Calculating the theoretical maximum rate of reaction for a UV-C LED in a free radical substitution reaction.

Stefan Nikolaj's blog

I bought a UV-C LED but didn't know what to do with it. In school I learned about free radical substitution with UV-C light, but given the low efficiency and power output of a UV-C LED I wanted to find out whether getting the materials would result in a fast reaction rate for a hobbyist like me, which I will define as being able to turn 1 mol of methane (CH_4) into 1 mol of carbon tetrachloride (CCl_4) in 1 day. I will only explore the theoretical maximum rate, since so many factors affect this reaction that I could never mention them all.

Free radical substitution is a way to do this and theoretically only requires methane and chlorine gas (which is why these results will stay purely theoretical. I thought about trying other halogens but all of them are very toxic in the gaseous state. First I want to discuss a bit of the theory and mention that I'm not a chemist or have done much chemistry in my life. I do know a lot about electronics, though, and passed IB Physics HL so I know physics too.

I explained free radicals and free radical substitution to myself through a simple analogy. Imagine two atoms bonded together in a molecule, like a real-life romantic couple. Let's say that they're boyfriend and girlfriend. They're happy together, they have a bond. Now, let's put them in a large field with different couples. Some are boyfriend-girlfriend (somewhat strong bond) and some are husband-wife (much stronger bond). Now, let's break those bonds using a highly energetic photon, or in the analogy – a relationship-ending negative event. Maybe one atom cheated on the other, maybe their life values changed, but regardless, their bond is broken. Both the boyfriend and girlfriend atom are now alone and looking for another partner. If enough partnerships get broken, then all those free boyfriends and girlfriends will start finding each other, and maybe for some the breakup will be so bad that they'll go for the same type of atom to avoid more negative experiences. Some married molecules will get broken, but less than ones that are just dating. Eventually, those that are dating will come to see that they found the right partner and will get married. Over time, only the married, strong bonds will be left, made up of all the atoms which should be together.

Now let's take this weird analogy into the real world. Free radical substitution has 3 main steps with corresponding chemical reactions (for the methane + chlorine example):

Initiation:

$Cl_2 \rightarrow Cl^{\cdot} + Cl^{\cdot}$

$CH_4 \rightarrow CH_3^{\cdot} + H^{\cdot}$

Propagation:

$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$

$CH_4 + Cl^{\cdot} \rightarrow CH_3^{\cdot} + HCl$

Termination:

$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$

$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3Cl$

$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3CH_3$

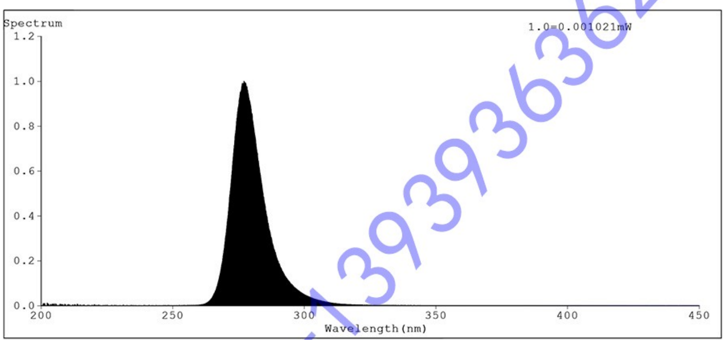
This, unfortunately, shows the biggest downside of free radical substitution – the large number of useless collisions which can either slow down the reaction by having to be re-initialized or creating a molecule which we don't want. CH_3Cl prefers chlorine over hydrogen since the difference of electronegativity between carbon and chlorine is higher, which should make it overall preferable to bond. However, CH_3Cl does require 3 more substitutions, meaning that for a molecule of methane, 4 chlorine radicals are needed. Since Cl_2 comes with 2 chlorine molecules, 2 moles of chlorine gas would be needed to make our beautiful carbon tetrachloride. To not make this extremely complicated, let's assume that only steps we like happen, since I don't have a degree in chemistry and knowledge of the kinematics, bonding and probabilities needed to accurately model this chaotic reaction. According to some studies I found online, chlorine likes UV light at around 260nm, so my 275nm LEDs are almost ideal, given the graphs. However, many graphs show vastly different distributions. Let's now look at the LED's characteristics itself.

The manufacturer gives this graph for the LED's power output at 100mA, which is the current I'm running the LED at.

EVERFINE

EVERFINE HAAS-2000 Test Report 2 Of 2

Spectrum Test Report



Peak WL:Lp=277.1nm HWL:Lhd=12.6nm

Photo Parameters:

Peak WL:Lp=277.1nm HWL:Lhd=12.6nm Fe = 15.081 mW

EUVC= 8.146mW EUVB= 4.4895mW EUVA= 7.2144e-005mW [weighting]

E_UVC= 8.6938mW E_UVB= 6.2763mW E_UVA= 0.11003mW

Electrical parameters:

V = 6.896 V I = 0.1000 A P = 689.8 mW PF = 1.000

IR = 0.0uA @5V

Status: Integral T = 1000 ms Ip = 30814 (47%)

Test Type: Fast Test; Delicacy = High; Tecool: ON

Model:JS-35AE	Number:1*100mA
Tester:	Date:2020-05-20
Temperature:25.0Deg	Humidity:50%
Manufactory:	Remarks:1

This nice graph shows the wide range of wavelengths output by the LED, all of which cover chlorine's effective spectrum. It also shows the power output – it's interesting how only 15.081mW of UV light are output for the 689.8mW of power put in. Since chlorine absorbs both UV-C and UV-B, I'll just take the total power output (15.081mW) as the actual power output and since 277.1nm is the peak wavelength, I'll take that as the actual wavelength, since the graph is relatively symmetric and the difference in wavelengths is not that large. Converting this to photons per second gives:

$$n_{photons} = \frac{P\,\lambda}{hc} = \frac{15.081 * 10^{-3} * 277.1 * 10^{-9}}{6.63 * 10^{-34} * 3 * 10^{8}} = 2.101 * 10^{16}$$

Even though that number looks very large, it's not. To react our 1 mol we would need 4 photons per molecule, which is:

$$4 * 6.022 * 10^{23} = 2.409 * 10^{24}$$

Finally, under perfect conditions, assuming that all interactions only take place between chlorine and the halogenoalkane, all the power goes into the reaction, and the rate does not decrease as it goes on, the time it would take to turn 1 mol of methane into 1 mol of carbon tetrachloride is:

$$\frac{2.409 * 10^{24}}{2.101 * 10^{16}} = 1.146 * 10^{8}\ seconds = 1.911 * 10^{6}\ minutes = 3.185 * 10^{4}\ hours = 1.326 * 10^{3}\ days$$

This is equal to 3.635 years. Not good. However, I have 4 LEDs, so hopefully combining them will get this done in under a year, and this is assuming perfect conditions. In actuality only half of the photons would likely need to be emitted because each photon makes 2 chlorine radicals, which still makes this reaction way too slow. Or, I have a more fun experiment to do: erase EEPROMs with the same UV-C LEDs. Woo!