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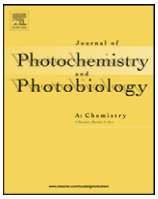

Short Note

How α-tocopherol quenches triplet state riboflavin? Insights from theory

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ABSTRACT

In the present study, the quenching mechanisms of triplet state riboflavin (RF) by α-tocopherol (α-T) have been explored employing density functional theory calculations. Three possible pathways, i.e., one-step H-atom transfer, direct electron-transfer and sequential proton-loss electron-transfer are proposed to account for the triplet state RF quenching by α-T in polar protic media.

1. Introduction

Riboflavin (RF), also known as vitamin B_2, is an endogenous photosensitizer, which can photogenerate various reactive oxygen species (ROS, e.g. $^1O_2$ and O_2^-) [1,2], and cause photosensitized DNA damage [3,4]. As the lowest triplet excited (T_1) state of a photosensitizer is mainly responsible for the photosensitive reactions owing to its relatively long life-time, it is of great importance to investigate the reactivity of the triplet state photosensitizer. Recently, it was reported that α-tocopherols (α-T), one of the most popular bio-antioxidants, can deactivate T_1 state RF in polar protic media [5]. However, the underlying quenching mechanisms of T_1 state RF by α-T still need further investigations. In view of the successful use of theoretical methods in illustrating the photosensitization and antioxidant mechanisms of various bioactive molecules [6–10], we attempt to gain some deeper insights into the T_1 state quenching mechanisms of RF by α-T using density functional theory (DFT) calculations.

2. Methods

Firstly, the electronic parameters of RF and α-T, including adiabatic electron affinity (AEA), vertical electron affinity (VEA), adiabatic ionization potential (AIP), vertical ionization potential (VIP), homolytic bond dissociation enthalpy (BDE) and H-atom affinity (HAA), were calculated by a combined DFT method, labeled as (RO)B3LYP/6-311 + G(2d,2p)//B3LYP/6-31G(d,p). The combined DFT method means B3LYP/6-31G(d,p) was used to optimize the molecular geometries and determine the vibrational frequencies in vacuo and then, single-point electronic energies (SPEs) were calculated by (RO)B3LYP functional at 6-311 + G(2d,2p) level in an implicit water model. The lowest triplet excitation energy (E_{T_1}) of RF and α-T compounds was estimated by TD-B3LYP/6-31G(d,p) method [11–13], whose effectiveness and accuracy in estimating the E_{T_1} of various photosensitizers have been proved [6–8]. During the calculations, the solvent (water) effect was taken into account on the single-point level by employing the self-consistent reaction field (SCRF) method with a polarizable continuum model (PCM) [14–16]. Considering the fact that the phytyl chain has little effect on the electronic properties of α-T, the phytyl chain was replaced by the methyl group during the calculations.

All of the calculations were implemented with Gaussian 03 package of programs [17].

3. Results and discussion

The first quenching pathway may involve direct energy transfer between triplet state RF and α-T (Eq. (1)). However, according to the theoretical results, the E_{T_1} of α-T is larger than that of RF, indicating that the direct energy transfer reaction is not favorable on thermodynamic grounds for the large energy gap.

$$RF(T_1) + \alpha\text{-}T \rightarrow RF + \alpha\text{-}T(T_1) \quad (1)$$

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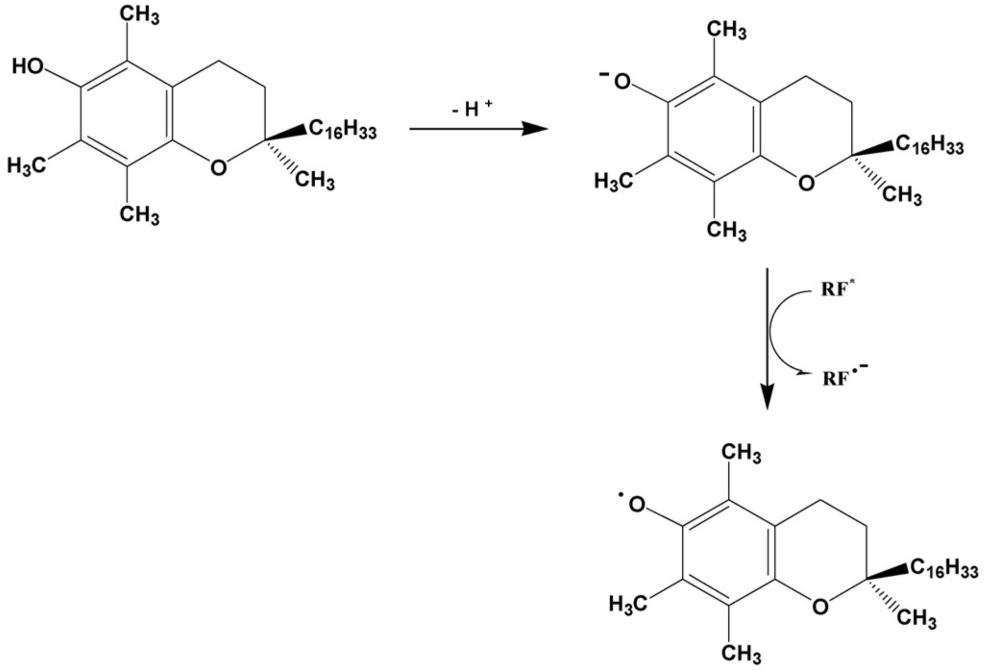

Fig. 1. Theoretically proposed sequential proton-loss electron-transfer-based quenching mechanism of triplet state riboflavin by α-tocopherol.

The second important quenching pathway may occur through direct electron-transfer (ET) from α-T to triplet state RF (Eq. (2)) with the prerequisite that the total energy of the reaction is negative.

$$RF(T_1) + \alpha\text{-}T \rightarrow RF^{\cdot -} + \alpha\text{-}T^{\cdot +} \quad (2)$$

Based on the theoretical T_1 state AEA or VEA (AEA_{T_1} or VEA_{T_1}) of RF and AIP or VIP of α-T (Table 1), the electron-transfer reaction from α-T to T_1 state RF is favorable from the thermodynamic point of view owing to the negative total reaction energy ($AIP + AEA_{T_1}$ or $VIP + VEA_{T_1}$).

Recently, it was proposed that sequential proton-loss electron-transfer (SPLET) plays important role during the free radical-scavenging processes of vitamin E in polar protic media [10,18]. We speculate SPLET may also act during the T_1 state RF quenching by α-T (Eq. (3), Fig. 1), which is supported by the theoretical results that the summation of the AIP of α-T_{anion} and AEA_{T_1} of RF or VIP of α-T_{anion} and VEA_{T_1} of RF is negative (Table 1). Therefore, SPLET

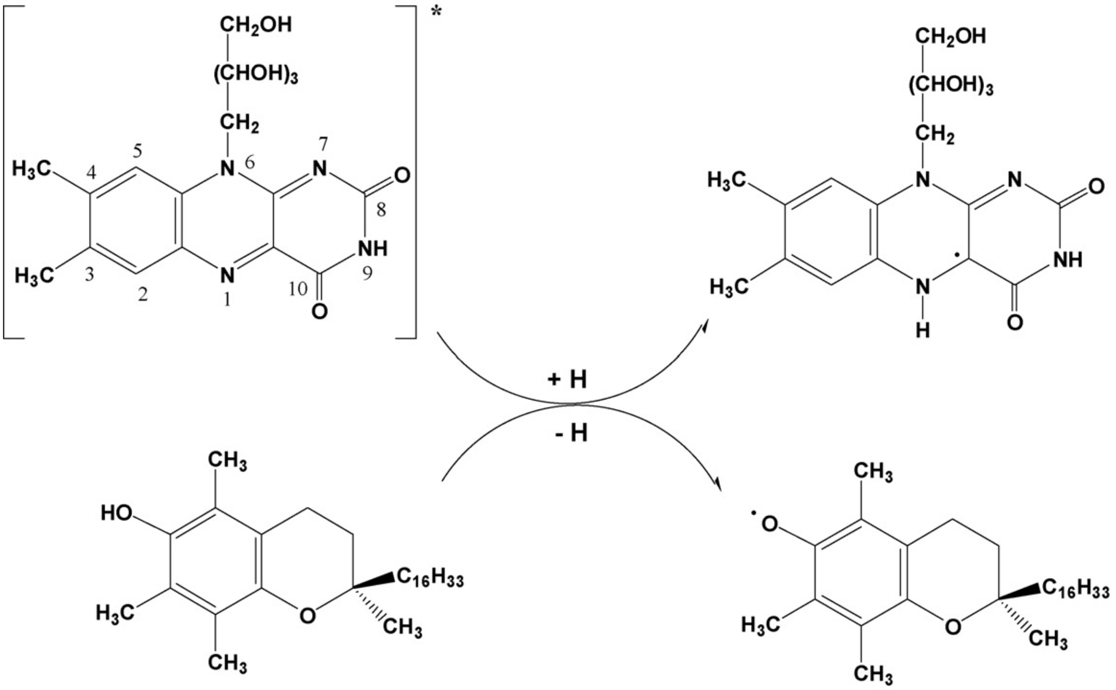

Fig. 2. Theoretically proposed H-atom transfer-based quenching mechanisms of triplet state riboflavin by α-tocopherol.

Table 1
Theoretically estimated lowest triplet excitation energy (E_{T_1}), adiabatic electron affinity (AEA), vertical electron affinity (VEA), adiabatic ionization potential (AIP), vertical ionization potential (VIP), homolytic bond dissociation enthalpy (BDE) and H-atom affinity (HAA) of α-tocopherol (α-T), anion of α-tocopherols (α-T_{anion}) and riboflavin (RF) in ground (S_0) state and triplet (T_1) state (in kcal/mol)

	E_{T_1}	AEA_{T_1} [a]	VEA_{T_1} [b]	AIP	VIP	BDE	HAA_{T_1} [c]
α-T	81.40			119.12	125.50	74.88	
α-T_{anion}				86.04	90.58		
RF	48.20[d]	−130.22	−127.20				105.07

[a] $AEA_{T_1} = AEA_{S_0} - E_{T_1}$.
[b] $VEA_{T_1} = VEA_{S_0} - E_{T_1}$.
[c] $HAA_{T_1} = HAA_{S_0} - E_{T_1}$.
[d] Data from Ref. [19].

accounts for an important pathway during the T_1 state RF quenching by α-T in polar protic media. Once $RF^{\bullet -}$ is generated, according to our previous study, it may then pass one electron to molecular oxygen to give birth to $O_2{}^{\bullet -}$ [19].

$$\alpha\text{-T} \rightarrow \alpha\text{-T}^{-} + H^{+}; \quad RF(T_1) + \alpha\text{-T}^{-} \rightarrow RF^{\bullet -} + \alpha\text{-T}^{\bullet} \tag{3}$$

Moreover, as the phenolic hydroxyl of α-T is ready to donate a H-atom [9,10], the quenching reaction may also occur through H-atom transfer (HAT) from α-T to T_1 state RF (Fig. 2). To explore the probability of this pathway from the thermodynamic point of view, the BDE, which has been successfully used to measure the molecular H-atom-donating ability [9,20,21], and HAA, an appropriate theoretical parameter to characterize the molecular H-atom-abstracting ability [9], of RF and α-T have been estimated. The O–H BDE of α-T was calculated to be 74.88 kcal/mol (Table 1). The HAA of T_1 state RF at the N1 position, which has been proved to be the thermodynamically favorable position to accept H-atom for RF, was 105.07 kcal/mol (Table 1). The HAA of T_1 state RF is larger than the BDE of α-T and thus, the H-atom transfer reaction from α-T to T_1 state RF is favorable on thermodynamic grounds.

In conclusion, the theoretical results indicate that one-step H-atom transfer, direct electron-transfer and sequential proton-loss electron-transfer are more favorable than direct energy transfer on thermodynamic grounds to be involved in the T_1 state RF quenching processes by α-T in polar protic media. The present findings have potential implications on the quenching behaviors of T_1 state RF by other antioxidants.

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