Mechanism of Inhibiting Action of Quinones in Oxidizing Polymers and Model Compounds

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SUMMARY: Quinones (Q) do not affect the liquid-phase oxidation of hydrocarbons and retard the solid-phase oxidation of polymers terminating chains in reactions with alkyl macroradicals. This difference is the result of specific influence of a polymer matrix on the kinetics of free radical reactions. Quinones were found to terminate chains in oxidizing polypropylene containing hydroperoxide groups by the reaction with hydroperoxyl radicals. This is the result of peroxide group's decomposition with hydrogen peroxide production and chain termination in the following reactions:

$$RO_2^\bullet + H_2O_2 \rightarrow ROOH + HO_2^\bullet$$
$$Q + HO_2^\bullet \rightarrow HQ^\bullet + O_2$$
$$RO_2^\bullet + HQ^\bullet \rightarrow ROOH + Q$$

The equilibrium reaction between hydroquinone (QH_2) and quinonimine (QI) was evidenced to proceed as a chain reaction with chain propagation in reactions of $^\bullet$QH with QI and HQI$^\bullet$ with QH_2. Analysis of the reactions of quinone with phenols (ArOH)

$$ArOH + Q \rightarrow ArO^\bullet + {}^\bullet QH$$

proved that it can be important as an additional way of chain termination in oxidizing polymers and hydrocarbons at elevated temperatures.

Introduction

Quinones are produced as products of phenol oxidation during inhibited oxidation of hydrocarbons and polymers in the result of consequent reactions [1)]

$$RO_2^\bullet + C_6H_5OH \rightarrow ROOH + C_6H_5O^\bullet$$

$$RO_2^\bullet + C_6H_5O^\bullet \rightarrow ROOC_6H_5O \rightarrow ROH + \dot{O}C_6H_4O$$

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The mechanism of quinonimine production from aromatic amines is similar. Quinones practically do not affect on oxidation of hydrocarbons and are treated as final inactive products of phenol oxidation.

In oxidizing polymers, quinones were found to be active antioxidants. They terminate the chains in reactions with alkyl macroradicals [2] and showed the high activity in retarding the oxidation of the preliminary oxidized polymer [3]. The reactivity of quinones in reactions of alkyl radical addition is analysed in this paper.

The chain mechanism of the equilibrium reaction between hydroquinone and quinonimine was found recently [4]. The chain propagation was shown to proceed as fast reactions of semiquinone radicals with quinone and quinonimine. The chains are initiated in the reaction of retrodisproportionation between hydroquinone and quinonimine. The reactivity of reagents in this reaction is discussed.

One of the consequences of this analysis is the thesis about an important role of the quinone reactions with phenols and amines. The reactivity of quinones as hydrogen atom acceptors in reactions with phenols and amines is the subject of discussion in this paper.

Quinones as alkyl and hydroperoxyl radical acceptors

p-Benzoquinone was studied as an inhibitor of solid isotactic polypropylene oxidation [2, 5]. The chain termination was proved to be the result of the reaction of quinone with alkyl macroradical. The rate of initiated oxidation v of polypropylene was found to be equal (v_i is the rate of initiation):

$$v = Const \times v_i \times pO_2 \times [Q]^{-1} \qquad (1)$$

This equation is consistent with the following kinetic scheme of oxidation (RH is the oxidized polymer).

$$\begin{aligned} \text{Initiator} &\rightarrow r^{\bullet} \rightarrow R^{\bullet} \\ R^{\bullet} + O_2 &\rightarrow RO_2^{\bullet} \\ RO_2^{\bullet} + RH &\rightarrow ROOH + R^{\bullet} \\ R^{\bullet} + Q &\rightarrow RQ^{\bullet} \\ R^{\bullet} + RQ^{\bullet} &\rightarrow RQR \end{aligned}$$

Rate constant of the reaction $R^{\bullet} + Q$ was estimated to be 3.8×10^4 kg mol^{-1} s^{-1} (387 K). Quinone (concentration 2.5×10^{-3} mol kg^{-1}) tenfold decreases the rate of polypropylene

oxidation. The oxidation of isooctane was found to be retarded to 10% in the presence of 3×10^{-2} mol s^{-1} of quinone under the same conditions [5]. Such a great difference of the retarding action of *p*-benzoquinone in oxidation of polymer and hydrocarbon is the result of a very fast reaction of alkyl radical with dioxygen in the liquid phase. A similar reaction of macroradical $R^{\bullet}$ with oxygen in the solid phase proceeds much slower due to an additional activation that is needed to change the angles of C—C bonds of the macroradical (from 120^0 to 109^0) in its reaction of dioxygen addition. This is the main reason why quinone competes successfully with dioxygen in the solid polymer matrix.

Reactivity of C=O and C=C bonds in reactions of free radical addition was analyzed in the scope of the parabolic model of bimolecular reaction [6]. This model treats the transition state of an addition reaction, for example

$$R^{\bullet} + OC_6H_4O \rightarrow ROC_6H_4O_2^{\bullet}$$

as the result of intersection of two potential parabolic curves. One of them refers to the vibration of the attacked C=O bond of quinone, and the other is related to the vibration of the forming C—O bond. Each elementary reaction may be characterised by the following parameters[6]: the enthalpy of reaction ΔH that includes the difference of zero vibration energies of the reacting bonds, the activation energy E that includes the zero vibration energy of the reacting C=O bond, the distance r between minimum points of two potential curves and coefficients b_i and b_f that characterize the dynamic properties of C=O (i) and C–O (f) bonds, respectively. The parabolic model helps to estimate from experimental data (ΔH and E) parameters $b_i r$ and r as characteristics of the whole group of structurally similar reactions. These parameters help to calculate the activation energy of any reaction of a chosen group using the following equation ($\alpha = b_i/b_f$) [6]:

$$E^{1/2} = b_i r (1 - \alpha^2)^{-1} \{1 - \alpha[1 - (b_i r)^{-2} (1 - \alpha^2) \Delta H]^{1/2} \qquad (2)$$

As the result of analysis of experimental data on addition of alkyl radicals and hydrogen atom to C=C and C=O bonds, the following empirical correlation between parameter r and strength of the formed R—O or R—C bond D was found

$$r \times 10^{13}/\mathrm{m} = (0.99 \pm 0.03) (D/\mathrm{kJ\ mol^{-1}}). \qquad (3)$$

This correlation proves that along with the enthalpy of the reaction the triplet repulsion plays a very important role in free radical addition reactions as well as in reactions with atom abstraction. This implies that the higher the strength of the formed R—O or R—C bond, the higher the energy of the nonbonding orbital of C...O...C or C...C...C in the transition state and the higher is the activation barrier of the reaction. As the result of combination of equations (2) and (3), we obtain the following empirical equation for estimation of the activation energy of an alkyl radical addition to quinone ($b_i r = 23.15$ (kJ/mol)$^{1/2}$, $\alpha = 1.57$):

$$E^{1/2} = 15.8\{1.57[1 + 2.73 \times 10^{-3} \Delta H]^{1/2} - 1\} \quad (4)$$

Quinones possess the oxidation activity and can react with hydrogen atom abstraction. That is why they react fast with such peroxyl radicals as $HO_2^{\bullet}$ and $>C(OH)O_2^{\bullet}$ [6-8].

$$Q + HO_2^{\bullet} \rightarrow HQ^{\bullet} + O_2$$

The forming semiquinone radicals then react rapidly with any peroxyl radical

$$RO_2^{\bullet} + HQ^{\bullet} \rightarrow ROOH + Q$$

These two reactions form a cycle of chain termination in oxidizing systems where $HO_2^{\bullet}$ are generated. Due to these reactions, quinones intensely retard the oxidation of preliminary oxidized polypropylene [7-11].

Chain mechanism of equilibrium reaction between hydroquinone and quinonimine

A new important result in the chemistry of quinones has been received recently by V. T. Varlamov[4]. He discovered that reduction of quinonimine (N-phenyl-1,4-benzoquinonemonoimine QI) by hydroquinone (2,5-di-*tert*-butyl-1,4-hydroquinone, QH_2) proceeds via the chain mechanism with very long chains (a few thousands). The initiator (tetraphenylhydrazine) was shown to accelerate this reaction [4], aromatic amines and quinones affect the reaction rate [12, 13]. The chain initiation reaction is performed in the reaction of retrodisproportionation between hydroquinone and quinonimime.

$$QH_2 + QI \rightarrow HQ^{\bullet} + HQI^{\bullet}$$

This reaction is endothermic and proceeds slowly ($k = 4.5 \times 10^{-3}$ l mol^{-1} s^{-1} at 298 K). Chain propagation is performed in the reactions

$$HQ^{\bullet} + QI \rightarrow Q + HQI^{\bullet}$$
$$HQI^{\bullet} + H_2Q \rightarrow H_2QI + HQ^{\bullet}$$

Both reactions are very fast. The rate constant of the first one was found to be 2×10^7 l mol^{-1} s^{-1}, and that of the second one is 1.6×10^7 l mol^{-1} s^{-1} (298 K) [4]. It is seen from the ratio of these rate constants (0.8) that the enthalpy of equilibrium is close to zero. Why do these reactions of chain propagation proceed so rapidly? The activation energy of the thermoneutral free radical reaction of the type $X^{\bullet} + HY \rightarrow XH + Y^{\bullet}$ strongly depends on the strength and polarity of the X—Y bond [6]. At first, the weaker is X—Y bond, the lower activation energy, due to triplet repulsion in the transition state X(↑)...H(↓)...Y(↑) between two electrons with parallel spins at X and Y atoms. In the reaction of hydrogen atom abstraction between $HQI^{\bullet}$ and H_2Q, we have the transition state reaction centre O...H...O. Since the bond ArO–OAr is very weak (this compound does not exist as a stable molecule) the activation energy at $\Delta H \approx 0$ is low [6]. At the second, the more is the difference in electron affinity of atoms X and Y, the lower activation energy due to attraction of X and Y atoms in transition state. In the reaction $HQ^{\bullet}$ + QI, we deal with the reaction centre of the type N...H...O. The difference in electron affinity between nitrogen and oxygen atom creates additional attraction and decreases the activation energy [6]. Both phenomena (triplet repulsion and difference in electron affinity) play the very important role in other free radical reactions of antioxidants [14, 15]. Chains are terminated in this system in reactions of disproportionation of semiquinone radicals: $HQ^{\bullet}$ + $HQ^{\bullet}$, $HQ^{\bullet}$ + $HQI^{\bullet}$ and $HQI^{\bullet}$ + $HQI^{\bullet}$. All these reactions are diffusionally controlled. So, quasistationary concentrations of both semiquinone radicals are low. However, the reaction proceeds as a chain process due to the very fast chain propagation. The values of chain length ν are given below [4] (T = 298 K, solvent C_6H_5Cl).

$[QH_2] \times 10^4$ l mol^{-1}	$[QI] \times 10^4$ l mol^{-1}	ν
1.0	2.0	2110
6.0	2.0	3660
4.0	10.0	2250
12.0	10.0	2780

Reaction of quinone with phenols and amines as an additional way of retardation of polymer oxidation

As has been shown earlier, quinonimine reacts with hydroquinone with semiquinone radical generation sufficiently rapidly to initiate the chain reaction between QH_2 and QI. Since quinone Q is formed as the product of phenol oxidation in oxidizing polymer or hydrocarbon, the reaction between quinone and phenol

$$ArOH + Q \rightarrow ArO^{\bullet} + HQ^{\bullet}$$

can affect the inhibiting activity of phenol, because the formed semiquinone radical $HQ^{\bullet}$ reacts with $RO_2^{\bullet}$

$$RO_2^{\bullet} + HQ^{\bullet} \rightarrow ROOH + Q$$

and results in the additional chain termination in RH oxidation.

The rate constants of reactions of quinone with phenols and aromatic amines may be calculated using the parabolic model of abstraction reactions [6]. The reactions of the type Q + HOAr and Q + $HNAr_2$ are endothermic. The activation energy of these reactions $E = \Delta H + 0.5RT$. The pre-exponential factor A of rate constant $k = A \exp(-E/RT)$ for these reactions depends on the value of ΔH. According parabolic model of endothermic reaction [6]

$$A = A_0 \{1 + \beta[\Delta H^{1/2} - \Delta H_{max}^{1/2}]\}^2, \qquad (5)$$

where A_0 is the standard pre-exponential factor for a chosen class of reactions with $\Delta H < \Delta H_{max.}$, $\beta = 1.6$ (mol/kJ)$^{1/2}$, and ΔH_{max} depends on the kinetic parameters of this class of reactions (b , r, α) according the following equation [6] :

$$\Delta H_{max} = (b_i r_e)^2 - 2\alpha\, b_i r_e\, (0.5hL\nu_f)^{1/2} + 0.5hL\nu_f (1 - \alpha^2) \qquad (6)$$

The calculated values of ΔH_{max} are written below (Ar_1OH is phenol, Ar_2OH is sterically hindered phenol, Ar_2NH is aromatic amine).

Reaction	Q + $HOAr_1$	Q + $HOAr_2$	Q + $HNAr_2$
$b_i r_e$/(kJ/mol)$^{1/2}$	12.61	13.31	10.13
ΔH_{max}/kJ mol^{-1}	47.3	76.6	12.4

Factor A_0 was taken equal to 2×10^9 l mol^{-1} s^{-1} as for the reaction ArO$^\bullet$ + HOAr. The values of ΔH were calculated as the difference between dissociation energies D of the broken bond O–H in ArOH or N–H in Ar_2NH and formed O–H bond of the *p*-benzosemiquinone radical (228.1 kJ mol^{-1}). Bond dissociation energies of antioxidants are taken from [16]. The results of calculation are presented in the tables 1-3.

Tab. 1. The calculated values of enthalpy, pre-exponential factor and rate constant of reaction of *p*-benzoquinone with phenols

Ar_1OH	ΔH	$A \times 10^{-10}$	k(400 K)	k(500 K)
	kJ mol^{-1}	l mol^{-1} s^{-1}	l mol^{-1} s^{-1}	l mol^{-1} s^{-1}
2–HOC_6H_4OH	113.9	20.0	1.6×10^{-4}	0.15
2–$CH_3C_6H_4OH$	133.4	14.4	3.3×10^{-7}	1.1×10^{-3}
3–$CH_3C_6H_4OH$	140.5	16.1	4.3×10^{-8}	2.0×10^{-4}
4–HOC_6H_4OH	126.2	25.4	5.0×10^{-6}	1.0×10^{-2}
1–Naphthol	117.3	10.7	3.1×10^{-5}	3.6×10^{-2}
2–Naphthol	127.7	13.1	1.4×10^{-7}	3.6×10^{-3}
4–$CH_3COC_6H_4OH$	145.4	17.3	1.1×10^{-8}	6.7×10^{-5}
4–$NH_2C_6H_4OH$	130.6	13.7	7.3×10^{-7}	1.9×10^{-3}
4–$CH_3OC_6H_4OH$	124.9	12.4	3.6×10^{-6}	6.7×10^{-3}
2,6–$(CH_3)_2C_6H_4OH$	130.8	13.8	6.9×10^{-7}	1.8×10^{-3}
4–$(CH_3)_2NC_6H_4OH$	102.7	7.7	1.8×10^{-3}	0.86
4–$C_6H_5C_6H_4OH$	133.3	14.3	3.4×10^{-7}	1.0×10^{-3}
2–CH_3–4–$(CH_3)_3CC_6H_3OH$	133.8	14.4	2.4×10^{-7}	9.1×10^{-4}
2,4,6–$(CH_3)_3C_6H_2OH$	122.7	11.9	6.8×10^{-6}	1.1×10^{-2}
2,3,5,6–$(CH_3)_4C_6HOH$	125.1	12.5	3.5×10^{-6}	6.4×10^{-3}
$(CH_3)_5C_6OH$	114.4	10.1	7.0×10^{-5}	6.8×10^{-2}
α–Tocopherol	103.6	7.9	5.3×10^{-4}	0.71

Tab. 2. The calculated values of enthalpy, pre-exponential factor and rate constant of the reaction of *p*-benzoquionone with sterically hindered phenols.

X	ΔH	$A \times 10^{-9}$	k(400 K)	k(500 K)
	kJ mol^{-1}	l mol^{-1} s^{-1}	l mol^{-1} s^{-1}	l mol^{-1} s^{-1}
H	121.3	4.3	3.7×10^{-7}	5.5×10^{-4}
$(CH_3)_3C$	113.6	3.3	2.9×10^{-6}	2.7×10^{-3}
$CH_3C(O)$	120.1	4.1	5.1×10^{-7}	7.0×10^{-4}
$C_6H_5CH_2$	114.3	3.4	2.4×10^{-6}	2.3×10^{-3}
$(CH_3)_3CO$	105.9	2.4	2.1×10^{-5}	1.4×10^{-2}
$(CH_3)_3COC(O)$	122.3	4.3	2.8×10^{-7}	4.3×10^{-4}
Cl	119.1	4.0	6.7×10^{-7}	8.7×10^{-4}
$C_6H_5(CH_3)_2C$	114.7	3.5	2.2×10^{-6}	2.2×10^{-3}
CH_3O	105.3	2.3	2.5×10^{-5}	1.4×10^{-2}
$CH_3OC(O)CH_2$	117.4	3.8	1.1×10^{-6}	1.2×10^{-3}
CH_3	113.6	3.3	2.9×10^{-6}	2.7×10^{-3}
NH_2CH_2	109.4	2.8	8.7×10^{-6}	6.2×10^{-3}
$HOC(O)CH_2$	111.5	3.0	5.0×10^{-6}	4.0×10^{-3}
NO	120.6	4.2	4.5×10^{-7}	6.3×10^{-4}
C_6H_5	112.3	3.7	4.8×10^{-6}	4.1×10^{-3}

A sufficient influence of the reaction Q + ArOH on the chain termination should be taken into account when its rate k[Q][ArOH] will be more than 1/4 of the rate of chain generation (ν_i). At $\nu_i > 10^{-8}$ mol l^{-1} s^{-1} and [Q] = [ArOH] = 10^{-2} mol l^{-1}, this reaction can affect the chain termination at $k > 10^{-5}$ l mol^{-1} s^{-1}. A few phenols at T = 400 K and many at T = 500 K obey to this criterium.

Tab. 3. The calculated values of enthalpy, pre-exponential factor and rate constant of the reaction of *p*-benzoquionone with aromatic amines

Ar_2NH	ΔH	$A \times 10^{-9}$	k(400 K)	k(500 K)
	kJ mol^{-1}	l mol^{-1} s^{-1}	l mol^{-1} s^{-1}	l mol^{-1} s^{-1}
$(C_6H_5)_2NH$	136.6	4.0	3.5×10^{-7}	1.3×10^{-3}
$(4\text{–}CH_3OC_6H_4)_2NH$	120.5	3.4	3.8×10^{-5}	5.3×10^{-2}
$(4\text{–}CH_3C_6H_4)_2NH$	129.4	3.7	2.9×10^{-6}	6.9×10^{-3}
$4\text{–}CH_3OC_6H_4NHC_6H_5$	127.8	3.6	4.6×10^{-6}	1.0×10^{-2}
$4\text{–}(CH_3)_3CC_6H_4NHC_6H_5$	132.2	3.8	1.2×10^{-6}	3.6×10^{-3}
$1\text{–}C_{10}H_7NH_2$	146.6	4.3	1.9×10^{-8}	1.2×10^{-4}
$2\text{–}C_{10}H_7NH_2$	151.4	4.5	4.7×10^{-9}	4.2×10^{-5}
$(2\text{–}C_{10}H_7)_2NH$	132.2	3.8	1.3×10^{-6}	3.7×10^{-3}
$4\text{–}C_8H_{17}NHC_6H_4NHC_8H_{17}$	118.8	3.3	6.2×10^{-5}	7.8×10^{-2}
$4\text{–}C_6H_5NHC_6H_4NHC_6H_5$	127.8	3.6	4.6×10^{-6}	1.0×10^{-2}
$4\text{–}C_6H_5NHC_6H_4NHCH(CH_3)_2$	121.1	3.4	3.2×10^{-5}	4.6×10^{-2}
$1\text{–}C_{10}H_7NHC_6H_5$	129.0	3.7	3.2×10^{-6}	7.6×10^{-3}
$2\text{–}C_{10}H_7NHC_6H_5$	134.8	3.9	5.9×10^{-7}	2.0×10^{-3}
$4\text{–}C_6H_5OC_6H_4NH\text{–}2'\text{–}C_{10}H_7$	121.4	3.5	3.0×10^{-5}	4.4×10^{-2}

Conclusion

The data presented and the results of calculation evidence that quinones and quinonimines are active intermediates in oxidizing polymers inhibited by phenol or aromatic amine . They retard the oxidation by different mechanisms.

1. Quinones accept alkyl radicals and terminate the chain oxidation. This mechanism is effective for solid phase oxidation of polymers at low oxygen pressures.

2. Quinones are easily reduced by $HO_2^{\bullet}$ radicals followed the reaction of $RO_2^{\bullet}$ with the semiquinone radical. These two reactions form the cycle of chain termination. This mechanism is effective in oxidizing polymer containing the hydroperoxide groups.

3. The endothermic reaction of quinone with phenol or amine results in the additional chain termination due to the fast reaction of the semiquinone radical with $RO_2^{\bullet}$.

Triplet repulsion plays very important role in all reactions of quinone mentioned above.

References

[1] N. M. Emanuel, E. T. Denisov, Z. K. Maizus, *Liquid-phase oxidation of hydrocarbons*, Plenum Press, N. Y. , 1967, p. 223.

[2] E. T. Denisov, *Role of alkyl radical reactions in polymer oxidation and stabilisation in Developments in Polymer Stabilisation* – 5 (Ed. G. Scott), Appl. Sci. Publishers, London, 1982, p. 23.

[3] E. T. Denisov, *Russian Chem. Rev.*, **65**, 505 (1996).

[4] V. T. Varlamov, *Dokl. Akad. Nauk*, **332**, 457 (1993).

[5] Yu. B. Shilov, E. T. Denisov, *Vysokomol. Soed., Ser.* **A16**, 1736 (1974).

[6] E. T. Denisov, *Russian Chem. Rev.*, **66**, 859 (1997).

[7] E. T. Denisov, *Macromol. Symp.* **115**, 41 (1997).

[8] E. T. Denisov, *Zhur. Fiz. Khim.*, **71**, 1385 (1997).

[9] Yu. B. Shilov, E. T. Denisov, *Vysokomol. Soed., Ser.* **A 24**, 837 (1982).

[10] Yu. B. Shilov, E. T. Denisov, *Vysokomol. Soed., Ser.* **A 26**, 1753 (1984).

[11] Yu. B. Shilov, E. T. Denisov, *Vysokomol. Soed., Ser.* **A 29**, 1359 (1987).

[12] V. T. Varlamov, *Dokl. Akad. Nauk*, **337**, 757 (1994).

[13] V. T. Varlamov, *Dokl. Akad. Nauk*, **345**, 339 (1995)

[14] E. T. Denisov, *Polym. Deg. Stability*, **49**, 71 (1995).

[15] E. T. Denisov, *Chem. Phys. Reports*, **14**, 1513 (1995).

[16] E. T. Denisov, *Handbook of Antioxidants*, CRC Press, Boca Raton, 1995, p. 47.