1. Based on Scheme 1 and 2, what is the definition of peroxyl radical clock? (Hint: competition between what two proceses?)

What does 'clocking' mean? And what type of molecules can serve as a 'clock'?

2. Scheme 3 describes the autoxidation of methyl linoleate and its product distribution based on the hydrogen (H)-atom donor present. When is the reaction under kinetic control and what are the products? Also, when is the reaction under thermodynamic control and what are the products?

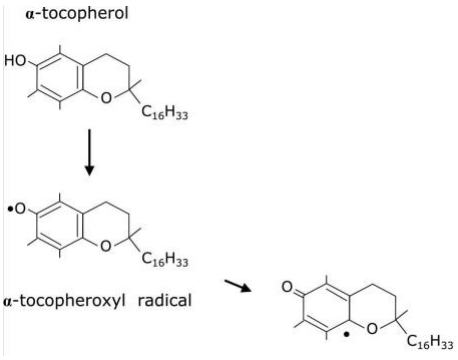
What type of analysis was applied into scheme 3 to derive the equations representing the kinetically controlled reactions (ML_{fast}) and the thermodynamically controlled reactions (ML_{slow})?

3. How is the allylbenzene radical clock different from the methyl linoleate radical clock and how did the author predict this difference?

4. How were the clocks calibrated? Why were the concentration of H-atom donor monitored during the course of the reaction?

5. It is mentioned in the experimental section that the clocking molecules (linoleate, allylbenzene, etc.) must be chromatographed on silica (aka purified via column chromatography) prior to use to remove any oxidations product. Can you predict how pre-existing oxidation products in the clocking molecules can affect the clocking results?

6.



The figure on the left describes the mechanism of H-atom abstraction from α-tocopherol. Based on this mechanism, can you explain why α-tocopherol as well as compounds 27, 28, and 29 in Scheme 5 are good H-atom donors?

Also, explain why the rate constant for compound 31 is much slower than compound 30 in Table 2.

For each of the compounds in scheme 5, please predict the position(s) in which H-atom can be abstracted from.

Bonus question:

The peroxyl radical clocks method have been applied into measuring rate constant for the H-atom transfer reaction of several biologically important lipids and sterols. For each of the pair of lipids/sterols below, can you predict which one has a faster rate constant and why?