Chem 128/228 (Spring 2003)
problem set 19 (further aspects of photochemistry)

What can be concluded from the following?

[a] Direct irradiation of compound **A** leads to the formation of **B** and **C**.
[b] When the same reaction is carried out to low conversion, only **B** is observed. It's only when 1/4 of **A** has been consumed that **C** shows up.
[c] Sensitized photolysis of some compound **H** leads to the formation of **D**, while direct photolysis of **H** does not produce **D**; only **E** is formed.
[d] Direct photolysis of some compound **Y** affords **W** and **X** as primary photo-products. Sensitization leads to the formation of the same amount (and with the same quantum efficiency) of **W**, but the amount of **X** is cut in half.
[e] Direct photolysis of some compound **F** leads to **V**. Sensitized photolysis, under conditions where energy transfer has been assured, leads to the complete recovery of the starting material.

Suppose that you plan to use a a photo[2+2]cycloaddition reaction as a key step in a total synthesis of some bioactive natural product. Luckily, you have access to the chemical literature. Luckily, you checked it. (-:

It turns out that a Stern-Volmer analysis had been conducted on two compounds, each similar to that you planned to use. The slope of the Stern-Volmer plot for the compound most closely related to your's was 5 times that of the simpler substance.

Assume that the studies were conducted in the same solvents and at the same temperatures, and that the rate of quenching was diffusion controlled. Assume, also, that the rate constant for the reaction of the simpler substance was determined to be 10^8 s^{-1}.

[a] Will the rate for the compound most closely related to yours be faster or slower?
[b] Determine the value of the rate constant. Show your work.

Which of the following transitions are formally allowed?

[a] singlet n,π^* to triplet n,π^*
[b] singlet n,π^* to triplet π,π^*
