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Elementary Reactions of Oxidation Inhibitors

E.T.Denisov

The review gives a systematic account and a critical analysis of the experimental data on the elementary reactions of phenols and aromatic amines in hydrocarbons undergoing oxidation. The results of the measurements and semiempirical estimates of the strength of the In-H bond (InH = inhibitor) in phenols and aromatic amines are examined. From the experimental data presented in the review, evidence is adduced for reaction mechanisms in the inhibited oxidation of hydrocarbons and a combined approach to the concept of the efficiency of the oxidation inhibitor is formulated.
The bibliography includes 110 references.

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I. INTRODUCTION

Inhibitors of oxidation reactions (antioxidants) have acquired considerable importance in modern chemistry. They are used widely to stabilise plastics, synthetic fibres, rubbers, lubricating oils, fats, and medicinal preparations. Experimental data on antioxidants have been compiled in monographs[1-6], symposia[7,8], and reviews[9-13]. Among the wide variety of organic compounds used as antioxidants, phenols and aromatic amines continue to attract most attention. In recent years, important new results were obtained in studies on the detailed mechanism of the action of these inhibitors. It was shown that the radicals formed from the inhibitor react with the hydrocarbons[14] and the hydroperoxide[15], thus participating in chain propagation. The exchange reactions between the radical of one inhibitor and the molecule of another play an important role[16]. The unique phenomenon of the regeneration of inhibitors in chain termination steps has been discovered[17]. The reactions of inhibitors with the hydroperoxide[18] and oxygen have been investigated[19,20]. The chemistry of stable free radicals

has developed rapidly[21-24] and extensive data on the reactions of peroxy-radicals with inhibitors have accumulated[25].

These new findings have made it necessary to revise the ideas about the mechanism of the inhibiting effect of phenols and amines, to analyse critically previous results and concepts, to compile data on elementary reactions involving oxidation inhibitors, and to formulate a mechanism of the action of inhibitors on the basis of modern results. Such an attempt is made in the present review.

II. STRENGTH OF THE In–H BOND IN PHENOLS AND AROMATIC AMINES

1. PHENOLS

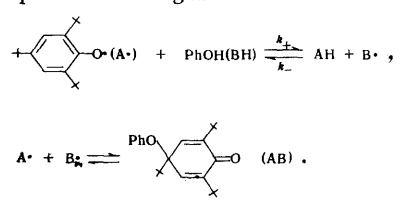
Peroxy-radicals react very rapidly with phenols[25]. At first sight, this can be explained by the low strength of the O–H bond. Therefore it is useful to examine the available data for the dissociation energy of the O–H bond in phenols ($D_{O\text{-}H}$). Several studies have been published recently in which quantities permitting the calculation of $D_{O\text{-}H}$ in phenols were determined by different methods.

1. Mahoney et al.[26] determined calorimetrically the heat of the reaction

$$2PhO^{\cdot} + C_6H_5NHNHC_6H_5 \rightleftharpoons 2PhOH + C_6H_5NNC_6H_5$$

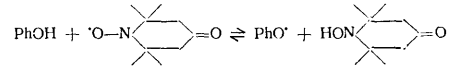
in benzene and found the difference $\Delta H_{PhO\cdot} - \Delta H_{PhOH}$ for certain stable phenoxy-radicals. Since $\Delta H_{PhOH} = \Delta H_{PhO\cdot} + \Delta H_H - D_{O\text{-}H}$, it follows that $D_{O\text{-}H} = \Delta H_{PhO\cdot} - \Delta H_{PhOH^+} + \Delta H_H$ and $\Delta H_H = 52.1$ kcal mole^{-1}. For tri-t-butylphenol, $\Delta H_{PhO\cdot} - \Delta H_{PhOH} = 29.14 \pm 0.08$ and $D_{O\text{-}H} = 29.1 \pm 52.1 = 81.2 \pm 0.1$ kcal mole^{-1}.

2. To measure the heat of formation of active phenoxy-radicals, a study was made[27] of the kinetics of the reaction between the tri-t-butylphenoxy-radical and various phenols and its heat was measured. The reaction includes two equilibrium stages:



The enthalpy of reaction is $\Delta\Delta H = -\Delta H_A + \Delta H_{AH} + \Delta H_B - \Delta H_{BH} + E_+' - E_-'$, the difference $\Delta H_A - \Delta H_{AH}$, measured by method 1 in chlorobenzene, is 28.25 ± 0.1 kcal mole^{-1}, E_-' was measured experimentally, and $E_+' \simeq 2$ kcal mole^{-1} since the recombination of phenoxy-radicals is rapid, its rate being limited by diffusion[27]; $D_{O\text{-}H} = \Delta\Delta H + E_-' + 78.3$ kcal mole^{-1}.

3. Vasserman et al.[28] and Kalashnikova et al.[29] measured the heats of the reversible reaction



and calculated from $D_{O\text{-}H}$ in hydroxylamine, which is 71.9 ± 3 kcal mole^{-1},[30] the values of $D_{O\text{-}H}$ for a number of phenols giving rise to stable phenoxy-radicals.

4. $D_{O\text{-}H}$ in phenols can be estimated from the activation energy for the reaction $PhOH + O_2 \xrightarrow{k_+} PhO^{\cdot} + HO_2^{\cdot}$. The reverse reaction $PhO^{\cdot} + HO_2^{\cdot} \xrightarrow{k_-} PhOH + O_2$ takes place in solution at a rate which is most probably diffusion-limited. This is supported by the finding that the rate of the analogous reaction $HO_2^{\cdot} + HO_2^{\cdot} \rightarrow HOOH + O_2$ in a hydrocarbon solution is limited by diffusion ($k \simeq 10^9$ litre mole^{-1} s^{-1}).[25] One can assume that $E_- = 1$ kcal mole^{-1} for the diffusion of $HO_2^{\cdot}$ in benzene, where k_+ was measured. The O_2 – H bond strength is 44–50 kcal mole^{-1}.[31] If we put $Q_{H\text{-}O_2} = 49$ kcal mole^{-1}, we obtain

$$q = E_- - E_+ = Q_{H\text{-}O_2} - D_{O\text{-}H} = E_+ + 48 \text{ kcal mole}^{-1}.$$

5. Hush[32] proposed a method for the estimation of $D_{O\text{-}H}$ from the critical oxidation-reduction potential[33], which can serve as a measure of the normal oxidation-reduction potential. The strength of the O–H bond in phenols is calculated from the formula[32] $D_{O\text{-}H} = FE_c + 57$ kcal mole^{-1}, where E_c is the critical potential in volts and $F = 23$ kcal equiv.$^{-1}$ V^{-1} is the Faraday. The results of the calculation of $D_{O\text{-}H}$ for phenols are presented in Table 1.

2. AROMATIC AMINES

The N–H bond dissociation energies in aromatic amines are unknown. $D_{N\text{-}H}$ can be estimated, as for phenols, from the activation energies for the reaction $InH + O_2 \rightarrow In^{\cdot} + HO_2$ (Denisova et al.[19]) by the formula $D_{N\text{-}H} = E + 48$ kcal mole^{-1}. It is also possible to estimate $D_{N\text{-}H}$ from the critical potentials for amines using the same formula as for phenols[32]: $D_{N\text{-}H} = FE_c + 57$ kcal mole^{-1}. The values of $D_{N\text{-}H}$ are presented in Table 2.

III. REACTION OF PEROXY-RADICALS WITH INHIBITORS

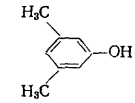
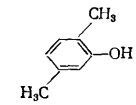
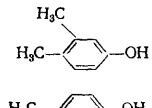
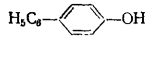
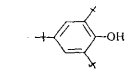
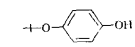
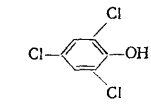
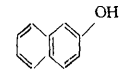
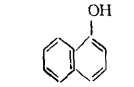
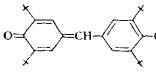
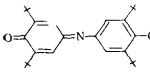
1. THE ISOTOPE EFFECT

If the peroxy-radical attacks the O–H bond of a phenol or the N–H bond of an amine, an isotope effect should be observed when hydrogen is replaced by deuterium. In a number of studies, where the inhibiting effect of phenols and aromatic amines on the oxidation of hydrocarbons was investigated[34-42], there was no isotope effect or it differed little from unity (1–1.3). A large isotope effect (10.6 for phenol at 65°C) was observed by Howard and Ingold[43] in the sensitised oxidation of styrene. The experimental difference between the activation energies[43] is $E_D - E_H = 1.1$ kcal mole^{-1}. Calculation yields a similar value[43]: $E_D - E_H = \frac{1}{2}h(\nu_{O\text{-}H} - \nu_{O\text{-}D}) = 1.36$ kcal mole^{-1}. The absence of an isotope effect in the reaction of $RO_2^{\cdot}$ and InH in the oxidation of other hydrocarbons can be accounted for by the formation of the hydroperoxide and rapid exchange via the reaction $InD + ROOH \rightleftharpoons InH + ROOD$. The oxidation of styrene yields a polymeric hydroperoxide which does not contain OOH groups and does not exchange hydrogen with the deuteriated inhibitor. An isotope effect was also observed for amines[44,45] and hydroxylamines[46] (Table 3).

2. THE REACTION MECHANISM

The isotope effect in experiments with deuteriated phenols and amines (Table 3) demonstrates convincingly that the rate-limiting stage in the reaction of $RO_2^{\cdot}$ with the inhibitor is the abstraction of a hydrogen atom: $RO_2^{\cdot} + InH \xrightarrow{k_7} ROOH + In$. The finding that phenolic ethers and tertiary aromatic amines do not exhibit an inhibiting effect is satisfactorily consistent with this mechanism. The molecular products of the reaction of inhibitors correspond

Table 1. The strength of O–H bonds in phenols.

Phenol	O–H bond strength, kcal mole^{-1}				
	method 1	method 2 C_6H_5Cl[27]	method 3 C_6H_6, C_7H_{16}[28,29]	method 4 C_6H_6[30]	method 5 C_2H_5OH — H_2O[31,32]
1	2	3	4	5	6
C_6H_5OH	—	—	—	83±3	84
p-$NO_2C_6H_4OH$	—	—	—	—	90
m-$NO_2C_6H_4OH$	—	—	—	—	83
p-$CH_3C_6H_4OH$	—	—	—	80±3	81
m-$CH_3C_6H_4OH$	—	—	—	—	82
o-$CH_3C_6H_4OH$	—	—	—	—	81
p-t-$C_4H_9C_6H_4OH$	—	84.4±1	—	—	—
p-$CH_3OC_6H_4OH$	—	79.1±1	—	75±3	—
p-BrC_6H_4OH	—	85.8±1	—	—	—
m-$C_2H_5OCOC_6H_4OH$	—	87.2±1	—	—	—
	—	86.2±1	—	—	—
	—	—	—	—	81
	—	—	—	—	81
	—	—	—	—	81
	81.2±0.1	—	78.8±3*	—	—
	79.8±0.2	—	—	—	—
	—	84.9±1	—	—	82
	—	—	—	77±3	80
	—	—	—	73±3	75.4
	78.5±0.5	—	75.8±3	—	—
	77.7±0.5		76.0±3	—	—

* Kalashnikova et al.[29] obtained erroneously another value of D_{O-H} for hydroxylamine, namely 71.9 kcal mole^{-1}. The error arose because they employed in the calculation D_{O-H} for the >NO–H bond in 4-dihydroxy-2,2,6,6-tetramethylpiperidine (D = 65 kcal mole^{-1}), while they investigated the equilibrium between phenol and 2,2,6,6-tetramethyl-1-hydroxy-4-oxopiperidine (D = 71.9 kcal mole^{-1})[30].

to the following sequence of transformations (for further details, see Denisov and Emanuel'[9]):

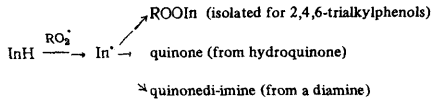


Table 2. Estimation of the N–H bond strengths in aromatic amines.

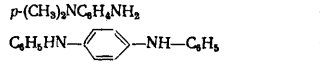
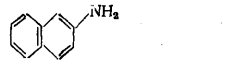
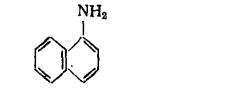
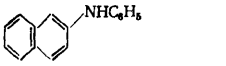
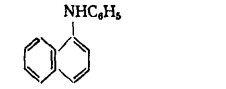
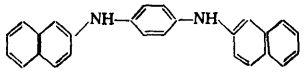
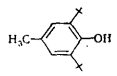
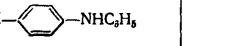
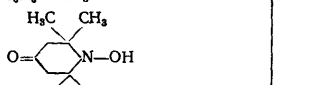
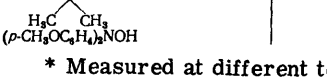
Amine	E_c, V (Ref.33)	D_{N-H}, kcal mole^{-1}	E(InH + O_2), kcal mole^{-1} (Ref.19)	D_N – H, kcal mole^{-1}
$C_6H_5NH_2$	1.135	88	—	—
$CH_3OC_6H_4NH_2$	0.892	77.5	—	—
p-$CH_3C_6H_4NH_2$	1.077	82	—	—
$C_6H_5NHCH_3$	1.053	81	—	—
$(C_6H_5)_2NH$	1.008	80	—	—
p-$(CH_3)_2NC_6H_4NH_2$	0.764	74.6	—	—
	0.710	73.3	—	—
	1.064	81.5	—	—
	0.841	76.3	30	78
	—	—	31	79
	—	—	32	80
	—	—	23	71

Table 3. The isotope effect in the reaction between $RO_2^{\cdot}$ and InH in styrene at 65°C.

Inhibitor	$(RO_2^{\cdot} + InH)$ litre mole^{-1} s^{-1}	k_H/k_D	References
	$2 \cdot 10^4$	10.6*	43
C_6H_5OH	—	~15	44
$(C_6H_5)_2NH$	$2 \cdot 10^4$	3.0	44
C_6H_5NH — β-$C_{10}H_7$	$5 \cdot 10^4$	3.0	44
C_6H_5NH — α-$C_{10}H_7$	$7 \cdot 10^4$	4.0	44
	—	3.0	45
$C_6H_5NHCH_3$	$4 \cdot 10^3$	3.0	45
	$5 \cdot 10^5$	3.0	46
	$5 \cdot 10^5$	2.0	46

* Measured at different temperatures: $k_H/k_D = 1.3 \exp(1100/RT)$.

a. The Polar Activated Complex $RO_2^{\cdot}$...H...In

Phenoxy-radicals react with phenols and amines, the corresponding rate constants being 10^4–10^6 litre mole^{-1}s^{-1} at 40–80°C. The question arises whether such high values of k_7 can be explained by the low strength of the In–H bond. We shall compare the values of k for the abstraction of H by the peroxy-radicals from tri-t-butylphenol (D_{O-H} = 81 kcal mole^{-1}, Table 1) and cumene (D_{C-H} = 76 kcal mole^{-1}): $\lg k\,(RO_2^{\cdot} + RH) = 6.51 - 10.13/\theta$ (Denisov[25]) and $\lg k\,(RO_2^{\cdot} + InH) = 6.58 - 3.4/\theta$ (Denisov[25]), where $\theta = 4.57 \times 10^{-3}\,T$. At 60°C, the ratio $k(RO_2^{\cdot} + InH)/k(RO_2^{\cdot} + RH) = 3 \times 10^4$. Thus the peroxy-radical

reacts with phenol 10^4 times faster than with cumene despite the fact that in cumene the C–H bond is somewhat weaker than the O–H bond of the phenol; the difference between the rate constants is associated with the difference between the activation energies. This can be explained by the markedly dipolar structure of the activated complex for the reaction between $RO_2^{\cdot}$ and InH, where the hydrogen atom is between two oxygen atoms (Fig. 1). Owing to the high electron affinity of oxygen atoms, a considerable proportion of the electron density of the O–H bond in the activated complex is located at the oxygen atom. The Coulombic attraction between $RO_2^{\delta-}$, $H^{\delta+}$, and $O^{\delta-}Ph$ causes a decrease of the potential barrier relative to that in the reaction between $RO_2^{\cdot}$ and RH. A similar situation obtains with aromatic amines, where the activated complex RO – O˙...H...N< is formed.

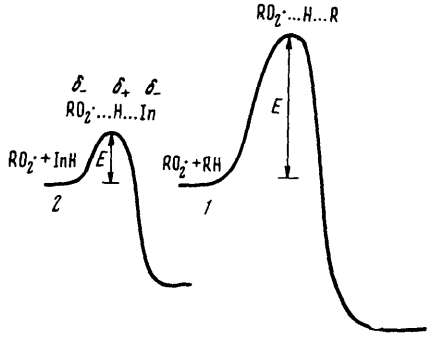


Figure 1. Schematic representation of the energy profiles for the reactions of the phenoxy-radicals with cumene (curve *1*) and ionol (curve *2*).

b. The $RO_2^{\cdot}$...HX Hydrogen Bond

Peroxy-radicals form a hydrogen bond of the type R'OO˙...HOR with the O–H group of water and alcohols[47–49]; this suggests that phenols and amines, which tend to form hydrogen bonds, react with peroxy-radicals via the preliminary formation of an association complex[50]:

$$RO_2^{\cdot} + InH \overset{k}{\rightleftharpoons} InH \ldots OOR \overset{k}{\rightarrow} In^{\cdot} + ROOH$$

Evidently the formation of the hydrogen bond between $RO_2^{\cdot}$ and InH increases the rate of reaction. It is not fortuitous that k_7 for the reaction of 2,6-dimethylphenol with the tetralylperoxy-radical[25] ($k_7 = 1.1 \times 10^4$ at 50°C) is higher than for the reaction involving 2,6-di-t-butylphenol[25] ($k_7 = 1.3 \times 10^3$): dimethylphenol forms a hydrogen bond with $RO_2^{\cdot}$, while di-t-butylphenol does not. In those cases where InH forms a hydrogen bond with the peroxy-radical, $k_7 = Kk$, $\Delta S_7^{\neq} = \Delta S_h + \Delta S^{\neq}$, $E_7 = E - Q_h$, and $\Delta H_7^{\neq} = \Delta H_h + \Delta H^{\neq}$, where the subscript h denotes a hydrogen bond. The quantity $K_{RO_2^{\cdot}\ldots HOPh}$ is unknown; for comparison, one can adduce K (phenol – dioxan) = 15.2 litre mole^{-1} in benzene at 25°C.[51]

3. DEPENDENCE OF k_7 ON THE STRUCTURE OF THE INHIBITOR.

The values of k_7 have been measured for a large number of phenols and amines[25] (the methods of measurement of k_7 have been described in a monograph[3]), but the vast majority of the measurements have been made at a single temperature. The activation energies for the reaction between $RO_2^{\cdot}$ and InH have been rarely measured. Table 4 shows that the values of E_7 are in the range 3.5–5.5 kcal mole^{-1}. However, one should bear in mind that the true activation energy for the reaction $RO_2^{\cdot}\ldots HIn \rightarrow ROOH + In^{\cdot}$ is higher and equal to $E_7 + \Delta H_h$ and $\Delta H_h = 3$–4 kcal mole^{-1}. The rate constant k_7 is almost independent of the structure of the peroxy-radical of the hydrocarbon (Table 4).

Table 4. Rate constants for the reaction between $RO_2^{\cdot}$ and InH.

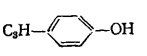
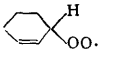
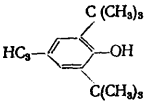
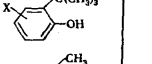
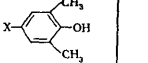
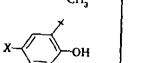
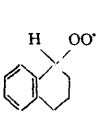
Inhibitor	$RO_2^{\cdot}$	Solvent	t, °C	lg k (litre mole^{-1} s^{-1})	lg A	E, kcal mole^{-1}	References
		cyclo-C_6H_{10}	49	3.88	7.02	4.5	52
ditto	$C_6H_5C(CH_3)_2OO\cdot$	$C_6H_5(CH_3)_2CH$	56	4.12	6.78	4.0	53
	~$CH_2(C_6H_5)CHOO\cdot$	$C_6H_5CH\text{-}CH_2$	40	4.00	7.92	5.6	54
ditto	$C_6H_5(CH_3)CHOO\cdot$	$C_6H_5C_2H_5$	60	4.34	6.58	3.4	55
α-$C_{10}H_7OH$	$C_6H_5(CH_3)CHOO\cdot$	$C_6H_5C_2H_5$	60	5.65	8.15	3.8	56
$(C_6H_5)_2NH$	$(CH_3)_2C(OO\cdot)CH_2CH\cdot(CH_3)_2$	$(CH_3)_2CHCH_2CH\cdot(CH_3)_2$	60	2.48	4.78	3.5	57

Table 5. Dependence of k_7 on the structure of the inhibitor.

InH	$RO_2^{\cdot}$	t°, C	Function	ρ	lg k_7, X=H	References
XC_6H_4OH	$C_6H_2(CH_3)_2COO\cdot$	62	σ	–3.7		35
ditto	$C_6H_5CH(OO\cdot)CH_2$~	65	σ+	–1.58	3.465	58
«	ditto	65	σ	–1.49	3.465	58
	»	65	σ+	–1.46	4.22	59
	»	65	σ+	–1.36	4.58	59
	»	65	σ+	–1.11	3.70	59
ditto		65	σ+	–1.36	3.89	60
$XC_6H_4NHCH_3$	$C_6H_5CH(OO\cdot)CH_2$	65	σ+	–1.6	3.60	45
$(XC_6H_4)_2NH$	ditto	65	σ+	–0.89	4.50	45

However, acylperoxy-radicals react with hydroquinone faster than do alkylperoxy-radicals[25]. Substituents in the benzene ring have a marked influence on the activity of the inhibitor: electropositive substituents increase and electronegative substituents decrease k_7. There is a linear correlation between $\lg k_7$ and σ^+ (Table 5).

4. EFFECT OF THE SOLVENT

When oxygen-containing compounds (H_2O, ROH, RCOOH, etc.) are added to the hydrocarbon, the rate of reaction of peroxy-radicals with the inhibitor decreases significantly[61-63]. This is primarily due to the formation of an intermolecular hydrogen bond In–H...Y, which blocks the susceptible O–H or N–H bond of the inhibitor and thus inhibits the reaction between $RO_2^\cdot$ and InH. In those cases where the solution contains the molecules of a hydroxy-compound (other than the inhibitor), the peroxy-radicals form with them a radical type hydrogen bond $RO_2^\cdot$...HOX, which causes additional inhibition of the reaction between peroxy-radicals and the inhibitor[62,63]. In the presence of compounds forming a hydrogen bond, we are dealing with the following series of stages in the inhibited oxidation reaction:

$$RO_2^\cdot + HIn \rightleftarrows RO_2^\cdot \ldots HIn \rightarrow ROOH + In^\cdot ,$$

$$InH + XOH \rightleftarrows InH \ldots O\begin{matrix}H\\X\end{matrix} ,$$

$$RO_2^\cdot + HOX \rightleftarrows RO_2^\cdot \ldots HOX ,$$

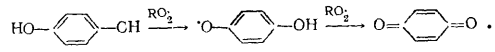
$$RO_2^\cdot \ldots HOX + InH \rightarrow ROOH + In^\cdot + HOX .$$

IV. REACTION OF In$^\cdot$ WITH $RO_2^\cdot$

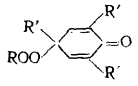
1. REACTION PRODUCTS

In the inhibited oxidation of hydrocarbons and polymers, free radicals (detected by ESR) are formed from the inhibitor. In the oxidation of octadecene at 171°C, a free radical (probably a nitroxide radical) is formed from phenyol-α-naphthylamine[64], its maximum experimental concentration being $[In^\cdot]_{max} \simeq 10^{-3}$ M for $[InH]_0 = 0.1$ M. A diphenylnitroxide radical is formed in the reaction of cumenylperoxy-radicals with diphenylamine[65]. Phenoxy-radicals have been detected in the oxidation of polypropylene by α-naphthol[66] {200°C, O_2 pressure 400 mmHg, $[In^\cdot]$ 10^{-5} M} and β-naphthol[66] {200°C, O_2 pressure 400 mmHg, $[In^\cdot]_{max} \simeq 2 \times 10^{-6}$ M}. The formation of labile coloured compounds was observed when the RH–O_2–amine system (diphenylamine, *N*-methylaniline, *NN'*-diphenyl-*p*-phenylenediamine)[67] was irradiated with electrons.

Molecular products are formed in the reaction of In$^\cdot$ radicals with $RO_2^\cdot$ and with one another. Hydroquinone is converted into quinone via the mechanism[68]:



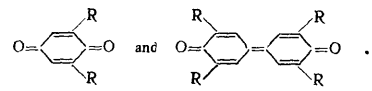
2,4,6-Trialkylphenols are converted into compounds of the type[69-71]



via the mechanism

$$InH \xrightarrow{RO_2^\cdot} In^\cdot \xrightarrow{RO_2^\cdot} ROOIn .$$

2,6-Dialkylphenol are converted into quinones[71-73]:



Diphenyl-*p*-phenylenediamine is converted quantitatively into quinonedi-imine[69], the reaction being analogous to that of hydroquinone.

2. THE STOICHIOMETRIC INHIBITION COEFFICIENT

The stoichiometric inhibition coefficient f is defined as the number of chains terminated by the inhibitor molecule and its reaction products under the given conditions. On the basis of the structures of the stable reaction products of hydroquinone, diphenyl-*p*-phenylenediamine, and 2,4,6-tri-t-butylphenol, one may conclude that $f = 2$ for these reference inhibitors. This permits the measurement of f for other inhibitors, by comparing the induction periods in initiated oxidation in the presence of the given and reference inhibitors. The values of f in cumene undergoing oxidation have been measured[69,74] and for the majority of phenols and aromatic amines proved to be close to two (the values of f are quoted in the author's handbook[25]).

3. REACTION OF THE DIPHENYLNITROGEN RADICAL WITH $RO_2^\cdot$

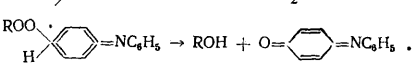
In the oxidation of cumene inhibited by diphenylamine, Thomas[65] detected a nitroxide radical by ESR. The same radical was also formed in cumene undergoing oxidation from a diphenylnitrogen radical (tetraphenylhydrazine served as a source of diphenylnitrogen radicals). Like diphenylamine, the diphenylnitroxide radical inhibits the oxidation of cumene, reacting with $RO_2^\cdot$ (the rate constant is 2.5×10^3 litre mole^{-1}s^{-1} at 68.5°C).[75] The ratio of the rate of formation of diphenylnitroxide radicals to the rate of initiation w_i is 0.11–0.19 for secondary peroxy-radicals and 0.20–0.33 for tertiary peroxy-radicals[76]. The following mechanism has been proposed for the reaction of diphenylamine (and other secondary amines) with peroxy-radicals[76,77]:

$$RO_2^\cdot + (C_6H_5)_2NH \rightleftarrows RO_2^\cdot \ldots HN(C_6H_5)_2 \rightarrow ROOH + (C_6H_5)_2N^\cdot ,$$

$$RO_2^\cdot + (C_6H_5)_2N \rightleftarrows ROON(C_6H_5)_2 \rightarrow [RO^\cdot + (C_6H_5)_2NO^\cdot] ,$$

$$[RO^\cdot + (C_6H_5)_2NO^\cdot] \rightarrow RO^\cdot + (C_6H_5)_2NO^\cdot ,$$

$$[RO^\cdot + (C_6H_5)_2NO^\cdot] \rightarrow \text{>C=O} + (C_6H_5)_2NOH \text{ (for s-}RO_2^\cdot\text{)}$$

$$(C_6H_5)_2N^\cdot + RO_2^\cdot \rightarrow$$  $$\rightarrow ROH +$$ 

This mechanism explains why the rate of formation of $(C_6H_5)_2NO^\cdot$ is always lower than w_i and why the ratio is smaller for secondary peroxy-radicals than for tertiary radicals. Diphenylnitroxide radicals terminate chains by reacting with $RO_2^\cdot$ and R$^\cdot$. The mechanism and the products of the reaction of $(C_6H_5)_2NO^\cdot$ and $RO_2^\cdot$ are so far unknown. Primary aromatic amines do not form oxides in reactions with peroxy-radicals[77]. It has been suggested that they give rise to nitroso-compounds[77]:

$$RO_2^\cdot + ArNH_2 \rightleftarrows ROO^\cdot \ldots HNHAr \rightarrow ROOH + ArN\dot{H} ,$$

$$ArN\dot{H} + ROO^\cdot \rightarrow [ArNHOOR] \rightarrow ArNO + ROH .$$

4. CHEMILUMINESCENCE IN THE REACTION OF $RO_2^{\cdot}$ WITH In$^{\cdot}$

In liquid-phase oxidation, chemiluminescence arises owing to the formation of excited molecules by the reaction between two peroxy-radicals[78]. This fact has served as a basis of the chemiluminescence methods for the investigation of oxidation reactions[78]. It was established recently that chemiluminescence can arise in liquid-phase oxidation in the presence of amines and polar molecules[79].

If an aromatic amine is added to cumene undergoing oxidation, the intensity of the luminescence decreases owing to the decrease in the rate of reaction between $RO_2^{\cdot}$ radicals. When an amine is added to cyclohexanol or chlorobenzene undergoing oxidation in the presence of t-butylalcohol and an initiator, the luminescence intensity increases despite the fall of $[RO_2^{\cdot}]$. Separate experiments showed that the decrease of luminescence is observed only in the presence of peroxy-radicals (initiator + O_2), aromatic amines, and polar (oxygen-containing) molecules (H_2O, ROH, R_2O). It was concluded that luminescence arises as a result of the reaction between peroxy-radicals and radicals generated from the aromatic amines. These are not nitroxide radicals, since luminescence is observed both with secondary amines (which give rise to nitroxide radicals) and with primary amines (which do not). Primary amines probably generate nitrogen radicals:

$$AmH + RO_2^{\cdot} \rightarrow Am^{\cdot} \xrightarrow{RO_2^{\cdot}} \Pi^* \rightarrow \Pi + h\nu$$

(only in the presence of polar molecules). The involvement of an amine radical in luminescence is confirmed by the finding that the addition of α-naphthol, which decreases $[Am^{\cdot}]$ owing to the reversible reaction

$$Am^{\cdot} + PhOH \rightleftharpoons AmH + PhO^{\cdot},$$

lowers the luminescence intensity. The occurrence of a new reaction generating chemiluminescence (in addition to the reaction between $RO_2^{\cdot}$ radicals) necessitates a very cautious approach to the employment of the chemiluminescence method for the investigation of the kinetics of the oxidation of organic compounds inhibited by amines and for the determination of its parameters.

V. REACTION OF INHIBITOR RADICALS WITH THE HYDROPEROXIDE

In a study of the effect of the hydroperoxide on the initiated oxidation of cumene in the presence of inhibitors, Thomas established[15] that the addition of the hydroperoxide accelerates the oxidation of cumene in the presence of phenol but has no influence if the oxidation of cumene is inhibited by 2,6-di-t-butylphenol and ionol. The experiments were performed at a low temperature (57.2°C) in the presence of azobisisobutyronitrile (8×10^{-3} M) when the additional initiation owing to the hydroperoxide was very insignificant. This can be accounted for by the reaction

$$PhO^{\cdot} + RO_2H \xrightarrow{k_{-7}} PhOH + RO_2^{\cdot},$$

as a result of which the concentration of peroxy-radicals increases in the presence of the hydroperoxide. The difference between the experiments with phenol and 2,6-di-t-butylphenol can be explained by the different reactivities of the phenoxy-radicals: a reactive phenoxy-radical is formed from phenol, while the 2,6-di-t-butylphenoxy-radical is relatively inactive and reacts slowly with the hydroperoxide. One can postulate the formation of a

Table 6. The reaction In$^{\cdot}$ + ROOH → InH + $RO_2^{\cdot}$

(In$^{\cdot}$ = )

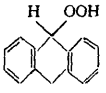
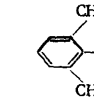
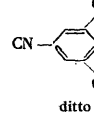
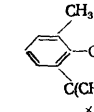
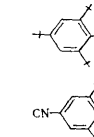
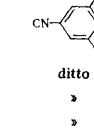
ROOH	Solvent	t, °C	lg k	References
$(CH_3)_3COOH$	CCl_4	0—21	6.33—8.3/θ	81
	C_6H_5Cl	24—60	4.11—5 8/θ	82
	C_6H_5Cl	24—60	5.60—8.6/θ	82

Table 7. The rate constant ratio k_{-7}/k_8 at 65°C in tetralin[83].

In$^{\cdot}$	ROOH	k_{-7}/k_8	k_{-7}, litre mole^{-1} s^{-1}
		$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{3}$
	ditto	$2.2 \cdot 10^{-5}$	$2.2 \cdot 10^{4}$
	»	$.6 \cdot 10^{-5}$	$2.6 \cdot 10^{4}$
m-$CH_3C_6H_4O^{\cdot}$	»	$3.7 \cdot 10^{-5}$	$3.7 \cdot 10^{4}$
$C_6H_5O^{\cdot}$	»	$5.2 \cdot 10^{-5}$	$5.2 \cdot 10^{4}$
ditto	$(CH_3)_3COOH$	$2.2 \cdot 10^{-5}$	$2.2 \cdot 10^{4}$
»	$C_6H_5(CH_3)_2COOH$	$2.2 \cdot 10^{-5}$	$2.2 \cdot 10^{4}$
»	$(C_6H_5)_3COOH$	$2.0 \cdot 10^{-6}$	$2.0 \cdot 10^{3}$
m-$CH_3OC_6H_4O^{\cdot}$		$2.3 \cdot 10^{-5}$	$2.3 \cdot 10^{4}$
p-Cl—$C_6H_4O^{\cdot}$	ditto	$2.8 \cdot 10^{-5}$	$2.8 \cdot 10^{4}$
	»	$1.7 \cdot 10^{-6}$	$1.7 \cdot 10^{3}$
	»	$9.2 \cdot 10^{-6}$	$9.2 \cdot 10^{3}$
ditto	$(CH_3)_3COOH$	$2.0 \cdot 10^{-6}$	$2.0 \cdot 10^{3}$
»	$C_6H_5(CH_3)_2COOH$	$2.0 \cdot 10^{-6}$	$2.0 \cdot 10^{3}$
»	$(C_6H_5)_3COOH$	$3.4 \cdot 10^{-7}$	$3.4 \cdot 10^{2}$
		$4.6 \cdot 10^{-7}$	$4.6 \cdot 10^{2}$
	ditto	$1.0 \cdot 10^{-8}$	10
	»	$4.9 \cdot 10^{-7}$	$4.9 \cdot 10^{2}$
ditto	$(CH_3)_3COOH$	$1.3 \cdot 10^{-7}$	$1.3 \cdot 10^{2}$
»	$C_6H_5(CH_3)_2COOH$	$1.5 \cdot 10^{-7}$	$1.5 \cdot 10^{2}$
»	$(C_6H_5)_3COOH$	$2 \cdot 10^{-8}$	20

* Calculated on the assumption that $k_8 = 10^9$ litre mole^{-1}s^{-1}.

hydrogen bond between phenol and the hydroperoxide, which should also retard the reaction between phenol and $RO_2^{\cdot}$:

$$PhOH + ROOH \rightleftharpoons PhOH \ldots \overset{H}{O}OR \quad \text{or} \quad PhOH \ldots \overset{OH}{O}R .$$

Calculation of the association constant from the relation between the rate of oxidation and [ROOH] yields an unreasonably large value of 300 litre mole^{-1} for the association constant of phenol with cumenyl hydroperoxide (at 57°C in cumene), while the same constant in carbon tetrachloride at 25°C is 12 litre mole^{-1} (determined from spectroscopic data). Evidently the hydrogen bond alone cannot account for this effect. A decrease of the relative overall rate constant for the reaction of the inhibitor with peroxy-radicals after the introduction of the hydroperoxide is observed also for aromatic amines[61]. As in the case of phenol, this is associated with the exchange reaction between the amine radical and the hydroperoxide (Denisov et al.[61] regarded this erroneously as a result of complex formation between the amine and the hydroperoxide).

The kinetics of inhibited oxidation in the presence of the hydroperoxide also demonstrate convincingly the occurrence of reaction between In$^{\cdot}$ and ROOH.

The inhibited oxidation of a hydrocarbon can be represented as follows taking into account the reaction between In$^{\cdot}$ and ROOH:

$$\text{initiator.} \rightarrow r^{\cdot} \xrightarrow{RH} R^{\cdot}, \quad (i)$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}, \quad (1)$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}, \quad (2)$$

$$ROOH + RH \rightarrow RO^{\cdot} + H_2O + R^{\cdot}, \quad (3)$$

$$R^{\cdot} + R^{\cdot} \rightarrow R\text{–}R, \quad (4)$$

$$R^{\cdot} + RO_2^{\cdot} \rightarrow ROOR, \quad (5)$$

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow \text{mol. products}, \quad (6)$$

$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot}, \quad (7)$$

$$ROOH + In^{\cdot} \rightarrow RO_2^{\cdot} + InH, \quad (-7)$$

$$RO_2^{\cdot} + In^{\cdot} \rightarrow ROOIn . \quad (8)$$

At a fairly high partial pressure of oxygen when $[RO_2^{\cdot}] \gg [R^{\cdot}]$ and in the presence of an initiator when $W_i \gg k_3[ROOH][RH]$, reactions (3)–(5) may be disregarded. If the inhibitor radical is incapable of chain propagation owing to the reaction with the hydroperoxide, reaction (7) is responsible for chain termination and therefore $W_i = fk_7[InH][RO_2^{\cdot}]$; the rate of oxidation (for sufficiently long chains) is $W = k_2[RH]w_i/fk_7InH$, where k_2 refers to the reaction between $RO_2^{\cdot}$ and RH. When reaction (-7) is rapid $\{k_{-7}[ROOH][In^{\cdot}] \gg k_8[In^{\cdot}][RO_2^{\cdot}]$, k_8 refers to the reaction between $RO_2^{\cdot}$ and $In^{\cdot}\}$, chain termination is due to reaction (8), $W_i = 2k_8[In^{\cdot}][RO_2^{\cdot}]$, $k_7[InH][RO_2^{\cdot}] = k_{-7}[In^{\cdot}][ROOH]$, and $W = k_2[RH][RO_2^{\cdot}] = k_2[RH]\{k_{-7}W_i[ROOH]/2k_8k_7[InH]\}^{1/2}$. The experimental results are consistent with these formulae: for ionol in cumene[15] and tetralin[80] undergoing oxidation, $W \propto W_i/[InH]$, and for phenol in cumene[15] and tetralin[80], $W \propto \sqrt{W_i}/[InH]$. For phenol, the ratio $k_{-7}/k_8 = 5.7 \times 10^{-5}$ in cumene[15] at 57.2°C and $k_{-7} = 2.3 \times 10^5$ litre mole^{-1}s^{-1}, i.e. is very high. The values of k_{-7} are listed in Tables 6 and 7.

VI. CHAIN PROPAGATION VIA THE REACTION OF In$^{\cdot}$ WITH THE HYDROCARBON

Phenoxy-radicals can abstract a hydrogen atom not only from the hydroperoxide but also from hydrocarbons. If the phenoxy-radical is reactive and the hydrocarbon has a fairly weak C–H bond, such a reaction will be comparatively fast and will affect the retarding action of the inhibitor. Bickel and Kooyman[14], who studied the kinetics of the inhibited oxidation of 9,10-dihydroanthracene, established that the relation $W/[InH]^{1/2} = C_1 + C_2[InH]$, which is consistent with the involvement of In$^{\cdot}$ in chain propagation via the reaction with the hydrocarbon, holds for 4-t-butyl-2,6-dimethylphenol. In a study of the sensitised oxidation of tetralin in the presence of phenols, Mahoney and Ferris[84] established the following relation between the rate of oxidation and the concentrations of phenol, the hydrocarbon, and the initiator: $w = \text{const.}\,[RH]^{3/2}[C_6H_5OH]^{-\frac{1}{2}}[\text{initiator}]^{\frac{1}{2}}$. This relation agrees satisfactorily with the oxidation mechanism involving reactions (i) and (1)–(6) and the following reactions involving the inhibitor:

$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot}, \quad (7)$$

$$RO_2^{\cdot} + In^{\cdot} \rightarrow ROOIn, \quad (8)$$

$$In^{\cdot} + In^{\cdot} \rightarrow In\text{–}In, \quad (9)$$

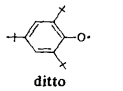
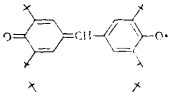
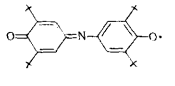
$$In^{\cdot} + RH \rightarrow InH + R^{\cdot} . \quad (10)$$

According to this mechanism, the rate of oxidation for $k_9[In^{\cdot}] \ll k_8[RO_2^{\cdot}]$ is

$$W = k_2\left(\frac{k_{10}w_i}{2k_7k_8}\right)^{1/2}[RH]^{3/2}[InH]^{-1/2} .$$

The constants k_{10} for stable phenoxy-radicals are listed in Table 8.

Table 8. Rate constants for the reaction In$^{\cdot}$ + RH → InH + R.

In	RH	t°,C	$\lg k$, $\theta = 4.57 \cdot 10^{-3}T$	References
	n-$C_{10}H_{22}$	120—150°	10.415—27.5/θ	
ditto	$(CH_3)_2CH(CH_2)_7CH_3$	90—150	9.28—25.5/θ	85
»	$C_6H_5CH_3$	100—150	8.78—23.0/θ	
»	$C_6H_5C_2H_5$	70—100	5.43—17.0/θ	
»	$C_6H_5CH(CH_3)_2$	100—160	4.69—16.5/θ	
»	$(C_6H_5)_2CH_2$	80—150	5.08—14.5/θ	
	$C_6H_5C_2H_5$	60—140	3.255—14.0/θ	86
	$C_6H_5C_2H_5$	80—130	3.48—14.8/θ	86

In 1955 Hammond et al.[35] established that the rate of oxidation of cumene in the presence of phenol and *N*-methylaniline is directly proportional to $\{[\text{initiator}]/[InH]\}^{\frac{1}{2}}$. On this basis, they proposed the following mechanism for chain termination involving the inhibitor:

$$RO_2^{\cdot} + InH \rightleftharpoons RO_2^{\cdot} \ldots InH ,$$

$$RO_2^{\cdot} + RO_2^{\cdot} \ldots InH \rightarrow ROOH + ROOIn .$$

This mechanism accounts for the relation $W \propto \{W_i/[InH]\}^{\frac{1}{2}}$ but it is inconsistent with the isotope effect for deuterium-substituted phenols and amines and the absence of an inhibiting effect of phenolic ethers and tertiary amines. There is also a difference between the kinetic relations which follow from the Boozer–Hammond mechanism and the mechanism involving In$^{\cdot}$ in chain propagation. According to the Boozer–Hammond mechanism, $W \propto [RH]$, while according to the mechanism involving reactions (7), (8), and (10), $W \propto [RH]^{3/2}$. The latter relation is in fact observed experimentally[35]. Therefore the mechanism involving the reaction between In$^{\cdot}$ and RH must be regarded as valid for phenols and amines in hydrocarbons undergoing oxidation; the Boozer–Hammond mechanism does not obtain in hydrocarbons in the presence of phenols and amines.

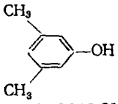
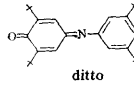
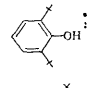
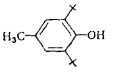
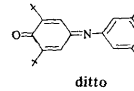
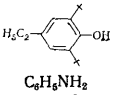
VII. THE EXCHANGE REACTION $In_1^{\cdot} + In_2H \rightleftharpoons In_1H + In_2^{\cdot}$

1. AMINE + PHENOL

In a study of the combined action of β-naphthylphenylamine and 2,6-di-t-butylphenol on the oxidation of ethylbenzene, Karpukhina et al.[16] established an interesting fact: if the phenol is present in a hydrocarbon undergoing oxidation, the amine is hardly consumed, a rapid decrease of its concentration in the oxidation process beginning only after the phenol has been used up. This finding cannot be accounted for by the fact that the amine reacts with peroxy-radicals more slowly than the phenol. On the contrary, for the amine $k_7 = 1.3 \times 10^5$ litre mole^{-1}s^{-1}, while for the phenol $k_7 = 0.95 \times 10^4$ litre mole^{-1}s^{-1} (ethylbenzene, 60°C). The unusual kinetics of the consumption of the amine in the presence of the phenol can be explained by the reaction Am$^{\cdot}$ + PhOH ⇌ AmH + PhO$^{\cdot}$. The reaction has been demonstrated in experiments with tetraphenylhydrazine[16]. The dissociation of tetraphenylhydrazine results in the formation of diphenylnitrogen radicals, which are converted into diphenylamine in the presence of ionol. In the absence of the phenol, very little diphenylamine is formed. The exchange reaction between Am$^{\cdot}$ and PhOH leads to a synergic effect: a mixture of the amine and the phenol gives rise to more prolonged inhibition of the oxidation of ethylbenzene at 120°C than either inhibitor separately[87–91].

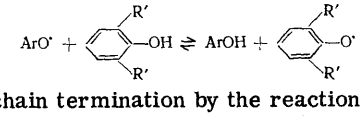
This can be explained by the fact that the amine gives rise to a radical capable of chain propagation by reaction with the hydrocarbon. Therefore the inhibition of the oxidation by the amine is incomplete despite the high rate constant k_7. The dialkylphenol forms relatively inactive phenoxy-radicals incapable of chain propagation, but it reacts with peroxy-radicals more slowly than does the amine. The rapid exchange reaction between Am$^{\cdot}$ and ArOH makes it possible to combine two valuable properties, namely the rapid chain termination by the reaction of $RO_2^{\cdot}$ with the amine and the inactivity of ArO$^{\cdot}$ in chain propagation reactions. β-Naphthylphenylamine is not consumed in oxidation in the presence of phenols giving rise to inactive phenoxy-radicals and the equilibrium Am$^{\cdot}$ + PhOH ⇌ AmH + PhO$^{\cdot}$ is displaced to the right. Investigation showed that this is true of 2,6-dialkylphenols, while in the case of *p*-substituted and mono-*o*-substituted phenols the effect of the replacement of Am$^{\cdot}$ by PhO$^{\cdot}$ is absent[55,91]. *p*-Phenylenediamine and also hydroxy-derivatives of diphenylamine and β-naphthylphenylamine likewise fail to give rise to this type of effect[92] (apparently the Am$^{\cdot}$ radicals derived from these amines are relatively inactive).

Table 9. Rate constants for the reaction ArO$^{\cdot}$ + In$^{\cdot}$H → ArOH + In$^{\cdot}$.

ArO$^{\cdot}$ radical	InH	Solvent	t°,C	lg k (litre mole^{-1} s^{-1})	References
	C_6H_5OH	C_6H_6	25—60	4.85— 5 5/0	82
ditto	C_6H_5OH	C_6H_6	24	0 49	81
»	o-$NO_2C_6H_4OH$	C_6H_6	20—90	4.78—12.1/0	93
»	p-$(CH_3)_3CC_6H_4OH$	C_6H_6	25—60	5.88— 5.3/0	93
»	p-$CH_3OC_6H_4OH$	C_6H_6	25	3.28	82
»	p-$CH_3OC_6H_4OH$	C_6H_6	24	3.48	94
»	p-$C_6H_5C_6H_4OH$	C_6H_6	24	2.10	
»	p-$(CH_3)_3CC_6H_4OH$	C_6H_6	24	1.66	
»	p-BrC_6H_4OH	C_6H_6	24	0.64	
»	p-$CH_3OCOC_6H_4OH$	C_6H_6	24	1.32	
»	p-CNC_6H_4OH	C_6H_6	24	1.88	
»	$(CH_3)_3CC_6H_4OH$	C_6H_6	24	1.02	
»		C_6H_6	24	1.19	94
»	m-$C_2H_5OCOC_6H_4OH$	C_6H_6	24	1 78	
»	m-CNC_6H_4CH	C_6H_6	24	2.90	
»	m-$ClC_6H_4NH_2$	CCl_4	23.5	0.60	81
»	C_6H_5NH-β-$C_{10}H_7$	$C_6H_5C_2H_5$	—30—23	4.61—4.0/0	55
	C_6H_5OH	o-$CH_3C_6H_4CH_3$	30—50	6.49—10.5/0	
ditto	p-$CH_3C_6H_4OH$	ditto	30	2.90	
»	p-$NO_2C_6H_4OH$	»	30	2.90	
»		»	30	0.49	95
»		»	30—50	3.84—5 5/0	
		o-$CH_3C_6H_4CH_3$	30	1.74	
ditto	$C_6H_5NH_2$	ditto	30—50	3.85—7.3/0	
»	$(C_6H_5)_2NH$	»	30—50	1.30—6.4/0	
»	$(p$-$NO_2C_6H_4)_2NH$	»	50	3.38	95
»	$(m$-$NO_2C_6H_4)NH$	»	50	3,32	
»	$(o$-$NO_2C_6H_4)_2NH$	»	50	3.90	

2. PHENOL + PHENOL

An analogous exchange mechanism was investigated by Mahoney[94] in mixtures of two inhibitors, one of which was a 2,6-dialkylphenol and the other a phenol with a substituent in the *para*-position. A 2,6-dialkylphenol reacts with $RO_2^{\cdot}$ relatively slowly, but it gives rise to inactive radicals. A phenol with a substituent in the *para*-position reacts rapidly with $RO_2^{\cdot}$, but the phenoxy-radical formed from it is reactive and can cause chain propagation by reaction with the hydrocarbon (if the latter has a weak C–H bond) and with the hydroperoxide (see above). When two such phenols are introduced sumultaneously, the rapid exchange process (equilibrium displaced to the right)



causes fast chain termination by the reaction of $RO_2^{\cdot}$ and ArOH, while the ArO$^{\cdot}$ radicals take little part in chain propagation reactions, since they undergo rapid exchange for the inactive 2,6-dialkylphenoxy-radicals. The rate constants for the exchange reactions involving phenoxy-radicals are listed in Table 9.

VIII. REACTION OF THE INHIBITOR WITH THE HYDROPEROXIDE

Rapid chain termination by inhibitors (phenols and aromatic amines) is due to the fact that the peroxy-radical is a powerful oxidant and the inhibitors are reductants. Another oxidant (the hydroperoxide), which can react with the inhibitor, is formed and is present, apart from $RO_2^{\cdot}$, in organic compounds undergoing oxidation. If its reaction with the inhibitor results in the formation of molecular products only, it leads merely to an additional consumption of the inhibitor. If it involves the formation of free radicals, it can serve as an additional source of initiation. This must be borne in mind in the analysis of the mechanism of the inhibited oxidation of hydrocarbons and polymers.

The reaction of phenols with cumenyl hydroperoxide was investigated in chlorobenzene solution[18]. The rate of reaction is $w = k[\mathrm{PhOH}][\mathrm{ROOH}]$. It results in the formation of radicals, which initiate the oxidation. This has been demonstrated in experiments on the oxidation of cumene with the hydroperoxide and *p*-methoxyphenol.

Under these conditions, the oxidation mechanism in the absence of an initiator includes reactions (1)–(6) and the following reactions with the inhibitor:

$$\mathrm{InH} + \mathrm{RO_2^{\cdot}} \rightarrow \mathrm{In^{\cdot}} + \mathrm{ROOH}\,, \qquad (7)$$

$$\mathrm{ROOH} + \mathrm{In^{\cdot}} \rightarrow \mathrm{RO_2^{\cdot}} + \mathrm{InH}\,, \qquad (-7)$$

$$\mathrm{In^{\cdot}} + \mathrm{RO_2^{\cdot}} \rightarrow \mathrm{InOOR}\,, \qquad (8)$$

$$\mathrm{InH} + \mathrm{ROOH} \rightarrow \mathrm{In^{\cdot}} + \mathrm{H_2O} + \mathrm{RO^{\cdot}}\,. \qquad (11)$$

The radicals formed by reaction (11) are partly destroyed in the cage and are partly released into the bulk phase, so that the rate constant for initiation owing to this reaction is $k_{i11} = 2ek_{11}$, where e is the probability of the release of the radicals into the bulk phase. The rate of oxidation $W = k_2[\mathrm{RH}][\mathrm{RO_2^{\cdot}}]$,

$$[\mathrm{RO_2^{\cdot}}] \simeq \sqrt{\frac{k_{-7}[\mathrm{ROOH}]^2 W_i}{2k_7k_8[\mathrm{InH}]}};\quad W_i = 2k_3[\mathrm{ROOH}][\mathrm{RH}] + 2ek_{11}[\mathrm{ROOH}][\mathrm{InH}]\,,$$

and

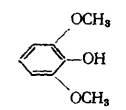
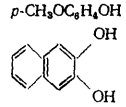
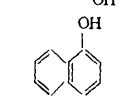
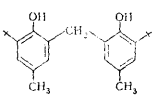
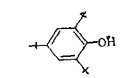
$$\frac{W^2[\mathrm{InH}]}{[\mathrm{ROOH}]^2} = \frac{k_2^2[\mathrm{RH}]^2 k_{-7}}{2k_7k_8}\cdot(2k_3[\mathrm{RH}] + 2ek_{11}[\mathrm{InH}])\,.$$

This type of relation is in fact observed experimentally, which indicates the formation of radicals in the reaction between the phenol and the hydroperoxide. By comparing k_{11} (determined from the rate of decomposition of the hydroperoxide) with k_{i11} {determined from the relation between W and [InH]}, $e = 0.27$ at 120°C was found. The formation of phenoxy-radicals in the reaction between ROOH and the phenol was demonstrated by the ESR method for tri-t-butylphenol. For sterically hindered phenols, it is reasonable to postulate the formation of a hydrogen bond between the phenol and the hydroperoxide. The reaction mechanism is as follows:

$$\mathrm{ROOH} + \mathrm{PhOH} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{ROO}\overset{\mathrm{H}}{\underset{\mathrm{HOPh}}{\diagup\diagdown}} \xrightarrow{k} \left[\mathrm{RO^{\cdot}} + \mathrm{H_2O} + \mathrm{PhO^{\cdot}}\right] \rightarrow \mathrm{RO^{\cdot}} + \mathrm{H_2O} + \mathrm{PhO^{\cdot}} + \text{mol. products}\,.$$

The experimental rate constant $k_{11} = Kk$, where K is the effective equilibrium constant (one must bear in mind that the phenol and the hydroperoxide forms several hydrogen-bonded association complexes, of which only one reacts). The rate constant k_{11} depends very markedly on the structure of the phenol (Table 10). The reaction between amines and peroxides has been discussed in a review[13].

Table 10. Rate constants for the reactions of phenols with cumenyl hydroperoxide[18] (solvent—chlorobenzene and n-decane in experiments with 2,4,6-tri-t-butylphenol).

Phenol	k_{11} at 140°C, litre mole^{-1} s^{-1}	E, kcal mole^{-1}	lg$A$ (litre mole^{-1} s^{-1})
	$6.5\cdot10^{-3}$	22.9±1.1	9.91±0.63
p-$CH_3OC_6H_4OH$	$4.3\cdot10^{-3}$	23.3±1.4	9.95±0.78
	$4.5\cdot10^{-3}$	25.8±0.8	11.33±0.45
	$6.7\cdot10^{-4}$	24.2±1.0	9.63±0.89
	$4.2\cdot10^{-4}$	26.0±0.7	10.36±0.42
p-$CH_3C_6H_4OH$	$2.0\cdot10^{-4}$	26.2±2.0	10.15±1.11
	$7.8\cdot10^{-5}$	25.9±1.0	9.60±0.54

The hypothesis has been put forward[96] that the inhibitor is involved in degenerate chain branching via its interaction with a pair of radicals in a solvent (or polymer) cage. On decomposition of the hydroperoxide by the reaction

$$\mathrm{ROOH} + \mathrm{RH} \rightarrow \mathrm{RO^{\cdot}} + \mathrm{H_2O} + \mathrm{R^{\cdot}}$$

or as a result of the consecutive reactions

$$\mathrm{ROOH} \rightarrow \mathrm{RO^{\cdot}} + \mathrm{HO^{\cdot}},\quad \mathrm{HO^{\cdot}} + \mathrm{RH} \rightarrow \mathrm{H_2O} + \mathrm{R^{\cdot}},$$

one cage contains both RO$^{\cdot}$ and R$^{\cdot}$ radicals. Some of these pairs recombine and some are released into the bulk phase. It is suggested that the inhibitor in the cage reacts with one of the radicals and thereby increases the probability of liberation of the radicals from the cage. A bifunctional inhibitor allegedly reduces the probability of the release of the radicals into the bulk phase by reacting with two radicals. However, in order to influence the liberation of the radicals from the cage (to increase or decrease the probability), the inhibitor must compete successfully with the diffusion of the radicals from the cage. In the usual solvents with low viscosity (benzene, heptane, etc.), the rate constants for the diffusion of molecules and radicals at about 20°C are very high (10^9–10^{10} litre mole^{-1}s^{-1}). The concentration of the inhibitor is usually low (10^{-4}–10^{-2} M). Therefore the specific rate of diffusion of the radical from the cage is always much higher than the rate of its reaction with the inhibitor even when the rate constant for this reaction is large {$k_7 \simeq 10^7$ litre mole^{-1}s^{-1}, $k_D \gtrsim 10^9$, $k_7[\mathrm{InH}] \leqslant 10^5$}.

Experiment confirmed this conclusion. Waits and Hammond[97] investigated the decomposition of the dinitrile of azocyclohexanecarboxylic acid in the presence of active acceptors of alkyl radicals such as I_2, Br_2, and diphenylpicrylhydrazyl, which react with alkyl radicals, the rate constant being close to k_D. It was established that free radical acceptors do not influence the yield of recombination products within the cage up to a concentration of 0.1 M. In a viscous medium (a polymer melt) at a high temperature (180°C and above), rapid release of radicals into the bulk phase from the cage is insured by intense segmental diffusion (if two macroradicals are formed).

The inhibitor has no influence on the initiation efficiency in the solid phase either, as shown by measurements of the rate of consumption of inhibitors (α-naphthol, α-naphthylamine) in polyethylene and polystyrene when the radicals are generated from azobisisobutyronitrile. Thus the hypothesis of the involvement of the inhibitor in initiation via the reaction of radicals in the cage is contrary to both experimental facts and theoretical estimates.

IX. REACTION OF THE INHIBITOR WITH OXYGEN

Phenols and aromatic amines react with molecular oxygen bimolecularly[19,20]:

$$InH + O_2 \rightarrow In^{\cdot} + HO_2^{\cdot}$$

The activation energy for this reaction is close to its endothermicity, which makes it possible to estimate the strength of the weakest bond in the inhibitor from the value of E (Tables 1 and 2). The pre-exponential factor varies over the range 10^9–10^{12} litre mole^{-1}s^{-1} (Table 11), i.e. is fairly close to the frequency factor for binary collisions in a liquid. According to the collision theory, in a liquid[93] $A = KP(6\nu/z)E/RT$, where P is the steric factor, ν the molecular vibration frequency in the liquid, z the number of neighbouring molecules surrounding the reacting molecules, E the activation energy, and K the equilibrium constant for the reaction $RH + O_2 = [RH + O_2]$. Hence we have $A = 2 \times 10^{14} P$ for $\nu = 10^{13}$ s^{-1}, $z = 12$, $E = 30$ kcal mole^{-1}, $K = 1$ litre mole^{-1}, and $T = 400$°K; when $A = 2 \times 10^{11}$, $P = 10^{-3}$.

Table 11. Rate constants for the reaction of InH with O_2 in benzene[19,20].

Inhibitor	k at 180°C, litre mole^{-1} s^{-1}	E, kcal mole^{-1}	lg$A$ (litre mole^{-1} s^{-1})
C_6H_5OH	$0.9 \cdot 10^{-4}$	35	12.845
p-$CH_3C_6H_4OH$	$1.2 \cdot 10^{-4}$	32	11.48
p-$CH_3OC_6H_4OH$	$7.4 \cdot 10^{-4}$	27	9.875
β-$C_{10}H_7OH$	$4.5 \cdot 10^{-4}$	29	10.65
α-$C_{10}H_7OH$	$2.0 \cdot 10^{-3}$	25	9.34
α-$C_{10}H_7NHC_6H_5$	$1.7 \cdot 10^{-5}$	32	10.545
β-$C_{10}H_7NHC_6H_5$	$5.6 \cdot 10^{-5}$	31	10.46
α-$C_{10}H_7NH_2$	$6.0 \cdot 10^{-5}$	30	10.175
β-$C_{10}H_7$—NH——NH—β-$C_{10}H_7$	$1.4 \cdot 10^{-2}$	23	9.145

It has been suggested[99,100] that the reaction of the inhibitor with oxygen is the main source of initiation in the induction period of the inhibited oxidation process. The finding[99] that in polypropylene undergoing oxidation α-naphthol was consumed in a first-order reaction and the specific rate of its consumption increased with oxygen pressure supported this hypothesis. In the initial period of the oxidation reaction, initiation is due to reactions involving oxygen: $RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}$ and $2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2$. The reaction between InH and O_2 plays a significant role if its rate is comparable to (or higher than) the rate of chain initiation w_0. Comparison of the experimental values of w_0 with the rate of reaction between InH and O_2 shows that, even for a comparatively active inhibitor such as α-naphthol, $W_0 \gg W(InH + O_2)$ in polymers undergoing oxidation.

Indeed in polyethylene at 118°C and an oxygen pressure of 1 atm, $W_0 = 1.5 \times 10^{-7}$ mole kg^{-1} s^{-1} and the rate of reaction of α-naphthol with oxygen for $[InH] = 10^{-3}$ mole kg^{-1} is approximately 2×10^{-11} mole kg s^{-1}; in polypropylene at 130°C and an oxygen pressure of 1 atm, $W_0 = 2.4 \times 10^{-6}$ mole kg^{-1} s^{-1} and $W(InH + O_2) \simeq 6 \times 10^{-11}$ mole kg^{-1} s^{-1} {$[\alpha$-naphthol$] = 10^{-3}$ mole kg^{-1}}.

X. REGENERATION OF THE INHIBITOR IN CHAIN TERMINATION STEPS

Chain termination in the reaction between the peroxy-radical and the inhibitor is accompanied by destruction of the latter. For the vast majority of phenols and amines, the stoichiometric inhibition coefficient[25] is close to two, which can be accounted for by the following chain termination mechanism:

$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot},$$
$$RO_2^{\cdot} + In^{\cdot} \rightarrow \text{mol. products}.$$

In a study of the oxidation of cyclohexanol[101], it was established that α-naphthylamine inhibiting the initiated oxidation of cyclohexanol is consumed at a rate smaller by a power of several tens than the rate of initiation. An analogous phenomenon is observed in the oxidation of other secondary and primary alcohols[102] and is characteristic not only of α-naphthylamine but also of other aromatic amines. This phenomenon is due to the regeneration of the aromatic amine in the alcohol undergoing oxidation and the repeated involvement of a single amine molecule in chain termination. The mechanism of the regeneration of the amine was discovered by Kharitonov and Denisov[103], who established the formation of diphenylamine from the diphenylnitrogen radical in cyclohexanol undergoing oxidation. Chain propagation in an alcohol undergoing oxidation is due to the hydroxyperoxy-radical $>C(OH)OO^{\cdot}$, which exhibits a dual reactivity: it can oxidise by abstracting a hydrogen atom from the molecule via its peroxy-group and it can reduce the radical by giving up to it the hydrogen atom from its hydroxy-group. The latter reaction leads to the regeneration of the inhibitor and irreversible destruction of the latter takes place as a result of the reaction of the radical In$^{\cdot}$ with the peroxy-group of the hydroxy-peroxy-radical:

$$>C(OH)OO^{\cdot} + InH \xrightarrow{k_7} >C(OH)OOH + In^{\cdot},$$
$$>C(OH)OO^{\cdot} + In^{\cdot} \xrightarrow{k_8'} InH + O_2 + >C{=}O,$$
$$>C(OH)OO^{\cdot} + In^{\cdot} \xrightarrow{k_8} InOO(HO)C \rightarrow \text{products}.$$

The degree of regeneration of the amine depends on the ratio of the rate constants for reactions (8) and (8′): $f = w_i/w_{InH}$; the rate of initiation w_i is equal to the rate of

chain termination, i.e. $w_i = \{k_7[InH] + (k_8 + k_8')[In^\cdot]\}[RO_2^\cdot]$ and $w_{InH} = k_7[InH][RO_2^\cdot] - k_8'[In^\cdot][RO_2^\cdot]$, whence we find

$$f = \frac{k_7[InH] + (k_8 + k_8')[In^\cdot]}{k_7[InH] - k_8'[In^\cdot]}, \quad [In^\cdot] = \frac{k_7[InH]}{k_8 + k_8'}, \quad f = 2\left(1 + \frac{k_8'}{k_8}\right).$$

The mechanism of the regeneration of α-naphthylamine in cyclohexanol undergoing oxidation was investigated recently in greater detail[104]. In an alcohol undergoing oxidation, chain termination takes place via the reactions:

$$\rangle\dot{C}OH + O_2 \xrightarrow{k_1} \rangle C(OH)OO^\cdot,$$
$$\rangle C(OH)OO^\cdot + \rangle CHOH \xrightarrow{k_8} \rangle C(OH)OOH + \rangle\dot{C}OH.$$

The hydroxyhydroperoxide formed decomposes into a ketone and hydrogen peroxide, the latter generating hydroperoxy-radicals by reaction with hydroxyperoxy-radicals:

$$\rangle C(OH)OOH \rightleftharpoons \rangle C{=}O + H_2O_2,$$
$$H_2O_2 + \rangle C(OH)OO^\cdot \rightarrow HO_2^\cdot + \rangle C(OH)OOH$$

Therefore an alcohol undergoing oxidation contains simultaneously hydroxyalkyl, hydroxyperoxy-, and hydroperoxy-radicals, each of which can reduce In$^\cdot$ to InH. To confirm the role that each of these radicals plays in the regeneration of α-naphthylamine, a study was made of the relation between f in an alcohol undergoing oxidation on the one hand and the partial pressure of oxygen and the concentration of hydrogen peroxide on the other. Since hydroxyalkyl radicals are consumed by the reaction with oxygen and are formed by reaction (2), their steady-state concentration is inversely proportional to the concentration of dissolved oxygen:

$$[\rangle\dot{C}OH] = \frac{k_2}{k_1}\frac{[\rangle CHOH]}{[O_2]}[\rangle C(OH)OO^\cdot].$$

By changing $[O_2]$, it is possible to follow the regeneration of the inhibitor by the reaction with hydroxyalkyl radicals. In the absence of oxygen, the regeneration can be achieved only by hydroxyalkyl radicals. In the experiments of Bardanyan et al.,[104] measurements were made of the rate of consumption of α-naphthylamine in cyclohexanol being oxidised at 120°C with $W_i = 1.86 \times 10^{-6}$ mole litre^{-1}s^{-1} and $[InH] = 8 \times 10^{-4}$ M at different partial pressures of oxygen. The experimental results[104] are presented below:

Partial oxygen pressure	= 0	61	160	300	760 mmHg.
f =	16.6	25	36	44	48

It is evident from these data that the degree of regeneration of the amine in the reaction with peroxy radicals is higher than in the reaction with hydroxyalkyl radicals and that the role of hydroxyalkyl radicals in regeneration at atmospheric oxygen pressure is insignificant. (Calculation shows that 95% of In$^\cdot$ is converted into InH as a result of the reaction with peroxy-radicals at an oxygen pressure of 1 atm.)

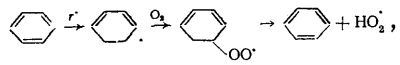
Experiments with different concentrations of hydrogen peroxide in cyclohexanol at 75°C and with $W_i = 3.7 \times 10^{-7}$ mole litre^{-1}s^{-1} showed that, as $[H_2O_2]$ increases, the coefficient f diminishes from $f = 90$ in pure cyclohexanol to $f = 20$ for $[H_2O_2] \geq 0.08$ M. Consequently hydroperoxy-radicals also reduce In$^\cdot$ to InH, but in this case k_8'/k_8 is significantly lower than for hydroxyperoxy-radicals. With increased concentration of hydrogen peroxide in the alcohol undergoing oxidation, the role of $HO_2^\cdot$ radicals in the regeneration of the inhibitor becomes more pronounced. The following values of k_8'/k_8, characterising the relative capacity of various radicals to regenerate the inhibitor, were obtained from experimental data for α-naphthylamine in cyclohexanol at 75°C: 47 ± 5 for the hydroxyperoxy-radical, 9 ± 2 for the hydroperoxy-radical, and 6 ± 2 for the hydroxyalkyl radical. The regeneration is characteristic of many aromatic amines.

Since the hydroxyperoxy-radical is a reductant, one may expect that chain termination in an alcohol being oxidised can be caused by oxidant molecules, for example quinones. It has been shown[105] that a quinone Q inhibits the oxidation of isopropyl alcohol owing to the reactions

$$\rangle C(OH)OO^\cdot + Q \rightarrow {}^\cdot QH + \rangle C{=}O + O_2,$$
$$\rangle\dot{C}OH + Q \rightarrow {}^\cdot QH + \rangle C{=}O.$$

At an oxygen partial pressure of 1 atm, 86% of chain termination is due to the first reaction, the quinone being regenerated in the oxidation process.

The regeneration of inhibitors in chain termination steps occurs also in the oxidation of certain unsaturated hydrocarbons, in particular 1,3-cyclohexadiene[106]. The oxidation of cyclohexadiene is propagated by hydroperoxy-radicals, which exhibit a reducing effect:



$$HO_2^\cdot + In^\cdot \rightarrow InH + O_2.$$

The degree of regeneration of the inhibitor depends on its structure and varies over a wide range (Table 12). In the case of phenols, regeneration is observed rarely (hydroquinone); this can probably be accounted for by the very rapid recombination of PhO$^\cdot$ and $RO_2^\cdot$.

Table 12. Inhibition coefficients f for different substances undergoing oxidation.

Inhibitor	Cyclohexene (Ref.109) (60°C, O_2)	Cyclohexene + 5% cyclohexanol (Ref.109) (60°C, O_2)	Cyclohexadiene [Ref.106(75°C)]	
			O_2	in the presence of O_2
α-$C_{10}H_7NH_2$		40	28	350
α-$C_{10}H_7NHC_6H_5$	1.9	11		
β-$C_{10}H_7NH_2$	2.8	21	—	—
β-$C_{10}H_7NHC_6H_5$	1.5	35	—	—
$(C_6H_5)_2NH$	1.4	35	>200	>200
p-$NH_2C_6H_4NH_2$	2.4	28		
β-$C_{10}H_7NH$——NH—β-$C_{10}H_7$	2.8	130	—	—
p-$(CH_3)_2CHNHC_6H_4NHC_6H_5$	1.8	450	—	—
β-$C_{10}H_7ONH$——NHOβ-$C_{10}H_7$	4.9	140	—	—
$(p$-$CH_3OC_6H_4)_2NH$	2.1	140	—	—
p-$(C_6H_5NH)C_6H_4NHC_6H_5$	3.5	175	—	—
			70	170
			90	1

In hydrocarbons undergoing oxidation, $f \simeq 2$ as a rule. An exception is provided by Chien's study[107], where a coefficient $f > 2$ (6–10) is quoted for 2,6-di-t-butylphenols in squalene and cyclohexene undergoing oxidation. The coefficient f was determined from the duration of the induction period in the initiated oxidation process. This measurement yields a correct value for f only if all the chains

are terminated by the inhibitor and $k_7[InH] \gg k_6[RO_2^{\cdot}]$. In the general case we have

$$W_i = k_6[RO_2^{\cdot}]^2 + fk_7[InH][RO_2^{\cdot}],\ W_{InH} = k_7[InH][RO_2^{\cdot}] \text{ and}$$

$$\frac{W_i}{W_{InH}} = f + \frac{k_6[RO_2^{\cdot}]}{k_7[InH]} = f + \frac{k_6 W_{InH}}{k_7^2[InH]^2}.$$

The coefficient f is found from the plot of w_i/w_{InH} against $w_{InH}/[InH]^2$. Such calculation based on Chien's data[107] yields $f = 2.3$ for ionol in squalene undergoing oxidation[108]. These experiments yielded an unduly high value of f because in the calculation no account was taken of chain termination by the reaction between $RO_2^{\cdot}$ radicals. Vardanyan's redetermination[108] of f for 2,6-di-t-butylphenols in cyclohexene at 80°C (in the presence of azobisisobutyronitrile as an initiator) yielded $f = 2$ for these phenols. Thus a check on Chien's results[107] failed to confirm the high values of f obtained in his study for 2,6-dialkylphenols.

XI. THE MECHANISM OF INHIBITED OXIDATION

In the absence of an inhibitor and an initiator, the mechanism of the oxidation of C–H bonds of organic compounds in the condensed phase can be represented by the following series of elementary reactions[3]:

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}, \quad (0)$$

$$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2, \quad (0)$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}, \quad (1)$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}, \quad (2)$$

$$ROOH \rightarrow RO^{\cdot} + HO^{\cdot}, \quad (3)$$

$$ROOH \rightarrow \text{mol. products}, \quad (M)$$

$$2RO_2^{\cdot} \rightarrow \text{mol. products} \quad (6)$$

After the introduction of an inhibitor, new elementary reactions involving InH and In$^{\cdot}$ take place:

$$RO_2^{\cdot} + InH \rightarrow ROOH + In^{\cdot}, \quad (7)$$

$$In^{\cdot} + RO_2H \rightarrow InH + RO_2^{\cdot}, \quad (-7)$$

$$In^{\cdot} + RO_2^{\cdot} \rightarrow \text{mol. products} \quad (8)$$

$$In^{\cdot} + In^{\cdot} \rightarrow \text{mol. products} \quad (9)$$

$$In^{\cdot} + RH \rightarrow InH + R^{\cdot}. \quad (10)$$

As a rule, the reactions of the inhibitor with the hydroperoxide and oxygen do not play a significant role. The kinetics of inhibited oxidation can be described by a set of differential equations. Each individual substance oxidised–inhibitor system is characterised by a definite set of rate constants for reactions (0)–(10). For a comprehensive kinetic analysis of such systems, it is insufficient to base the treatment solely on experimental results. Firstly, there are very few systems in which each elementary stage has been investigated. Secondly, in the experiment it is always possible that a number of factors (and elementary reactions) have not been taken into account. There is a possibility that the presence of substances (impurities) may complicate the mechanism, etc. Therefore, in a study of complex reactions such as the inhibited oxidation processes, the experimental research techniques can be usefully supplemented by the so called numerical experiment where the mechanism is specified in the form of a set of differential equations and rate constants and a computer calculation yields the rates of accumulation of reaction products. The numerical experiment yields the reaction kinetics for strictly specified mechanism and constants; the element of uncertainty associated with incomplete control over the reaction mechanism in a real experiment is excluded here; the reaction mechanism can be varied at will, which makes it possible to establish clearly the role of a particular elementary reaction in the overall process. Such a calculation has been carried out[110] for the simplest case where the inhibitor is involved only in reaction (7) and In$^{\cdot}$ is involved only in reaction (8). A more complicated mechanism, including reactions (7)–(10) was examined with the following rate constants: $W = \{k_0 + k_0'[RH]\}[RH][O_2] = 10^{-10}$ mole litre^{-1} s^{-1}, $k_2[RH] = 50$ s^{-1}, $k_3 = 2 \times 10^{-6}$ s^{-1}, $k_M = 5 \times 10^{-5}$ s^{-1}, $k_6 = 10^6$ litre mole^{-1}s^{-1}, $k_7 = 2 \times 10^5$ litre mole^{-1}s^{-1}, $k_{-7} = 10^5$ litre mole^{-1}s^{-1}, $k_8 = 10^9$ litre mole^{-1}s^{-1}, $k_9 = 10^8$ litre mole^{-1}s^{-1}, and $k_{10} = 10$ litre mole^{-1}s^{-1}. To elucidate the role of each of these reactions involving In$^{\cdot}$, a numerical experiment was carried out including the mechanism of individual (but not all) reactions of the In$^{\cdot}$ radical.

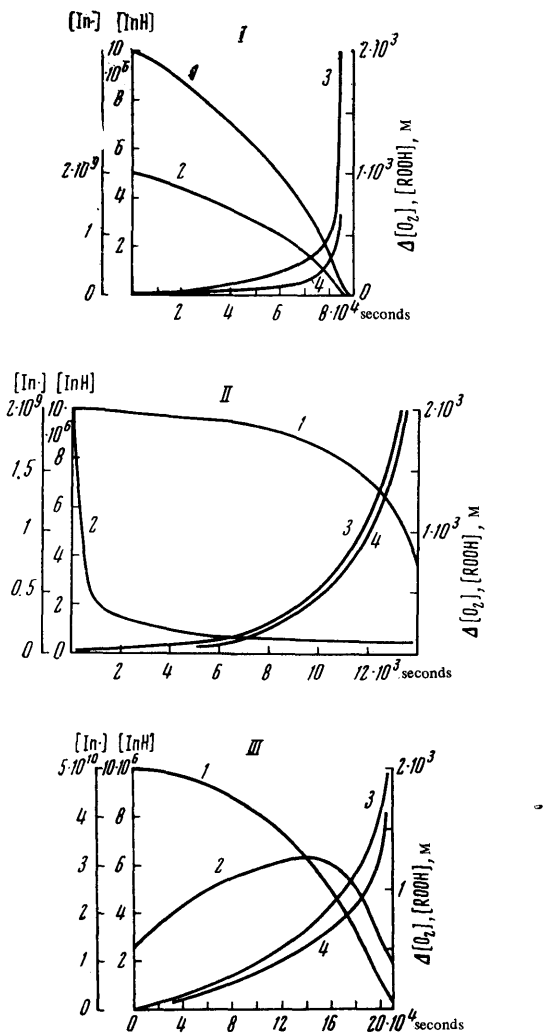


Figure 2. Kinetic curves for the consumption of InH (curve *1*) and In$^{\cdot}$ (curve *2*), the absorption of O_2 (curve *3*) and the accumulation of ROOH (curve *4*) in mechanisms I, II, and III respectively.

Mechanism I: the inhibitor and the radical In$^{\cdot}$ react with $RO_2^{\cdot}$, the rate constants for the remaining reactions of In$^{\cdot}$ being zero. In this case the oxidation develops very slowly and the transition from slow inhibited oxidation to rapid oxidation takes place abruptly (Fig. 2, I). The concentration of In$^{\cdot}$ varies in parallel with [InH]. At the end of the induction period, the concentration of ROOH is less than that of the absorbed oxygen.

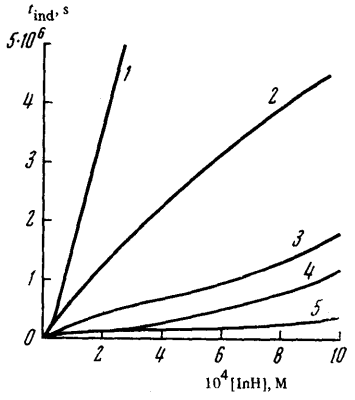


Figure 3. Dependence on the induction period on the concentration of inhibitor: 1) mechanism I; 2) mechanism III + Q with $k_Q = 1$; 3) mechanism III + Q with $k_Q = 0.2$; 4) mechanism III + Q with $k_Q = 0.02$; 5) mechanism II; Q = inhibitor decomposing the hydroperoxide; $[Q]_0 = 10^{-3}$ M.

Mechanism II: the radical In$^{\cdot}$ reacts only with $RO_2^{\cdot}$ and ROOH. Fig. 2, II shows that the oxidation develops more rapidly than in mechanism I, the proportion of the hydroperoxide decomposing during the induction period is small, and the concentration of In$^{\cdot}$ decreases rapidly during the reaction. The reaction emerges from the induction period smoothly long before the complete consumption of the inhibitor.

Mechanism III: the radical In$^{\cdot}$ reacts with $RO_2^{\cdot}$, In$^{\cdot}$, and RH. The oxidation develops faster than in mechanism I; the reaction emerges from the induction period smoothly, the concentration of In$^{\cdot}$ passing through a maximum (Fig. 2, III). Comparison of mechanisms (I)–(III) (Fig. 2) shows that a change in mechanism causes a significant change in the kinetics of the accumulation of In$^{\cdot}$. There is also a change in the nature of the relation between the induction period and [InH] (Fig. 3). For mechanism I, the relation is close to linear. When In$^{\cdot}$ causes chain propagation via the reaction with RH, the induction period ceases to depend on [InH] beyond a certain value $[InH]_{min}$. For mechanism II, the relation between t_{ind} and [InH] is represented by a line with positive curvature. In the presence of an additional inhibitor Q decomposing the hydroperoxide, the t_{ind}–[InH] relation is represented by an inverted S-shaped curve (Fig. 3). Evidently different mechanisms of inhibitor action lead to different relations between t_{ind} and [InH]. However, one should bear in mind that the mechanism of inhibitor action cannot be inferred unambiguously from the t_{ind}–[InH] relation.

XII. CRITERIA OF THE EFFICIENCY OF INHIBITORS

We have seen that the mechanism of the action of inhibitors is fairly complicated. The efficiency of the inhibiting effect depends on a series of reactions involving In$^{\cdot}$, $RO_2^{\cdot}$, InH, and ROOH, i.e. is determined by a series of reactions. Therefore the efficiency of the inhibitor cannot be expressed by any one parameter but must be represented in the general case by a set of formulae (inequalities), which take account of the contributions by all the reactions on which the rate of the oxidation process depends.

If the radicals In$^{\cdot}$ are only weakly involved in chain propagation,

$$k_8[RO_2^{\cdot}] \gg k_{10}[RH] + k_7[ROOH] \quad \text{or}$$
$$k_8 W_i / f k_7 [InH] \gg k_{10}[RH] + k_{-7}[ROOH],$$

the inhibiting effect is stronger for higher values of k_7 and [InH]:

$$f k_7 [InH][RO_2^{\cdot}] \gg k_6 [RO_2^{\cdot}]^2 \text{ and } f k_7 [InH] \gg \sqrt{W_i k_6} \quad \text{(IV)}$$

If In$^{\cdot}$ is involved in chain propagation via reaction (10), then strong inhibition requires that the following inequality should hold:

$$k_2[RH][RO_2^{\cdot}] + k_{10}[RH][In^{\cdot}] \ll k_2[RH]\sqrt{W_i/k_6} \quad \text{or}$$
$$1 + \frac{k_7[InH]}{k_2[RH]} \ll k_2 \left\{ \frac{2k_8}{k_6} \frac{k_7[InH]}{k_{10}[RH]} + \frac{2k_9}{k_6} \left(\frac{k_7[InH]}{k_{10}[RH]} \right)^2 \right\}^{1/2}.$$

The above inequality is valid when another inequality holds:

$$\frac{1}{k_{10}} \gg \frac{k_6[RH]}{8k_2^2 k_8} \left(1 + \frac{1}{k_7[InH]} \right) + \frac{\sqrt{k_6}}{4k_2\sqrt{2k_9}} \left(\frac{1}{k_2} + \frac{[RH]}{k_7[InH]} \right), \quad \text{(V)}$$

i.e. when k_{10} is fairly large, it is impossible to achieve effective inhibition by increasing [InH] if

$$\frac{1}{k_{10}} \ll \frac{k_6[RH]}{8k_2^2 k_8} + \frac{\sqrt{k_6}}{4k_2^2\sqrt{2k_9}}.$$

If In$^{\cdot}$ causes chain propagation via the reaction with the hydroperoxide, we obtain the following inequality for effective inhibition:

$$[RO_2^{\cdot}] \ll \sqrt{W_i/k_6}, \quad [RO_2^{\cdot}] = \left\{ \frac{W_i k_{-7}[ROOH]}{2k_7 k_8 [InH]} \right\}^{1/2}$$

and

$$k_{-7} \ll \frac{2k_7 k_8 [InH]}{k_6 [ROOH]} \quad \text{(VI)}$$

In certain cases one should also bear in mind the reaction of the inhibitor itself with the hydroperoxide:

$$ROOH + InH \rightarrow RO^{\cdot} + H_2O + In^{\cdot} \quad (11)$$

When account is taken of this reaction in the presence of InH, $W_i = W_0 + 2k_3[ROOH] + 2ek_{11}[ROOH][InH]$. If we consider the case where In$^{\cdot}$ is responsible for chain propagation only via the reaction with the hydroperoxide, then, when account is taken of reaction (11), we obtain the following inequality for effective inhibition:

$$\frac{k_{-7}[ROOH](1 + ek_{11}[InH]/k_3)}{2k_7 k_8} \ll \frac{1}{k_6} \quad \text{or}$$
$$\frac{k_{-7}}{[InH]} + \frac{ek_{-7}k_{11}}{k_3} \ll \frac{2k_7 k_8}{k_6 [ROOH]}. \quad \text{(VII)}$$

Inequalities (IV)–(VII) represent a combined kinetic criterion for an effective inhibitor in the given compound being oxidised. These inequalities take into account all the reactions involving the inhibitor currently known.

They reflect both the specific characteristics of the inhibitor, its kinetic features (the constants k_7, k_{-7}, k_8, k_9, k_{10}, and k_{11}), and the specific features of the substance being oxidised (W_0, k_2, and k_{10}), its peroxy-radicals (k_2, k_6, k_7, and k_8), and its hydroperoxide (k_3, k_{-7}, and k_{11}).

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The review shows that the principal reactions involved in oxidation inhibited by phenols and aromatic amines have now been established. The rate constants for reactions with peroxy-radicals have been measured for many phenols and aromatic amines. Unfortunately in the vast majority of cases these measurements have been made at only one temperature, which makes it difficult to employ the results at other temperatures. The reactions of phenoxy- and phenylnitrogen radicals have been less well investigated, particularly in the case of the reactive radicals In$^{\cdot}$, such reactions playing a major role in inhibited oxidation. There are few data for the rates of the reactions between In$^{\cdot}$ and $RO_2^{\cdot}$ and between In$^{\cdot}$ radicals alone. Overall, a quantitative study of the mechanism of the action of inhibitors requires further research to establish from the available fragmentary data a well-founded mechanism of inhibitor action.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow