Kinetics and mechanism of oxidation of vitamin E by sulphate radical anion in aqueous acetonitrile solution

Midadhu Saitha Swaraga & Mundra Adinarayana
Dept of Chemistry, Osmania University,
Hyderabad 500 007, India
E-mail: mundra_adinarayana@hotmail.com
Received 29 October 2002; revised 19 August 2003

The photooxidation of vitamin E (α-tocopherol) in the presence of peroxydisulphate (PDS) in aqueous solution at natural pH (7.5) has been carried out in a quantum yield reactor using a high pressure mercury vapour lamp. The rate of photooxidation increases with increase in [vitamin E], [PDS] and light intensity. The quantum yield increases with increase in [vitamin E] and is independent of [PDS] and light intensity. The plots of log (rate) versus log [PDS] and the log (rate) versus log [vitamin E] are linear with a slope of less than one indicating fractional order dependence of rate on [PDS] as well as on [vitamin E]. On the basis of experimental results and product analysis a probable mechanism is suggested.

Vitamin E is a naturally occurring α-tocopherol present in plant oils. It is a major lipid soluble antioxidant in mammalian membranes. Vitamin E is known to be essential component of diet of animals and humans. The antioxidant activity of the tocopherols is mainly due to their ability to donate their phenolic hydrogens to lipid free radicals.

The oxidations of tocopherol by the reactive oxygen species, hydroxyl (·OH), perhydroxy (·OOH) and superoxide (O$_2^-$) radicals was studied in micelles and liposomes. The oxidizing ability of these radicals has been found to be in the order "OH > ·OOH > O$_2^-$".

In order to find the efficiency of α-tocopherol in scavenging SO$_4^{2-}$ and to understand the mechanism of oxidation of α-tocopherol by SO$_4^{2-}$, a systematic study of photooxidation of α-tocopherol in the presence of peroxydisulphate has been undertaken.

Experimental

Vitamin E (α-tocopherol) was from Sigma and was used as received. The solutions of vitamin E was always prepared afresh using a HPLC grade acetonitrile and that of peroxydisulphate with doubly distilled water. The PDS solution was standardised cerimetrically with ferroin indicator. The concentration of vitamin E is determined by measuring the absorbance at its λ$_{max}$ (294 nm) and from the known molar absorption coefficient value at this wavelength. Irradiations were carried out in a quantum yield reactor model QYR-20 using high pressure mercury lamp. In general, intensity measurements were carried out using ferrioxalate actinometry. In a typical reaction, vitamin E and PDS solutions were mixed in a specially designed 1 cm path length cuvette, which is suitable, both for irradiation in the reactor as well as absorbance measurements. The absorbance measurements were carried out on Hitachi UV-visible spectrophotometer model 3410. The progress of the reaction was followed by measuring the absorbance at the λ$_{max}$ of vitamin E by interrupting irradiation at regular intervals of time. The reaction rates have been calculated from the plots of absorbance versus time using a computer program. The quantum yields have been calculated from the rates and calculated light intensity absorbed by PDS at 254 nm. This is the wavelength at which peroxydisulphate is activated to radical reactions. The light intensity at 254 nm was measured by peroxydisulphate actinometry. The light intensity absorbed by PDS at 254 nm was calculated from Eq. (1):

$$ I_{PDS} = \frac{\varepsilon_{PDS}[PDS]}{\varepsilon_{PDS}[PDS]+\varepsilon_{Vitamin E}[Vitamin E]} \times I_t \quad (1) $$

$I_{PDS}$ = Intensity of light absorbed by PDS; $I_t$ = total intensity of light at 254nm obtained from PDS actinometry; $\varepsilon_{PDS}$ = molar absorption coefficient of PDS at 254nm (24.1 dm$^3$mol$^{-1}$cm$^{-1}$); and $\varepsilon_{Vitamin E}$ = molar absorption coefficient of vitamin E (348 dm$^3$mol$^{-1}$cm$^{-1}$) at 254nm.

Results and discussion

The photooxidation of vitamin E (α-tocopherol) in the presence of peroxydisulphate (PDS) in 75% (v/v) acetonitrile-water at pH 7.5 has been carried out in a quantum yield reactor using a high pressure mercury vapour lamp. The rates of oxidation of vitamin E is measured under different experimental conditions. The reaction rates of photooxidation of vitamin E by
PDS are found to increase with increase in [vitamin E] [PDS] and of light intensity (Table 1). The order in [PDS] and [vitamin E] has been found to be fractional each. The quantum yields are calculated from the rates of oxidation of vitamin E and calculated light intensity absorbed by PDS at 254 nm. The quantum yields of the reaction have been found to depend on [vitamin E] but independent of [PDS] and light intensity (Table 1). Nagoaka et al. proposed a mechanism for the oxidation of tocopherols by peroxy radicals indicating its role as an antioxidant. Initially the tocopherol molecule and the peroxy radical approach each other and their electron clouds overlap, forming a transition state of the type (LOO\(^-\)-TOH\(^+\)). When a tocopherol molecule and a peroxy radical approach each other to an appreciable extent (LOO\(^-\)-TOH\(^+\)) proton tunneling takes place and the chromanol molecule loses a hydrogen atom to a lipid peroxy radical forming the chromanoxyl radical.

In presence of peroxy radical, \(\alpha\)-tocopherol is primarily oxidized to 8a\(^-\)-peroxy-substituted tocopherones which degrades to \(\alpha\)-tocopherol-quinone. Generally, first step in the oxidation of a chromanol is the formation of resonance stabilised chromanoxyl (chroman 6-oxyl) radical due to the donation of the phenolic hydrogen to a lipid peroxy radical. Evidence for the formation of tocopheroxyl radical from the tocopherol is available from E.S.R and electron nuclear double resonance studies. It is reported that carbon-centered alkyl radicals generally add to the phenoxyl oxygen while oxygen centered radicals prefer to add to an ortho- or para-position of the phenoxyl radicals. It is reported that oxidation of the \(\alpha\)-tocopherol in polar protic solvents usually involve different pathways and lead to different products than oxidations in inert, polar aprotic solvents. In protic solvents, where electron mobility is enhanced, the \(\alpha\)-tocopheroxyl radical will donate an electron to another radical, and the resultant \(\alpha\)-tocopheroxyl cation can react with alcohols and other protic solvents to give quinone type products. Nishikimi et al. studied the oxidation of tocopherols, at physiological pH, by \(\text{O}_2^\cdot\) generated by a xanthine-xanthine oxidase system. All tocopherols (\(\alpha\), \(\beta\), \(\gamma\) and \(\delta\)) were oxidized to corresponding tocopherol quinones. Dogliotti and Hayon studied the photolysis of peroxydisulphate in aqueous solution, and they reported the formation of sulphate radical anion. It is an important source of free radicals and is used as an initiator in free-radical induced oxidations. Sulphate radical anion which is produced on photolysis of peroxydisulphate in the initiation step might react with \(\alpha\)-tocopherol to produce phenoxy radical. The light intensity has no effect on the quantum yields indicating that it might be mainly involved in the activation of PDS to sulphate radical anion in the initiation step. The rates are found to depend on PDS suggesting that the sulphate radical anion might react with vitamin E in the rate determining step (Table 1). The fractional order dependence of rate of oxidation of vitamin E by sulphate radical anion on [PDS] and [vitamin E] (Table 1) indicates that \(\alpha\)-tocopherol molecule and \(\text{SO}_4^\cdot\) approach each other and their electron clouds overlap forming an intermediate in a fast step having a charge transfer character. This charge transfer complex disproportionates in a slow step transferring hydrogen atom from vitamin E to sulphate radical.

**Table 1—Effect of [PDS], [vitamin E] and light intensity on the rate and quantum yield of oxidation of vitamin E by sulphate radical anion (SO\(_4^\cdot\)) in aqueous solution.**

<table>
<thead>
<tr>
<th>[PDS]×10(^4) mol dm(^{-3})</th>
<th>[vitamin E]×10(^3) mol dm(^{-3})</th>
<th>(10^5\times) [Intensity] Quanta s(^{-1})</th>
<th>(Rate)×10(^7) mol dm(^{-3}) s(^{-1})</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>5.00</td>
<td>2.16</td>
<td>1.15±0.03</td>
<td>0.443±0.01</td>
</tr>
<tr>
<td>4.00</td>
<td>5.00</td>
<td>2.16</td>
<td>1.86±0.03</td>
<td>0.478±0.008</td>
</tr>
<tr>
<td>6.00</td>
<td>5.00</td>
<td>2.16</td>
<td>2.54±0.04</td>
<td>0.468±0.007</td>
</tr>
<tr>
<td>8.00</td>
<td>5.00</td>
<td>2.16</td>
<td>3.00±0.02</td>
<td>0.477±0.004</td>
</tr>
<tr>
<td>4.00</td>
<td>1.00</td>
<td>2.16</td>
<td>0.750±0.03</td>
<td>0.086±0.003</td>
</tr>
<tr>
<td>4.00</td>
<td>2.00</td>
<td>2.16</td>
<td>0.86±0.02</td>
<td>0.125±0.003</td>
</tr>
<tr>
<td>4.00</td>
<td>10.00</td>
<td>2.16</td>
<td>2.30±0.04</td>
<td>0.884±0.015</td>
</tr>
<tr>
<td>5.00</td>
<td>5.00</td>
<td>2.16</td>
<td>2.02±0.03</td>
<td>0.424±0.006</td>
</tr>
<tr>
<td>5.00</td>
<td>5.00</td>
<td>2.55</td>
<td>2.38±0.03</td>
<td>0.415±0.005</td>
</tr>
<tr>
<td>5.00</td>
<td>5.00</td>
<td>3.14</td>
<td>2.83±0.04</td>
<td>0.398±0.005</td>
</tr>
</tbody>
</table>
anion. Further sulphate radical anion being an oxygen centered radical preferentially adds to the para position of phenoxy radical resulting in the formation of \( \alpha \)-tocopheroxylium cation which reacts with water giving \( \alpha \)-tocopherol quinone as the final product. The IR spectrum of the product showed absorptions at 1637 cm\(^{-1}\) and 1645 cm\(^{-1}\) supporting the proposed tocopherol quinone formation. The increase in quantum yield of oxidation of vitamin E with increase in [vitamin E] suggest that vitamin E might be acting as a sensitizer to activate PDS to give SO\(_4^{2-}\). On the basis of the experimental results and the above discussion the following reactions (Scheme I) have been suggested for the photooxidation of vitamin E by PDS in presence of light.

**Acknowledgement**

The authors thank Prof P. Jayaprakash Rao Department of Chemistry, Osmania University for helpful discussions. MSS is thankful to the CSIR.
New Delhi, for fellowship. MA is thankful to UGC, New Delhi for granting Major Research Project.

References