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Determination of the absolute redox potential of Rutin: Experimental and theoretical studies

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Abstract

The conditional formal potential, $E^{\circ\prime}$, of Rutin has been studied by cyclic voltammetry using a Rutin film deposited at the multi-wall carbon nanotubes modified glassy carbon electrode (GCE) as the working electrode in different pH phosphate buffered solutions. The experimental standard redox potential, E°, of Rutin is obtained to be 0.88 V versus SHE (Standard Hydrogen Electrode). High-level ab initio calculations have been also performed on a chemical model of Rutin and the absolute reduction potential has been calculated. The theoretical standard reduction potential relative to SHE (0.83 V) is in relatively good agreement with experiment.

Keywords: Rutin; Standard redox potential; Cyclic voltammetry; G3MP2; CPCM

1. Introduction

Electron-transfer reactions, which constitute a well-known class of chemical reactions, play an important role in chemistry and biology. For instance, a photoinitiated electron-transfer reaction is the first step in photosynthesis [1]. The standard redox potential, which measures the propensity of a molecule to donate or accept an electron in solution, is fundamental to understanding chemical and biological electron-transfer reactions [2]. The accurate theoretical calculation of electrode potentials therefore plays an important role in explaining the nature of these important reactions [3]. For these reasons, the accurate theoretical calculation of electrode potential has recently attracted considerable attention (see, for example, recent works by Liu–Guo [2,3], Wass [4], Truhlar–Cramer [5–7], Houk [8], and Garza [9]). Previously, we have reported the determination of experimental redox potential of some organic and biological compounds using cyclic voltammetry, chronoamperometry and rotating disk electrode voltammetry, together with the theoretical calculation of redox potential using popular quantum mechanical methods [10–12]. Very recently, we have also reported accurate calculation of absolute reduction potential of some quinone derivatives in non-aqueous solution of acetonitrile using a high level of theory [13]. In all cases we have found excellent agreement between theory and experiment, indicating that computational chemistry offers a useful tool for studying electrochemistry.

In the present work, we apply theoretical and experimental methods to the study of Rutin (Scheme 1), a very important biological molecule. Rutin, also known as vitamin P, is one of the most bioactive flavonoids and is thought to be an activating factor for vitamin C [14]. Flavonoids are benzo-g-pyrone derivatives and are a large family of naturally occurring organic compounds widely distributed in plants [15]. They have broad pharmacological activity such as alleged anti-aging, and are used in a great variety of health products [16]. For example, Rutin is used in many countries to relieve capillary impairment and to treat venous insufficiency of the lower limbs and is also ingredient of a large number of multivitamin preparations and herbal remedies [16].

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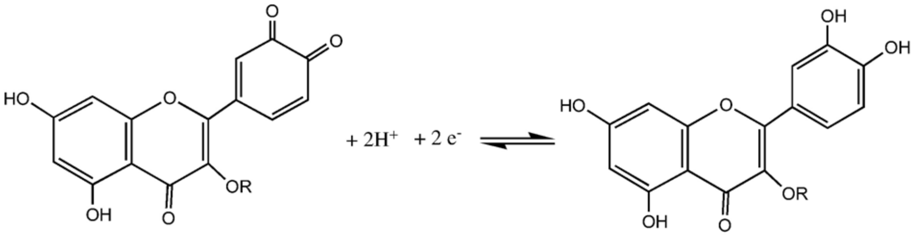


Scheme 1. The two-electron, two-proton redox reaction of Rutin (R = Rutinoside) and the model compound used in the ab initio calculations (R = H).

Rutin, which has been shown to have antioxidative action *in vitro* and *in vivo*, can act directly by entering the redox reactions, and indirectly by chelation of iron. Thus it is important to determine its exact standard redox potential [17,18].

2. Experimental and theoretical methods

2.1. Experimental: materials and methods

Rutin (3′, 4′, 5, 7-tetrahydroxyflurone-3β-D-rutinoside) was obtained from Fluka and used as received. The multi-wall carbon nanotubes (MWCNT) (>95% purity, 10–20 nm diameter, 5–20 μm length) were purchased from Nanolab Inc (Brighton, MA) and used without further purification. Dimethyl formamide (DMF) and all chemical reagents used for buffer solution preparation were reagent grade from Merck. The immobilizing solution of MWCNT was prepared by introducing 5 mg of MWCNT into 5 ml of DMF. The buffer solutions were prepared with doubly distilled water and using H_3PO_4, NaH_2PO_4 and NaOH.

Cyclic voltammograms were drawn using an Autolab potentiostat/galvanostat PGSTAT 30 (ECO Chemic Utrecht, The Netherlands), GPES 4.9 software and a personal computer for data storage and processing. A glassy carbon electrode (GCE), which was modified with Rutin film deposited on MWCNT, was used as the working electrode and an Ag/AgCl (sat.), KCl (3 M) was the reference electrode. The pH was measured with a Metrohm model 691 pH/mV meter.

The Rutin multi-wall carbon nanotubes (RMWCNT) modified GCE was constructed as described previously [17]. Thus, the GCE was polished mechanically with 0.05 μm alumina slurry and then rinsed with doubly distilled water. The GCE was then immersed in 0.1 M sodium bicarbonate solution and was activated by a continuous potential cycling at range of −1.1 to 1.6 V at a scan rate of 100 mV s^{-1}, until stable voltammograms were obtained. For preparation of the modified electrode, a 5 μl of DMF-MWCNT solution (1 mg/1 ml) was placed directly onto the activated GCE surface and dried at room temperature to form a MWCNT film at the GCE surface. Then the MWCNT modified GCE was then immersed in 0.3 mM Rutin solution (pH 3) and was modified using 16 cycles of potential scan between 350 and 600 mV at 25 mV s^{-1}.

3. Theoretical calculations

Standard ab initio molecular orbital theory calculations [19] were carried out using Gaussian 03 [20] software. For the calculations, we have used a very similar molecule to Rutin,

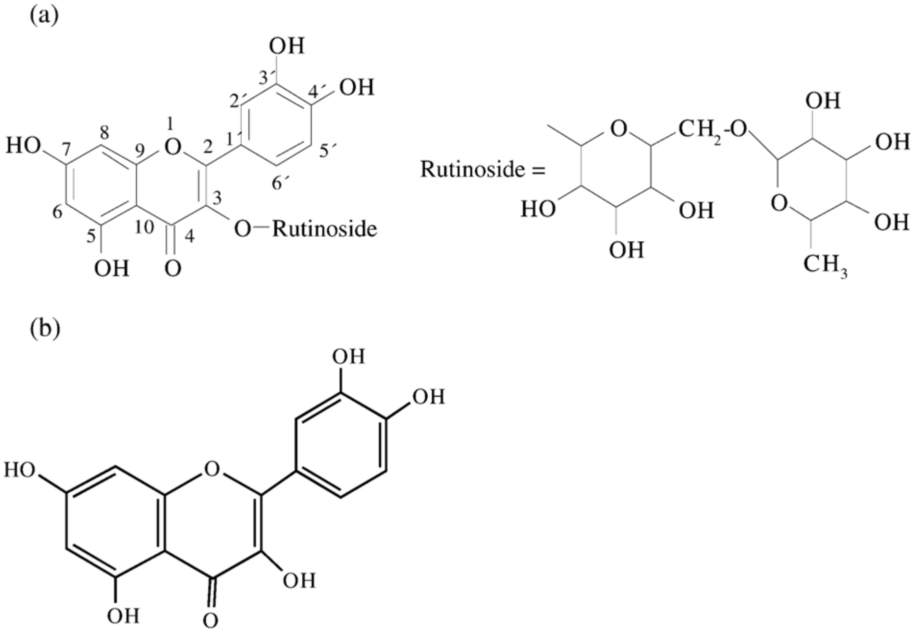


Fig. 1. The structure of Rutin (a) and the model used for the G3MP2 ab initio calculations (b).

RH_2, as shown in Fig. 1(b), as a model since Rutin is too large for high-level ab initio calculations. The Gibbs free energy of each species was calculated using the high-level composite method, G3MP2, which was introduced by Curtiss et al. [21]. This method uses a UMP2(fu)/6-31G(d) optimized geometry and a scaled UHF/6-31G(d) zero-point-energy (by a factor of 0.8929). Then a base energy evaluated at the UQCISD(T)/6-31G(d) level is corrected to UQCISD(T)/G3MP2 large using an additivity approximation at the UMP2 level [22]. This level of theory has been demonstrated to provide an accuracy of 1.41 and 1.46 kcal/mol for calculation of ionization energies and electron affinities when assessed against a large test set of thermochemical data [21]. The average absolute deviation of G3MP2 results from 299 experimental data has been reported to be as small as 1.30 kcal/mol [21].

In order to calculate solvation energies, a continuum model of solvation, the Conductor-like Polarizable Continuum Model (CPCM) [23,24], has been used at the recommended level of theory, B3-LYP/6-31+G(d) [25,26]. The radii of United Atom topological model applied on radii optimized for the density functional theory calculations (UAKS radii), have been chosen for solvation energies as recommended [27]. The rest of the parameters in the solvation models, have been kept as default values [27]. Geometries of the studied species in aqueous solution have been re-optimized fully in the presence of solvent using B3-LYP/6-31+G(d) level of theory. The average error of the calculated solvation energies from the experimental data for neutral molecules at the employed level of theory has been reported to be 0.88 kcal mol^{-1} [25].

4. Results and discussion

4.1. Voltammetric investigations of Rutin

The oxidation reaction and also the formal redox potential of flavonoids such as Rutin depend strongly on their chemical structure. The chemical structure of Rutin is given in Fig. 1 from which it can be seen that Rutin has an ortho-hydroquinone ring in its structure. Previous studies indicate that the response of the Rutin film is pH dependent, and the cyclic voltammograms of Rutin in different pH phosphate buffer contain a single pair of oxidation–reduction peaks, which correspond to the oxidation of 3′, 4′-dihydroxy substituent on the ortho-ring of Rutin and the reduction of the 3′, 4′-diquinone respectively [18]. It was recently reported that the electrochemical behaviour of a Rutin film deposited at the MWCNT modified GCE is reversible, [17] while the Rutin film deposited at the GCE has shown quasireversible behaviour [28]. In the present work, in order to determine the exact conditional formal potential ($E^{\circ\prime}$) of Rutin, the electrochemical behaviour of RMWCNT modified GCE was investigated in different pH buffered solutions.

Table 1
The results of G3MP2 calculations of RH_2 and R as models for Rutin and its oxidized form, together with solvation free energies of species calculated at B3-LYP/6-31+G(d) level of theory

	R	RH_2	Scheme (1)
G3MP2 Energy [a]	−797.73078	−798.96914	–
G3MP2 Enthalpy [a]	−797.72984	−798.96819	–
G3MP2 Free Energy [a]	−797.78195	−799.02072	–
$\Delta G^{\circ}(g)$ / kJ mol^{-1}	−2094576.5	−2097828.9	−3199.8
$\Delta G^{\circ\rightarrow *}$ / kJ mol^{-1}	7.9	7.9	−15.8
ΔG(solv.) / kJ mol^{-1}	−60.1	−69.7	2199.6 [b]
$\Delta G^{*}(t)$ / kJ mol^{-1}	−2094628.7	−2097890.6	−1016.1

[a] G3MP2 Energies are in atomic unit, Hartree (1 Hartree=2625.5 kJ mol^{-1}).

[b] The solvation energy of H^+ has been considered −1104.6 kJ mol^{-1} (−264.0 kcal mol^{-1}) to be consistent with other species. The correction of 7.9 kJ mol^{-1} (1.9 kcal mol^{-1}) for the change in standard state has been considered in the $\Delta G^{\circ\rightarrow *}$ term.

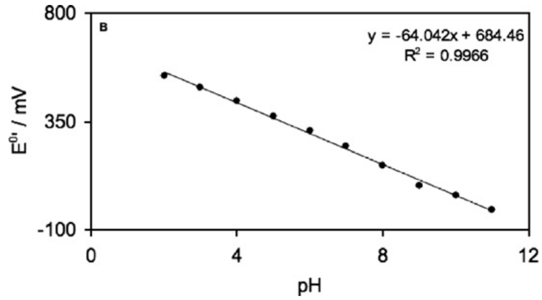


Fig. 2. Plot of conditional formal potential, $E^{\circ\prime}$, versus pH. Conditional formal potentials are taken from cyclic voltammograms of a RMWCNT modified GCE in 0.5 M phosphate buffer at a scan rate of 25 mV s^{-1} at pHs of 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11. For details of cyclic voltammograms see ref. [17].

The conditional formal potential $E^{\circ\prime}$, which will be used for determination of the standard redox potential, E°, can then be obtained from the equation $E^{\circ\prime}=E_{p.a}-\alpha(E_{p.a}-E_{p.c})$ and considering $\alpha=0.4$ [17]. Fig. 2 shows the measured values of $E^{\circ\prime}$, of the $Rutin_{ox}/Rutin_{red}$ redox couple as a function of pH. As can be seen in Fig. 2, $E^{\circ\prime}$ is pH dependent, and could be fitted with the equation $E^{\circ\prime}=-64.04$ pH$+684.5$ with a correlation coefficient (R) of 0.9983. Based on the relation between E°’ and pH, Eq. (1) [29,30], the standard redox potential of Rutin, E°, was obtained from the intercept of Fig. 2 and is equal to 0.68 V versus Ag/AgCl (sat.), KCl (3 M).

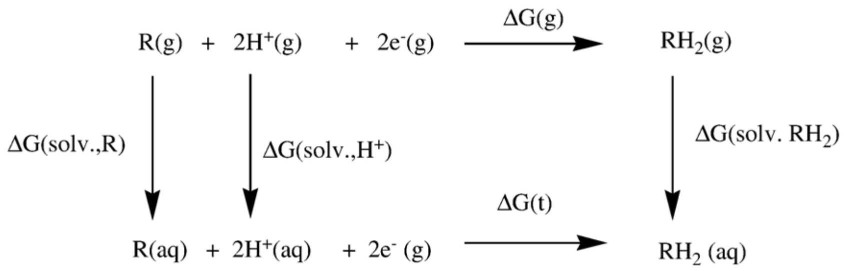
$$E^{\circ\prime} = E^{\circ} - 2.303(mRT/nF)\mathrm{pH} \tag{1}$$

In Eq. (1) m and n are the number of protons, H^+, and electrons in the redox reaction, respectively and all other symbols have their conventional meaning. In the studied range of pH, both m and n are two [17]. Considering the standard electrode potential of the Ag/AgCl reference electrode as 0.20 V [31] relative to the Standard Hydrogen Electrode (SHE), the standard reduction potential of Rutin is 0.88 V versus SHE.

5. Theoretical computation of electrode potential

As noted above, in order to facilitate high-level ab initio calculations, the electrode potential of Rutin was calculated using the model compound shown in Fig. 1(b), which we will refer to as RH_2. RH_2 can be reduced from its oxidized form, R, via the following 2-electron half reaction (see Scheme 1):

$$\mathrm{R(aq.)} + 2\mathrm{H}^{+}\mathrm{(aq.)} + 2\mathrm{e}^{-} \rightarrow \mathrm{RH_2(aq.)} \tag{2}$$



Scheme 2. Thermodynamic cycle used to calculate total free energy of reaction (1) from its components.

The standard Gibbs free energy change of this reaction, $\Delta G^*(t)$ is related to the absolute reduction potential via Eq. (3) [32]:

$$E^\circ = -\Delta G^*(t)/nF \tag{3}$$

where: n is number of electrons transferred ($n=2$ in this case) and F is the Faraday constant (96485 C mol^{-1}) [29]. As Scheme 2 shows, $\Delta G^\circ(t)$ can be calculated from its components by introducing a thermodynamic cycle,

$$\begin{aligned}\Delta G^*(t) = {} & \Delta G^\circ(g) + \Delta G^*(\text{solv., RH}_2) - \Delta G^*(\text{solv., R}) \\ & - 2G^*(\text{solv., H}^+) + \Delta n \Delta G^{\circ\rightarrow *}\end{aligned} \tag{4}$$

where: $\Delta G^\circ(g)$ is the change of Gibbs free energy of Scheme 1 in the gas-phase; $\Delta G^*(\text{solv., RH}_2)$ and $\Delta G^*(\text{solv., R})$ are solvation energies of RH_2 and R in water, respectively; $\Delta G^{\circ\rightarrow *}$ is the correction for the change in standard state from 1 atm for gas-phase calculations “ ° ” to 1 mol L^{-1} for solution phase “ * ” which is 7.9 kJ mol^{-1} for each component (RT Ln (24.46)) [33]; Δn is the change of moles of Scheme 1 and has a value of −2 in the present system. We have used the literature value of −1104.6 kJ mol^{-1} (−264.0 kcal mol^{-1}) for aqueous $\Delta G^*(\text{solv., H}^+)$ which has been recently reported by Truhlar and Cramer [5]. As noted in this previous study, the correction of 1.9 kcal mol^{-1} (7.9 kJ mol^{-1}) for the change in standard state, converts the value of −264.0 kcal mol^{-1} to −265.9 kcal mol^{-1}, which is consistent with the older literature value [5]. However, this correction should not be taken into account twice.

In order to calculate $\Delta G^\circ(g)$, the Gibbs free energies of R and RH_2 have been calculated in the gas-phase using the G3MP2 level of theory as described before (Table 1). For the free electron, we have followed the Ion Convention (IC), which has been used in the “Gaseous Ion Energetics” compilation in the GIANT Tables [34]. However, we have also compared the results with those obtained using the Electron Convention based on Fermi–Dirac statistics (EC-FD) [35]. Based on this convention, the energy and entropy of the free electron were reported to be 3.720 kJ mol^{-1} and 22.734 J mol^{-1} K^{-1} at 298 K, respectively [35]. There is only a small discrepancy in the final results between these two conventions, which will be discussed later in this article. The Gibbs free energy of $H^+(g)$ has been reported to be −26.3 kJ mol^{-1} [33].

Using Eqs. (3) and (4) the absolute reduction potential of R has been calculated as 5.27 V. To allow comparison with experiment, and in that way assess the validity of this theoretical value, it is necessary to calculate the reduction potential of R relative to SHE. Therefore, the absolute value of reduction potential of Standard Hydrogen Electrode (SHE) is required. In the present work we have selected the value of 4.44 V for SHE, which can be found in electrochemistry textbooks [29] and continues to be used in recent studies [2,3]. Therefore, E° has been calculated as 0.83 V versus SHE. The experimental redox potential for Rutin was measured above as 0.88 V using cyclic voltammetry. There is thus a discrepancy of only 0.05 V (or 4.8 kJ mol^{-1}) between theory and experiment, which is typical of the expected error in the theoretical calculations at this level of theory. This good agreement between the experimental and theoretical values for the reduction potential verifies that the model used for the high-level ab initio calculations was close enough to the structure of the real Rutin molecule to include the major of electronic and stereo interactions.

Finally, it is worth noting that, using electron convention, based on Fermi–Dirac statistics (EC-FD) [35], we obtained a value of 0.82 V for the reduction potential of the studied molecule which compares well with the ion convention (IC) value (0.83 V) and the experimental value (0.88 V). It is clear that both the EC-FD and IC conventions can be used in the calculation of accurate electrode potentials.

6. Conclusions

The results obtained in this study show that the conditional formal potential, $E^{\circ\prime}$, of a Rutin film deposited at the MWCNT modified GCE is strongly dependent on solution pH. The experimental standard redox potential, E°, of Rutin was found to be equal to 0.88 V versus SHE. The calculated reduction potential for the studied model has been 0.83 V, which is in good agreement with experiment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bpc.2007.10.010.

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