SAMPLE SIGNAL TO NOISE CALCULATION

Experiment: Photolyze 4-Bromo-Butene using 248 nm light in the presence of O2. Measure the decay of buten-4-yl radical (CH2CHCH2CH2) by direct absorption at 309 nm, and so infer the rate constant for the reaction

CH2CHCH2CH2 + O2 = products (1)

(I am actually planning to do this experiment this summer in collaboration with Leah Ruslen, Jason Clevenger, Dr. Hans-Heinrich Carstensen, and Prof. R.W. Field.)

For the calculation we will assume a crossed-beam geometry, everything in the gas phase and premixed, and a single-pass absorption. (One can do better with more complicated geometries, but there are associated headaches.)

The 248 nm light will come from an excimer laser, pulse energy about E=0.1 J, with a pulse length of ~50 ns.

The 309 nm light will come from a continuous source (either a doubled dye laser or a lamp with a monochromator), we will assume here that we can get 1 microwatt of light of the appropriate wavelength through the sample and onto a detector.

First we need to estimate the timescale. At the high pressure limit, we expect that Reaction 1 will go with a rate similar to that of ordinary alkyl radicals, i.e. ~1E9 liter/mole second. The reaction will be slower at lower pressures (or at higher temperatures, we will discuss this paradox later in class). If we had one atmosphere of O2, [O2] = P/RT ~ .05 mole/liter. So the time constant for the radical's decay due to this reaction τ ~1/k[O2] ~

20 ns. This is a little too fast for us since the excimer pulse will not be over yet.

We can slow the reaction down by lowering the partial pressure of O2. How slow can we go? At some point, we expect the radical to react with other radicals or with the residual bromobutene instead of reacting with O2. The rate constants for these side reactions will be comparable to or slower than the reaction with O2, and the concentrations of these species will be less than the initial concentration of bromobutene employed. So we will be safe if [O2] is in the range

.01 M > [O2] > [initial bromobutene]

so τ >100 ns. The initial concentration of bromobutene must be set correctly so that the 248 nm light will penetrate to an appropriate depth into the sample cell. It is convenient if the penetration depth is > 1 cm, i.e. if the Beers Law exponent

ε_{248} [initial bromobutene](1 cm) < 1

We will measure the UV absorption coefficient for 4-bromobutene experimentally to set this condition precisely, but for now we will assume ε_{248} ~100 liter/mole cm. (I have measured this now, it is actually only ~10 liter/mole cm.) Hence we want [initial bromobutene]<0.01 moles/liter ~ 0.2 atm. To get the best signal, we will want [initial bromobutene] near the top of this range (so most of the 248 nm photons are used to make radicals we can detect), but this may give us problems, since the side reactions may be faster than the reaction with O2. If we can afford to sacrifice signal, we can use more dilute bromobutene, and have less trouble with side reactions.

What is the signal? Here we need to choose some geometrical parameters. Set the probe beam to have a height H and a width W, and the photolysis beam to have the same height H but a different width L (this is the depth of the region where the two beams cross). All these numbers will typically be O(cm). Set the edge of the probe beam to be just inside the sample cell, so there is little volume irradiated by the 248 nm light upstream of the probed region. The number of 248 nm photons absorbed in the region probed will be (E*248nm/hc)(1-exp(- ε_{248} *[initial bromobutene]*W)), and the average concentration in the probed region will be this number divided by the volume: H*W*L. To get mole units, we have to divide this number by Avagadro's number N=6E23. Some fraction f (called "the quantum yield") of the bromobutene molecules which absorb a 248 nm photon will fragment to form the desired radical plus a Br atom. We will be optimistic and assume f=1. So:

concentration of radicals ~ f*E*248nm*(1-exp(ε_{248} *[initial bromobutene]*W))/(hcHWLN)

~ .0002 moles/liter*(1-exp(- ε_{248} *[initial bromobutene]*W)/HWL)

where H,W,L are in cm

For H,W,L ~ 1 cm and a high [initial bromobutene], the concentration of radicals formed ~ 1E-4 moles/liter.

The probe beam will be absorbed by the radicals. We expect ε_{309} ~ 1000 liter/mole cm. Beer's Law says

Fractional absorption of probe ~ 1-exp(- ε_{309} *[radicals]*L)

so for [radicals] ~ 1E-4 moles/liter and L~1 cm we expect to absorb about 10% of the 309 nm probe beam. This is a strong absorption, so we expect that this would be detectable (more on this below). So at least for high [initial bromobutene] we expect to see some signal immediately after the photolysis pulse. Beer's Law is only valid if there are many more molecules than photons (otherwise the photons can excite all the molecules, and excited molecules typically will not absorb any more photons, in fact they will emit instead). Let us make sure that we have enough molecules and radicals to absorb all the photons.

First the bromobutene: We claim we can photolyze ~ 1E-4 moles/liter of bromobutene to make radicals.

This means [initial bromobutene]>1E-4 moles liter. This appears to be no problem,

from above we know that [initial bromobutene]<0.01 moles/liter.

[initial bromobutene]~0.001 moles/liter ~ 0.02 atm ~15 torr looks like a reasonable working range

where the radical concentration would be ~1E-5 moles/liter and the probe beam would be attenuated by ~1%. (In light of the weaker than expected 248 nm absorption, we may need to use a bit more bromobutene, closer to 0.2 atm. The question then is how hot do we need to heat bromobutene to get its vapor pressure up to ~150 torr, not 15 torr). A key question is whether we can get 15 torr of bromobutene into the gas phase; it's reported boiling point is 100 C, so probably we can achieve this vapor pressure pretty easily, maybe even at room temperature.

Second, the butenyl radicals: We claim we can absorb 1-10% of the probe beam, and that the probe beam will be a microwatt. The probe photon flux

is

1E-6 Joule/sec * 309 nm / hc = 1.6E12 photons/sec which is not very much compared with the number of radicals we will make:

1E-5 moles/liter*.001 liter/cc*6E23 radicals/mole = 6E15 radicals/cc per pulse of the 248 nm laser.

We have established that we can run in a regime where we are absorbing ~1% of the probe beam, the timescale is ~1E-6 second, and all the pressures and temperatures are reasonable. What are the expected sources of noise/background/interferences?

If we block the light beams, we expect a very small noise level due to the dark-current of the photodetector and electromagnetic noise pickup by our electronics. One would need to check for the particular type of photodetector used, but off-hand I expect these noise sources to be negligible compared to the photodetector response to 1E12 photons/ second. With the probe beam hitting the photodetector, we will have additional noise due to fluctuations in the light intensity (e.g. many lasers have power fluctuations of about 1%) and due to the shot noise (discussed more below). The power fluctuations are likely a very serious problem for us, since they can be larger than the expected signal and for some types of light sources these fluctuations occur at a high enough frequency that we might confuse them with our signal. There are two ways to reduce this problem: 1) pick off a piece of the probe beam and measure the difference between the light power going through the sample and the reference beam or 2) frequency-modulate the laser beam at a very high frequency (faster than any fluctuations) and measure the difference between the absorption when the laser is on top of an absorption with that when it is not on the absorption with a phase-locked demodulator. (This trick is called FM spectroscopy).

If we allow the 248 nm beam into the sample, we have additional background due to scattered light and possibly also due to fluorescence (if anything in the cell or on the windows fluoresces.) This can be a serious problem, since the pulsed laser is much brighter (~1E17 photons/50 ns) than the probe beam (~1E12 photons/sec, i.e. 5E4 photons/50 ns). The scatter can be reduced by painting things black and by taking care with the geometry of the apparatus, and by putting a filter in front of the photodetector that rejects 248 nm light, but it is difficult to completely reject so many photons. The normal way to deal with this is to not use any data collected during the laser pulse, which often looks like a big spike at the beginning of the kinetic trace. Fortunately, the scattered light decays away quickly; fluorescence can last longer. If something in the system fluoresces strongly at 309 nm on the same time scale as the chemical reaction we are probing, the experiment may be impossible as currently configured.

Now let us examine the shot noise. In order to measure the kinetics, we will want to discretize the signal into different time intervals. For ~1E-6 second, 50 ns bins may be about right. As mentioned above, over each 50 ns interval, about 5E4 photons will hit our photodetector. We expect a fluctuation of about the square root of the this number (~ 200) due to quantum statistics (we call this "shot noise"). On the other hand, we expect about 1% of the photons passing through the sample (i.e. 500 photons) to be absorbed by our radical immediately after the photolysis pulse (less will be absorbed later as the radical concentration decays). So our S/N on each point in our time trace is only about 2/1, not great. We can average several laser pulses, though, so this is actually not too bad. For example, if we average 100 time traces, we expect the signal to noise on those traces (due to shot noise) to be about 20/1, certainly good enough to read a rate constant. Note that the shot noise is much less important if our only goal is to detect the radical (not its time dependence). Then we would just

integrate all the signal for a couple of microseconds, and expect a single-pulse S/N (due to shot noise) around 10/1 instead of 2/1.

Interferences? We don't expect any of the molecules in the system to absorb at 309 nm except the radical of interest. We need to check to confirm this. The 248 nm photon energy of 115 kcal/mol is almost double the energy required to break the C-Br bond, so potentially the photolysis could make many different products. Multiphoton absorption is also possible, with unknown consequences. The chemicals will also have impurities which might absorb/react/fluoresce. The products of the reactions between O2, butenyl radical, and Br might absorb at 309 nm or at 248 nm; their influence on the results can be minimized by completely flushing the sample between laser pulses.

Kinetic complication: The butenyl radical formed will likely be very hot (highly vibrationally excited). The background gas pressure will have to be high to ensure that it is thermalized before reacting with O2; possibly the butenyl radical will react unimolecularly immediately when it is formed, so we may not form the thermalized butenyl we are attempting to detect. It would be better to photolyze with lower energy photons to reduce these complications.

Summary: The experiment looks possible, but the S/N is small enough that it is not a sure thing in the proposed configuration. A longer path-length configuration (e.g. collinear probe and photolysis beams, or multipassing the probe beam) would help. With the numbers assumed here, the biggest problem is likely to be probe beam light fluctuations, and signal averaging may be necessary. The probe light power and stability, the absorption spectra of butenyl radical, and the photophysics of bromobutene are key unknowns.