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Cyclic mechanisms of chain termination in the oxidation of organic compounds

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Abstract. All the mechanisms known at present for cyclic (repeated) chain termination involving aromatic amines, quinones, nitroxyl radicals, and variable-valence metal complexes in the oxidation of hydrocarbons, polymers, alcohols, and aliphatic amines are surveyed. The mechanisms are classified and the factors needed for the realisation of a particular mechanism are analysed. The reasons for the limitation of the number of cycles in the cyclic chain termination mechanism are considered. The bibliography includes 84 references.

I. Introduction

Inhibitors of oxidation (antioxidants) play an important role in modern technology for the production of polymers,[1–4] lubricants,[5] hydrocarbon fuel,[6] solvents, intermediate products in organic synthesis,[7] and foodstuffs.[8] They also perform the function of protecting living organisms from the harmful influence of oxygen, light, and radiation. Studies in the fields of synthesis and physicochemical and biochemical properties of antioxidants and intermediate products formed from them have been developed intensely during the last three decades. An important place among these studies is occupied by the studies of elementary reactions of inhibitors and of the radicals derived from them.[9–11]

The oxidation of organic compounds with oxygen in the liquid phase proceeds as a rule by a chain mechanism involving participation of peroxyl radicals in the chain propagation. Therefore, compounds that are able to react rapidly with peroxyl radicals and thus cause chain termination occupy a prominent place among antioxidants. Phenols, thiophenols, and aromatic amines are effective oxidation inhibitors and are irreversibly consumed in reactions with peroxyl radicals. When the oxidation is propagating rapidly at a sufficiently high temperature or under the action of very intense light, these inhibitors permit the process to be decelerated for only a short period.

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In this connection, the inhibiting systems that ensure the possibility of regenerating the inhibitor consumed in the chain termination steps are of interest. This permits the oxidation to be retarded effectively by adding a relatively small amount of an inhibitor.

The cyclic mechanism of chain termination was discovered in a study of oxidation of alcohols[12–14] in which aromatic amines have been used as inhibitors. A short time later, the ability of copper ions to terminate repeatedly the chains during oxidation of cyclohexanol was found.[15] The cyclic mechanisms of chain termination are due to the dual reactivity of the hydroxyperoxyl radicals formed in the oxidation of an alcohol. This has been confirmed in relation to *p*-benzoquinone,[16] which terminates the chains in the oxidation of alcohols by the cyclic mechanism, but has virtually no influence on the oxidation of hydrocarbons.

The possibility of the repeated chain termination with stable nitroxyl radicals in the oxidation of polymers was discovered in 1972.[17] Later, a fundamentally new three-component system ensuring the cyclic chain termination in the oxidation of hydrocarbons was suggested. Apart from nitroxyl radicals, an important role in this system is played by an alcohol (primary or secondary) and an organic (citric) acid, which are responsible for the acid catalysis.[18] Certain aspects of the cyclic chain termination during oxidation have been considered in a number of reviews.[19–23] However, in the present review all the currently known systems and mechanisms for the cyclic chain termination in the oxidation of organic compounds are considered comprehensively for the first time, and the reasons enabling the realisation of these mechanisms are also analysed.

II. Chain termination with phenols and aromatic amines in the oxidation of hydrocarbons

Oxidation of hydrocarbons[9] and of many other organic compounds[24,25] involves alkyl ($R^{\cdot}$) and peroxyl ($RO_2^{\cdot}$) radicals and proceeds by a chain mechanism that includes the following elementary stages:

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

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

$$ROOH \longrightarrow RO^{\cdot} + OH^{\cdot}, \quad (3)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow RR, \quad (4)$$

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

$$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow ROOR + O_2. \quad (6)$$

At a partial pressure of oxygen of 10–100 kPa and with sufficiently intense stirring of the liquid phase (which facilitates the diffusion of oxygen into the compound being oxidised) alkyl radicals are converted very rapidly (over a period of 10^{-6}–10^{-4} s) into peroxyl radicals. Chain termination occurs via reaction (6), which accounts for the limitation of the chain length.

$$v = \frac{k_2[RH]}{(2k_6 v_i)^{0.5}},$$

where v_i is the rate of initiation and k_2 and k_6 are rate constants of the corresponding stages. The lower the rate of reaction (6), the longer the chain. The chain regime is realised when

$$k_2^2[RH]^2 > 2k_6 v_i.$$

As the hydroperoxide is accumulated, the initiation rate increases and the oxidation accelerates.

The introduction of an inhibitor InH (phenol or amine) accelerates the chain termination due to the occurrence of the following reactions:[9-11]

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

$$RO_2^{\cdot} + In^{\cdot} \longrightarrow Mol, \quad (8)$$

$$In^{\cdot} + In^{\cdot} \longrightarrow Mol, \quad (9)$$

(Mol are molecular products).

If the concentration of the inhibitor is sufficiently high, so that

$$k_7[InH] > (2k_6 v_i)^{0.5},$$

then the chain termination will proceed via reactions (7)–(9) and the chain length will be equal to

$$v = \frac{k_2[RH]}{f k_7[InH]},$$

where f is the stoichiometric coefficient of inhibition. The reactions (8) and (9) occur very rapidly (their rate constants are 10^8–10^9 dm^3 mol^{-1} s^{-1}), the rate of the chain termination being limited by the reaction (7). Within the framework of this scheme, which is typical of oxidation of hydrocarbons, $f \cong 2$ in the case where reaction (8) predominates or $f \cong 1$ if the reaction (9) predominates. The f values determined experimentally fall in this range.[26]

The $In^{\cdot}$ radicals can react with ROOH and RH to give the $RO_2^{\cdot}$ and $R^{\cdot}$ radicals,[23] which are then involved in the chain propagation:

$$In^{\cdot} + RH \longrightarrow InH + R^{\cdot}, \quad (10)$$

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

When the temperature is fairly high (>400 K), the inhibitor starts to react with the hydroperoxide and with oxygen at a noticeable rate thus initiating chains:[23]

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

$$InH + O_2 \longrightarrow In^{\cdot} + HO_2^{\cdot}. \quad (12)$$

The quinolide peroxides InOOR, resulting from the recombination of phenolic and peroxyl radicals, redissociate into radicals, which initiate oxidation at fairly high temperatures:[11]

$$InOOR \longrightarrow InO^{\cdot} + RO^{\cdot}. \quad (13)$$

The decomposition of *p*-alkoxy-substituted phenoxyl radicals affords alkyl radicals, which continue the oxidation chain.[11]

$$ROC_6H_4O^{\cdot} \longrightarrow R^{\cdot} + OC_6H_4O. \quad (14)$$

The semiquinone radicals continue the chain by reacting with oxygen.[27]

$$O_2 + HOC_6H_4O^{\cdot} \longrightarrow HO_2^{\cdot} + OC_6H_4O. \quad (15)$$

Thus, the kinetics of the inhibited oxidation depend, on the one hand, on a number of reactions involving ROOH, $RO_2^{\cdot}$, and O_2 and, on the other hand, on the reactions involving the inhibitor and the radicals derived from it.

The duration of the retarding action of an inhibitor is determined by its concentration and reactivity, and also by the conditions and the regime of the chain oxidation. At a constant initiation rate and with intense chain termination by the inhibitor $[fk_7[InH]_0 > (k_6 v_i)^{0.5}]$, the induction period τ is equal to $f[InH]_0 v_i^{-1}$, i.e. it is directly proportional to the concentration of the added inhibitor and to the inhibition coefficient. Under the conditions of autooxidation, when the hydroperoxide formed acts as an initiator, a feedback appears between the efficiency of the chain termination with the inhibitor and the induction period τ. Problems of the mechanism and the efficiency of oxidation inhibitors have been considered in detail in a number of monographs and reviews.[3,6,9-11] It is noteworthy that the induction period of the inhibited oxidation depends in all cases on the coefficient f and on the concentration of the inhibitor. The reactions (7)–(15) associated with the participation of the inhibitor may be divided into two groups: reactions having no influence on the coefficient f [reactions (7), (–7), and (10)], and reactions, the occurrence of which influences the f value [reactions (8), (9), (11)–(15)].

It seems that oxidation could be retarded if a large amount of an inhibitor is added. However, both theory and experience indicate that the use of high concentrations of an inhibitor reduces its efficiency and leads sometimes to a shortening rather than to an extension of the induction period. This is accounted for by the following reasons. An increase in the concentration of an inhibitor leads to an increase in the quasi-steady concentration of the $In^{\cdot}$ radicals, and, consequently, the chain propagation reactions involving these radicals [reactions (10), (–7), (14), and (15)] proceed more intensely. The rate of the initiation reactions [(11) and (12)] involving the inhibitor is directly proportional to its concentration. Therefore, it is expedient to increase the concentration of the inhibitor only up to a value at which initiation involving it is insignificant.

There are also other reasons why high antioxidant concentrations are undesirable. First, the evaporation of the inhibitor from the polymer sample or its washing-out in the case where it is in contact with a liquid accelerates at high concentrations. Second, high concentrations of an antioxidant may be toxic for a human organism. Third, antioxidants deteriorate the mechanical properties of polymeric articles. Fourth, the introduction of large quantities of a fairly expensive antioxidant increases substantially the cost of an article or a product. In some cases, this contradictory situation can be resolved by using antioxidants that provide repeated chain termination per one initial molecule of the inhibitor, owing to the realisation of the cyclic chain termination mechanism. In these cases, prolonged retardation of the oxidation can be achieved with a small amount of an inhibitor.

An important role in the identification and investigation of cyclic mechanisms of chain termination has been played by experiments dealing with the measurement of the coefficient f. It should be noted that this coefficient is stoichiometric only when it is determined by the reactions (7)–(9). In the case where cyclic chain termination occurs, the coefficient f is influenced by the competition between the irreversible destruction of the $In^{\cdot}$ radicals on the one hand, and the conversion of $In^{\cdot}$ into the initial InH on the other hand. In these systems, f should be considered and said to be the inhibition coefficient.

The coefficient f has been measured by various methods. When aromatic amines were used as inhibitors, f was defined as the ratio v_i/v_{InH}, where v_{InH} is the rate of consumption of the amine in an experiment with a constant rate of initiation.

The concentration of the amine was determined by colorimetry after its conversion into a brightly coloured compound.[12-14] When stable nitroxyl radicals were used as inhibitors, the variation of their concentration during the experiment has been monitored by EPR.[17,18] The consumption of a quinone has been evaluated from the increase in the rate of the initiated oxidation during the experiment.[16] In the case where variable-valence metals were used as inhibitors, the evaluation was based on the induction period.

III. Cyclic chain termination in the oxidation of alcohols, alkenes, and amines

A high value of the inhibition coefficient ($f = 28$) was detected for the first time in the oxidation of cyclohexanol in the presence of α-naphthylamine (393 K, *tert*-butyl peroxide as the initiator, $P_{O_2} = 10^5$ kPa).[12] For the oxidation of n-decane under the same conditions, $f = 2.5$. In the case of the oxidation of n-decane–cyclohexanol mixtures, the coefficient f increased with increase in the cyclohexanol concentration, from 2.5 (in pure n-decane) to 28 (in pure alcohol).[12] When the oxidation of cyclohexanol was carried out in the presence of tetraphenylhydrazine, the diphenylamino radicals produced from tetraphenylhydrazine were reduced to diphenylamine.[14] This conclusion has been confirmed in another study.[28] Diphenylamine was formed only in the presence of the initiator, no matter whether the process was conducted under an oxygen atmosphere or under an inert atmosphere. In the former case, the amino radical was reduced by the hydroperoxyl radical derived from the alcohol, and in the latter case, it was reduced by the hydroxyalkyl radical:

$$(C_6H_5)_2N^{\cdot} + C_6H_{10}(OH)OO^{\cdot} \longrightarrow (C_6H_5)_2NH + O_2 + C_6H_{10}O, \quad (16)$$

$$(C_6H_5)_2N^{\cdot} + C_6H_{10}(OH)^{\cdot} \longrightarrow (C_6H_5)_2NH + C_6H_{10}O. \quad (17)$$

On the basis of these results the following mechanism was suggested for the cyclic chain termination:[14]

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

$$>C(OH)OO^{\cdot} + In^{\cdot} \longrightarrow >C=O + O_2 + InH. \quad (18)$$

The oxidation of primary and secondary alcohols in the presence of α-naphthylamine, β-naphthylamine, or phenyl-α-naphthylamine is characterised by high values of the inhibition coefficient ($f \gg 2$).[12-14] Alkylperoxyl and α-ketoperoxyl radicals, like the peroxyl radicals derived from tertiary alcohols, are incapable of reducing the amino radicals. For example, when oxidation of *tert*-butanol is inhibited by α-naphthylamine, f is equal to 2, which coincides with the value found in the oxidation of alkanes.[14] However, the addition of hydrogen peroxide to the *tert*-butanol being oxidised leads to the realisation of the cyclic chain termination mechanism (α-naphthylamine as the inhibitor, 393 K, cumyl peroxide as the initiator, $P_{O_2} = 100$ kPa).[29] This is due to the participation of the $HO_2^{\cdot}$ radicals formed in the chain termination:

$$RO_2^{\cdot} + H_2O_2 \longrightarrow ROOH + HO_2^{\cdot}, \quad (19)$$

$$RO_2^{\cdot} + AmH \longrightarrow ROOH + Am^{\cdot}, \quad (20)$$

$$Am^{\cdot} + HO_2^{\cdot} \longrightarrow AmH + O_2, \quad (21)$$

where AmH is an amine (in this particular case, it is α-naphthylamine).

Since the peroxyl radicals derived from the alcohol dissociate to a carbonyl compound and $HO_2^{\cdot}$

$$>C(OH)OO^{\cdot} \longrightarrow >C=O + HO_2^{\cdot}, \quad (22)$$

three reactions, in which the amino radicals formed from the amine are reduced, proceed in parallel under the conditions of the oxidation of the alcohol:

$$Am^{\cdot} + HO_2^{\cdot} \longrightarrow AmH + O_2, \quad (21)$$

$$Am^{\cdot} + >C(OH)OO^{\cdot} \longrightarrow >C=O + O_2 + AmH, \quad (23)$$

$$Am^{\cdot} + >C^{\cdot}(OH) \longrightarrow >C=O + AmH. \quad (24)$$

In the presence of dissolved oxygen, the hydroxyalkyl radicals are converted very rapidly into the hydroxyperoxyl radicals, therefore, only $>C(OH)OO^{\cdot}$ and $HO_2^{\cdot}$ participate in the reduction of the amino radicals. The higher is the temperature, the more effectively the decomposition of the hydroxyperoxyl radicals proceeds and the higher is the proportion of the $HO_2^{\cdot}$ radicals participating in the regeneration of the amine.

Our investigation has shown[30] that in the case of repeated chain termination with aromatic amines in the oxidation of alcohols, the situation is more complicated. In parallel with the reaction (23), the following reaction proceeds:

$$>C(OH)OO^{\cdot} + Am^{\cdot} \longrightarrow AmO^{\cdot} + >C(OH)O^{\cdot}. \quad (25)$$

The nitroxyl radical, in its turn, gives rise to a new cyclic mechanism of chain termination according to reactions:

$$>C(OH)OO^{\cdot} + AmO^{\cdot} \longrightarrow >C=O + O_2 + AmOH, \quad (26)$$

$$>C(OH)OO^{\cdot} + AmOH \longrightarrow >C(OH)OOH + AmO^{\cdot}. \quad (27)$$

The intermediate formation of nitroxyl radical has been detected in the oxidation of isopropanol retarded by diphenylamine; chain termination occurs by cyclic mechanisms involving both $Am^{\cdot}$ and $AmO^{\cdot}$.[30] In the case where the oxidation of isopropanol is decelerated by bis(*p*-methoxyphenyl)amine, only the cycle involving nitroxyl radicals is realised.[30]

Organic acids retard the formation of nitroxyl radicals via reaction (25).[31] Apparently, the formation of a hydrogen bond of the N...HOC(O)R type leads to shielding of nitrogen, which precludes the addition of oxygen to it, yielding the nitroxyl radical. Thus, the products of the oxidation of hydrocarbons (acids) have an influence on the mechanism of the cyclic chain termination.

As noted above, the duration of the retarding action of an inhibitor is directly proportional to the f value. In systems with a cyclic chain termination mechanism, the coefficient f depends on the ratio of the rate constants for the two reactions, in which the inhibitor is regenerated and irreversibly consumed. In the oxidation of alcohols, amino radicals are consumed irreversibly via reaction (25) and via the following reaction:

$$RO_2^{\cdot} + (C_6H_5)_2N^{\cdot} \longrightarrow RO_2C_6H_4NHC_6H_5 \longrightarrow ROH + OC_6H_4NC_6H_5. \quad (28)$$

The formation of the nitroxyl radical [reaction (25)] and of quinone imine [reaction (28)] precludes the possibility of the recovery of amine and, hence, either of the above reactions interrupts the cycle at the amino radical

$$f = 1 + \frac{k_{23}}{k_{25} + k_{28}}.$$

Table 1 presents the inhibition coefficients and the termination rate constants in systems with a cyclic mechanism of chain termination with aromatic amines. Naturally, these are effective rate constants, which characterise primarily the rate-limiting stage of the chain termination process.

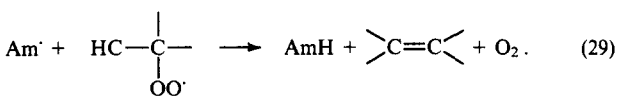
The question of why the amino radicals ensure cyclic chain termination in those systems in which the $HO_2^{\cdot}$ and $>C(OH)OO^{\cdot}$ radicals are formed, but not in the oxidation of hydrocarbons where alkylperoxyl radicals $RO_2^{\cdot}$ are the chain-propagating species, deserves special attention.[42]

Disproportionation of the amino and peroxyl radicals that involves both the O–H and C–H bonds is, in principle, possible:

$$Am^{\cdot} + HO-\underset{\displaystyle OO^{\cdot}}{\overset{\displaystyle |}{\underset{|}{C}}}- \longrightarrow AmH + O=C\!\!\diagup\!\!\diagdown + O_2, \quad (23)$$

Table 1. Inhibition coefficients and rate constants for the reactions of peroxyl radicals with aromatic amines in systems with a cyclic mechanism of chain termination.

Amine	Substrate	Peroxyl radical	T/K	f	$k/10^4$ dm^3 mol^{-1} s^{-1}	Ref.
$(C_6H_5)_2NH$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	343	>23	–	30
$(C_6H_5)_2NH$	$CH=CHCH=CHCH_2CH_2$	$HO_2^{\cdot}$	348	200	–	32
$(C_6H_5)_2NH$	*trans*-$C_6H_5CH=CHCOOC_2H_5$	$HO_2^{\cdot}$	323	20	36.0	33
$(C_6H_5)_2NH$	*trans*-$C_6H_5CH=CHCOOCH_3$	$HO_2^{\cdot}$	323	20	28.0	33
$(C_6H_5)_2NH$	*trans*-$C_6H_5CH=CHCOOC_6H_5$	$HO_2^{\cdot}$	323	20	1.1	33
$(C_6H_5)_2NH$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	56	0.5	34
$(C_6H_5)_2NH$	$(CH_3)_2N(CH_2)_2OCO(CH_3)C=CH_2$	$RO_2^{\cdot}$	323	10	0.6	35
$(4\text{-}CH_3OC_6H_4)_2NH$	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	313	26	6.5	36
$(4\text{-}CH_3OC_6H_4)_2NH$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	343	22	–	30
$(4\text{-}CH_3OC_6H_4)_2NH$	cyclo-$[N(CH_3)(CH_2)_5]$	$RO_2^{\cdot}$	323	52	7.3	37
$(4\text{-}CH_3OC_6H_4)_2NH$	$N(CH_2CH_3)_3$	$RO_2^{\cdot}$	313	80	44.0	38
$(4\text{-}CH_3OC_6H_4)_2NH$	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	70	150	38
$(4\text{-}CH_3OC_6H_4)_2NH$	$CH_3CON(CH_2CH_3)_2$	$RO_2^{\cdot}$	348	30	>10	39
$(4\text{-}CH_3OC_6H_4)_2NH$	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	18	2.2	40
$(4\text{-}CH_3OC_6H_4)_2NH$	$(C_4H_9)_2NH$	$RO_2^{\cdot}$	348	29	4.2	40
$(4\text{-}CH_3OC_6H_4)_2NH$	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	25	0.82	40
$(4\text{-}CH_3OC_6H_4)_2NH$	$C_6H_5CH_2NHCH_3$	$RO_2^{\cdot}$	333	>10	3.7	38
$(4\text{-}CH_3OC_6H_4)_2NH$	$(CH_3)_2N(CH_2)_2OCO(CH_3)C=CH_2$	$RO_2^{\cdot}$	323	18	1.2	35
$(4\text{-}CH_3OC_6H_4)_2NH$	$(CH_3)_2NC_4H_9$	$RO_2^{\cdot}$	323	16	10.6	41
$(4\text{-}CH_3OC_6H_4)_2NH$	$(CH_3)_2N(CH_2)_2OCOCH_2CH_3$	$RO_2^{\cdot}$	323	26	8.0	41
$1\text{-}C_{10}H_7NH_2$	$(CH_3)_2N(CH_2)_2OCO(CH_3)C=CH_2$	$RO_2^{\cdot}$	323	10	0.6	35
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	16	0.08	40
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	56	0.13	34
$1\text{-}C_{10}H_7NH_2$	$CH=CHCH=CHCH_2CH_2$	$HO_2^{\cdot}$	348	28	–	32
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	28	3.2	12
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	413	30	–	12
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	28	–	13
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	348	15	–	14
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	348	90	–	29
$1\text{-}C_{10}H_7NH_2$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	348	90	–	29
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH + H_2O_2$	$HO_2^{\cdot}$	398	22	–	29
$1\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	>4	4.2	38
$1\text{-}C_{10}H_7NH_2$	$CH_3(CH_2)_3OH$	$RO_2^{\cdot}$	347	12	–	13
$1\text{-}C_{10}H_7NH_2$	$CH_3(CH_2)_3OH$	$RO_2^{\cdot}$	383	17	–	13
$1\text{-}C_{10}H_7NH_2$	$CH_3(CH_2)_3OH$	$RO_2^{\cdot}$	347	12	–	13
$1\text{-}C_{10}H_7NH_2$	$CH_3CH(OH)CH_2CH_3$	$RO_2^{\cdot}$	347	12	–	13
$1\text{-}C_{10}N_7NH_2$	$(CH_3)_3COH + H_2O_2$	$RO_2^{\cdot}$	358	9	–	13
$1\text{-}C_{10}H_7NH_2$	$(CH_3)_3COH + H_2O_2$	$HO_2^{\cdot}$	348	22	–	29
$1\text{-}C_{10}H_7NH_2$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	348	90	–	29
$1\text{-}C_{10}H_7NH_2$	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	313	–	0.16	36
$1\text{-}C_{10}H_7NH_2$	cyclo-$[N(CH_3)(CH_2)_5]$	$RO_2^{\cdot}$	323	–	0.20	37
$1\text{-}C_{10}H_7NH_2$	$N(CH_2CH_3)_3$	$RO_2^{\cdot}$	313	–	1.3	38
$1\text{-}C_{10}H_7NH_2$	$(C_4H_9)_2NH$	$RO_2^{\cdot}$	348	26	0.15	40
$1\text{-}C_{10}H_7NH_2$	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	30	0.16	40
$2\text{-}C_{10}H_7NH_2$	$CH_3(CH_2)_3OH$	$RO_2^{\cdot}$	347	6	–	13
$2\text{-}C_{10}H_7NH_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	28	0.2	34
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	$(CH_3)_2N(CH_2)_2OCO(CH_3)C=CH_2$	$RO_2^{\cdot}$	323	26	12.0	35
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	$CH=CHCH=CHCH_2CH_2$	$HO_2^{\cdot}$	348	6.5	–	32
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	$CH=CHCH=CHCH_2CH_2$	$HO_2^{\cdot}$	313	22	–	32
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	cyclo-$[N(CH_3)(CH_2)_5]$	$RO_2^{\cdot}$	323	43	8.2	37
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	17	21.0	38
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	*trans*-$C_6H_5CH=CHCOOC_2H_5$	$HO_2^{\cdot}$	323	40	26.0	33
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	*trans*-$C_6H_5CH=CHC_6H_5$	$HO_2^{\cdot}$	323	40	17.0	33
$2\text{-}C_{10}H_7NHC_6H_4NH\text{-}2'\text{-}C_{10}H_7$	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	313	22	4.0	36
$4\text{-}C_6H_5NHC_6H_4NHCH(CH_3)_2$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	200	–	34
$1\text{-}C_{10}H_7NHC_6H_5$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	15	–	34
$2\text{-}C_{10}H_7NHC_6H_5$	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	393	26	0.9	34
$2\text{-}C_{10}H_7NHC_6H_5$	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	36	1.2	40
$(4\text{-}C_6H_5NH\text{-}4'\text{-}C_6H_4O)_2Si(CH_3)_2$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	343	18	–	30
$2\text{-}C_{10}H_7NHC_6H_5$	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	52	1.2	40
$2\text{-}C_{10}H_7NHC_6H_5$	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	20	1.0	38



$$Am^{\cdot} + HC(OO^{\cdot})C \longrightarrow AmH + >C{=}C< + O_2 . \quad (29)$$

We present below the heats (ΔH) of disproportionation of the diphenylamino radicals both with hydroxyl radicals and with alkyl-containing peroxyl radicals:[42]

Peroxyl radical	$-\Delta H$ / kJ mol^{-1}
$HO_2^{\cdot}$	161
$(CH_3)_2C(OH)O_2^{\cdot}$	145
cyclo-$C_6H_{10}(OH)O_2^{\cdot}$	135
$C_6H_5C(CH_3)_2O_2^{\cdot}$	95
cyclo-$C_6H_{11}O_2^{\cdot}$	84

It can be seen that all these reactions are exothermic, and the ΔH values are fairly close to one another. All these reactions should seemingly proceed equally rapidly. The question as to how easily the amino radicals react with the O–H and C–H bonds of the peroxyl radicals can be answered by analysing these reactions in terms of the parabolic model of transition state.[43–45] This model treats the transition state in a radical abstraction reaction as the point of intersection of two nonperturbed parabolic terms, one of which describes the potential energy of the bond being attacked, whereas the other describes the potential energy of the bond being formed. The model makes it possible to calculate, using experimental data (activation energy, rate constant), an important characteristic of the elementary step, namely the distance by which the hydrogen atom being attacked shifts. This permits, in turn, the calculation of the activation energy for a thermally neutral reaction of this class. By a class of reactions is meant a set of all structurally similar reactions, characterised by the same distance of the displacement of an atom in the elementary step. For example, all the $RO_2^{\cdot}$ + RH reactions, in which an aliphatic hydrogen atom is attacked, belong to the same class.

Each elementary reaction is characterised in this model by enthalpy ΔH_e, which incorporates the difference between the zero point energies of the reacting bonds, and also by activation energy E_e, which is the sum of the activation energy E measured experimentally and the zero point vibration energy of the bond being attacked (in the case of the O–H bond, the latter is 21 kJ mol^{-1}). The activation energies for all the thermally neutral reactions of radical abstraction ($E_{e,o}$) and the coefficients α of reactions of this class are identical.[45]

Analysis of experimental data has shown that, when amino radicals react with hydrocarbons, phenols, and hydroperoxides, they are extremely reactive toward specifically the O–H bonds.[46] The $E_{e,o}$ values for the reactions of amino radicals with various compounds are presented below:[46]

Compound	$E_{e,o}$ / kJ mol^{-1}
ROOH	39.0
ArOH	41.8
AmOH	32.2
AlkH	69.7
AralkH	81.7

The reactions of amino radicals with the O–H bonds ($E_{e,o}$ varies from 32 kJ mol^{-1} to 42 kJ mol^{-1}) and their reactions with the C–H bonds ($E_{e,o}$ varies from 70 kJ mol^{-1} to 82 kJ mol^{-1}) are very different, which leads to the following significant fact.

The activation energies for reactions are known to decrease as ΔH decreases. According to the parabolic model,[45] for highly exothermic reactions with fairly high ΔH_e values the activation energy $E = 0.5\,RT$. The transition from higher activation energies to $E = 0.5\,RT$ occurs at a certain minimum value of ΔH_e ($\Delta H_{e,min}$), which depends on $E_{e,o}$ for the class of reactions being considered. The higher $E_{e,o}$, the higher $\Delta H_{e,min}$ and the broader the ΔH range, in which $E > 0.5\,RT$.

For the reaction of amino radicals with the O–H bond in ROOH, $\Delta H_{e,min} = -39.4$ kJ mol^{-1}, which is substantially smaller in magnitude than $\Delta H_{e,min}$ for the reactions of diphenylamino radicals with $HO_2^{\cdot}$ and $(CH_3)_2C(OH)O_2^{\cdot}$ (−161 to −135 kJ mol^{-1}, see above). Thus all these reactions require virtually no activation energy, i.e. proceed fairly rapidly. The $E_{e,o}$ value for the reactions of Am$^{\cdot}$ with the C–H bond is markedly higher,[46] and the $\Delta H_{e,min}$ value corresponding to it is −141.1 kJ mol^{-1}. In the case of the reactions of diphenylamino radicals with β-C–H bonds in the alkylperoxyl radicals, $\Delta H = 84-95$ kJ mol^{-1}, which is smaller than $\Delta H_{e,min}$. Hence, these reactions should proceed with activation energies $E > 0.5\,RT$, i.e. their rates are much lower than the rate of interaction of Am$^{\cdot}$ with the O–H bond in the corresponding peroxyl radical.

To give the ultimate answer to the question of why the cyclic chain termination mechanism is realised in those systems where $HO_2^{\cdot}$ and >C(OH)OO$^{\cdot}$ radicals act as the chain-propagating species but is not realised during the oxidation of hydrocarbons, one should compare the rate constants for the disproportionation reactions in which Am$^{\cdot}$ affords the starting AmH [reactions (23) and (27)] with the rate constant for the irreversible destruction of Am$^{\cdot}$ [reaction (28)]. The diphenylamino radical reacts with $RO_2^{\cdot}$ via two parallel routes (25) and (28) at approximately identical rates.[30] The rate constant for the overall reaction k is known to be 6×10^8 dm^3 mol^{-1} s^{-1}.[47] This implies that the rate constant for the addition of the peroxyl radical to the aromatic ring of the diphenylamino radical k_{28} is 3×10^8 dm^3 mol^{-1} s^{-1}. The cyclic mechanism is realised if the inequality $k_{21} > k_{28}$ or $k_{23} > k_{28}$ inequality holds. Therefore, it is necessary to evaluate the rate constants for the disproportionation of Am$^{\cdot}$ and $RO_2^{\cdot}$ and for the regeneration of AmH. It should be noted that, according to the parabolic model, in the case of highly exothermic reactions the pre-exponential factor A is related to the enthalpy of the reaction at $\Delta H_e > \Delta H_{e,min}$ by the following relationship:[48]

$$\left(\frac{A}{A_0}\right)^{0.5} = 1 - \beta\left[|\Delta H_e|^{0.5} - |\Delta H_{e,min}|^{0.5}\right] .$$

For this class of reactions, $A_0 = A$ at $\Delta H_e < \Delta H_{e,min}$, and the coefficient β for the reactions

$$RO_2^{\cdot} + R'OOH \longrightarrow ROOH + R'O_2^{\cdot}, \quad (30)$$

is 1.6 kJ$^{-0.5}$ mol$^{-0.5}$.[42] The activation energy, which is equal to $0.5\,RT$ for exothermic reactions with $\Delta H_e > \Delta H_{e,min}$ and is greater than $0.5\,RT$ for reactions with $\Delta H_e < \Delta H_{e,min}$, can be calculated from the equations of the parabolic model.[45]

The activation energies and rate constants for the reactions (21), (23), and (29) of the diphenylamino radical with various $RO_2^{\cdot}$ calculated in this way are presented below:[42]

Peroxyl radical	E / kJ mol^{-1}	k / dm^3 mol^{-1} s^{-1}
$C_6H_5C(CH_3)_2O_2^{\cdot}$	16.6	1.5×10^7
cyclo-$C_6H_{11}O_2^{\cdot}$	19.8	3.1×10^6
$HO_2^{\cdot}$	1.4	8.4×10^9

One can see that the rate constants for the disproportionation of the amino and peroxyl radicals (k_{29}) involving the C–H bond are substantially lower than the rate constants for the addition of $RO_2^{\cdot}$ to the aromatic ring of the amino radical ($k_{28} = 3 \times 10^8$ dm^3 mol^{-1} s^{-1}). Conversely, the reaction of Am$^{\cdot}$ with $HO_2^{\cdot}$ proceeds very rapidly and can compete successfully with the addition reaction. Thus, the result obtained in terms of the parabolic model is in good agreement with the experiment.

The reason for the different reactivities of Am$^{\cdot}$ with respect to alkyl- and hydroxyl-containing peroxyl radicals lies in the energy characteristics of the transition states of the C...H...N and O...H...N types. In the former case, the triplet repulsion makes a substantial contribution to the energy of the transition state, because the C–N bond is fairly strong, and the energy of its nonbonding orbital is high.[45] In the latter case, the hypothetical

compound ROOAm incorporates a weak N–O bond, and the contribution of the triplet repulsion to $E_{e,o}$ is slight. Apart from the triplet repulsion, the electronegativities of the atoms forming the reaction centre of the transition state are also significant:[45] the higher the difference between the electronegativities of the atoms, the lower the $E_{e,o}$ activation barrier. In this respect, too, the relationship between the C...H...N and O...H...N reaction centres counts in favour of the latter: the electron affinities of the C and N atoms are close to each other, whereas the electronegativities of the O and N atoms are substantially different.

An evaluation based on the equations of the parabolic model[45] indicates that a reaction of the type (18) involving phenoxyl radicals also requires no activation energy (in this case, $\Delta H_e > \Delta H_{e,min} = 57$ kJ mol^{-1}). However, the addition of $RO_2^{\cdot}$ to the aromatic ring of the phenoxyl radical occurs very rapidly, so that the rate constant for this reaction is determined by diffusion processes.[11] The data on the $E_{e,o}$ values are also consistent with this: for ArO$^{\cdot}$ + HOOR reactions (the O...H...O) reaction centre and for Am$^{\cdot}$ + HOOR reactions (the N...H...O reaction centre), these values are 45.3 kJ mol^{-1} and 39.0 kJ mol^{-1}, respectively.[46] At the same time, calculation of the pre-exponential factor in terms of the parabolic model indicates that the rate constant k_{-7} for the reaction of ROOH with the participation of amino radical is several times higher than that for the reaction involving phenoxyl radical, the enthalpies of these reactions being identical. Thus, the irreversible destruction of ArO$^{\cdot}$ in its reactions with $HO_2^{\cdot}$ and $>C(OH)O_2^{\cdot}$ occurs more rapidly than the conversion of ArO$^{\cdot}$ into ArOH, and the cyclic mechanism of chain termination is not realised with phenols. An exception is provided by hydroquinones, which are considered below.

Aromatic amines also cause cyclic chain termination in the oxidation of primary and secondary aliphatic amines (Table 1). AmH is recovered from Am$^{\cdot}$ via the reaction of Am$^{\cdot}$ with the N–H bond of the $RCH(NHR')O_2^{\cdot}$ peroxyl radical. Together with AmH, the reaction yields the imine $RCH{=}NR'$ and O_2, i.e. a process similar to reaction (23) occurs. The rapid occurrence of this reaction involving primary and secondary amines is apparently due to the fact that the triplet repulsion in this case is weak, because a transition state of the N...H...N type is formed and the energy of the dissociation of the N–N bond is substantially lower than that for the N–C and C–C bonds. This can be seen from a comparison of the D_{C-C}, D_{N-N} and D_{N-C} dissociation energies (see handbooks[26,49]):

Compound	D/ kJ mol^{-1}
CH_3-CH_3	376
H_2N-NH_2	275
$H_2N-NHC_6H_5$	219
$CH_3-NHC_6H_5$	299
$(C_6H_5)_2N-N(C_6H_5)_2$	119

Cyclic chain termination with aromatic amines also occurs in the oxidation of tertiary aliphatic amines (see Table 1). To explain this fact, a mechanism of the conversion of Am$^{\cdot}$ into AmH involving the β-C–H bonds [reaction (29)] has been suggested;[39] however, its realisation is hampered by its high activation energy. Since tertiary amines have low ionisation potentials and readily participate in reactions with electron transfer, the cyclic mechanism in systems of this type is realised apparently as a sequence of such reactions, similar to what occurs in the systems containing complexes of variable-valence metals (see below).

IV. Cyclic chain termination with quinones in the oxidation of alcohols and polymers

Quinones (Q) are well known as inhibitors of radical polymerisation; they terminate chains by adding alkyl radicals via the following reactions[50]

$$R^{\cdot} + Q \longrightarrow RQ^{\cdot}, \quad (31)$$

$$RQ^{\cdot} + R^{\cdot} \longrightarrow RQR. \quad (32)$$

At the same time, quinones do not retard oxidation of hydrocarbons, since alkyl radicals react very rapidly with oxygen (see Section II) to give alkylperoxyl radicals, which scarcely react with quinones. Quinones exhibit their inhibiting properties only in the oxidation of polymers; the chain termination results from their interaction with alkyl macroradicals,[51] which is due to the specific features of the oxidation of polymers in the solid phase and also due to the fact that alkyl macroradicals react with O_2 in a polymeric matrix relatively slowly.[3] Quinones decelerate the oxidation of alcohols very effectively and for long periods by ensuring cyclic chain termination via the following reactions[16]

$$>C(OH)OO^{\cdot} + Q \longrightarrow >C{=}O + O_2 + HQ^{\cdot}, \quad (33)$$

$$>C(OH)OO^{\cdot} + HQ^{\cdot} \longrightarrow >C(OH)OOH + Q. \quad (34)$$

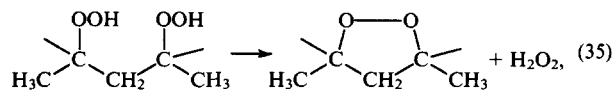
The processes of oxidation of cyclohexadiene, 1,2-substituted ethenes, and aliphatic amines are decelerated by quinone or hydroquinone by a similar mechanism. The values of the stoichiometric inhibition coefficients and of the rate constants (f and k) for the corresponding reactions involving peroxyl radicals [$HO_2^{\cdot}$, $>C(OH)OO^{\cdot}$, and $>C(NHR)O_2^{\cdot}$] are presented in Table 2. The f coefficients in these reactions are relatively high, varying from 8 to 70. Evidently, the irreversible consumption of quinone in these systems is due to the addition of $RO_2^{\cdot}$ to the aromatic ring of the quinone followed by the decomposition of the resulting adduct.

The data on the deceleration of the oxidation of polymers (polyethylene, polypropylene) by quinones deserve particular attention.[51] It has been noted above that benzoquinone, which retards the initiated oxidation of polymers, behaves as a typical acceptor of alkyl radicals. It decreases the rate of chain oxidation, which obeys the following dependence:

$$v \sim v_i P_{O_2}[Q]^{-1}.$$

In this case, the chain termination occurs stoichiometrically: one quinone molecule terminates two chains.

However, when stilbenequinone is introduced into a preliminarily oxidised polymer containing hydroperoxy-groups, a totally different picture is observed.[52] In this case, quinone acquires the ability to repeatedly terminate the chains ($f = 20$ in the oxidation of polypropylene with a concentration of the hydroperoxy-groups [POOH] = 0.13 mol kg^{-1}, $T = 356$ K). The chain termination at $P_{O_2} = 10^5$ Pa occurs predominantly via the reaction with peroxyl radicals. The increase in the efficiency of the retarding action of the quinone is due to the fact that in the oxidised polypropylene containing associated β-OOH groups, the latter decompose to give hydrogen peroxide, which serves as the source of the $HO_2^{\cdot}$ radicals and these radicals ensure cyclic chain termination via interaction with quinones:[52]



(35)

$$PO_2^{\cdot} + H_2O_2 \longrightarrow POOH + HO_2^{\cdot}, \quad (36)$$

$$Q + HO_2^{\cdot} \longrightarrow {}^{\cdot}QH + O_2, \quad (37)$$

$$PO_2^{\cdot} + HO_2^{\cdot} \longrightarrow POOH + Q \quad (38)$$

($PO_2^{\cdot}$ is the peroxyl macroradical).

It is evident from Table 2 that quinones react rapidly with the hydroperoxyl radicals. Calculation shows that the change in the enthalpy in the reaction (33) is relatively small. The calculation was based on the ΔH_f data for quinone and hydroquinone[49] and on the D_{O-H} value for hydroquinone[53] (350.3 kJ mol^{-1}). The dissociation energy of the O–H bond in the 4-$HOC_6H_4O^{\cdot}$ semiquinone radical is 228.1 kJ mol^{-1}. The dissociation energies

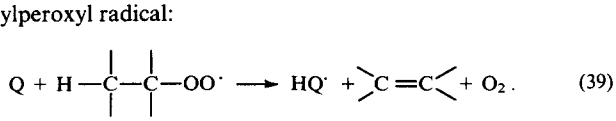
Table 2. Inhibition coefficients and rate constants for the reactions of quinones and hydroquinones with $RO_2^{\cdot}$ in systems with a cyclic mechanism of chain termination.

InH	RH	$RO_2^{\cdot}$	T/K	f	$k/10^4$ dm^3 mol^{-1} s^{-1}	Ref.
4-HOC_6H_4OH	cyclo-[$N(CH_3)(CH_2)_5$]	$RO_2^{\cdot}$	323	14	3.2	38
4-HOC_6H_4OH	$N(CH_2CH_3)_3$	$RO_2^{\cdot}$	313	>20	14.0	38
4-HOC_6H_4OH	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	20	7.2	38
4-HOC_6H_4OH	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	313	–	0.7	36
4-HOC_6H_4OH	$CH_3CON(CH_2CH_3)_2$	$HO_2^{\cdot}$	348	10	0.94	39
4-HOC_6H_4OH	*trans*-$C_6H_5CH=CHCOOC_2H_5$	$HO_2^{\cdot}$	323	15	14.0	33
4-HOC_6H_4OH	*trans*-$C_6H_5CH=CHC_6H_5$	$RO_2^{\cdot}$	323	15	0.3	33
4-OC_6H_4O	cyclo-[$N(CH_3)(CH_2)_5$]	$RO_2^{\cdot}$	323	8	4.0	38
4-OC_6H_4O	$N(CH_2CH_3)_3$	$RO_2^{\cdot}$	313	>10	29.0	38
4-OC_6H_4O	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	16	2.7	38
4-OC_6H_4O	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	344	23	29.0	16
4-OC_6H_4O	cyclo-[$(CH=CH)_2CH_2CH_2$]	$HO_2^{\cdot}$	348	70	–	32
4-OC_6H_4O	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	313	–	1.0	36
4-OC_6H_4O	$(CH_3)_2N(CH_2)_3CH_3$	$RO_2^{\cdot}$	323	12	4.2	41
4-OC_6H_4O	$(CH_3)_2N(CH_2)_2OCOC(CH_3)_3=CH_2$	$HO_2^{\cdot}$	323	34	1.6	35
$C_6H_5NC_6H_4O$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	343	12	20.0	30
Stilbenequinone	Polypropylene	$HO_2^{\cdot}$	365	20	–	42

of the O–H and C–H bonds in the corresponding peroxyl radicals[42] and enthalpies of the reaction (33) are presented in Table 3. It can be seen from this Table that the ΔH_f value for reaction (33) varies from -25 kJ mol^{-1} in the case of $HO_2^{\cdot}$ to 1.7 kJ mol^{-1} in the case of hydroxycyclohexylperoxyl radical. The activation energies for this reaction were calculated from the equations of the parabolic model;[45] parameters of a similar reaction of phenoxyl radicals with hydroperoxide ($E_{e,o}$ = 45.3 kJ mol^{-1}, α = 1) were used for the calculation. The activation energies of these reactions were found to be relatively low and equal to 14–26 kJ mol^{-1}. The low activation barriers to these reactions are accounted for by the fact that the transition state of the O...H...O type arising in the reaction (33) is characterised by the absence of the triplet repulsion, which makes a substantial contribution to the activation energy in other reactions. For the $ArO^{\cdot}$ + ROOH reaction, the pre-exponential factor A is equal to 10^8 dm^3 mol^{-1} s^{-1}. Therefore, with allowance for the fact that benzoquinone incorporates two reaction centres, we may take $A = 2\times10^8$ dm^3 mol^{-1} s^{-1} for the reaction (33).

Table 3 presents the results of the calculations of the rate constants for reactions (33) involving $HO_2^{\cdot}$ and two hydroperoxyl radicals. Comparison of the calculated and experimental values of k_{33} can be carried out using the reaction of benzoquinone with the peroxyl radical derived from isopropanol as an example. According to the data of Denisov,[16] the $k_{33}/2k_t$ ratio in this case at 344 K is 9.4 litre$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$, whereas the rate constant for the disproportionation of two $RO_2^{\cdot}$ radicals is 1.1×10^9 dm^3 mol^{-1} s^{-1}.[26] Hence we obtain $k_{33} = 3.1\times10^5$ dm^3 mol^{-1} s^{-1}. The theoretical calculation from the equations of the parabolic model gives $k_{33} = 2\times10^8\exp(-21.2/RT) = 1.2\times10^5$ dm^3 mol^{-1} s^{-1} (344 K), i.e. a closely similar value. Thus, the calculation permits the rate constants for reaction (33) to be evaluated with sufficient accuracy.

The question arises as to why quinones terminate chains via reaction (33) and not via reaction with the β-C–H bond of the alkylperoxyl radical:



(39)

The cleavage of the C–H and C–O bonds in the reaction (39) is compensated to a substantial degree by the formation of the π-C–C and O–H bonds of the semiquinone radical. Table 3 presents the ΔH values for the reaction (39) involving two hydrocarbon peroxyl radicals $C_6H_5(CH_3)_2CO_2^{\cdot}$ and cyclo-$C_6H_{11}O_2^{\cdot}$. The reaction is endothermic in both cases (ΔH = 40–50 kJ mol^{-1}). However, the fact that such reactions proceeding via a transition state of the C...H...O type are characterised by high thermally neutral activation energies $E_{e,o}$ is more significant. The difference between the $E_{e,o}$ values for reactions involving an $ArO^{\cdot}$...H...R transition state [an analogue of reaction (39)] and an $ArO^{\cdot}$...H...OOR transition state [an analogue of reaction (33)] amounts to 69.8–45.3 = 24.5 kJ mol^{-1}. This accounts for the high activation energy for reaction (39) involving the $C_6H_5(CH_3)_2CO_2^{\cdot}$ and cyclo-$C_6H_{11}O_2^{\cdot}$ radicals (~74 and ~79 kJ mol^{-1}, respectively). If we take the pre-exponential factor A to be equal to 2×10^9 dm^3 mol^{-1} s^{-1}, then the rate constants for the reaction (39) will assume the values given in Table 3. With the rate constants being so small, reaction (39) cannot influence the oxidative chain termination via the interaction of two $RO_2^{\cdot}$ radicals {the rate constant for the latter is 10^5–10^7 dm^3 mol^{-1} s^{-1};[26] in these cases, the inequality $(2k_6v_i)^{0.5} \ll 2k_{39}[Q]$ always holds}. What is the reason for such high $E_{e,o}$ values and, hence, for the high activation energies characteristic of the reactions involving transition states of the O...H...C type? Comparison of reactions of various types has shown that this is the strong triplet repulsion.[45] It is this repulsion that precludes rapid occurrence of reaction (39), as also in the reactions involving amino radicals. In the case of aminoperoxyl radicals (primary and secondary amines), the high rate of the reaction

$$Q + \gtrdot C(NHR)O_2^{\cdot} \rightarrow HQ^{\cdot} + \gtrdot C{=}NR + O_2 \qquad (40)$$

is due to the low activation barrier $E_{e,o}$, which is only 39 kJ mol^{-1} for the N...H...O type transition state.[46] This is explained by weak triplet repulsion in compounds AmOOR and by an additional attraction between the N and O atoms owing to their different

Table 3. Some energy and kinetic parameters of the reactions of benzoquinone with the O–H [reaction (33)] and C–H bonds [reaction (39)] of peroxyl radicals.

Peroxyl radical	D_{O-H} or D_{C-H},[a]	ΔH,[a]	E,[a]	k(333 K)[b]
$HO_2^{\cdot}$	203.4	–24.7	13.7	1.4×10^6
$(CH_3)_2C(OH)O_2^{\cdot}$	219.9	–8.9	21.2	9.5×10^4
cyclo-$C_6H_{10}(OH)O_2^{\cdot}$	229.8	1.7	26.0	1.7×10^4
$C_6H_5(CH_3)_2CO_2^{\cdot}$	270.0	41.9	73.6	3.4×10^{-2}
cyclo-$C_6H_{11}O_2^{\cdot}$	280.3	52.9	78.9	3.4×10^{-3}

[a] kJ mol^{-1}; [b] dm^3 mol^{-1} s^{-1}

Table 4. Rate constants for the reactions of alkylperoxyl radicals with alcohols (the method of selective inhibition).[54]

Hydrocarbon	Alcohol	T/K	k/dm^3 mol^{-1} s^{-1}	Ref.
cyclo-C_6H_{10}	CH_3OH	313	0.3	53
cyclo-C_6H_{10}	C_2H_5OH	333	1.9	53
cyclo-C_6H_{10}	$(CH_3)_2CHOH$	333	2.0	53
cyclo-C_6H_{10}	$CH_3(CH_2)_3OH$	333	1.2	53
cyclo-C_6H_{10}	cyclo-$C_6H_{11}OH$	333	2.5	53
cyclo-C_6H_{10}	$C_6H_5CH_2OH$	333	5.6	53
$CH_3(CH_2)_{14}CH_3$	$CH_3(CH_2)_8CH_2OH$	404	1.8×10^2	54
$CH_3(CH_2)_{14}CH_3$	$CH_3CH(OH)(CH_2)_5CH_3$	404	2.3×10^2	54
$CH_3(CH_2)_{14}CH_3$	$CH_2(OH)CH_2(OH)$	404	78	54
$CH_3(CH_2)_{14}CH_3$	$[CH_2(OH)CH_2]_2$	404	87	54
$CH_3(CH_2)_{14}CH_3$	$CH_2(OH)CH_2CH(OH)CH_3$	404	1.2×10^2	54
$CH_3(CH_2)_{14}CH_3$	$CH_2(OH)C(CH_3)_2CH_2OH$	404	3.4×10^3	54
$CH_3(CH_2)_{14}CH_3$	$CH_3CH_2C(CH_2OH)_3$	404	9.4×10^2	54
$CH_3(CH_2)_{14}CH_3$	$O[CH_2CH(OH)CH_2OH]_2$	404	1.6×10^3	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_3(CH_2)_8CH_2OH$	404	22.5	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_3(CH_2)_7CH_2OH$	404	23.0	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_3CH(OH)(CH_2)_5CH_3$	404	22.5	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_2(OH)(CH_2)_2CH_2OH$	404	14.0	54
$[CH_3(CH_2)_4COO(CH2)_2OCH_2]_2$	$CH_2(OH)CH_2CH(OH)CH_3$	404	15.6	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_2(OH)C(CH_3)_2CH_2OH$	404	1.2×10^2	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_3CH_2C(CH_2OH)_3$	404	1.2×10^2	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$O[CH_2CH(OH)CH_2OH]_2$	404	71	54
$[CH_3(CH_2)_4COO(CH_2)_2OCH_2]_2$	$CH_3[CH(OH)]_2CH_3$	404	27	54

electron affinities (as also in the case of reactions of amino radicals with the O–H groups of the peroxyl radicals). (Apparently, quinones react with the peroxyl radicals derived from tertiary amines with transfer of an electron).

The selectivity of the reaction of benzoquinone with hydroxyperoxyl radicals and its inertness with respect to alkylperoxyl radicals has been used for the development of an original method for measuring the rate constants for the reactions of alkylperoxyl radicals with alcohols.[54] For this purpose, the initiated oxidation of a mixture of a hydrocarbon and an alcohol is carried out in the presence of benzoquinone. The latter is added in a concentration that is high enough to ensure that all the hydroxyperoxyl radicals derived from the alcohol react with it (are destroyed) and is low enough to cause no noticeable chain termination via the reaction of quinone with the alkyl radicals. This 'operating' range of the benzoquinone concentrations is $(1-10) \times 10^{-3}$ mol dm^{-3}. The rate constants for the reactions of a number of alkylperoxyl radicals with alcohols found by this method are presented in Table 4.

V. Cyclic chain termination mechanisms involving nitroxyl radicals

Nitroxyl radicals react rapidly with alkyl radicals[53] and efficiently retard the radical polymerisation of hydrocarbons. At the same time, only aromatic nitroxyls are capable of reacting with alkylperoxyl radicals,[53] and in this case the chain termination in the oxidation of saturated hydrocarbons occurs stoichiometrically. However, in the processes of oxidation of alcohols, alkenes, and primary and secondary aliphatic amines in which the chain reaction involves the $HO_2^{\cdot}$, $>C(OH)O_2^{\cdot}$, and $>C(NHR)O_2^{\cdot}$ radicals, respectively, nitroxyl radicals are capable of terminating the chains repeatedly by a cyclic mechanism.[30,32,40] For example, chain termination in the oxidation of alcohols occurs via the following reactions

$$AmO^{\cdot} + HO_2^{\cdot} \longrightarrow AmOH + O_2, \quad (41)$$

$$AmOH + HO_2^{\cdot} \longrightarrow AmO^{\cdot} + H_2O_2. \quad (42)$$

Reaction (41) is the rate-determining stage. During the oxidation a kinetic equilibrium is established between the two forms of the inhibitor — $AmO^{\cdot}$ and AmOH.[38] The kinetic characteristics of this mechanism are presented in Table 5.

Let us try to account for the rapidity of reactions (41) and (42). The disproportionation of radicals (41) is an exothermic reaction. For example, the enthalpies of disproportionation of 2,2,6,6-tetramethylpiperidinoxyl with $HO_2^{\cdot}$, $(CH_3)_2C(OH)O_2^{\cdot}$, and cyclo-$C_6H_{10}(OH)O_2^{\cdot}$ are -109, -92, and -82 kJ mol^{-1}, respectively. The $E_{e,o}$ value for the abstraction of an H atom from the O–H bond in ROOH by a nitroxyl radical is 45.6 kJ mol^{-1} and is matched by the value $\Delta H_{e,min} = -58$ kJ mol^{-1}. Since $\Delta H < \Delta H_{e,min}$, the activation energy $E \simeq 0.5RT$ for these reactions is low,[48] and the rate constant is correspondingly high. Therefore, in the systems in which hydroperoxyl and hydroxyperoxyl radicals participate in the chain propagation, the cyclic chain termination mechanism is realised.

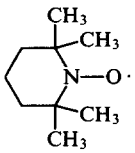
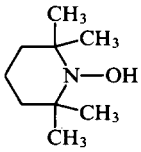
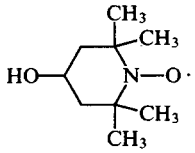
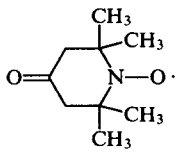
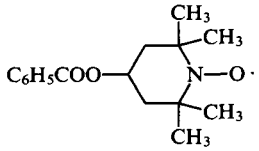
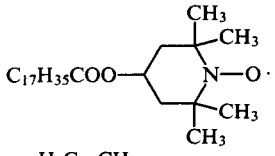
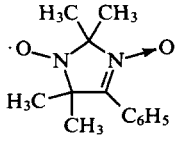
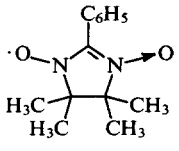
The reactions of disproportionation of nitroxyl and alkylperoxyl radicals are also exothermic. For example, 2,2,6,6-tetramethylpiperidinoxyl abstracts an H atom from the β-C–H bond of cumylperoxyl and cyclohexylperoxyl radicals. The enthalpies of these reactions are -42 and -32 kJ mol^{-1}. The activation energy for the radical abstraction ($E_{e,o}$) for the $AmO^{\cdot}$ + RH reaction is 58 kJ mol^{-1}, and the corresponding $\Delta H_{e,min}$ value is -125 kJ mol^{-1};[42] that is, $\Delta H_{e,min}$ substantially exceeds ΔH in magnitude. Thus, both reactions under consideration

$$AmO^{\cdot} + RO_2^{\cdot} \longrightarrow AmOH + O_2 + R_{-H},$$

should require appreciable activation energies. According to a calculation,[42] for the reaction of $AmO^{\cdot}$ with $C_6H_5(CH_3)_2CO_2^{\cdot}$, $E = 23.7$ kJ mol^{-1} and $k = 1.1 \times 10^6$ dm^3 mol^{-1} s^{-1}, and for the reaction of $AmO^{\cdot}$ with cyclo-$C_6H_{11}O_2^{\cdot}$, $E = 27.4$ kJ mol^{-1} and $k = 2.0 \times 10^5$ dm^3 mol^{-1} s^{-1}. The recombination of nitroxyl radicals with alkyl radicals proceeds as a rule much more rapidly.[53]

Why are the $E_{e,o}$ values in the reactions of nitroxyl radicals with O–H bonds lower than those in their reactions with C–H bonds? As in the case of disproportionation of $RO_2^{\cdot}$ with amino radicals, the low $E_{e,o}$ values are accounted for by triplet repulsion.[57] When a transition state of the O...H...O type is formed (the $AmO^{\cdot}$ + $HO_2^{\cdot}$ reaction), the triplet repulsion is close to zero, because the O–O bond in the labile compound AmOOH is very weak. Conversely, the triplet repulsion in the reaction of $AmO^{\cdot}$

Table 5. Some kinetic characteristics of the cyclic mechanism of the chain termination on nitroxyl radicals in the oxidation of alcohols and amines.

Inhibitor	Substrate	$RO_2^{\cdot}$	T/K	f	$k/10^4$ dm^3 mol^{-1} s^{-1}	Ref.
$(4\text{-}CH_3OC_6H_4)_2NO^{\cdot}$	$(CH_3)_2CHOH$	$RO_2^{\cdot}$	343	50	–	30
	$CH_3CON(CH_2CH_3)_2$	$RO_2^{\cdot}$	348	30	3.5	39
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	100	21.0	39
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	100	8.1	39
	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	348	50	8.4	39
	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	140	34.0	39
	*trans*-$C_6H_5CH=CHCOOC_2H_5$	$HO_2^{\cdot}$	323	> 100	19.0	33
	trans-$C_6H_5CH=CHCOOCH_3$	$HO_2^{\cdot}$	323	> 100	12.0	33
	$CH_3CON(C_2H_5)_2$	$RO_2^{\cdot}$	348	50	1.3	39
	trans-$C_6H_5CH=CHC_6H_5$	$HO_2^{\cdot}$	323	> 100	3.2	33
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	200	2.4	39
	$(CH_3)_2C=CHC(O)CH_3$	$HO_2^{\cdot}$	323	> 100	2.2	33
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	160	14.0	39
	$C_2H_5OCOCH=CHCOOC_2H_5$	$HO_2^{\cdot}$	323	> 100	1.2	7
	$CH_2=C(CH_3)COOCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	323	30	2.6	35
	$CH_3CH_2COOCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	323	10	0.2	7
	cyclo-$[(CH_2)_5NCH_3]$	$RO_2^{\cdot}$	323	90	7.2	39
	$(CH_3CH_2)_3N$	$RO_2^{\cdot}$	313	25	57.0	39
	cyclo-$C_6H_{11}N(CH_3)_2$	$RO_2^{\cdot}$	323	92	18.0	39
	$C_6H_5CH_2NHCH_3$	$RO_2^{\cdot}$	323	16	4.2	39
	*trans*-$C_6H_5CH=CHCOOC_2H_5$	$HO_2^{\cdot}$	323	> 100	14.0	33
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	100	2.8	39
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	100	15.2	39
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	313	> 4	1.3	36
	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	100	7.9	39
	$CH_2=C(CH_3)CO_2CH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	323	70	0.8	35
	$CH_3(CH_2)_3N(CH_3)_2$	$RO_2^{\cdot}$	323	80	5.6	39
	$CH_3CH_2CO_2CH_2CH_2N(CH_3)_2$	$RO_2^{\cdot}$	323	10	0.3	7
	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	348	120	21	40
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	–	3.0	40
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	–	12.6	40
	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	–	19.0	40
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	–	2.5	40
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	–	16.6	40
	Polypropylene	$RO_2^{\cdot}$, $R^{\cdot}$	387	14	–	17
	Oxidized polypropylene	$HO_2^{\cdot}$	388	> 40	–	56
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	–	0.7	40
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	–	6.6	40
	$C_6H_5CH_2NH_2$	$RO_2^{\cdot}$	338	–	7.2	40
	cyclo-$C_6H_{11}OH$	$RO_2^{\cdot}$	348	–	5.9	40
	cyclo-$C_6H_{11}NH_2$	$RO_2^{\cdot}$	348	–	0.9	40
	$[CH_3(CH_2)_3]_2NH$	$RO_2^{\cdot}$	348	–	9.4	40

with the C–H bond is fairly great, due to the high dissociation energy of the AmO–R bond. This accounts for the difference between the activation energies and between the rate constants for the reactions considered above. Thus, the possibility of the realisation of a cyclic chain termination mechanism in the reactions of Am$^{\cdot}$ and AmO$^{\cdot}$ with peroxyl radicals, incorporating O–H groups, is caused by the weak triplet repulsion in the disproportionation reactions in which the corresponding inhibitor (AmH or AmOH) is recovered.

$HO_2^{\cdot}$ radicals are also generated in the oxidation of polymers, in particular, in the oxidation of polypropylene,[58] when intramolecular chain transfer affords associated hydroperoxy-groups.[3] The thermal decomposition of the latter yields H_2O_2, which reacts with peroxyl macroradicals and thus generates the $HO_2^{\cdot}$ radicals, which are responsible for the cyclic chain termination via reactions (41) and (42).[52,58]

The nitroxyl radicals also participate in other cyclic mechanisms of chain termination. One of these mechanisms involves alternation of reactions involving the R$^{\cdot}$ and $RO_2^{\cdot}$ radicals. This mechanism has been discovered in a study of the retarding effect of 2,2,6,6-tetramethyl-4-benzoylpiperidin-*N*-oxyl on the initiated oxidation of polypropylene.[17] It has been shown [17,59,60] that the nitroxyl radical terminates the oxidation chain by reacting with the alkyl macroradical of polypropylene being oxidised. The resulting compound AmOR is fairly reactive with respect to the peroxyl radicals AmO$^{\cdot}$ being regenerated in this reaction. Thus, the cycle includes the following two reactions (mechanism I):[59–62]

$$R^{\cdot} + AmO^{\cdot} \longrightarrow ROAm, \quad (43)$$

$$RO_2^{\cdot} + ROAm \longrightarrow AmO^{\cdot} + ROOH + Y, \quad (44)$$

where Y is a polypropylene macromolecule with a double bond formed by the abstraction of the H atom from the β-C–H bond and by the cleavage of the O–N bond in ROAm. This conclusion was confirmed later in a study of radiation-induced chemical oxidation of octane;[63] in this work, AmOR was identified as a reaction product.

The ether AmOR is thermally unstable. At elevated temperatures it dissociates with cleavage of the R–O bond, which leads to the appearance of an [Am$^{\cdot}$ + R$^{\cdot}$] radical pair in the cage of the polymer or of the hydrocarbon being oxidised; disproportionation of this radical pair gives hydroxylamine and an alkene. The peroxyl radical reacts rapidly with hydroxylamine thus regenerating the nitroxyl radical. This scheme was suggested and justified in a number of papers.[64–68] The cyclic mechanism (II) includes the following stages:

$$R^{\cdot} + AmO^{\cdot} \longrightarrow ROAm, \quad (43)$$

$$ROAm \longrightarrow [R^{\cdot} + AmO^{\cdot}], \quad (45)$$

$$[R^{\cdot} + AmO^{\cdot}] \longrightarrow AmOH + Y, \quad (46)$$

$$AmOH + RO_2^{\cdot} \longrightarrow AmO^{\cdot} + ROOH. \quad (47)$$

The fact that hydroxylamine has been found among the products of the transformations of nitroxyl during the oxidation of hydrocarbons is evidence in support of this mechanism. Both mechanisms described above are realised in parallel and supplement each other. The result of the competition between them depends primarily on the temperature, since the thermal decomposition of the product ROAm requires a fairly high activation energy. The problem of the competition between the mechanisms I and II of cyclic chain termination has been considered by Denisov.[21] In the case of the oxidation of polypropylene at the initiation rate $v_i = 10^{-7}$ mol kg^{-1} s^{-1} and for $[O_2] = [AmO^{\cdot}] = 10^{-3}$ mol kg^{-1}, the ratio of the rates of chain termination via reactions (44) and (46) varies as a function of the temperature in the following way:[62]

T/K	350	365	380	388	400	420
v_I/v_{II}	50.0	9.55	2.14	1.00	0.33	0.029

It is obvious that when the temperature is not very high and the ether AmOR is stable, the mechanism I predominates, that is, the regeneration of AmO$^{\cdot}$ from AmOR is ensured by the reaction of AmOH with the peroxyl radical. At higher temperatures, when AmOR becomes unstable, the mechanism II predominates. It should be taken into account that only some of the radical pairs formed upon decomposition of ROAm disproportionate giving AmOH and an alkene. The remaining radical pairs pass into the bulk, and the radical R$^{\cdot}$ reacts with O_2 to give $RO_2^{\cdot}$ and thus initiate a new oxidation chain. Hence, the regeneration of AmO$^{\cdot}$ from AmOH is inevitably accompanied by the initiation of the process, which certainly decreases the efficiency of the inhibition.

As the oxidation of the polymer proceeds and hydroperoxyl groups which decompose to give H_2O_2 accumulate, the cyclic chain termination mechanisms involving the $HO_2^{\cdot}$ radical [reactions (41) and (42)] become more significant. Below we present the results illustrating the relative efficiency of the chain termination mechanisms involving the R$^{\cdot}$ and $RO_2^{\cdot}$ radicals (mechanisms I and II), on the one hand, and the mechanism involving the $HO_2^{\cdot}$ radicals, on the other hand, obtained for the oxidation of polypropylene.[62] Polypropylene was oxidised at 388 K and $P_{O_2} = 10^5$ Pa in the presence of an initiator (cumyl peroxide) and with an inhibitor (2,2,6,6-tetramethyl-4-stearylpiperidin-*N*-oxyl),[56] the consumption of which was monitored by EPR. The inhibiting activity was characterised by the coefficient

$$f = \frac{v_i}{v_{AmO^{\cdot}}},$$

where v_i and $v_{AmO^{\cdot}}$ are the initiation rate and the rate of consumption of the nitroxyl radical, respectively, and by the parameter F:

$$F = \frac{v_i}{v}\left(1 - \frac{v^2}{v_0^2}\right)[AmO^{\cdot}]^{-1},$$

where v_0 and v are the rates of oxidation of the polymer without an inhibitor and with the inhibitor AmO$^{\cdot}$, respectively. The parameter F characterises the efficiency of AmO$^{\cdot}$ as an inhibitor terminating the chains. In experiments on the oxidation of polypropylene containing no hydroperoxy-groups the following values were found: $f = 4$ and $F = 7$ kg mol^{-1}, whereas for the oxidation of polypropylene that had been preliminarily oxidised and contained 4.12×10^{-2} mol kg^{-1} of hydroperoxy-groups, these parameters were: $f = 40$ and $F = 1060$ kg mol^{-1}.

Thus, there is a clear dissimilarity between the cyclic chain termination mechanism involving only R$^{\cdot}$ and $RO_2^{\cdot}$ radicals and the mechanism involving $HO_2^{\cdot}$ radicals produced from H_2O_2.

Recently, a new cyclic mechanism of chain termination by nitroxyl radicals, including the formation of amino radicals as intermediate species, has been found.[69,70] It was shown that the addition of 4,4′-dioctyldiphenylnitroxyl radical to hexadecane being oxidised ($T = 433$ K) leads to the formation of the corresponding diphenylamine as an intermediate compound during its transformations. The following cyclic mechanism of chain termination was suggested:

$$AmO^{\cdot} + R^{\cdot} \longrightarrow AmOR, \quad (43)$$

$$AmOR \longrightarrow [Am^{\cdot} + RO^{\cdot}] \longrightarrow AmH + Y, \quad (48)$$

$$RO_2^{\cdot} + AmH \longrightarrow ROOH + Am^{\cdot}, \quad (49)$$

$$RO_2^{\cdot} + Am^{\cdot} \longrightarrow RO^{\cdot} + AmO^{\cdot}. \quad (50)$$

A specific feature of this mechanism is the reaction (48), in which AmOR cleaves at the N–O bond rather than at the C–O bond as observed for the inhibition by alicyclic nitroxyl radicals. An alternative mechanism of the regeneration of the amino radical from the nitroxyl radical is also possible:

$$AmO^{\cdot} + RO_2^{\cdot} \longrightarrow [Am^{\cdot} + O_2 + RO^{\cdot}] \longrightarrow AmH + R'{=}O + O_2. \quad (51)$$

In this case, the cyclic chain termination mechanism can be realised only with participation of peroxyl radicals.

$$RO_2^{\cdot} + AmH \longrightarrow ROOH + Am^{\cdot}, \quad (49)$$

$$RO_2^{\cdot} + Am^{\cdot} \longrightarrow RO^{\cdot} + AmO^{\cdot}, \quad (50)$$

$$RO_2^{\cdot} + AmO^{\cdot} \longrightarrow AmH + R'{=}O + O_2. \quad (51)$$

Thus, nitroxyl radicals can participate in various cyclic mechanisms of chain termination. In the oxidation of alcohols, peroxides, and amines, when peroxyl radicals possess both oxidising and reducing ability, the cyclic mechanism of chain termination includes reactions of peroxyl radicals with $AmO^{\cdot}$ and AmOH. The cyclic mechanism occurring under the conditions of polymer oxidation includes the $R^{\cdot} + AmO^{\cdot}$ and $RO_2^{\cdot} + AmOR$ reactions. At elevated temperatures AmOR becomes thermally unstable, and the mechanism that includes homolysis of AmOR at the C–O or N–O bonds with the generation of $AmO^{\cdot}$ (AmOH) or $Am^{\cdot}$ (AmH) radicals is realised.

VI. Cyclic chain termination mechanisms involving acid catalysis

We have by no means described all the cyclic mechanisms of chain termination involving nitroxyl radicals. A new interesting branch of modern antioxidant chemistry deals with cyclic mechanisms involving acid catalysis. The first inhibiting system of this type was discovered in 1988.[18] It consisted of an alcohol (primary or secondary), a stable nitroxyl radical (2,2,6,6-tetramethylpiperidin-*N*-oxyl), and an organic (citric) acid. This three-component system effectively retarded the initiated oxidation of ethylbenzene. Each component taken by itself and binary combinations of these components did not retard oxidation of ethylbenzene or retarded it only slightly. Intense chain termination was ensured only by the presence of all three components of this system.

The important role of the acid was established in experiments on the oxidation of ethylbenzene containing an alcohol and nitroxyl radicals, when air or air mixed with gaseous HCl was passed through the reactor. The concentration of the peroxyl radicals in the hydrocarbon being oxidised was determined by the chemiluminescence method. The intensity of chemiluminescence was evaluated in terms of $I \sim [RO_2^{\cdot}]^2 \sim \upsilon_i^2/2k_t$, where k_t is the rate constant for the disproportionation of $RO_2^{\cdot}$. When a mixture of air with HCl was used, the intensity of the chemiluminescence decreased by approximately two orders of magnitude.[18]

The H_2O_2 + $AmO^{\cdot}$ (2,2,6,6-tetramethylpiperidin-*N*-oxyl) + HA (citric acid) system also exhibits an extremely high inhibiting effect. The data presented below demonstrate how the individual components of this system and the whole system influence the rate of the chain oxidation of ethylbenzene (343 K, $P_{O_2} = 10^5$ Pa, $\upsilon_i = 5.21 \times 10^{-7}$ mol dm^{-3} s^{-1}):[71]

$[AmO^{\cdot}]/10^{-4}$ mol dm^{-3}	$[HA]/10^{-4}$ mol dm^{-3}	$[H_2O_2]/10^{-3}$ mol dm^{-3}	$\upsilon/10^{-6}$ mol dm^{-3} s^{-1}
0	0	0	4.92
5	0	0	3.78
5	5	0	3.00
5	5	2.5	0.22

It can be seen that complete termination of the chain process is ensured only by the three-component system.

The very effective retardation of the oxidation of the hydrocarbon by this system can be explained in terms of the following mechanism:[71,72]

$$AmO^{\cdot} + HA \rightleftharpoons [AmOH^{+\cdot}, A^-], \quad (52)$$

$$RO_2^{\cdot} + [AmOH^{+\cdot}, A^-] \longrightarrow ROOH + [AmO^+, A^-], \quad (53)$$

$$[AmO^+, A^-] + H_2O_2 \longrightarrow AmOH + HA + O_2, \quad (54)$$

$$RO_2^{\cdot} + AmOH \longrightarrow ROOH + AmO^{\cdot}. \quad (47)$$

According to this mechanism, H_2O_2 is consumed during oxidation of hydrocarbons at a rate of $\frac{1}{2}\upsilon_i$, whereas the rate at which nitroxyl radicals are consumed via the reaction (46) is much lower. Only a small portion of the $R^{\cdot}$ radicals react with $AmO^{\cdot}$, since the latter react very rapidly with oxygen. The kinetic characteristics of the inhibited oxidation are fully consistent with the suggested scheme for the cyclic chain termination. When the concentration of H_2O_2 is relatively low, the chain termination rate is limited by the stage (54), and then the function F assumes the following form:[71]

$$F = 2\frac{k_{36} + k_{54}K_{52}[AmO^{\cdot}][HA]}{(2k_t\upsilon_i)^{0.5}}[H_2O_2].$$

If the concentration of H_2O_2 is large, the stage (54) occurs rapidly and the reaction (53) becomes the rate-limiting stage of the cyclic chain termination. Under these conditions

$$F = 2\frac{k_{53}K_{52}[AmO^{\cdot}][HA] + k_{36}[H_2O_2]}{(2k_6\upsilon_i)^{0.5}}.$$

The mechanism of chain termination consisting of the reactions (47), (52), (53), and (54) is notable because the acid protonates nitroxyl and thus converts it into a donor of hydrogen atom for the peroxyl radical, while hydrogen peroxide reduces the AmO^+ cation to hydroxylamine, which reacts rapidly with $RO_2^{\cdot}$. Thus, the acid and hydrogen peroxide transform $AmO^{\cdot}$, which is unreactive with respect to $RO_2^{\cdot}$, into $AmOH^+$ and AmOH, and the latter inhibit effectively the oxidation of hydrocarbons.

Recently an analogous mechanism for cyclic chain termination has been proposed for quinones.[73] Quinones, which can act as acceptors of alkyl radicals, do not decelerate the oxidation of hydrocarbons at concentrations of up to 5×10^3 mol dm^{-3}, because the $R^{\cdot}$ radicals react very rapidly with oxygen. However, the ternary quinonemonoanilide (Q) + H_2O_2 + acid (HA) system effectively retards the initiated oxidation of methyl oleate and ethylbenzene.[73] This is indicated by the following results obtained for the oxidation of ethylbenzene (343 K, $P_{O_2} = 10^5$ Pa, $\upsilon_i = 5.21 \times 10^{-7}$ mol dm^{-3} s^{-1}).

$[Q]/10^{-4}$ mol dm^{-3}	$[H_2O_2]/10^{-3}$ mol dm^{-3}	$[HA]/10^4$ mol dm^{-3}	$\upsilon/10^{-7}$ mol dm^{-3} s^{-1}
0	0	0	4.92
5.0	0.0	0	3.01
0.0	1.25	0	3.27
0.0	0.0	5.0	3.93
5.0	1.25	5.0	2.39
5.0	12.5	5.0	0.69

The following mechanism, analogous to the mechanism involving nitroxyl radicals, has been suggested for the retarding influence of this system:

$$Q + HA \rightleftharpoons [QH^+, A^-], \quad (55)$$

$$RO_2^{\cdot} + [QH^+, A^-] \longrightarrow ROOH + [Q^{+\cdot}, A^-], \quad (56)$$

$$[Q^{+\cdot}, A^-] + H_2O_2 \longrightarrow QH^{\cdot} + O_2 + HA, \quad (57)$$

$$RO_2^{\cdot} + QH^{\cdot} \longrightarrow ROOH + Q, \quad (58)$$

$$[Q^{+\cdot}, A^-] + RH \longrightarrow R^{\cdot} + HA + Q. \quad (59)$$

In conformity with this mechanism, the function F depends on the concentrations of the components of the inhibiting mixture in the following way:

$$F = \frac{2K_{55}k_{56}k_{57}[Q][H_2O_2][HA]}{(k_{57}[H_2O_2] + k_{59}[RH])(2k_6\upsilon_i)^{0.5}}.$$

Experimental data on the kinetics of oxidation of methyl oleate and ethylbenzene are in good agreement with the scheme consisting of the reactions (55)–(59).

The cyclic mechanism of chain termination with quinone imines involving acid catalysis is very important for an understanding of the retarding influence of aromatic amines on the oxidation of hydrocarbons and of other organic compounds via the reaction (28). Hydrogen peroxide arises during the oxidation of alcohols due to the decomposition of $RO_2^{\cdot}$ to yield $HO_2^{\cdot}$ and ketone and due to the decomposition of >C(OH)OOH giving ketone and H_2O_2. In addition, H_2O_2 is formed in the hydrolysis of alkyl hydroperoxide through the action of water or acids, which also arise in the system during oxidation of hydrocarbons. Thus, two of the three components needed for the realisation of the cyclic chain termination mechanism involving acid catalysis result from the oxidation of the hydrocarbon, while the third component — quinone imine — results from the oxidation of the starting inhibitor (amine). It is possibly owing to this mechanism that aromatic amines exhibit high inhibiting capacity during oxidation at elevated temperatures (>400 K).

VII. Ions and complexes of variable-valence metals as catalysts for chain termination in the oxidation of alcohols, amines, and alkenes

Compounds of variable-valence metals (Mn, Fe, Co, Ce) are well known as catalysts for oxidation of hydrocarbons and aldehydes. They accelerate oxidation by destroying hydroperoxides and initiating the formation of free radicals.[9] Salts and complexes containing transition metals in a lower valence state react rapidly with peroxyl radicals and so when these compounds are added to a hydrocarbon prior to its oxidation an induction period arises.[9] The chain termination occurs stoichiometrically ($f \simeq 1$) and stops when the metal passes to a higher valence state due to oxidation. On the addition of an initiator or hydroperoxide the induction period disappears.

Another situation is observed when salts or complexes of metals with variable valence states are added to an alcohol (primary or secondary) subjected to oxidation: in this case, a prolonged deceleration of the initiated oxidation occurs, owing to repeated chain termination. This was discovered for the first time in relation to the oxidation of cyclohexanol in the presence of a copper salt.[15] Copper and manganese ions also exert a decelerating influence on the initiated oxidation of cyclohexadiene,[32] aliphatic amines,[39] and 1,2-disubstituted ethenes.[33] This is accounted for by the dual redox nature of the peroxyl radicals $HO_2^{\cdot}$, $>C(OH)O_2^{\cdot}$, and $>C(NHR)O_2^{\cdot}$, and by the ability of ions (complexes) of heavy metals to accept an electron when they are in a higher valence state, and to release an electron when they are in a lower valence state, for example:

$$>C(OH)O_2^{\cdot} + Cu^{2+} \longrightarrow >C=O + O_2 + H^+ + Cu^{1+}, \quad (60)$$

$$>C(OH)O_2^{\cdot} + Cu^{1+} \longrightarrow >C(OH)OO^- + Cu^{2+}. \quad (61)$$

Table 6 presents the results of a kinetic study of the reactions (60) and (61). Copper and manganese compounds exhibit the highest inhibiting activity. The chain termination on variable-valence metals in the systems in which hydroperoxyl and hydroxyperoxyl radicals act as the chain-propagating species is characterised by very large coefficients: $f \simeq 10^4 - 10^6$.

Both reactions (60) and (61) may include several stages. If an aqueous solution of a copper salt, for example sulfate, is used, the following mechanism involving the incorporation of $RO_2^{\cdot}$ into the inner coordination sphere of the metal ion is possible for the reaction (60):

$$>C(OH)O_2^{\cdot} + Cu_{aq}^{2+} \rightleftharpoons >C(O_2^{\cdot})OH \cdot Cu_{aq}^{2+}, \quad (62)$$

$$>C(O_2^{\cdot})OH \cdot Cu_{aq}^{2+} + H_2O \rightleftharpoons >C(O_2^{\cdot})O^- \cdot Cu_{aq}^{2+} + H_3O^+, \quad (63)$$

$$>C(O_2^{\cdot})O^- \cdot Cu_{aq}^{2+} \longrightarrow >C=O \cdot Cu_{aq}^{1+} + O_2, \quad (64)$$

$$>C=O \cdot Cu_{aq}^{1+} \rightleftharpoons >C=O + Cu_{aq}^{1+}. \quad (65)$$

In the case of metal complexes with strongly bound ligands, the outer-sphere transfer of an electron from the radical to the ion and back is more probable.

When variable-valence metals are used as catalysts in the oxidation of hydrocarbons, the chain termination via reactions (60) and (61) manifests itself late in the process. This case has been specially studied in relation to the oxidation of paraffins to fatty acids in the presence of a K–Mn catalyst,[80] which ensures a high oxidation rate and a high selectivity of formation of the target product. As the reaction proceeds, alcohols are accumulated in the reaction mixture, their oxidation being accompanied by the formation of hydroxyperoxyl radicals. The more extensively has the oxidation proceeded, the higher is the concentration of alcohols in the oxidised paraffin, and, hence, the higher is the kinetically equilibrium concentration of these radicals. The latter enter into reactions resembling the reactions (60) and (61) with Mn^{2+} and Mn^{3+} ions and thus cause chain termination. When

Table 6. Rate constants for the reactions of metal salts and complexes with peroxyl radicals in systems with a cyclic mechanism of chain termination.

Metal complex[a]	Substrate	T/K	k/dm^3 mol^{-1} s^{-1}	Ref.
$Mn(CO_2CH_3)_2$	$(C_4H_9)_2NH$	348	2.5×10^6	39
$Mn(CO_2CH_3)_2$	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	313	1.1×10^6	36
$Mn(CO_2CH_3)_2$	cyclo-$C_6H_{11}NH_2$	348	7.3×10^7	40,74
$Mn(CO_2CH_3)_2$	$C_6H_5CH_2NH_2$	338	2.8×10^8	40
$Mn(CO_2CH_3)_2$	$CH_2=C(CH_3)C(O)OC_2H_4N(CH_3)_2$	323	1.2×10^7	35
$Mn(CO_2CH_3)_2$	$C_3H_7OCOC_2H_4N(CH_3)_2$	323	1.5×10^7	7
$Mn(CO_2CH_3)_3$	$CH_2=CHCOOC_2H_4N(CH_3)_2$	323	1.2×10^7	35
$MnSt_2$	cyclo-C_6H_8	348	1.9×10^6	32
$MnSt_2$	cyclo-$C_6H_{11}OH$	348	6.8×10^6	75
$MnSt_2$	$(C_4H_9)_2NH$	348	3.5×10^6	40,74
$MnSt_2$	cyclo-$C_6H_{11}NH_2$	348	1.6×10^8	40,74
$MnSt_2$	$CH_3CON(C_2H_5)_2$	348	7.8×10^5	39
$Mn(Acac)_2$	cyclo-$C_6H_{11}NH_2$	363	9.8×10^7	76
$MnEN(Sal)_2$	cyclo-$C_6H_{11}NH_2$	348	3.1×10^8	76
$FeSt_3$	cyclo-$C_6H_{11}OH$	348	1.3×10^4	75
$FeSt_3$	cyclo-$C_6H_{11}NH_2$	348	1.2×10^6	39,40
$Fe(Acac)_3$	cyclo-$C_6H_{11}NH_2$	348	1.0×10^5	39,40
$Fe(DMG)_2Py_2$	cyclo-C_6H_8	348	2.3×10^3	77
$Fe(DMG)_2Py_2$	$(CH_3)_2CHOH$	344	1.0×10^3	78
$CoCl_2$	cyclo-$C_6H_{11}OH$	348	6.1×10^4	39

Table 6 (continued)

Metal complex	Substrate	T/K	k/dm^3 mol^{-1} s^{-1}	Ref.
$Co(CO_2CH_3)_2$	cyclo-$C_6H_{11}NH_2$	348	1.2×10^5	39,40
$CoSt_2$	cyclo-$C_6H_{11}OH$	348	2.8×10^5	75
$CoSt_2$	cyclo-$C_6H_{11}NH_2$	348	3.2×10^4	40
Co(III)$(Acac)_3$	$(CH_3)_2CHOH$	344	2.9×10^2	78
$Co(Acac)_2$	cyclo-$C_6H_{11}OH$	348	6.4×10^6	40
$Co(Acac)_2$	cyclo-$C_6H_{11}NH_2$	348	6.4×10^4	40
$Co(Acac)_3$	cyclo-$C_6H_{11}NH_2$	348	6.3×10^4	40
$Co(C_6H_{11}CO_2)_2$	cyclo-$C_6H_{11}OH$)	348	8.7×10^4	39
Co(II)$(DMG)_2NH_3Cl$	cyclo-C_6H_8	348	8.4×10^2	77
Co(II)$(DMG)_2NH_3Cl$	$(CH_3)_2CHOH$	344	5.0×10^3	78
Co(II)$(DMG)_2NH_3I$	cyclo-C_6H_8	348	2.3×10^4	77
Co(II)$(DMG)_2NH_3I$	$(CH_3)_2CHOH$	344	3.1×10^2	78
Co(II)$(DMG)_2PyI$	$(CH_3)_2CHOH$	344	7.0×10^4	78
Co(II)$(DMG)_2Py_2$	$(CH_3)_2CHOH$	344	1.2×10^4	78
Co(EN)$(Slm)_2$	cyclo-$C_6H_{11}OH$	348	3.3×10^5	76
Co(II)Prf	cyclo-$C_6H_{11}OH$	348	3.6×10^4	76
$Ni(Sal)_2$	$C_8H_{17}OH$	363	1.6×10^4	76
$Ni(Sal)_2$	cyclo-$C_6H_{11}NH_2$	353	2.8×10^4	76
$NiEN(Slm)_2$	$C_8H_{17}OH$	363	7.9×10^3	76
$NiEN(Slm)_2$	cyclo-$C_6H_{11}NH_2$	353	1.5×10^4	76
$NiEN(Slm)_2$	$C_8H_{17}OH$	363	3.5×10^4	76
$NiEN(Slm)_2$	cyclo-$C_6H_{11}NH_2$	353	6.6×10^4	76
NiENSlmTln	cyclo-$C_6H_{11}NH_2$	353	1.7×10^5	76
$CuSO_4$	cyclo-$C_6H_{11}OH$	348	8.8×10^6	15
$CuCl_2$	*trans*-$C_6H_5CH=CHCOOC_2H_5$	323	5.9×10^5	33
$CuCl_2$	*trans*-$C_6H_5CH=CH=CHCOOCH_3$	323	5.6×10^5	33
$CuCl_2$	*trans*-$C_6H_5CH=CHC_6H_5$	323	2.6×10^5	33
$Cu(CO_2CH_3)_2$	$C_6H_5CH_2NH_2$	338	1.5×10^8	39
$Cu(CO_2CH_3)_2$	$C_3H_7COOC_2H_4N(CH_3)_2$	323	1.3×10^7	79
$Cu(CO_2CH_3)_2$	$C_4H_9N(CH_3)_2$	323	1.0×10^7	79
$Cu(CO_2CH_3)_2$	$C_6H_5CH=CHCOOC_2H_5$	323	2.2×10^5	33
$Cu(CO_2CH_3)_2$	$C_6H_5CH=CHCOOCH_3$	323	4.5×10^5	33
$Cu(CO_2CH_3)_2$	$C_6H_5CH=CHC_6H_5$	323	5.3×10^5	33
$CuSt_2$	cyclo-C_6H_8	348	1.9×10^6	77
$CuSt_2$	cyclo-$C_6H_{11}OH$	348	2.9×10^6	75
$CuSt_2$	$(C_4H_9)_2NH$	348	4.1×10^6	40
$CuSt_2$	cyclo-$C_6H_{11}NH_2$	348	9.5×10^7	39
$CuSt_2$	cyclo-$C_6H_{11}NH_2$	348	1.0×10^7	76
$CuSt_2$	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	313	2.7×10^5	36
$Cu(Acac)_2$	$C_6H_5CH_2NH_2$	338	1.3×10^6	39
$Cu(Acac)_2$	cyclo-$C_6H_{11}NH_2$	348	7.2×10^5	39
$Cu(DMG)_2$	cyclo-C_6H_8	348	1.3×10^5	77
$Cu(DMG)_2$	cyclo-C_6H_8	348	1.5×10^5	77
$Cu(DMG)_2$	$(CH_3)_2CHOH$	344	5.0×10^5	78
$Cu(Sal)_2$	cyclo-C_6H_8	348	1.7×10^5	77
$Cu(Sal)_2$	$(CH_3)_2CHOH$	344	1.2×10^5	78
$Cu(DPG)_2$	$(CH_3)_2CHOH$	344	5.9×10^4	78
$Cu(DMG)_2$	$(CH_3)_2CHOH$	344	3.7×10^4	78
Cu(4-NO_2-Slm)$_2$	cyclo-$C_6H_{11}NH_2$	363	2.8×10^8	76
$Cu(Slm)_2$	cyclo-$C_6H_{11}NH_2$	363	1.4×10^8	76
Cu(4-HO-Slm)$_2$	cyclo-$C_6H_{11}NH_2$	363	9.2×10^7	76
Cu(4-CH_3O-Slm)$_2$	cyclo-$C_6H_{11}NH_2$	363	1.1×10^8	76
$CuEN(Slm)_2$	cyclo-$C_6H_{11}NH_2$	348	7.5×10^7	76
$CuEN(Slm)_2$	cyclo-$C_6H_{11}NH_2$	363	3.6×10^7	76
$Cu(EN)_2(Slm)_2$	cyclo-$C_6H_{11}NH_2$	348	4.7×10^6	76
$Cu(EN)_3(Slm)_2$	cyclo-$C_6H_{11}NH_2$	348	7.9×10^5	76
$CuC_6H_4(Slm)_2$	cyclo-$C_6H_{11}NH_2$	348	7.9×10^6	76
CuC_6H_4-$C_6H_4(Slm)_2$	cyclo-$C_6H_{11}NH_2$	348	2.6×10^6	76
Cu(II)Prf	cyclo-$C_6H_{11}NH_2$	348	7.3×10^5	39
CuPrf	$C_6H_5CH_2NH_2$	338	1.5×10^6	39
$CeSt_3$	cyclo-$C_6H_{11}OH$	348	1.1×10^5	75
$CeSt_3$	cyclo-$C_6H_{11}NH_2$	348	8.6×10^5	39

[a] Notation: AcacH — acetylacetone, StH — stearic acid, DMGH — dimethylglyoxime, SlmH — salicylaldoxime, 4-X-SlmH — 4-X-salicylanilide, ENSlm — *o*-salicylalethenediimine, ENH_2 — ethylene diamine, TlnH — toluidine, SalH — salicylic acid, Prf — porphyrin, DPGH —diphenylglyoxime.

the rate of chain termination with the hydroxyperoxyl radicals becomes equal to the rate of generation of the chain-propagating radicals, the oxidation virtually ceases.

The oxidation of alcohols is also retarded by bases,[81-83] which is apparently due to the decomposition of the hydroxyperoxyl radical giving ketone and superoxide ion $O_2^{-\cdot}$:

$$>C(OH)O_2^{\cdot} + B^- \longrightarrow >C=O + O_2^{-\cdot} + BH. \quad (66)$$

The superoxide ion cannot continue the chain and is destroyed via disproportionation with $RO_2^{\cdot}$.

VIII. Conclusion

Studies of the mechanisms of cyclic chain termination in oxidation processes carried out for three decades have demonstrated on the one hand that they are extremely diverse and, on the other hand, that they are highly structurally selective. The 19 currently known mechanisms, which are presented in Table 7, can be divided into three groups.

The first group includes mechanisms with the participation of such inhibitors as aromatic amines, nitroxyl radicals, quinones, and compounds of variable-valence metals (Mn, Fe, Co, Cu, Ce). These inhibitors or, more precisely, the inhibiting pairs (AmH and Am$^{\cdot}$, Q and QH$^{\cdot}$, AmO$^{\cdot}$ and AmOH, and M^{n+} and M^{n+1}) retard oxidation only provided that the chain is continued by the $HO_2^{\cdot}$, $>C(OH)O_2^{\cdot}$, or $>CH(NHR)O_2^{\cdot}$ radicals. The latter disproportionate very rapidly with hydrogen atom acceptors such as Am$^{\cdot}$, AmO$^{\cdot}$, or Q. This leads to the recovery of the reduced form of the inhibitor, which again reacts rapidly with a peroxyl radical; this ensures the effective chain termination. The number of cycles is determined by the ratio of the rate of the reaction of the peroxyl radical, in which the inhibitor is recovered, to the rate of its irreversible consumption. The direction of the transformation of $RO_2^{\cdot}$ is largely determined by the nature of the reaction centre of disproportionation. Analysis has shown that the triplet repulsion in the transition state of an elementary step of the regeneration of the inhibitor by the peroxyl radical needs to be very weak. It is also essential that the atoms between which the electron transfer occurs (for example, N and O) should differ in electron affinity. Thus, the structure of the peroxyl radical is the crucial factor for the mechanisms of the first group.

The second group of mechanisms, by which the inhibitors (nitroxyl radicals) are recovered, involves successive participation of the R$^{\cdot}$ and $RO_2^{\cdot}$ radicals in the reactions with AmO$^{\cdot}$ and AmOH. The possibility of the realisation of these mechanisms depends on the conditions of the oxidation, which should ensure fairly rapid interaction of the alkyl radicals with AmO$^{\cdot}$, and this requires that the reaction of R$^{\cdot}$ with oxygen does not occur very rapidly. This requirement is fulfilled in the oxidation of solid

Table 7. Cyclic mechanisms of chain termination in the liquid-phase oxidation of organic compounds.

Inhibiting system	Radical	Mechanism	Ref.
AmH, Am$^{\cdot}$	$HO_2^{\cdot}$	$HO_2^{\cdot} + AmH \longrightarrow H_2O_2 + Am^{\cdot}$, $Am^{\cdot} + HO_2^{\cdot} \longrightarrow AmH + O_2$	29, 32, 33
AmH, Am$^{\cdot}$	$>C(OH)O_2^{\cdot}$	$>C(OH)OO^{\cdot} + AmH \longrightarrow >C(OH)OOH + Am^{\cdot}$ $>C(OH)OO^{\cdot} + Am^{\cdot} \longrightarrow >C=O + O_2 + AmH$	14, 18, 19, 28, 29, 30, 34
AmH, Am$^{\cdot}$	$>C(NHR)O_2^{\cdot}$	$>C(NHR)OO^{\cdot} + AmH \longrightarrow >C(NHR)OOH + Am^{\cdot}$ $>C(NHR)OO^{\cdot} + Am^{\cdot} \longrightarrow >C=NR + O_2 + AmH$	35-41
AmO$^{\cdot}$, AmOH	$HO_2^{\cdot}$	$AmO^{\cdot} + HO_2^{\cdot} \longrightarrow AmOH + O_2$ $AmOH + HO_2^{\cdot} \longrightarrow AmO^{\cdot} + H_2O_2$	32, 33, 56
AmO$^{\cdot}$, AmOH	$>C(OH)O_2^{\cdot}$	$>C(OH)OO^{\cdot} + AmO^{\cdot} \longrightarrow >C=O + O_2 + AmOH$ $>C(OH)OO^{\cdot} + AmOH \longrightarrow >C(OH)OOH + AmO^{\cdot}$	30
AmO$^{\cdot}$, AmOH	$>C(NHR)O_2^{\cdot}$	$>C(NHR)OO^{\cdot} + AmO^{\cdot} \longrightarrow >C=NR + AmOH$ $>C(NHR)OO^{\cdot} + AmOH \longrightarrow >C(NHR)OOH + AmO^{\cdot}$	35, 36, 39, 40
Q, HQ$^{\cdot}$	$HO_2^{\cdot}$	$Q + HO_2^{\cdot} \longrightarrow HQ^{\cdot} + O_2$ $HQ^{\cdot} + HO_2^{\cdot} \longrightarrow Q + H_2O_2$	30, 32, 33, 42, 58
Q, HQ$^{\cdot}$	$>C(OH)O_2^{\cdot}$	$>C(OH)OO^{\cdot} + Q \longrightarrow >C=O + O_2 + HQ^{\cdot}$ $>C(OH)OO^{\cdot} + HQ \longrightarrow >C(OH)OOH + Q$	16, 52-54
Q, HQ$^{\cdot}$	$>C(NHR)O_2^{\cdot}$	$>CC(NHR)OO^{\cdot} + Q \longrightarrow >C=NR + O_2 + HQ^{\cdot}$ $>CC(NHR)OO^{\cdot} + HQ^{\cdot} \longrightarrow >C(NHR)OOH + Q$	36, 38-41
M^{n+}, M^{n+1}	$HO_2^{\cdot}$	$M^{n+} + HO_2^{\cdot} \longrightarrow M^{n+1} + HO_2^-$ $M^{n+1} + HO_2^{\cdot} \longrightarrow H^+ + O_2 + M^{n+}$	32, 33, 77
M^{n+}, M^{n+1}	$>C(OH)O_2^{\cdot}$	$>C(OH)OO^{\cdot} + M^{n+} \longrightarrow >C(OH)O_2^- + M^{n+1}$ $>C(OH)OO^{\cdot} + M^{n+1} \longrightarrow >C=O + O_2 + H^+ + M^{n+}$	15, 39, 40, 75-79
M^{n+}, M^{n+1}	$>C(NHR)O_2^{\cdot}$	$>C(NHR)OO^{\cdot} + M^{n+} \longrightarrow >C(NHR)O_2^- + M^{n+1}$ $>C(NHR)OO^{\cdot} + HQ^{\cdot} \longrightarrow >C=NR + O_2 + H^+ + M^{n+}$	35, 39, 40, 74, 77, 79
AmO$^{\cdot}$, AmOR	R$^{\cdot}$, $RO_2^{\cdot}$	$AmO^{\cdot} + R^{\cdot} \longrightarrow AmOR$ $AmOR + RO_2^{\cdot} \longrightarrow ROOH + Alkene + AmO^{\cdot}$	

Table 7. (continued)

Inhibiting system	Radical	Mechanism	Ref.
$AmO^{\cdot}$, AmOR	$R^{\cdot}$, $RO_2^{\cdot}$	$AmO^{\cdot} + R^{\cdot} \longrightarrow AmOR$ $AmOR \longrightarrow [AmO^{\cdot} + R^{\cdot}] \longrightarrow AmOH + Alkene$ $AmOH + RO_2^{\cdot} \longrightarrow ROOH + AmO^{\cdot}$	64–68
$AmO^{\cdot}$, AmOR	$R^{\cdot}$, $RO_2^{\cdot}$	$AmO^{\cdot} + R^{\cdot} \longrightarrow AmOR$ $AmOR \longrightarrow [Am^{\cdot} + RO^{\cdot}] \longrightarrow AmH + Alkene$ $AmH + RO_2^{\cdot} \longrightarrow ROOH + Am^{\cdot}$ $Am^{\cdot} + RO_2^{\cdot} \longrightarrow AmO^{\cdot} + RO^{\cdot}$	69, 70
I_2	$R^{\cdot}$, $RO_2^{\cdot}$	$R^{\cdot} + I_2 \longrightarrow RI + I^{\cdot}$ $RI + RO_2^{\cdot} \longrightarrow R^{\cdot} + ROOI$ $2\,ROOI \longrightarrow I_2 + O_2 + ROOR$	84
$AmO^{\cdot}$	$RO_2^{\cdot}$	$AmO^{\cdot} + HA \rightleftharpoons [AmOH^{+\cdot}, A^-]$, $RO_2^{\cdot} + [AmOH^{+\cdot}, A^-] \longrightarrow ROOH + [AmO^+, A^-]$, $[AmO^+, A^-] + H_2O_2 \longrightarrow AmOH + HA + O_2$, $RO_2^{\cdot} + AmOH \longrightarrow ROOH + AmO^{\cdot}$.	30, 71, 72
Q, H_2O_2, HA	$RO_2^{\cdot}$	$Q + HA \rightleftharpoons (QH^+, A^-)$, $(QH^+, A^-) + RO_2^{\cdot} \longrightarrow (Q^{+\cdot}, A^-) + ROOH$, $(Q^{+\cdot}, A^-) + H_2O_2 \longrightarrow HQ^{\cdot} + HA + O_2$, $RO_2^{\cdot} + HQ^{\cdot} \longrightarrow ROOH + Q$	73
B	$>C(OH)O_2^{\cdot}$	$>C(OH)O_2^{\cdot} + B^- \longrightarrow >C{=}O + O_2^{-\cdot} + BH$	81–83

polymers, since in this case, the solubility of O_2 and the rate of its reaction with $R^{\cdot}$ are lower than those in a liquid under similar conditions. Mechanism of this sort can also occur in the liquid phase, when the concentration of the dissolved oxygen is relatively low ($[O_2] \ll [ArO^{\cdot}]$). For the dissociation of the intermediate product at the O–C or N–O bond, a sufficiently high temperature is needed.

The third group of mechanisms includes acid catalysis as a necessary stage of the cycle. An acid protonates an inhibitor in the oxidised form ($AmO^{\cdot}$, Q) and thus transforms the corresponding species into a potential hydrogen donor. The cycle begins with attack by $RO_2^{\cdot}$ on the protonated inhibitor. Of course, the reduction of the cationic form of the inhibitor with hydrogen peroxide also plays an important role. Mechanisms of this sort should be characteristic of the oxidation in the systems in which hydrogen peroxide and an acid are generated, and this refers to many organic compounds.

Evidently, catalysis with bases is characteristic of systems in which the $HO_2^{\cdot}$ or $>C(OH)O_2^{\cdot}$ radicals act as the chain-propagating species in the oxidation. Repeated chain termination has also been observed in the presence of sulfur-containing inhibitors,[23] but the exact mechanism of these processes is still unknown.

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