Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc

Petroleum & Coal 47 (1), 33-39, 2005

ON THE ENERGETICS OF PHENOL ANTIOXIDANTS ACTIVITY

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Received 1 July 2004; accepted 10 June 2005

Abstract

In this article a systematic study of several phenolic antioxidants (BHT, α-tocopherol, tocopheryl acetate and their derivatives) is presented. The optimal geometries, energies and QSAR properties of the studied structures were obtained by semi empirical quantum-chemical method AM1. Predicted characteristics are in good agreement with the trends available from experimental studies of antioxidants action. Our results show that high antioxidant activity of tocopherols can not be explained with the enhanced stability of the tocopheroxyl radical through interaction between the p-orbitals on the two oxygen atoms.

Key words: *antioxidant, sterically hindered phenol, polymer oxidation, BHT, tocopherol*

Thermally initiated degradation of polymers may proceed at elevated temperatures even in the absence of oxygen. However, generally it occurs in the presence of oxygen and it may become important already at relatively low temperatures. Thermal oxidation of thermoplastics and elastomers may occur during every stage of their life cycle. It can take place already during the polymerization, following processing, and on storage. The rate of thermal degradation is pronounced during the polymer treatment. Thermal degradation during the lifetime of the plastics depends mainly on the environmental conditions [1].

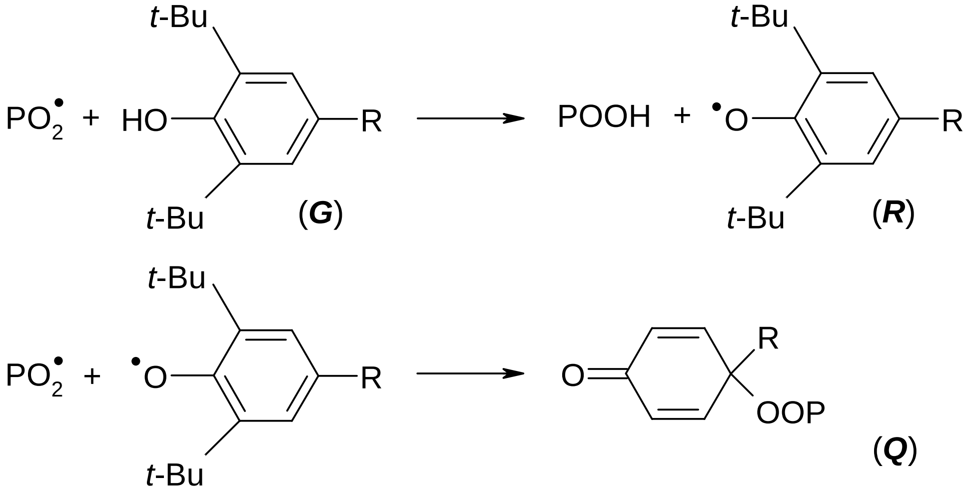
Thermal oxidation of polymers generally corresponds to a free radical chain reaction [1, 2, 3]. It involves initiation reactions generating free radicals, propagation reactions yielding hydroperoxides, and termination reactions eliminating free radicals from the system. Initiating polymer radicals are formed through the action of heat or the combination of heat and mechanical stress (especially under processing conditions). The radicals formed in the initiation, propagation, and chain branching steps are not only able to fix oxygen and/or abstract hydrogen. They may be subject to unimolecular decomposition reactions, too. These reactions lead to chain scissions, i.e. to a decrease in polymer molecular weight. On the other hand, bimolecular termination reactions give rise to crosslinking and an increase in polymer molecular weight. The main consequence of thermal oxidation is the loss of mechanical properties of polymers.

Substances reducing or inhibiting thermal oxidation are generally called antioxidants. Antioxidants may intervene in any step in the thermal oxidation. They are often divided into two general groups: primary antioxidants, which act as free-radical scavengers to interrupt or prevent oxidation reactions; and secondary antioxidants, which react with hydroperoxide groups (their formation is a stage in the oxidation reaction chain) to convert them to non-radical products [1, 4, 5].

The primary antioxidants are typically compounds containing sterically hindered phenolic OH groups, secondary aromatic amines, and sterically hindered amines (HALS). Primary antioxidants can be used for prestabilization and long-term stabilization of the polymers [1, 5].

The secondary antioxidant group consists of phosphites, phosphonites, thioesters, and metal salts. They are used in combination with primary antioxidants during processing and for long-time stabilization under severe thermal conditions [1].

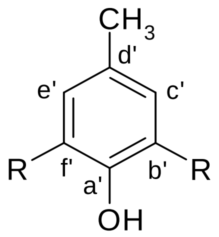
Hindered phenols are radical-trapping antioxidants for oxy, and especially peroxy radicals [1, 5, 6, 7]. The phenoxy radicals with their bulky substituents are stabilized by sterical hindrance and cannot attack the polymer. These radicals are transformed to quinonoid structures that can recombine with other peroxy radicals (Scheme 1).



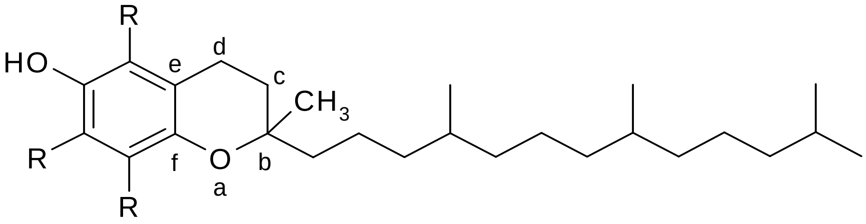
Scheme 1: Antioxidant action of the sterically hindered phenols. P denotes the polymer chain.

Butylated hydroxytoluene (2,6-di-*tert*-butyl-4-methylphenol, BHT) is the simplest representative of sterically hindered phenols group. The natural compound α-tocopherol is also used as an antioxidant. This active form of vitamin E is known to be one of the best chain breaking phenolic antioxidants. It reacts more rapidly with alkylperoxyl radicals than other similar phenolic antioxidants that lack the fused 6-membered heterocyclic ring [8]. It was shown that the melt processing activity of α-tocopherol in polyethylene and polypropylene is much higher than that of the synthetic hindred phenol Irganox 1010 [9].

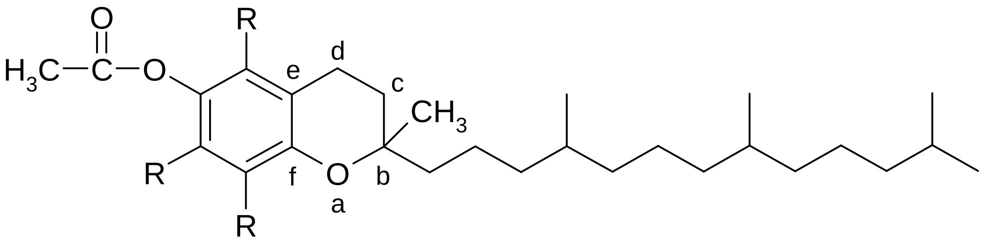
The action of hindered phenols was experimentally studied by several authors [6-12] and reaction products were identified. On the other hand, no theoretical works dealing with structural and energy characterization of the reaction intermediates and products are available. With respect to this fact, the aim of this study is a deeper insight into the energetics of the antioxidant effect of sterically hindered phenols using the AM1 quantum chemical calculation method [13]. We have studied BHT, α-tocopherol, tocopheryl acetate and four model molecules derived from these three compounds (Fig. 1) to find possible effects of the substituents in *ortho* position to phenolic OH group. Finally, the molecular dynamics simulation using MM+ method [14] at constant temperature (T = 300 K) will be used to determine the torsional oscillations near the active oxygen atom. Obtained information may be useful for the prediction and/or choice of suitable candidates for possible technological applications.



R=H (**I**), CH_3 (**II**), *tert*-butyl (**III**, BHT)



R=H (**IV**), CH_3 (**V**, α–tocopherol)



R=H (**VI**), CH_3 (**VII**, tocopheryl acetate)

Figure 1: Studied hindered phenols

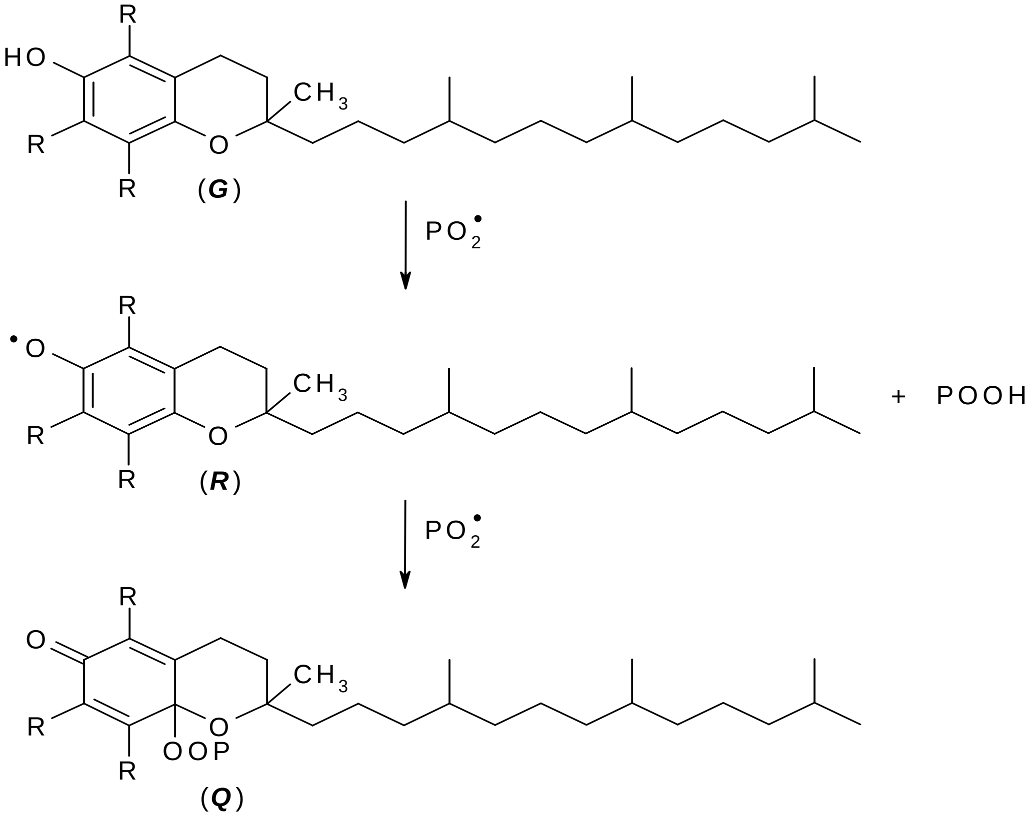
Quantum Chemical Methods

The ground-state geometry of studied molecules were optimized at the Hartree-Fock level using the standard semiempirical AM1 (Austin Model 1) method [15, 16] of the MOPAC 7.0 program package [17] (energy cut-off of 10^{-5} kJ·mol^{-1}, final RMS energy gradient under 0.01 kJ·mol^{-1} Å^{-1}). On the basis of the optimized geometries, the QSAR properties [18], i.e. hydratation energy, surface area and volume of the molecules, were evaluated. The time dependence of the vibrational motion between active phenolic oxygen atom and its neighbor molecular fragment for thermal equilibrium at T = 300 K was calculated using molecular dynamics. The run time was set to the 1 ps value and the scan was performed with 0.001 ps step.

Results and discussion

At the beginning, the conformational analysis has been carried out for the studied compounds (denoted by letter ***G***), their fenoxy radicals (***R***) and model quinonoide products (***Q***) where P (polymer chain in Scheme 1 and 2) was replaced with methyl group. We do not expect, that longer aliphatic chain (ethyl, propyl,…) may vary the results and trends significantly. The optimized ground-state and radical structures have the planar phenyl ring. On the other hand the quinonoide systems are non-planar. The deviations from the planarity can be described using the torsional angles α(d–e–f–a) in tocopherol-type and tocopheryl acetate-type molecules or α(f’–a’–b’–c’) and β(c’–d’–e’–f’) in BHT-type molecules (marking of the atoms is shown in Fig. 1).

The next interesting geometric parameter for all systems might be the $R_{O–C}$ bond length between the active oxygen atom and its carbon neighbor located in phenyl ring (see Tab. 1). In our study we have restricted our attention to the most stable conformations because the differences between various conformations in interatomic distances are practically negligible. The effect of the substituents localized in *ortho* positions on the $R_{O–C}$ distance is negligible. The calculated partial charges reveal small charge increase on active oxygen (compare **I**, **II**, **III** and **IV**, **V** molecules, see Table 1). In Table 1 we present the ionization potentials (IP) of the studied molecules, too. The values between 8.31 and 8.88 eV are typical for most organic molecules. Higher quantities were obtained for BHT-type molecules (**I**, **II** and **III**) due to the lower π-conjugation.



Scheme 2: Antioxidant action of the α-tocopherol. P denotes the polymer chain.

Table 1 Calculated AM1 heat of formations H_f, ionization potentials IP, relative charge on active oxygen q_O, distance $R_{O–X}$ and reaction heat $\Delta_r H$ values.

Molecule	Ground state (*G*)				Radical (*R*)			Quinonoid structure (*Q*)			Reaction heat	
	H_f (kJ·mol^{-1})	IP (eV)	q_O	$R_{O–C}$ (10^{-10} m)	H_f (kJ·mol^{-1})	q_O	$R_{O–C}$ (10^{-10} m)	H_f (kJ·mol^{-1})	q_O	$R_{O–C}$ (10^{-10} m)	$\Delta_r H_1$ (kJ·mol^{-1})	$\Delta_r H_2$ (kJ·mol^{-1})
I	–125.367	8.88	–0.253	1.377	25.962	–0.290	1.248	–67.039	–0.280	1.237	151.326	–93.001
II	–182.499	8.70	–0.255	1.379	–40.886	–0.300	1.248	–127.728	–0.282	1.237	141.614	–86.844
III	–243.297	8.62	–0.262	1.377	–112.496	–0.303	1.248	–212.804	–0.286	1.236	130.801	–100.307
IV	–562.202	8.43	–0.254	1.380	–421.026	–0.306	1.249	–520.393	–0.273	1.237	141.175	–99.367
V	–635.230	8.31	–0.260	1.383	–508.806	–0.316	1.250	–600.708	–0.279	1.237	126.424	–91.901
VI	–703.440	8.50	–0.254	1.402	–421.026	–0.306	1.249	–520.393	–0.273	1.237	282.413	–99.367
VII	–775.875	8.49	–0.234	1.399	–508.806	–0.316	1.250	–600.708	–0.279	1.237	267.069	–91.901

Note: $H_f(H) = –0.042$ kJ mol^{-1}, $H_f(CH_3–OO) = –32.182$ kJ mol^{-1}, $H_f(CH_3–CO) = –48.421$ kJ mol^{-1}

Formation of the radical on the oxygen atom leads to the shortening of the interatomic distances $R_{O–C}$ of about 0.05 Å. The presence of the unpaired electron leads to the charge decrease on the oxygen. The quinonoid form of the reaction products has the non-planar structure. The torsional angles α and β (see the angles definition above) are summarized in Table 2.

Table 2 Calculated hydratation energies, QSAR properties (surface area *S* and volume *V*) of ground state forms (***G***) and AM1 torsional angles *α* and *β* of quinonoid forms (***Q***).

Molecule	$\Delta_{hydr}H$ (kJ·mol^{-1})	S (10^{-20} m^2)	V (10^{-30} m^3)	ΔR_{O-X} (10^{-10} m)	α (deg)	β (deg)
I	–32.019	276	406	0.043	–8	13
II	–16.427	325	503	0.040	–13	16
III	4.180	454	757	0.068	–29	26
IV	–15.424	748	1307	0.037	37	
V	3.469	800	1432	0.031	31	
VI	10.283	830	1436	0.016	37	
VII	19.437	865	1550	0.013	31	

On the basis of the optimized AM1 geometry, the QSAR properties have been calculated. The negative values of hydratation energies are obtained for **I**, **II** and **IV** molecules while the positive values were indicated for the **III**, **V**, **VI** and **VII** structures. It seems that this quantity very well corresponds with the antioxidant activity. We suppose that higher values correspond with better antioxidant effect. With increasing number of atoms in molecule increases also the volume and surface area of the molecule. The ratios (values in $10^{10} \times V/S$) of these quantities increase from **I** (1.47), **II** (1.55), **III** (1.67) to **IV** (1.75), **V** (1.79), **VI** (1.73) and **VII** (1.79). The highest magnitudes of these ratios are indicated for the systems with the best antioxidant effectiveness – **III** for BHT-type molecules and **V** or **VII** for α-tocopherol and tocopheryl acetate, respectively. This parameter might be in direct relation to the diffusion process. The antioxidants with large volumes have decreased mobility in polymer matrix and their diffusion to polymer surface may be restricted. It has been demonstrated, that the rate of diffusion of additives decreases with increasing molecular weight of the additive [1]. Some phenolic antioxidants are rather volatile and may be lost from polymer samples even at low temperatures. Then, if the additive is able to diffuse, there may be continuous migration to the polymer surface followed by loss to the surrounding medium. Through this mechanism, polymer may be depleted from antioxidants and left without protection [1].

Preparation of new materials for technological applications requires good intuition on the possible mechanisms that determine the oxidation processes in polymers. Information contained in many-electron wave functions is too complex and thus it is very unlike to get physical insight into the structure-function relationship for an additive in this way. The calculated values of heat of formations (H_f) and/or heat of reactions ($\Delta_r H_1$ for radical formation $\boldsymbol{G} \rightarrow \boldsymbol{R}$ and $\Delta_r H_2$ for quinonoid structure formation $\boldsymbol{R} \rightarrow \boldsymbol{Q}$) offer a reasonable compromise from the energy point of view. Table 1 summarizes all energy values calculated within AM1 approach for studied molecules, their radical and quinonoid forms. As can be seen, the abstraction of the hydrogen atom from the active phenolic oxygen leads to comparable $\Delta_r H_1$ values. Formation of radical from molecules **VI**, **VII**, i.e. abstraction of CH_3CO fragment, requires approximately twice higher energy than the O–H bond splitting-off. The ability to form radical is better for the compounds with non-hindered active oxygen. The energy difference between the radical and quinonoid forms increases for BHT-type compounds from **I** to **III** and for tocopherol group from **V** to **IV**. Finally, the large energy gaps for the radical formation indicate, that the thermal homolytic cleavage of the O–X (X= H, CH_3CO) bond is not probable process. Therefore antioxidant itself can not act as a source of radicals in the system, even if the phenolic group is not hindered. Dominant is the reaction of peroxy radicals and/or molecular oxygen with antioxidant. The interaction between thermally excited polyenes in the case of PVC dehydrochlorination [19] and the antioxidant molecule may take place, too. On the other hand, sterical hindrance in the radical may be very important under certain circumstances. Our study of the α-tocopherol (**V**) (commercial name Irganox E201) and tocopheryl acetate (**VII**) effect on poly(vinyl chloride) thermal dehydrochlorination (DHC) at 180 °C in air demonstrated, that α-tocopherol causes significant increase in the DHC rate, while tocopheryl acetate is able to slow down

DHC reaction [20, 21]. The effectiveness of tocopheryl acetate was almost identical with Irganox 1010 which is one of the most effective synthetic sterically hindered phenolic antioxidant. This clearly demonstrates that sterically non-hindered radical formed from tocopherol can attack the polymer and intervenes in the DHC process. It is well known fact that radicals present in PVC matrix negatively influence DHC [22]. In the case of tocopheryl acetate abstraction of CH_3CO fragment requires more energy, and formed $CH_3CO^{\bullet}$ radical can contribute to radical termination (recombination) reactions and thus the rate of thermal DHC is lower than DHC rate of the pure polymer.

Some recently published papers dealing with antioxidant power of tocopherols *in vivo* and in polyethylene and polypropylene [6, 8, 9] cite works of Burton and his co-workers [23, 24]. They suppose that excellent antioxidant capability of tocopherols is related to the enhanced stability of the tocopheroxyl radical (produced in the rate limiting reaction) through interaction between the *p*-orbitals on the two oxygen atoms. However, our calculations showed that this interaction is not probable due to the long 5.5 Å distance between the two oxygen atoms. Moreover, the electronic density shows a nodal plane between these oxygen atoms. These findings indicate that the excellent antioxidant activity of tocopherols can not be explained in this way.

Molecular dynamics simulations offer a better view on the thermal stability as well as on the vibrational oscillations of the bond that breaks during the radical formation. Simulations have been performed using AM1 method at constant temperature (T = 300 K). The results, elongation of the O–X (X= H, CH_3CO) bond on the 1 picosecond time scale are included in the Table 2. The time course of the bond elongation for molecules **V** and **VII** are shown in Figures 3 and 4, respectively. We have found that molecules **I** and **II** are non-sensitive to the thermal effects at the beginning of the simulation. The highest bond elongation after simulated heating process (thermal bath) is observed for molecule **III** in BHT group and molecule **IV** (in tocopherol group). The bonds containing heavier acetate fragment (molecules **VI** and **VII**) have the quasi oscillating nature.

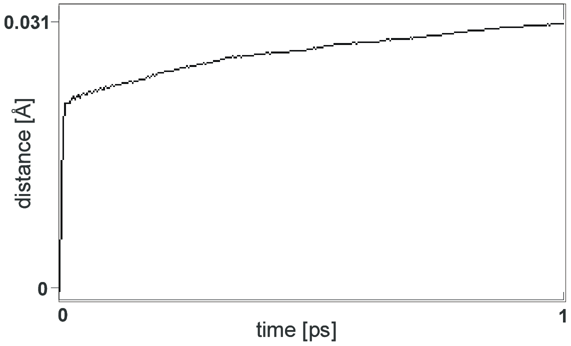


Figure 3: Time course of O-H bond elongation in 1 ps time scale for tocopherol V.

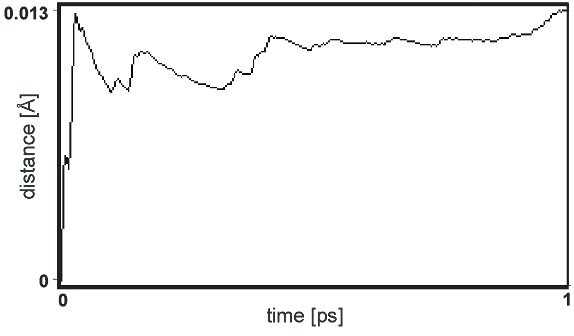


Figure 4 Time course of O–C(O)CH_3 bond elongation in 1 ps time scale for tocopheryl acetate (**VII**).

Conclusion

In this article a systematic study of phenolic antioxidants (BHT, α-tocopherol, tocopheryl acetate and their derivatives) is presented. The optimal geometries, energies and QSAR properties of the studied structures were obtained by semiempirical quantum-chemical method AM1. Influence of the substituents in *ortho* position to phenolic OH group on the energetics and C–O bond length was investigated, too. The molecular dynamics calculations indicate also good thermal resistance for compounds **VI** and **VII** containing CH_3CO fragment. The predicted characteristics are in good agreement with the trends available from experimental studies of antioxidant action [1, 6-12, 20, 21]. Our results show that the excellent antioxidant activity of tocopherols can not be explained with the supposed enhanced stability of the tocopheroxyl radical through interaction between the *p*-orbitals on the two oxygen atoms.

It may be concluded that this type of antioxidants still represents a perspective basis for material research in polymer science and industry. Deeper understanding of the reaction mechanism, energetics and molecular properties of the relevant intermediates and products is necessary for optimal modifications of the antioxidants.

Acknowledgements

This work has been supported by Science and Technology Assistance Agency under the contract No APVT-20-005004.

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