# Reactivity of C—H and O—H bonds in reactions with aminyl and nitroxyl radicals and cyclic mechanisms of chain termination in oxidizable alcohols and olefins

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The parabolic model of transition state has been used to analyze the problem of why aromatic amines and nitroxyl radicals cause the cyclic mechanism of chain termination in oxidizable alcohols and olefins (where $HO_2^{\cdot}$ and $>C(OH)O_2^{\cdot}$ radicals participate in chain propagation) and not in oxidizable hydrocarbons. The differences are caused by the existence of a weak triplet repulsion in transition states with the N...H...O and O...H...O reaction centers, while the triplet repulsion is strong in transition states with reaction centers of the C...H...O and C...H...N type in oxidizable hydrocarbons.

**Key words:** free radicals, oxidation of organic compounds, parabolic model, transition state, triplet repulsion, cyclic mechanism of chain termination.

Aromatic amines retard oxidation of hydrocarbons, they terminate chains by reactions with peroxyl radicals and are consumed with the stoichiometric coefficient $f$ = 2—3.[1] A quite different situation is observed for oxidation of alcohols, in which amines cause the cyclic mechanism of chain termination[2] in such a way that one molecule of an inhibitor results in the termination of a great number of chains ($f$ = 10—200). The same phenomenon is observed for the oxidation of cyclohexadiene[3] and 1,2-disubstituted ethylenes.[4] The cyclic mechanism of chain termination is caused by the participation of hydroperoxyl (alcohols, olefins) and hydroxyperoxyl (alcohols) radicals in the reactions[2]:

$$AmH + HO_2^{\cdot}\ (>C(OH)OO^{\cdot}) \rightarrow Am^{\cdot} + H_2O_2\ (>C(OH)OOH), \quad (1)$$

$$Am^{\cdot} + HO_2^{\cdot}\ (>C(OH)OO^{\cdot}) \rightarrow AmH + O_2\ (O_2 + >C{=}O). \quad (2)$$

It is the fast reduction of the aminyl radical ($Am^{\cdot}$) to the amine (AmH) by the peroxyl radical that provides the multiple (cyclic) mechanism of chain termination in the system, in which $HO_2^{\cdot}$ and $>C(OH)OO^{\cdot}$ radicals are generated. A similar cycle is realized in oxidizable alcohols, for example, in 2-propanol, involving nitroxyl radicals $AmO^{\cdot}$:[5]

$$AmO^{\cdot} + Me_2C(OH)OO^{\cdot} \rightarrow AmOH + Me_2C{=}O + O_2, \quad (3)$$

$$Me_2C(OH)OO^{\cdot} + AmOH \rightarrow AmO^{\cdot} + Me_2C(OH)OOH. \quad (4)$$

In principle, the reduction of $Am^{\cdot}$ to AmH, like that of $AmO^{\cdot}$ to AmOH, can also occur *via* disproportionation with the alkylperoxyl radical:

$$R^1CH_2CH(OO^{\cdot})R^2 + Am^{\cdot} \rightarrow AmH + R^1CH{=}CHR^2 + O_2, \quad (5)$$

$$R^1CH_2CH(OO^{\cdot})R^2 + AmO^{\cdot} \rightarrow AmOH + R^1CH{=}CHR^2 + O_2. \quad (6)$$

However, no cyclic mechanisms are observed in oxidizable hydrocarbons.[1,6] In the present work, this problem is analyzed from the viewpoint of the parabolic model of transition state of radical detachment reactions.[7]

## Enthalpy of disproportionation of aminyl and nitroxyl radicals with peroxyl radicals

The differences between reactions (2) and (3), on the one hand, and reactions (5) and (6), on the other hand, probably are associated with their different exothermicities. Therefore, it is reasonable to compare the enthalpies of these reactions $\Delta H = \Delta H^{\circ}_{298}$. For this comparison, the following peroxyl radicals were chosen: $HO_2^{\cdot}$, *cyclo*-$C_6H_{11}O_2^{\cdot}$, $C_6H_5Me_2CO_2^{\cdot}$, $Me_2C(OH)O_2^{\cdot}$, and *cyclo*-$C_6H_{10}(OH)O_2^{\cdot}$, whose reactions with aromatic amines were studied.[1—3,6] The enthalpy of the reaction of the type

$$In^{\cdot} + RO_2^{\cdot} \rightarrow InH + O_2 + R'H, \quad (7)$$

where R'H is the corresponding olefin (reactions (5) and (6)) or ketone (reactions (2) and (3)), respectively, and InH is the inhibitor, can be calculated considering the reaction

$$RO_2^{\cdot} \rightarrow R'H + O_2 + H^{\cdot}, \quad (8)$$

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**Table 1.** Enthalpies of formation of radicals and of reaction (8) (kJ mol$^{-1}$)

| RH | $\Delta_f H^\circ$(RH) | $\Delta_f H^\circ$($RO_2$) | $\Delta_f H^\circ$(R'H) | $\Delta H_8$ |
|---|---|---|---|---|
| *cyclo*-$C_6H_{12}$ | −123.1 | −67.7 | −5.4 | 280.3 |
| $PhCHMe_2$ | 3.9 | 61.0 | 113.0 | 270.0 |
| $Me_2CHOH$ | −272.6 | −219.5 | −217.6 | 219.9 |
| *cyclo*-$C_6H_{11}OH$ | −294.6 | −241.8 | −230.1 | 229.8 |

whose enthalpy $\Delta H_8$ is the following

$$\Delta H_8 = \Delta_f H^\circ(R'H) + \Delta_f H^\circ(H^\cdot) - \Delta_f H^\circ(RO_2^\cdot). \qquad (9)$$

Then

$$\Delta H_7 = \Delta H_8 - D_{In-H}. \qquad (10)$$

The calculation was performed in the following way. The $\Delta_f H^\circ(RO_2^\cdot)$ values were calculated by the empiric dependence[8] and corrected by the recommended values of $\Delta_f H^\circ$(ROOH):[9]

$$\Delta_f H^\circ(RO_2^\cdot) = 1.015\Delta_f H^\circ(RH) + 57.2 \text{ kJ mol}^{-1}. \qquad (11)$$

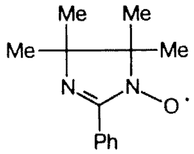
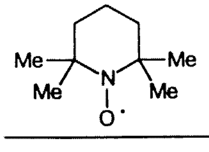
The values $\Delta_f H^\circ$(RH), $\Delta_f H^\circ$(R'H), and $\Delta_f H^\circ(H^\cdot)$ = 218 kJ mol$^{-1}$ were determined previously.[10,11] The results of this calculation are presented in Table 1.

The energy of dissociation of the O—H bond to $HO_2^\cdot$ calculated using the published data[11] is equal to 203.4 kJ mol$^{-1}$. Diphenylaminyl, α- and β-naphthylaminyl, phenyl-α-naphthylaminyl, and di(4-methoxyphenyl)aminyl radicals, for which the cyclic mechanism of chain termination in oxidation of alcohols[2] and olefins has been experimentally proven,[3,4] were chosen as aminyl radicals. The following nitroxyl radicals were chosen: $(4\text{-}MeOC_6H_4)_2NO^\cdot$ radical, for which the cyclic mechanism of chain termination in oxidizable 2-propanol has been proven,[5] 2,2,6,6-tetramethylpiperidine-1-oxyl, for the analog of which the cyclic mechanism of chain termination involving $HO_2^\cdot$ in oxidizable polypropylene has been proven[12]; and three nitroxyl radicals (Table 2) differing in the strength of the O—H bonds formed. The values of dissociation energies of the N—H and O—H bonds formed in reaction (7) are taken from the handbook.[13] It is obvious from the comparison of the $\Delta H_7$ values (see Table 2) that there is no basic difference between disproportionation reactions involving O—H and C—H bonds of peroxyl radicals. However, it is known from the experiment that peroxyl radicals with O—H bonds participate in the cyclic mechanism of chain termination, while alkylperoxyl radicals do not participate. Therefore, one should search for this difference in the specific character of the elementary act of disproportionation of these radicals.

## Role of triplet repulsion and electronegativity in disproportionation reactions of $RO_2^\cdot$ with $Am^\cdot$ and $AmO^\cdot$

The analysis of rate constants of reactions of peroxyl radicals with amines[14] and of aminyl radicals with hydroperoxides and phenols[15] shows that the aminyl radicals are highly reactive toward O—H bonds. By contrast, they react with C—H bonds slowly with high activation energies. Nitroxyl radicals also react with O—H bonds much more rapidly than with C—H bonds. In light of the aforementioned results, it is reasonable to pose the question of whether the discussed difference in behavior of hydroxyl and alkylperoxyl radicals is associated with the difference in the reactivity of C—H and O—H bonds with respect to aminyl and nitroxyl radicals.

**Table 2.** Enthalpies $\Delta H$ of disproportionation reactions of aminyl (nitroxyl) and peroxyl radicals $HO_2^\cdot$, $Me_2C(OH)O_2^\cdot$, *cyclo*-$C_6H_{10}(OH)O_2^\cdot$, $C_6H_5Me_2CO_2^\cdot$, and *cyclo*-$C_6H_{11}O_2^\cdot$

| $Am^\cdot$ ($AmO^\cdot$) | $-\Delta H$/kJ mol$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | $HO_2^\cdot$ | $Me_2C(OH)O_2^\cdot$ | *cyclo*-$C_6H_{10}(OH)O_2^\cdot$ | $PhMe_2CO_2^\cdot$ | *cyclo*-$C_6H_{11}O_2^\cdot$ |
| 2-$C_{10}H_7NH^\cdot$ | 176.1 | 159.6 | 149.7 | 109.5 | 99.2 |
| 1-$C_{10}H_7NH^\cdot$ | 171.3 | 154.8 | 144.9 | 104.7 | 94.4 |
| $Ph_2N^\cdot$ | 161.3 | 144.8 | 134.9 | 94.7 | 84.4 |
| 1-$C_{10}H_7(Ph)N^\cdot$ | 153.7 | 137.2 | 127.3 | 87.1 | 76.8 |
| $(4\text{-}MeOC_6H_4)_2N^\cdot$ | 145.2 | 128.7 | 118.8 | 78.6 | 68.3 |
| $Bu^t_2C{=}NO^\cdot$ | 135.1 | 118.6 | 108.7 | 68.5 | 58.2 |
| $PhCO(Bu^t)NO^\cdot$ | 119.6 | 103.1 | 93.2 | 53.0 | 42.7 |
|  | 108.8 | 92.3 | 82.4 | 42.2 | 31.9 |
|  | 87.8 | 71.3 | 61.4 | 21.2 | 10.9 |

As is known, the lower is $\Delta H$, the lower is the activation energy of any reaction of radical detachment. At a sufficiently high absolute value of $\Delta H$, the activation energy of the exothermic reaction becomes close to zero. According to the parabolic model of transition state,[7] the activation energy $E > 0.5RT$ for $\Delta H_e > \Delta H_{e,\min}$ and $E = 0.5RT$ at $\Delta H_e < \Delta H_{e,\min}$. The $\Delta H_e$ value includes the difference in null energies of bonds involved in the reaction. In turn, $\Delta H_{e,\min}$ is related to the activation energy of the thermoneutral reaction $E_{e,0}$ at the enthalpy $\Delta H_{e,0} = 0$ by the following equation[7]:

$$\Delta H_{e,\min} = -(1+\alpha)^2\alpha^{-2}E_{e,0} + \\ + 2(1+\alpha)\alpha^{-2}(E_{e,0}0.5h\nu L)^{1/2} + (1-\alpha^{-2})0.5h\nu L. \quad (12)$$

Here $E_{e,0}$ includes the energy of the null vibration of the bond that is cleaved, coefficient $\alpha^2$ is the ratio of force constants of bonds that are cleaved and formed, h is Planck's constant, ν is the frequency of a bond that is cleaved, and L is Avogadro's number. The activation energy $E_{e,0}$ characterizes the whole class of the reactions. For example, for the reaction $RO_2^{\cdot}$ + AmH, $E_{e,0}$ = 39.4 kJ $mol^{-1}$. The values of coefficient α, the energies of null vibrations of bonds that are cleaved $\Delta D_0 = 0.5h\nu L$, the activation energies $E_{e,0}$ taken from the handbook,[13] and the values of $\Delta H_{e,\min}$ calculated by formula (12) are presented in Table 3. It clearly follows from the comparison of $\Delta H$ presented in Table 2 with the $\Delta H_{e,\min}$ values that $\Delta H_e < \Delta H_{e,\min} = -39.4$ kJ $mol^{-1}$ for the reactions of aminyl radicals with O—H-containing peroxyl radicals. By contrast, for reactions of $Am^{\cdot}$ with alkylperoxyl radicals, $\Delta H_e > \Delta H_{e,\min} = -156$ kJ $mol^{-1}$. This means that the reactions of $Am^{\cdot}$ radicals with C—H bonds of $RO_2^{\cdot}$ occur with noticeable activation energies despite a high exothermicity.

A similar situation is observed for disproportionation reactions involving nitroxyl radicals. In all cases of the reactions of $AmO^{\cdot}$ with O—H-containing $RO_2^{\cdot}$, $\Delta H_e < \Delta H_{e,\min} = -58$ kJ $mol^{-1}$. By contrast, the reactions of $AmO^{\cdot}$ with C—H bonds of alkylperoxyl radicals occur with $\Delta H_e > \Delta H_{e,\min} = -125$ kJ $mol^{-1}$, *i.e.*, they have the activation energy $E > 0.5RT$. The difference in $\Delta H_{e,\min}$ is thus caused by different values of $E_{e,0}$ for the reactions of $Am^{\cdot}$ and $AmO^{\cdot}$ with O—H and C—H bonds.

It is reasonable to ask why $E_{e,0}$ for these classes of the reactions differ so strongly. This problem has been analyzed previously.[7,14,15] In point of fact, $E_{e,0}$ depends on such factors as the triplet repulsion and electronegativity of the atoms in the reaction center of the transition state. In the reactions with the transition state of the N...H...C and O...H...C types, strong triplet repulsion occurs due to the high energy of the antibonding orbital of N—C and O—C, respectively. Therefore, these reactions are characterized by a high value of $E_{e,0}$ and a high value of $|\Delta H_{e,\min}|$. In the reactions with the O...H...O transition state, the triplet repulsion is close to zero due to a very weak O—O bond. Therefore, the disproportionation of $AmO^{\cdot}$ *via* the reaction with the O—H bond of $RO_2^{\cdot}$ is fast. The reactions with the transition state of the N...H...O type occur more rapidly due to a weak triplet repulsion and an additional attraction of the N and O atoms, which have different electron affinities.[7]

**Table 3.** Thermoneutral activation energies $E_{e,0}$ and limiting values $\Delta H_{e,\min}$ (formula (12)) for reactions of aminyl ($Am^{\cdot}$) and nitroxyl ($AmO^{\cdot}$) radicals with hydroperoxides ROOH and hydrocarbons

| Reaction | α | $\Delta D_0$ | $E_{e,0}$ | $-\Delta H_{e,\min}$ |
|---|---|---|---|---|
| | | /kJ $mol^{-1}$ | | |
| $Am^{\cdot}$ + HOOR | 1.064 | 21.1 | 39.0 | 39.4 |
| $Am^{\cdot}$ + RH | 0.866 | 17.4 | 69.7 | 146.1 |
| $AmO^{\cdot}$ + HOOR | 1.000 | 21.2 | 45.6 | 58.0 |
| $AmO^{\cdot}$ + RH | 0.802 | 17.4 | 58.0 | 124.6 |

The activation energy $E_e$ can be calculated using $E_{e,0}$ and $\Delta H_e$ by the formula[7]:

$$E_e^{1/2} = E_{e,0}^{1/2}(1-\alpha)^{-1}\{1 - \alpha[1 - \\ - (1-\alpha)(1+\alpha)^{-1}E_{e,0}^{-1}\Delta H_e]^{1/2}\}. \quad (13)$$

It is related to the Arrhenius activation energy $E$ by the simple correlation[7]:

$$E_e = E + 0.5h\nu L - 0.5RT. \quad (14)$$

The values of $E$ for the reactions presented in Table 2 were calculated by formulas (13) and (14), and parameters α and $E_{e,0}$ are presented in Table 3. The results of this calculation in the form of curves are presented in Fig. 1. It is distinctly seen from Fig. 1 that the dispro-

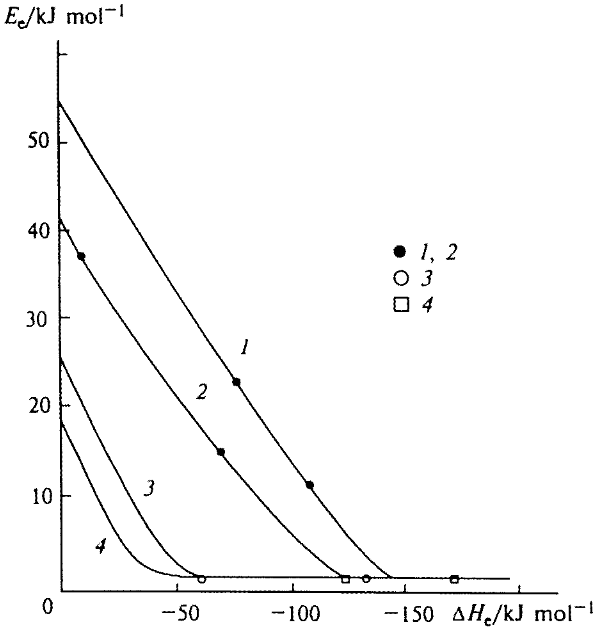


**Fig. 1.** Dependence of the activation energy $E_e$ on the enthalpy $\Delta H_e$ of disproportionation reactions of an aminyl radical with alkylperoxyl radical (*1*), nitroxyl radical with alkylperoxyl (*2*) and hydroperoxyl (*3*) radicals, and an aminyl radical with a hydroxyperoxyl radical (*4*).

portionation of Am$^{\cdot}$ and AmO$^{\cdot}$ with alkyl $RO_2^{\cdot}$ radicals occurs with a considerably higher activation energy than that with O—H-containing radicals. In the latter case, all aminyl and nitroxyl radicals react with the activation energy close to zero ($E = 0.5RT$).

### Estimation of the competition between the disproportionation of In$^{\cdot}$ with $RO_2^{\cdot}$ and addition of $RO_2^{\cdot}$ $(HO^{\cdot})_2$ to In$^{\cdot}$

For the quantitative estimation of the probability of the cyclic chain termination involving the radical-inhibitor In$^{\cdot}$, rate constants of disproportionation and regeneration of InH (reaction (7)) should be compared as well as those of the reaction of $RO_2^{\cdot}$ with In$^{\cdot}$ and irreversible consumption of InH. It is known that peroxyl radicals add to the aromatic ring of the aminyl radical to finally form quinonimine[16]:

$$RO_2^{\cdot} + Ph_2N^{\cdot} \rightarrow ROOPhNPh \rightarrow ROH + OC_6H_4NPh. \quad (15)$$

The addition of $RO_2^{\cdot}$ to the nitrogen atom accompanied by the generation of the nitroxyl radical occurs in parallel:

$$Ph_2N^{\cdot} + RO_2^{\cdot} \rightarrow Ph_2NOOR \rightarrow Ph_2NO^{\cdot} + RO^{\cdot}. \quad (16)$$

The ratio of the rates of these two reactions is[5] 1 : 1, while the overall rate constant $k = 6 \cdot 10^8$ L mol$^{-1}$ s$^{-1}$ ($T$ = 293 K).[17] Thus, the rate constant of the first reaction $k_{ad} = 3 \cdot 10^8$ L mol$^{-1}$ s$^{-1}$. It is likely that the reaction of peroxyl radicals with nitroxyl radicals also occurs *via* their addition to the aromatic ring to form, for example, the corresponding nitrone. Peroxyl radicals react with di(4-methoxyphenyl)nitroxyl with $k = 6 \cdot 10^5$ L mol$^{-1}$ s$^{-1}$ ($T$ = 333 K).[18] These data can be used to estimate the ratio of the rate constants of two reactions we are interested in: disproportionation (reaction (2)) and addition of $RO_2^{\cdot}$ (or $HO_2^{\cdot}$) to the aromatic ring (reaction (15)).

For correct comparison, it should be taken into account that the reactions considered are strongly exothermic (see Table 2). For these reactions, as has been recently shown,[19] the pre-exponential factor $A$ depends on the enthalpy of the reaction, more exactly, on the difference in enthalpies: $\Delta H_e$ and $\Delta H_{e,min}$. This is associated with the fact that the more exothermic the reaction, the greater the cross-section of the collision resulting in the reaction (at $\Delta H_e < \Delta H_{e,min}$). The dependence of the $A$ factor on $\Delta H_e$ is described, according to the parabolic model, by the following formula[19]:

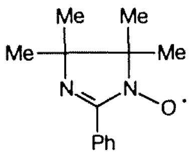
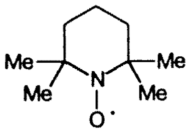
$$(A/A_0)^{1/2} = 1 + \beta(|\Delta H_e|^{1/2} - |\Delta H_{e,min}|^{1/2}), \quad (17)$$

where $A_0$ is the standard pre-exponential factor for the given class of reactions. The reaction of disproportionation of $HO_2^{\cdot}$ radicals is the closest to the reactions considered (see Table 2):

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow HOOH + O_2. \quad (18)$$

This reaction occurs almost without activation energy with $k = 1.0 \cdot 10^{10}$ L mol$^{-1}$ s$^{-1}$ in the gas phase[20] and in $CCl_4$.[1] For the reaction of exchange of a hydrogen atom ROO$^{\cdot}$ + HOOR$'$, which is analogous in structure of the transition state, the pre-exponential factor $A_0 = 10^8$ L mol$^{-1}$ s$^{-1}$ in the liquid phase. The $E_{e,0}$ value for the reaction $RO_2^{\cdot}$ + R$'$OOH is[7] $E_{e,0}$ = 43.1 kJ mol$^{-1}$ and that calculated by formula (12) $\Delta H_{e,min}$ = −50.6 kJ mol$^{-1}$. Using $A$, $A_0$, $\Delta H_e$ (see Table 2), and $\Delta H_{e,min}$ values, we determine the coefficient $\beta$ = 1.6 (kJ mol$^{-1}$)$^{1/2}$.

**Table 4.** Activation energies $E$ (kJ mol$^{-1}$) and rate constants $k$ (L mol$^{-1}$ s$^{-1}$) of disproportionation reactions of aminyl and nitroxyl radicals with peroxyl radicals (calculation by formulas (13) and (14))

| Am$^{\cdot}$ (AmO$^{\cdot}$) | $PhCMe_2O_2^{\cdot}$ | | *cyclo*-$C_6H_{10}(OH)O_2^{\cdot}$ | | $HO_2^{\cdot}$, |
|---|---|---|---|---|---|
| | $E$ | $k$ | $E$ | $k$ | $k$ |
| 1-$C_{10}H_7NH^{\cdot}$ | 13.6 | $4.4 \cdot 10^7$ | 16.7 | $9.6 \cdot 10^6$ | $9.6 \cdot 10^9$ |
| $Ph_2N^{\cdot}$ | 16.6 | $1.5 \cdot 10^7$ | 19.8 | $3.1 \cdot 10^6$ | $8.4 \cdot 10^9$ |
| 1-$C_{10}H_7(Ph)N^{\cdot}$ | 18.9 | $6.5 \cdot 10^6$ | 22.3 | $1.3 \cdot 10^6$ | $7.8 \cdot 10^9$ |
| $(4\text{-}MeOC_6H_4)_2N^{\cdot}$ | 21.7 | $2.4 \cdot 10^6$ | 25.1 | $4.6 \cdot 10^5$ | $7.2 \cdot 10^9$ |
| $Bu^t_2C{=}NO^{\cdot}$ | 15.0 | $2.7 \cdot 10^7$ | 18.3 | $5.4 \cdot 10^6$ | $3.7 \cdot 10^9$ |
| $PhCO(Bu^t)NO^{\cdot}$ | 20.0 | $4.4 \cdot 10^6$ | 23.5 | $8.2 \cdot 10^5$ | $2.6 \cdot 10^9$ |
|  | 23.7 | $1.1 \cdot 10^6$ | 27.4 | $2.0 \cdot 10^5$ | $2.0 \cdot 10^9$ |
|  | 31.5 | $6.9 \cdot 10^4$ | 35.7 | $1.0 \cdot 10^4$ | $9.6 \cdot 10^8$ |

The results of the calculation of $E$ (formulas (13) and (14)) and $k = A\exp(-E/RT)$ (formula (17)) for disproportionation of aminyl and nitroxyl radicals (see Table 2) with $RO_2^{\cdot}$ and $HO_2^{\cdot}$ radicals are presented in Table 4. It is seen that $HO_2^{\cdot}$ enters the reaction of disproportionation with $Am^{\cdot}$ and $AmO^{\cdot}$ 2—4 orders of magnitude more rapidly than with $RO_2^{\cdot}$. On the other hand, the addition of $RO_2^{\cdot}$ to the aromatic ring of the diphenylaminyl radical occurs[16] with the rate constant $k = 3 \cdot 10^8$ L mol$^{-1}$ s$^{-1}$. As is seen from comparison with this value, all aminyl radicals react more rapidly with $HO_2^{\cdot}$ (and the cyclic chain termination is observed in these systems), but all of them react more slowly with C—H bonds of $RO_2^{\cdot}$ and, therefore, there is no cyclic chain termination in hydrocarbons!

Thus, in oxidizable alcohols and olefins, aminyl and nitroxyl radicals cause the cyclic chain termination due to their high reactivity with respect to O—H bonds, which is caused by a low triplet repulsion and different electronegativities of transition states of N and O atoms. In oxidizable hydrocarbons, these mechanisms are impossible due to slow reactions of the same radicals with C—H bonds of $RO_2^{\cdot}$, which is caused by strong triplet repulsion in the O...H...C and N...H...C transition states. In such systems, the irreversible consumption of $Am^{\cdot}$ in the reaction with $RO_2^{\cdot}$ and consumption of $AmO^{\cdot}$ in the reactions with alkyl and peroxyl radicals predominate.

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