

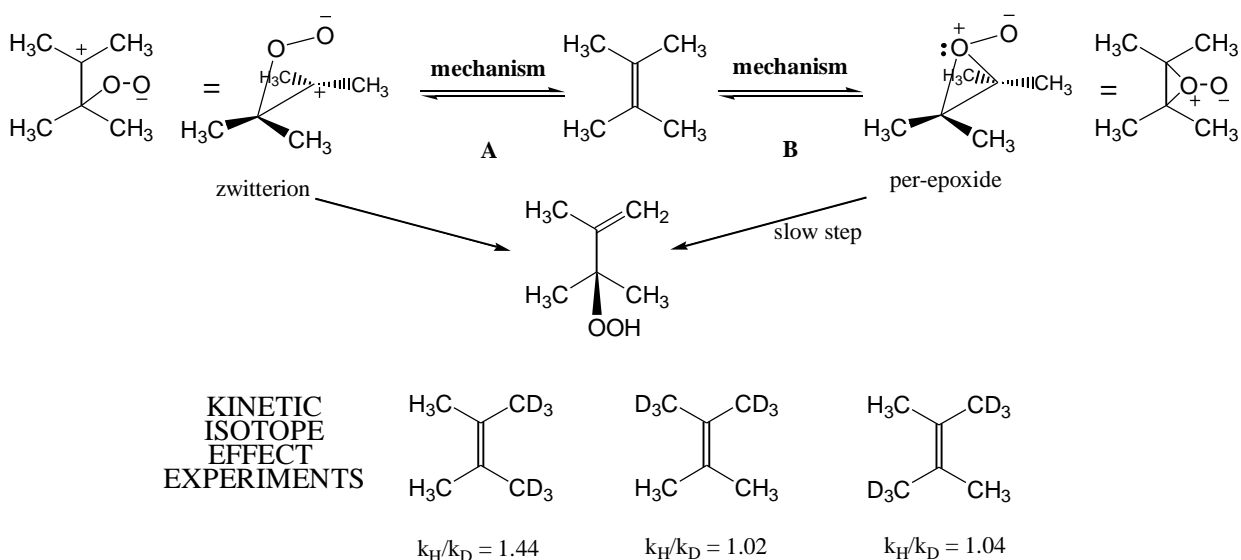
QUIZ #3 (100 points)

NAME: _____ ANSWER KEY

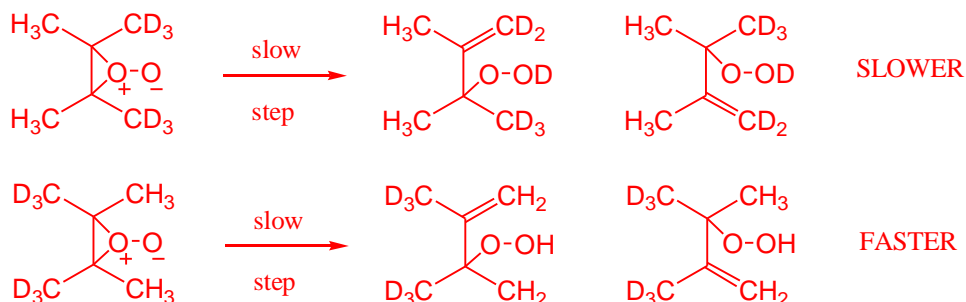
Answer all questions as completely as you can. Clearly show your work and reasoning.

- (1) Two mechanisms are shown below for the reaction of singlet oxygen (generated photochemically from normal, triplet oxygen) with tetramethylethylene. Mechanism A gives a zwitterion, while mechanism B gives a cyclic per-epoxide; the intermediates then swiftly react by hydrogen abstraction to give the final product. *Please note that the per-epoxide is expected to be geometrically rigid.*

Isotopically substituted versions of tetramethylethylene were used to try to differentiate the two mechanisms. The isotope effects are shown below, relative to tetramethylethylene itself. Which mechanism do you think is more likely, based on the isotope effects observed? Briefly explain your answer. (50 pts)



Only the per-epoxide intermediate has a geometry, such that a C-H bond in a methyl group must be broken on one of two cis-methyl groups. Only the cis-double-labeled material shows a relatively stronger isotope effect. Therefore, the per-epoxide is more likely.

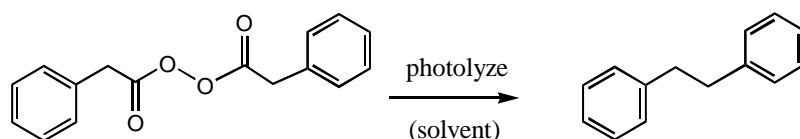


If the zwitterion intermediate were formed, then geminal methyl groups would show the isotope effect most strongly $(CD_3)_2C=C(CH_3)_2$.

(2) Are the effects described in (1) above primary or secondary isotope effects? Briefly explain your answer. (20 pts)

Since a C-H or C-D bond is broken in the process, this is a primary effect.

(3) Briefly describe a cross-over labeling experiment. You may use the reaction shown below as an example for your description (30 pts).



In a crossover experiment, one suspects that a pair of intermediates is formed, which might diffuse and then recombine, or which might quickly recombine within the solvent cage of their formation. If diffusion occurs, there is a chance for the intermediates to react with intermediates from other molecules. The resulting intermolecular products are cross-over products, as opposed to the intramolecular products formed solely from solvent cage recombination.

