28th of October, 2016

Comparision between Two Bromine Containing Free Radical Initiators in PRESAGE® Dosimeter

Hyeonsuk Park

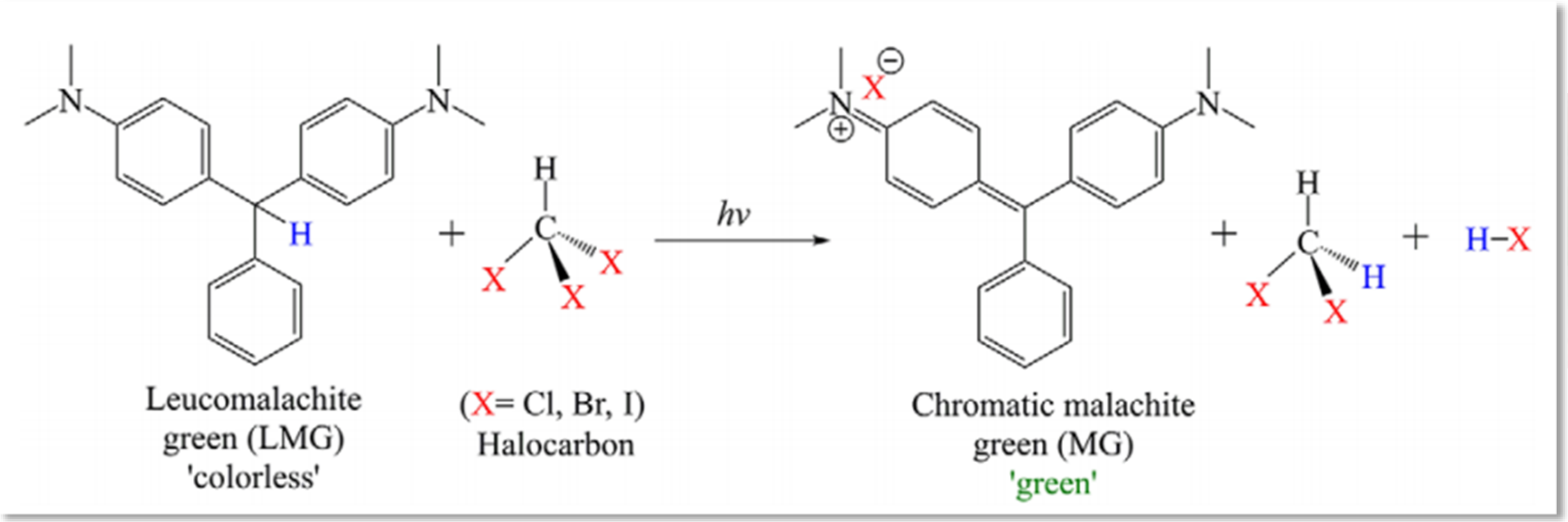
ssook7979@gmail.com

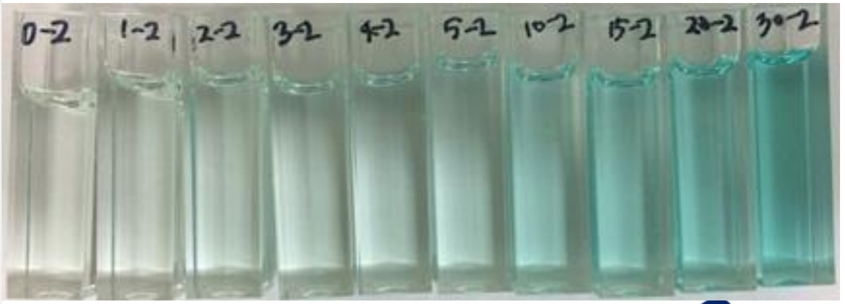
서울대학교 SEOUL NATIONAL UNIVERSITY

Contents

Introduction

- Presage is solid type dosimeter
  - Which contains **halocarbon radical initiator** and **Leucomalachite green (LMG) dye**
  - **Halocarbon initiator** is **ionized** upon irradiation and **oxidizes LMG** to be **green colored MG**





(Alqathami et al., Phys. Med. Biol. 61, 2016)

Introduction

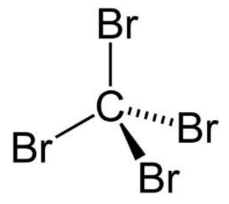
- There has been a lot of studies regarding **the effect of changing LMG and initiator ratio** or **comparing among different halogen containing initiator**.
- But lack of studies about **same halogen containing initiator** or the **effect of adding subsidiary material**.

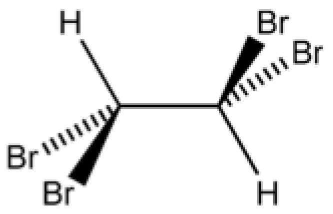
- The aim of this study
  - To see the **effect of adding LMG solvent** and
  - **Compare the two radical initiators $C_2H_2Br_4$ and CBr_4** which contains **same halogen atom**, **Bromine**
  - While **maintaining the water-equivalency** of dosimter.

Materials and Methods

- Chemical Formula for Presage dosimeters

	Initiator	LMG solvent
Formulation A	CBr_4 0.56 wt%	Cyclohexanone 7 wt%
Formulation B	CBr_4 0.56 wt%	Cyclohexanone 3 wt%
Formulation C	$C_2H_2Br_4$ 0.56 wt%	-
Formulation D	$C_2H_2Br_4$ 0.56 wt%	Cyclohexanone 3 wt%





- All formulation contained same a mount of Dibutyltin Dilaurate catalyst (0.05 wt%)
- Crystal Clear 200 (Smooth-On, Easton, PA USA) urethane was used as a base.

Materials and Methods

- Effective atomic number (Z_{eff}) calculation

➢ The elemental composition of the **Smooth-On Crystal Clear series** is **C:63.3 %, H: 9.4 %, N: 5.0 %, O: 21.3 %** (M. Alqathami et al., Radiation Physics and chemistry 81(7), 2012).

➢ The **effective atomic numbers** of all dosimeters were calculated using **Mayneord equation**.

$$Z_{eff} = \sqrt[2.94]{\sum_{i=1}^{n} a_i Z_i^{2.94}}$$

where $\mathbf{a_i}$ is the **fractional contributions** of each element to the total number of electrons in the mixture and $\mathbf{Z_i}$ is the **atomic number** of each element.

Materials and Methods

- Irradiation
  - X-RAD320 biological irradiation (Precision X-Ray Inc., USA)
  - 250 kVp, 15 mA with 2 mm Al filter
  - 35 cm SSD with 10×10 cm^2 field size

- Absorbance measurements
  - Perkin-Elmer Lambda 35 UV-Vis spectrophotometer
  - Wavelength range of 500-700 nm
  - 4 points along the length of the cuvette were measured and averaged.
  - To test the post-irradiation effect, absorbance was measured over 4 days.

Results and discussion

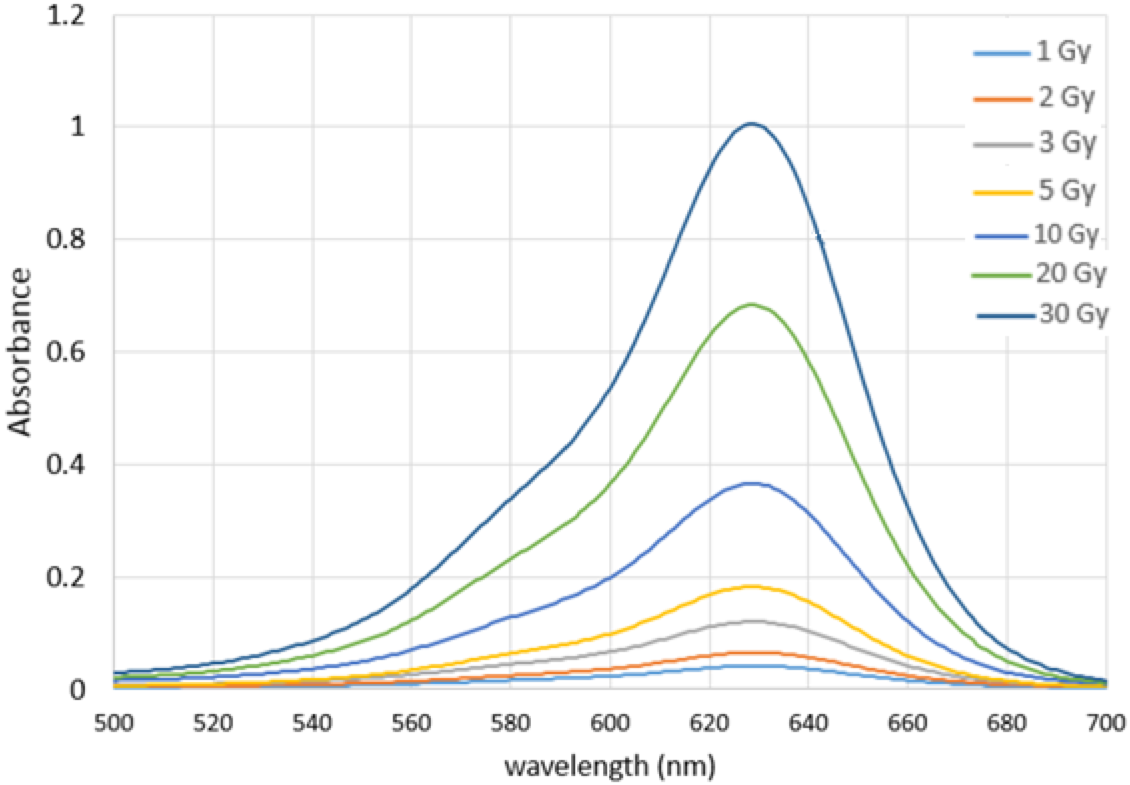
- Effective atomic number calculations

	Formulation A	Formulation B	Formulation C	Formulation D	water
W_H (wt %)	9.32	9.32	9.32	9.32	11.19
W_C (wt %)	63.34	63.43	63.43	63.42	-
W_N (wt %)	5.05	5.05	5.04	5.04	-
W_O (wt %)	20.72	20.72	20.75	20.74	88.81
W_{Br} (wt %)	0.58	0.50	0.52	0.53	-
W_{Sn} (wt %)	0.01	0.01	0.01	0.01	-
Z_{eff}	**7.49**	**7.49**	**7.46**	**7.45**	**7.42**

- All dosimeters showed similar values to water.

Results and discussion

- Absorption spectrum

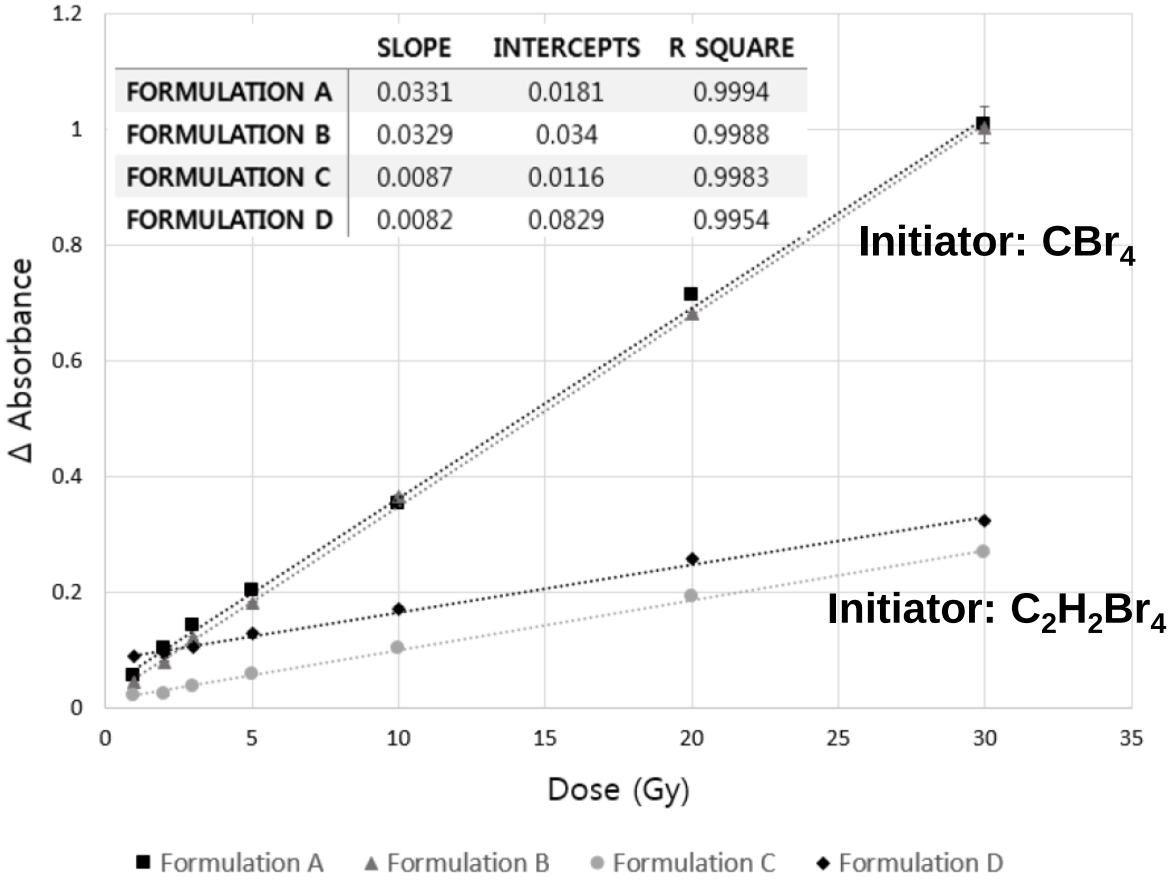


(Absorption spectrum of Formulation B)

- The maximum absorption occurred at **629 or 630 nm**.
- The **Maximum peak values** were **increased along with the exposed dose**.
- All dosimeters showed the same absorption trends.

Results and discussion

- Calibration curves (2 hrs after irradiation)

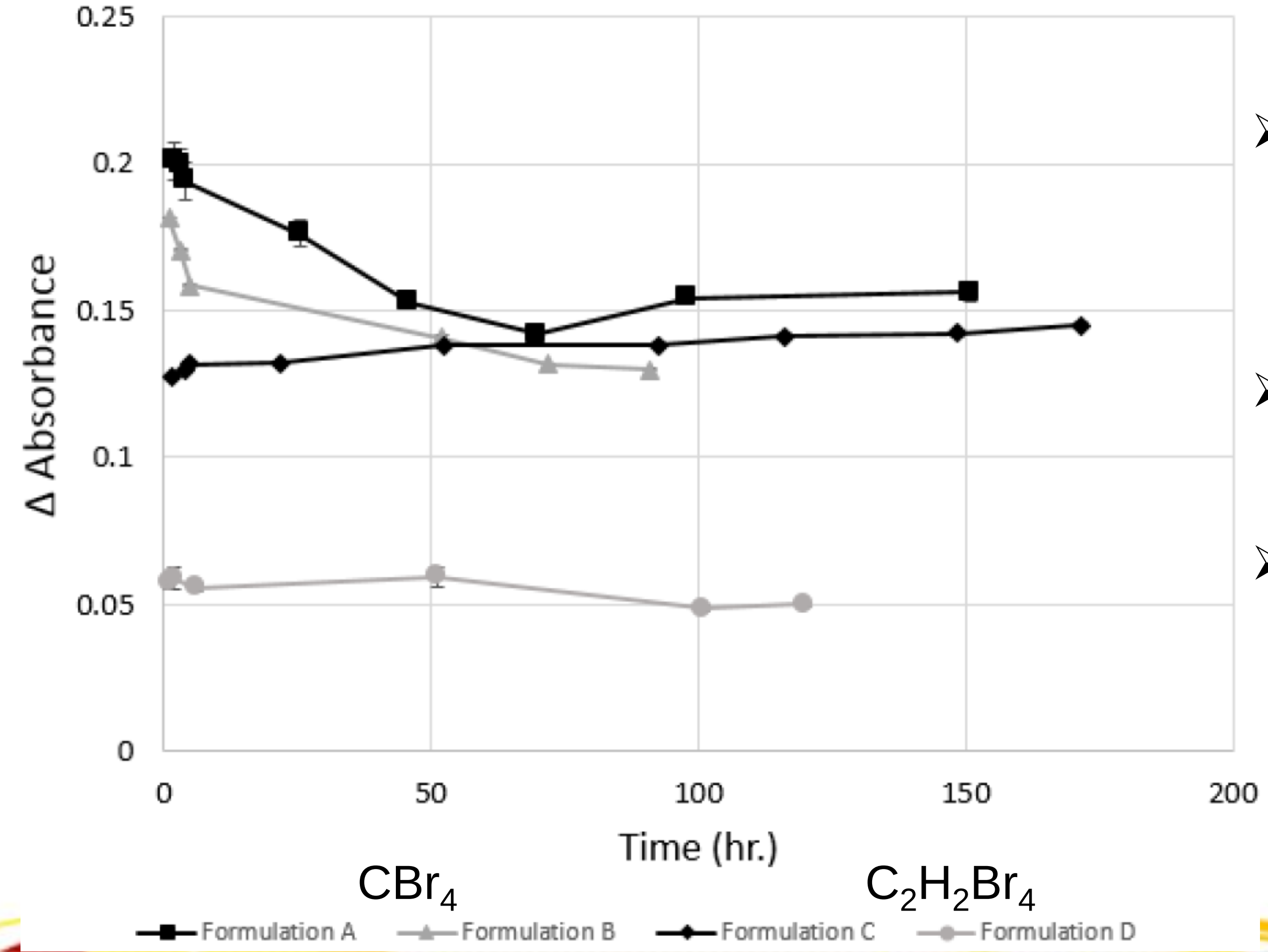


	SLOPE	INTERCEPTS	R SQUARE
FORMULATION A	0.0331	0.0181	0.9994
FORMULATION B	0.0329	0.034	0.9988
FORMULATION C	0.0087	0.0116	0.9983
FORMULATION D	0.0082	0.0829	0.9954

- All calibration curve showed **high linearity** (R^2>0.99).
- **CBr_4** initiator is about **4 times more sensitive** than **$C_2H_2Br_4$** initiator although they have **similar amount of C-Br bond**.
- There is **no significant effect** of adding **cyclohexanone** on **sensitivity**.

Results and discussion

- Post-irradiation effect (5 Gy)



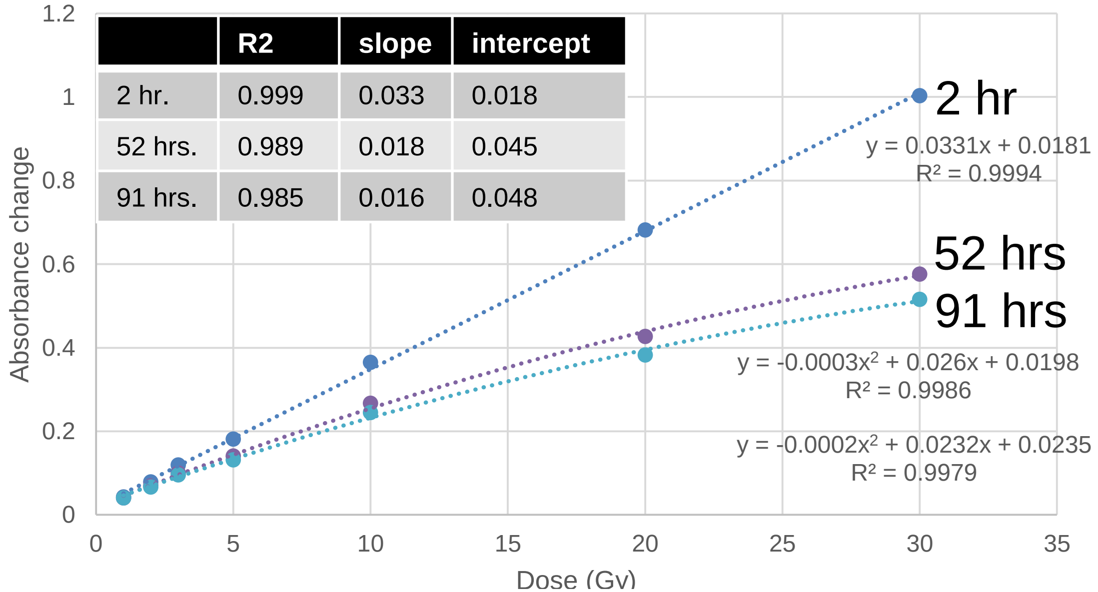
CBr_4 $C_2H_2Br_4$

- ➢ The absorbance of the **CBr_4** containing dosimeters (Formulation A,B) **decreased rapidly** before they were stabilized (**23.16 %** and **28.46 %** each).
- ➢ While **$C_2H_2Br_4$** containg dosimeters (Formulation C,D) changed **12.14 %** and **12.68 %** each.
- ➢ There is **no significant effect** of adding **cyclohexanone** in case of $C_2H_2Br_4$.

Results and discussion

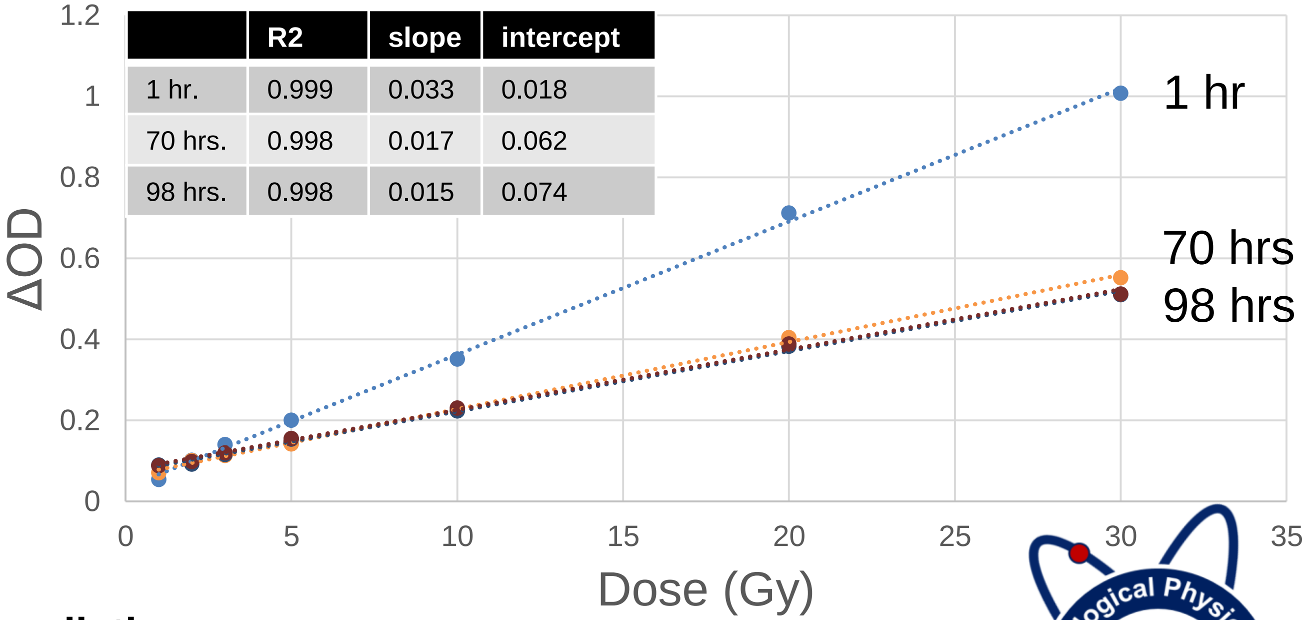
- Effect of solvent on CBr_4 initiator

3 wt% solvent with CBr_4



	R2	slope	intercept
2 hr.	0.999	0.033	0.018
52 hrs.	0.989	0.018	0.045
91 hrs.	0.985	0.016	0.048

7 wt% solvent with CBr_4



	R2	slope	intercept
1 hr.	0.999	0.033	0.018
70 hrs.	0.998	0.017	0.062
98 hrs.	0.998	0.015	0.074

- There were an effect of **reduced solvent** on CBr_4 in **post-irradiation response**.
- Some time after the irradiation, **3 wt% solvent** containing formulation **lost its linearity continuously** while **7 wt% solvent** containg formulation **maintain its high linearity (R^2>0.99)** over time.

Results and discussion

- The cyclohexanone solvent **reduces the ionization energy** of CBr_4 into CBr_3 + Br^-.

CBr_4 + Cyclohexanone	$\longrightarrow$	CBr_4^+ (Unstable)
CBr_4^+	$\longrightarrow$	CBr_3•Br
CBr_3•Br	$\xrightarrow{4.14\ eV}$	CBr_3+Br^-

$$CBr_4 \xrightarrow{10.27\ eV\ or\ 9.85\ eV} CBr_3 + Br^-$$

(H. Zhang et al., J. Phys. Chem. A, 2005)

Results and discussion

- The **reduction of linearity** in 3 wt% cyclohexanone and CBr4 initiator may be related to the **reduction of the amount of solvent**.
- **Cyclohexanone**, as a nonpolar solvent, seems act as a **cage** which **prevent recombination of the once ionized initiator**.
- Because of the **reduction in solvent**, the **ion recombination occurred fast** especially at high dose.

Conclusion

- **CBr_4** was **more sensitive** to the radiation and emitted 4 times more free radials upon irradiation **with no additional effective atomic number**.
- But the **absorbance after irradiation was highly variable** with time.
- For **stable measurement**, **$C_2H_2Br_4$** would be more appropriate as a free radical initiator.
- The solvent **cyclohexanone** may affect the performance of the dosimeter especially when it is used with **CBr_4**.
- **CBr_4** can be considered as a **high sensitive dosimeter** with **fast scanning device**.
- With appropriate solvent, **CBr_4** can be used as a **high sensitive** initiator while maintaining its **water-equivalency.**

Discussion & Question

Thank you for your attention