization of ArO• (75 kJ/mol for the unsubstituted phenoxyl radical[32]) due to delocalization of the unpaired electron, results in a low dissociation energy for the O–O bond. The dimer bond is rather weak (ΔH° = 30–120 kJ/mol, Table 10), and dimerization of ArO• is therefore reversible. At the same time in many cases the equilibrium is completely shifted to the right and recombination of some ArO• is irreversible. Such radicals include mono-, di-, and certain trisubstituted radicals (Table 11).

The mechanism and kinetics of ArO• decay in liquid solutions is largely determined by the nature of the

TABLE 11. Rate Constants and Activation Parameters for Recombination 6-1 of Aroxyl Radicals[a]

formula of ArO$^\bullet$	solvent	T, K	k_1, $M^{-1} \cdot s^{-1}$	log (A_1/($M^{-1} \cdot s^{-1}$))	E_1, kJ/mol	ref
$C_6H_5O^\bullet$	water + 0.1 M H_2SO_4	293–298	1.3×10^9			128
$C_6H_5O^\bullet$	chlorobenzene + 1 × 10^{-3} M *p*-toluenesulfonic acid	303	2×10^8	12	19	129, 130
$3\text{-}OHC_6H_4O^\bullet$	water, pH 7.0	298	1.5×10^8			131
$4\text{-}NH_2C_6H_4O^\bullet$	water, pH 10.5	293–298	1×10^9			132
	benzene	303	5×10^9	8.8	-5	129, 130
$4\text{-}C_6H_5C_6H_4O^\bullet$	*n*-hexane	293	5.5×10^9	10.3	1	124
$2\text{-}C_6H_5C_6H_4O^\bullet$	*n*-hexane	293	1.8×10^9	9.8	3	124
	di-*n*-butyl phthalate	293	5.0×10^6	10.3	21	124
	*n*-hexane	293	2.2×10^9	9.7	2	32
$4\text{-}CH_3C_6H_5O^\bullet$	water, pH 8.0	285 ± 2	5.5×10^7			133

[a] Mean errors are k_1, 20%; E_1 ±2 kJ/mol; log (A_1/($M^{-1} \cdot s^{-1}$)), ±0.4.

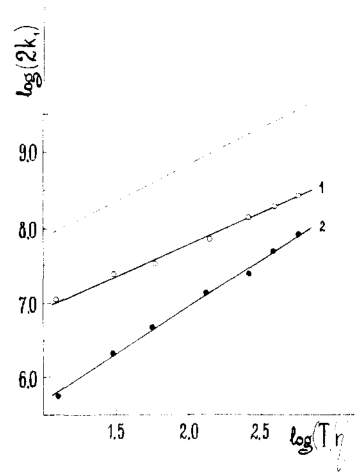
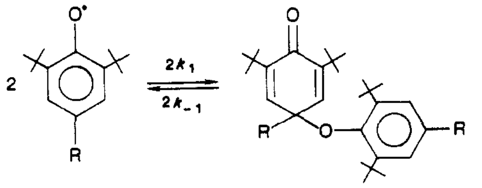


Figure 2. log ($2k_1$) vs. log (T/η) relationship (T = 293 K; η in cP) for (1) recombination of 2,6-dimethyl-4-(1,3-dioxo-2-indanyl)phenoxyl (6) and (2) disproportionation of the 2,6-di-*tert*-butyl-4-(1,3-dioxo-2-indanyl)phenoxyl radical (1). The dotted line is the relationship predicted by eq 6-7.[127]

substituents at the para and ortho positions relative to the monovalent oxygen.

ArO$^\bullet$ containing three substituents in the ortho and para positions, for example, 2,6-di-*tert*-butyl-4R- and 2,6-diphenyl-4R-phenoxyl radicals with R not containing any mobile α-hydrogen atoms, may for considerable periods of time remain in equilibrium with their corresponding dimers[32,126]



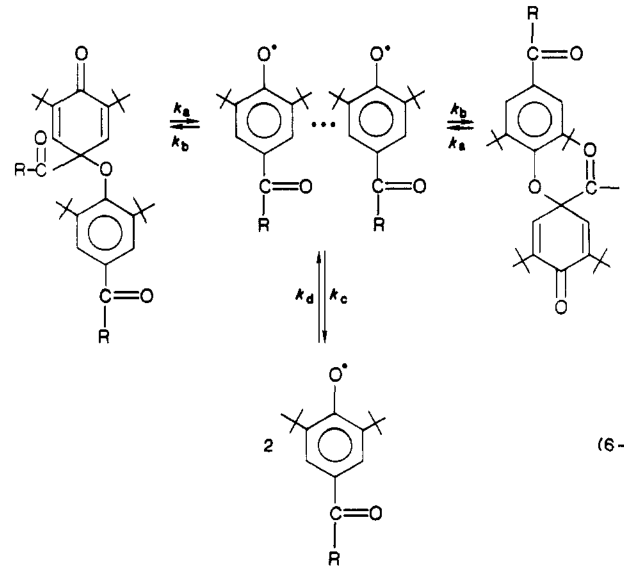
(6-1)

Dimers of some ArO$^\bullet$ are stable in solution and sometimes may be recovered as solids. Most such dimers, e.g., dimers of 2,6-di-*tert*-butyl-4R- or 2,6-diphenyl-4R-phenoxyl radicals, have structures of quinol ethers ("head-to-tail"). This dimer structure has been convincingly demonstrated by NMR analysis.[105] The dimer structure of certain aroxyl radicals has been discussed in ref 32.

2. Kinetics of Reversible Recombination of Aroxyl Radicals

The kinetics of reaction 6-1 for ArO$^\bullet$ have been studies by NMR, ESR, flash photolysis, and pulsed radiolysis. The rate constants of ArO$^\bullet$ recombination (k_1) and dimer dissociation (k_{-1}) heavily depend on the chemical type, volume, and position of the substituent in the phenol moiety (Tables 10 and 11).

Analysis of recombination of 2,6-di-*tert*-butyl-4R-phenoxyl radicals by NMR led the authors of ref 126 to propose the following scheme for reaction 6-1:



(6-1)

R = OCH_3, OC_2H_5

As a result of dissociation of dimer with the rate constant k_a an intermediate product of unknown structure, the complex between the radicals, is formed. The complex may be reconverted to the initial dimer with a rate constant k_b, converted to a dimer in which the radicals have swapped places (also with the rate constant k_b), or dissociate to two free radicals with a rate constant k_c. The radicals combine into a complex with a rate constant k_d. If these complexes are in quasi-steady concentrations and $k_b \gg k_c$ (the validity of such an assumption is verified by experimental data of ref 126), we have $\boldsymbol{k}_1 = k_d$.

The calculated $\boldsymbol{k}_1$ values are several orders of magnitude smaller than k_{diff} (Table 10); i.e., the complex between radicals is formed at far from every encounter between them. In all probability, recombination of these radicals is a pseudodiffusion reaction (see section B of this chapter). In fact, investigation of solvent viscosity effect on recombination rate of related 2,6-di-*tert*-butyl- and 2,6-di-*tert*-butyl-4-methylphenoxyl radicals has shown these reactions to be pseudodiffusion ones; indeed, $f_{\mathrm{eff}} \simeq 10^{-2}$.[32] Recombination of many other ArO$^\bullet$ is diffusion- or pseudodiffusion-controlled.[31,32] Figure 2 shows as an example the relationship between the recombination rate of the 2,6-dimethyl-4-(1,3-dioxo-2-indanyl)phenoxyl radical and solvent viscosity. From Figure 2 it follows that $\boldsymbol{k}_1 < k_{\mathrm{diff}}$ and $\boldsymbol{k}_1 \sim \eta^{-1}$; i.e., the reaction is a pseudodiffusion one.

From the data of Tables 10 and 11 it follows that $\boldsymbol{k}_1$ greatly increases if the *tert*-butyl groups in the ortho positions of the phenoxyl moiety are replaced with phenyl or methoxy groups. The reason lies with the lower screening of monovalent oxygen by the last two substituents in comparison with *tert*-butyl groups. (The *tert*-butyl group is known to create considerable steric limitations, higher in fact than either the phenyl or methoxy group, which is relfected by the respective steric constants of these substituents, E_s.)

Further, recombination of many mono- and diphenyl-substituted phenoxyls and 2,6-diphenyl-4-alkoxy-substituted phenoxyls is limited by molecular mobility.[32] The reactivity anisotropy of these radicals is largely averaged out during the encounter time, and the numerical values of $2\boldsymbol{k}_1$ are close to the corresponding σk_{diff} (eq 6-6, 6-7). The constant $\boldsymbol{k}_1$ decreases with increasing number of carbon atoms in the alkoxyl substituent of the 2,6-diphenyl-4-alkoxyphenoxyl radical (Table 10). The explanation is that the area of the reaction spots remains almost unchanged as the radical volume increases; as a result, f_g and, consequently, f_{eff} and $\boldsymbol{k}_1$ decrease. $\boldsymbol{k}_1$ increases further if the alkoxyl substituent is replaced with the phenyl substituent, due apparently to the more severe steric limitations to radical dimerization. An even further decrease of $\boldsymbol{k}_1$ results from substitution of phenyl groups at ortho positions with more bulky cyclohexyl groups (Table 10).[106]

Thus the steric limitations imposed by the substitutent in the aroxyl radicals have a controlling effect on their recombination kinetics.

In analysis of activated reaction it is conventional to use the concept of steric hindrance around the reaction site. Obviously, steric hindrances reduce the rate of activated recombination of radicals.[32]

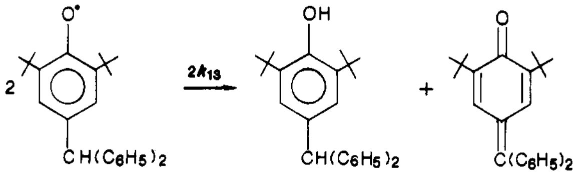
3. Dimer Dissociation

The dissociation rate constant of the dimers of 2,6-diphenyl-4R-phenoxyl radicals, $\boldsymbol{k}_{-1}$, strongly depends, as does $\Delta \boldsymbol{H}^{\ddagger}_{-1}$, on the nature of the substituent (Table 10): $\boldsymbol{k}_{-1}$ decreases and $\Delta \boldsymbol{H}^{\ddagger}_{-1}$ increases with increasing acceptor properties of the substituent. A similar relation is observed for dissociation of 2,4,6-tri-*tert*-butylphenoxyl dimers with strically unhindered phenoxyl radicals.[18,70]

The $\boldsymbol{k}_{-1}$ values for dissociation of 2,4,6-tri-*tert*-butylphenoxyl radical with meta- and para-substituted phenoxyls correlate with the σ^+ parameters of the substituents and have $\rho = -3.3$.[70] The ratio of $\boldsymbol{k}_{-1}$ to rate constant of hydrogen abstraction by the 2,4,6-tri-*tert*-butylphenoxyl radical from a sterically unhindered ArOH is practically independent of substituent. The authors of ref 70 measured relatively high $\boldsymbol{k}_{-1}$ for radicals with substituents in the ortho positions, whereas $\Delta \boldsymbol{H}^{\ddagger}_{-1}$ were smaller than expected from electronic effect considerations. The reason is that ortho substituents create steric hindrances to dimerization; see above. This is why the quinol ethers produced from the 2,4,6-tri-*tert*-butylphenoxyl radical and ortho-substituted phenoxyl radicals are less stable. For example, in the case of 2,6-dimethylphenoxyl and 2,4,6-trichlorophenoxyl radicals the strain energy of the C–O bond formed in dimerization is 20 kJ/mol.[70]

4. Hydrogen-Transfer Kinetics in Aroxyl Self-Reactions

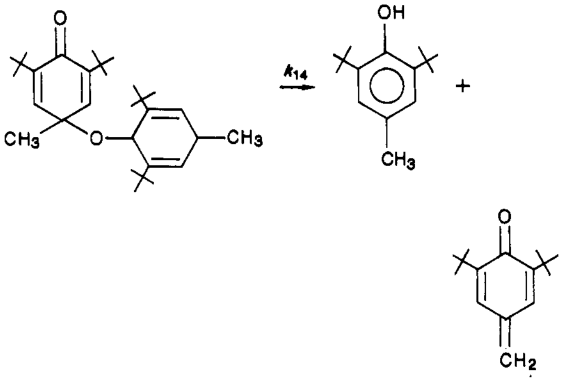
2,6-Di-*tert*-butyl-4R-phenoxyl radicals where the substituents R contain mobile α-H atoms undergo disproportionation at a rather rapid rate;[30,32,125,134–140] e.g.



(6-13)

The reaction products are ArOH and quinone methide. Where R does not create substantial steric hindrances in 2,6-di-*tert*-butyl-4R-phenoxyl radicals (for instance, R = CH_3 or C_2H_5), disproportionation is accompanied by formation of the corresponding dimer via reaction 6-1.

In this case quinone methide and ArOH may be formed either through reaction 6-13 or through unimolecular cleavage of the dimer;[32] e.g.



(6-14)

The ArO$^\bullet$ decays here in two steps. First, an equilibrium establishes itself very quickly (eq 6-1), and then reactions 6-13 or 6-14 follow. Below we give two alternative schemes of radical decay.[32,125,137–140]

SCHEME 1

$$2R^\bullet \underset{2k_{-1}}{\overset{2k_1}{\rightleftharpoons}} D \xrightarrow{k_{14}} \text{stable products}$$

Under the condition $k_{-1} \gg k_{14}$ we obtain

$$-\mathrm{d}[\mathrm{R}^\bullet]/\mathrm{d}t = 2\boldsymbol{k}_{14}\boldsymbol{k}_1[\mathrm{R}^\bullet]^2/[\boldsymbol{k}_{-1}(1 + 4\boldsymbol{k}_1[\mathrm{R}^\bullet]/\boldsymbol{k}_{-1})] \tag{6-15}$$

If $4\boldsymbol{k}_1[\mathrm{R}^\bullet]/\boldsymbol{k}_{-1} \gg 1$, then the irreversible radical decay (decrease of their quasi-steady concentration) will follow first-order kinetics with $k_{\mathrm{obsd}} = \boldsymbol{k}_{14}/2$; if $4\boldsymbol{k}_1[\mathrm{R}^\bullet]/\boldsymbol{k}_{-1} \ll 1$, the decay will follow second-order kinetics with $2k_{\mathrm{obsd}} = 2\boldsymbol{k}_1\boldsymbol{k}_{14}/\boldsymbol{k}_{-1}$. Thus in the case of high concentrations, radicals decay by a first-order reaction, and in the case of low concentrations, by a second-order reaction.

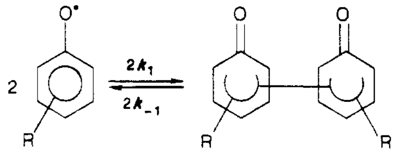
SCHEME 2

$$\mathrm{D} \underset{2\boldsymbol{k}_1}{\overset{2\boldsymbol{k}_{-1}}{\rightleftarrows}} 2\mathrm{R}^\bullet \xrightarrow{2\boldsymbol{k}_{13}} \text{stable products}$$

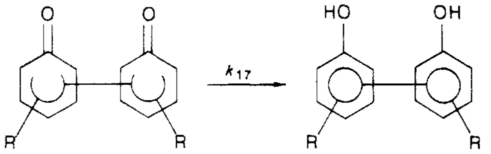
Under the condition $\boldsymbol{k}_1 \gg \boldsymbol{k}_{13}$ we have

$$-\mathrm{d}[\mathrm{R}^\bullet]/\mathrm{d}t = 2\boldsymbol{k}_{13}[\mathrm{R}^\bullet]^2/(1 + 4\boldsymbol{k}_1[\mathrm{R}^\bullet]/\boldsymbol{k}_{-1}) \tag{6-16}$$

Similarly, for $4\boldsymbol{k}_1[\mathrm{R}^\bullet]/\boldsymbol{k}_{-1} \gg 1$, radical decay will occur with first-order kinetics and $k_{\mathrm{obsd}} = \boldsymbol{k}_{13}\boldsymbol{k}_{-1}/(2\boldsymbol{k}_1)$, and for $4\boldsymbol{k}_1[\mathrm{R}^\bullet]/\boldsymbol{k}_{-1} \ll 1$, radical decay will be a second-order reaction with $2k_{\mathrm{obsd}} = 2\boldsymbol{k}_{13}$. Decay of ArO• having no substituents in at least one of its ortho or para positions occurs in two steps[30,32,124,129,130]



(6-1)

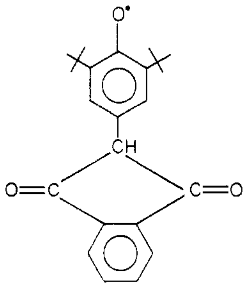


(6-17)

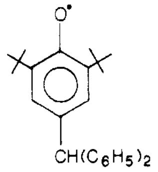
Reaction 6-17 is enolization.

5. Disproportionation

The kinetics of disproportionation of radicals of the structures



1



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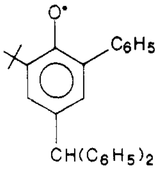
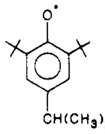
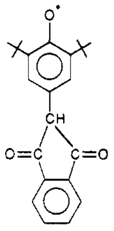
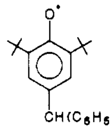
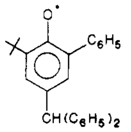


3

is strictly second-order.[125,127] It has been estimated that for these radicals $\boldsymbol{K}_1 \gtrsim 10^{-3}$ M.[125,127] Steric hindrances about the reactive sites (oxygen atom and para-carbon atom) in radicals **1–3** created by the *tert*-butyl group(s) and the diphenylmethyl or 1,3-dioxo-2-arylindan-2-yl group prevent formation of the dimer, quinol. Formation of the diketo dimer is also impossible because of steric hindrances.

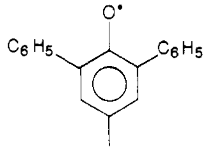
Quinonemethides were observed to accumulate symbatically with decay of ArO• **1–3**.[124,125,127] Quinone methides are the final products of oxidation of the starting ArOH with chemical agents.[26,125,127,134–139] The kinetic and activation parameters for reaction 6-13 are given in Table 12.

TABLE 12. Rate, Equilibrium, and Activation Parameters for Disproportionation 6-13 of Aroxyl Radicals at 293 K[a]

radical	solvent	$\boldsymbol{k}_{13}$, $\mathrm{M^{-1} \cdot s^{-1}}$	$\boldsymbol{E}_{13}$, kJ/mol	$\boldsymbol{A}_{13}$, $\mathrm{M^{-1} \cdot s^{-1}}$	ref
	chloro-benzene[b]	0.785	28.8	1.6×10^5	135
	toluene	7.5×10^7	12	2.5×10^{10}	127
	benzene	0.6	17	5.5×10^2	125
	benzene	2.0×10^4	8	6.0×10^5	125

[a] The mean errors are $\boldsymbol{k}_{13}$, 10%; $\boldsymbol{E}_{13}$, ±1 kJ/mol; $\boldsymbol{A}_{13}$, 40%. [b] At 283 K.

Disproportionation of ArO• **4–7** occurs, under pulsed radical generation conditions, in two steps.[125,127] First equilibrium 6-1 rapidly establishes itself and then reaction 6-13 or 6-14 follows.



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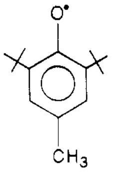

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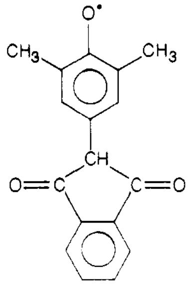

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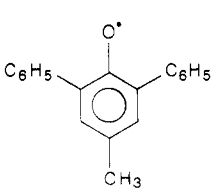

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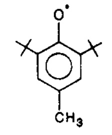
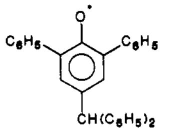
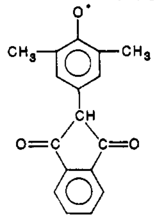
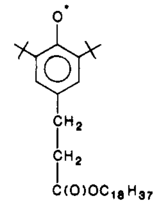
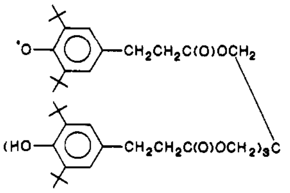
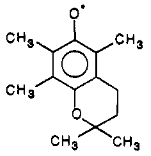
Disproportionation (Schemes 1 and 2) of radicals **4–7** (the slow stage) obeys first-order kinetics with $k_{\mathrm{obsd}} = \boldsymbol{k}_{13}\boldsymbol{k}_{-1}/(2\boldsymbol{k}_1)$ if disproportionation takes route 6-13 or $k_{\mathrm{obsd}} = \boldsymbol{k}_{14}/2$ if disproportionation takes route 6-14. The rate, equilibrium, and thermodynamic parameters for reaction 6-1 involving radicals **4–7** are given in Table 10. The kinetic and activation parameters for disporportionation routes 6-13 and 6-14 are presented in Table 13.

The disproportionation kinetics of radical **5**, the ArO• obtained from the important InH ionol, was the subject

TABLE 13. Rate, Equilibrium, and Activation Parameters for Reactions 6-13 and 6-14 of Reversibly Recombining Aroxyl Radicals[a]

radical formula	T, K	k_{13}, $M^{-1} \cdot s^{-1}$	E_{13}, kJ/mol	A_{13}, $M^{-1} \cdot s^{-1}$	k_{14}, s^{-1}	E_{14}, kJ/mol	A_{14}, $M^{-1} \cdot s^{-1}$	ref
	295[b]	1.0×10^3	13	1.0×10^7	0.02	88	7.5×10^{13}	137
	298[b]	1.6×10^4	4	5.0×10^4	6.3×10^{-3}	77	1.6×10^{11}	138
	293[b]	3.0×10^3			1.0×10^{-2}			125
	293[b]	3.0×10^3			1.35×10^{-2}			136
	323[b]	2.2×10^4	20	7.5×10^6				139
	293[b]	2.8×10^6	4	1.5×10^7	0.4	67	3.0×10^{12}	125
	293[c]	5.0×10^6	12	8.5×10^8	0.25	71	1.0×10^{12}	125
	293[d]	2.0×10^8	−18	1.0×10^5	42	29	6.0×10^6	127
	293[c]	7.8×10^8	−22	1.0×10^5	13	34	1.5×10^7	127
	299[b]	2.0×10^2	29	2.5×10^7				139
	323[b]	1.2×10^3	16	3.9×10^5				139
	323[b]	1.1×10^3	30	6.6×10^7				140

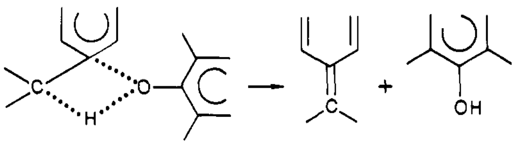
[a] Measurement accuracy was widely different and is presented in the references. [b] In benzene. [c] In acetonitrile. [d] In 1,1,2,2-tetrachloroethane.

of a number of studies[125,136-140] (Table 13). The k_{14} results are in fair agreement throughout. For instance, within experimental error k_{14} obtained in flash photolysis experiments[125] coincides with k_{14} obtained by ESR in ref 136 and 140 (Table 13).

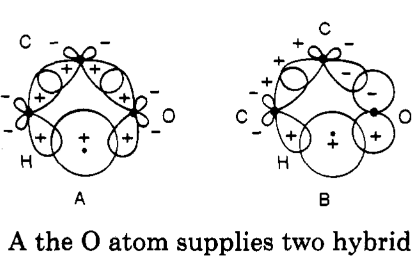
To establish the mechanism of two-step disproportionation is undisputable interest. In ref 32, 124, 125, and 127 all the elementary constants (k_1, k_{-1}, k_{13}, k_{14}), and in many cases the corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, have been measured. These data provide sufficient ground for speculation about the reaction mechanism. Disproportionation of ArO$^{\bullet}$ 6 follows reactions 6-1 and 6-14. Indeed, if we presume that disproportionation takes route 6-13, then for a given ArO$^{\bullet}$ we have $k_{13} \gtrsim k_1$ (cf. Table 13), which is contrary to the initial assumption of $k_1 \gg k_{13}$; besides, large negative values of $\Delta H^{\ddagger}{}_{13}$ will result (Table 13).

Very probably the disproportionation of the other ArO$^{\bullet}$ investigated also occurs by reactions 6-1 and 6-14. The arguments are as follows.

1. Reaction 6-14, provided it takes place at all, is concerted decomposition to complex fragments involving scission of the C–O and C–H bonds in a four-center transition state



This transition state merits a more detailed discussion. Carbon atoms participating in the formation of the cycle are saturated and occupy a configuration between sp^2 and sp^3. The transition state may be schematically represented as



In variant A the O atom supplies two hybrid orbitals, whereas in variant B it supplies only one p orbital; in both variants the O atom supplies one electron. The plus and minus signs at the blades of the orbitals have been written in accordance with the prescriptions of ref 141. In both versions, six electrons are involved and the blades of the orbitals are in-phase. This means that the reaction is allowed for symmetry rules and must have a low or moderate activation energy.[141] Such activation energies have indeed been measured experimentally (29–88 kJ/mol, Table 13).

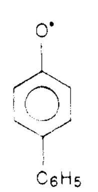
2. Let us now consider more closely the activation parameters for reaction 6-14 (Table 13). $\Delta \boldsymbol{H}^{\ddagger}_{14}$ (see above), $\Delta \boldsymbol{S}^{\ddagger}_{14} = -110$ to 0 J/(mol·K), or $\boldsymbol{A}_{14} = 10^{7}$–$10^{13}$ s^{-1} are consistent for dissociation through a four-center transition state. The authors of ref 138, who analyzed $\boldsymbol{A}_{14}$ values for decomposition of the dimer of ArO$^{\bullet}$ **5**, were of the same opinion. Reaction 6-(−1) is in fact a simple breakdown into two large groups. Clearly, in both the gas phase and the liquid phase it must hold that $\Delta \boldsymbol{S}^{\ddagger}_{-1} > \Delta \boldsymbol{S}^{\ddagger}_{14}$ ($\boldsymbol{A}_{-1} > \boldsymbol{A}_{14}$), since the transition state of reaction 6-(−1) is "looser" than the cyclic transition state of reaction 6-14.

The data of ref 32 and 125 allow one to make such a comparison for dissociation of a given dimer; in this case the condition $\Delta \boldsymbol{S}^{\ddagger}_{-1} > \Delta \boldsymbol{S}^{\ddagger}_{14}$ must always be true. As follows from Tables 10 and 13, this condition does hold for ArO$^{\bullet}$ **4–6**, giving further support to the mechanism (6-1, 6-14).

Yet it can hardly be claimed at present that either mechanism (6-1, 6-14) or (6-1, 6-13) is a sure fact for ArO$^{\bullet}$ **4**, **5**, and **7**. Besides, it makes no sense to insist on the general nature of the mechanism of ArO$^{\bullet}$ disproportionation, since the precise routes of scission reactions are often very sensitive to even slight variations in the nature of the solvent, reaction conditions, and reactant structure.[141] Knowing the radical disproportionation mechanism bears rather an academic interest, for it is necessary to know, in the analysis of inhibited oxidation kinetics, the rate with which ArO$^{\bullet}$ decays (cf. section III), whereas the mechanism itself is insignificant.

6. Recombination of Mono- and Disubstituted Aroxyls

The kinetics of decay of mono- and disubstituted ArO$^{\bullet}$ of structures **8–10** have been investigated in ref 124. Under the experimental conditions used ($T \gtrsim 293$ K), the initial radical concentration decreased only down to a quasi-steady concentration as a result of equilibrium 6-1, whereafter the relatively slow enolization 6-17 takes place. The thermodynamic data for the reaction 6-1 of ArO$^{\bullet}$ **8–10** are given in Table 10.



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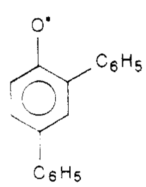

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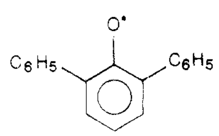


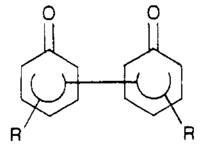
10

The equilibrium concentration of radicals decreases slowly via reaction 6-17. Under the experimental conditions used, 4[R$^{\bullet}$] was more than an order of magnitude greater than $\boldsymbol{K}_1$ (Table 10); therefore, the radical decay obeyed a first-order law with $k_{\mathrm{obsd}} = k_{17}/2$ (see Scheme 1). The measured k_{17} for ArO$^{\bullet}$ **9** are presented in Table 14.

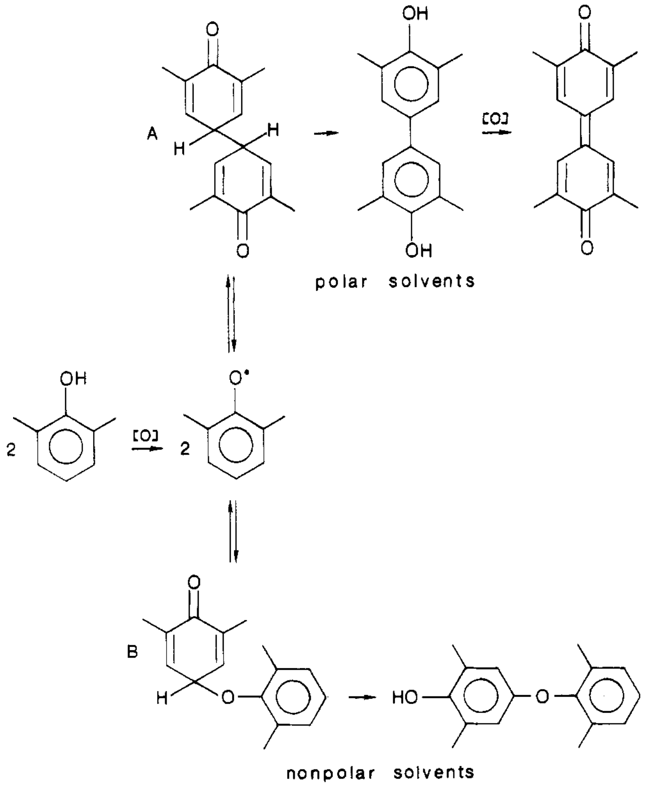
From the data of Table 14 it follows that k_{17} has a weak dependence on the polarity and viscosity of the solvent. One may expect enolization to be acid-catalyzed.[130] In fact, k_{17} increased when acetic acid or formic acid was added to benzene or toluene.[124] In acetic acid $\boldsymbol{k}_{17}$ was an order of magnitude higher than the standard value in benzene or toluene (Table 14). In the stronger formic acid k_{17} is so high that recombination becomes the limiting step.

It is interesting that the recombination of unsubstituted phenoxyl or methyl-substituted phenoxyl radicals in water strictly follows second-order kinetics.[30] Yet, an increase of pH of solvent causes some decrease of the recombination rate constant.[30] This means that enolization has some effect on the observed decay rate.

The structure of the primary labile dimers (eq 6-1 and 6-17)



may be inferred from the structure of the stable final products, also bound with the C–C or C–O bond. Chemical oxidation of 2,6-dimethoxyphenol or 2,6-diphenylphenol in dimethylformamide and acids (polar solvents) yields predominantly diphenoquinone, whereas oxidation in benzene and other nonpolar solvents yields phenoxyphenol.[105] A buildup of colored diphenoquinone symbatically with radical decay was observed in the flash photolysis of these ArOH in air-saturated polar solvents.[124] Consequently, the reaction may be schematically represented as



The dipole moment of labile dimer A is obviously higher than that of dimer B, which explains the prevalent formation of diphenoquinone in polar media.

TABLE 14. Rate and Activation Parameters for Enolization 6-17 of the Dimer of the 2,4-Diphenylphenoxyl Radical at 293 K[a]

solvent	k_{17}, s^{-1}	$\Delta H^{\ddagger}_{17}$, kJ/mol	$\Delta S^{\ddagger}_{17}$, J/(mol·K)
carbon tetrachloride	2.0	67	−4
toluene	4.3	59	−25
benzene	4.2	63	−13
tetrahydrofuran	6.2	42	−80
chlorobenzene	6.5	63	−8
chloroform	8.2	44	−71
dichloromethane	7.1	61	−17
acetone	8.3	38	−92
acetonitrile	20.0	42	−71
acetic acid	31.0	46	−55
di-*n*-butyl phthalate	2.4	63	−17

[a] Reference 124. Determination errors are k_{17}, 20%; $\Delta H^{\ddagger}_{17}$, ±2 kJ/mol; $\Delta S^{\ddagger}_{17}$, ±15 J/(mol·K).

D. Semiquinone Radicals

In the absence of scavengers, neutral semiquinone radicals ($QH^\bullet$) decay through bimolecular self-reactions[30]

$$QH^\bullet + QH^\bullet \xrightarrow{2k_1} Q + QH_2 \tag{6-1}$$

resulting in formation of *p*- or *o*-quinone and a coresponding hydroquinone (catechol). Reaction 6-1 is disproportionation. In the absence of oxidants or other active agents the quinone radical anions also decay through bimolecular self-reactions (dismutation)[30]

$$Q^{\bullet -} + Q^{\bullet -} \xrightarrow[2H^+]{2k_{18}} Q + QH_2 \tag{6-18}$$

The disproportionation and dismutation of semiquinone radicals have been studied by pulsed radiolysis, flash photolysis with optical and ESR recording, and the ESR technique in combination with a rotating sector. The decay of *p*-semiquinone radicals has been investigated much more thoroughly. The rate constants of reactions 6-1 and 6-18 are listed in Tables 15 and 16.

1. Disproportionation

Disproportionation of many sterically unhindered semiquinones is either a (pseudo)diffusion-controlled or activated reaction.

In ref 144 the ESR technique has been used to investigate the decay of neutral *p*-benzosemiquinone and 4-hydroxy-1-naphthoxyl radicals. It has been shown that disproportionation of these radicals is limited by molecular mobility,[144] and disproportionation of the latter radical should be classified as a pseudodiffusion reaction (cf. section VI.B.2). Detailed kinetic studies of $QH^\bullet$ of *p*-benzoquinone, naphthoquinone-1,4, and duroquinone in solvents of different viscosity were carried out in ref 142, 154, and 155 (cf. Table 15). The conclusions concerning the reaction type made by the authors of the different references have been very similar.

In investigations of the decay of semiquinone radicals generated by photoreduction of quinones (Q)

$$Q^* + SH \rightarrow QH^\bullet + S^\bullet \tag{6-19}$$

one faces the problem of whether there is a cross-reaction between $QH^\bullet$ and $S^\bullet$

$$QH^\bullet + S^\bullet \rightarrow \text{products} \tag{6-20}$$

and what its contribution to $QH^\bullet$ decay rate is.

Normally reaction 6-20 would not make much of a contribution to $QH^\bullet$ decay via reaction 6-1, characterized by $k_1 = 10^7$–10^9 $M^{-1} \cdot s^{-1}$.[154] In ref 156 it was shown that the decay rate of the durosemiquinone radical in ethanol is independent of its preparation history, whether by reaction 6-19 or reaction 6-21

$$Q^*_T + QH_2 \rightarrow 2QH^\bullet \tag{6-21}$$

It has been shown in CIDNP and magnetic field effect experiments that any or all of the following reactions occur in the cage during quinone photoreduction with an aliphatic alcohol.[157,158]

$$QH^\bullet + (CH_3)_2\dot{C}OH \rightarrow Q + (CH_3)_2CHOH \tag{6-22a}$$

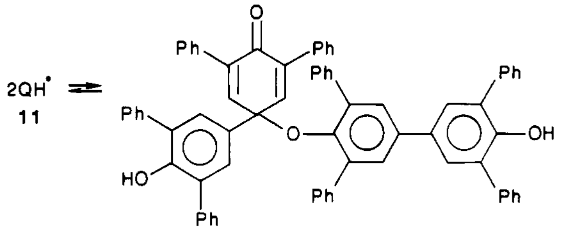
$$\rightarrow QH_2 + CH_2{=}C(CH_3)OH \tag{6-22b}$$

$$\rightarrow QH_2 + (CH_3)_2CO \tag{6-22c}$$

However, in the bulk of solvent reactions 6-22a–c cannot contribute to $QH^\bullet$ decay since the alcohol radicals are oxidized by the starting quinone.[159]

$$(CH_3)_2\dot{C}OH + Q \rightarrow (CH_3)_2CO + QH^\bullet \tag{6-23}$$

The disproportionation kinetics of the 2,6-diphenyl-4-(3,5-diphenyl-4-hydroxyphenyl)phenoxyl radical (11) in benzene, toluene, and 1-propanol deviated from the second-order law. In these solvents reversible dimerization



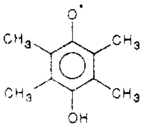
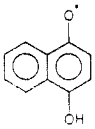
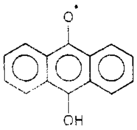
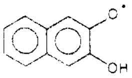
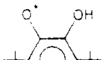
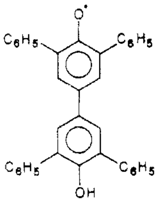
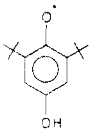
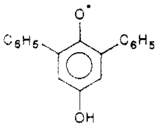
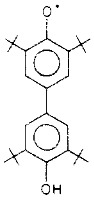
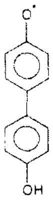
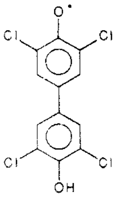
(6-24)

took place apart from disproportionation.[147] Dimers of this structure are formed from different 2,6-diphenyl-4R-phenoxyl radicals (see section VI.C), and the assumption that there must be an equilibrium 6-24 is valid. In acid solutions such dimers are unstable (cf. section VI.C) and dissociate to Q and QH_2. Therefore in acids the decay of $QH^\bullet$ 11 strictly follows second-order kinetics[147] (Table 15).

2. Dismutation

It is believed that reaction 6-18 occurs via one-electron transfer.[150,160] The dianion formed in reaction 6-18 is rapidly protonated, since the pK_a of hydroquinone (catechol) derivatives is usually much greater than the pK_a of $QH^\bullet$ (section VII). The k_{18} values of *p*-benzoquinone radical anions fit nicely into the Marcus relationship between electron-transfer rate constant and reaction heat for a broad range of reactions.[160] The results of ref 150 on the effect of the donor–acceptor properties of substituents in *p*-benzoquinone radical anions on their decay rate show that the reaction involves electron transfer. The ratio of the one-electron

TABLE 15. Rate, Equilibrium, and Activation Parameters for Disproportionation 6-1 of Semiquinone Radicals at Room Temperature[a]

radical formula	solvent	k_1, $M^{-1} \cdot s^{-1}$	log (A_1/($M^{-1} \cdot s^{-1}$))	E_1, kJ/mol	ref
$4\text{-}HOC_6H_4O^{\bullet}$	toluene/2-propanol (15:85 (v/v))	1.8×10^8	11	16	142
$2\text{-}HOC_6H_4O^{\bullet}$	water, pH 2.0	2.0×10^8			131
	toluene/2-propanol (15:85 (v/v))	1.4×10^8	10	11	142
	water, pH 3.0 + 1-3 M 2-propanol	6.5×10^8			143
	2-propanol	1.0×10^8			159
	2-propanol	2.5×10^7			145
	water, pH 7.0	3.0×10^7			131
	tetrahydrofuran	5.0×10^4	7.6	17	146
	acetic acid	5.0×10^8			147
	2-propanol	8.5×10^5	10.6	26	159
	acetic acid	1.2×10^8			148
	toluene	6.5×10^4			147
	acetonitrile	2.8×10^8			149
	acetic acid	8.5×10^8			149

[a] The mean errors are k_1, 15%; E_1, ±2 kJ/mol; log (A_1/($M^{-1} \cdot s^{-1}$)), ±0.7.

TABLE 16. Dismutation 6-18 Rate Constants for Quinone Radical Anions at Room Temperature

starting quinone	solvent	k_{18},[a] $M^{-1} \cdot s^{-1}$	ref
1,4-benzoquinone	methanol + 0.1 M tetraethylammonium perchlorate	1.65	150
	water, pH 7.0	8.0×10^7	151
duroquinone	water, pH 9.0	1.6×10^7	143
cyano-1,4-benzoquinone	methanol + 0.1 M tetraethylammonium perchlorate	1.65×10^3	150
9,10-anthraquinone-2-sulfonate	water, pH 4.0	6.3×10^8	152
methyl 9,10-anthraquinone-2-sulfonate	water + 5 M sodium chloride	4.0×10^8	153

[a] Mean determination error in k_{18} is 15%.

TABLE 17. Rate Constants for Recombination 6-1 of Ketyl Radicals at Room Temperature[a]

starting ketone	solvent	k_1, $M^{-1} \cdot s^{-1}$	ref
benzophenone	water	8.0×10^8	165, 166
	1-propanol	2.5×10^7	166
4,4′-dimethylbenzophenone	1-propanol	1.6×10^6	166
4,4′-dimethoxybenzophenone	1-propanol	3.2×10^7	166
4,4′-dichlorobenzophenone	1-propanol	6.0×10^7	166
4-bromobenzophenone	1-propanol	5.0×10^7	166

[a] Determination errors in k_1 do not exceed 20%.

potentials (cf. section VIII.E) of a number of pairs in water (pH 7.0), $E_7^1(Q/Q^{\bullet -})$ and $E_7^2(Q^{\bullet -}/Q^{2-})$, shows that $E_7^2 > E_7^1$ and that one radical anion may oxidize the other in water at pH 7.0.

At the same time it is known that $Q^{\bullet -}$ decay is decelerated as the basicity or pH of aqueous solution is increased (within, of course, pH > pK_a), and in strongly basic solutions $Q^{\bullet -}$ are relatively stable.[161,162] On these grounds the authors of ref 145 proposed a protonation mechanism for the decay of $Q^{\bullet -}$

$$Q^{\bullet -} + H^+ \overset{K_a}{\rightleftharpoons} QH^\bullet \qquad (6\text{-}25)$$

which is followed by disproportionation of the resultant $QH^\bullet$ by reaction 6-1. For such a mechanism

$$2k_{18}^{\text{obsd}} = 2\boldsymbol{k}_1[H^+]/K_a \qquad (6\text{-}26)$$

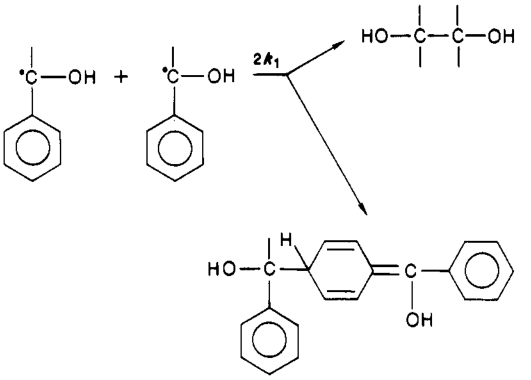
From eq 6-26 it is apparent that k_{18} decreases as pH increases. The two mechanisms (one-electron transfer and protonation + disproportionation) are not mutually exclusive and probably there are conditions in which they may coexist.

The k_{18} values (Table 16) are about an order of magnitude smaller than the corresponding k_1 for the same radicals (cf. Table 15). The most conspicuous reason for such a relationship between the constants is the mutual repulsion between the like-charged radical anions.[30] Investigation of the effect of the viscosity of a water–glycerol binary mixture on the rate of reaction 6-18 for p-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquionine 2-sulfonate radical anions has shown that these reactions are (pseudo)diffusion-controlled.[155] In not too viscous media the $2k_{18}$ are smaller than the corresponding k_{diff} estimated by formula 6-8. The main reason for such a relationship consists obviously in the steric factor $f_{\text{eff}} = 0.1$–0.5 for these reactions. Reaction 6-18 takes place only upon direct contact of the reactants with their sites characterized by the highest electron density and unpaired electron density (primarily the oxygen atoms of $Q^{\bullet -}$). To support this assumption we refer to the results for spin exchange between duroquinone radical anions,[163] which is characterized by $f_{\text{eff}} = 0.45$.

E. Ketyl Radicals

1. Recombination

In the absence of atmospheric oxygen, free radicals, oxidant–reductant, and other active agents, aromatic ketyl radicals ($BPH^\bullet$) decay by recombination into pinacols and isopinacols[164–168]



(6-1)

The corresponding k_1 are presented in Table 17.

Disproportionation of $BPH^\bullet$

$$2BPH^\bullet \rightarrow BP + BPH_2 \qquad (6\text{-}27)$$

is energetically unfavorable and makes virtually no contribution to $BPH^\bullet$ decay.[169] For benzophenone ketyl radical $2\boldsymbol{k}_1 \simeq \sigma k_{\text{diff}}$ (eq 6-6) in water, and $2\boldsymbol{k}_1 \sim \eta^{-1}$ in water–glycerol mixtures. This reaction is diffusion-controlled. Similarly, recombination of ketyl radicals in n-hexane is a diffusion-controlled reaction.[166] The suggestion was made that recombination of ketyl radicals of benzophenone and acetophenone may take place at each one of their random encounters in solution in the singlet state only when the intermediate dimers, isopinacols, are yielded by the reaction apart from pinacols.[122]

Investigators of the decay of photogenerated ketyl radicals have to face the problem of whether there is a cross-reaction between $BPH^\bullet$ and solvent or donor radicals (compare section VI.D). Alcohol radicals effectively reduce the starting ketones and do not contribute materially to $BPH^\bullet$ decay.[166] n-Hexane's and indole's radicals undergo cross-recombination, and in this case the $[BPH^\bullet]^{-1}$ vs. t plot is not a straight line.[112,166] Aliphatic alcohols solvate ketyl radicals, decelerating their recombination[165,166,168] (cf. section VI.H).

For recombination of ketyl radicals of 4,4′-dichlorobenzophenone and 4-bromobenzophenone in viscous solvents the $2k_1$ have been found to be larger than σk_{diff} (eq 6-6).[166] It has been proposed that recombination of these heavy-atom-containing radicals removes the spin forbiddance[166] ($\sigma > {}^1/_4$; see eq 6-6).

Generally, recombination of $BPH^\bullet$ is reversible. Compounds such as benzopinacol, 4,4′-dibromobenzopinacol, and 4,4′,4″,4‴-tetramethoxybenzopinacol in benzene and 2-propanol are in equilibrium with the corresponding $BPH^\bullet$ at 353–414 K.[168]

TABLE 18. Rate and Activation Parameters of Reaction 6-28 for Aromatic Ketone Radical Anions at Room Temperature[a]

starting ketone	solent	k_{28}, $M^{-1} \cdot s^{-1}$	log (A_{28}/ ($M^{-1} \cdot s^{-1}$))	E_{28}, kJ/ mol	ref
benzophenone	water, pH 11.0	3.2×10^6			164
	water, pH 12.0	2.9×10^5	13	44	166
4,4′-dimethyl-benzophenone	1-propanol + 10^{-2} M KOH	2.5×10^5	12	37	166
4,4′-dimethoxy-benzophenone	1-propanol + 10^{-2} M KOH	2.8×10^5	11	31	166
4,4′-dichloro-benzophenone	1-propanol + 10^{-2} M KOH	1.2×10^5	10	26	166
4-bromobenzo-phenone	1-propanol + 10^{-2} M KOH	3.2×10^5	12	38	166
acetophenone	water, pH 12.2	4.8×10^8			161

[a] Determination errors are k_{28}, 20%; E_{28}, ±2 kJ/mol; log ($A_{28}/(M^{-1} \cdot s^{-1})$), ±1.

2. Self-Reactions of Radical Anions

In the absence of oxygen, free radicals, and other active agents the radical anions of aromatic ketones decay by second-order kinetics[164-166]

$$BP^{\bullet -} + BP^{\bullet -} \xrightarrow{2k_{28}} \text{products} \qquad (6\text{-}28)$$

The elementary reaction is electron transfer[166] or formation of the C–C bond in twice-ionized pinacol.[164]

At pH > 10 or high alkali concentrations in water–alcohol solutions, the contribution of the reaction

$$BPH^{\bullet} + BP^{\bullet -} \rightarrow \text{products} \qquad (6\text{-}29)$$

to the observed $BP^{\bullet -}$ decay rate may be neglected.[164,166] The corresponding k_{28} and activation parameters are presented in Table 18.

F. Aminyl Radicals

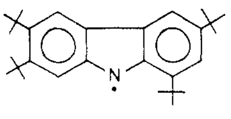
1. Neutral Radicals

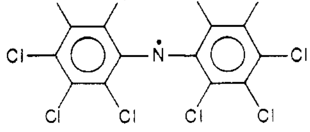
Recombination of arylaminyl radicals (Am•), like that of aroxyls and ketyls, is often reversible[170,171]

$$Am^{\bullet} + Am^{\bullet} \underset{2k_{-1}}{\overset{2k_1}{\rightleftharpoons}} D \qquad (6\text{-}1)$$

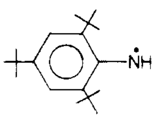
However, Am• may also decay irreversibly (cf. section VI.C.5).

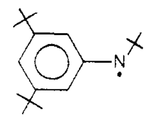
Most Am• are short-lived and can be detected by flash photolysis or by ESR only at low temperatures. Steric screening of the aminyl nitrogen is an important factor controlling the stability of Am•. For instance, the screened radicals



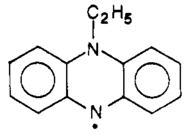


are monomers. The sterically hindered radicals



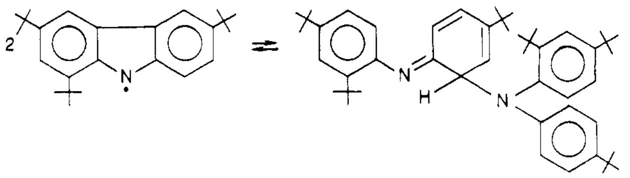


have lifetimes of the order of hours.[171] Unpaired electron delocalization also improves the radical stability. For example, a relatively stable radical is 9-*N*-ethylphenazyl[172]



Unpaired electron delocalization in aminyl radicals affects their ESR spectra and reactivities. Aromatic aminyl π radicals form products not only in N–N but also in C–N and C–C combinations.[171]

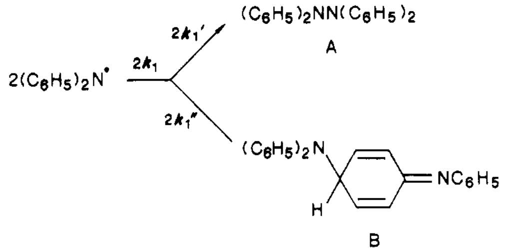
Strong screening of aminyl nitrogen may result in C–N dimerization[173]



(6-1)

The reversible recombination of the diphenylaminyl radical merits a more detailed discussion because the starting AmH is an important inhibitor.

Recombination of $(C_6H_5)_2N^{\bullet}$ results in formation of tetraphenylhydrazine (rate constant $2k_1'$) and the C–N dimer (rate constant $2k_1''$)



(6-1)

In hydrocarbons $k_1''/k_1' = 1.4$.[100]

The values of $k_1 = k_1' + k_1''$ for $(C_6H_5)_2N^{\bullet}$ and other are listed in Table 19. At elevated temperatures A is in equilibrium with $(C_6H_5)_2N^{\bullet}$. A complex series of reactions takes place in the system: B reacts with $(C_6H_5)_2N^{\bullet}$ to yield $(C_6H_5)_2NH$ plus Am• of *p*-semidine.[100] The latter radical undergoes further conversions to ultimately form oligomeric semidines.[100]

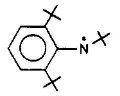
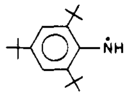
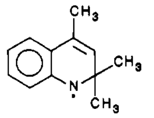
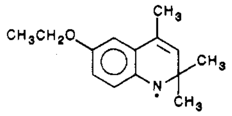
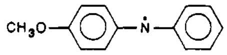
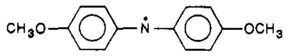
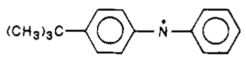
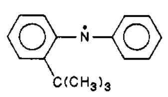
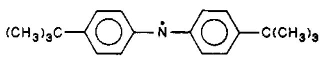
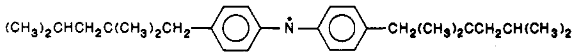
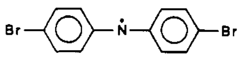
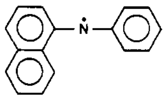
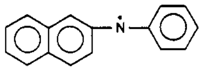
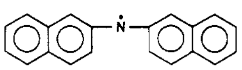
Recombination of $(C_6H_5)_2N^{\bullet}$ and other diarylaminyl radicals has a small activation energy (10–15 kJ/mol); nevertheless, recombination is an activation-controlled reaction.[100,122] The formation of a sterically strained transition state in reaction 6-1 of these radicals manifests itself in low preexponential factor of recombination A_1.[177] A Hammett relationship was found between log k_1 for diarylaminyl radicals and σ constants of the substituents.[177]

Oxidation of *N*-phenyl-2-naphthylamine and photolysis of 1,4-di(2-naphthyl)-2-tetrazine yield the 2-naphthylphenylaminyl radical[180]

Then C–C and C–N dimers are formed as a result of recombination of these Am•.[180]

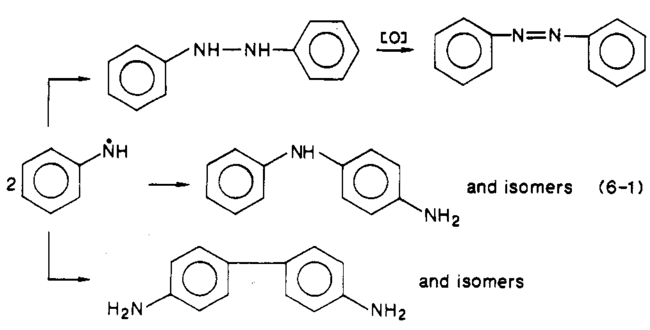
Sterically unhindered neutral Am• recombine predominantly to hydrazines. The decay of phenylaminyl radical in water (pH 9.8) obeyed second-order kinetics (Table 19). The measured $2k_1$ (Table 19) is higher than the theoretical value $k_{diff} = 1.2 \times 10^9$ $M^{-1} \cdot s^{-1}$ calculated

TABLE 19. Rate Constants for Recombination 6-1 of Aminyl Radicals at Room Temperature[a]

aminyl radical	solvent	k_1, $M^{-1} \cdot s^{-1}$	ref
$C_6H_5\dot{N}H$	water, pH 9.8	2.0×10^9	174
	methylcyclohexane[b]	0.2	175
	di-*tert*-butyl peroxide	4.5	176
$(C_6H_5)_2N^{\bullet}$	cyclohexane	2.0×10^7	100
	toluene	1.5×10^7	122
	c	2.7×10^7	177
	*n*-hexane	4.0×10^7	178
	benzene	2.0×10^7	178
	*n*-hexane	3.0×10^7	178, 179
	benzene	2.5×10^6	178, 179
	*c*	3.0×10^6	177
	*c*	1.1×10^6	177
	*c*	5.5×10^6	177
	*c*	5.5×10^4	177
	*c*	1.7×10^6	177
	*c*	1.2×10^6	177
	*c*	3.0×10^7	177
	*c*	3.1×10^8	177
	*c*	1.9×10^8	177
	*c*	2.2×10^8	177

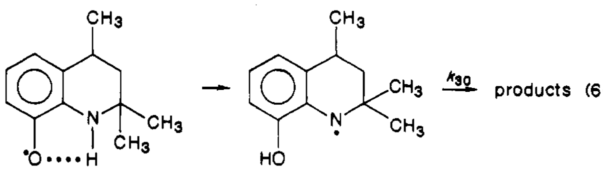
[a] Mean determination error is ca 15%. [b] At 259.2 K. [c] Solvent is toluene/di-*tert*-butyl peroxide (85:15 (v/v)).

with eq 6-6 and is apparently slightly overestimated. There is no question that recombination of phenylaminyl radicals is a diffusion-controlled reaction.[174] Recombination yields the following products:[174]



(6-1)

A somewhat unusual route of decay of the phenylaminyl radical was observed in ref 181, where the aromatic radicals obtained from 2,2,4-trimethyl-1,2,3,4-tetrahydro-8-hydroxyquinoline, an effective InH, were studied by ESR and flash photolysis techniques. Under photolysis this compound produces an $ArO^{\bullet}$, which isomerizes to $Am^{\bullet}$



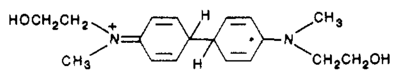
(6-30)

The $Am^{\bullet}$ decays slowly into unidentified products. It has been determined that $k_{30} = 4.0 \pm 0.5$ s^{-1} (*n*-hexane,

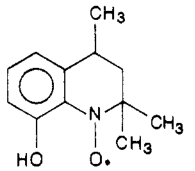
TABLE 20. Rate Constants of Aromatic Amine Radical Cation Decay by Second-Order Reaction at Room Temperature[a]

starting amine	solvent	k, $M^{-1}\cdot s^{-1}$	reaction	ref
$C_6H_5NH_2$	water, pH 2.0	4.9×10^5	6-31	174
$C_6H_5NH_2$	water, pH 2.0	8.2×10^8	6-32	174
$C_6H_5NH_2$	water, pH 3.25	2.0×10^8	6-32	111
$C_6H_5NH_2$	water, pH 7.0	8.0×10^8	6-33	21
N-(β-hydroxyethyl)-*N*-methylaniline	water, pH 3.5	1.4×10^6	3-31	183
dimer of *N*-(β-hydroxyethyl)-*N*-methylaniline[b]	water, pH 3.5	2.0×10^5	6-32	183
$(C_6H_5)_3N$	acetonitrile	1.1×10^3	6-32	184
$(p\text{-}C_2H_5C_6H_4)_3N$	acetonitrile	1.1×10^1	6-32	184

[a] Mean determination error is ca. 15%. [b] The corresponding radical cation has the structure



298 K). Atmospheric oxygen promotes decay of the Am•; the ESR spectrum of the product of such a decay, a nitroxyl radical of structure[181]



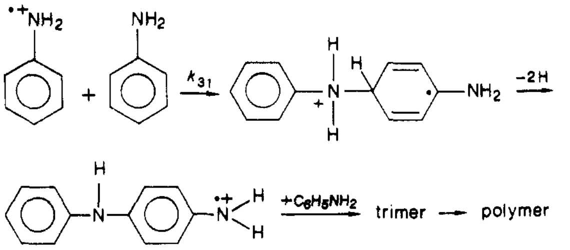
was recorded.

2. *Radical Cations*

The decay of radical cations of aromatic amines is a complex process often involving a cation's interaction with the starting AmH

$$RNH_2^{\bullet +} + RNH_2 \xrightarrow{k_{31}} \text{products} \qquad (6\text{-}31)$$

The main product of aniline oxidation in acidic aqueous solutions is a polymer that is formed via the reactions[174]



(6-31)

The k_{31} values for $C_6H_5NH_2^{\bullet +}$ and other radicals are listed in Table 20. The rate constant of reaction 6-32

$$RNH_2^{\bullet +} + RNH_2^{\bullet +} \xrightarrow{2k_{32}} \text{products} \qquad (6\text{-}32)$$

was determined in an investigation of the decay of $C_6H_5NH_2^{\bullet +}$ in acid solutions using the flash photolysis technique, i.e., under relatively high radical concentrations.[174] The value of $2k_{32}$ determined in ref 174 (Table 20) is greater than k_{diff} (eq 6-8) and is apparently somewhat overestimated. The k_{32} obtained in ref 111 (Table 20) appears to be more correct. Thus the aniline radical cations generated in acid media participate in two reactions, reactions 6-31 and 6-32. The decay of $C_6H_5NH_2^{\bullet +}$ at pH 7.0, equal to the pK_a of $C_6H_5NH_2^{\bullet +}$ (section VII), obviously follows the reaction[21]

$$C_6H_5NH_2^{\bullet +} + C_6H_5NH^{\bullet} \xrightarrow{k_{33}} \text{products} \quad (6\text{-}33)$$

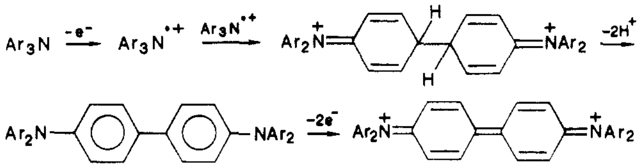
(See Table 20.)

The decay of the radical cation of *N,N'*-diphenyl-*p*-phenylenediamine in acid EPA solutions at room temperature and lower temperatures takes the route 6-32 and is a dismutation reaction.[182]

The radical cation of *N*-(β-hydroxyethyl)-*N*-methylaniline decays in water by reaction with the starting amine (Table 20) and produces the dimer $D^{\bullet +}$.[183] In deoxygenated solutions $D^{\bullet +}$ participate in dismutation[183]

$$D^{\bullet +} + D^{\bullet +} \xrightarrow{2k_{32}} D + D^{2+} \qquad (6\text{-}32)$$

By oxidation of triarylamines containing no substituents in the para position one obtains short-lived radical cations that undergo dimerization to tetraarylbenzidine.[170] Under the effect of an oxidizing agent (an electrode potential, a copper(II) salt, or some other agent), tetrarylbenzidine oxidizes further to dication[170,184]



(6-33)

Tris-para-substituted triarylaminyl radical cations with electron-accepting substituents are also unstable and go on to react with each other by forming ortho combinations.[170]

G. 1,3-Dioxo-2-arylindan-2-yl Radicals

The rate, equilibrium, and thermodynamic parameters for reaction 6-1 involving 1,3-dioxo-2-arylindan-2-yl radicals (A•) are presented in Table 21. Structural formulas of these radicals (12–25) are given in Chart 1.

$$A^{\bullet} + A^{\bullet} \underset{2k_{-1}}{\overset{2k_1}{\rightleftarrows}} D, \quad \boldsymbol{K}_1 = \boldsymbol{k}_{-1}/\boldsymbol{k}_1 \qquad (6\text{-}1)$$

In the absence of other active radicals, equilibrium systems such as C–C dimer/A• are stable in hydrocarbon solvents.[108,185] The kinetics of radical recombination (dimer dissociation) have been studied by flash photolysis in ref 108 and 185–187. Investigation of recombination of A• **12–19** in solvents of different viscosity has shown that for A• **12–15** reaction 6-1 is diffusion-controlled at $\eta \gtrsim 5$ cP and activated at $\eta \lesssim 2$ cP.[185] Recombination of A• **16–18** is diffusion-limited over the entire viscosity range ($0.6 \leq \eta \leq 18.4$ cP).[185] The reactivity anisotropy of A• **12–15**, **17**, and **18** is completely averaged as the reactants undergo translation or rotation during their encounter time.

Recombination of A• **16**, which contains bulkier phenyl substituents, is pseudodiffusion-controlled at $\eta \gtrsim 0.6$ cP.[31] Recombination of A• **19** is activation-controlled, its rate not depending on η, and $\boldsymbol{H}^{\ddagger}_1 > B$; cf. eq 6-9.[185]

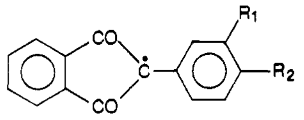
Consider now the relationship between the structure and reactivity for radicals **12–19** in chlorobenzene (Table 21). The $\boldsymbol{K}_1$ values for radicals of similar structure (**12–18**) are strongly dependent upon the nature of the substituent in the phenyl fragment (Table 21). The steric hindrances to recombination of A• **12–18** (or dissociation of the corresponding dimers in nonviscous solvents) may be considered to be roughly the same, and differences in $\boldsymbol{K}_1$ may be attributed to

TABLE 21. Rate, Equilibrium, and Thermodynamic Data for Reaction 6-1 Involving 1,3-Dioxo-2-arylindan-2-yl Radicals at 293 K[a]

radical	$10^{-7}k_1$, $M^{-1}{\cdot}s^{-1}$	$10k_{-1}$, s^{-1}	10^9K_1, M	$\Delta H^{\ddagger}_1$	$\Delta H^{\ddagger}_{-1}$	ΔH°	$-\Delta S^{\ddagger}_1$	$\Delta S^{\ddagger}_{-1}$	ΔS°	ref
12	80	0.9	0.14	10	84	75	42	8	50	*b*
13	50	2.5	0.5	15	82	67	25	21	46	*b*
14	30	2.7	0.9	14	94	80	33	54	88	*b*
15	35	1.75	0.5	15	85	70	29	17	46	*b*
16	45	0.015	0.0035	105	62	51	42	−105	−63	*b*
17	180			12			25			*b*
18	250			13			21			*b*
19	0.055	90	17000	13	76	64	93	29	122	*b*
20	40	0.044	1.1	−5	74	79	18	8	97	*c*
21	34	0.065	1.9	−3	74	77	84	8	97	*c*
22	50	0.11	2.2	−4	74	78	88	13	101	*c*
23	60	0.07	1.2	0	79	78	71	25	92	*c*
24	20	0.0012	0.060	−1	84	85	92	4	92	*c*
25	10	0.0003	0.030	−2	84	86	88	−4	92	*c*

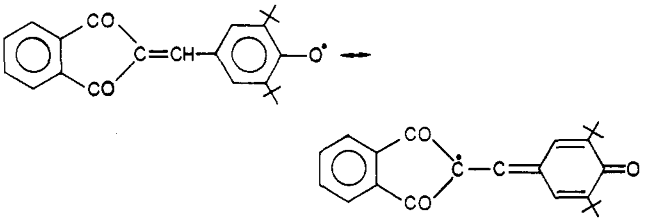
[a] ΔH is in kJ/mol; ΔS is in J/(mol·K). Mean errors are K_1, 10%; k_1, 15%; k_{-1}, 15%; ΔH°, $\Delta H^{\ddagger}_1$, $\Delta H^{\ddagger}_{-1}$, ±2 kJ/mol; ΔS°, $\Delta S^{\ddagger}_1$, $\Delta S^{\ddagger}_{-1}$, ±8 J/(mol·K). [b] Reference 185. [c] Reference 186.

CHART I

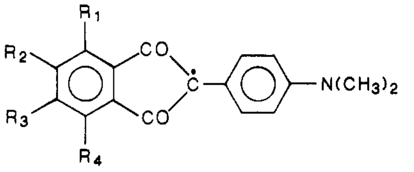


12-18

12, R_1 = H; R_2 = $N(CH_3)_2$
13, R_1 = H; R_2 = $N(C_2H_5)_2$
14, R_1 = H; R_2 = $N(n\text{-}C_3H_7)_2$
15, R_1 = H; R_2 = $N(n\text{-}C_4H_9)_2$
16, R_1 = H; R_2 = NPh_2
17, R_1 = R_2 = OCH_3
18, R_1 = Br; R_2 = $N(CH_3)_2$



19



20-25

20, R_1 = Cl; R_2 = R_3 = R_4 = H
21, R_2 = Cl; R_1 = R_3 = R_4 = H
22, R_2 = Br; R_1 = R_3 = R_4 = H
23, R_2 = I; R_1 = R_3 = R_4 = H
24, R_2 = $N(CH_3)_2$; R_1 = R_3 = R_4 = H
25, R_1 = R_4 = Ph; R_2 = R_3 = H

electronic effects. However, in dissociation of the C–C dimer or related structure A• **19** equilibrium 6-1 is shifted toward the A• side, as compared with A• **12–18** (Table 21). The reason is that dissociation of the dimer of A• **19** results in relatively stable radicals where the unpaired electron is delocalized along the developed system of π bonds, including the p orbital of the oxygen atom. Introduction of a bromine atom at the ortho position with respect to the dimethylamino group of 1,2-bis[[4-(dimethylamino)phenyl]phthaloyl]ethane (dimer of **18**) results in complete displacement of the equilibrium to the dimer formation side. The bromine atom turns the dimethylamino group out of the plane of the ring, thereby disrupting the conjugation of the lone electron pair of the nitrogen atom with the dioxophenylindanyl fragment, and as consequence considerably reduces the degree of delocalization of the unpaired electron. Similarly, due to the mutual repulsion of hydrogens in the triphenylaminyl group of A• **16**, the diphenylamino group is deconjugated from the phenyl ring bonded to the trivalent carbon. Radical **16** happens to be more reactive than any one of the A• **12–15**—its recombination is molecular mobility limited up to η = 0.6 cP.[31,185]

The k_1 values for recombination of dioxoarylindanyl radicals in a viscous solvent ($\eta \gtrsim 5$ cP) decrease in the series A• **12**, **13**, **14**, **15**, **16**.[31,185] As for ArO• (cf. section VI.C), this is due to the increasing volume and van der Waals surface of radicals in the series, while the reaction spot surface area remains the same.

Comparison of K_1 and ΔH° for reaction 6-1 of ArO• (Table 10), triphenylmethyl radicals,[32] and A• (Table 21) shows that the dimers of the last radicals dissociate to a much smaller degree and are characterized by significant bond dissociation energies.

H. Solvent Effect on Reversible Recombination Kinetics

In the previous sections of this chapter we have shown that solvent viscosity has in many instances a decisive effect on the rates of fast self-reactions between inhibitor radicals. At the same time one may not disgard the possible formation of solvation complexes with the solvent (S).

$$R^\bullet + S \rightleftarrows R_S^\bullet \qquad (6\text{-}34)$$

In the literature there has been mention of the effect of the so-called "specific" solvation (complexing with the solvent) and "nonspecific" solvation on radical reactivity; see, e.g., ref 11 and 188. In this section we summarize the available information concerning the effect of solvent on the rates of reversible recombination and disproportionation of aromatic radicals

$$R^\bullet + R^\bullet \underset{2k_{-1}}{\overset{2k_1}{\rightleftarrows}} D \qquad (6\text{-}1)$$

$$RH^\bullet + RH^\bullet \xrightarrow{2k_1} R + RH_2 \qquad (6\text{-}1)$$

derived chiefly by fast reaction technique. The kinetic data are presented in Tables 10–21 and may be also

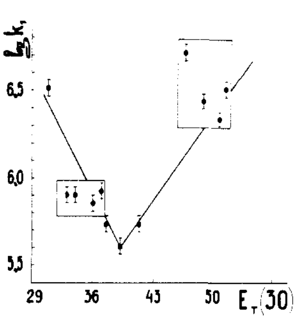


Figure 3. log $\boldsymbol{k}_1$ vs. $E_T(30)$ relationship for recombination of 2,6-di-*tert*-butyl-4-(β-phthalylvinyl)phenoxyl radical.[189]

found in ref 32, 35, and 36.

1. Rates and Equilibria in Self-Reactions

Obviously, the solvent effect on the rates of activated and molecular mobility limited reactions should be analyzed in different ways (cf. section B of this chapter).

If recombination is molecular mobility limited (is diffusion- or pseudodiffusion-controlled), one may expect that

$$\boldsymbol{K}_1 \eta \varphi = \text{const} \tag{6-35}$$

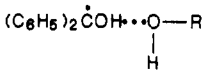
i.e., is independent of solvent at constant pressure and temperature. (φ is microfriction factor, see section VI.B1.) Equation 6-35 is satisfied to a good accuracy by 2,6-di-*tert*-butyl-, 2,6-di-*tert*-butyl-4-methyl-, and 2,6-dimethoxyphenoxyl radicals.[31] 2,6-Di-*tert*-butyl-substituted phenoxyl radicals are incapable of forming solvation complexes $R_S^{\bullet}$ through reaction with monovalent oxygen because of steric hindrances.[136] For nonsubstituted phenoxyls and the simplest alkyl-substituted phenoxyls there also has been no evidence to support the existence of $R_S^{\bullet}$. For phenyl-substituted aroxyls and a number of other phenyl-substituted aromatic radicals the authors of ref 106 and 189 found empirical relationships—the more or less clearly defined dependences on the Dimroth–Reichardt solvent parameter $E_T(30)$; see Figure 3. The situation is somewhat amended if we take into account the viscosity and "microfriction" factors; still eq 6-35 will not be obeyed as closely as it is for 2,6-di-*tert*-butyl-substituted phenoxyl radicals. In this case we have to describe it as "specific" solvation of radical by the solvent (eq 6-34). Phenyl-substituted aroxyl radicals are known to possess a developed system of conjugated bonds and low steric hindrances around the monovalent oxygen (section VI.C), thereby promoting formation of $R_S^{\bullet}$ of different types. The existence of charge-transfer complexes between 2,4,6-triphenylphenoxyl radicals and molecules of different solvents has been experimentally demonstrated in ref 190. An attempt to find an explanation of the V-shaped $\boldsymbol{k}_1$ vs. $E_T(30)$ curves has been made in ref 106. It was found that 2,6-diphenyl-4-methoxyphenoxyl and other phenyl-substituted aromatic radicals recombined most slowly in chloroform, whereas 2,4,6-triphenylphenoxyl radicals recombined most slowly in pyridine and chloroform.[106] There have been conjectures regarding the possible formation of π–σ complexes between chloroform and 2,6-diphenyl-4R-phenoxyl radicals.[191] The 1,3-dioxo-4-[(diphenylamino)phenyl]indan-2-yl radicals A$^{\bullet}$ **16** (see section VI.G) recombine most slowly in solvents whose molecules also contain the group >CHCl and probably form similar π–σ complexes with this radical.[189]

In many cases radical solvation involves participation of free-valence atoms or, in other words, the sites with the highest unpaired electron density.[188] These atoms also bind the radicals in a dimer; therefore, recombination may be expected to cause desolvation. In experiments on high-pressure recombination of radical A$^{\bullet}$ **16** it has been shown that radical recombination in the solvent cage does cause desolvation.[192]

The energy required for desolvation may be so high that a reaction which is (pseudo)diffusion-controlled in a nonsolvating solvent will be activated in a solvating medium of identical viscosity, and $\Delta \boldsymbol{H}^{\ddagger}_1$ will be much greater than B (eq 6-9). Indeed it has been measured in chloroform that $\Delta \boldsymbol{H}^{\ddagger}_1 = 3.5B$.[189]

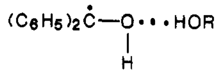
Thus radical solvation by a solvent may change the reaction control from (pseudo)diffusion to activation and thereby inhibit it. This is the reason behind the slowest recombination of A$^{\bullet}$ **16**, ArO$^{\bullet}$ **7**, and ArO$^{\bullet}$ **9** in chloroform than in any other nonviscous solvent.[32,189]

Solvation of ketyl radicals of benzophenone with 1-propanol or ethanol is responsible for the fact that their recombination, which is diffusion-controlled in water, becomes activated in alcohol solutions.[166] In ref 166 there are arguments favoring the solvate structure i rather than ii.



$(C_6H_5)_2\dot{C}OH\cdots\underset{H}{\underset{|}{O}}-R$

i



$(C_6H_5)_2\dot{C}-\underset{H}{\underset{|}{O}}\cdots HOR$

ii

It may be speculated that radicals might also take part in the (pseudo)diffusion-controlled recombination as solvation complexes $R_S^{\bullet}$. In some cases it has been possible to find experimental support for this logical assumption.[166]

On the basis of $\boldsymbol{K}_1$ values for reversible recombination 6-1 of phenyl-substituted aroxyls, it may be concluded that radical solvation increases the more polar the aprotic solvent, since the corresponding $\boldsymbol{K}_1$ apparently increase.[106]

V-Shaped $\boldsymbol{k}_1$ vs. $E_T(30)$ relationships have also been recorded for activated recombination of 2,6-diphenyl-4-(diphenylmethyl)-, 2,4,6-triphenyl-, and 2,6-di-*tert*-butyl-4-(β-phthalylvinyl)phenoxyl radicals.[106,189] In these cases $\boldsymbol{k}_1$ varies over a broader range than in the case of radicals whose recombination is limited by molecular mobility, which is consistent with the general observation that solvent affects more the slow reactions than the fast reactions.[106]

The effect of the composition of binary solvent mixtures on the recombination rate of a number of ArO$^{\bullet}$, A$^{\bullet}$ **16**, and 2,6-diphenyl-4-hydroxyphenoxyl radicals has been studied.[106,193,194] In near-ideal solvent mixtures one observes a monotonous variation of the self-reaction rate with mixture composition.[106] It has been found that the relationships between the self-reaction rate and composition of strongly nonideal binary mixtures have extrema that are due to changes in solvent structure.[106,193,194] Correlations between the product $\boldsymbol{k}_1\eta$ and mixing heat have been established.[194]

2. Dissociation Kinetics

Solvent has a considerable effect on rates of dissociation of aromatic radical dimers, too.[32] The following general behavior has been discovered: the rate of dissociation of the majority of ArO• and A• dimers increases with solvent polarity.[106,189] Therefore, the dipole moment of the transition state of reaction 6-(−1) is higher than that of the starting dimer D. The investigated examples include dimers of 2,6-diphenyl-4-methoxyphenoxyl radical, ArO• **7** (see section VI.C), and A• **12** (see section VI.G). (Dissociation of 2,6-diphenyl-4-methoxyphenoxyl radical dimer is limited by diffusion; what we mean, therefore, is the effect of the dielectric properties of solvent on dimer dissociation rate in the solvent cage.) Only the "nonspecific" solvation affects the kinetics of dissociation of the A• **12** dimer, as well as its recombination rate and equilibrium parameters. For dissociation of this dimer it has been found that log $\boldsymbol{k}_{-1}$ is a linear function of the Kirkwood parameter $(\epsilon - 1)/(2\epsilon + 1)$; $\boldsymbol{k}_1$ weakly depends on the solvent. Isokinetic (for reaction 6-(−1)) and isoequilibrium relationships with characteristic temperatures β = 408 K and $\beta°$ = 651 K have been obtained. For dissociation of this dimer, $\delta_M \ln \boldsymbol{k}_{-1} = \gamma\delta_M \ln \boldsymbol{K}_1$, where δ_M is the Leffler–Grunwald operator. The high γ (γ = 0.8) and the increase of the dipole moment of transition state of reaction 6-(−1) over that of D mean that the transition state is more like a radical pair than a dimer.[189]

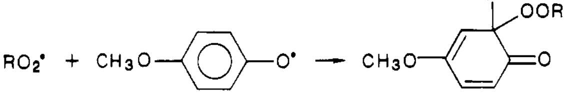
I. Reactions of Aroxyl and Aminyl Radicals with Peroxyl Radicals

The In• radicals formed via reaction 7 in the course of inhibited oxidation of RH go on to react with $RO_2^•$, reaction 8; see the IHO scheme in section II.A. The quasi-steady concentration of In• depends on whether the reaction is fast or not. If the In• radicals participate in the chain propagation process via reactions with RH and ROOH, the rate of reaction 8 will determine the rate of inhibited oxidation of RH (see section IX).

The authors of ref 18 estimated k_8 for a number of ArO• by studying the inhibited oxidation of 9,10-dihydroanthracene as a function of [RH], [InH], and v_i at 333 K in chlorobenzene with 2,2,3,3-tetraphenylbutane as the initiator. The following k_8 values were obtained:

X in p-XC_6H_4OH	OCH_3	C_6H_5	CH_3	$C(CH_3)_3$	H
$k_8 \times 10^{-8}$, $M^{-1}{\cdot}s^{-1}$	7.8	3.9	2.4	1.1	1.6

Reaction 8 is seen to be fast, the k_8 values varying between 10^8 and 10^9 $M^{-1}{\cdot}s^{-1}$; depending on the substituent. The products of this reaction have not been studied thoroughly, but an analogy with 2,4,6-trisubstituted phenoxyl radicals (see below), it may be assumed that the process involves addition of $RO_2^•$ to the phenyl ring at the ortho or para position in relation to monovalent oxygen



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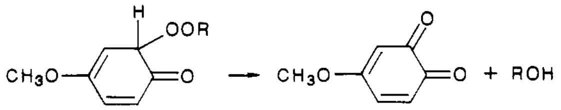
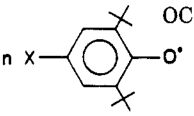
followed by formation of alochol and quinone



(6-36)

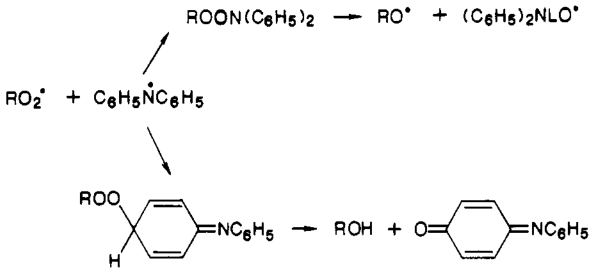
Phenoxyl radicals substituted in the 2, 4, and 6 positions decay slowly (see section VI.C) and, under the standard conditions of RH oxidation, react exclusvely with $RO_2^•$. As a result quinolide peroxides are formed that are stable at moderate temperatures (T < 350 K) but decompose at higher temperatures to free radicals.[43] Peroxyls may couple ArO• radicals both at para and ortho positions. The ortho/para ratio depends on the type of substituent. For instance, addition of $RO_2^•$ to 2,4,6-tri-*tert*-butylphenoxyl is 8 times faster at the para position than at the ortho position, whereas the ortho position is preferred in the addition to 2-methyl-4,6-di-*tert*-butylphenoxyl.[43] The k_8 values of $RO_2^•$ reactions with 2,4,6-trisubstituted phenoxyl radicals have been measured in ref 83. ESR has been used to study the ArO• buildup rate in benzene in the presence of the corresponding ArOH, with azobisisobutyronitrile as the source of cyanisopropyl radicals. In such experiments the ArO• concentrations passed through a maximum, such that $[ArO^•]_{max} = k_7k_8^{-1}[ArOH]$. Therefore, the ratio k_7/k_8 could be calculated according to the $[ArO^•]_{max}$ vs. [ArOH] relationship and k_8 could be determined by using literature values of k_7 (benzene, 333 K)



X in	OCH_3	C_6H_5	$C(CH_3)_3$	Cl	CN	$O(O)C_6H_5$
$k_8 \times 10^{-8}$, $M^{-1}{\cdot}s^{-1}$	7.2	6.0	3.2	1.7	2.7	1.9

It is seen that, as for most ArO•, the values of k_8 are within 10^7–10^8 $M^{-1}{\cdot}s^{-1}$. The constant k_8 tends to decrease as the electron-donor substituents are replaced with electron-acceptor ones, which indicates that there is a relationship between the reaction 8 rate of ArO• and $RO_2^•$ and the electron density at the para and ortho positions of the phenyl ring of ArO•. The activation energy varies widely, from −33 to +10 kJ/mol, but symbatically varies the preexponential factor A_8 from 10^3 to 10^{10} $M^{-1}{\cdot}s^{-1}$; i.e., there is an apparent compensation effect.

Aminyl radicals react with $RO_2^•$ by two routes to form N–O and C–O bonds, respectively.[195] Decomposition of the resultant unstable peroxide yields a nitroxyl radical in the first case and an imino quinone in the second



(8a)

(8b)

In the case of diphenylaminyl radical the ratio of the rates of reactions 8a and 8b will depend on the structure of $RO_2^•$: for secondary $RO_2^•$ the yield of nitroxyl radicals (reaction 8a) is 0.11–0.19, whereas for tertiary $RO_2^•$ it is 0.20–0.33.[195] The rate constant of reaction between radicals $RO_2^•$ and $(C_6H_5)_2N^•$ has been measured by using the flash photolysis technique in cyclohexane at room temperature.[100]

The corresponding $k_8 \simeq 6 \times 10^8$ $M^{-1}{\cdot}s^{-1}$ ($RO_2^•$ is cyclohexylperoxyl radical).[100]

Associated with the reaction between $RO_2^•$ and Am• (reaction 8) is the phenomenon of chemiluminescence of amine-inhibited oxidation of polar organic molecules.[196] Under liquid-phase oxidation, chemiluminescence arises in the disproportionation of secondary (primary) $RO_2^{\bullet}$ in which a triplet-excited carbonyl compound is formed[197]

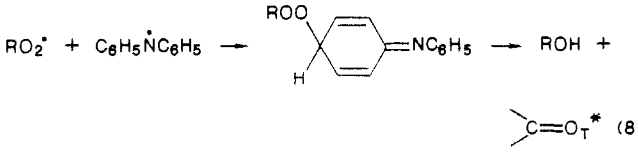
$$2RO_2^{\bullet} \rightarrow ROOOOR \rightarrow {>}C{=}O^{*}_{T} + O_2 + ROH \quad (6)$$

$$>C{=}O^{*}_{T} \rightarrow {>}C{=}O + h\nu \quad (6\text{-}37)$$

Upon addition of an AmH the concentration of $RO_2^{\bullet}$ is decreased, and thereby the $RO_2^{\bullet}$ disproportionation rate and chemiluminescence intensity are reduced, too. After all the AmH has been consumed in the oxidizing RH (v_i = const) chemiluminescence returns to its original level. On addition of primary and secondary AmH to chlorobenzene in the presence of alcohols, ethers, esters, or even water, the chemiluminescence increased 1.5–7-fold. The luminescence is due to reaction 8, $RO_2^{\bullet}$ + $Am^{\bullet}$, since additions of ArOH quench the luminescence in these systems. The quenching effect of ArOH is due to the exchange reaction

$$ArOH + Am^{\bullet} \rightarrow ArO^{\bullet} + AmH \quad (15)$$

whereby the $RO_2^{\bullet}$ decay not via reaction with $Am^{\bullet}$, which causes chemiluminescence, but with $ArO^{\bullet}$, which does not cause chemiluminescence. After all the ArOH has been consumed the chemiluminescence is enhanced again, since when only AmH is present $RO_2^{\bullet}$ reacts with $Am^{\bullet}$ (reaction 8). Important for the formation of the electronically excited product is the polar environment; there is no luminescence when there is no such environment (e.g., in a RH). Probably, quinone imine is the product



(8)

which causes luminescence.[39]

VII. Acid–Base Equilibrium Reactions of Inhibitor Radicals

Many free inhibitor radicals participate in acid–base equilibrium reactions.[198] The reactivity of the acidic and basic forms of free radicals is substantially different. Therefore, by varying the acidity (basicity) of the medium or the solution pH, one may directionally control the radical reactivity. Using strongly acidic or basic solutions, it is sometimes possible to extend the lifetime, or even stabilize, the otherwise short-lived radicals. For example, relatively high concentrations of quinone radical anions ($Q^{\bullet -}$) may be obtained in strongly basic solvent.[162]

The acid–base equilibria

$$R^{\bullet} + H^{+} \rightleftharpoons RH^{\bullet +} \quad (7\text{-}1)$$

$$R^{\bullet -} + H^{+} \rightleftharpoons RH^{\bullet} \quad (7\text{-}2)$$

are usually established sooner than radical decay in bimolecular reactions. The equilibrium constants for reactions 7-1 and 7-2 were determined by flash photolysis, pulse radiolysis, and ESR techniques. To obtain the pK_a of radicals (Table 22) one plots some selected parameter, e.g., optical absorption at maximum, against the pH of the aqueous solution.

TABLE 22. pK_a Values of Inhibitor Free Radicals Taking Part in Reactions 7-1 and 7-2 in Water at Room Temperature

starting compd	pK_a	ref
1,4-benzoquinone[a]	4.1 ± 0.1	109
duroquinone[a]	5.1 ± 0.2	109
2-methyl-1,4-benzoquinone[a]	4.45 ± 0.1	109
1,4-naphthoquinone[a]	4.1 ± 0.2	143
9,10-anthraquinone[a]	5.3 ± 0.2	143
9,10-anthraquinone-2-sulfonate[a]	3.9 ± 0.2	161
9,10-anthraquinone-2-disulfonate[a]	3.2 ± 0.1	114
aniline[b]	7.0 ± 0.1	21
diphenylamine[b]	4.2 ± 0.1	199, 200
p-phenylenediamine[b]	5.9 [illegible] 0.1	200
N,*N*-dimethyl-*p*-phenylenediamine[b]	6.1 ± 0.1	200
acetophenone[a]	9.9 ± 0.2	161
benzophenone[a]	9.2 ± 0.1	161
phenol[b]	−1.95 ± 0.1	201
o-cresol[b]	−1.8 ± 0.1	201
m-cresol[b]	−1.9 ± 0.1	201
p-cresol[b]	−1.7 ± 0.1	201
catechol[b]	−1.65 ± 0.1	201
catechol[a]	>7.0	202
resorcinol[b]	−1.45 ± 0.1	201
hydroquinone[b]	−0.77 ± 0.05	201

[a] Reaction 7-2. [b] Reaction 7-1.

The acid–base equilibrium reactions of semiquinone radicals have mostly been studied by pulsed radiolysis (Table 22). In ref 201, 203, and 204 equilibrium 7-1 has been investigated for aroxyl radical–aroxyl radical cation. It has been shown that in acid aqueous solutions (up to 12 M sulfuric acid) unsubstituted phenoxyl radicals are not protonated.[204] At the same time it was observed that the 2,4,6-triphenylphenoxyl radical and the corresponding radical cation were present in about equal concentrations in water–ethanol solution that contained 15 N sulfuric acid.[204] It has been demonstrated that four water molecules are required to remove the proton from the phenoxyl radical cation[203]

$$PhOH^{\bullet +} + 4H_2O \rightleftharpoons PhO^{\bullet} + H_9O_4^{+} \quad (7\text{-}1)$$

The ESR-measured pK_a values for various aroxyl radical cations are presented in Table 22. As expected, pK_a values increase with the electron-donor property of the substituent in the aroxyl radical.

Normally, neutral radicals decay in bimolecular reactions faster than the respective radical ions (section VI.D–F). Further, radical anions are more active reductants than the respective neutral radicals (see section VIII.E). These properties may be used to find the pK_a of radicals. Such radical titration techniques have been used to determine the dissociation constants of radicals that are difficult to obtain by spectrophotometric methods.

The rates of protonation of benzophenone and *p*-cyanoacetophenone radical anions were measured in ref 205 with the aid of the pulsed radiolysis technique. The radical anions decayed via reactions 7-2 and 7-3.

$$R^{\bullet -} + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RH^{\bullet} + OH^{-} \quad (7\text{-}3)$$

The following results have been obtained at room temperature: $k_2 \simeq 1.2 \times 10^{10}$ $M^{-1} \cdot s^{-1}$ and $k_3 \simeq 7.8 \times 10^{4}$ s^{-1} for benzophenone radical anion ($BP^{\bullet -}$) in water containing 2.5 M *tert*-butyl alcohol.[205] The rather high values $k_2 \simeq 10^{10}$ $M^{-1} \cdot s^{-1}$ and $k_{-3} = 5 \times 10^{9}$–10^{11} $M^{-1} \cdot s^{-1}$ indicate that the acid–base equilibrium is established very rapidly.

Linear correlations have been found between the pK_a of radicals and the Hammett and Taft constants,[28] redox potentials of ketones, aldehydes, and quinones (for ketyl and semiquinone radicals),[198,206] and the difference in the π-electronic energies of the acid and basic forms of conjugated radicals.[207] There is promise in the quantum-chemical calculation of radical affinity for proton (PA). In the absence of entropy and solvation effects, PA should be expected to correlate with the corresponding pK_a values.[208]

Dissociation constants of neutral radicals (radical cations; cf. Table 22) provide useful information for kinetic analysis of oxidation of organic compounds in water inhibited with phenol-, carbonyl-, or arylaminyl-based compounds.

Acid–base equilibrium reactions of radicals can also occur in nonpolar media. The authors of ref 39 came up with a fact very important for the theory of inhibited oxidation: in cyclohexane the diphenylaminyl radical is protonated by cumyl hydroperoxide

$$(C_6H_5)_2\dot{N} + ROOH \rightleftarrows (C_6H_5)_2\dot{N}H^+,RO_2^- \qquad (4\text{-}6)$$

VIII. Oxidation–Reduction Reactions of Inhibitor Radicals

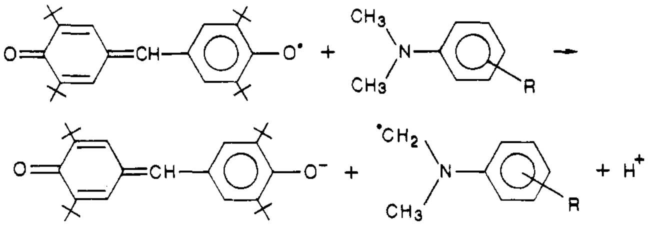
A. General Comments

In many cases free aromatic radicals are generated in solutions containing metal compounds, hydrogen donors, electron donors, and electron acceptors. Aromatic radicals can react with these agents. The reduction of aroxyl and aminyl radicals through abstraction of a hydrogen atom from a donor (hydrocarbon, hydroperoxide, a second inhibitor, etc.) has been discussed in sections III and IV. These reactions play an exclusive role in inhibited oxidation and largely control the inhibition effect. Apart from the inhibitors, to the solution of the oxidized compound are sometimes added transition-metal compounds that show an inhibiting or promoting (depending on conditions) effect on the oxidation process.[209] The combined effect of the inhibitor and transition-metal compound may be, first, a sharp deceleration of reaction followed by its promotion.[210] The complex series of reactions taking place in such a system normally includes reaction of the inhibitor radical with the metal compound.[210] Oxidation–reduction reactions of In• are important if inhibited oxidation takes place in the presence of metal compounds.

B. Reduction of Aroxyl Radicals

Aroxyl radicals oxidize those compounds which contain a nucleophilic heteroatom or a labile hydrogen atom.[18,105,211,212] Aroxyls are usually converted by the reaction to the corresponding phenolates (phenols) or cyclohexadienones.[18,105,211,212] There has been much discussion in the literature concerning the mechanism of such reactions, i.e., whether the mechanism involves electron or hydrogen transfer. In ref 213, the mechanism of the elementary reactions of the 2,6-diphenyl-4-stearoxyphenoxyl radical and galvinoxyl with C_1–C_4 aliphatic alcohols in the corresponding neat alcohols or benzene–alcohol mixtures has been identified by using the spin-trap technique. At ca. 373 K primary alcohols and *tert*-butyl alcohol were oxidized mainly via electron transfer reaction, while secondary alcohols were oxidized mainly via hydrogen abstraction reactions (the solvent was the corresponding alcohol). At 338 K the reaction is more specific: the reaction route that dominated at 373 K becomes the sole route at 338 K.

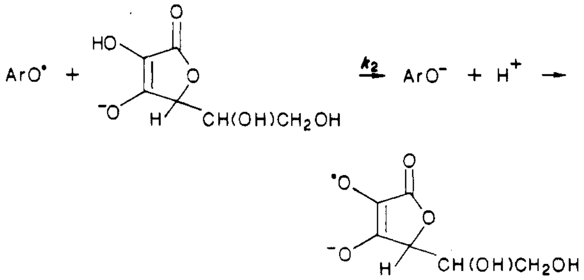
As shown in ref 212 stable aroxyls oxidize organic compounds having no labile hydrogens via electron transfer



(8-1)

Galvinoxyl and indophenoxyl are reduced to the respective phenolate anions through reaction with OH^- and the anion p-$CH_3C_6H_4NO_2^{\bullet -}$.[212]

Methoxy- and dimethoxyphenoxyl radicals oxidize ascorbate anion in water at pH 10–11[214]



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For this reaction, $k_2 \sim 10^8$–10^9 $M^{-1}{\cdot}s^{-1}$, and it may be used for near-quantitative removal of ArO• from an aqueous solution.[214]

Aroxyls exhibit not only electron-accepting but also electron-donor properties.[212,215-217] At low temperatures galvinoxyl has been found to from charge-transfer complexes (CTC) with a number of electron donors and acceptors.[216] It has been shown that the CTC are not always the intermediates of an electron-transfer reaction between galvinoxyl and donor.[216]

C. Oxidation–Reduction Reactions of Radicals with Metals and Metal Compounds

As strong reducing agents, alkali metals reduce indophenoxyl and galvinoxyl via the reaction[212]

$$ArO^{\bullet} + K \rightarrow ArO^- + K^+ \qquad (8\text{-}3)$$

Reactions of aromatic radicals with metal salts and complexes have been studied very thoroughly.[33,218] A radical may react with metal compound $M^{n+}L_M$ by different elementary routes. The following reactions are known for aromatic radicals:[33,131]

$$R^{\bullet} + M^{n+}L_m \rightarrow R^- + M^{(n+1)+}L_m \text{ (electron transfer)} \qquad (8\text{-}4a)$$

$$\rightarrow R^+ + M^{(n-1)+}L_m \text{ (electron transfer)} \qquad (8\text{-}4a')$$

$$\rightarrow {}^{\bullet}RM^{n+}L_{m-1} + L \text{ (ligand substitution)} \qquad (8\text{-}4b)$$

$$\rightarrow R^{\bullet}\cdots M^{n+}L_m \text{ (CTC formation)} \qquad (8\text{-}4c)$$

In the following we consider examples of such reactions and their principal distinguishing features.

2,4,6-Tri-*tert*-butylphenoxyl, galvinoxyl, and indophenoxyl are oxidized with Lewis acids MHal_n ($\mathrm{M} = \mathrm{Sb^V, Nb^V, Tl^{IV}, Sn^{IV}, Al^{III}}$; $\mathrm{Hal} = \mathrm{Cl^-, Br^-}$) as well as with $\mathrm{VOCl_3}$ and $\mathrm{AgClO_4}$ in various solvents

$$\mathrm{ArO^\bullet + M^{n+} \xrightarrow{k_4} ArO^+ + M^{(n-1)+}} \qquad (8\text{-}4a')$$

That reaction 8-4 really takes place has been convincingly demonstrated by ESR, NMR, spectrophotometric, and polarographic techniques.[212] The stability of the diamagnetic salts produced in reaction 8-4 depends on the radical structure, the type of oxidant, and the medium. It has been found that $k_4 \simeq 10^1$–$10^3\ \mathrm{M^{-1}\cdot s^{-1}}$ for different MHal_n.[212]

Galvinoxyl is oxidized with $\mathrm{RuCl_3}$ and $\mathrm{RhCl_3}$ and reduced with $\mathrm{Fe(acac)_2}$ and $\mathrm{Co(acac)_2}$ in 1-propanol.[219] 2,6-Diphenyl-4-stearoxyphenoxyl radical in the same solvent is oxidized with $\mathrm{RuCl_3}$ and $\mathrm{RhCl_3}$, the reaction having third-order kinetics (the first with respect to radical and second with respect to metal chloride).[219] It has been proposed that the reaction proceeds through an intermediate complex[219]

$$\mathrm{ArO^\bullet + MCl_3 \rightleftarrows ArO^\bullet\cdots MCl_3} \qquad (8\text{-}4c)$$

$$\mathrm{ArO^\bullet\cdots MCl_3 + MCl_3 \rightarrow products} \qquad (8\text{-}5)$$

The kinetics of oxidation of aromatic radicals with copper(II) compounds have been investigated in ref 131, 148, 220, and 221. Despite their relatively low redox potentials, copper(II) compounds are known to exhibit high reactivity toward free radicals. This fact has been established for alkyl radicals.[218] According to Kochi's hypothesis,[218] this high reactivity of copper(II) in relation to free alkyl radicals is due to formation of an intermediate organocopper compound; where the alkyl radicals do react, they are either oxidized or react with the solvent. Owing to the high lability of many copper(II) compounds, e.g., $\mathrm{Cu(H_2O)_6{}^{2+}}$, the radicals undergo oxidation in the inner sphere of the ion

$$\mathrm{Cu^{II}L_n + R^\bullet \overset{-L}{\rightleftarrows} Cu^{II}L_{n-1}R \rightarrow Cu^I + R^+} \qquad (8\text{-}6)$$

Analysis of the data for oxidation of aroxyl and semiquinone radicals shows that Kochi's hypothesis presents a good tool for their description, and it may be safely concluded that oxidation follows reaction 8-6. Moreover, in some cases it is possible to interrupt the reaction at the labile complex formation step (see section VIII.D).

Kinetic and activation parameters of reaction 8-7 have been obtained for oxidation of phenyl-substituted *p*-benzosemiquinone radicals ($\mathrm{QH^\bullet}$) with acetylacetonate or benzoylacetonate of copper(II) (Table 23)[221]

$$\mathrm{QH^\bullet + Cu^{II} \xrightarrow[AcOH]{k_7} Q + Cu^I + H^+} \qquad (8\text{-}7)$$

Reaction 8-7 takes place only where there is acid present, which facilitates replacement of ligand with radical.[221]

It is important that the semiquinone oxidation rate decreases as the oxidative potential of the radical, reflected by the parameter $-E_{1/2}$ (Table 23), increases.

TABLE 23. Rate Constants and Enthalpies of Activation of Reaction 8-7 for Ortho-Substituted 4-Hydroxyphenoxyl Radicals and Copper(II) Benzoylacetonate and Half-Wave Potentials of Reduction of Starting Quinones at 293 K[a]

subst in radical	$k_7 \times 10^{-5}$,[b] $\mathrm{M^{-1}\cdot s^{-1}}$	$\Delta H^{\ddagger}_7$,[c] kJ/mol	$-E_{1/2}$,[d] V
2,6-diphenyl-3,5-dichloro	1.1	40	0.10
2,6-diphenyl-3-chloro	4.4	34	0.15
2-phenyl	2.3	38	0.18
2-(3-chlorophenyl)	2.9	38	0.19
2-(4-chlorophenyl)	2.8	36	0.20
2,6-diphenyl	10	32	0.21
2-*tert*-butyl-6-phenyl	2.3	38	≥0.30

[a] Reference 221. [b] Determination error is 15%. [c] Determination error is ±2 kJ/mol. [d] Data of ref 222.

Addition of an electron-acceptor substituent, chlorine atom, to the meta position relative to the monovalent oxygen results in increased $-E_{1/2}$ and decreased k_7 (Table 23).

A strong donor, the radical anion of the sodium salt of 2-sulfo-9,10-anthraquinone, is rapidly oxidized with copper(II) perchlorate in water and water–glycerol mixtures: in viscous ($\eta \gtrsim 10$ cP) solvents the reaction is a pseudodiffusion one[220] (cf. section VI.B). Similarly, ketyl radical of benzophenone, also a strong donor, is rapidly oxidized with copper acetate in acetic acid; $k_4 = (4.5 \pm 0.2) \times 10^6\ \mathrm{M^{-1}\cdot s^{-1}}$ has been determined at room temperature.[33] Another strong electron donor is the 3-hydroxynaphthoxy-2-yl radical, which is also quickly oxidized with the chloride, sulfate, and acetate salts of copper(II) at room temperature in water (pH 6.8): $k_4 = (3.2 \pm 0.6) \times 10^6\ \mathrm{M^{-1}\cdot s^{-1}}$ for all of the above-mentioned salts.[33]

The chloranyl radical anion is oxidized with copper(II) chloride in a 9:1 (v/v) water–1-propanol mixture: $k_4 = (1.0 \pm 0.1) \times 10^9\ \mathrm{M^{-1}\cdot s^{-1}}$ at room temperature.[33]

Thus, in water or acetic acid in the form of labile aquo complexes or acetates copper(II) compounds oxidize, in one step, those radicals that possess sufficiently high electron-donor properties. It is virtually impossible to detect the intermediate complex $\mathrm{Cu^{II}L_{n-1}R}$ (cf. eq 8-6) since it is always present in very low concentrations.

While investigating the absorption spectra and decay kinetics of the 2,6-diphenyl-4-hydroxyphenoxyl radical ($\mathrm{QH^\bullet}$) in acetonitrile, the authors of ref 148 observed promotion of $\mathrm{QH^\bullet}$ decay when a solution of $\mathrm{Cu(acac)_2}$ was added in increasing concentrations and the symbatic building of the second intermediate—the complex.

$$\mathrm{QH^\bullet + Cu^{II} \rightleftarrows Q^{\bullet -}Cu^{II} + H^+} \qquad (8\text{-}8)$$

Addition of acetic acid ($C \gtrsim 5 \times 10^{-3}$ M) to solutions shifts equilibrium 8-8 to the left; this is accompanied by oxidation 8-7 of $\mathrm{QH^\bullet}$ with divalent copper.

The $\mathrm{Q^{\bullet -}Cu^{II}}$ complexes break down via the bimolecular self-reaction

$$\mathrm{Q^{\bullet -}Cu^{II} + Q^{\bullet -}Cu^{II} \xrightarrow{2k_9} products} \qquad (8\text{-}9)$$

slower than $\mathrm{QH^\bullet}$ and $\mathrm{Q^{\bullet -}}$ decay in self-reactions 6-1 and 6-18, respectively.

Thus by adding copper(II) compounds to $\mathrm{QH^\bullet}$ solutions in acetonitrile it is possible to inhibit radical decay, whereas addition of acetic acid in combination with Cu(II) to the same solutions can render the process as fast as one could wish. By adding copper(II) com-

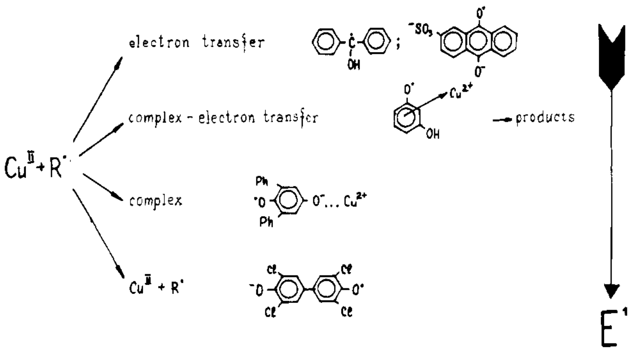


Figure 4. Scheme of reaction between copper(II) compounds and free radicals of inhibitor.[123]

pounds it is possible to control the lifetime of the radical particles over very broad ranges.

We would like to note the following tendency in reactions of aroxyl and semiquinone radicals with copper(II) compounds. For radicals possessing high electron-donor properties the intermediate complex $Cu^{II}R$ (cf. eq 8-6) is short-lived and oxidation is a single-step process. If the radical is a weaker donor, it is sometimes possible to record the absorption spectrum of the complex, which then decomposes to reduction–oxidation products. For still weaker donors the reaction stops at the complex formation stage, and the complexes decay through bimolecular self-reactions 8-9. The weakest donors do not react with Cu^{II}. Examples derived from ref 131, 148, 220, and 221 are shown in Figure 4.

The paramagnetic transition-metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Mo^{3+}, Fe^{2+}, Cu^{2+}) reduce the lifetimes of the radical anions of the disodium salts of 2,6-disulfo-9,10-anthraquinone and 2-methyl-9,10-anthraquinone in water or water–2-propanol mixtures owing to the reduction–oxidation reactions involved.[113,223]

1,4-Benzoquinone (Q) radicals enter reduction–oxidation reactions with iron(II,III) ions in water–1-propanol mixtures[224]

$$Q^{\bullet-} + Fe^{2+} \xrightarrow{+2H^+} QH_2 + Fe^{3+} \qquad (8\text{-}10)$$

$$QH^{\bullet} + Fe^{2+} \xrightarrow{+H^+} QH_2 + Fe^{3+} \qquad (8\text{-}11)$$

$$QH^{\bullet} + Fe^{3+} \xrightarrow{-H^+} Q + Fe^{2+} \qquad (8\text{-}12)$$

For all three reactions at room temperature, $k_{10-12} \simeq 10^7\ M^{-1}{\cdot}s^{-1}$.[224]

Using the stopped-flow method, the authors of ref 225 studied the kinetics of oxidation of the 2,5-di-*tert*-butyl-1,4-benzoquinone radical anion with Co(II), Fe(II), and Mg(II) tetraphenylporphyrins in tetrahydrofuran. The results at room temperature were $k(Co^{II}) = (5 \pm 2) \times 10^5$, $k(Fe^{II}) = (9 \pm 4) \times 10^6$, and $k(Mg^{II}) \simeq 10^7\ M^{-1}{\cdot}s^{-1}$. It is believed that in all cases the first step is electron transfer between the radical anion and the central ion; this reduces, for example, Co^{II} to Co^{I} and (in case of Fe^{II}) the porphyrin ring.[225]

To improve the inhibiting effect of phenolic inhibitors the aroxyl (semiquinone) radicals must be removed from solution as soon as possible by combining them into molecular products.[37] As follows from the data of this section, compounds of transition metals, e.g., copper(II), are good for this purpose. Of course, one must make sure that reactions of these compounds with other agents, hydroperoxides in particular, are not detrimental.

D. Labile Complexes between Aroxyl and Semiquinone Radicals and Metal Compounds

Charge transfer between a reacting donor and acceptor may only be partial. Then charge-transfer complexes are formed.

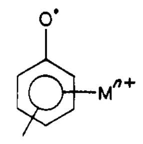
The oxidation–reduction reactions between radicals and metal compounds taking place in the inner or outer sphere terminate in decomposition of the intermediate collision complex to the final products. However, if no oxidation–reduction occurs, there may be formed charge-transfer complexes, associates, or coordination compounds with radical ligands. Apart from the chemical affinity of the radical for the particular metal compound, the important factors include the paramagnetic interactions between unoccupied or partially occupied orbitals of the metal and the vacant orbitals of the radical. Complexes between radicals and metal compounds (ions) are interesting because complex formation affects the radical reactivity. In many cases this results in a relative stabilization of the radical. Coordination between radical and metal may greatly increase the radical stability with respect to the decomposition process.

Depending on the completeness of charge transfer, the complexes may be nominally represented with the formulas[218] $R^{\bullet}M^{n+}$, $R^{+}M^{(n-1)+}$, and $R{:}^{-}M^{(n+1)+}$. The radical ligand has an unpaired electron that is also delocalized along the metal shell. In many cases there has been observed hyperfine splitting in the radicals' ESR spectrum due to the interaction of the unpaired electron with the paramagnetic metal nucleus.[33,218] Nevertheless the spectra show that the radical remains what it was.

The labile complexes of aroxyl and semiquinone radicals, especially *o*-semiquinone radicals, with metal compounds have been studied in great detail. In ref 131 and 217 variations in the absorption spectra and decay kinetics of 2-methylphenoxyl, 3-hydroxyphenoxyl, and 3-hydroxy-5-methylphenoxyl radicals in water have been detected in the presence of $Cu^{+}{}_{aq}$, $Cu^{2+}{}_{aq}$, $Mn^{2+}{}_{aq}$, and $Fe_2{}^{+}{}_{aq}$ ions, which could presumably be bound into complexes

$$ArO^{\bullet} + M^{n+} \rightleftarrows ArO^{\bullet}{\cdots}M^{n+} \qquad (8\text{-}13)$$

The complexes have been ascribed the π–v structure[131,217]



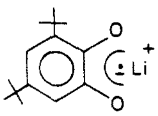
Complexes of the 3-hydroxyphenoxyl and 3-hydroxy-5-methylphenoxyl radicals decay with first-order kinetics and $k = (3.0 \pm 0.5) \times 10^3\ s^{-1}$ for both radicals in water at room temperature (pH 2.0); cf. Figure 4.[131]

In a nonpolar medium the 2-methylphenoxyl radical forms complexes with $Co(acac)_2$.[215] The complexes decay via bimolecular self-reactions 8-9 slower than the starting radicals.[215]

The existence of complexes between the stable 2,4,6-tri-*tert*-butylphenoxyl radical and $Co(acac)_2$ has been demonstrated by ESR in ref 226 and 227. There was a coupling between the unpaired electron and cobalt nucleus: besides the triplet due to the aroxyl radical they observed an octet due to the complex.[226]

The authors of ref 131, who studied the effect of Cu^{+}_{aq} and Cu^{2+}_{aq} ions on the decay kinetics and absorption spectra of the *p*-benzoquinone radical anion ($Q^{\bullet -}$) in water at pH 6.0, discovered that $Q^{\bullet -}$ formed complexes of 1:1 composition with these ions. The complexes decayed via reaction 8-9. The following k_9 values were found at room temperature: $k_9 = (8.0 \pm 1.0) \times 10^6\ M^{-1} \cdot s^{-1}$ for $Cu^{+}Q^{\bullet -}$ and $k_9 = (1.9 \pm 0.3) \times 10^6\ M^{-1} \cdot s^{-1}$ for $Cu^{2+}Q^{\bullet -}$, which is 1–2 orders smaller than the dismutation 6-18 rate constants (cf. section VI.D). Thus the reaction of $Q^{\bullet -}$ with copper ions results in more stable radicals. The reason for such an increase in stability seems to consist in unpaired electron delocalization along the electronic shell of copper and the appearance of steric hindrances during self-reactions of complexes, reaction 8-9.[131] Similarly, the complex of the 2-hydroxyphenoxyl radical with Cu^{2+}_{aq} was consumed 2 orders of magnitude slower in self-reactions 8-9 than the starting 2-hydroxyphenoxyl radicals underwent disproportionation.[131]

With the help of ESR it has been shown that there exist a large variety of *tert*-butyl-substituted complexes of *o*-semiquinone radicals with metal compounds of groups 1–4 and 8 of the periodic table,[228,229] and their properties have been investigated. The ESR data show that most of the complexes remain π radicals, the degree of transfer of the spin density to the metal ion being low.[230] The nature of the oxygen–metal bond has a significant effect on unpaired electron density distribution in *o*-semiquinone and on the hyperfine coupling with the paramagnetic nuclei of the central atom. The complexes with alkali metal ions (e.g., **26**) may be considered as contact pairs. The complexes with Tl^{I} and In^{III} are obviously chelates (compound **27**). The radical identified in ref 231 as tin-containing radical **28** may, on the basis of the ESR data, be described as an organometallic radical. The π-electron system of the radical includes a total of nine electrons delocalized with respect to eight centers. The metal is coupled to the radical ligand via the hybrid orbitals of oxygen located in the point plane of the π-electron system. The ESR spectra show splitting on the protons of the *o*-semiquinone aromatic ring and the magnetic nuclei of the metal and ligands L. Typically the splitting constants vary only slightly in passing from free radicals to chelate complexes. This is indicative of a low degree of spin density transfer from the radical ligand to the ML_m fragment. At the same time the hyperfine coupling constants are extremely sensitive both to the nature of the atoms and to the geometry of the M environment.[228]



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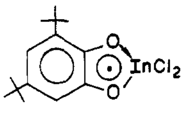

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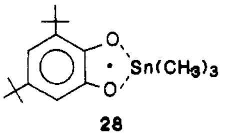

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E. Redox Potentials of Free Radicals

Any prediction of the direction and rate of the oxidation–reduction reactions of inhibitors and free radicals must be based on an adequate knowledge of the one-electron redox potentials E^1 of such pairs as

TABLE 24. One-Electron Redox Potentials vs. NHE of Quinoid and Phenolic Compounds in Aqueous Solutions at Room Temperature[a]

starting compd	E^1, V	E^2, V	pH	ref
1,4-benzoquinone	0.099	0.480	7.0	232
duroquinone	–0.244	0.355	7.0	232
9,10-anthraquinone-2-sulfonate	–0.375	0.075	7.0	232
9,10-anthraquinone-2,6-disulfonate	–0.32		7.0	234
menaquinone	–0.203	0.207	7.0	232
phenol		>0.5	13.5	235
4-methoxyphenol		0.320	13.5	235
resorcinol		0.304	11.6	235
hydroquinone		0.057	11	235
catechol		0.139	11	235
3,3′,5,5′-tetrachloro-4,4′-diphenoquinone	0.26		7	149
3,3′,5,5′-tetrabromo-4,4′-diphenoquinone	0.26		7	149

[a] Determination errors vary from ±0.001 to ±0.01 V and are given in the cited references.

$$R + e^- \rightleftarrows R^{\bullet -} \qquad (8\text{-}14)$$

$$RH - e^- \rightleftarrows R^{\bullet} + H^+ \qquad (8\text{-}15)$$

$$RH^{\bullet} - e^- \rightleftarrows R + H^+ \qquad (8\text{-}16)$$

$$R^{\bullet} + e^- \rightleftarrows R^- \qquad (8\text{-}17)$$

Of special interest are E^1 in water measured relative to the normal hydrogen electrode at pH 7.0 (E_7^1), $T = 298$ K, or at some other pH.

Experimental determination of the E^1 of short-lived radicals often meets with difficulties because it is necessary to generate radicals and measure their E^1 before they decay. Equilibria must be established sooner than radicals decay by other reactions, including self-reactions. In most cases equilibria like 8-14 are the ones that satisfy this requirement since they yield relatively long-lived radical anions.

Quinone radical anions ($Q^{\bullet -}$) take part in reversible electron-transfer reactions with other quinones, viologens, or dye molecules (A)[232,233]

$$Q^{\bullet -} + A \underset{k_{-18}}{\overset{k_{18}}{\rightleftarrows}} Q + A^{\bullet -} \qquad (8\text{-}18)$$

The E_7^1 values for quinone/quinone radical anion pairs obtained by pulse radiolysis are given in Table 24.

Equilibrium 8-18 sets in rather fast. The radicals decay by reactions $Q^{\bullet -} + Q^{\bullet -}$, $A^{\bullet -} + A^{\bullet -}$, and $Q^{\bullet -} + A^{\bullet -}$ much slower.[232,233] It has been demonstrated that the concomitant spectral changes were due to none other but electron transfer; the observed first-order rate constant (relaxation to equilibrium) is in this case expressed by

$$k_{obsd} = k_{-18}[Q] + k_{18}[A],\ s^{-1} \qquad (8\text{-}19)$$

To determine the one-electron potential $E_7^1(Q/Q^{\bullet -})$ the equilibrium rate constants K_{18} were measured. As A, a reference compound of known one-electron potential was used. For known K_{18} it is easy to obtain the desired E_7^1 values by using the formula

$$E_7^1(Q/Q^{\bullet -}) = E_7^1(A/A^{\bullet -}) - 0.059 \log K_{18},\ V \qquad (8\text{-}20)$$

The second potential of quinones $E^2(Q^{\bullet -}/Q^{2-})$ (see

Table 24) is usually calculated from the measured E^1-($Q/Q^{\bullet -}$) and known two-electron potentials $E^\circ = {}^1/_2(E^1 + E^2)$. In ref 235 E^2 were measured by pulse radiolysis in reactions of aroxyl radical with different di- and trihydroxybenzenes and aromatic diamines in alkaline media (hydroquinone was the reference compound). The E^2 values are given in Table 24.

Knowing the one-electron potentials enables one to calculate exactly the quasi-equilibrium concentrations of radical anions in solutions in the presence of electron donors or acceptors and predict with sufficient confidence the rates of the reduction–oxidation reactions of radical anions. The reorganization energy of water as solvent is about the same for different pairs, and the rate of electron transfer in any series of compounds is mainly determined by the free energy of reaction or ΔE^1.

The available information (Table 24) will no doubt be beneficial in the analysis of the kinetics of ArOH-inhibited oxidation in aqueous solutions.

On many occasions radicals become involved in irreversible reduction–oxidation reactions because of the very fast decay of either the radicals themselves or their oxidation (reduction) products. In such cases E^1 can be of no use. Yet, for comparing the redox properties of radicals in specific series of radicals, one may have to resort either to the so-called "kinetic" potentials $E_k{}^1$ or the half-height potentials of the polarographic reduction or oxidation waves (cf., e.g., ref 33 and 236).

IX. Kinetic Topology of Inhibited Oxidation of Hydrocarbons

A. General Principles of Kinetic Topology of Inhibited Oxidation

The conclusion we draw from the kinetic data on inhibited oxidation of RH set forth in previous sections is that even for a system consisting of a particular InH added to a particular RH, the oxidation may take one of several possible routes or mechanisms determined by a number of key reactions (cf. Table 1). If we have investigated an InH in a given system so that we know all the elementary reaction rate constants involving RH, InH, $RO_2^\bullet$, $In^\bullet$, ROOH, and O_2, we will be in a position to calculate the RH oxidation kinetics under any conditions. If we do not know the rate constants for all elementary reactions, we may solve the problem by staging a series of experiments. Yet this oversimplified approach falls short of providing us with answers to a number of general questions: How is the inhibited oxidation mechanism related to the InH and RH structures and reactivity of $RO_2^\bullet$? What particular InH will be most effective under given conditions in a given system? And so on. Answeres to these, and like, questions can be obtained by using the approach set forth in ref 38, 78, and 237–239. In summary, the principles of this approach are as follows.

1. The elementary reactions accompanying RH oxidation in the presence of an InH may be many in number (see the IHO scheme, section II.A), but the actual reaction mechanism is determined by only a few of them, which may be called key ones. For example, the reactions involved in cumene oxidation in the presence of *p*-cresol at 320–380 K are reactions 2, 7, −7, 9, and 10. However, the rates of reactions $In^\bullet$ + ROOH (reaction −7) and $In^\bullet$ + RH (reaction 10) are much smaller than the rate of the reaction $RO_2^\bullet$ + $In^\bullet$ (reaction 8). Therefore, when $v_2 > v_i$, where v_2 pertains to reaction $RO_2^\bullet$ + RH (reaction 2), reactions 2 and −7 will be the crucial ones, and the oxidation rate $v = k_2[RH]v_i/2k_7[InH]$; i.e., the rate is controlled by reactions 2 and 7, which are the key ones. The ratio of the rate constants of these reactions, k_7/k_2, will be a characteristic of InH effectiveness. For InH causing chain termination by reaction with $RO_2^\bullet$, the following mechanisms, each consisting of a set of elementary steps, can be singled out as principal; see Table 1.

2. If we use a different InH or a different oxidizing RH or change the oxidation conditions, the mechanism may change, too. Therefore to enable a systematic approach it may be helpful to consider the domain of existence of a particular inhibited oxidation mechanism. For one InH and one RH it will be a set of conditions under which the mechanism in question persists. But the concept of the domain of existence may be broadened if we extend it to a range of oxidizing compounds and a range of InH.

3. The domain of existence of each mechanism depends on the relative rates of a large number of elementary acts. For instance, the following seven inequalities must be valid in order to channel the reaction according to mechanism III, where the chains are terminated via reaction 7: $k_2[RH] \gg k_7[InH]$; $k_2[RH] > 2k_7[InH]$; $k_{-7}[ROOH] < k_8[RO_2^\bullet]$; $k_{10}[RH] \ll k_8[RO_2^\bullet]$; $v_i \gg (k_{11}[ROOH] + k_{12}[O_2])[InH]$; $k_{13}[InOOR] \ll v_i$; $k_{14} \ll k_8[RO_2^\bullet]$. In real situations the realization of each mechanism depends on the relative rates of all the elementary reactions involved. This multiparameter relationship may be simplified if we use correlation equations. To this end the range of InH must be broken down into groups, each falling under a specific set of correlation equations. For example, depending on their structure the ArOH may be divided into the following three groups.

Group A consists of phenols reacting with $RO_2^\bullet$, ROOH, and O_2, the $ArO^\bullet$ being active enough to react with RH and ROOH under certain conditions. The products of their reactions with $RO_2^\bullet$ are not peroxides InOOR, and the $ArO^\bullet$ do not decompose to active radicals. This group includes all ArOH except 2,6-di-*tert*-alkyl-substituted and *o*- or *p*-alkoxy-substituted phenols. For such ArOH, mechanisms I, II, III, IV, VI, VII, and IX may be valid (cf. Table 1).

Group B consists of phenols generating inactive $ArO^\bullet$ that under oxidation conditions are practically unable to react with RH and ROOH, the ArOH themselves being capable of slowly reacting with ROOH and $RO_2^\bullet$. By reacting with $RO_2^\bullet$, aroxyls of these ArOH form peroxides that decompose to free radicals. Therefore such ArOH can react by only mechanisms I, II, III, and V.

Group C consists of phenols with alkoxy substituents producing the $ArO^\bullet$ which dissociate to an alkyl radical that propagates the chain. Such ArOH can react by mechanisms I–IX.

All reactions in which ArOH or $ArO^\bullet$ take part depend on the bond dissociation energy of the phenol's O–H bond. Therefore within each group of ArOH the activation energies and rate constants of each elementary step may be expressed in terms of one parameter,

TABLE 25. Correlation Equations for the Key Reactions of Phenol-Inhibited Oxidation of Hydrocarbons

reaction no.[a]	$\log (k/(M^{-1} \cdot s^{-1}))$[b]
sec-$RO_2^\bullet$ + RH (2)	$9.0 - 3000/T + (330/T) \log k_2^*$
tert-$RO_2^\bullet$ + RH (2)	$8.2 - 3000/T + (330/T) \log k_2^*$
ROOH → $RO^\bullet$ + $HO^\bullet$ (3)	$13 - 7400/T$
Group A Phenols[c]	
$RO_2^\bullet$ + InH (7)	$7.2 - 2400/T + (330/T) \log k_7^*$
$In^\bullet$ + ROOH (−7)	$7.2 + 1260/T - (710/T) \log k_7^*$
$RO_2^\bullet$ + $In^\bullet$ (8)	8.5
$In^\bullet$ + $In^\bullet$ (9)	8.5
$In^\bullet$ + RH (10)	$9.2 - 1800/T + (520/T) \log k_7^* + 530/T \log k_2^*$
InH + ROOH (11)	$1.0 - 8100/T + (570/T) \log k_7^*$
InH + O_2 (12)	$9.9 - 8700/T + (570/T) \log k_7^*$
Group B Phenols[c]	
$RO_2^\bullet$ + InH (7)	$7.2 - 2410/T + (330/T) \log k_7^*$
InOOR → $InO^\bullet$ + $RO^\bullet$ (13)	$14 - 7225/T$
$In^\bullet$ + ROOH (−7)	$7.2 + 530/T - (710/T) \log k_7^*$
Group C Phenols[c]	
$In^\bullet$ → Q + $r^\bullet$ (14)	$12.7 - 5810/T$

[a] See IHO scheme in section II.A. [b] Index of k is the number of the corresponding reaction in the leftmost column. [c] Phenol groups are described in the text; see section IX.A.

viz., D_{ArO-H}. On the other hand, the activation energies for reactions in which RH takes part may be expressed in terms of the R–H bond dissociation energy. It should not be overlooked that tertiary $RO_2^\bullet$ react somewhat slower than either the secondary or primary ones.

4. It is therefore possible to reduce the variety of structural factors, the relative impact of which on oxidation is determined by the rate constants of a total of nine reactions, to only two parameters, namely, D_{R-H} and D_{ArO-H}. However, there is not enough literature data available on the R–H and ArO–H bond dissociation energies. On the other hand, the rate constants of reactions 2 and 7 have been measured for a great number of compounds.[35,36] For this reason this information is used to characterize the initial reactivity of $RO_2^\bullet$, $In^\bullet$, RH, and InH[78,238,239] (Table 25). For convenience, we introduce the parameters $k_2^* = k_2$ at 333 K and $k_7^* = k_7$ at 333 K.

5. For each mechanism its domain may now be expressed as a certain volume in three-dimensional space: "k_2^*, k_7^* and conditions" (T, v_i, [InH], [RH], [ROOH], [O_2]). The domain will be defined by the ranges of k_2^* and k_7^* and experimental conditions (e.g., temperature). One domain will be separated from another by a boundary "strip", i.e., ranges of k_2^* and k_7^* and conditions for which signs of both mechanisms will be evident. The boundary conditions between any two domains may be formulated as the appropriate inequalities and expressed in terms of parametric formulas (Table 26). The boundary strip has a finite width, so that the transition from one mechanism to another is smooth. Following suggestions of ref 78, we may define the width of the boundary strip as the range of factor values that cause the ratio of the rates of crucial reactions to vary e times. This corresponds to a 3-fold variation of one of the parameters which determine the boundary.

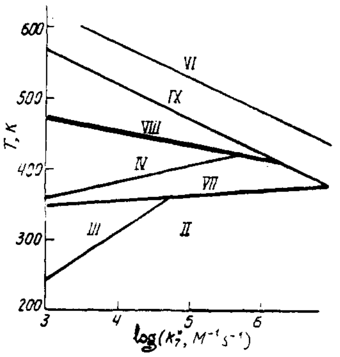

Figure 5. Graphic representation of the domains of relaization of different mechanisms of phenol-inhibited oxidation of hydrocarbons in T vs. $\log k_7^*$ coordinates with $k_2^* = 1\ M^{-1} \cdot s^{-1}$, [RH] = 10 M, $f = 2$, [InH] = [ROOH] = [O_2] = 10^{-3} M, and $v_i = 10^{-7}$ $M \cdot s^{-1}$. The mechanism numbering and the key reactions of each mechanism are given in Table 1.

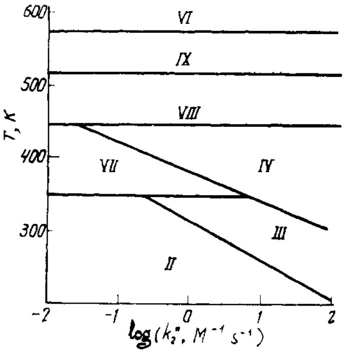

Figure 6. Graphic representation of the domains of realization of different mechanisms of phenol-inhibited oxidation of hydrocarbons in T vs. $\log k_2^*$ coordinates with $k_7^* = 10^4\ M^{-1} \cdot s^{-1}$, [RH] = 10 M, $f = 2$, [InH] = [ROOH] = [O_2] = 10^{-3} M, and $v_i = 10^{-7}$ $M \cdot s^{-1}$. The mechanism numbering and the key reactions of each mechanism are given in Table 1.

Figures 5 and 6 show domains of inhibited oxidation mechanisms as a function of the InH activity, expressed through k_7^*, and RH oxidizability, expressed through k_2^* and T. This presentation allows us to make certain conclusions. First, we may now pinpoint the chief factors that control the mechanism. They are D_{R-H}, D_{ArO-H}, and T. Affecting but not controlling the mechanism are the concentrations of RH and ArOH.

TABLE 26. Equations for Domain Boundary Strips and Their Presentation in the $T = X/Y$ Form[a]

mechanism	key reactions	domain boundary equation	X	Y
II, III	2, 7[b]	$k_2[RH] = fk_7[InH]$	$600 + 330(\log k_7^* - \log k_2^*)$	$1.8 + \log ([RH]/f[InH])$
III, IV	8, 10[b]	$k_8 v_i = k_7 k_{10}[RH][InH]$	$4200 + 90 \log k_7^* - 530 \log k_2^*$	$7.9 + \log ([RH][InH]/v_i)$
III, IV–VI	7, 12[b]	$fk_{12}[InH][O_2] = v_i$	$8700 - 570 \log k_7^*$	$9.9 + \log (f[InH][O_2]/v_i)$
III–VII	−7, 8[b]	$k_8 v_i = k_7 k_{-7}[ROOH][InH]$	$1140 + 380 \log k_7^*$	$5.9 + \log ([ROOH][InH]/v_i)$
III–VIII	8, 14[b]	$k_8 v_i = k_7 k_{14}[InH]$	$8210 - 330 \log k_7^*$	$11.4 + \log ([InH]/v_i)$
III–IX	7, 11[b]	$fk_{11}[InH][ROOH] = v_i$	$8100 - 570 \log k_7^*$	$10 + \log (f[InH][ROOH]/v_i)$
II, III	2, 7[c]	$k_2[RH] = fk_7[InH]$	$600 + 330 (\log k_7^* - \log k_2^*)$	$1.8 + \log([RH]/f[InH])$
III–V	2, 7, 13[c]	$k_{13}[InH] = v_i$	7225	$14 + \log (f[InH]/v_i)$

[a] This form enables one to get an analytical relationship between $\log k_2^*$, $\log k_7^*$, [InH], [ROOH], f, v_i, and T for the domain boundary strip. Units of M and $M^{-1} \cdot s^{-1}$ are used. [b] For phenols of the A group; see text. [c] For phenols of the B group; see text.

Factors such as v_i, $[O_2]$, and [ROOH] will affect the mechanism only under specific conditions. Second, from analysis of the analytical formulas it follows that there are structural ranges responsible for a particular mechanism. It appears that it is not always possible to implement, by merely varying the conditions, a particular mechanism for a given RH–InH pair. For example, mechanism III (Table 1) may be realized only for such pairs for which

$$D_{R\text{-}H} < 0.36D_{ArO\text{-}H} + 142, \text{ kJ/mol} \qquad (9\text{-}1)$$

Third, using this approach it is possible to derive parametric equations for the rate of inhibited oxidation and employ them for rough estimates of v_i.

B. The Optimum Inhibitor

The inhibiting effect is characterized by duration and extent of reaction inhibition (effectiveness). The latter, for chain terminations, may be expressed in terms of the chain length $\nu = v/v_i$. The ArOH that under specific conditions provides for the minimum chain length is the more effective. From the data of Table 26 it follows that the inhibiting effectiveness depends on the oxidation mechanism, types of reagents (RH and ArOH), and conditions (T, v_i, reagent concentrations). In Table 26 all the parameters relating to reactions that involve ArOH and ArO$^\bullet$ are in terms of k_7*. From consideration of the equations for v under different mechanisms, it follows that in all cases v is smaller the higher the k_7*. Hence the InH characterized by a maximum k_7* will be the most effective one in any case.

Another important characteristic of an ArOH is the duration of its inhibiting period τ, which, provided the InH is consumed only for chain terminations, is determined by its initial concentration $[ArOH]_0$, coefficient f, and initiation rate v_i. Under these conditions the rate of consumption of InH is $v_{InH} = v_i/f$. Side reactions, e.g., reactions of InH with O_2 and ROOH, will reduce the effective inhibition period. The effectiveness of an InH as an inhibiting agent is higher the smaller the contribution of side reactions to the total consumption of InH. Therefore the optimum InH will be the one that ensures the minimum chain length ν with a relatively low loss of InH through side reactions. The important factor is the relative fraction of InH loss via side reactions $\omega = fv'_{InH}/v_i$, where v'_{InH} is the rate of InH consumption via side reactions. Suppose for an effective InH, $\omega \leq 0.25$. Since k_{11} and k_{12} increase symbatically with k_7* (cf. Table 25), the optimum InH is therefore expected to satisfy contradictory requirements: it must be maximally active in chain termination but react as slowly as possible with O_2 and ROOH. If the main side route of InH consumption is its reaction with O_2, the condition $\omega \leq 0.25$ will mean that $4k_{12}[InH][O_2] \leq v_i$, which, after substitution of the correlation equation from Table 25 and necessary manipulations, takes the form

$$\log k_7^* \leq 15.3 - [18.4 - 1.8 \log (v_i/f[InH][O_2])] \times 10^{-3}T \qquad (9\text{-}2)$$

(Units of M and s are used in eq 9-2 and equations below.)

Obviously, the InH that has the maximum k_7* and satisfies inequality 9-2 will be the best one. As follows from eq 9-2, the optimum k_7* value will be lower the higher the temperature and InH and O_2 concentrations. At $v_i = 10^{-7}$ M·s^{-1}, $[InH] = [O_2] = 10^{-3}$ M, and $f = 2$, the optimum $\log k_7^* = 8$ ($T = 350$ K), 7 (400 K), 6 (450 K), and 5 (500 K). For ArOH $k_7^* \leq 10^7$ M^{-1}·s^{-1}.

If it is the reaction of InH with ROOH that is the main route of InH consumption, the inequality, upon substitution of the correlation equation and transformation, takes the form

$$\log k_7^* \leq 14.2 - [18.6 - 1.8 \log (v_i/f[InH][ROOH])] \times 10^{-3}T \qquad (9\text{-}3)$$

It follows from eq 9-3 that at higher temperatures the range of suitable ArOH is narrower. At $v_i = 10^{-7}$ M·s^{-1} and $f = 2[ArOH] = [ROOH] = 10^{-3}$ M, the optimum values of $\log k_7^*$ are 6.9 (350 K), 5.8 (400 K), 4.8 (450 K), and 3.8 (500 K).

In the general case ArOH reacts both with O_2 and ROOH. Therefore to use an ArOH as effectively as possible the total rate of these reactions must be relatively low; i.e.

$$f(k_{11}[ROOH] + k_{12}[O_2])[ArOH] \leq 0.25v_i \qquad (9\text{-}4)$$

The competition between reactions 11 and 12 depends on T, $[O_2]$, and [ROOH]

$$v_{11}/v_{12} = k_{11}[ROOH]/k_{12}[O_2] \qquad (9\text{-}5)$$

$$\log (v_{11}/v_{12}) \simeq 600/T + \log ([ROOH]/[O_2]) \qquad (9\text{-}6)$$

At temperatures standard for oxidation (350–450 K) and $[ROOH] \geqslant 0.1[O_2]$, the prevalent reaction is that between ArOH and ROOH (reaction 11).

Similarly, one may estimate the optimum InH for quasi-steady oxidation of RH. For example, if the prevalent mechanism is III (see Table 1), the rate of InH consumption with allowance for initiation and InH consumption via reaction with ROOH is

$$v_{InH} = v_if^{-1} + k_{11}[InH][ROOH]_s \qquad (9\text{-}7)$$

$$v_i = v_{i0} + (k_3 + 2ek_{11}[InH])[ROOH]_s \qquad (9\text{-}8)$$

and

$$v_{InH} = v_{i0}f^{-1} + k_3f^{-1} + k_{11}(2e + f^{-1})[InH][ROOH]_s \qquad (9\text{-}9)$$

($[ROOH]_s$ was defined in section II.B.)

Using the data of ref 47, assuming $[InH] = 0.5[InH]_0$, and considering the case $\beta\nu \ll 1$, we obtain upon substitution of $[ROOH]_s$ in eq 9-9

$$v_{InH} = v_{i0}f^{-1} + \beta\frac{k_2[RH]}{fk_7[InH]}v_{i0}[1 + 0.5k_3^{-1}k_{11}(1 + f)][InH]_0 \qquad (9\text{-}10)$$

(β is defined in Table 5 (see also section II.B); ν is the chain length.)

After differentiating v_{InH} with respect to k_7* and putting $dv_{InH}/dk_7^* = 0$, we find k_7* for which the v_{InH} is minimum

$$\log k_7^* = 14.2 - 17.5 \times 10^{-3}T + 1.8 \times 10^{-3}T \log (k_3/(1 + f)[InH]_0) \qquad (9\text{-}11)$$

We shall call the value of k_7* that satisfies the demand of v_{InH} to be minimum the optimum value $k_7^*{}_{opt}$.

Table 27 contains formulas for k_7* of an optimum InH for different inhibited oxidation mechanisms. As

TABLE 27. Equations for the Selection of Optimum Inhibitor from Group A Phenols[a]

mechanism	key reactions	$\log (k_7{}^*{}_{\text{opt}}/(\text{M}^{-1}\cdot\text{s}^{-1}))$
III–VIII	2, 7, −7, 8, 10, 14[b]	$14.2 - 18.6 \times 10^{-3}T + 1.8 \times 10^{-3}T \log (\upsilon_i/\{f[\text{InH}][\text{ROOH}]\})$
III	2, 7[c]	$14.2 - 17.5 \times 10^{-3}T + 1.8 \times 10^{-3} T \log (k_3/\{(1 + f)[\text{InH}]_0\})$
IV	2, 8, 10[c]	*d*
VII	2, −7, 8[c]	*d*
VIII	2, 8, 14[c]	$14.2 - 17.5 \times 10^{-3}T + 1.8 \times 10^{-3}T \log (k_3/\{(1 + f)[\text{InH}]_0\})$
III	2, 7[e]	$14.2 - 17.5 \times 10^{-3}T + 1.8 \times 10^{-3}T \log (k_3/(1 + f)[\text{InH}]_0)$
IV	2, 8, 10[e]	$1.8 \times 10^{-3}T \log (k_3/(1 + f)[\text{InH}]_0)$
VII	2, −7, 8[e]	$15.2 - 17.5 \times 10^{-3}T + 1.8 \times 10^{-3}T \log (k_3/\{(1 + f)[\text{InH}]_0\})$
VIII	2, 8, 14[e]	$13.6 - 17.5 \times 10^{-T} + 1.8 \times 10^{-3}T \log (k_3/\{(1 + f)[\text{InH}]_0\})$

[a] The phenols are characterized in section IX.A. [b] The oxidation reaction proceeds in the following regime: υ_i = const, side reaction 11 (see IHO scheme in section II.A). [c] The regime is the following: $\upsilon_i = k_3[\text{ROOH}]$, ROOH is present at quasi-steady concentration. [d] The optimum InH is that possessing the maximum $k_7{}^*$. [e] The regime is the following: $\upsilon_i = k_3[\text{ROOH}]$, ROOH concentration is nonsteady.

follows from Table 27, such formulas are identical for mechanisms III and VII, whereas the InH for which $k_7{}^*$ is maximum is the optimum one for mechanisms IV and VII.

C. Effective Inhibition Temperatures

It is important to know temperatures at which a compound of a given class may be used as an effective InH. In the case of ArOH the problem may be solved on the quantitative level if we rely on the approach and equations presented in this paper. The inhibitors that terminate chains remain effective as long as they ensure short enough reaction chains $\nu \leq \nu_{\max}$, where $\nu_{\max}$ is the maximum possible chain length in a system. On the other hand, for an InH to be effective, its $k_7{}^*$ should not, as we have shown above, be greater than some optimum value $k_7{}^*{}_{\text{opt}}$. Using the correlations of Table 25 and the formulas for $k_7{}^*{}_{\text{opt}}$ of Table 27, one may obtain $T_{\max}$, above which the inhibition by a given mechanism stops being effective. For example, in the case of mechanism III, $\nu = k_2[\text{RH}]/fk_7[\text{InH}]$, and putting $\nu = \nu_{\max}$, taking the logarithm, and substituting the equations of Table 25, we obtain

$$\log \nu_{\max} = 1.8 - 600/T + 300/T \log (k_2{}^*/k_7{}^*) + \log ([\text{RH}]/[\text{InH}]) \quad (9\text{-}12)$$

Substituting in eq 9-12 the formulas for $k_7{}^*{}_{\text{opt}}$ (for side reaction 11), we come up with the formulas given in Table 28. This table consists formulas for estimating $T_{\max}$ under different oxidation mechanisms for any $k_2{}^*$ and the $k_7{}^*$ of the optimum InH, assuming reaction with ROOH as the main side route. Evaluation of $T_{\max}$ for *n*-alkane oxidation under the conditions $[\text{InH}] = [\text{ROOH}] = 10^{-3}$ M and $\upsilon_i = 10^{-7}$ M·s^{-1} gives $T_{\max} = 440$ K (mechanism III), 445 K (mechanism IV, reactions 2, 7, 8, and 10), 520 K (mechanism IV, reactions 9 and 10), 400 K (mechanism VII), and 425 K (mechanism VIII). Referring to Figure 6, we see that for *n*-alkanes in the presence of ROOH, mechanism VII is preferable to mechanisms II and IV because of the very strong R–H bond. Therefore the most confident of all estimates will be $T_{\max}$ for mechanism VII (Table 28). Apparently all such estimates are approximate since the correlation equations themselves are approximate. For instance, in the case of oxidation by mechanism III and for an error in the difference of measured activation energies $(E_2 - E_1) = 6$ kJ/mol, the error in $T_{\max}$ will be ±30 K ($T_{\max} = 440 \pm 30$).

X. Conclusions

The review presents a state-of-the-art report on the activity of phenols and amines as inhibitors of oxidation of organic compounds. The inhibiting effect of these compounds depends on the rate constants of their reactions with peroxyl radicals k_7, but it is not this reaction alone that controls the inhibitor effectiveness. Also important are reactions of inhibitor radicals In$^\bullet$, including In$^\bullet$ + In$^\bullet$ (reaction 9), In$^\bullet$ + ROOH (reaction −7), and In$^\bullet$ + RH (reaction 10). Kinetic analysis of the situation has shown that, depending on the conditions and activity of InH, RH, and In$^\bullet$, some reactions are more important than others and may be called "key" ones. Using the parametric relation between the rate constants of reactions involving InH, In$^\bullet$, and RO$_2{}^\bullet$, one may generally reduce the variety of reactions in such systems to the following two key reactions: RO$_2{}^\bullet$ + InH (reaction 7) and RO$_2{}^\bullet$ + RH (reaction 2). This enables one to tackle the problem of estimating the effectiveness of inhibition of different RH with a whole class of InH under different conditions and allows one to choose the optimum InH and to estimate the temperature ranges of effective inhibition, opting for inhibition mechanism depending on conditions and InH structure.

The inhibition effectiveness is largely determined by inhibitor radical reactivity. Very important are reactions of In$^\bullet$ termination (reaction 9) and abstraction of hydrogen atom from RH (reaction 10), which we have

TABLE 28. Formulas for the Upper Temperature Limit $T_{\max}$ of Inhibiting Action of Phenols Presented in the $T_{\max} = X/Y$ Form[a]

mechanism	key reactions	X	Y
III	2, 7[b]	$600 + 330 \log (k_7{}^*/k_2{}^*)$	$1.1 + \log ([\text{RH}]/f[\text{InH}])$
IV	2, 8, 10[b]	$2700 + 420 \log k_7{}^* - 600 \log k_2{}^*$	$5.0 + 1.5 \log [\text{RH}] - 0.5 \log (f[\text{InH}]\upsilon_i)$
IV	2, 9, 10[b]	$1800 + 520 \log k_7{}^* - 530 \log k_2{}^*$	$4.3 + \log [\text{RH}] - 0.5 \log (f[\text{InH}]\upsilon_i)$
VII	2, −7, 8[b]	$1170 + 520 \log k_7{}^* - 330 \log k_2{}^*$	$4.1 + \log [\text{RH}] + 0.5 \log ([\text{ROOH}]/f[\text{InH}]\upsilon_i)$
VIII	2, 8, 14[b]	$4700 - 330 \log k_2{}^*$	$6.8 + \log [\text{RH}] - 0.5 \log (f[\text{InH}]\upsilon_i)$
III	2, 7[c]	$5290 - 330 \log k_2{}^*$	$6.9 + \log [\text{RH}] - 0.6 \log (\upsilon_i/[\text{ROOH}]) - 0.4 \log (f[\text{InH}]\upsilon_i)$
IV	2, 8, 10[c]	$8660 - 600 \log k_2{}^*$	$14.5 + 1.5 \log [\text{RH}] - 1.3 \log \upsilon_i + 0.3 \log (f[\text{InH}]) + 0.8 \log [\text{ROOH}]$
IV	2, 9, 10[c]	$9180 - 530 \log k_2{}^*$	$13.7 + \log [\text{RH}] - 1.4 \log \upsilon_i + 0.9 \log (f[\text{InH}][\text{ROOH}])$
VII	2, −7, 8[c]	$8550 - 330 \log k_2{}^*$	$13.5 + \log [\text{RH}] + 1.4 \log [\text{ROOH}] + 0.4 \log (f[\text{InH}]) - 1.4 \log \upsilon_i$

[a] Group A phenols under consideration; cf. section IX.A. It is assumed that υ_i = const. The $T_{\max} = X/Y$ form enables one to get an analytical relationship between $T_{\max}$ and $\log k_2{}^*$, $\log k_7{}^*$, [RH], [ROOH], [InH], υ_i, and f. $k_2{}^*$ and $k_7{}^*$ are in M$^{-1}\cdot$s^{-1}, any concentration is in M, and υ_i is in M·s^{-1}. [b] It is assumed that $\nu_{\max} = 5$. [c] The $k_7{}^*$ value is expressed by eq 9-3. It is assumed that $\nu_{\max} = 10$.

considered in much detail in this review (cf. sections III, IV, and VI).

Reaction 9, which appears to be simple at first glance, may proceed by a very complex route, including formation of a labile dimer. Of phenolic inhibitors the most effective are those which under identical conditions form aroxyl radicals that rapidly disproportionate, generating initial phenol.[37] Recombination of many aroxyl radicals is limited by molecular mobility, even though it is often characterized by $2k_9 < k_{\text{diff}}$. The data on the acid–base and redox potential properties of inhibitor radicals (sections VII and VIII) may prove useful for analyzing inhibited oxidation of organic compounds in polar solvents, inclusive of water.

Considering the huge body of rate constant data available at present and the more profound knowledge of inhibition mechanisms, it may be possible to make a qualitative leap in solving the inhibitor choice problem, calculating the kinetic behavior of various inhibitors in many real systems.

XI. References

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