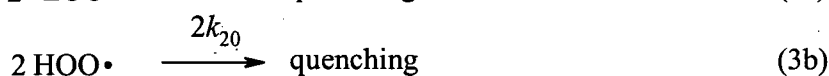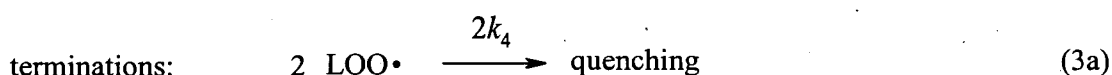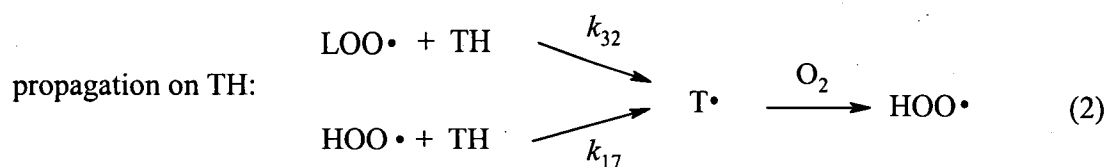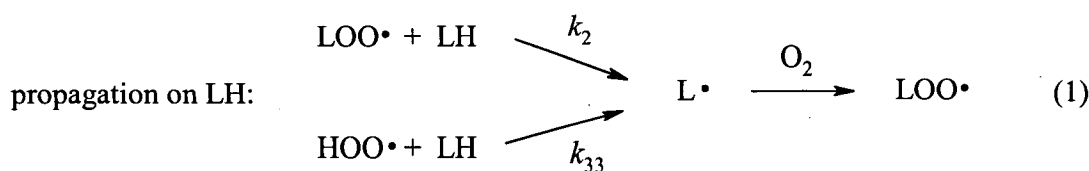**Derivation of Equation 31.**

In a binary mixture of linoleic acid (LH) and γ-terpinene (TH), the following sequence of reactions summarizes the overall AIBN-initiated peroxidation (for simplicity of representation the peroxidation products are omitted; the numbering of the rate constants is that of the corresponding reactions in the full paper) of both hydrocarbons:

propagation on LH:
$$\text{LOO}^\bullet + \text{LH} \xrightarrow{k_2}$$
$$\text{HOO}^\bullet + \text{LH} \xrightarrow{k_{33}} \text{L}^\bullet \xrightarrow{O_2} \text{LOO}^\bullet \qquad (1)$$

propagation on TH:
$$\text{LOO}^\bullet + \text{TH} \xrightarrow{k_{32}}$$
$$\text{HOO}^\bullet + \text{TH} \xrightarrow{k_{17}} \text{T}^\bullet \xrightarrow{O_2} \text{HOO}^\bullet \qquad (2)$$

terminations:
$$2\ \text{LOO}^\bullet \xrightarrow{2k_4} \text{quenching} \qquad (3a)$$
$$2\ \text{HOO}^\bullet \xrightarrow{2k_{20}} \text{quenching} \qquad (3b)$$
$$\text{HOO}^\bullet + \text{LOO}^\bullet \xrightarrow{k_{29}} \text{quenching} \qquad (3c)$$
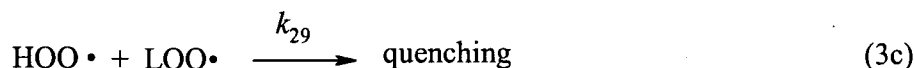
Since in stationary conditions the rate of initiation R_i (see the paper) must equal the rates of termination

$$R_i = 2k_4[\text{LOO}]^2 + 2k_{20}[\text{HOO}]^2 + k_{29}[\text{HOO}][\text{LOO}] \qquad (4)$$

which assuming [LH]>>[TH] can be simplified in the form

$$R_i \approx 2k_4[\text{LOO}]^2 + k_{29}[\text{HOO}][\text{LOO}] \qquad (4a)$$

Given that the steady-state concentration of HOO• is equal to

$$[\text{HOO}]_{ss} = \frac{k_{32}[\text{TH}][\text{LOO}]_{ss}}{k_{29}[\text{LOO}]_{ss} + k_{33}[\text{LH}]} \qquad (5)$$

substituting equation 5 in 4a, a cubic equation in [LOO]$_{ss}$ is obtained.

1   To avoid the resolution of such an equation, the steady-state concentration of LOO• can

2   be written in the following way

$$[\text{LOO}]_{ss} \approx \frac{R_i^{1/2}}{(2k_4 + \frac{k_{29}k_{32}[\text{TH}]}{k_{33}[\text{LH}] + k_{29}[\text{LOO}]_{ss}})^{1/2}} \qquad (6)$$

4   After a few cycles[1], this equation converges to the correct value of [LOO•]$_{ss}$ which through

5   equation 5 yields the steady-state concentration of HOO•.

6   The peroxidation rate of LH, in the presence of TH, therefore, is:

$$R_{\text{LH}}^{\text{TH}} = k_2[\text{LH}] \times [\text{LOO}]_{ss} + k_{33}[\text{LH}] \times [\text{HOO}]_{ss} \qquad (7)$$

8   Assuming that the cross-termination 3c is a diffusion-controlled process ($k_{29} = 2 - 10 \times 10^9$

9   M^{-1}s^{-1}) and fitting equation 7 (using the rate constants k_{32} and k_{33} as floating parameters) to

10   experimental {[TH], $R_{\text{LH}}^{\text{TH}}$} pairs, it is possible to obtain the best-fit values for the rate constants

11   k_{32} and k_{33} or k_{34} when 1,4-cyclohexadiene (CHD) is used in place of TH (see Table S1).

12   For relatively high concentrations of LH (> 0.5 M), it is possible to neglect, in equations 5

13   and 6, the term $k_{29}[\text{LOO}]$ with respect to $k_{33}[\text{LH}]$. The steady-state concentration of LOO•,

14   therefore, becomes

$$[\text{LOO}]_{ss} \approx \frac{R_i^{1/2}}{(2k_4 + k_{29}(k_{32}/k_{33})[\text{TH}]/[\text{LH}])^{1/2}} \qquad (8)$$

17   while

$$[\text{HOO}]_{ss} \approx \frac{(k_{32}/k_{33})R_i^{1/2}[\text{TH}]/[\text{LH}]}{(2k_4 + k_{29}(k_{32}/k_{33})[\text{TH}]/[\text{LH}])^{1/2}} \qquad (9)$$

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[1] In the first cycle, the initial value [LOO]$_0$ can be $R_i^{1/2}/(2k_4)^{1/2}$ which will give with equation 6 a new value

[LOO]$_1$. In the second cycle, [LOO]$_1$ will be used in the denominator of equation 6 and a new value [LOO]$_2$

will be obtained, and so forth. When two consecutive values are very close each other the cyclic

calculation can be stopped and the final value will be the correct solution of the cubic equation.

1   Equation 7 can therefore be written in the form

2

$$R_{LH}^{TH} \approx \frac{k_2[LH]R_i^{1/2} + k_{32}[TH]R_i^{1/2}}{[2k_4 + k_{29}(k_{32}[TH]/k_{33}[LH])]^{1/2}} \qquad (10)$$

3
4
5   numbered as equation 31 in the full paper.
6

7

8   **Table S1.** Summary of the rate constants[a] ($M^{-1}s^{-1}$) for LH, TH, CHD, HOO• and LOO• in

9   acetonitrile and cyclohexane at 50°C.

	LH	TH	CHD	HOO•	LOO•
Acetonitrile:					
LOO•	160 (k_2)[b]	2200 (k_{32})[c]	1200 (k_{34})[c]	$10\times10^9 (k_{29})$[d]	$3\times10^7 (2k_4)$[e]
HOO•	350 (k_{33})[c]	2800 (k_{17})[f]	890 (k_{13})[b]	$8\times10^7 (2k_{20})$[g]	
Cyclohexane:					
LOO•	160 (k_2)[b]	2200 (k_{32})[c]	1200 (k_{34})[c]	$3\times10^9 (k_{29})$[d]	$3\times10^7 (2k_4)$[e]
HOO•	350 (k_{33})[c]	2800 (k_{17})[f]	890 (k_{13})[b]	$1.3\times10^9 (2k_{20})$[h]	

10
11   [a] Uncertainties vary but for some rate constants derived by simulation may be as high as ± 50%.

12   [b] Evaluated from a value at 30°C and the Arrhenius pre-exponential factor for H-atom

13   abstraction, $A \sim 10^{8.5}$ $M^{-1}s^{-1}$ (ref.21b). [c] Evaluated by computer simulation of the {[TH] or [CHD],

14     $R_{LH}^{TH\ or\ CHD}$} pairs (see text). [d] By assumption. [e] Evaluated from the oxidizability of LH and k_2 at

15   50°C. [f] Evaluated from the oxidizability of TH and $2k_{20}$ at 50°C. [g] Evaluated from the ratio of TH

16   oxidizabilities in acetonitrile and cyclohexane and the value given for $2k_{20}$ in cyclohexane.

17   [h] Evaluated from a value at 30°C in *n*-decane (ref. 21b).