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Formation of singlet oxygen from solutions of vitamin E

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Abstract

Vitamin E offers protection against oxidative stress and is an efficient quencher of singlet oxygen. A recent report suggests that photo-excitation of vitamin E results in the formation of a triplet state (Naqvi et al, Photochem.Photobiol.Sci. 2, 381 (2003)). This leads to the possibility of the triplet state of vitamin E being able to sensitize singlet oxygen and if this is the case it would be counter productive in terms of the biological protective function of vitamin E. We report the production of singlet oxygen, detected by 1270 nm luminescence, from pulsed laser excitation (308 nm) of vitamin E and an analogue, 2,2,5,7,8-pentamethyl-6-hydroxy-chroman (PMHC), with quantum yields between ~0.1 to 0.2. The luminescence was identified as singlet oxygen from self quenching by vitamin E with solvent-dependent rate constants similar to published values. Whilst the beneficial antioxidant aspects of vitamin E are well established, these results indicate that vitamin E when directly excited can sensitize singlet oxygen formation and may therefore be capable of inducing biochemical and biological damage. The results are discussed in relation to recent reports on the deleterious effects of vitamin E dietary supplementation and pro-oxidant effects of vitamin E.

Keywords

Laser flash photolysis; singlet oxygen; vitamin E

INTRODUCTION

Vitamin E is a lipid-soluble antioxidant present in cellular membranes and lipoproteins. It plays a key role in the suppression of free radical-induced lipid peroxidation *in vivo* by functioning as a chain-breaking antioxidant [1,2]. Vitamin E is present in eight different forms (α -, β -, γ -, δ -, tocopherol/tocotrienols). α -Tocopherol (α -T) is most potent as an antioxidant and is preferentially retained in the body suggesting a specific mechanism for the uptake of this form [3,4]. There is growing evidence for non-antioxidant roles played by vitamin E in the areas of growth regulation and signalling [5,6]. Such claims need careful evaluation given the well established knowledge base on how vitamin E protects against a wide range of pathological conditions, including atherosclerosis, cancer, diabetes and ageing [2,7]. In particular, recent studies from trials involving dietary supplementation with high levels of vitamin E have not shown the expected beneficial protection against gastric cancers by vitamin E [8]. In the most recent study, a statistically significant relationship between vitamin E dosage and increase in mortality from all causes was deduced on supplementation with >150 IU/day [9].

Singlet oxygen may be formed by energy transfer from a photoexcited state of a sensitizer [10] or from thermal decomposition of some endoperoxides [11]. It is a highly reactive form of molecular oxygen and is capable of damaging biomolecules such as proteins [12], nucleic acids [11] and lipids [13]. Cellular systems are protected to some extent from the deleterious effects of singlet oxygen by antioxidants, in particular vitamins E and C. In mice, topically applied vitamin E prevents UV-induced cancers in the skin, but is simultaneously degraded to oxidation products (quinone) and tocopherol dimers and trimers [14]. In contrast, in some studies α -T has found to be ineffective in preventing other UV-induced effects such as erythema and immunosuppression [15]. It is possible that photoinduced tocopheroxyl radicals induce lipid peroxidation and deplete the cellular supply of other antioxidants [16]. Several studies have shown that vitamin E and its analogues are very effective quenchers of singlet oxygen with second order rate constants of $\sim 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [17-19]. This evidence shows how at least mechanistically vitamin E protects the cell from harmful oxidants and this is particularly important given that singlet oxygen has been observed from photoexcitation of a range of biomolecules [10, 20]. Singlet oxygen is formed by energy transfer from either excited singlet or triplet states of the sensitizer, although the latter are more frequently involved due to their longer lifetime in fluid solution [10]. Several reports indicate that triplet states of phenols, often with relatively high yield, are formed by intersystem crossing from the excited singlet state [21, 22]. However, triplet states of phenols are difficult to observe directly using flash photolysis methods because they have low extinction coefficients and their spectra overlap with the simultaneously formed phenoxyl radicals. This difficulty has been overcome by Naqvi et al who have presented evidence for the existence of the triplet state of α -T, by observing triplet β -carotene that can only be formed via a triplet-triplet energy transfer process [23]. We now present evidence, based on direct detection of singlet oxygen by time-resolved infrared luminescence, that α -T is capable of acting as a singlet oxygen sensitizer when excited in the UVB region at 308 nm. Whilst it is usually assumed triplet states will sensitize formation of singlet oxygen this is not always the case because of other competing reactions, such as electron transfer from an excited state to produce the superoxide radical, O_2^- . Measurements have also been undertaken with the vitamin E analogue 2,2,5,7,8-pentamethyl-6-hydroxy-chroman (PMHC). Whilst lacking the phytyl chain of vitamin E, PMHC contains the same head group and chromophore as vitamin E, functions similarly as an antioxidant in model homogenous systems [1], and may be obtained in pure form.

MATERIALS AND METHOD

Solvents (spectroscopic grade) and vitamin E (>97% purity) were obtained from Sigma-Aldrich Company Ltd. Trimethylhydroquinone, zinc chloride and isoprene used in the preparation of PMHC were obtained from Sigma-Aldrich Company Ltd and used as received. PMHC was prepared as described [24] and purified by recrystallization from ethanol followed by sublimation under reduced pressure. Further recrystallization from petroleum ether afforded white needle-like crystals (m.p. 95.0-95.3 °C, lit value 94-94.5 [24]) in 90% yield. The purified material gave a single spot on TLC. ^1H δ NMR (400 MHz, CDCl_3) 4.0 (s, 1H), 2.5 (t, 2H), 2.0 (s, 3H), 1.95 (s, 6H), 1.6 (t, 2H), 1.10 (s, 6H). MS (EI) m/z : 220 (M^+ , 220 (100)). (CI) m/z 221 (M^+ , H^+ (100)).

Absorption spectra were measured using Perkin-Elmer 410 double beam uv-vis spectrophotometer. For singlet oxygen measurements, samples contained in a 1 cm quartz cuvette were illuminated with 308 nm laser pulses ($\sim 15 \text{ ns}$, ca 1.5 mJ/pulse) from a Lumonics Pulsemaster PM-846i XeCl excimer laser. Singlet oxygen emission from the central region of the cuvette was detected by time-resolved phosphorescence using a 1270 nm interference filter and a Ge photodiode (North Coast 8171) cooled to 77 K.

RESULTS AND DISCUSSION

Singlet oxygen lifetimes and self-quenching by vitamin E

The time-resolved luminescence profiles from pulsed laser excitation (308 nm) of aerated solutions of vitamin E ($0.23 \text{ mmol dm}^{-3}$) in n-hexane (Figure 1A) show a fast spike ascribed to fluorescence and scattered laser radiation, followed by a strictly mono-exponential process over some tens of microseconds. Saturation with oxygen resulted in an increase of the signal by 40% compared with the aerated solution, without significantly affecting the lifetime (τ) of the decay. However, deaeration by bubbling with argon very substantially reduced the signal intensity. In further experiments in cyclohexane solution, increasing the vitamin E concentration resulted in an increased luminescence intensity measured at zero time after the laser pulse, whilst the lifetime (τ) of the emission decreased (Figure 1B), indicating quenching. A plot of the first order rate constant (k_1 , equal to $1/\tau$) versus vitamin E concentration was linear (Figure 2) i.e.

$$k_1 = k_0 + k_q [\text{Vitamin E}] \quad (1)$$

In cyclohexane, the slope of this plot gave a second order rate constant for quenching of singlet oxygen (k_q) of $(1.2 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, compared with a previous value of $8.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [17]. From the intercept, k_0 , the lifetime in pure cyclohexane (τ_0) was $21.9 \pm 0.2 \mu\text{s}$ (literature value in cyclohexane 17 - 24 μs [19]). Similar experiments in n-hexane and methanol gave τ_0 values of 35 μs and 9.1 μs , compared with literature values of 30-31 μs and 9-12 μs respectively [19]. The results from equivalent experiments with the vitamin E analogue, PMHC, gave similar results summarised in Table 1. Compared with literature values, the only major discrepancy is in the rate constant for singlet oxygen quenching by PMHC in cyclohexane where the present value of $7.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (literature $2.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) shows a reduction in reactivity between methanol and cyclohexane similar to that for vitamin E. The effect of oxygen concentration on luminescence intensity and the extrapolated luminescence lifetimes in the three solvents are entirely consistent with the observed emission being due to singlet oxygen luminescence at 1270 nm. The decrease in luminescence lifetime (τ) with increasing vitamin E or PMHC concentration corresponds to quenching of singlet oxygen by these compounds with established rate constants of ca. $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The experiments therefore show that photoexcitation of vitamin E at 308 nm results in the production of singlet oxygen that is recognised by its characteristic intrinsic lifetime in the solvents investigated and by its quenching by vitamin E. The kinetics of this process are discussed further below.

Quantum yields of singlet oxygen (Φ_Δ)

The quantum yields for singlet oxygen formation, Φ_Δ , from photoexcitation of vitamin E and PMHC were estimated by comparison with those of known standards phenanthrene and naphthalene. The relative yield (Y_Δ) of singlet oxygen was estimated from the luminescence intensity extrapolated to the zero time of excitation by the laser pulse. The value of Φ_Δ for vitamin E was obtained from a comparison of the extrapolated signal intensities for solutions of vitamin E and a reference compound with matched absorbance at the laser wavelength of 308 nm using equation (2). Plots of Y_Δ versus A_{308} will also be linear for samples with absorbance values less than ~ 0.1 over the pathlength used for the measurement.

$$\frac{Y_\Delta^{\text{vitE}}}{Y_\Delta^{\text{ref}}} = \frac{\Phi_\Delta^{\text{vitE}} A_{308}^{\text{vitE}}}{\Phi_\Delta^{\text{ref}} A_{308}^{\text{ref}}} \quad (2)$$

Figure 3A shows plots of Y_{Δ} versus A_{308} for both vitamin E and naphthalene. Taking Φ_{Δ} for naphthalene [10, 25] as 0.73 gives a singlet oxygen quantum yield from 308 nm excitation of vitamin E of 0.085 ± 0.005 , whereas a similar experiment using phenanthrene as the standard ($\Phi_{\Delta} = 0.44$) [10, 26] gave Φ_{Δ} (vitamin E) as 0.11 ± 0.03 . An average value of 0.097 is shown in Table 1. The same experiment with PMHC in cyclohexane gave a similar Φ_{Δ} of 0.12 ± 0.01 . Further experiments were undertaken in methanol solution (Figure 3B), where values of Φ_{Δ} increased to 0.17 ± 0.025 and 0.16 ± 0.012 for vitamin E and PMHC respectively. The increase in Φ_{Δ} in methanol compared with cyclohexane corresponds to the increase in triplet quantum yield for phenols with increasing solvent polarity [22]. For example, for 4-*tert*-butylphenol the triplet yield increases from 0.27 in cyclohexane to 0.67 in ethanol. Vitamin E is rather difficult to purify and the sample used contained up to 3% impurities. The similarity in Φ_{Δ} values for vitamin E and the model compound PMHC demonstrates that the singlet oxygen originates from the vitamin E and not from the impurities.

The lifetime of the excited singlet state of vitamin E has been measured as 1.1 ns in hexane [27]. The relatively small increase in yield of the 1270 nm emission from singlet oxygen on fivefold increase in oxygen concentration (air versus oxygen saturated solutions) is inconsistent with an energy transfer process from such a short-lived singlet state. We propose that the formation of singlet oxygen results from energy transfer from a longer-lived triplet state with a lifetime in the absence of oxygen of about a microsecond. Whilst the triplet excited state of vitamin E has not been observed directly, there is evidence for its formation via triplet energy transfer to form triplet β -carotene after electronic excitation of vitamin E [23]. Direct spectroscopic observation of a triplet state has been reported for phenol and methylated phenols, in which the intensity at $\lambda > 300$ nm is low ($\epsilon < 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [21] and overlaps with the stronger absorption of the phenoxy radical [28] which is formed simultaneously at moderate laser powers. For non-sterically hindered phenols the quantum yield for triplet formation (Φ_T) is as high as ca. 0.6 in cyclohexane and fluorescence lifetimes of between 1 and 2 ns were measured [22]. In contrast, sterically hindered phenols such as 2,6-di-*tert*-butylphenol [29] were found to have very short singlet state lifetimes (ca. 50 ps) and correspondingly low values of Φ_T (< 0.01). This is expected because of the lower probability of the singlet state undergoing intersystem crossing before relaxation of the singlet state. For phenol itself in acetonitrile (Φ_T 0.5) a transient absorption at 235 nm was observed that could be ascribed to the triplet state. Therefore there is every reason to expect that for vitamin E, with a relatively unhindered phenolic group and a fluorescence lifetime of 1.1 ns in hexane [27], there will be a moderate yield of the triplet, but that the triplet-triplet absorption spectrum at $\lambda > 300$ nm may not be readily observed.

Mechanism of singlet oxygen sensitization

We now turn to discuss briefly the overall process of vitamin E sensitizing singlet oxygen. Firstly, it is interesting to note the ability of the nascent singlet oxygen to escape from the collision complex and avoid the back reaction (quenching) of singlet oxygen before escape from the solvent cage, possibly through different geometries of the transition states for formation and quenching of singlet oxygen [30]. The fact that we observe a shortening of the singlet oxygen lifetime with increasing vitamin E concentration demonstrates that separation of the collision complex does occur, and there is diffusion of singlet oxygen and Vitamin E in bulk solvent following triplet formation. Thus the ability of the nascent singlet oxygen to escape from the collision complex and, as in this case, avoid the back reaction of the nascent singlet oxygen being quenched through a charge transfer process (see equation (3)) is significant. This process has been reported by ourselves [31] and others [17].

The possibility of forming the α -tocopheroxyl radical appears to have been previously excluded [32].

Environmental conditions can be expected to play an important role in the overall efficiency of all these processes. The results presented here for formation of singlet oxygen in cyclohexane and methanol may be taken to approximate to the non-polar interior hydrocarbon chain and interfacial regions respectively of a cellular lipid bilayer membrane. The results obtained here show that the singlet oxygen is significantly self quenched by vitamin E at the concentrations used of up to 0.5 mmol dm⁻³, shortening the lifetime from that in the pure solvents to ca. 10 microseconds. This degree of self-quenching is likely to be insignificant *in vivo* where vitamin E concentrations may be lower and the presence of other reactive solutes reduces the singlet oxygen lifetime to less than 0.5 μ s [33, 34]. The laser wavelength (308 nm) used in this study and the long wavelength absorption band of vitamin E fall within the UVB region (290–320 nm) which represents a small fraction of the solar spectrum. Whilst vitamin E is well recognised as providing photoprotection to the skin, it has been noted that the effect may disappear at high doses and that vitamin E undergoes photodegradation in the skin [14]. It may be that singlet oxygen generated from the triplet excited state of vitamin E plays a role in these processes. Further studies are required to ascertain the impact of these findings *in-vivo* with the aim to establish the biological consequences arising from the main conclusion of this work that triplet vitamin E can sensitize singlet oxygen.

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Figure 1.

Time-resolved luminescence at 1270 nm from solutions of vitamin E illuminated with a 308 nm, 15 ns laser pulse. A: Solutions of vitamin E ($0.23 \text{ mmol dm}^{-3}$) in n-hexane saturated by bubbling with a) oxygen, b) air, and c) argon. B: Luminescence decays in oxygen-saturated cyclohexane solutions of vitamin E at concentrations of a) 0.1, b) 0.2 and c) 0.4 mmol dm^{-3} .

Figure 2.

Plots of first order rate constant for time-resolved singlet oxygen luminescence decay versus vitamin E or PMHC concentration in oxygen-saturated solutions: vitamin E in methanol (◆); vitamin E in cyclohexane (■); and PMHC in cyclohexane (□).

Figure 3. Luminescence signal intensities at 1270 nm, obtained by extrapolation of decays to zero time, versus absorbance at 308 nm (1 cm pathlength) for A) oxygen-saturated solutions of naphthalene (□) and vitamin E (○) in cyclohexane; B) naphthalene (○) and PMHC (■) in methanol.

TABLE 1

Quantum yields for singlet oxygen formation and kinetics of self-quenching of singlet oxygen for Vitamin E and PMHC in various solvents.

Samples	Methanol		Cyclohexane	
	τ_{exp} (μ s)	k_0 ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	τ_{exp} (μ s)	k_0 ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)
Vitamin E	9.1 ± 1.1 (9 - 12) *	$(2.8 \pm 0.3) \times 10^8$ (3.0×10^8) #	21.9 ± 0.2 (17-24) *	$(1.2 \pm 0.2) \times 10^8$ (8.4×10^7) #
PMHC	14.8 ± 2.7	$(4.1 \pm 0.2) \times 10^8$ (3.4×10^8) #	24.3 ± 0.35	$(7.5 \pm 0.1) \times 10^7$ (2.4×10^7) #

* Literature values from Wilkinson et al [19]

Literature values from reference [17].