

Problem set 17; chem. 128/228, spring 2003
(photochemistry - some practical considerations)

1. The following situation applies under two common circumstances – 1) when a strongly absorbing impurity is produced (or is present in the starting material because you neglected to remove it and didn't think that it would matter (-:) and 2) the initially formed, and desired, photoproduct absorbs more strongly than the starting material (secondary photolysis is observed if the reaction is run to completion). The same sort of thought exercise is useful when considering photostationary state equilibrium – of the variety encountered when one is dealing with the E/Z isomerization of an alkene (*e.g.* retinal and vision).

Irradiation of compound **A** leads to the production of **B**, the desired synthetic target molecule. The extinction coefficient maximum for **A** in the wavelength region of interest is 100. At some time during the photolysis another compound, call it **C**, was detected. The photolysis was stopped, **C** was separated from the other materials, and its UV spectrum was recorded. Its extinction coefficient maximum for **C**, in the region of importance for the conversion of **A** to **B**, turned out to be 10,000.

Suppose that the photolysis is carried out so that at some time, *t*, the concentration of **C** was 1/4 that of **A**. Determine the absorbance for each substance at this time. Which substance, **A** or **C**, will absorb most of the incident light under this condition?

2. Suppose that you wish to irradiate compound **A** and to attain the n,π^* excited state. **A** absorbs in two distinct regions – 1) between 240 and 260 nm with an ϵ_{max} of 10^4 (π,π^*), and 2) between 310 and 330 nm with an ϵ_{max} of 50 (n,π^*).

[a] What glass filter sleeve should be selected?

[b] What concentration of **A** should be used to assure that it absorbs at least 90% of the incident radiation? Assume a path length of “1 unit”.

3. Suppose that you wish to determine whether compound **B** could serve as a triplet sensitizer for a reaction that you are interested in studying. A prerequisite is that the triplet energy for ^3B be greater than or equal to that of the energy of the triplet excited state one wishes to generate (call it ^3A). Suppose that $E(^3\text{A}) = 75$ kcal/mol. Suppose, too, that the 0-0 transition in the phosphorescence spectrum for ^3B appears at 410 nm.

(a) What is $E(^3\text{B})$?

(b) Could **B** be a useful sensitizer?