

ANTIOXIDANT POTENTIAL OF NOVEL DESIGNED PHENOLIC
DERIVATIVES: COMPUTATIONAL INSIGHTSDinesh R. Pandithavidana¹, ✉, Kushani S. K. Hewage¹<https://doi.org/10.23939/chcht14.04.448>

Abstract. Density functional theory calculations were applied for designed phenolic antioxidant derivatives. The reaction enthalpies related to various mechanisms of primary antioxidant action were deliberated in detail. How antioxidant activity of designed phenolic compounds has been perturbed by electron donor and withdrawing substituents present at *ortho*, *meta* and *para* positions, allylic conjugation and the dimerization effect were computed.

Keywords: density functional theory, phenolic antioxidants, HAT mechanism, SET–PT mechanism.

1. Introduction

Among numerous types of antioxidant compounds, phenolic antioxidants form an important class of chain-breaking compounds, which have a potential to quench reactive radical intermediates formed during the oxidative processes of both biological and commercial importance materials [1-3]. Phenolic compounds are also mainly classified as secondary metabolites in plants and are divided into phenolic acids and polyphenols [3]. These compounds may exist as mono and polysaccharides, linked to one or more phenolic group, or can occur as derivatives, such as ester or methyl esters [2]. Among the numerous classes of phenolic antioxidants, the phenolic acids, flavonoids, and tannins are considered as the main dietary phenolic compounds [3]. According to the recent investigations, the possible role of antioxidants in prevention of human diseases has taken a leading role. Antioxidants are also capable to defend against a number of disease conditions such as aging, atherosclerosis, cancer, asthma, arthritis, and autoimmune diseases. Antioxidants as external supplements are used to maintain the concentration of free radicals as low as possible and to avoid the oxidative stress [4]. They are heavily used in food industry to maintain the quality of the ready-to-eat foods, and to boost the shelf life [5, 6].

The computational chemistry has become a versatile tool to investigate a wide range of thermodynamic properties which are hardly measurable, as well as to predict the trends between them. The efficiency of an antioxidant can be successfully estimated by analyzing the potential energy surface (PES) of the reaction with a certain radical. This potential energy surface permits calculation of the activation and reaction energies, entailing that both kinetic and thermodynamic approaches to the interested reaction are presented [6]. The computed parameters also provide useful information on the radical scavenging power without considering reaction pathway.

There are three major proposed mechanisms which can be used to clarify how antioxidants release the atomic hydrogen from their conjugated OH group to scavenge free radicals: (1) the hydrogen atom transfer (HAT) mechanism, (2) the single electron transfer–proton transfer (SET–PT) mechanism and (3) the sequential proton loss–electron transfer (SPLET) mechanism as illustrated in the Scheme [7, 8].

One of the most important parameters characterizing the antioxidant or radical scavenging activity of many natural and synthetic compounds is the bond dissociation enthalpy (BDE) that can be used to study the antioxidant potential of the HAT mechanism. The adiabatic ionization potential (IP) and the proton dissociation enthalpy (PDE) are utilized to determine antioxidant capacity of the SET–PT mechanism. Thus, the proton affinity (PA) and the electron transfer enthalpy (ETE) are used as thermodynamic parameters to investigate the antioxidant efficiency of the SPLET mechanism [7-9].

Although the Gibbs free energy represents a criterion of the thermodynamically feasible process, Klein and co-authors [9] have revealed for their investigated reactions that the absolute values of the entropic component are much smaller than the enthalpy component. Thus, comparison of BDEs, IPs, PDEs, Pas, and ETEs can illustrate which mechanism is thermodynamically preferred. Although these three mechanisms may or may not co-exist, the net end result of all these mechanisms is almost the same.

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