

Thermo-induced lipid oxidation of culinary oils: a kinetic study of the oxidation products by magnetic resonance spectroscopies

Supporting Information

*Adriano Silvagni, Lorenzo Franco, Alessandro Bagno, and Federico Rastrelli**

Dipartimento di Scienze Chimiche, Università di Padova,

via Marzolo, 1 - 35131 Padova (Italy)

federico.rastrelli@unipd.it

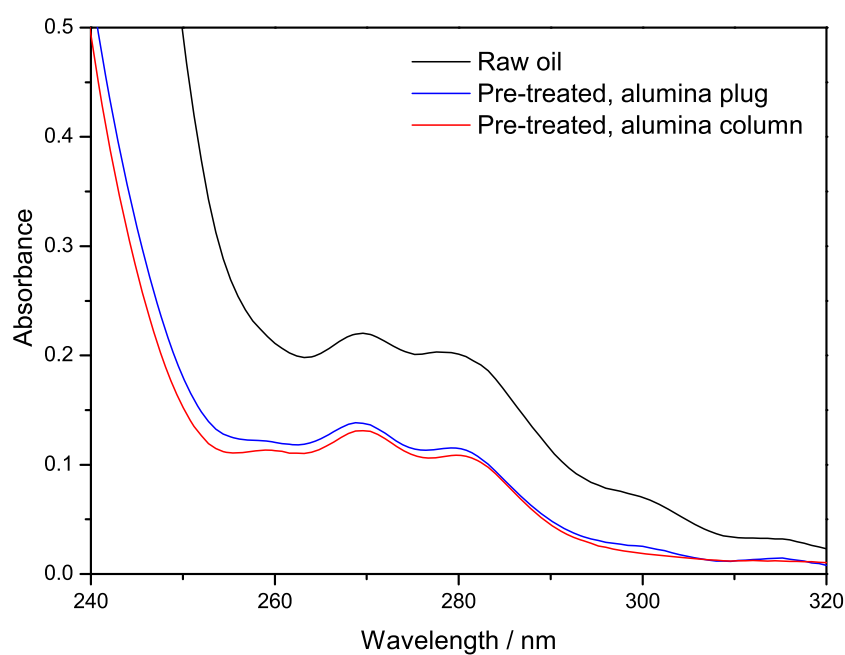


Figure S1. UV-Vis spectrum of an olive oil sample before and after pre-treatment to remove peroxides.

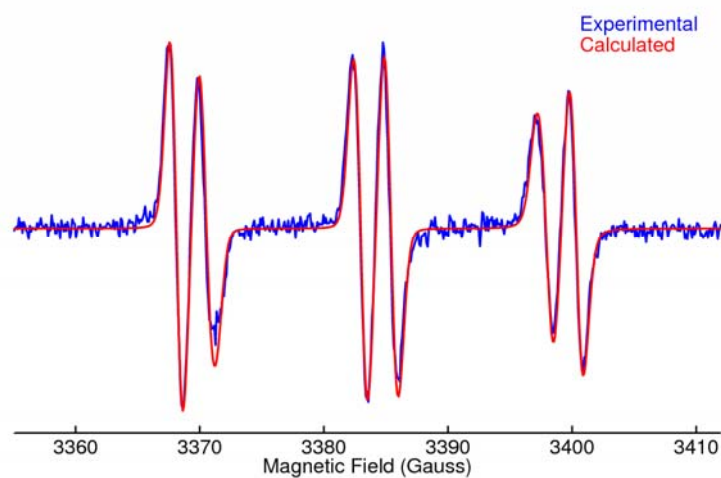


Figure S2. Experimental (blue) and calculated (red) EPR spectra resulting from a sample of peanut oil with added PBN and heated for 10 minutes at 180 °C open to air. The calculated spectrum consists of a 65% contribution from radical **1** and a 35% contribution from radical **2**.

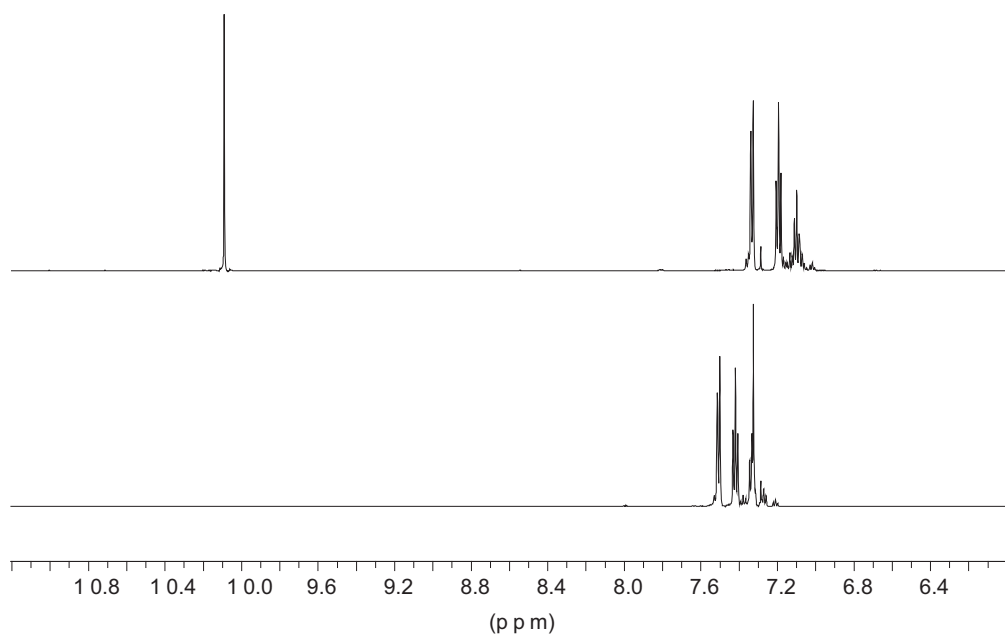
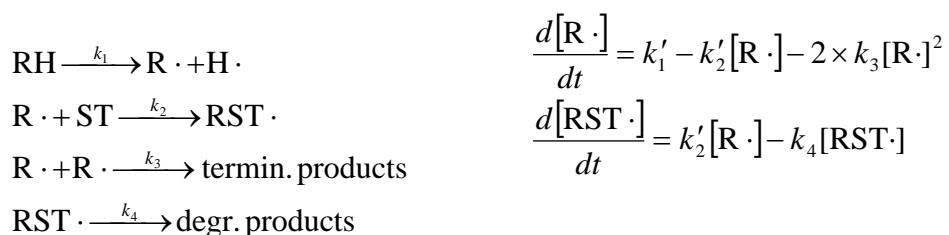


Figure S3. ^1H NMR spectrum of cumene hydroperoxide recorded in plain CDCl_3 (lower trace) and in CDCl_3 :DMSO = 9:1 mixture (upper trace). The DMSO oxygen coordinates to the peroxidic hydrogen, thus shifting its signal downfield.

Estimates of the kinetic constants

General procedure. In order to stabilize the results of the multiparametric fitting, after finding an initial best-fit set, we allowed a single kinetic constant to vary and determined the confidence interval on each one. All the estimated errors reported in the table are evaluated at a 95% confidence level.

Estimates of k_1 from EPR spectra (ST = spin trap)



Estimated parameters:

$k_1' = k_1[RH] = (1.08 \pm 0.03) \times 10^{-4} \text{ M s}^{-1}$; $k_2' = k_2[ST] = (2.73 \pm 0.03) \times 10^{-1} \text{ s}^{-1}$; $k_4 = (2.79 \pm 0.04) \times 10^{-3} \text{ s}^{-1}$. k_3 was set to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ according to ref. [S1] and not varied during the fitting procedure.

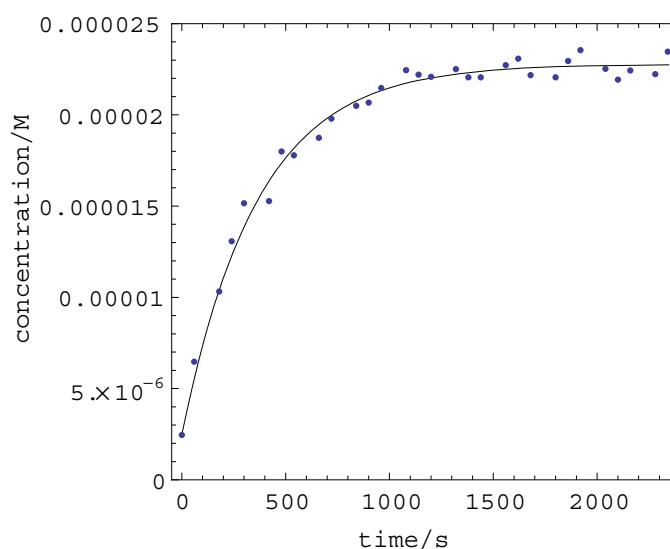


Figure S4. Best fitting curve to the experimental data set of radical **2** (degassed sample) as resulting from the kinetic model described in the text.

Even though it is difficult to compare the above rate constants with literature values measured under different conditions [S2, S3], we can nevertheless validate our values on a qualitative basis. In fact, prolonged heating of fatty acid methyl esters at 105 °C (see Fig. 1 of ref. [S4]) indeed shows that PBN adducts are fairly stable, especially those originating from methyl oleate and linoleate. As a consequence, the degradation constant k_4 is expected to be small, which is what we also find for our system.

Similarly, we find the constant k_2 to be quite small, indicating that the reaction between an alkyl radical and the PBN is not so fast as one would expect. Fig. 4 of the paper highlights that the formation of adduct 1, albeit originating from an alkyl radical and a subsequent degradation product of the PBN-peroxyl radical adduct, is markedly faster than the direct reaction between an alkyl radical and the PBN itself. As a consequence, step 2 of the above kinetic scheme appears to be intrinsically slow.

Estimates of k_n ($n= 3, 8$) from NMR spectra

Constants	Pre-treated sample	Raw sample	Units
k_1'	$(1.08 \pm 0.03) \times 10^{-4} \text{ (a)}$	$(1.08 \pm 0.03) \times 10^{-4} \text{ (a)}$	M s^{-1}
k_2'	10^6	10^6	s^{-1}
k_3'	0.50 ± 0.01	0.31 ± 0.02	s^{-1}
k_{3b}	$(2.52 \pm 0.05) \times 10^5$	$(1.83 \pm 0.07) \times 10^5$	$\text{M}^{-1} \text{s}^{-1}$
k_4	$(8.8 \pm 0.1) \times 10^6$	$(9.1 \pm 0.3) \times 10^6$	$\text{M}^{-1} \text{s}^{-1}$
k_5	$(4.4 \pm 0.1) \times 10^{-4}$	$(7.3 \pm 0.3) \times 10^{-4}$	s^{-1}
k_6	$(7.1 \pm 0.1) \times 10^2$	$(5.9 \pm 0.2) \times 10^2$	s^{-1}
k_7	$(2.5 \pm 0.1) \times 10^2$	$(2.1 \pm 0.1) \times 10^2$	s^{-1}
k_8	$(4.26 \pm 0.07) \times 10^3$	$(3.07 \pm 0.08) \times 10^3$	s^{-1}

An estimate of k_2' value is not possible from the fitting procedure, since it is associated to a very fast process preceding a slow reaction (k_3') and it can span a very wide range. Its value was thus fixed at 10^6 s^{-1} , which is the maximum known

value for k_2 , ($10^9 \text{ M}^{-1}\text{s}^{-1}$ [S1]) multiplied by the average oxygen concentration in oil under normal conditions (10^{-3} M [S5]).

References

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- [S2] Maeda, Y; Ingold, K. U. *J. Am. Chem. Soc.* **1979**, *101*, 4975-4981
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- [S5] Parenti, A.; Spugnoli, P. ; Masella, P.; Calamai, L. *Eur. J. Lipid Sci. Technol.* **2007**, 1180-1185