Kinetics of Molecular Decomposition under Irradiation of Gold Nanoparticles with Nanosecond Laser Pulses – A 5-Bromouracil Case Study

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Complete derivation of the reaction kinetics:

$$BrU \overset{k1}{\rightarrow} small\,fragments \qquad (1)$$

$$BrU \overset{k2}{\rightarrow} U \qquad (2)$$

$$U \overset{k3}{\rightarrow} small\,fragments \qquad (3)$$

Based on equation (1) and (2) the decomposition of BrU is following a (pseudo-) first order reaction that can be described by the following equation:

$$\frac{d[BrU]}{dt} = -k_1[BrU] - k_2[BrU] \qquad (4)$$

According to equation (2) and (3) the generation and decomposition of U can be described by:

$$\frac{d[U]}{dt} = -k_3[U] + k_2[BrU] \qquad (5)$$

From equation (4) we get for the concentration of *[BrU]* after an irradiation time *t*:

$$[BrU] = [BrU]_0 e^{-(k_1+k_2)t} \qquad (6)$$

Where *[BrU]₀* is the initial concentration of BrU before the irradiation. If we insert this expression for *[BrU]* into equation (5) we get:

$$\frac{d[U]}{dt} + k_3[U] = k_2[BrU]_0 e^{-(k_1+k_2)t} \qquad (7)$$

By using the integral method, which allows to solve differential equations of the type: $\frac{dy}{dx} + f(x)y = g(x)$ by multiplication with $e^{\int f(x)dx} = e^{\int k_3 dt} = e^{k_3 t}$, we get:

$$e^{k_3 t}\frac{d[U]}{dt} + e^{k_3 t}k_3[U] = k_2[BrU]_0 e^{-(k_1+k_2)t}e^{k_3 t} \qquad (8)$$

Which can be rearranged to:

$$\frac{d([U]e^{k_3 t})}{dt} = k_2[BrU]_0\, e^{-(k_1+k_2-k_3)t} \qquad (9)$$

by using $\frac{d([U]e^{k_3 t})}{dt} = e^{k_3 t}\frac{d[U]}{dt} + e^{k_3 t}k_3[U]$. Thus the integration of equation (9):

$$\int_{[U_0]e^0}^{[U]e^{k_3 t}} d([U]e^{k_3 t}) = k_2[BrU]_0 \int_0^t e^{-(k_1+k_2-k_3)t}dt \qquad (10)$$

gives us:

$$[U]e^{k_3 t} - [U_0] = \frac{k_2[BrU]_0}{k_3-k_1-k_2}\left(e^{-(k_1+k_2-k_3)t} - 1\right) \qquad (11)$$

With $[U_0] = 0$, since there has been initially no U in the solution, we get for [U]:

$$[U] = \frac{k_2[BrU]_0}{k_3-k_1-k_2}\left(e^{-(k_1+k_2)t} - e^{-k_3 t}\right) \qquad (12)$$

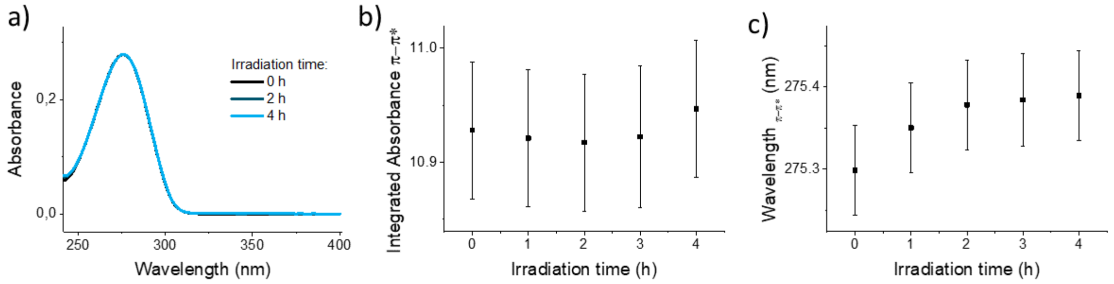
Consequently, the ratio of [U] and be [BrU] can be determined using equation (6) and (12):

$$\frac{[U]}{[BrU]} = \frac{k_2}{k_3-k_1-k_2}\left(1 - e^{-(k_3-k_1-k_2)t}\right) \qquad (13)$$

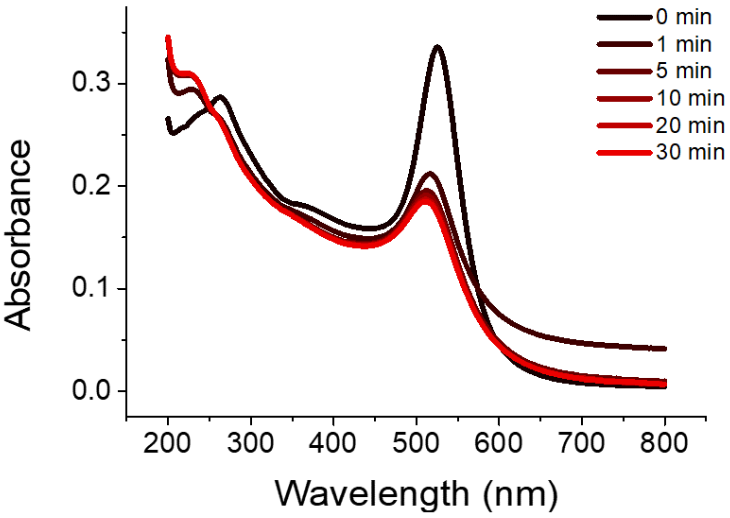
By using the Taylor expansion: $e^x \approx 1 + x$ we can simplify the expression for short illumination times t to:

$$\frac{[U]}{[BrU]} \approx k_2 t \qquad (14)$$

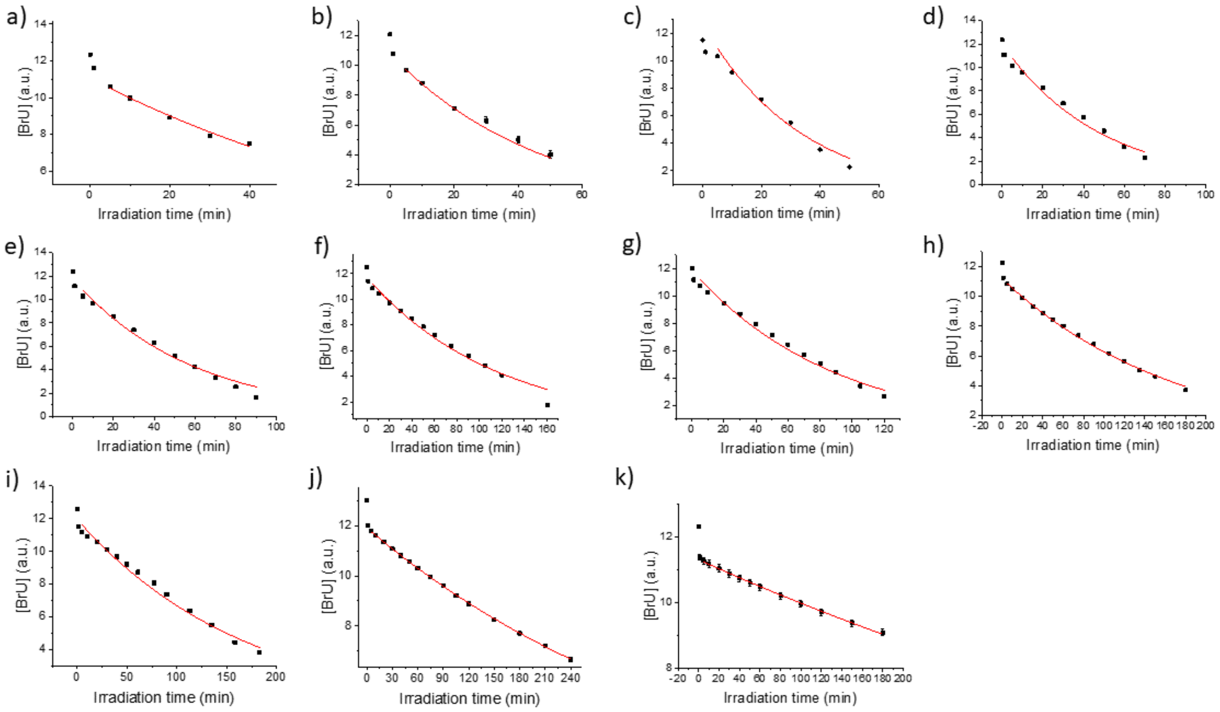
<u>Irradiation of BrU in the absence of AuNPs:</u>



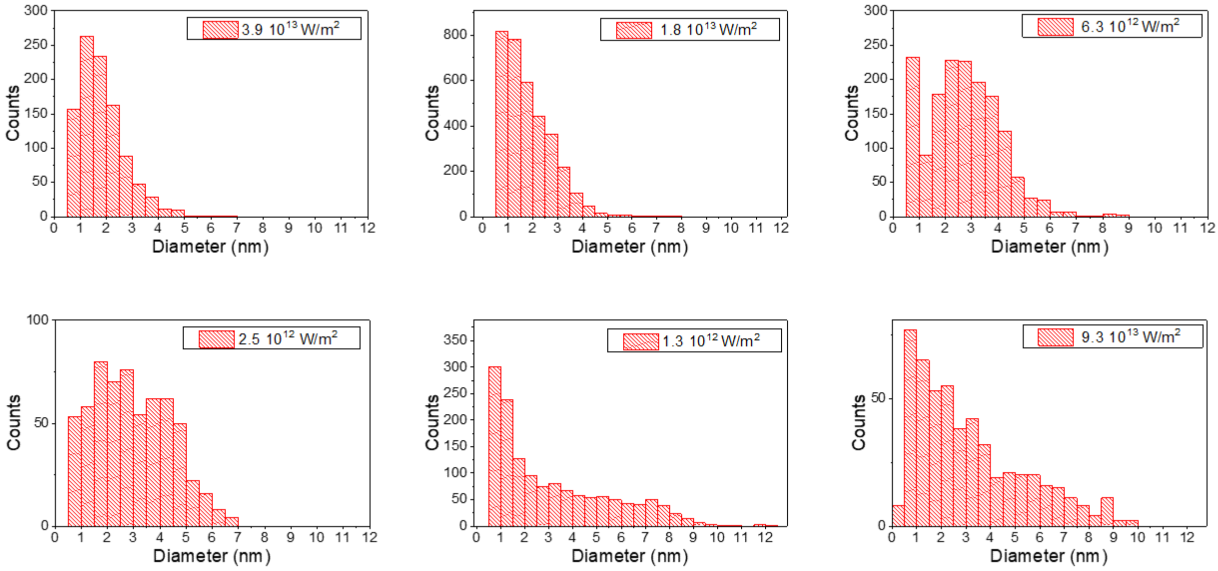
SI1: a) UV-Vis spectra of BrU solution irradiated with a focused 532 nm ns laser pulses with a repetition rate of 15 Hz with a maximum laser fluence of 4 10^{13} W/m^2 after 0 h, 2 h and 4 h of irradiation. b) Integrated Absorbance of the π- π resonance of BrU as a function of the illumination time. c) Center wavelength of the π- π* resonance as a function of the illumination time.*



SI2: Exemplary set of UV-Vis spectra of an AuNPs solution irradiated with a focused 532 nm ns laser pulses with a repetition rate of 15 Hz with a maximum laser fluence of 3.4 10^{12} W/m^2 used as background correction.



SI3: Concentration [BrU] plotted as a function of the irradiation time for different laser fluences: a) 19.9·10^{12} W/m^2 b) 13.7·10^{12} W/m^2 c) 10.3·10^{12} W/m^2 d) 5.48·10^{12} W/m^2 e) 4.83·10^{12} W/m^2 f) 3.39·10^{12} W/m^2 g) 3.23·10^{12} W/m^2 h) 2.13·10^{12} W/m^2 i) 1.92·10^{12} W/m^2 j) 1.45·10^{12} W/m^2 k) 1.05·10^{12} W/m^2.



SI4: Histograms of the AuNPs sizes after laser illumination with different fluences.

Error calculation:

The error of the surface area of the irradiated surface area A_s has been calculated based on the error of *P(r),* which is given by:

$$\Delta P(r) = \frac{\Delta N(r)}{N_{ges}} + \frac{N(r)}{{N_{ges}}^2} \cdot \Delta N_{ges} \qquad (15)$$

with

$$N = \sqrt{N} \qquad (16)$$

Thus we get:

$$\Delta A_S = \left[\sum_r \left| \frac{\partial}{\partial P(r)} \frac{V_{gold}}{\sum_r P(r) \cdot \frac{4}{3} \cdot \pi \cdot r^3} \cdot \sum_r 4\pi \cdot P(r) \cdot r^2 \right|^2 \cdot \Delta P(r)^2 \right]^{1/2} \qquad (17)$$

Which can be written as:

$$\Delta A_S = \left[\left[\frac{V_{gold} \cdot \sum_r \frac{4}{3} \pi \cdot r^3 \cdot \Delta P(r)}{\left(\sum_r P(r) \cdot \frac{4}{3} \cdot \pi \cdot r^3 \right)^2} \cdot \sum_r 4\pi \cdot P(r) \cdot r^2 \right]^2 + \left[\frac{V_{gold}}{\sum_r P(r) \cdot \frac{4}{3} \cdot \pi \cdot r^3} \cdot \sum_r 4\pi \cdot r^2 \cdot \Delta P(r) \right]^2 \right]^{1/2}$$

(18)

The error for the illuminated surface area of the AuNPs is given by:

$$\Delta A_{ill} = \frac{V_{ill}}{V_{total}} \cdot \Delta A_S \qquad (19)$$

The error for the absorbed heat by an individual AuNP:

$$Q = \frac{Abs\cdot\sum_r P(r)\cdot\frac{4}{3}\cdot\pi\cdot r^3}{V_{gold}\cdot N_{AuNP\ 40nm}\cdot l}\cdot I \qquad (20)$$

has been calculated by:

$$\Delta Q = \left[\sum_r \left|\frac{\partial}{\partial P(r)}\,\frac{Abs\cdot\sum_r P(r)\cdot\frac{4}{3}\cdot\pi\cdot r^3}{V_{gold}\cdot N_{AuNP\ 40nm}\cdot l}\cdot I\right|^2 \cdot \Delta P(r)^2\right]^{\frac{1}{2}} = \frac{Abs\cdot\sum_r \frac{4}{3}\cdot\pi\cdot r^3\cdot\Delta P(r)}{V_{gold}\cdot N_{AuNP\ 40nm}\cdot l}\cdot I \qquad (21)$$

Table 1: Ratio of [U] and [BrU] as a function of the irradiation time. Data presented in Fig. 3a).

Irradiation time (min)	0	1	5	10	20	30
[U]/[BrU]	0,0319	0,0524	0,0417	0,0462	0,0545	0,0749
Δ[U]/[BrU]	0,0017	0,0019	0,0021	0,0019	0,0022	0,0022
Irradiation time (min)	40	50	60	70	80	90
[U]/[BrU]	0,1006	0,1192	0,1318	0,1534	0,1685	0,1899
Δ[U]/[BrU]	0,0022	0,003	0,0033	0,0052	0,0081	0,0167

Table 2: Concentration [BrU] as a function of the irradiation time. Data presented in Fig. 3b).

Irradiation time (min)	0	1	5	10	20	30	40	50	60	70	80	90
[BrU]	12,37	11,14	10,28	9,67	8,54	7,40	6,30	5,20	4,29	3,37	2,56	1,62
Δ[BrU]	0,14	0,14	0,14	0,12	0,12	0,11	0,11	0,11	0,11	0,13	0,14	0,15

Table 3: Reaction rates as a function of the laser repetition rates. Data presented in Figure 4.

40 mM BrU				
Frequency (Hz)	k1 (puls^{-1})	Δk1 (puls^{-1})	k2 (puls^{-1})	Δk2 (puls^{-1})
4	2,02184E-5	8,18345E-7	2,74703E-6	2,13321E-7

6	1,99022E-5	7,23873E-7	1,46826E-6	2,55005E-7
8	1,89349E-5	8,85859E-7	4,55324E-6	4,93752E-7
10	1,82486E-5	7,50822E-7	1,34997E-6	1,57657E-7
12	1,68431E-5	7,07432E-7	2,77589E-6	4,15534E-7
14	1,53243E-5	3,71962E-7	1,95252E-6	2,16141E-7
35 mM BrU				
Frequency (Hz)	k1 (puls^{-1})	Δk1 (puls^{-1})	k2 (puls^{-1})	Δk2 (puls^{-1})
3	1,84951E-5	9,57881E-7	3,83911E-7	3,40785E-8
5	1,73793E-5	1,36372E-6	1,73427E-6	3,44217E-7
7	1,54995E-5	1,31419E-6	2,31902E-6	4,55786E-7
10	1,59941E-5	6,67977E-7	1,78483E-6	1,29012E-7
12	1,68431E-5	7,07432E-7	2,77589E-6	4,15534E-7
15	1,30933E-5	7,38898E-7	1,10882E-6	8,34434E-8

Table 4: Reaction rates as a function of the laser repetition rates. Data presented in Figure 5 a).

Laser fluence 10^{12}(W/m^2)	k1 (min^{-1})	Δk1 (min^{-1})	k2 (min^{-1})	Δk2 (min^{-1})
19,91	0,00586	0,0011	0,00152	1,6E-4
13,74	0,0191	0,00146	0,00361	3,0E-4
10,26	0,02113	0,00196	0,00374	5,2E-4
5,48	0,01869	0,00118	0,00188	8,0E-5
4,83	0,01529	8,3E-4	0,00175	8,4E-5
3,40	0,00789	4,7E-4	8,22E-4	5,5E-5
3,23	0,0097	4,5E-4	0,00137	5,3E-5
2,13	0,00508	2,7E-4	7,85E-4	7,1E-5
1,92	0,00566	2,7E-4	5,14E-4	4,9E-5
1,45	0,00204	9,3E-5	3,51E-4	2,8E-5

1,05	0,00119	2,7E-5	8,16E-5	7,1E-6

Table 5: AuNP surface area as a function of the laser fluence. Data presented in Figure 6 d).

Laser fluence (W/m^2)	3,93E13	1,75E13	6,29E12	2,46E12	1,30E12	9,30E11
As (cm^2/ml)	0,00199	0,00187	0,00138	0,00130	8,8E-4	9,2E-4
ΔAs (cm^2/ml)	4,0E-4	2,3E-4	2,2E-4	2,9E-4	1,9E-4	3,1E-4

Table 6: Illuminated AuNP surface area as a function of the laser fluence. Data presented in Figure 6 f).

Laser fluence (W/m^2)	3,93E13	1,75E13	6,29E12	2,46E12	1,30E12	9,30E11
A_{ill} (cm^2/ml)	1,10E-4	1,23E-4	1,23E-4	1,72E-4	1,62E-4	2,07E-4
ΔA_{ill} (cm^2/ml)	2,2E-5	1,5E-5	2,0E-5	3,8E-5	3,5E-5	6,8E-5

Table 7: Heat absorbed by an individual AuNP as a function of the laser fluence. Data presented in Figure 7.

Laser fluence (W/m^2)	3,93E13	1,75E13	6,29E12	2,46E12	1,30E12	9,30E11
Q_{abs} (J)	1,42E-13	6,9E-14	6,8E-14	3,9E-14	4,9E-14	3,3E-14
ΔQ_{abs} (J)	3,5E-14	1,1E-14	1,3E-14	8,8E-15	1,1E-14	1,1E-14