Electronic Supplementary Information

Tunneling Effect in Vitamin E Recycling by Green Tea

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Table S1  \( k_r^H, k_r^D, k_s^H, k_s^D, 2k_d^H \) and \( 2k_d^D \) values for reactions (1)–(3) in EtOH/H\(_2\)O and EtOD/D\(_2\)O at 15–37 °C.

Fig. S1  Rise-and-decay curves of \([\alpha-\text{Toc}\cdot]\) during reaction (2-H) and the subsequent reaction (3-H) in EtOH/H\(_2\)O at 15–37 °C, and the curves simulated according to eqns (9)–(16).

Fig. S2  Rise-and-decay curves of \([\alpha-\text{Toc}\cdot]\) during reaction (2-D) and the subsequent reaction (3-D) in EtOD/D\(_2\)O at 15–37 °C, and the curves simulated according to those similar to eqns (9)–(16).

Fig. S3  Arrhenius plots of \( k_s^H \) and \( k_s^D \) values for reactions (2-H) and (2-D) in EtOH/H\(_2\)O and EtOD/D\(_2\)O, respectively.

Fig. S4  Decay curves of \( \alpha-\text{Toc}\cdot \) absorbance at 429 nm during reaction (3-D) and the competitive reaction (1-D) between \( \alpha-\text{Toc}\cdot \) and EGC-D in EtOD/D\(_2\)O at 25 °C.

Fig. S5  Decay curves of \( \alpha-\text{Toc}\cdot \) absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between \( \alpha-\text{Toc}\cdot \) and EC-H in EtOH/H\(_2\)O at 25 °C.
Fig. S6  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-D) and the competitive reaction (1-D) between $\alpha$-Toc• and EC-D in EtOD/D$_2$O at 25 °C.

Fig. S7  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and ECG-H in EtOH/H$_2$O at 25 °C.

Fig. S8  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and EGCG-H in EtOH/H$_2$O at 25 °C.

Fig. S9  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-D) and the competitive reaction (1-D) between $\alpha$-Toc• and EGCG-D in EtOD/D$_2$O at 25 °C.

Fig. S10 Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and MR in EtOH/H$_2$O at 25 °C.

Fig. S11  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and MC in EtOH/H$_2$O at 25 °C.

Fig. S12  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and MG in EtOH/H$_2$O at 25 °C.

Fig. S13  Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and EC-H in EtOH/H$_2$O.

Fig. S14 Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and ECG-H in EtOH/H$_2$O.

Fig. S15  Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and EGCG-H in EtOH/H$_2$O.

Fig. S16 Arrhenius plot of $k_r^D$ values for reaction (1-D) between $\alpha$-Toc• and EGCG-D in EtOD/D$_2$O.

Fig. S17 Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and MC in EtOH/H$_2$O.

Fig. S18 Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and MG in EtOH/H$_2$O.
Table S1  \( k^H, k^D, k^H, k^D, 2k^H \text{ and } 2k^D \) values for reactions (1)–(3) in EtOH/H\(_2\)O and EtOD/D\(_2\)O at 15–37 °C

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Reaction rate constant / M(^{-1})s(^{-1})</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>37 / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC-H</td>
<td>( k^H )</td>
<td>7.90 \times 10^2</td>
<td>9.63 \times 10^2</td>
<td>1.20 \times 10^3</td>
<td>1.46 \times 10^3</td>
<td>1.78 \times 10^3</td>
</tr>
<tr>
<td>EC-D</td>
<td>( k^D )</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
</tr>
<tr>
<td>ECG-H</td>
<td>( k^H )</td>
<td>2.38 \times 10^3</td>
<td>2.84 \times 10^3</td>
<td>3.43 \times 10^3</td>
<td>4.18 \times 10^3</td>
<td>5.22 \times 10^3</td>
</tr>
<tr>
<td>ECG-D</td>
<td>( k^D )</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
</tr>
<tr>
<td>EGC-H</td>
<td>( k^H )</td>
<td>2.00 \times 10^4</td>
<td>2.24 \times 10^4</td>
<td>2.41 \times 10^4</td>
<td>2.71 \times 10^4</td>
<td>2.98 \times 10^4</td>
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<tr>
<td>EGC-D</td>
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<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
</tr>
<tr>
<td>EGCG-H</td>
<td>( k^H )</td>
<td>1.82 \times 10^4</td>
<td>2.02 \times 10^4</td>
<td>2.31 \times 10^4</td>
<td>2.50 \times 10^4</td>
<td>2.83 \times 10^4</td>
</tr>
<tr>
<td>EGCG-D</td>
<td>( k^D )</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
</tr>
<tr>
<td>MR</td>
<td>( k^H )</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
<td>&lt; 10^2</td>
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<tr>
<td>MC</td>
<td>( k^H )</td>
<td>3.30 \times 10^3</td>
<td>3.96 \times 10^3</td>
<td>4.48 \times 10^3</td>
<td>5.38 \times 10^3</td>
<td>6.32 \times 10^3</td>
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<tr>
<td>MP</td>
<td>( k^H )</td>
<td>1.38 \times 10^5</td>
<td>1.61 \times 10^5</td>
<td>1.75 \times 10^5</td>
<td>1.87 \times 10^5</td>
<td>1.88 \times 10^5</td>
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<tr>
<td>MG</td>
<td>( k^H )</td>
<td>1.47 \times 10^3</td>
<td>1.78 \times 10^3</td>
<td>2.11 \times 10^3</td>
<td>2.46 \times 10^3</td>
<td>3.06 \times 10^3</td>
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<tr>
<td>α-TocH</td>
<td>( k^H )</td>
<td>6.80 \times 10^3</td>
<td>7.50 \times 10^3</td>
<td>8.20 \times 10^3</td>
<td>9.00 \times 10^3</td>
<td>1.00 \times 10^4</td>
</tr>
<tr>
<td>α-TocD</td>
<td>( k^D )</td>
<td>2.70 \times 10^2</td>
<td>3.20 \times 10^2</td>
<td>4.00 \times 10^2</td>
<td>4.55 \times 10^2</td>
<td>5.45 \times 10^2</td>
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<tr>
<td>α-Toc•</td>
<td>( 2k^H )</td>
<td>1.08 \times 10^3</td>
<td>1.13 \times 10^3</td>
<td>1.21 \times 10^3</td>
<td>1.25 \times 10^3</td>
<td>1.40 \times 10^3</td>
</tr>
<tr>
<td>α-Toc•</td>
<td>( 2k^D )</td>
<td>8.80 \times 10^2</td>
<td>8.90 \times 10^2</td>
<td>9.50 \times 10^2</td>
<td>1.01 \times 10^3</td>
<td>1.15 \times 10^3</td>
</tr>
</tbody>
</table>

\( a \) Reliable data was not obtained.
Fig. S1  Rise-and-decay curves of \([\alpha\text{-Toc}^\bullet]\) during reaction (2-H) and the subsequent reaction (3-H) in EtOH/H\(_2\)O at 15–37 °C (red curves), and the curves simulated according to eqns (9)–(16) (black curves). In the simulation, \(k_s^H\) and \(2k_d^H\) are set to the values given in Table S1, and [ArO\(_\bullet\)]\(_0\) are set to 7.50×10\(^{-2}\), 7.60×10\(^{-2}\), 7.85×10\(^{-2}\), 8.15×10\(^{-2}\) and 8.46×10\(^{-2}\) mM at 15, 20, 25, 30 and 37 °C, respectively. \([\alpha\text{-TocH}]_0 = 6.33\) mM and \(\varepsilon = 3420\) M\(^{-1}\)cm\(^{-1}\).
Fig. S2  Rise-and-decay curves of [α-Toc•] during reaction (2-D) and the subsequent reaction (3-D) in EtOD/D$_2$O at 15–37 °C (red curves), and the curves simulated according to those similar to eqns (9)–(16) (blue curves). In the simulation, $k_s^D$ and $2k_d^D$ are set to the values given in Table S1, and [ArO•]$_0$ are set to 0.255, 0.240, 0.230, 0.218 and 0.215 mM at 15, 20, 25, 30 and 37 °C, respectively. [α-TocD]$_0$ = 2.12 mM and $\varepsilon$ = 3420 M$^{-1}$cm$^{-1}$.  

\[ k_s^D = 1.00 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \]
\[ 2k_d^D = 1.45 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \]
**Fig. S3** Arrhenius plots of $k_s^H$ and $k_s^D$ values for reactions (2-H) and (2-D) in EtOH/H$_2$O and EtOD/D$_2$O (open and filled circles, respectively). The solid lines show the best-fitting lines by standard linear least-squares analyses.

**Fig. S4** Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-D) and the competitive reaction (1-D) between $\alpha$-Toc• and EGC-D in EtOD/D$_2$O at 25 °C. The prepared [EGC-D] for the data shown with red, blue, green and black curves were $3.96 \times 10^{-5}$, $7.92 \times 10^{-5}$, $1.19 \times 10^{-4}$ and $1.58 \times 10^{-4}$ M, respectively.
Fig. S5  Decay curves of \( \alpha \)-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between \( \alpha \)-Toc• and EC-H in EtOH/H\( _2 \)O at 25 °C.  The prepared [EC-H] for the data shown with black, dark-grey, red and light-gray curves were \( 3.57 \times 10^{-4} \), \( 7.14 \times 10^{-4} \), \( 1.07 \times 10^{-3} \) and \( 1.43 \times 10^{-3} \) M, respectively.

Fig. S6  Decay curves of \( \alpha \)-Toc• absorbance at 429 nm during reaction (3-D) and the competitive reaction (1-D) between \( \alpha \)-Toc• and EC-D in EtOD/D\( _2 \)O at 25 °C.  The prepared [EC-D] for the data shown with red, blue, green and black curves were \( 3.44 \times 10^{-4} \), \( 6.88 \times 10^{-4} \), \( 1.03 \times 10^{-3} \) and \( 1.38 \times 10^{-3} \) M, respectively.
Fig. S7  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and ECG-H in EtOH/H$_2$O at 25 °C. The prepared [ECG-H] for the data shown with black, dark-grey, red and light-gray curves were $3.84 \times 10^{-5}$, $7.69 \times 10^{-5}$, $1.15 \times 10^{-4}$ and $1.53 \times 10^{-4}$ M, respectively.

Fig. S8  Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and EGCG-H in EtOH/H$_2$O at 25 °C. The prepared [EGCG-H] for the data shown with black, dark-grey, red and light-gray curves were $1.79 \times 10^{-5}$, $3.58 \times 10^{-5}$, $5.38 \times 10^{-5}$ and $7.17 \times 10^{-5}$ M, respectively.
**Fig. S9** Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-D) and the competitive reaction (1-D) between $\alpha$-Toc• and EGCG-D in EtOD/D$_2$O at 25 °C. The prepared [EGCG-D] for the data shown with red, blue, green and black curves were $3.20 \times 10^{-5}$, $6.39 \times 10^{-5}$, $9.56 \times 10^{-5}$ and $1.28 \times 10^{-4}$ M, respectively.

**Fig. S10** Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and MR in EtOH/H$_2$O at 25 °C. The prepared [MR] for the data shown with black, dark-grey, red and light-gray curves were $9.18 \times 10^{-4}$, $1.84 \times 10^{-3}$, $2.75 \times 10^{-3}$ and $3.67 \times 10^{-3}$ M, respectively.
**Fig. S11** Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) between $\alpha$-Toc• and MC in EtOH/H$_2$O at 25 °C. The prepared [MC] for the data shown with black, dark-grey, red and light-gray curves were $1.07 \times 10^{-3}$, $2.14 \times 10^{-3}$, $3.20 \times 10^{-3}$ and $4.27 \times 10^{-3}$ M, respectively.

**Fig. S12** Decay curves of $\alpha$-Toc• absorbance at 429 nm during reaction (3-H) and the competitive reaction (1-H) with MG in EtOH/H$_2$O at 25 °C. The prepared [MG] for the data shown with black, dark-grey, red and light-gray curves were $6.44 \times 10^{-4}$, $1.29 \times 10^{-3}$, $1.93 \times 10^{-3}$ and $2.58 \times 10^{-3}$ M, respectively.
**Fig. S13** Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and EC-H in EtOH/H$_2$O. The solid line shows the best-fitting line by a standard linear least-squares analysis.

**Fig. S14** Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and ECG-H in EtOH/H$_2$O. The solid line shows the best-fitting line by a standard linear least-squares analysis.
**Fig. S15** Arrhenius plot of $k_r^H$ values for reaction (1-H) between $\alpha$-Toc• and EGCG-H in EtOH/H$_2$O. The solid line shows the best-fitting line by a standard linear least-squares analysis.

**Fig. S16** Arrhenius plot of $k_r^D$ values for reaction (1-D) between $\alpha$-Toc• and EGCG-D in EtOD/D$_2$O. The solid line shows the best-fitting line by a standard linear least-squares analysis.
**Fig. S17** Arrhenius plot of $k_r^H$ values for reaction (1-H) with MC in EtOH/H$_2$O. The solid line shows the best-fitting line by a standard linear least-squares analysis.

**Fig. S18** Arrhenius plot of $k_r^H$ values for reaction (1-H) with MG in EtOH/H$_2$O. The solid line shows the best-fitting line by a standard linear least-squares analysis.