Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information

Additivity rule holds in hydrogen-transfer reactivity of unsaturated fatty acids with a peroxyl radical: mechanistic insight into lipoxygenase

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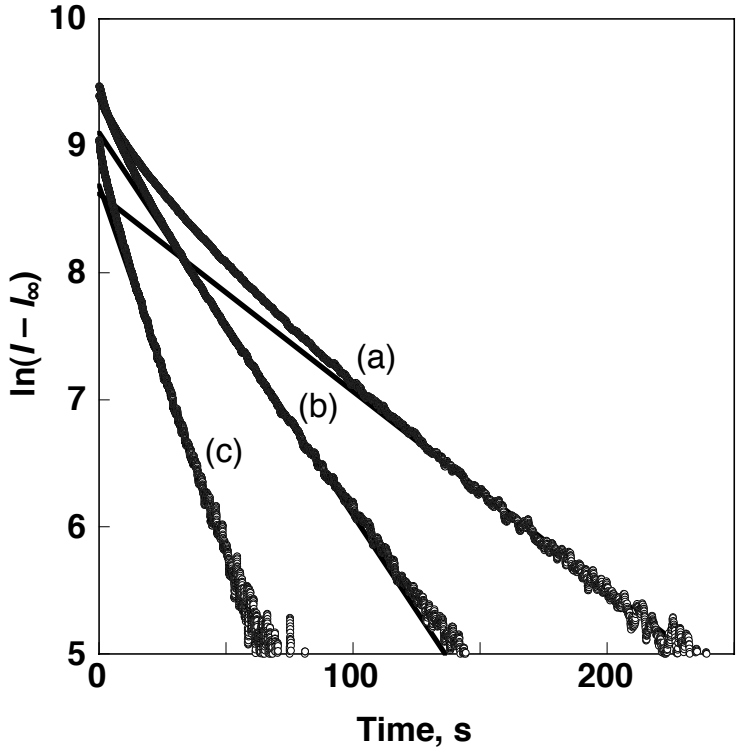

Fig. S1 First-order plots for the decay of the ESR signal due to cumylperoxyl radical in the presence of various concentrations of arachidonic acid at 203 K; (a) 0.01 mol dm^{-3}, (b) 0.02 mol dm^{-3} and (c) 0.04 mol dm^{-3}. The pseudo-first-order rate constants were determined from the slopes of the linear correlations (the contribution of the bimolecular decay at the initial stage was excluded).

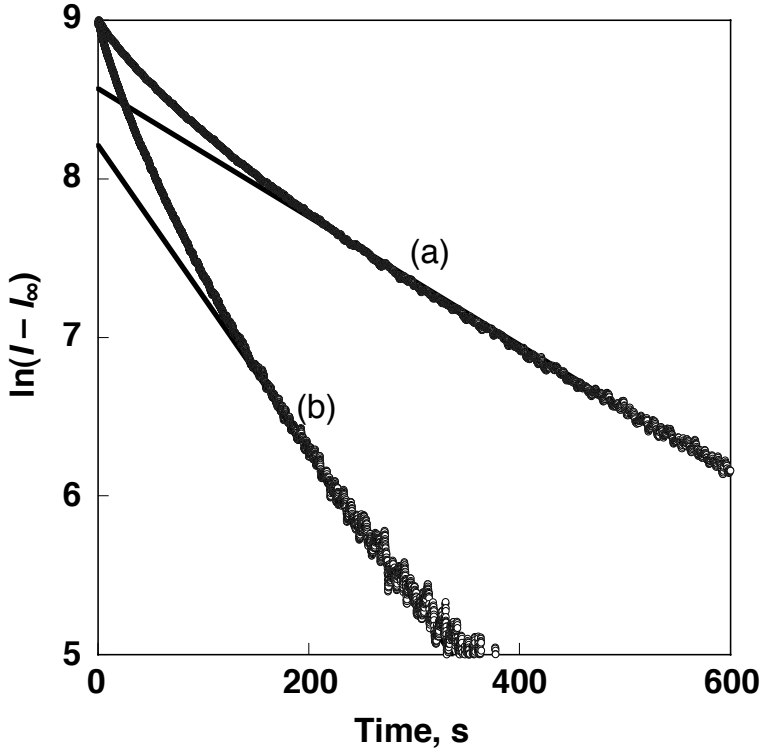

Fig. S2 First-order plots for the decay of the ESR signal due to cumylperoxyl radical in the presence of various concentrations of linoleic acid at 203 K; (a) 0.01 mol dm^{-3} and (b) 0.02 mol dm^{-3}. The pseudo-first-order rate constants were determined from the slopes of the linear correlations (the contribution of the bimolecular decay at the initial stage was excluded).

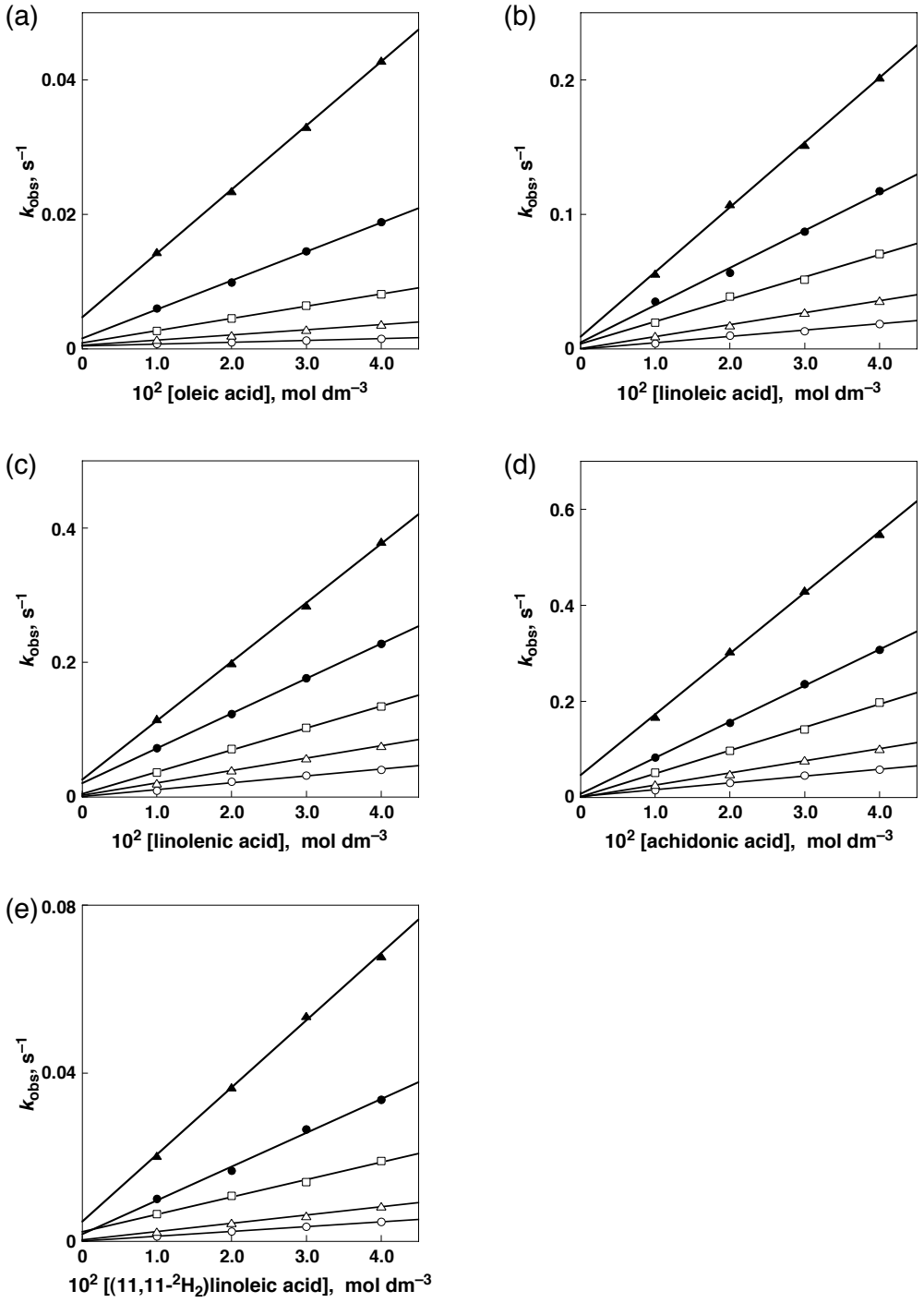

Fig. S3 Plots of pseudo-first-order rate constants (k_{obs}) *vs*. concentrations of unsaturated fatty acids for hydrogen transfer from unsaturated fatty acids to cumylperoxyl radical in O_2-saturated EtCN at 203 K (○), 213 K (△), 223 K (□), 233 K (●) and 243 K (▲).

Table S1 Rate constants (k_H and k_D) for hydrogen transfer from unsaturated fatty acids to cumylperoxyl radical in O_2-saturated EtCN.

	k_H or k_D , mol^{-1} dm^3 s^{-1}				
unsaturated fatty acid	**203 K**	**213 K**	**223 K**	**233 K**	**243 K**
oleic acid	**(2.65 ± 0.04) x 10^{-2}**	**(7.63 ± 0.24) x 10^{-2}**	**(1.82 ± 0.03) x 10^{-1}**	**(4.31 ± 0.11) x 10^{-1}**	**(9.50 ± 0.11) x 10^{-1}**
linoleic acid	**(4.71 ± 0.33) x 10^{-1}**	**(8.88 ± 0.19) x 10^{-1}**	**1.66 ± 0.10**	**2.78 ± 0.16**	**4.81 ± 0.10**
linolenic acid	**1.02 ± 0.09**	**1.84 ± 0.02**	**3.26 ± 0.05**	**5.19 ± 0.03**	**8.78 ± 0.19**
arachidonic acid	**1.42 ± 0.05**	**2.52 ± 0.09**	**4.82 ± 0.18**	**7.52 ± 0.13**	**(1.27 ± 0.00) x 10**
[11,11-$^2H_2$]linoleic acid	**(1.14 ± 0.01) x 10^{-1}**	**(1.98 ± 0.08) x 10^{-1}**	**(4.12 ± 0.22) x 10^{-1}**	**(8.04 ± 0.42) x 10^{-1}**	**1.60 ± 0.04**

Table S2 Activation parameters for hydrogen transfer from unsaturated fatty acids to cumylperoxyl radical in O_2-saturated EtCN

unsaturated fatty acid	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}
oleic acid	34.7 ± 0.3	–101 ± 1
linoleic acid	21.9 ± 0.3	–140 ± 1
linolenic acid	20.1 ± 0.3	–143 ± 1
arachidonic acid	20.6 ± 0.5	–137 ± 2
[11,11-$^2H_2$]linoleic acid	25.5 ± 1.3	–135 ± 6