

Lecture #20

Reaction Mechanisms Involving Several Intermediates

EXAM #3 Next Tuesday April 4th covering chapters 1, 10, 11

Essentially (except no quencher, [Q]) shows how Eq. 11 is obtained from Eqs. 1-7 of:

“The concentration dependence of the normalized photostability of 1,3,5,7,8-pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex (PM-597) methanol solutions”

Wade N. Sisk and Wesley Sanders [Journal of Photochemistry and Photobiology A: Chemistry](#) Volume 167, Issues 2-3, 1 October 2004, Pages 185-189

1. From the 8 self-sensitized photooxidation reaction mechanism below, utilize the steady state approximation for all intermediates to show that the the rate of DO₂ production is given by

$$\frac{d[DO_2]}{dt} = - \frac{k_5 k_3 k_1 [D]^2}{(k_2 + k_3) \{ (k_5 + k_6) [D] + k_Q [Q] + k_7 \}}$$

An intermediate is a species which is produced and consumed so as not to appear in the final overall reaction. 2.

2. First you might want to list the three intermediates.

3. If $(k_5 + k_6)[D] \gg k_7 + k_Q[Q]$ the above rate law simplifies to what expression?

4. How could you determine whether the DO₂ production rate is first order or second order with respect to D?

5. How would the inclusion of a ³D quenching step affect the expression for DO₂ production?

The a ³D quenching step (9th step):



8-step self-sensitized photooxidation mechanism

