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Chapter

Thermodynamics and Kinetics of *Camellia sinensis* Extracts and Constituents: An Untamed Antioxidant Potential

Douglas Vieira Thomaz

Abstract

Given the relevance of impairing reactive oxygen species (ROS) buildup in tissues, the use of exogenous antioxidants is highly regarded as a valid prophylaxis against oxidative stress and its deleterious effects on organisms. In this regard, *Camelia sinensis* uses as a remarkable antioxidant source have been reported in various folk and standard medicine systems around the world. In this chapter, the thermodynamics and kinetics of *Camelia sinensis* constituents is concisely discussed focusing on the implications of its redox profiling toward antioxidant capacity. Notwithstanding, the biological repercussion of ROS reduction as well as its therapeutic potential is also addressed to provide readers a basic background on the relevance of investigating the physicochemical features of medicinal plants.

Keywords: redox, black tea, electrochemistry, free radicals, reactive oxygen species

1. Introduction

1.1 The principles of antioxidant thermodynamics in biological systems

Antioxidant capacity has been described by many authors as an important property of phytomedicines due to the extent of biological effects linked to it [1–3]. This key feature in plant-based drugs and nutraceuticals is widely exploited by industry to increase product appeal as well as to improve the health benefits allegedly promised by their consumption [3–5]. The main premise behind the antioxidant lore is that it counteracts the oxidative stress generated by biological systems [6, 7]. In this sense, the regular intake of free radical scavengers would safeguard the proper attunement of homeostatic balance by diminishing oxidative stress [8, 9].

The natural workings of biological systems, although quite complex at first glance, are based on two simple reactions which quite often occur in close connection to each other [8]. These reactions are reduction and oxidation, commonly shortened to redox reactions. The oxidation is based on electrons (e) leaving the chemical species (A), as represented in Eq. (1), while reduction is based on a chemical species (A) accepting electrons (e), as represented in Eq. (2). These reactions can occur simultaneously, leading to a redox couple, as showcased in Eq. (3).

$$A^0 \rightarrow A^{+1} + 1e^{-1} \tag{1}$$

$$A^{+1} + 1e^{-1} \rightarrow A^0 \tag{2}$$

$$A^0 \leftrightarrow A^{+1} + 1e^{-1} \tag{3}$$

Regarding all processes which are related to the occurrence of life, redox reactions are deeply important since biological systems feed on the chemical energy produced by oxidation [8]. To a certain extent, cells behave quite like thermal power plants, thereby "burning" certain nutrients to obtain energy for self-sustainability. This process is however imperfect, as oxidation byproducts may be highly reactive, therefore degrading functional biomolecules which come in contact with them [5, 9, 10]. These reactive byproducts are the often-demonized reactive oxygen species (ROS), which include oxygen-bearing free radicals and other reactive compounds [11, 12]. An overview of ROS and other reactive chemicals is showcased in **Table 1**.

Albeit ROS are widely known for their negative effects on organisms, these compounds do have remarkable importance to sustain life. Although such statement might be seemingly paradoxical, oxidative stress and ROS buildup are essential to proper inflammatory response as well as immunologic defense [8, 11, 12]. Moreover, the relevance of ROS in the natural workings of cell physiology is still being discovered, since these compounds have been linked to many biochemical pathways and cell signaling processes. For instance, superoxide anion showcases affinity to sulfur residues bound to iron coordination complexes as the heme in cytochromes, while some non-radical ROS may showcase affinity to exposed sulfur-bearing amino acids such as cysteine, thence selectively targeting these moieties [11–13]. Therefore, the true concept behind antioxidants is not the full disruption of oxidative stress, but the balance of this natural phenomenon toward proper homeostasis.

Non-radical ROS	Radical ROS
O_2 (oxygen)	$\cdot^- O_2$ (superoxide anion)
H_2O_2 (hydrogen peroxide)	$\cdot OH$ (hydroxyl)
O_3 (ozone)	$\cdot HO_2$ (perhydroxyl)
Obtainable through excitation	
$^1O_2$ (singlet oxygen)	
Obs.: Radical ROS are obtainable by sequential single-electron oxidation of water and its oxidation products, namely, hydroxyl radical, hydrogen peroxide, superoxide anion, and molecular oxygen. Singlet oxygen is obtainable through excitation of molecular oxygen.	

Table 1.
Overview of ROS and other reactive chemicals.

Enzymes	Nonenzymatic	Proteins
Catalase	Bilirubin	Lactoferrin
Superoxide dismutase	Uric acid	Metallothionein
Glutathione peroxidase	Glutathione	Transferrin
Glutathione reductase	Lipoic acid	Ceruloplasmin
Thioredoxin reductase	Melatonin	Ferritin

Table 2.
*Endogenous antioxidants reported in literature.*

Considering that all chemicals showcase intrinsic physicochemical features regarding their proneness to undergo redox reactions, the feasibility of antioxidant capacity can be linked to the thermodynamics of selected compounds in comparison to endogenous antioxidants of both chemical and enzymatic nature [8, 11, 14–16]. Thus, the Gibbs free energy, enthalpy and entropy of alleged antioxidants can be compared to those of endogenous free radical scavengers and oxireductive enzymes in order to assess the thermodynamic feasibility of antioxidant capacity [9, 17, 18]. **Table 2** showcases the main endogenous antioxidants reported in literature.

The activity of endogenous antioxidants is remarkably high in order to counteract the effect of the oxidative stress promoted by cell physiology; however, the presence of compounds bearing higher thermodynamic proneness to reduce ROS could safeguard the whole biological material in site. This antioxidant capacity can be assessed by many methods, such as thermodynamic evaluation through spectrophotometry, electrochemistry, and other approaches. However, redox reactions may be dependent on mass transfer through solution or other processes which reduce reaction speed, which thence raises the importance of also evaluating the kinetics of antioxidant capacity.

2. Basic physicochemical features of *Camellia sinensis* antioxidants

Camellia sinensis, also known as green or black tea according to its production method, is a widely commercialized herb whose therapeutic applications are highly
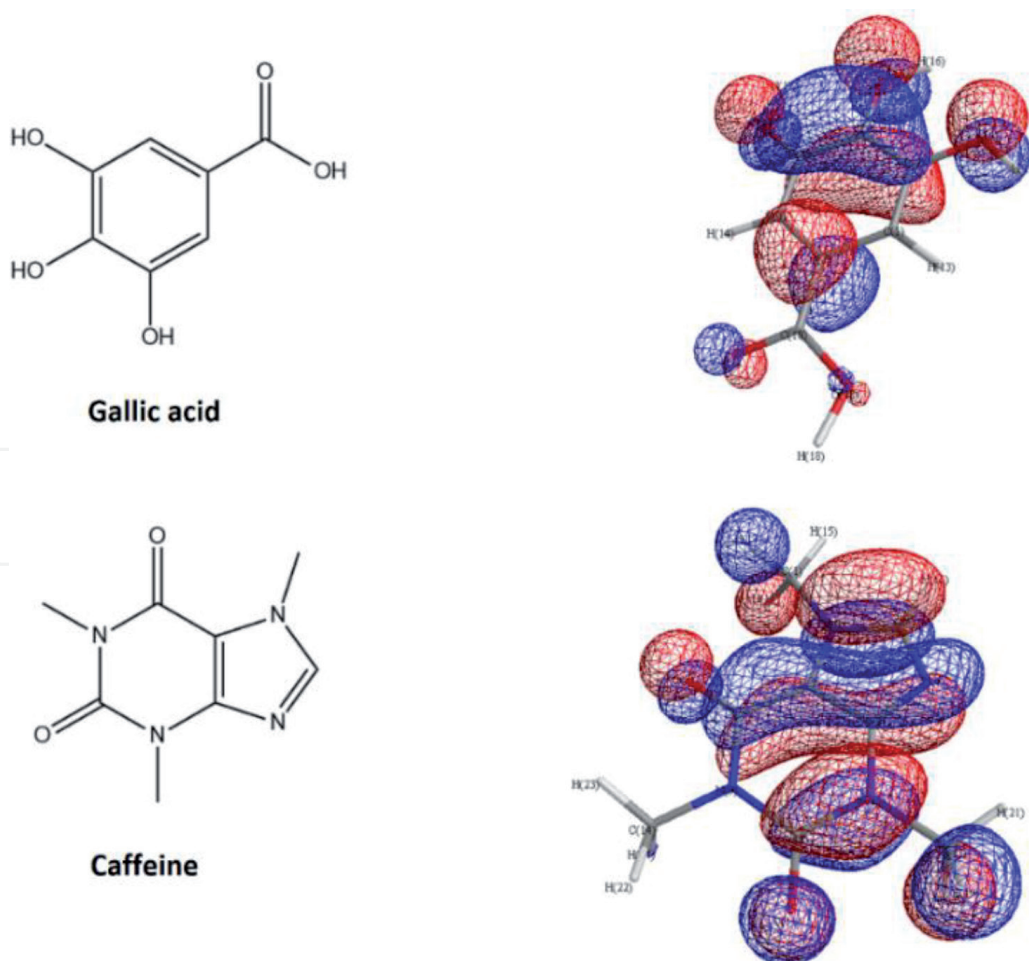
Figure 1.
Known constituents of C. sinensis*, gallic acid, and caffeine, which are acknowledged to exert antioxidant power, and graphical rendering of HOMO-0 for each constituent. Negative charges are rendered in blue, and positive charges are rendered in red.*

regarded in the folk medicine of many regions around the globe [19–23]. This plant is acknowledged to harbor a chemically diverse metabolism, and its constituents are known to promote strong antioxidant action in biological systems [18, 24]. **Figures 1** and **2** showcase some major constituents of *C. sinensis* which are known to exert anti-oxidant action as well as the surface rendering of the first state of their highest occupied molecular orbital (HOMO-0) using standard Hückel molecular orbital theory [25, 26].
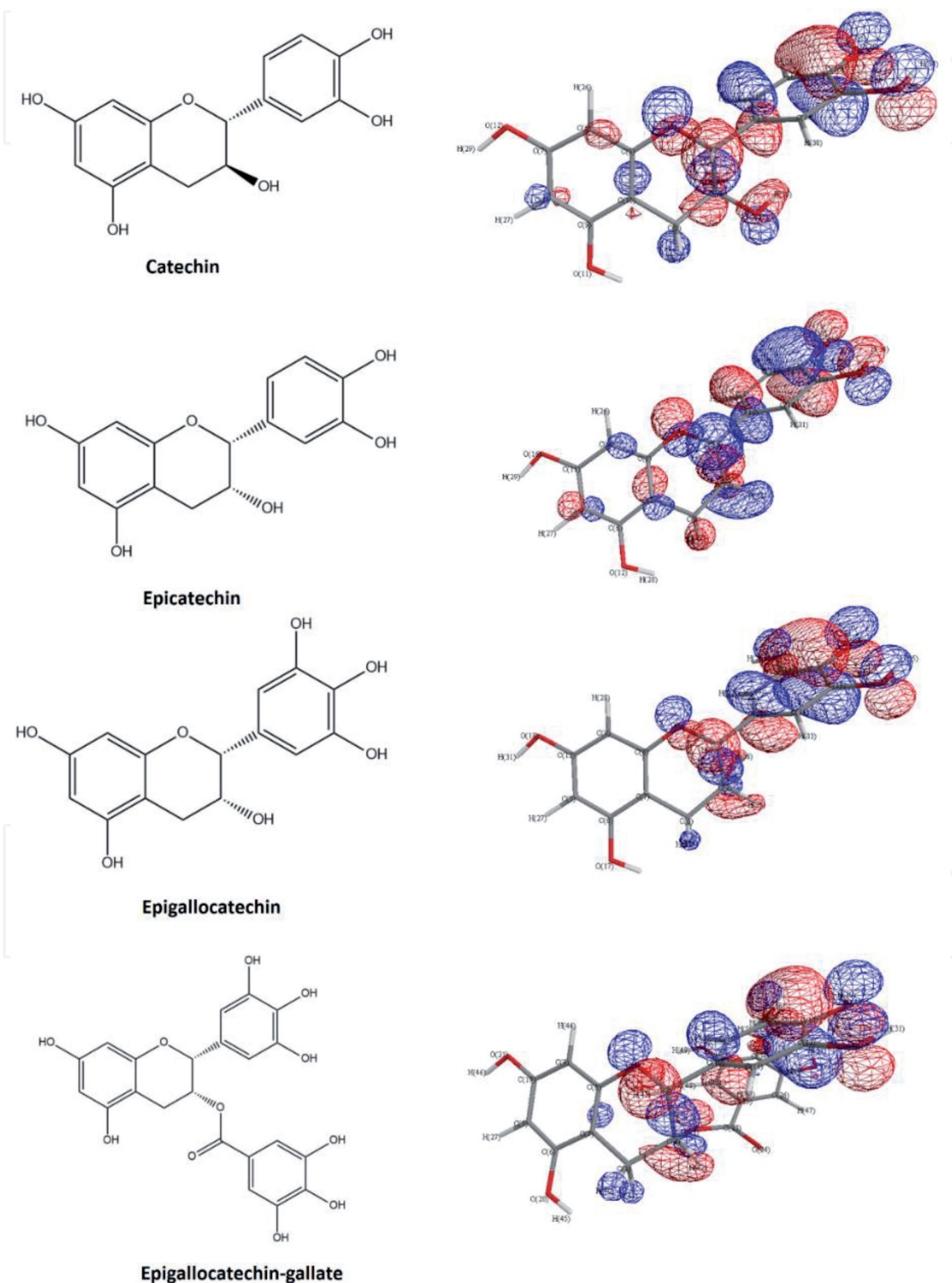
Figure 2.
Known flavonoid constituents of C. sinensis*, which are acknowledged to exert antioxidant power, and graphical rendering of HOMO-0 for each constituent. Negative charges are rendered in blue and positive charges are rendered in red.*

Constituent	HOMO-0 (eV)	LUMO-0 (eV)	ΔE (|LUMO-HOMO|)
Catechin	−10.885	1.293	12.178
Epicatechin	−10.938	1.254	12.192
Epigallocatechin	−10.528	2.382	12.91
Epigallocatechin gallate	−10.549	−3.117	7.432
Gallic acid	−11.026	−3.01	8.016
Caffeine	−9.26	2.047	11.307

Obs.: ΔE also displayed in eV.

Table 3.
HOMO-0, LUMO-0, and energy gaps (ΔE) for each major C. sinensis *constituent.*

As showcased in **Figures 1** and **2**, the resonance systems promoted by aromatic rings in both the flavonoids, as well as gallic acid and caffeine, allow the inference that the inductive effect of functional groups may be transmitted along the molecule [25, 26]. This assumption is supported by both Hückel molecular orbital theory and its implications in medicinal chemistry through the vinylogy principle [27]. In this sense, all these molecules could undergo redox reactions due to their easily excitable electrons in the conjugated aromatic systems (flavonoids) and single aromatic ring (gallic acid and caffeine) [25]. Notwithstanding, this interpretation is further corroborated by experimental data as well as by the evaluation of their energy gap (ΔE) in comparison to that of other known antioxidants such as alpha-tocopherol, which showcase ΔE of 10.2011 eV when analyzed under the same method [25, 26, 28, 29]. **Table 3** showcases the ΔE of major *C. sinensis* constituents.

The ΔE of chemical compounds is an important parameter to evaluate the thermodynamic feasibility of redox processes; hence lower values suggest easier electron transfer and therefore higher possibility of occurrence [25, 26]. Nonetheless, complex approaches such as density functional theory (DFT) are often employed to gather thermodynamic data from ab initio computational models in order to investigate the proneness of chemicals to undergo oxidation [28].

3. Thermodynamics of redox systems and ways to explore it

Thermodynamic data obtained through ab initio or empiric/semi-empiric approaches such as DFT and Hückel molecular orbital theory can also be combined to other physicochemical investigations in order to render more reproducible models regarding energy shifts in redox reactions. Among the most associated techniques are quantum chemistry and electrochemistry [28], which provide relevant information concerning energy parameters and the kinetics of chemical processes.

When energy levels are concerned, the overall behavior of a system can be investigated by the fundamental laws of thermodynamics, as summarized in Eq. (4).

$$\Delta G = \Delta H - T \Delta S \tag{4}$$

wherein ΔG stands for Gibbs free energy, ΔH stands for enthalpy, T stands for temperature, and ΔS stands for entropy. Note that all energy parameters are approached as variations between different states of the system.

Considering that Gibbs free energy can also be expressed according to Eq. (5), we can thence declare the dependence of energy to the equilibrium constant of reactions, as showcased in Eqs. (6) and (7).

$$\Delta G \;=\; -RTLn\,K_{eq} \tag{5}$$

$$A_{red} \;\leftrightarrow\; A_{ox} + 1e^{-1} \tag{6}$$

$$K_{eq} \;=\; \frac{A_{ox}}{A_{red}} \tag{7}$$

wherein R stands for the universal gas constant.

From these relations, both Van't Hoff and Nernst equation are achievable. Taking Nernst equation for instance, one can clearly see how electric potential is a thermodynamic parameter, as showcased in Eqs. (8) and (9).

$$\Delta G \;=\; -nF\,\Delta E \tag{8}$$

$$\Delta E \;=\; -\frac{RT}{nF}Ln\,\frac{A_{ox}}{A_{red}} \tag{9}$$

wherein n stands for the number transferred electrons in the system and F stands for the Faraday constant.

Considering that electric potential is a thermodynamic parameter, the antioxidant capacity is therefore conditioned by both energy levels of oxidized and reduced forms and the reaction rate thereby associated. In this context, electrochemical tests such as chronoamperometry and voltammetry can be used to investigate the electric potentials associated to redox reactions, as well as the kinetic profile they follow [8, 16].

4. Investigating the basics of *Camellia sinensis* antioxidant thermodynamics and kinetics

Many authors reported that *C. sinensis* antioxidant power is remarkable due to the capacity of its constituents to promptly reduce standard free radicals such as 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) [18, 24, 30, 31]. Although results are often noteworthy, colorimetric tests tend to be biased due to the strong color of *C. sinensis* extracts, which may lead to imprecise results. In this regard, many authors pursued the exploration of the redox behavior of this plant using electrochemical methods, which may provide less color-biased results due to their unique dependence on electron transfer [17, 32, 33].

The electroanalytical investigation of plantstuff is a growing field on science due to its promising perspectives regarding the quality control, authenticity, and physicochemical characterization of plant secondary metabolites [32–34]. Nonetheless, most voltammetric assays can be applied to plants without strenuous pretreatment of the vegetal sample [32]. However, given that plant secondary metabolites of phenolic origin such as those of *C. sinensis* showcase electrochemical processes which are mainly controlled by mass transfer in the bulk solution [17], as well as proneness of oxidation products to undergo adsorption on electrode surface, a careful electrode surface renewal protocol needs to be adopted.

Regarding the basic background on voltammetric studies, these tests involve the interpolation of two functions, namely, electric potential *versus* time ($E \times t$) and

electric current *versus* time ($I \times t$). When graphically displayed, a voltammogram is the plot of electric current *versus* the applied electric potential following a specific signal pattern during a defined time interval ($I \times E$). Therefore, any change in electric current which is non-capacitive by nature can be attributed to redox processes taking place in the electrochemical cell [35–37].

During voltammetric investigation, the scanning of electric potential toward positive values, aka anodic scan, leads to the visualization of oxidative processes, while the reverse scan, aka cathodic scan, leads to the visualization of reduction processes [35, 37]. Taking these concepts into account, the redox profiling and electrochemical characterization of both isolated plant constituents and vegetal extracts can be elucidated by varying the kind of scan which is being performed [10, 17, 33, 34]. **Figure 3** showcases an example of a cyclic voltammogram presenting a response which could be attributed to a reversible redox reaction, while **Figure 4** depicts an overview of the main mechanisms which are involved in the electrooxidation of *C. sinensis* constituents [7, 27, 38–40].

Literature reports that *C. sinensis* extracts showcase anodic peaks at electric potentials bellow 0.5 V when analyzed under voltammetry [17, 18, 30, 31, 41], which is nonetheless a remarkable feature. Considering that most of the endogenous antioxidant arsenal operates at electric potentials close to this value, the reductive power of *C. sinensis* constituents is noteworthy, since they could undergo oxidation thereby stabilizing ROS or restituting endogenous antioxidants [8, 10, 27, 42].

Notwithstanding, many authors showcased evidence of redox reversibility in the processes which take place at 0.5 V in *C. sinensis* extracts, which suggests that the antioxidant compounds could undergo followed redox reactions to promote the reduction of ROS in biological systems [32, 33]. When compared to voltammetric profiles of isolated compounds, *C. sinensis* voltammograms evidence the richness of electroactive compounds which are present in this plant, which further corroborates to the appeal of this plant in the development of therapeutic and nutraceutical products to balance oxidative stress in biological systems.
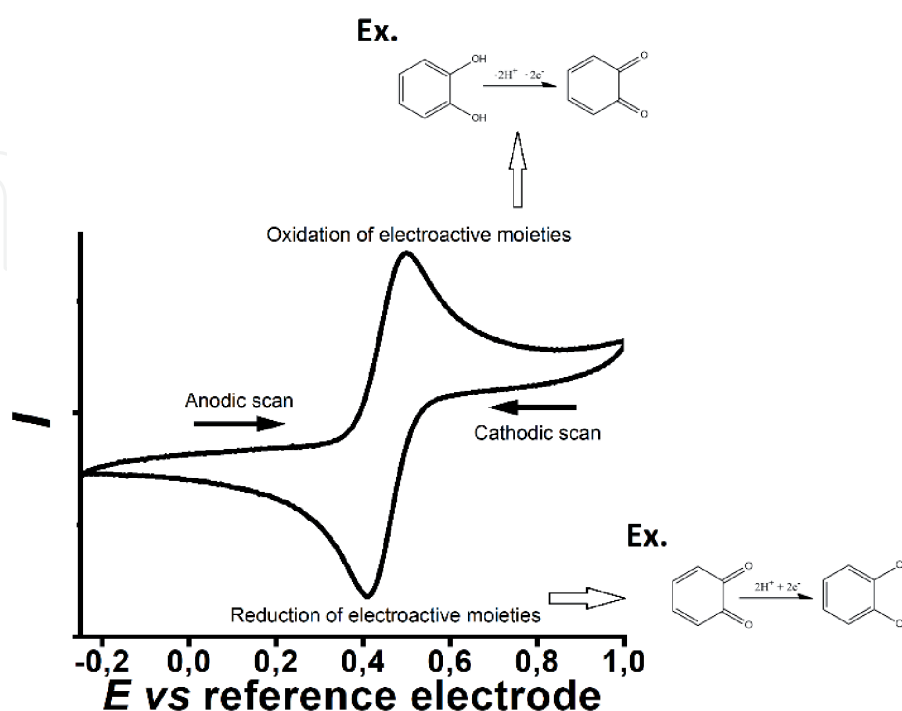
Figure 3.
Example of a cyclic voltammogram presenting a response which could be attributed to a reversible reaction.
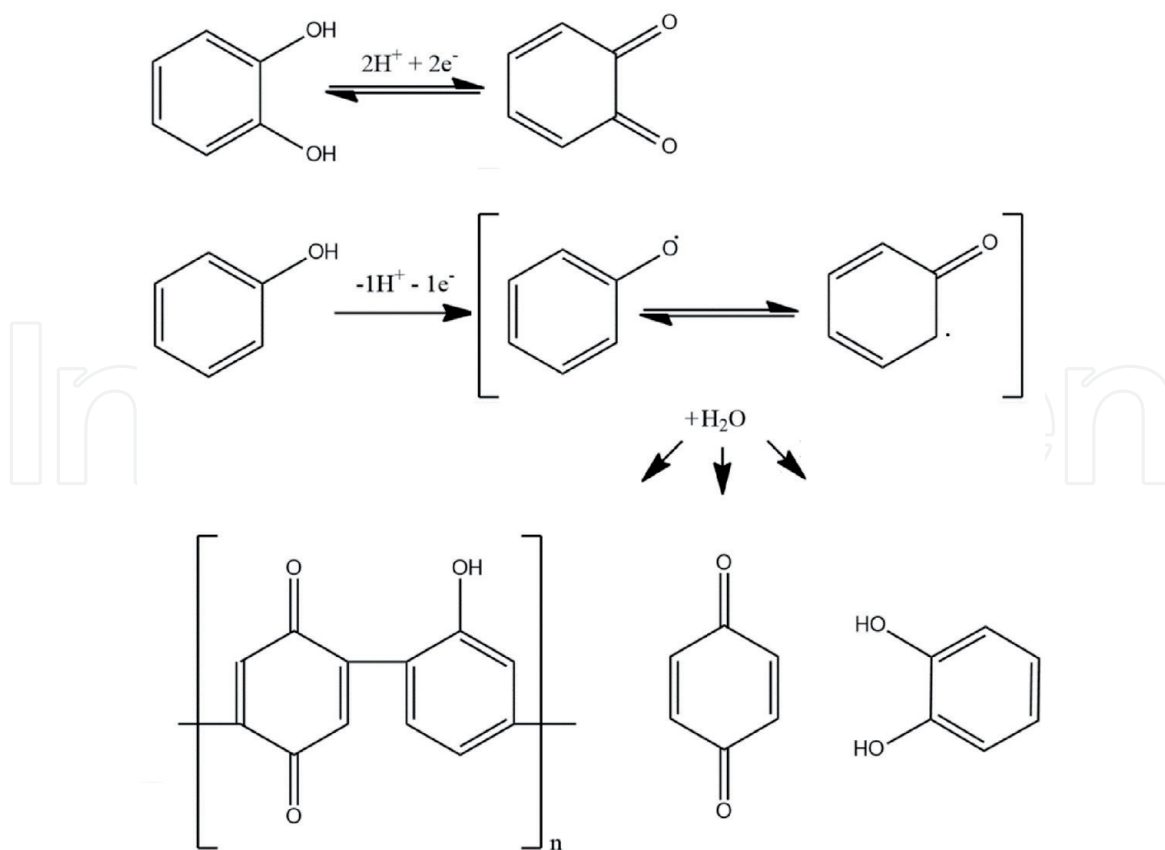
Figure 4.
Main mechanisms involved in the electrooxidation of phenolic compounds which are occurrent in C. sinensis*.*
Note that catechol oxidation is reversible, while phenol undergoes irreversible oxidation, leading to both 1,2 and
1,4 catechol and an electro-polymerized product.

5. Conclusions

This chapter aimed to provide readers with a basic background on the relevance of investigating the physicochemical features of *Camelia sinensis*, as well as concisely discuss the implications of the redox profiling in the understanding of antioxidant capacity. It was observed that several methods can be used to investigate the underlying thermodynamic and kinetic features which are intrinsically linked to the antioxidant power of phytomedicines. Moreover, literature extensively reports the remarkable antioxidant power of *C. sinensis* extracts and constituents, therefore highlighting the relevance of this plant as an important asset for the development of therapeutic and nutraceutical formulations.

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