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Research paper

DFT studies of the effectiveness of p-substituted diphenyl amine antioxidants in styrene-butadiene rubber through their Cu(II) coordination ability

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In the memory of Professor Stanislav Biskupič (1949 – 2016).

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ABSTRACT

Structures of a series of diphenyl amine (DPA) antioxidants and of their complexes with Cu^{2+} were optimized at B3LYP level of theory. DPAs may be divided into two groups according to their molar antioxidant effectiveness (AEM). The effectiveness of high-AEM DPA antioxidants at 130 °C rises with decreasing spin densities at Cu atoms and with the increasing electron density Laplacian at Cu–N bond critical points in the ^{2}[DPA...Cu]$^{2+}$ complexes similarly as in the case of p-phenylene diamine antioxidants. No such trends are observed at 25 °C and for low- AEM DPA antioxidants.

1. Introduction

Rubber products undergo degradation which is mainly caused by oxygen, ozone, heat and dynamic stress. The thermal oxidation of rubber is an autocatalytic, free radical chain reaction where the oxidation products are carboxylic acids, ketones, aldehydes, epoxides, etc. The rate of the oxidation process can be reduced using antioxidants (AOxs). Chain-breaking AOxs, such as arylamines, donate labile hydrogen to a peroxy radical so interrupting the propagation step [1].

The mechanism of the AOx action of diarylamines Ar_2NH based on $Ar_2NO^{\cdot}$ radicals formation originates in late 1960s [2]. A few years later the differences in the mechanism at lower and higher temperatures were observed [3]. According to the recent picture of this catalytic inhibition mechanism [4] the diarylamine is first oxidized by a peroxyl radical.

$$> NH + RO_2^{\cdot} \rightarrow > N^{\cdot} + ROOH \quad (1)$$

$$> N^{\cdot} + RO_2^{\cdot} \rightarrow > NO^{\cdot} + RO^{\cdot} \quad (2)$$

The secondary alkyl radical can react with $Ar_2NO^{\cdot}$ to form a secondary N-alkoxydiarylamine

$$> NO^{\cdot} + R^{\cdot} \rightarrow > NOR \quad (3)$$

which is unstable at higher temperatures and decomposes to complete the inhibition cycle

$$2 > NOR \rightarrow 2 > NH + R'COR'' \quad (4)$$

One complete inhibition cycle traps two radicals (one peroxyl and one alkyl). Side reactions lead to non-radical products which stop the catalytic inhibition chain

$$> NOR \rightarrow > NOH + > C = C < \quad (5)$$

Or alternatively they can contribute to the inhibition

$$> NOH + RO_2^{\cdot} \rightarrow > NO^{\cdot} + ROOH \quad (6)$$

$$> NOR \rightarrow > N^{\cdot} + RO^{\cdot} \quad (7)$$

It implies that at high temperatures the rate determining step is not the hydrogen transfer but the subsequent re-generation of the amine via N—O homolysis and in-cage disproportionation. It is evident that there is a switch in behavior between low temperatures (where the protection is non-catalytic with low stoichiometric factors for inhibition) and high temperatures (above ca 100 °C), where the protection becomes catalytic (high stoichiometric factors).

Simon et al. [5–10] investigated the AOx efficiency in polyisoprene rubber (PIR) and similar matrices by non-isothermal DSC measurements and proposed the method of the AOx efficiency quantification as follows:

The degradation process starts with the formation of free radicals during the induction period. The AOx activity can be evaluated

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as the ratio of the lengths of the induction periods t_i of the stabilized (PIR+AOx) and unstabilized (PIR) polymer as the protection factor (*PF*)

$$PF = \frac{t_i(\mathrm{PIR}+\mathrm{AOx})}{t_i(\mathrm{PIR})} \quad (8)$$

The values of protection factors change with temperature and AOx concentrations. The Molar Antioxidant Effectiveness (*AEM*) can be defined as

$$AEM = \frac{PF-1}{m} \quad (9)$$

where m is the concentration of antioxidant in polymer matrix expressed in mol kg^{-1}.

Recent studies how to explain the action of diphenyl amine antioxidants are focused mainly on N,N'-substituted p-phenylenediamines (PPDs) with industrial applications [11–24] in order to enable their target synthesis. Very recently we have proposed the method of AOx effectiveness prediction of PPD antioxidants based on their NMR data [22,23]. We have found that their AEM increases with increasing ^{1}H NMR shifts of both amine hydrogens, ^{15}N NMR shifts of the nitrogen between aromatic rings (N1 site) and probably ^{13}C NMR shifts of the tertiary carbon atom neighboring to the nitrogen between aromatic ring and the side aliphatic chain (N2 site). On the other hand, AEM increases with decreasing ^{15}N NMR shifts of the amine nitrogens between the aromatic ring and the side aliphatic chain (N2 site). This is very surprising because similar reactions at both nitrogen sites are supposed.

Alternatively we have modified for this purpose the method of a Cu^{2+} probe attached to oxygen active sites of various AOxs [25–27]. The authors of this method have shown that the relative stability of the metalated species at various coordination sites strongly depends on their position and nature. The spin density of the copper ion upon ligand coordination becomes small whereas the ligand spin density approaches 1. Thus the neutral ligand is oxidized to a radical cation while Cu(II) is reduced to Cu(I). Consequently, the metal-ion affinity as well as the charge and spin density of Cu atoms can be used as a measure of the AOx effectiveness. We have found that in PPD AOxs [24] the copper atom prefers bonding to the nitrogen atom between aromatic rings (N1 site). We have observed linear relations between AEM and Cu atomic charges, Cu spin densities as well as the Laplacian of electron density at Cu–N bond critical points. The AEM values rise with increasing PPD affinity to Cu^{2+} ions, decreasing charges and spin densities at Cu atoms and the increasing electron density transfer in Cu–N bonds in the ^{2}[PPD...Cu]$^{2+}$ complexes with copper atoms bonded at the nitrogen between aromatic rings (N1 site) unlike the remaining N site. Cu bonding to tertiary carbon atoms is excluded due to the absence of frontier molecular orbitals density at these atoms in PPD molecules.

Due to the limited number of PPDs (only four in [24]) the above treatments should be verified on a wider set of AOxs. In our previous study [28] on a series of ten p-substituted diphenyl amine (DPA) AOxs no correlation between AEM and NMR chemical shifts of amine nitrogen and hydrogen atoms has been found at 25 °C. AEM values at 130 °C increase with NMR chemical shifts of nitrogen atoms between aromatic rings and hydrogen atoms bonded to them with very good statistical parameters (except nitro- and nitroso-compounds). The aim of our recent study is to test the suitability of the above mentioned method (based on the Cu^{2+} complexation ability) on the series of p-substituted diphenylamines [25–27] as well.

2. Method

The geometries of the neutral AOx molecules under study in singlet spin ground states as well as of corresponding [Aox...Cu]$^{2+}$ cations in doublet ground spin states containing Cu – N bonds were optimized using Becke three-parameter B3LYP hybrid functional [29] and standard 6-311G* basis sets from Gaussian09 library [30] for all atoms. Stability of the optimized structures (see Figs. S1 – S8 in Supplementary Information) was confirmed by vibrational analysis (no imaginary vibrations). All the above mentioned calculations were performed using Gaussian09 program package [30]. The Cu^{2+} metal-ion affinity to AOx is evaluated as the molecule-ion interaction energy E_{int} [25–27].

$$E_{int} = E_{Complex} - E_{AOx} - E_{Ion} \quad (10)$$

where $E_{Complex}$ is the DFT energy of the ^{2}[AOx...Cu]$^{2+}$ complex, E_{AOx} is the DFT energy of the isolated AOx molecule and E_{Ion} is the DFT energy of the isolated Cu^{2+} ion (−1639.39803 hartree). Electron structure of the systems under study has been evaluated in terms of NBO (Natural Bond Orbitals) population analysis [31–35] (such as atomic charges and spin populations). Alternatively, QTAIM (Quantum Theory of Atoms-in-Molecules) topological analysis of electron density [36] has been performed using AIM2000 software [37] in terms of atomic charges (integrated over atomic basins up to 0.001 e/bohr^3 value) and spin densities at relevant atoms. Electron density Laplacians at bond critical points, $\nabla^2\rho_{BCP}$, which describe the electron density transfer in the case of ionic and complex bonds ($\nabla^2\rho_{BCP} > 0$ for unshared bonds [36]), have been evaluated as well. MOLDRAW [38] software was used for visualization and geometry manipulation purposes.

3. Results and discussion

At first it must be mentioned that we were not successful in geometry optimization of ^{2}[Aox...Cu]$^{2+}$ complexes with Cu – N bonding of all DPA antioxidants investigated in [28]. Some of them preferred π-complex formation between Cu and phenyl aromatic rings, the structure with Cu – N bonding was unstable and thus unusable for our purposes. Consequently, our study is restricted to AOxs in Table 1. These ones may be divided into two groups which are treated separately. AEM values of compounds (A1) – (A3) are high (over 1000 kg/mol) and significantly depend on the temperature unlike AEM values of compounds (B1) – (B5) (see Table 1). Such a behavior can be explained by relatively high stability of a secondary N-alkoxydiarylamine and a small reaction rate of its decomposition according to Eq. (4). As the compound (A1) has been investigated in our previous study [24], we present the results for Cu^{2+} bonded to both nitrogen atoms in this compound as well.

The results of our study for experimental AEM data [8] obtained at 25 °C (AEM_{25}) and 130 °C (AEM_{130}) are presented in Figs. 1–4. Unlike our previous study on PPD [24] no similar trends between AEM and interaction energies E_{int} can be observed for A1 – A3 compounds (Fig. 1). Concerning B1 – B5 compounds some less obvious proportionality might be observed (except B5 at 25 °C and except B3 at 130 °C).

According to our results (Fig. 2), AEM values at 25 °C (AEM_{25}) are proportional to positive Cu atom charges for (A1) – (A3) compounds, especially if the side nitrogen site in (A1) is considered. No such relation can be observed for AEM at 130 °C (AEM_{130}). It must be mentioned that AEM values of PPD at 130 °C [24] decrease with Cu charges. Similar relations for (B1) – (B5) compounds are indistinct.

NBO and QTAIM spin densities at Cu atoms exhibit opposite signs (Fig. 3). Nevertheless, AEM_{130} values decrease with their absolute values for (A1) – (A3) compounds if the side nitrogen site