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Reactivity of Quinones As Alkyl Radical Acceptors

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Abstract—The enthalpies of the addition of 11 alkyl radicals to *ortho*- and *para*-benzoquinones and substituted *para*-benzoquinones and the enthalpies of formation of various alkoxyphenoxyl radicals have been calculated. Experimental data for the addition of alkyl radicals to quinones are analyzed in terms of the intersection of two parabolic potential curves, and parameters characterizing this class of reactions are calculated. The classical potential barrier of the thermally neutral reaction of alkyl radical addition to benzoquinone is $E_{e,0}$ = 82.1 kJ/mol. This class of reactions is compared to other classes of free-radical addition reactions. The interaction between the electrons of the reaction center and the π electrons of the aromatic ring is a significant factor in the activation energy. Activation energies, rate constants, and the geometric parameters of the transition state have been calculated for 40 reactions of alkyl radical addition to quinones. Strong polar interaction has been revealed in the addition of polar macroradicals to quinones, and its contribution to the activation energy has been estimated. Kinetic parameters, activation energies, and rate constants have been calculated for the reverse reactions of alkoxyphenoxyl radical decomposition to quinone and alkyl. The competition between chain termination and propagation reactions in alkoxyphenol-inhibited hydrocarbon oxidation is discussed.

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INTRODUCTION

Quinones (Q) are acceptors of alkyl radicals ($R^{\bullet}$) and well-known inhibitors of radical polymerization [1–3]. The addition of Q to a macroradical yields a low-reactivity alkoxyphenoxyl radical, resulting in chain termination:

$$R^{\bullet} + Q \longrightarrow RQ^{\bullet},$$

$$R^{\bullet} + RQ^{\bullet} \longrightarrow RQR.$$

At the same time, *ortho*- and *para*-alkoxyphenols are very active antioxidants [4–6]. Their oxidation-inhibiting efficiency depends, in particular, on the decomposition of the phenoxyl radicals forming from them, the reaction responsible for chain propagation [4, 6]:

$$R^1O_2^{\bullet} + ROC_6H_4OH \longrightarrow R^1OOH + ROC_6H_4O^{\bullet},$$

$$ROC_6H_4O^{\bullet} \longrightarrow R^{\bullet} + OC_6H_4O,$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}.$$

Thus, the reactivity of quinones as acceptors of alkyl radicals and the reactivity of alkoxyphenoxyl radicals in the reverse decomposition reaction are of interest to both radical polymerization and antioxidant chemistry.

In the present work, the parabolic model (intersecting parabolas method, IPM) [7, 8] is used in the analysis and kinetic calculation of the parameters of addition reactions. The geometric parameters of the transition state (TS) in the reactions considered were calculated using the reduced parabolic model (RIPM) [9–11]. The data thus obtained allowed a theoretical analysis to be carried out for the temperature limit of the efficiency of alkoxyphenols as antioxidants.

COMPUTATIONAL PROCEDURE

Enthalpy of the Addition of Alkyl Radicals to Quinones

In the reaction

$$R^{\bullet} + Q \longrightarrow RQ^{\bullet} \quad \text{(add)}$$

the radical $R^{\bullet}$ adds to the oxygen atom of quinone to form the alkoxyphenoxyl radical $RQ^{\bullet}$. The enthalpy of this reaction, ΔH_{add}, is

$$\Delta H_{\text{add}} = \Delta H_f^0(RQ^{\bullet}) - \Delta H_f^0(R^{\bullet}) - \Delta H_f^0(Q). \quad (1)$$

The enthalpies of formation of the alkyl and phenoxyl radicals were calculated using the enthalpies of formation of the corresponding molecules and the dissociation energies of the bonds whose cleavage produces these radicals:

$$\Delta H_f^0(R^{\bullet}) = \Delta H_f^0(RH) + D_{R-H} - \Delta H_f^0(H^{\bullet}), \quad (2)$$

$$\Delta H_f^0(RQ^{\bullet}) = \Delta H_f^0(RQH) + D_{O-H} - \Delta H_f^0(H^{\bullet}). \quad (3)$$

Because the enthalpy of formation of the alkoxyphenols is unknown, for R = CH_3 [4], ΔH_f^0(RQH) was derived from the difference of the enthalpies of formation of ROMe and MeOMe using the modified increment rule [12]:

$$\begin{aligned}&\Delta H_{\mathrm{f}}^{0}(\mathrm{RQH})\\&= \Delta H_{\mathrm{f}}^{0}(\mathrm{MeQH}) + \Delta H_{\mathrm{f}}^{0}(\mathrm{ROMe}) - \Delta H_{\mathrm{f}}^{0}(\mathrm{MeOMe}).\end{aligned} \tag{4}$$

The enthalpies of formation of RH are known [13], the strengths of C–H bonds are also available [14, 15], $\Delta H_{\mathrm{f}}^{0}(\mathrm{H}^{\bullet}) = 218$ kJ/mol [13], and $\Delta H_{\mathrm{f}}^{0}$ (*para*-benzoquinone) = –122.9 kJ/mol [13]. The enthalpies of formation of substituted quinones and alkoxyphenols were calculated using the increment rule [12], the enthalpy of formation of 4-methoxyphenol is $\Delta H_{\mathrm{f}}^{0}(4\text{-}\mathrm{MeOC_6H_4OH}) = -242 \pm 7$ kJ/mol [4], and the O–H bond dissociation energies for phenols were taken from a handbook [4] or were calculated from available data using the additivity rule applied to the effects of substituents on $D_{\mathrm{O-H}}$.

Kinetic Parameters of the Addition Reaction in the Framework of the IPM

In the IPM, bimolecular addition is characterized by the enthalpy ΔH_{e}, the classical potential barrier E_{e}, the coefficient α, the product br_{e} (where $2b^2$ is the force constant of the attacked C=O bond and r_{e} is the total elongation of the reacting bonds in the TS), and the preexponential factor A. Except ΔH_{e} and E_{e}, all parameters are constant for a given class of reactions. The enthalpy ΔH_{e} includes the algebraic sum of zero-point energies of the bonds that form or break in the elementary reaction:

$$\Delta H_{\mathrm{e}} = \Delta H + 0.5hN_{\mathrm{A}}\sum \nu_i, \tag{5}$$

$$\begin{aligned}0.5hN_{\mathrm{A}}\sum \nu_i &= 0.5hN_{\mathrm{A}}(2\nu_{\mathrm{C=O}} - 3\nu_{\mathrm{C-O}})\\&= 0.2\ \mathrm{kJ/mol}.\end{aligned} \tag{6}$$

As a result of alkyl addition to quinone, two C=O groups disappear ($0.5hN_{\mathrm{A}}\nu = 10$ kJ/mol [8]) and three C–O bonds are formed ($0.5hN_{\mathrm{A}}\nu = 6.6$ kJ/mol [7]), so $0.5hN_{\mathrm{A}}\sum \nu_i = 0.2$ kJ/mol.

The classical potential barrier E_{e} is related to the Arrhenius activation energy $E = RT\ln(A/k)$ through a simple equation ($0.5hN_{\mathrm{A}}\nu_{\mathrm{C=O}} = 10$ kJ/mol):

$$E_{\mathrm{e}} = RT\ln(A/k) + 0.5hN_{\mathrm{A}}\nu_{\mathrm{C=O}} - 0.5RT. \tag{7}$$

The preexponential factor for $\mathrm{R}^{\bullet}$ addition to the carbonyl group of quinone is taken to be $A = 10^8$ l mol^{-1} s^{-1}, as in the case of $\mathrm{R}^{\bullet}$ addition to the C=C bond [8]. The coefficient α is expressed as $\alpha = b_{\mathrm{C=O}}/b_{\mathrm{C-O}}$. For the C=O group, the frequency of stretching vibrations is $\nu = 1765$ cm^{-1} [13] and, therefore, $b = 2\pi\nu\sqrt{\mu} = 58.38 \times 10^{10}$ (kJ/mol)$^{1/2}$ m^{-1}, where μ is the reduced mass of the C=O bond. For the ordinary bond C–O, $b = 38.14 \times 10^{10}$ (kJ/mol)$^{1/2}$ m^{-1} [7] and, hence, $\alpha = 1.531$. Thus, $\mathrm{R}^{\bullet}$ addition to quinones as a class of reactions is characterized by the following parameters and corrections: $\alpha = 1.531$, $b = 58.38 \times 10^{10}$ (kJ/mol)$^{1/2}$ m^{-1}, $\Delta H_{\mathrm{e}} = \Delta H + 0.2$ kJ/mol, and $E_{\mathrm{e}} = E + 10 - 0.5RT$.

The br_{e} value calculated from experimental data using the equation

$$br_{\mathrm{e}} = \alpha\sqrt{E_{\mathrm{e}} - \Delta H_{\mathrm{e}}} + \sqrt{E_{\mathrm{e}}} \tag{8}$$

is given in Results and Discussion. This value allows one to calculate the activation energy of any reaction of this class from the enthalpy of this reaction:

$$\sqrt{E_{\mathrm{e}}} = B\left\{\alpha\sqrt{1 + \frac{\Delta H_{\mathrm{e}}}{Bbr_{\mathrm{e}}}} - 1\right\}, \tag{9}$$

where $B = br_{\mathrm{e}}/(\alpha^2 - 1)$.

TS Interatomic Distances in the Addition Reaction

We have recently developed an algorithm for calculating TS interatomic distances for free-radical addition reactions [9, 10]. This algorithm includes calculating the interatomic distances in the reaction center using the RIPM [9] and correlating these distances with the results of DFT calculations [10]. The calculation was performed using the following formulas. The distance $r^{\#}(\mathrm{C}\ldots\mathrm{O})$ between the C and O atoms of the carbonyl group of quinone (these atoms bear a free valence) is calculated by the formula [11]

$$r^{\#}(\mathrm{C\underline{\ldots}O}) \times 10^{10},\ \mathrm{m} = r(\mathrm{C{-}O}) + \frac{\beta D_{\mathrm{e}}^{\#}}{b_{\mathrm{f}}^{\#}}, \tag{10}$$

where $r(\mathrm{C{-}O}) = 1.416 \times 10^{-10}$ m is the length of the C–O bond formed in alkoxyphenol [13], $D_{\mathrm{e}}^{\#} = \Delta H_{\mathrm{e}} + E_{\mathrm{e}}$, $2(b_{\mathrm{f}}^{\#})^2$ is the effective force constant of the bond forming in the TS, and the coefficient $\beta = 0.826$ is obtained by comparing RIPM and DFT data. The coefficient $b_{\mathrm{f}}^{\#}$ was calculated by the correlation equation [9]

$$\begin{aligned}&b_{\mathrm{f}}^{\#}\ (\mathrm{kJ^{1/2}mol^{-1/2}\ m^{-1}})\\&= 2.28 \times 10^{9}D_{\mathrm{e}}^{\#} - 3.32 \times 10^{6}(D_{\mathrm{e}}^{\#})^2.\end{aligned} \tag{11}$$

According to DFT data, the elongation of the carbonyl bond in the TS of these reactions is insignificant and is given by the formula [11]

$$r^{\#}(\mathrm{C{=}O}) \times 10^{-10},\ \mathrm{m} = r(\mathrm{C{=}O}) + \frac{\sqrt{E_{\mathrm{e}}}}{b_{\mu}}. \tag{12}$$

The length of the C=O bond is 1.210×10^{-10} m [13].

Table 1. Enthalpies of the formation of alkoxyphenoxyl radicals and of the addition of alkyl radicals to *para*- and *ortho*-benzoquinones (kJ/mol)

$R^{\bullet}$	$\Delta H_f^0(R^{\bullet})$	$\Delta H_f^0(ROMe) - \Delta H_f^0(MeOMe)$	$\Delta H_f^0(RQ^{\bullet})$	$-\Delta H_{add}$
para-OC_6H_4O (ΔH_f^0 = –122.9 kJ/mol)				
$C^{\bullet}H_3$	147.6	0.0	–114.9	139.6
$MeC^{\bullet}H_2$	120.2	–32.2	–147.1	144.4
$Me_2C^{\bullet}H$	89.3	–67.8	–182.7	149.1
$Me_3C^{\bullet}$	47.8	–99.6	–214.5	139.4
cyclo-$C_6^{\bullet}H_{11}$	67.4	–87.5	–202.4	146.9
$PhC^{\bullet}H_2$	207.4	102.1	–12.8	97.3
$MePhC^{\bullet}H$	176.0	74.1	–40.8	93.9
$Me_2PhC^{\bullet}$	140.7	46.1	–68.8	86.6
$CH_2{=}CHC^{\bullet}H_2$	170.0	79.5	–35.4	82.5
$Ph^{\bullet}$	338.6	116.3	1.4	214.3
$CH_2{=}C^{\bullet}H$	298.5	77.0	–37.9	213.5
$Me(MeOC(O))C^{\bullet}H$	250.1	–395.7	–510.6	137.6
$Me(MeOC(O))C^{\bullet}Me$	285.8	–431.0	–545.9	137.2
$Me(MeC(O)O)C^{\bullet}H$	262.4	–433.4	–548.3	163.0
ortho-OC_6H_4O (ΔH_f^0 = –104.6 kJ/mol)				
$C^{\bullet}H_3$	147.6	0.0	–109.0	152.0
$MeC^{\bullet}H_2$	120.2	–32.2	–141.2	156.8
$Me_2C^{\bullet}H$	89.3	–67.8	–176.8	161.5
$Me_3C^{\bullet}$	47.8	–99.6	–208.6	151.8
cyclo-$C_6^{\bullet}H_{11}$	67.4	–87.5	–196.5	159.3
$PhC^{\bullet}H_2$	207.4	102.1	–6.9	109.7
$MePhC^{\bullet}H$	176.0	74.1	–34.9	106.3
$Me_2PhC^{\bullet}$	140.7	46.1	–62.9	99.0
$CH_2{=}CHC^{\bullet}H_2$	170.0	79.5	–29.5	94.9
$Ph^{\bullet}$	338.6	116.3	7.3	226.7
$CH_2{=}C^{\bullet}H$	298.5	77.0	–32.0	225.9

RESULTS AND DISCUSSION

Enthalpy of $R^{\bullet}$ Addition to Quinones

The calculated enthalpies of formation of *para*- and *ortho*-alkoxyphenoxyl radicals and the enthalpies of the addition of $R^{\bullet}$ radicals to quinones are listed in Tables 1 and 2.

The enthalpy of $R^{\bullet}$ addition to *para*-benzoquinone varies in a wide range of –82 to –214 kJ/mol, and the

Table 2. Enthalpies of the formation of alkoxyphenoxyl radicals and of the addition of alkyl radicals to benzoquinones (kJ/mol)

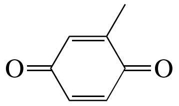
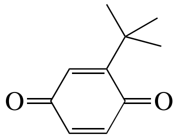
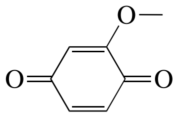
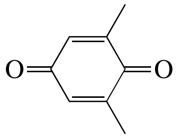
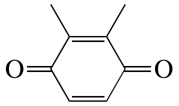
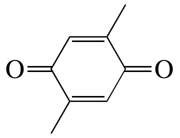
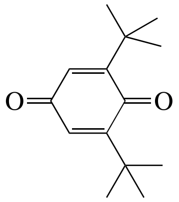
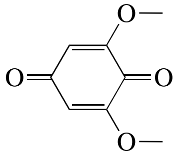
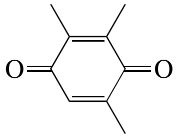
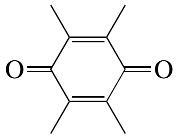
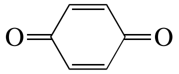
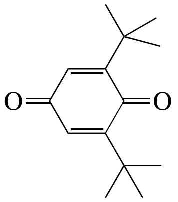
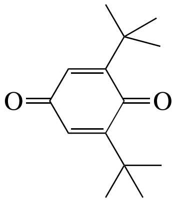
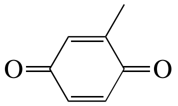
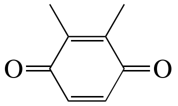
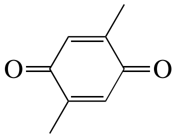
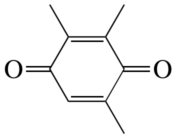
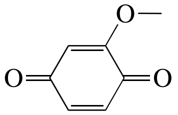
$R^\bullet$	Q	ΔH_f^0 (Q)	ΔH_f^0 (RQH)	D(RQ–H)	ΔH_f^0 ($RQ^\bullet$)	ΔH_{add}
$C^\bullet H_3$		–155.2	–272.0	343.4	–146.6	–139.0
$C^\bullet H_3$		–221.5	–330.6	343.4	–205.2	–131.3
$C^\bullet H_3$		–286.7	–389.2	341.6	–265.6	–126.5
$C^\bullet H_3$		–198.5	–308.4	331.4	–195.0	–144.1
$C^\bullet H_3$		–188.3	–304.7	332.3	–190.4	–149.7
$C^\bullet H_3$		–188.3	–308.0	341.1	–184.9	–144.2
$C^\bullet H_3$		–320.1	–422.6	327.1	–313.5	–141.0
$C^\bullet H_3$		–450.5	–546.2	334.5	–429.7	–126.8
$C^\bullet H_3$		–226.1	–333.1	331.2	–219.9	–141.4
$C^\bullet H_3$		–260.5	–380.4	342.4	–256.0	–143.1
$Bu^\bullet$		–122.9	–317.0	347.8	–187.2	–145.3

Table 2. (Contd.)

$R^{\bullet}$	Q	ΔH_f^0 (Q)	ΔH_f^0 (RQH)	D(RQ–H)	ΔH_f^0 ($RQ^{\bullet}$)	ΔH_{add}
$Me_3C^{\bullet}$		–320.1	–534.2	331.3	–420.9	–148.6
$C_6H_5^{\bullet}$		–320.1	–317.8	337.2	–198.6	–217.1
$PhC^{\bullet}HR$		–155.2	–197.9	343.4	–72.5	–93.3
$PhC^{\bullet}HR$		–188.3	–229.7	331.4	–116.3	–104.0
$PhC^{\bullet}HR$		–188.3	–233.9	341.1	–110.8	–98.5
$PhC^{\bullet}HR$		–221.4	–254.3	331.2	–141.1	–95.7
$PhC^{\bullet}HR$		–286.7	–357.3	341.4	–233.7	–80.8

same enthalpy for *ortho*-benzoquinone ranges between –99 and –227 kJ/mol. In the first approximation, the more reactive the $R^{\bullet}$ radical (the stronger the R–H bond), the lower the enthalpy of the reaction.

Radical	$Ph^{\bullet}$	$Et^{\bullet}$	$PhC^{\bullet}H_2$
D_{C-H}, kJ/mol	474	422	375
ΔH, kJ/mol	–214	–144	–97

The enthalpy of $R^{\bullet}$ addition is higher for *para*-benzoquinone than for *ortho*-benzoquinone. Methyl substituents in benzoquinone exert a weak effect on the enthalpy of addition of methyl radicals (Table 2), and methoxy substituents substantially raise the enthalpy (Table 2).

Comparison with Other Classes of Addition Reactions

The initial experimental data and the br_e values calculated by formulas (7) and (8) are presented in Table 3.

The reactions appearing in Table 3 are characterized by similar br_e values; therefore, they belong to one class. The average br_e value is 22.94 ± 0.59 $(kJ/mol)^{1/2}$, implying the following classical potential barrier for the thermally neutral reaction [8]:

$$E_{e,0} = \left\{\frac{br_e}{1+\alpha}\right\}^2 = 82.1 \pm 4.3 \text{ kJ/mol}. \qquad (13)$$

Let us compare the parameters of this reaction to the parameters of other classes of addition reactions.

Reaction	ΔH, kJ/mol	E, kJ/mol	$E_{e,0}$, kJ/mol
$C^{\bullet}H_3$ + *para*-OC_6H_4O	–139.9	6.6	82.1
$C^{\bullet}H_3 + Me_2CO \longrightarrow Me_3CO^{\bullet}$	–26.0	33.0	58.5
$C^{\bullet}H_3 + Me_2CO \longrightarrow Me_2C^{\bullet}OMe$	–9.5	35.9	52.4
$C^{\bullet}H_3 + CH_2{=}CHMe$	–100.0	19.3	76.3
$C^{\bullet}H_3 + CH_2{=}CHCH{=}CH_2$	–146.9	12.0	86.0
$C^{\bullet}H_3 + CH_2{=}CHPh$	–144.7	7.7	79.4

Clearly, the addition of a methyl radical to *para*-benzoquinone is most similar in ΔH, E, and $E_{e,0}$ to $C^{\bullet}H_3$ addition to styrene and butadiene-1,3. This is likely due to the fact that the reaction center of the TS in these reactions is adjacent to π electrons of the double bond or aromatic ring. The interaction of the π electrons of the ring with the electrons of the reaction center raises the activation energy (the effect of the repulsion of electron pairs in the TS [10]). At the same time, the reactions $Me^{\bullet}$ + quinone and $Me^{\bullet} + Me_2CO \longrightarrow Me_2C^{\bullet}OMe$, with identical structures of the reaction center, differ strongly in terms of $E_{e,0}$ from radical addition to quinones.

Theoretical Calculation of E and k for $R^{\bullet}$ Addition to para- and ortho-Benzoquinones

The activation energies were calculated by formula (9), and the rate constants of the addition of 11 radicals with various structures to *ortho*- and *para*-benzoquinones were determined using the Arrhenius formula. The results of these calculations are presented in Table 4. The activation energy of addition varies between 14 and 29 kJ/mol, and the rate constants range from 1.2×10^8

Table 3. Addition of radicals to quinones: initial kinetic data and calculated br_e values

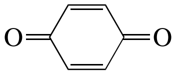
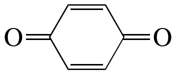
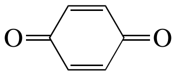
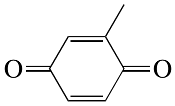
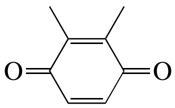
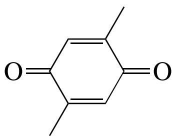
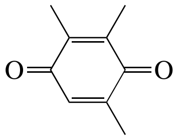
$R^{\bullet}$	Q	ΔH_{add}, kJ/mol	$k(T)$, l mol^{-1} s^{-1}	E_{add}, kJ/mol	br_e, (kJ/mol)$^{1/2}$	References
$C^{\bullet}H_3$		–139.6	4.5×10^7 (298)	3.7	22.40	[16]
$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$		–144.4	2.0×10^7 (342)	6.5	23.21	[17]
$PhC^{\bullet}HCH_2$~		–93.9	1.01×10^5 (323)	20.4	22.36	[1]
$PhC^{\bullet}HCH_2$~		–93.3	5.29×10^4 (323) 1.38×10^5 (353)	20.3 19.3	22.30 22.11	[1]
$PhC^{\bullet}HCH_2$~		–104.0	2.39×10^4 (323)	24.3	23.65	[1]
$PhC^{\bullet}HCH_2$~		–98.5	1.85×10^4 (333) 4.01×10^4 (363)	25.8 25.7	23.50 23.47	[1]
$PhC^{\bullet}HCH_2$~		–95.7	4.98×10^3 (323)	26.6	23.45	[1]
				Average	22.94 ± 0.59	

Table 4. Theoretical activation energies, rate constants, and geometric parameters of the TS for the addition of radicals to *ortho*- and *para*-benzoquinones

$R^{\bullet}$	ΔH_{add}, kJ/mol	E_{add}, kJ/mol	k(350 K), l mol^{-1} s^{-1}	$r^{\#}$(C…O) × 10^{10}, m	$r^{\#}$(C=O) × 10^{10}, m
para-Benzoquinone					
$C^{\bullet}H_3$	–139.6	6.6	2.07×10^7	1.792	1.241
$MeC^{\bullet}H_2$	–144.4	5.1	3.47×10^7	1.790	1.240
$Me_2C^{\bullet}H$	–149.1	3.7	5.61×10^7	1.789	1.238
$Me_3C^{\bullet}$	–139.4	6.7	2.00×10^7	1.792	1.241
cyclo-$C_6^{\bullet}H_{11}$	–146.9	4.3	4.56×10^7	1.790	1.239
$PhC^{\bullet}H_2$	–97.3	22.7	8.19×10^4	1.809	1.255
$MePhC^{\bullet}H$	–93.9	24.2	4.89×10^4	1.811	1.256
$Me_2PhC^{\bullet}$	–86.6	27.4	1.63×10^4	1.814	1.258
$CH_2{=}CHC^{\bullet}H_2$	–82.5	29.3	8.48×10^3	1.816	1.259
$Ph^{\bullet}$	–214.3	1.4	1.24×10^8	1.775	1.235
$CH_2{=}C^{\bullet}H$	–213.5	1.4	1.24×10^8	1.775	1.235
ortho-Benzoquinone					
$C^{\bullet}H_3$	–152.0	2.8	7.64×10^7	1.788	1.237
$MeC^{\bullet}H_2$	–156.8	1.5	1.19×10^8	1.786	1.235
$Me_2C^{\bullet}H$	–161.5	1.4	1.24×10^8	1.785	1.235
$Me_3C^{\bullet}$	–151.8	2.3	9.07×10^7	1.788	1.237
cyclo-$C_6^{\bullet}H_{11}$	–159.3	1.4	1.24×10^8	1.785	1.236
$PhC^{\bullet}H_2$	–109.7	17.5	4.89×10^5	1.804	1.251
$MePhC^{\bullet}H$	–106.3	18.9	3.02×10^5	1.805	1.252
$Me_2PhC^{\bullet}$	–99.0	22.0	1.04×10^5	1.808	1.254
$CH_2{=}CHC^{\bullet}H_2$	–94.9	23.7	5.81×10^4	1.810	1.256
$Ph^{\bullet}$	–226.7	1.4	1.24×10^8	1.775	1.235
$CH_2{=}C^{\bullet}H$	–225.9	1.4	1.24×10^8	1.775	1.235

to 1.6×10^4 l mol^{-1} s^{-1} (350 K). The activation energies thus calculated fall rather close to experimental E values.

Radical	$C^{\bullet}H_3$	$MeC^{\bullet}H_2$	$RPhC^{\bullet}H$
E(exp.), kJ/mol	3.7	6.5	20.4
E(calcd.), kJ/mol	6.6	5.1	24.2
ΔE, kJ/mol	2.9	1.4	3.8

TS Geometry in $R^{\bullet}$ Addition to >C=O

The geometry of the TS in methyl addition to the O atom of acetone was calculated earlier by the DFT method [11]. In this reaction, the TS configuration is nonlinear (Fig. 1).

The algorithm developed for the calculation of interatomic distances in the TS of addition reactions [9, 10] makes it possible to calculate the distances $r^{\#}$(C…O) and $r^{\#}$(C=O) for the reactions examined here. The $r^{\#}$(C…O) and $r^{\#}$(C=O) data calculated using formulas (10)–(12) are listed in Table 4. The addition of $R^{\bullet}$ to quinone is a very exothermic reaction and, hence, its TS is early. The C=O bond elongates insignificantly, specifically, by (1–2) × 10^{-11} m, and, by contrast, the C…O distance between the approaching $C^{\bullet}$ atom and the O atom of the carbonyl group is much longer than the C–O bond (1.416×10^{-10} m). The distance $r^{\#}$(C…O)

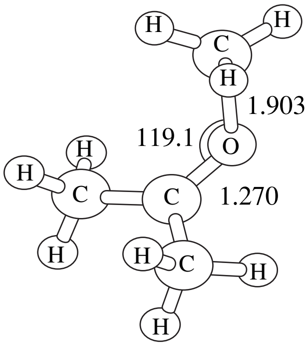


Fig. 1. Geometry of the transition state of the reaction of methyl radical addition to the oxygen atom of acetone (calculated by the DFT method [10]).

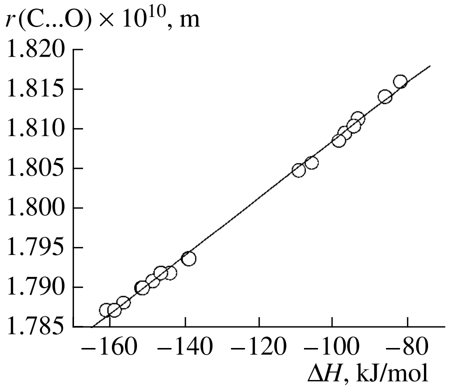


Fig. 2. Correlation between the interatomic distance C...O in the TS and the enthalpy of alkyl radical addition to benzoquinones.

and the enthalpy of the reaction are linearly correlated (Fig. 2) in the following analytical form:

$$r^{\#}(\mathrm{C}\ldots\mathrm{O}) \times 10^{10} = 1.85 + (3.93 \pm 0.05)\Delta H. \quad (14)$$

Polar Effect in Addition Reactions

When a radical having a polar group adds to quinone, the polar reaction center C=O...C and the polar group X of the $\mathrm{RXC^{\bullet}H}$ radical interact in the TS. This interaction makes a contribution (ΔE_{μ}) to the activation energy [7, 8]. This contribution can be positive or negative. It can be estimated from experimental data, specifically, the Arrhenius activation energy (E_{μ}) that characterizes the addition of $\mathrm{RXC^{\bullet}H}$ to quinone. For this purpose, the parameter $(br_e)_{\mu}$, which characterizes the classical potential barrier of the reaction examined, is calculated and is then compared to the parameter br_e of the reaction of nonpolar $\mathrm{R^{\bullet}}$ with quinone Q. The contribution from the polar interaction to the activation energy is estimated by the formula [7]

$$\Delta E_{\mu} = \{(br_e)_{\mu}^2 - (br_e)^2\}(1+\alpha)^{-2}. \quad (15)$$

Table 5 contains the initial experimental data (reaction rate constants) and the ΔE_{μ} increments calculated by formula (15) for the addition of *para*-benzoquinone to macroradicals that are capable of carrying on free-radical polymerization and contain polar groups. It can be seen that, for the three reactions considered, the polar interaction greatly increases the activation energy: its contribution is 29.8 kJ/mol for the methyl acrylate macroradical, 27.8 kJ/mol for methyl methacrylate, and 52.1 kJ/mol for vinyl acetate.

Decomposition of Alkoxyphenoxyl Radicals

Alkoxyphenols have a weak O–H bond and are widely used as antioxidants [4]. Their inhibiting effect on hydrocarbon oxidation is complicated by the decomposition, at elevated temperatures, of the phenoxyl radicals that they produce. The decomposition of an alkoxyphenoxyl radical yields an alkyl radical that continues the chain oxidation of the substrate:

$$\begin{gathered}\mathrm{ROC_6H_4O^{\bullet}} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{OC_6H_4O}, \\ \mathrm{R^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{RO_2^{\bullet}}.\end{gathered} \quad (\mathrm{d})$$

Since the decomposition of the alkoxyphenoxyl radical (reaction (d)) is the reverse of $\mathrm{R^{\bullet}}$ addition to quinone (reaction (add)), these reactions have the same TS, $\Delta H_d = -\Delta H_{add}$, and $E_d = E_{add} + \Delta H_d$. The values of ΔH_{add}, E_{add} (see Table 4), E_d, and k_d for the decomposition of 11 *para*- and 11 *ortho*-alkoxyphenoxyl radicals are presented in Table 6. When calculating k_d, we used the preexponential factor $A_d = 10^{14}$ s^{-1}. This value is typical of

Table 5. Contribution from the polar effect (ΔE_{μ}) to the activation energy in the addition of polar macroradicals to *para*-benzoquinones

Monomer	ΔH_{add}, kJ/mol	T, K	k_{add}, l mol^{-1} s^{-1}	E_{add}, kJ/mol	br_e, (kJ/mol)$^{1/2}$	ΔE_{μ}, kJ/mol
$\mathrm{CH_2{=}CHCOOMe}$	137.6	317	1.2×10^3	31.7	26.78	29.8
$\mathrm{CH_2{=}CMeCOOMe}$	137.2	317	2.4×10^3	29.9		
$\mathrm{CH_2{=}CMeCOOMe}$	137.2	323	2.92×10^3	29.9	26.54	27.8
$\mathrm{CH_2{=}CMeCOOMe}$	137.2	333	2.96×10^3	30.8		
$\mathrm{CH_2{=}CHOC(O)Me}$	163.0	317	5.0×10	40.8	29.33	52.1

Table 6. Theoretical activation energies and the rate constants of decomposition of the *ortho*- and *para*-alkoxyphenoxyl radicals

R	ΔH_d, kJ/mol	E_{add}, kJ/mol	E_d, kJ/mol	k_d(400 K), s^{-1}
		para-Benzoquinone		
CH_3	139.6	6.6	146.2	8.10×10^{-6}
$MeCH_2$	144.4	5.1	149.5	3.00×10^{-6}
Me_2CH	149.1	3.7	152.8	1.11×10^{-6}
Me_3C	139.4	6.7	146.1	8.35×10^{-6}
cyclo-C_6H_{11}	146.9	4.3	151.2	1.80×10^{-6}
$PhCH_2$	97.3	22.7	120.0	2.14×10^{-2}
MePhCH	93.9	24.2	118.1	3.78×10^{-2}
Me_2PhC	86.6	27.4	114.0	1.30×10^{-1}
$CH_2{=}CHCH_2$	82.5	29.3	111.8	2.51×10^{-1}
Ph	214.3	1.4	215.7	6.80×10^{-15}
$CH_2{=}CH$	213.5	1.4	214.9	8.66×10^{-15}
		ortho-Benzoquinone		
CH_3	152.0	2.8	154.8	6.10×10^{-7}
$MeCH_2$	156.8	1.5	158.3	2.13×10^{-7}
Me_2CH	161.5	1.4	162.9	5.34×10^{-8}
Me_3C	151.8	2.3	154.1	7.53×10^{-7}
cyclo-C_6H_{11}	159.3	1.4	160.7	1.58×10^{-7}
$PhCH_2$	109.7	17.5	127.2	2.45×10^{-3}
MePhCH	106.3	18.9	125.2	4.47×10^{-3}
Me_2PhC	99.0	22.0	121.0	1.58×10^{-2}
$CH_2{=}CHCH_2$	94.9	23.7	118.6	3.26×10^{-2}
Ph	226.7	1.4	228.1	1.63×10^{-16}
$CH_2{=}CH$	225.9	1.4	227.3	2.08×10^{-16}

the homolytic cleavage of molecules [14]. It can be seen that E_d varies in a wide range of 112 to 216 kJ/mol.

The calculated E_d data make it possible to estimate the temperature at which alkoxyphenol loses its antioxidant efficiency. In a substrate being oxidized, alkoxyphenol RQH and its phenoxyl radical react as follows (the reactions are numbered as in [4]):

$$R^1O_2^{\bullet} + RQH \longrightarrow R^1OOH + RQ^{\bullet}, \qquad (VII)$$

$$R^1O_2^{\bullet} + RQ^{\bullet} \longrightarrow R^1OH + \text{quinone}, \qquad (VIII)$$

$$RQ^{\bullet} \longrightarrow R^{\bullet} + Q. \qquad (d)$$

The critical point can be assumed to be the point at which the rate of $RQ^{\bullet}$ radical decomposition is equal to the halved initiation rate w_i:

$$k_7[RQH][R^1O_2^{\bullet}] = k_d[RQ^{\bullet}] = 0.5w_i. \qquad (16)$$

From the condition that the concentrations of the radicals involved in the chain propagation reaction (d) and in the chain termination reactions (VII) and (VIII) are quasi-stationary, we derive the following relationship between the concentrations of the peroxyl and phenoxyl radicals:

$$2k_8[RQ^{\bullet}][R^1O_2^{\bullet}] = w_i. \qquad (17)$$

From this relationship and the differential equation for the rate of accumulation of peroxyl radicals in the hydrocarbon being oxidized, we obtain the following expression for their stationary concentration:

$$[RO_2^{\bullet}] = \frac{k_8 w_i}{4k_7[RQH]}\left\{1 + \sqrt{1 + \frac{8k_7k_d[RQH]}{k_8 w_i}}\right\}. \qquad (18)$$

Substituting this expression into Eqs. (16) and (17), we obtain the following expression for the critical (boundary) $k_{d,\max}$ value at which inhibition by alkoxyphenol becomes inefficient:

$$k_{d,\max}k_7 = k_8 w_i/[RQH]. \qquad (19)$$

Taking the logarithm of this equation and introducing the Arrhenius expressions for the rate constants k_7 and k_d, we arrive at

$$(RT\ln 10)\log\left(\frac{A_d A_7[\mathrm{RQH}]}{k_8 w_i}\right) = E_d + E_7. \qquad (20)$$

This expression enables one to estimate the maximum oxidation temperature (T_{max}) above which alkoxyphenol is inefficient. Below, we present T_{max} values calculated for a variety of R radicals in alkoxyhenols RQH. This calculation was carried out for $k_8 \approx 10^9$ l mol^{-1} s^{-1} ($\log A_d$ = 14.0 and $\log A_7$ = 7.5 [4]). In this case, Eq. (20) takes the form

$$T_{max} = \frac{52.25(E_d + E_7)}{12.5 + \log\{[\mathrm{RQH}]/w_i\}}. \qquad (21)$$

The T_{max} values (K) calculated for a series of alkoxyphenols are presented below. The activation energy E_7 for the reactions of secondary peroxyl radicals with alkoxyphenols in a hydrocarbon medium is E_7 = 14.0 kJ/mol [4].

$[RQH]/w_i$	Me	Me_2CH	$PhCH_2$	Me_2PhC	CH_2=CçCH_2	Ph
10^3 s	539	562	451	431	424	773
10^4 s	507	528	424	405	398	727
10^5 s	478	497	400	382	375	685

It can be seen that T_{max} varies in a wide range (from 375 to 773 K), depending on the structure of R and on the $[RQH]/w_i$ ratio, which is proportional to the induction period. The temperature limit for the efficient action of quinones as polymerization inhibitors can be determined in a similar way. At a sufficiently high temperature, a macroradical with a terminal $RQ^{\bullet}$ group becomes thermally unstable and will sooner decompose than react with another macroradical to terminate the chain.

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