Kinetics and Catalysis, Vol. 45, No. 6, 2004, pp. 826–846. Translated from Kinetika i Kataliz, Vol. 45, No. 6, 2004, pp. 877–896.

PEROXIDES-XI

Geometric Parameters of the Transition State in Radical Reactions of Antioxidants

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Received June 20, 2003

Abstract—An algorithm for calculating interatomic distances in a transition state of radical abstraction reactions through the enthalpy of a reaction is developed. The algorithm is based on a combination of quantum-chemical calculations with the calculation by the intersecting-parabolas method. Using this method and experimental data (enthalpies and activation energies of reactions), interatomic distances in a reaction center are calculated for the reactions of antioxidants with a symmetrical transition state of the N…H…N and O…H…O types and a nonsymmetrical transition state of the N…H…C, O…H…C, and O…H…N types. These distances are compared with other characteristics of the reactions and reactants. The influence of such factors as the enthalpy of the reaction, triplet repulsion in the transition state, electronegativity of atoms in the reaction center, and steric repulsion of reactants on the geometric parameters of the transition state is examined. The results obtained are used to calculate the increments characterizing the influence of various factors on interatomic distances of radical reactions considered.

INTRODUCTION

Antioxidants (phenols and aromatic amines) and related radicals are involved in various radical reactions [1–5]. Kinetic data on these reactions were analyzed by the intersecting-parabolas method to estimate the parameters and derive formulas for calculating the activation energies and rate constants of the reactions from the enthalpy [6–14]. A new geometric parameter, namely, the stretch of reacting bonds in a transition state, is introduced in the intersecting-parabolas method for considering a bimolecular reaction. We have recently compared this parameter (r_e) with the results of quantum-chemical calculations of the geometry of the transition state for a series of radical reactions [15, 16]. This combined approach makes it possible to calculate the geometric parameters of transition states of radical reactions with an accuracy close to that of quantum chemical methods (GAUSSIAN-98, density functional theory) using experimental data (the activation energy and the enthalpy of reaction). In this study, we used this approach to construct an algorithm and calculate interatomic distances in transition states of radical reactions involving antioxidants.

CALCULATION PROCEDURES

In the framework of the intersecting-parabolas method, the radical abstraction reaction

$$X^{\cdot} + HY \longrightarrow XH + Y^{\cdot}$$

is characterized by the following parameters [12–14]:

(1) the enthalpy ΔH_e including a difference between zero-point energies of breaking and forming bonds;

(2) the classical activation barrier E_e including the zero-point energy of a breaking bond;

(3) the parameter r_e, which is equal to the total stretch of breaking and forming bonds in the transition state;

(4) the parameter b ($2b^2$ is the force constant of a breaking bond);

(5) the parameter α (α^2 is equal to the ratio of force constants of breaking and forming bonds); and

(6) the preexponential factor A_0 calculated per one equireactive bond in a molecule.

The reaction rate constant relates to E and A_0 by the Arrhenius equation

$$k = nA_0\exp(-E/RT), \quad (1)$$

where n is the number of equally reactive bonds in a reacting molecule. Analysis of experimental data shows that ΔH_e and E_e are the individual characteristics of a reaction, and parameters b, α, A_0, and r_e characterize a class of reactions and are the same for all reactions of this class [14]. The above parameters are related by the expression [7]

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \quad (2)$$

The parameter br_e makes it possible to calculate the activation energy $E_{e,0}$ of a thermally neutral reaction for which $\Delta H_e = 0$

$$E_{e,0} = \frac{(br_e)^2}{(1+\alpha)^2}. \quad (3)$$

The position of an abstracted hydrogen atom in the transition state in the section r_e is characterized by the distance $r^{\#}$, which can be estimated using formula [14]

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$$r^{\#} = \frac{r_e\sqrt{E_e}}{\alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}}. \quad (4)$$

Two basically different transition states, namely, symmetrical and nonsymmetrical, can be formed in radical-abstraction reactions.

Symmetrical transition states take place in reactions of the type

$$Y_f^{\cdot} + HY_i \longrightarrow Y_fH + Y_i^{\cdot},$$

in which breaking and forming bonds are equivalent with respect to the force constant, the bond length r(Y–H), and the zero-point energy. These reactions are exemplified by the reaction of a phenoxy radical with phenol or the reaction of a peroxy radical with hydroperoxide. For these reactions, $\alpha = 1$ and $\Delta H_e = \Delta H$. The formulas for calculation of the activation energy E have the following simple forms [14]:

$$\sqrt{E_e} = \frac{br_e}{2} + \frac{\Delta H}{2br_e}, \quad (5)$$

$$E = E_e - 0.5hN_A\nu(\text{Y–H}) - 0.5RT, \quad (6)$$

where ν(Y–H) is the vibration frequency of the breaking bond, and h and N_A are Planck's constant and Avogadro's number, respectively.

Nonsymmetrical transition states take place in reactions of the type

$$X^{\cdot} + HY \longrightarrow XH + Y^{\cdot},$$

where the breaking and forming bonds differ with respect to such characteristics as the force constant, the bond lengths r(Y–H) and r(X–H), and the zero-point energy of the bond. These are, for instance, the reactions of peroxy and phenoxy radicals with an amine, a peroxy radical with hydrocarbon, and others. For these reactions, $\alpha \neq 1$ and $\Delta H_e \neq \Delta H$. In this case, formulas for calculating the activation energy E are

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left[1 - \alpha\sqrt{1 - \frac{1-\alpha^2}{(br_e)^2}\Delta H_e}\right], \quad (7)$$

$$\Delta H_e = D(\text{Y–H}) - D(\text{X–H}) + 0.5hN_A(\nu(\text{Y–H}) - \nu(\text{X–H})), \quad (8)$$

$$E_e = E + 0.5(hN_A\nu(\text{Y–H}) - RT), \quad (9)$$

where ν(Y–H) and ν(X–H) are the vibration frequencies of breaking and forming bonds, respectively. When the coefficient α is close to unity and the reaction enthalpy is low, the activation energy E_e can be calculated from formula [14]

$$\sqrt{E_e} = \frac{br_e}{1+\alpha} + \frac{\alpha\Delta H_e}{2br_e}. \quad (10)$$

For the reactions considered in this work, the characteristics of reacting bonds can take the following values [17]:

Bond	r(Y–H) × 10^{10}, m	$0.5hN_A\nu_i$, kJ/mol	$b \times 10^{-10}$, (kJ/mol)$^{1/2}$ m^{-1}
C–H	1.096	17.4	37.43
N–H	1.009	20.0	43.06
O–H (in alcohol)	0.970	21.7	47.01
O–H (in phenol)	0.970	21.5	46.65
O–H (in hydroxylamine)	0.970	21.5	46.65
O–H (in hydroperoxide)	0.970	21.2	46.00

The interatomic distance Y…H…X in the transition state is the sum consisting of three terms [15]

$$r(\text{Y…H…X}) = r(\text{Y–H}) + r(\text{X–H}) + \beta r_e, \quad (11)$$

where r(Y–H) and r(X–H) are the corresponding bond lengths in the YH and XH molecules, and r_e is the stretch of these bonds in the transition state calculated by the intersecting-parabolas method using formula (2). With the use of the coefficient β, the distance r(Y…H…X) becomes equal to that obtained by quantum-chemical calculations. The coefficient β was calculated in [15, 16] and has the following values:

Reaction	$RO_2^{\cdot} + RH$	$HO_2^{\cdot} + H_2O_2$	$Et^{\cdot} + EtH$	$N^{\cdot}H_2 + NH_3$
Transition state	O…H…C	O…H…O	C…H…C	N…H…N
β	1.44	1.49	1.13	1.11

For the reactions with a transition state of the N…H…C type, the coefficient β is assumed to be 1.12 (average between β(C…H…C) and β(N…H…N), whereas for a transition state of the N…H…O type, $\beta = 1.44$ (by analogy to a transition state of the C…H…O type). Other parameters for the reaction classes considered are presented in Table 1.

Since r_e can be expressed through $E_{e,0}$, α, and β, the following formula is obtained for the distance r(Y…H…X):

$$r(\text{Y…H…X}) = r(\text{Y–H}) + r(\text{X–H}) + (1+\alpha)\beta b^{-1}\sqrt{E_{e,0}}. \quad (12)$$

Table 1. Parameters of the intersecting-parabolas method calculated by formulas (12), (17), (20), and (21) for reactions involving antioxidants

Reaction	α	$E_{e,0}$, kJ/mol	$\beta b^{-1} \times 10^{12}$, $mol^{1/2}\ kJ^{-1/2}\ m$	$r(Y\ldots H\ldots X) \times 10^{10}$, m	$\frac{dr(Y\ldots H)}{d(\Delta H)} \times 10^{10}$, m mol J^{-1}	$\Delta r \times 10^{10}$, m
$RO^{\bullet}$ + Ar^1OH	0.992	50.5	3.19	2.392	1.12	0.452
$RO^{\bullet}$ + Ar^2OH	0.992	63.2	3.19	2.445	1.00	0.505
$RO_2^{\bullet}$ + Ar^1OH	1.014	43.3	3.19	2.363	1.22	0.423
$RO_2^{\bullet}$ + Ar^2OH	1.014	51.1	3.19	2.399	1.12	0.459
$RO_2^{\bullet}$ + AmH	0.936	39.0	3.46	2.397	1.29	0.418
$Ar^1O^{\bullet}$ + Ar^1OH	1.000	39.7	3.19	2.342	1.27	0.402
$Ar^1O^{\bullet}$ + Ar^2OH	1.000	43.6	3.19	2.361	1.21	0.421
$Ar^2O^{\bullet}$ + Ar^2OH	1.000	51.6	3.19	2.398	1.11	0.458
$Ar^1O^{\bullet}$ + R^1H	0.802	62.9	3.85	2.616	1.08	0.550
$Ar^1O^{\bullet}$ + R^2H	0.802	78.3	3.85	2.680	0.97	0.614
$Ar^1O^{\bullet}$ + R^3H	0.802	69.5	3.85	2.644	1.03	0.578
$Am^{\bullet}$ + Ar^1OH	1.083	29.5	3.09	2.329	1.48	0.350
$Am^{\bullet}$ + Ar^2OH	1.083	33.5	3.09	2.351	1.39	0.372
$Am^{\bullet}$ + AmH	1.000	33.8	3.62	2.439	1.56	0.421
$Am^{\bullet}$ + R^3H	0.869	81.7	2.99	2.610	0.77	0.505
$AmO^{\bullet}$ + Ar^1OH	1.000	45.8	3.19	2.372	1.18	0.432
$AmO^{\bullet}$ + Ar^2OH	1.000	52.8	3.19	2.404	1.10	0.464
$AmO^{\bullet}$ + AmH	0.927	38.3	3.09	2.347	1.20	0.368
$AmO^{\bullet}$ + R^3H	0.802	69.7	3.85	2.645	1.03	0.579

Note: Ar^1OH and Ar^2OH are phenol and a sterically hindered phenol, respectively; R^1H, R^2H, and R^3H are a paraffin, an olefin, and an alkylarene, respectively.

The bond lengths are known with an accuracy of $\pm 0.005 \times 10^{-10}$ m, the average accuracy in determination of the classical barrier from experimental data is ±1.5 kJ/mol [11], and the error in r_e estimation does not exceed 0.01×10^{-10} m. Therefore, the total error in $r(Y\ldots H\ldots X)$ estimation is $\Delta = (0.005 + 0.005 + 0.01) \times 10^{-10}$ m $= 0.02 \times 10^{-10}$ m.

The position of a hydrogen atom in the reaction center of the transition state is characterized by the distances $r(Y\ldots H)$ and $r(X\ldots H)$. These distances depend on the activation energy E_e and the reaction enthalpy ΔH_e. They are expressed by formulas [14]

$$r(Y\ldots H) = r(Y\text{–}H) + \beta b^{-1}\sqrt{E_e}, \quad (13)$$

$$r(X\ldots H) = r(X\text{–}H) + \alpha\beta b^{-1}\sqrt{E_e - \Delta H_e}. \quad (14)$$

The activation energy E_e can be expressed through the enthalpy of the reaction (see formula (10)). Then, formulas (13) and (14) take the form

$$r(Y\ldots H) = r(Y\text{–}H) + \beta b^{-1}\sqrt{E_{e,0}} + \frac{\alpha\beta\Delta H_e}{2b(1+\alpha)\sqrt{E_{e,0}}}, \quad (15)$$

$$r(\mathrm{X}\ldots\mathrm{H}) = r(\mathrm{X}\text{–}\mathrm{H}) + \alpha\beta b^{-1}\sqrt{E_{\mathrm{e},0}} - \frac{\alpha\beta\Delta H_\mathrm{e}}{2b(1+\alpha)\sqrt{E_{\mathrm{e},0}}}. \quad (16)$$

The formulas are valid for any ΔH_e values at $\alpha = 1$ and for any α when $\Delta H_\mathrm{e} \ll (br_\mathrm{e})^2/(1-\alpha^2)$. The error in estimation of these distances is 0.01×10^{-10} m.

RESULTS AND DISCUSSION

Influence of the Enthalpy of Reaction

For reactions of the same class, the parameter br_e is constant [15]. This implies that, according to Eqs. (13) and (14), the distances r(X…H) and r(Y…H) in the transition state vary from one reaction to another within the same class, while the distance r(Y…H…X) remains unchanged. This is also confirmed by the quantum chemical calculation [15, 16]. Therefore, each class of radical abstraction reactions can be characterized by the activation energy of a thermally neutral reaction $E_{\mathrm{e},0}$ and also by the interatomic distance r(Y…H…X) in the transition state. These distances for the reactions of antioxidants under consideration are presented in Table 1.

For equal lengths and force constants of breaking and forming bonds, a hydrogen atom in the transition state of a thermally neutral reaction $\Delta H_\mathrm{e} = 0$ lies exactly in the middle of the section $r(\mathrm{Y_i}\ldots\mathrm{H}\ldots\mathrm{Y_f})$, that is, $r(\mathrm{Y_i}\ldots\mathrm{H}) = r(\mathrm{Y_f}\ldots\mathrm{H})$ (see formulas (15) and (16)). This fact agrees with the results of quantum-chemical calculations [15]. In reactions with nonsymmetrical transition states, a hydrogen atom in a thermally neutral reaction is shifted toward an atom with the bond having a higher force constant as follows from formulas (15) and (16). The distances r(Y…H) and r(X…H) for transition states of the reactions under discussion with $\Delta H_\mathrm{e} = 0$ are presented in Table 2.

Exothermic reactions with symmetrical transition states are always characterized by the inequality $r(\mathrm{Y_i}\ldots\mathrm{H}) < r(\mathrm{Y_f}\ldots\mathrm{H})$; that is, an early transition state takes place. On the contrary, for endothermic reactions, $r(\mathrm{Y_i}\ldots\mathrm{H}) > r(\mathrm{Y_f}\ldots\mathrm{H})$; that is, a late transition state is observed. According to formulas (15) and (16), when the enthalpy of the reaction ΔH changes, the interatomic distances r(Y…H) and r(X…H) vary as follows:

$$\frac{\mathrm{d}r(\mathrm{Y_i}\ldots\mathrm{H})}{\mathrm{d}\Delta H} = \frac{\beta}{4b\sqrt{E_{\mathrm{e},0}}}, \qquad \frac{\mathrm{d}r(\mathrm{Y_f}\ldots\mathrm{H})}{\mathrm{d}\Delta H} = -\frac{\beta}{4b\sqrt{E_{\mathrm{e},0}}}. \quad (17)$$

The derivatives $\mathrm{d}r(\mathrm{Y_i}\ldots\mathrm{H})/\mathrm{d}\Delta H$ and $\mathrm{d}r(\mathrm{Y_f}\ldots\mathrm{H})/\mathrm{d}\Delta H$ for radical reactions with symmetrical transition states differ by sign, and their values are presented in Table 1. Tables 3–7 contain the enthalpies, activation energies, and geometric parameters for the reactions of antioxidants with symmetrical transition states or transition states close to symmetrical ones.

A different situation is observed for the position of a hydrogen atom in the transition state for reactions with nonsymmetrical transition states. When $E = E_{\mathrm{e},0}$, a hydrogen atom in the transition state is already shifted toward the X or Y atoms for $\Delta H_\mathrm{e} = 0$. Therefore, the following inequality is true for exothermic reactions:

$$r(\mathrm{Y}\ldots\mathrm{H}) < r_0(\mathrm{Y}\ldots\mathrm{H}) = r(\mathrm{Y}\text{–}\mathrm{H}) + \beta b^{-1}E_{\mathrm{e},0}^{1/2}, \quad (18)$$

where r_0(Y…H) = r(Y…H) in the reaction with $\Delta H_\mathrm{e} = 0$. For endothermic reactions,

$$r(\mathrm{Y}\ldots\mathrm{H}) > r_0(\mathrm{Y}\ldots\mathrm{H}) = r(\mathrm{Y}\text{–}\mathrm{H}) + \beta b^{-1}E_{\mathrm{e},0}^{1/2}. \quad (19)$$

According to formulas (11) and (12), a shift of a hydrogen atom relative to the center of Δr in the transition state of the reaction with $\Delta H_\mathrm{e} = 0$ is

$$\Delta r = r(\mathrm{Y}\ldots\mathrm{H}) - 0.5r(\mathrm{Y}\ldots\mathrm{X}) = 0.5[r(\mathrm{Y}\text{–}\mathrm{H}) - r(\mathrm{X}\text{–}\mathrm{H})] - \alpha\beta b^{-1}E_{\mathrm{e},0}^{1/2}. \quad (20)$$

As can be seen from formula (20), this is caused by the difference between the lengths and force constants of the breaking and forming bonds. A relationship between the interatomic distances and the enthalpy of reaction is described by the following formulas for the corresponding derivatives (obtained by differentiating Eqs. (15) and (16) after inserting formula (10)):

$$\frac{\mathrm{d}r(\mathrm{Y}\ldots\mathrm{H})}{\mathrm{d}\Delta H} = \frac{\alpha\beta}{2(1+\alpha)b\sqrt{E_{\mathrm{e},0}}}, \qquad \frac{\mathrm{d}r(\mathrm{X}\ldots\mathrm{H})}{\mathrm{d}\Delta H} = -\frac{\alpha\beta}{2(1+\alpha)b\sqrt{E_{\mathrm{e},0}}}. \quad (21)$$

The derivatives and r(Y…H) values are presented in Table 1. However, the slope in the distance–enthalpy coordinates changes slightly on going from one reaction to another (from 1.5×10^{-10} to 3.0×10^{-10} mol mJ^{-1}) due to the compensating influence of different factors. The enthalpies, the activation energies, and the geometric parameters for the reactions of antioxidants with nonsymmetrical transition states are presented in Tables 8 and 9.

To consider the problem of the factors affecting interatomic distances in the transition state, it is important to know the characteristics of different classes of reactions. Each class of radical reactions is characterized by the interatomic distance r(Y…H…X) in the transition state and bond stretch upon transition state formation: $\Delta r = r(\mathrm{Y}\ldots\mathrm{H}\ldots\mathrm{X}) - r(\mathrm{Y}\text{–}\mathrm{H}) - r(\mathrm{X}\text{–}\mathrm{H})$.

Triplet Repulsion

Let us compare the values of $\Delta r \times 10^{10}$ m (bond stretch in the transition state) for the reactions of oxygen-centered radicals with a C–H bond of aliphatic hydrocarbons R^{1}H and an O–H bond of sterically unhindered phenols Ar^{1}OH (Ar^{2}OH is sterically hindered phenol, and AmOH is hydroxylamine).

$X^{\cdot}$	$RO^{\cdot}$	$RO_2^{\cdot}$	$Ar^1O^{\cdot}$	$Ar^2O^{\cdot}$	$AmO^{\cdot}$
$\Delta r(X^{\cdot} + R^1H) \times 10^{10}$, m	0.504	0.524	0.550	0.640	0.550
$\Delta r(X^{\cdot} + Ar^1OH) \times 10^{10}$, m	0.439	0.406	0.389	0.408	0.418
$\Delta\Delta r \times 10^{10}$, m	0.065	0.118	0.161	0.232	0.132
$\Delta E_{e,0}$, kJ/mol	2.7	13.0	19.6	41.8	17.2

For the reactions of the O-centered radicals with the C–H bond of hydrocarbon, the bond stretch in the transition state is $(0.06–0.23) \times 10^{-10}$ m longer than that in the reactions with the O–H bond of phenol. This agrees with the fact that the height of the classical barrier $E_{e,0}$ for reactions with a C–H bond is higher than that for reactions with an O–H bond. The latter is the result of a stronger triplet repulsion in a transition state of the C…H…O type compared to that in a transition state of the O…H…O type [14]. The same regularity is observed for Δr in the reactions $X^{\cdot}$ + R^1H and $X^{\cdot}$ + ROOH. The average value of Δr is $(0.419 \pm 0.015) \times 10^{-10}$ m, and $\Delta\Delta r = (0.130 \pm 0.015) \times 10^{-10}$ m.

$X^{\cdot}$	$RO_2^{\cdot}$	$Ar^1O^{\cdot}$	$Ar^2O^{\cdot}$	$AmO^{\cdot}$
$\Delta r(X^{\cdot} + R^1H) \times 10^{10}$, m	0.524	0.550	0.640	0.550
$\Delta r(X^{\cdot} + ROOH) \times 10^{10}$, m	0.411	0.406	0.441	0.419
$\Delta\Delta r \times 10^{10}$, m	0.113	0.144	0.199	0.131
$\Delta E_{e,0}$, kJ/mol	13.3	19.6	34.3	17.4

Influence of π Bonds

Analysis of the $E_{e,0}$ values showed a substantial effect of the presence of π bonds in the α-position to the reaction center of the transition state on the classical barrier [14]. π electrons react with the reaction center and thus enhance the triplet repulsion and increase $E_{e,0}$. How does this interaction reflect the bond stretch in the transition state? Below the Δr values for transition states of several reactions are presented (R^1H is paraffin, R^2H is olefin, and R^3H is alkylaromatic hydrocarbon). The respective parameters r_e for the reactions $R^{\cdot}$ + RH are taken from the [8] and those for the reactions $RO^{\cdot}$ + RH are available from [18].

$X^{\cdot}$	$R^{\cdot}$	$RO^{\cdot}$	$RO_2^{\cdot}$	$Ar^1O^{\cdot}$	$AmO^{\cdot}$
$\Delta r(X^{\cdot} + R^1H) \times 10^{10}$, m	0.522	0.504	0.524	0.550	0.550
$\Delta r(X^{\cdot} + R^2H) \times 10^{10}$, m	0.562	0.544	0.585	0.613	0.620
$\Delta r(X^{\cdot} + R^3H) \times 10^{10}$, m	0.537	0.519	0.551	0.577	0.578

It is seen that a double bond in the α-position to the reaction center of the transition state increases Δr by $(0.055 \pm 0.012) \times 10^{-10}$ m, whereas the presence of a phenyl ring increases this value by $(0.022 \pm 0.006) \times 10^{-10}$ m. Thus, π electrons react with electrons of the reaction center and increase the bond stretch in the transition state.

Electronegativity of X and Y Atoms

Such a factor as the difference between the electronegativities of atoms forming a reaction center also manifests itself in the transition-state geometry. This follows from comparison of the bond stretches in the transition state Δr for reaction centers of the O…H…O and N…H…O types.

$X^{\bullet}$	$RO_2^{\bullet}$	$Ar^1O^{\bullet}$	$Ar^2O^{\bullet}$	$AmO^{\bullet}$
$\Delta r(X^{\bullet} + Ar^1OH) \times 10^{10}$, m	0.441	0.389	0.407	0.418
$\Delta r(X^{\bullet} + AmH) \times 10^{10}$, m	0.405	0.348	0.371	0.368
$\Delta\Delta r \times 10^{10}$, m	0.036	0.041	0.036	0.050

These data show that the interatomic distance in the N…H…O reaction center is much shorter than that in the O…H…O reaction center: $\Delta\Delta r = (0.041 \pm 0.006) \times 10^{-10}$ m. This occurs due to the difference in electron affinities of oxygen and nitrogen atoms and the mutual Coulomb repulsion of these atoms in the transition state.

Steric Hindrance

Another factor, namely, steric repulsion of reactants in the transition state, manifests itself in the reactions of radicals with sterically hindered phenols Ar^2OH [14]. This factor reflects the transition-state geometry, which is seen from comparison of the reactions of radicals with Ar^1OH and of sterically hindered phenols Ar^2OH with *tert*-butyl substituents in the *ortho*-position.

Table 2. Interatomic distances calculated by formulas (15) and (16) for thermally neutral radical reactions ($\Delta H_e = 0$) involving an antioxidant

Reaction	α	$\beta b^{-1} E_{e,0}^{1/2} \times 10^{10}$, m	$r(Y\ldots H) \times 10^{10}$, m	$\alpha\beta b^{-1} E_{e,0}^{1/2} \times 10^{10}$, m	$r(X\ldots H) \times 10^{10}$, m
$RO^{\bullet} + Ar^1OH$	0.992	0.227	1.197	0.225	1.195
$RO^{\bullet} + Ar^2OH$	0.992	0.254	1.224	0.252	1.122
$RO_2^{\bullet} + Ar^1OH$	1.014	0.210	1.180	0.213	1.183
$RO_2^{\bullet} + Ar^2OH$	1.014	0.228	1.198	0.231	1.201
$RO_2^{\bullet} + AmH$	0.936	0.216	1.225	0.202	1.172
$Ar^1O^{\bullet} + Ar^1OH$	1.000	0.201	1.171	0.201	1.171
$Ar^1O^{\bullet} + Ar^2OH$	1.000	0.211	1.181	0.211	1.181
$Ar^2O^{\bullet} + Ar^2OH$	1.000	0.229	1.199	0.229	1.199
$Ar^1O^{\bullet} + R^1H$	0.802	0.305	1.401	0.245	1.215
$Ar^1O^{\bullet} + R^2H$	0.802	0.341	1.437	0.273	1.243
$Ar^1O^{\bullet} + R^3H$	0.802	0.321	1.417	0.257	1.227
$Am^{\bullet} + Ar^1OH$	1.083	0.168	1.138	0.182	1.191
$Am^{\bullet} + Ar^2OH$	1.083	0.179	1.149	0.194	1.203
$Am^{\bullet} + AmH$	1.000	0.210	1.219	0.210	1.219
$Am^{\bullet} + R^3H$	0.869	0.270	1.366	0.235	1.244
$AmO^{\bullet} + Ar^1OH$	1.000	0.216	1.186	0.216	1.186
$AmO^{\bullet} + Ar^2OH$	1.000	0.232	1.202	0.232	1.202
$AmO^{\bullet} + AmH$	0.927	0.191	1.200	0.177	1.147
$AmO^{\bullet} + R^3H$	0.802	0.321	1.417	0.257	1.227

Table 3. Activation energies and interatomic distances in transition states calculated by formulas (5), (6), (9), (15), and (16) for reactions of 1,1-dimethylethoxy radicals with phenols

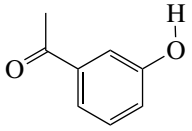
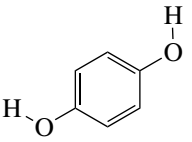
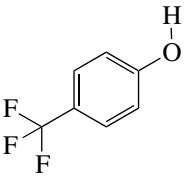
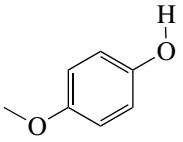
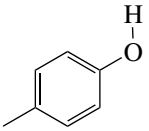
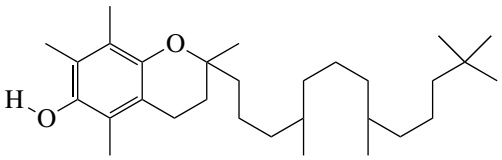
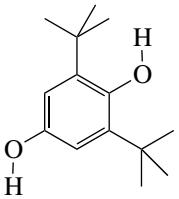
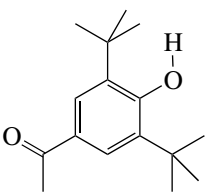
Phenol	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(PhO…H) × 10^{10}, m	r(RO…H) × 10^{10}, m
	$(CH_3)_3CO^{\bullet}$ + Ar^1OH				
	–58.4	5.3	1.62×10^8	1.131	1.261
	–82.9	1.4	8.20×10^8	1.118	1.274
PhOH	–65.9	2.7	3.95×10^8	1.122	1.270
	–52.5	7.4	7.86×10^7	1.137	1.255
	–89.1	1.4	9.00×10^8	1.118	1.274
	–72.7	1.8	5.39×10^8	1.119	1.273
	–104.9	1.4	2.00×10^9	1.118	1.274
	$(CH_3)_3CO^{\bullet}$ + Ar^2OH				
	–108.2	1.8	5.39×10^8	1.119	1.326
	–87.1	7.0	9.02×10^7	1.136	1.309

Table 3. (Contd.)

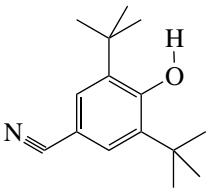
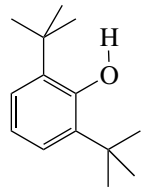
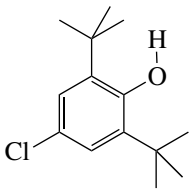
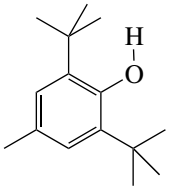
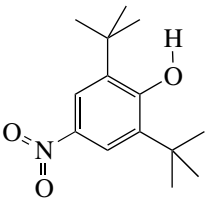
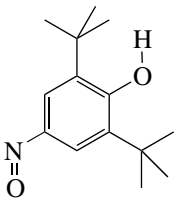
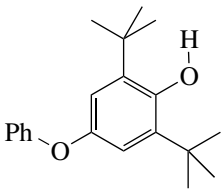
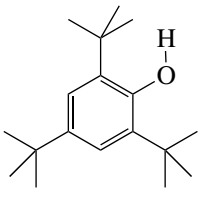
Phenol	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(PhO…H) × 10^{10}, m	r(RO…H) × 10^{10}, m
	–82.5	8.5	5.39×10^7	1.141	1.304
	–88.5	6.5	1.07×10^8	1.134	1.311
	–90.4	5.5	1.51×10^8	1.131	1.314
	–95.9	4.2	2.36×10^8	1.127	1.318
	–76.9	10.4	2.80×10^7	1.146	1.299
	–88.9	6.4	1.09×10^8	1.134	1.311
	–97.7	3.6	2.90×10^8	1.125	1.320
	–95.2	4.4	2.20×10^8	1.128	1.317

Table 4. Activation energies and interatomic distances in transition states calculated by formulas (5), (6), (9), (15), and (16) for reactions of peroxy radicals (*sec*-$RO_2^{\bullet}$) with phenols

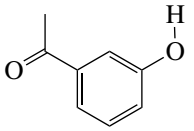
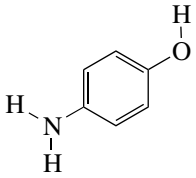
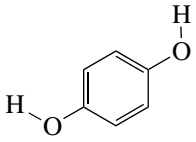
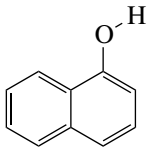
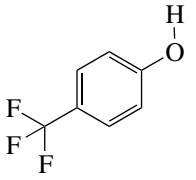
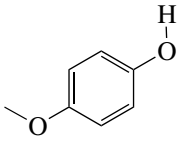
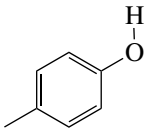
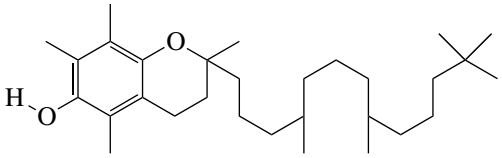
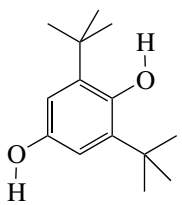
Phenol	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(PhO…H) × 10^{10}, m	r(ROO…H) × 10^{10}, m
sec-$RO_2^{\bullet}$ + Ar^1OH					
	11.0	28.6	1.80×10^3	1.192	1.171
	–8.8	18.5	5.68×10^4	1.168	1.195
	–13.5	16.3	1.21×10^5	1.162	1.201
	–22.1	12.4	4.61×10^5	1.152	1.211
PhOH	3.5	24.6	6.97×10^3	1.183	1.180
	16.9	31.8	5.94×10^2	1.200	1.163
	–19.7	13.5	3.20×10^5	1.155	1.208
	–3.3	21.2	2.26×10^4	1.175	1.188
	–35.5	6.8	3.17×10^6	1.135	1.228
sec-$RO_2^{\bullet}$ + Ar^2OH					
	–38.8	11.6	6.23×10^5	1.150	1.249

Table 4. (Contd.)

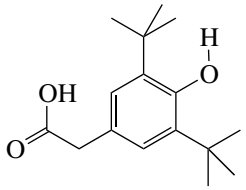
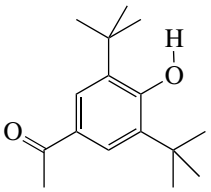
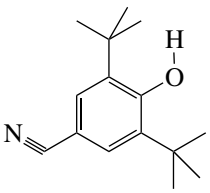
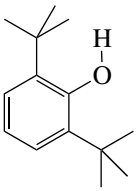
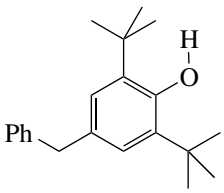
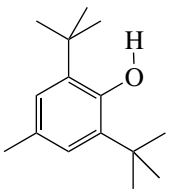
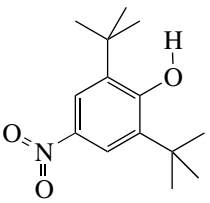
Phenol	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(PhO…H) × 10^{10}, m	r(ROO…H) × 10^{10}, m
	–28.6	16.1	1.30×10^5	1.162	1.237
	–17.7	21.3	2.15×10^4	1.175	1.224
	–13.1	23.7	9.74×10^3	1.181	1.218
	–19.1	20.7	2.73×10^4	1.173	1.226
	–25.8	17.4	8.27×10^4	1.165	1.234
	–26.5	17.1	9.26×10^4	1.165	1.234
	–7.5	26.5	3.60×10^3	1.188	1.211

Table 5. Activation energies and interatomic distances in transition states calculated by formulas (5), (6), (9), (15), and (16) for reactions of the phenoxy radical $C_6H_5O^{\bullet}$ with phenols

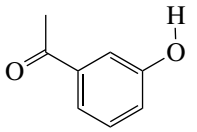
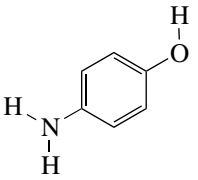
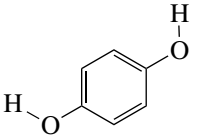
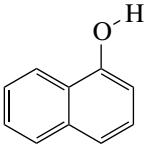
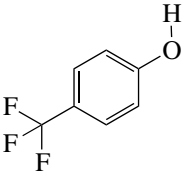
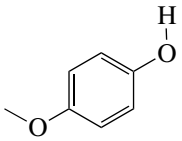
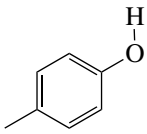
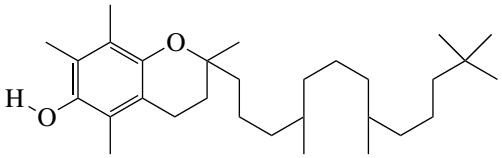
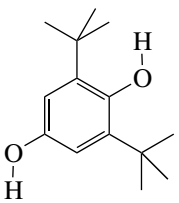
ArOH	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(ArO…H) × 10^{10}, m	r(PhO…H) × 10^{10}, m
$C_6H_5O^{\bullet}$ + Ar^1OH					
	7.5	23.5	3.12×10^5	1.181	1.161
	–12.3	13.7	8.90×10^6	1.155	1.187
	–17.0	11.6	1.85×10^7	1.150	1.192
	–25.6	7.9	6.66×10^7	1.139	1.203
PhOH	0.0	19.6	1.17×10^6	1.171	1.171
	13.4	26.6	1.06×10^5	1.188	1.154
	–23.2	8.9	4.70×10^7	1.142	1.200
	–6.8	16.3	3.66×10^6	1.162	1.180
	–39.0	2.5	4.17×10^8	1.122	1.220
$C_6H_5O^{\bullet}$ + Ar^2OH					
	–42.3	4.9	1.87×10^7	1.129	1.232

Table 5. (Contd.)

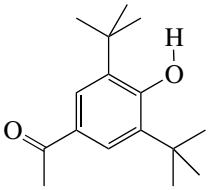
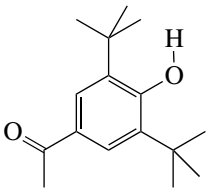
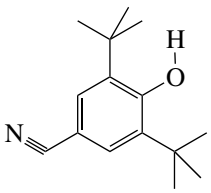
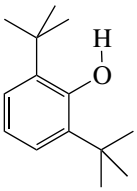
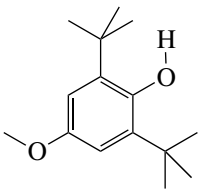
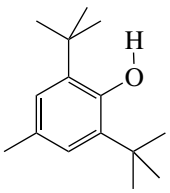
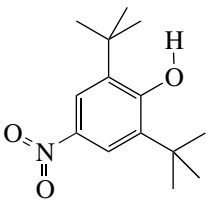
ArOH	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(ArO…H) × 10^{10}, m	r(PhO…H) × 10^{10}, m
	–32.1	8.9	4.71×10^6	1.142	1.219
	–21.2	13.5	9.65×10^5	1.155	1.206
	–16.6	15.6	4.77×10^5	1.161	1.200
	–22.6	12.9	1.19×10^6	1.153	1.208
	–41.9	5.0	1.78×10^8	1.130	1.231
	–30.0	9.8	3.50×10^6	1.144	1.217
	–11.0	18.1	1.97×10^5	1.167	1.194

Table 6. Activation energies and interatomic distances in transition states calculated by formulas (5), (6), (9), (15), and (16) for reactions of the bis(1,1-dimethylethyl)nitroxy radical with phenols

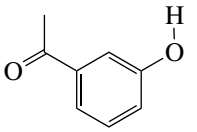
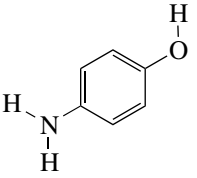
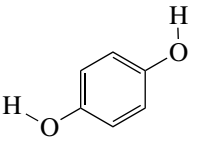
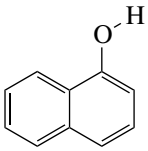
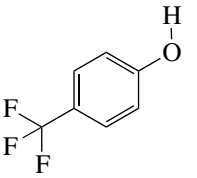
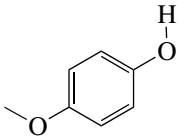
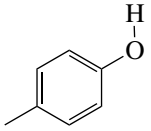
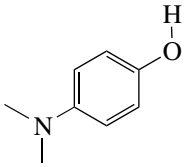
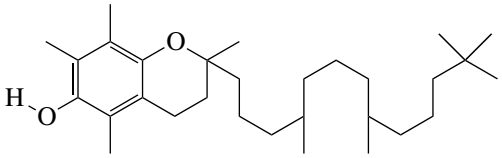
PhOH	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(PhO…H) × 10^{10}, m	r(AmO…H) × 10^{10}, m
$[(CH_3)_3C]_2NO^{\bullet}$ + Ar^1OH					
	33.9	44.2	2.49×10^1	1.283	1.089
	14.1	33.0	1.17×10^3	1.254	1.118
	9.4	30.5	2.75×10^3	1.247	1.125
	0.8	26.1	1.26×10^4	1.235	1.137
PhOH	26.4	39.9	1.11×10^2	1.272	1.100
	39.8	47.8	7.37×10	1.291	1.108
	3.2	27.3	8.29×10^3	1.238	1.134
	19.6	36.0	4.15×10^2	1.262	1.110
	–13.8	19.1	1.41×10^5	1.166	1.206
	–12.6	19.6	1.17×10^5	1.168	1.204

Table 6. (Contd.)

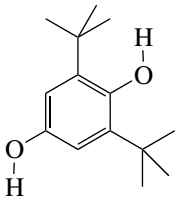
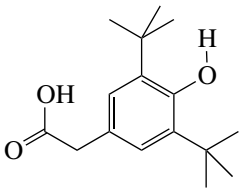
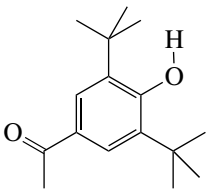
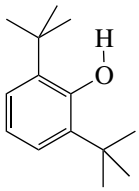
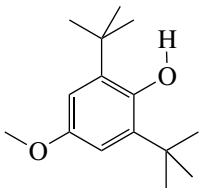
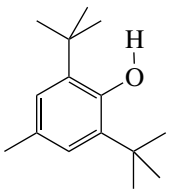
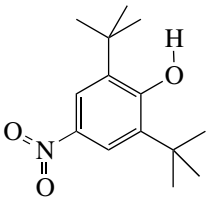
PhOH	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(PhO…H) × 10^{10}, m	r(AmO…H) × 10^{10}, m
		$[(CH_3)_3C]_2NO^{\bullet}$ + Ar^2OH			
	–15.9	24.7	2.03×10^4	1.184	1.220
	–5.7	29.6	3.85×10^3	1.196	1.208
	5.2	35.0	5.93×10^2	1.208	1.196
	3.8	34.3	7.58×10^2	1.206	1.198
	–15.5	24.9	1.90×10^4	1.185	1.219
	–3.6	30.6	2.71×10^3	1.198	1.206
	15.4	40.4	9.43×10^1	1.219	1.185

Table 7. Enthalpies, activation energies, and interatomic distances in transition states calculated by formulas (5), (6), (9), (15), and (16) for reactions of the diphenylaminyl radical $Ph_2N^{\bullet}$ with amines

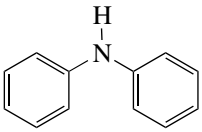
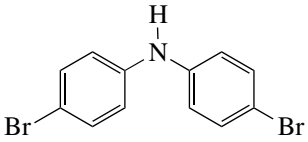
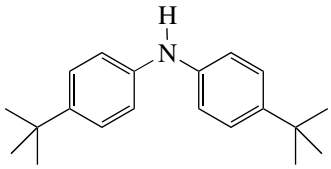
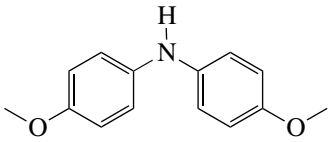
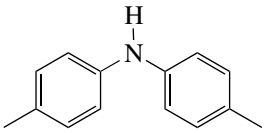
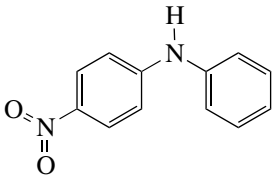
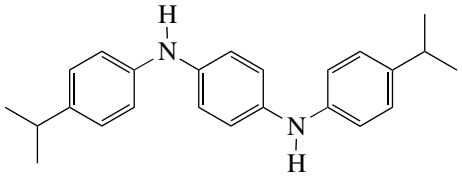
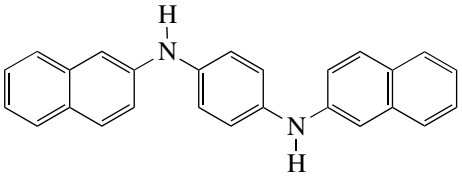
Amine	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(Am…H) × 10^{10}, m	r(Ph$_2$N…H) × 10^{10}, m
	0.0	15.3	5.21×10^5	1.220	1.220
	–0.5	15.0	5.77×10^5	1.219	1.221
	–5.9	12.4	1.41×10^6	1.211	1.229
	–16.1	7.7	7.09×10^6	1.195	1.245
	–7.2	11.8	1.73×10^6	1.209	1.231
	8.2	19.5	1.23×10^5	1.233	1.207
	–31.3	1.5	1.19×10^8	1.171	1.269
	–18.1	6.9	1.87×10^7	1.192	1.248

Table 7. (Contd.)

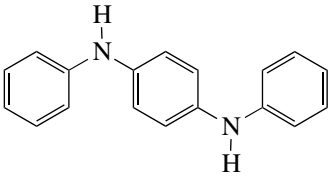
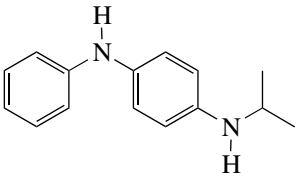
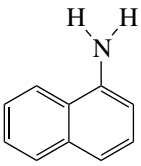
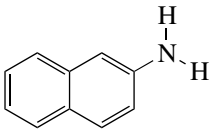
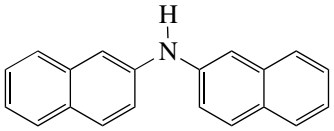
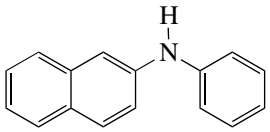
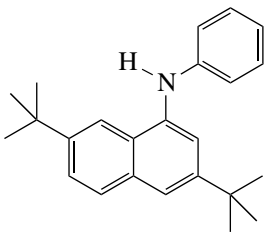
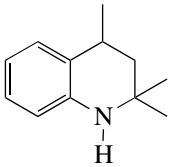
Amine	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(Am…H) × 10^{10}, m	r(Ph$_2$N…H) × 10^{10}, m
	–8.8	11.1	4.41×10^6	1.206	1.234
	–15.5	8.0	6.40×10^6	1.196	1.244
	10.0	20.5	1.74×10^5	1.236	1.204
	14.8	23.1	7.14×10^4	1.243	1.197
	–4.5	13.1	1.11×10^6	1.213	1.227
	–1.8	14.4	7.09×10^5	1.217	1.223
	–19.8	6.1	1.23×10^7	1.189	1.251
	–3.8	17.2	2.71×10^5	1.214	1.226

Table 8. Enthalpies, activation energies, and interatomic distances in transition states calculated by formulas (6), (7), (9), (15), and (16) for reactions of *sec*-$RO_2^{\bullet}$ with amines

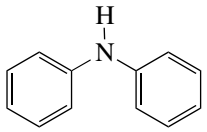
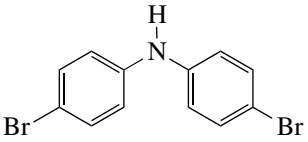
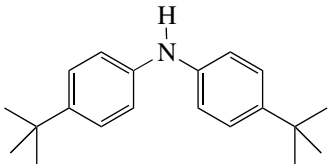
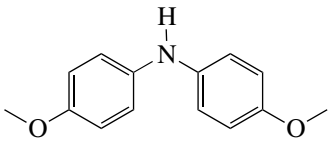
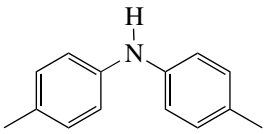
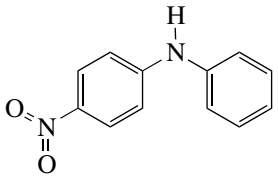
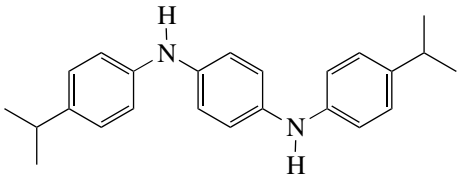
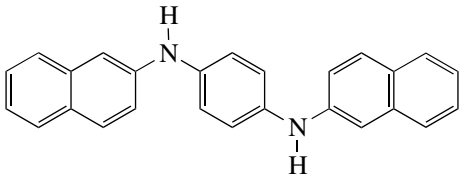
Amine	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(Am…H) × 10^{10}, m	r(ROO…H) × 10^{10}, m
	–0.8	19.6	1.19×10^5	1.222	1.175
	–1.3	19.3	1.32×10^5	1.212	1.175
	–6.7	16.8	3.11×10^5	1.214	1.182
	–16.9	12.3	1.46×10^6	1.201	1.196
	–8.0	16.2	3.85×10^5	1.213	1.184
	7.4	23.6	3.01×10^4	1.233	1.164
	–31.9	6.2	2.37×10^7	1.181	1.216
	–18.9	11.4	3.98×10^6	1.198	1.199

Table 8. (Contd.)

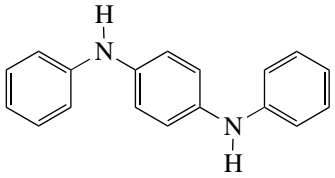
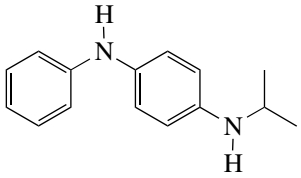
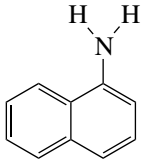
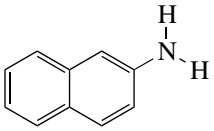
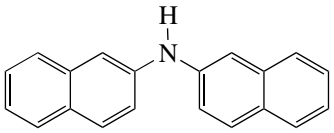
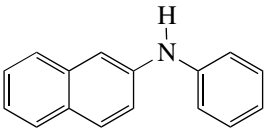
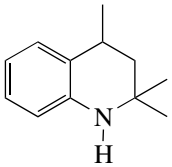
Amine	ΔH, kJ/mol	E, kJ/mol	k(350 K), l mol^{-1} s^{-1}	r(Am…H) × 10^{10}, m	r(ROO…H) × 10^{10}, m
	–9.6	15.5	9.72×10^5	1.211	1.186
	–16.3	12.5	1.36×10^5	1.202	1.195
	9.2	24.5	4.41×10^4	1.236	1.161
	14.0	27.0	1.87×10^4	1.242	1.155
	–5.3	17.4	2.53×10^5	1.216	1.181
	–2.6	18.7	1.62×10^5	1.248	1.148
	3.0	21.4	6.40×10^4	1.252	1.145

Table 9. Enthalpies, activation energies, and interatomic distances in transition states calculated by formulas (6), (7), (9), (15), and (16) for reactions of phenoxy radicals with cumene

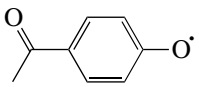
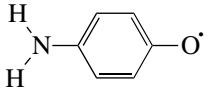
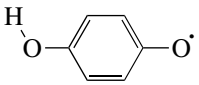
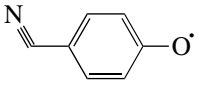
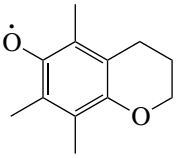
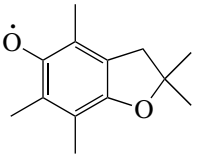
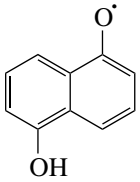
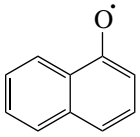
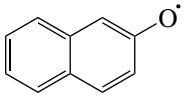
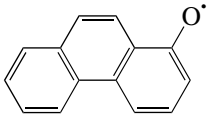
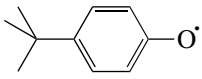
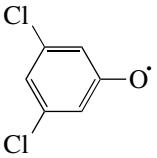
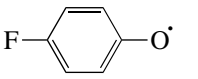
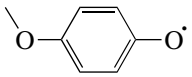
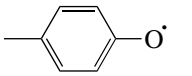
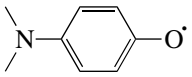
Phenoxyl	ΔH, kJ/mol	E, kJ/mol	k_{10}(400 K), l mol^{-1} s^{-1}	r(C…H) × 10^{10}, m	r(O…H) × 10^{10}, m
	–16.9	44.8	1.41×10^2	1.398	1.246
	–2.0	51.1	21.4	1.412	1.232
	2.7	53.1	15.5	1.416	1.228
	–15.5	45.4	1.19×10^2	1.399	1.245
	23.9	62.9	0.60	1.436	1.208
	28.7	65.2	0.30	1.440	1.204
	21.2	61.6	0.89	1.433	1.211
	11.3	57.0	3.58	1.424	1.220
	0.9	52.3	14.6	1.414	1.230
	0.0	51.9	16.4	1.413	1.231
PhO$^{\bullet}$	–14.3	45.8	1.02×10^2	1.400	1.244
	–5.4	49.6	33.2	1.408	1.236
	–31.5	39.0	8.05×10^2	1.384	1.260

Table 9. (Contd.)

Phenoxyl	ΔH, kJ/mol	E, kJ/mol	k_{10}(400 K), l mol^{-1} s^{-1}	r(C…H) × 10^{10}, m	r(O…H) × 10^{10}, m
	–10.3	47.5	62.0	1.404	1.240
	8.9	55.9	5.0	1.422	1.222
	–7.5	48.7	43.5	1.406	1.238
	25.9	63.9	45.2	1.438	1.206

X$^{\bullet}$	$RO_2^{\bullet}$	$Ar^1O^{\bullet}$	$Ar^2O^{\bullet}$	$AmO^{\bullet}$
Δr(X$^{\bullet}$ + Ar^1OH) × 10^{10}, m	0.406	0.389	0.407	0.348
Δr(X$^{\bullet}$ + Ar^2OH) × 10^{10}, m	0.441	0.407	0.443	0.371
$\Delta\Delta r$ × 10^{10}, m	0.035	0.016	0.036	0.023

In these reactions, steric repulsion in the transition state increases the interatomic distance X…H…OAr^2, on the average, by $\Delta\Delta r$ = (0.027 ± 0.008) × 10^{-10} m.

CONCLUSIONS

All factors influencing the classical barrier of the reaction $E_{e,0}$ manifest themselves in the transition-state geometry by the elongation or shortening of the interatomic distance in the reaction center.

Factor	Triplet repulsion	Electronegativity	π-Bond	Steric repulsion
Reaction center	O…H…O	N…H…O	O…H…R^2	Ar^2O…H…X
Comparison center	O…H…C	O…H…O	O…H…R^1	Ar^1O…H…Ar^1
$\Delta\Delta r$ × 10^{10}, m	0.130	0.041	0.055	0.027

The reaction enthalpy has no effect on the distance r(X…H…Y) but affects the distances r(Y…H) and r(X…H), which follows from formulas (10)–(12). The increments obtained in this work make it possible to construct the geometry of a reaction center of the reactions of antioxidants using the distance r(Y…H…X) for the same class of reactions.

ACKNOWLEDGMENTS

This study was supported by the Division of Chemistry and Materials Science of the Russian Academy of Sciences in the framework of the program Theoretical and Experimental Investigation of the Chemical Bond Nature and Mechanisms of the Most Important Chemical Reactions and Processes.

REFERENCES

1. Howard, J.A., *Adv. Free Radical Chem.*, 1972, vol. 4, p. 49.
2. Denisov, E.T. and Khudyakov, I.V., *Chem. Rev.*, 1987, vol. 87, p. 1313.
3. Roginskii, V.A., *Fenol'nye antioksidanty. Reaktsionnaya sposobnost' i effektivnost'* (Phenolic Antioxidants: Reactivity and Effectiveness), Moscow: Nauka, 1988.
4. Denisov, E.T. and Azatyan, V.V., *Inhibition of Chain Reactions*, London: Gordon and Breach, 2000.
5. Denisov, E.T. and Denisova, T.G., *Handbook of Antioxidants*, Boca Raton: CRC, 2000.
6. Denisov, E.T. and Denisova, T.G., *Kinet. Katal.*, 1993, vol. 34, no. 3, p. 424.

7. Denisov, E.T. and Drozdova, T.I., *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 176.
8. Denisov, E.T., *Kinet. Katal.*, 1994, vol. 35, no. 5, p. 671.
9. Denisov, E.T., *Kinet. Katal.*, 1995, vol. 36, no. 3, p. 381.
10. Denisov, E.T., *Khim. Fiz.*, 1995, vol. 14, no. 10, p. 21.
11. Denisov, E.T. and Drozdova, T.I., *Kinet. Katal.*, 1997, vol. 38, no. 1, p. 43.
12. Denisov, E.T. and Varlamov, V.T., *Kinet. Katal.*, 1997, vol. 38, no. 1, p. 36.
13. Denisov, E.T., Denisova, T.G., Geletii, Yu.V., and Balavuan, Zh., *Neftekhimiya*, 1997, vol. 37, no. 5, p. 402.
14. Denisov, E.T., *Usp. Khim.*, 1997, vol. 66, no. 10, p. 953.
15. Shestakov, A.F. and Denisov, E.T., *Izv. Akad. Nauk, Ser. Khim.*, 2003, no. 2, p. 306.
16. Denisova, T.G. and Emel'yanova, N.S., *Kinet. Katal.*, 2003, vol. 44, no. 4, p. 485.
17. *Handbook of Chemistry and Physics*, Lide, D., Ed., Boca Raton: CRC, 1992.
18. Denisova, T.G. and Denisov, E.T., *Zh. Fiz. Khim.*, 1991, vol. 65, no. 5, p. 1208.