SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Delaney Ryan
FACULTY ADVISOR:	Aliaksandra Lisouskaya and Ian Carmichael
PROJECT PERIOD:	May – July 2023 (Summer 2023)
PROJECT TITLE:	Characterization of tributyl phosphate radicals by electron spin resonance
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**(X) Energy Conversion and Efficiency** **(X) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Learn how to use the electron paramagnetic resonance (EPR) spectrometer	Learned about the theory of EPR and mastered how to work the device. Able to independently conduct successful EPR experiments for several hours at room temperature and at low temperatures (77 K).	100%
Performing on-site irradiation of samples using an X-ray tube in an EPR resonator	Got acquainted with the safety methods for working with radiation sources. Performed X-ray irradiation of samples in the EPR resonator for experiments with spin traps, which makes it possible to perform in-situ irradiation and simultaneously measure the spectrum at room temperature. Trained to do Fricke dosimetry.	100%
Become more familiar with MATLAB coding and the Bruker Xenon software.	Can fit EPR spectra relatively well on both programs and convert the results to the appropriate units.	85%
Learn how to use the Schlenk line for the Freeze Pump Thaw technique	Studied the degassing method by the Freeze-Pump-Thaw technique. Wrote the standard operating procedure for Schlenk lines with the help of Alexandra. Perform degassing using Schlenk lines individually but need help with quartz tube sealing.	80%
Become more familiar with radiation chemistry, radicals, spin adducts, etc.	Read a considerable amount of literature this summer to expand understanding of the field.	80%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	N/A
EXTERNAL AWARDS RECEIVED	N/A
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	The paper is prepared for publication in the Journal of Physical Chemistry A
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	N/A
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Notre Dame Summer Undergraduate Research Symposium, Characterization of tributyl phosphate radicals by electron spin resonance, July 26, 2023, University of Notre Dame Jordan Hall of Science
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	N/A
INTERNAL COLLABORATIONS FOSTERED	N/A
EXTERNAL COLLABORATIONS FOSTERED	N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	N/A

OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	N/A

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

The Vincent P. Slatt Fellowship for Undergraduate Research in Energy Systems and Processes has been one of the greatest and most valuable experiences I have had in my lifetime. I began my research in the Radiation Laboratory in January of this year, and while I loved my five hours in lab every week, it sometimes felt like I wasn't spending enough time there to be making a real impact. But working there for ten weeks has shown me that I do add value to the lab with the work that I do, and I truly enjoy being there because of the research and the fantastic people I've come to know. This experience has consistently exceeded every expectation I came into the program with. Lab personnel were incredibly helpful, respectful, and responsive. Even faculty I didn't work with would be willing to help when an experiment wasn't working properly. I also really enjoyed how well-rounded my experience was. I wasn't just experimenting all the time. I read literature, helped edit and write a paper, learned how to use different software programs (Origin, MATLAB, and Bruker Xenon), and got to watch in-person lectures most weeks on topics that were in the same field as mine. I don't know what else could have been done to make my experience better.

FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

Introduction

Tributyl phosphate (TBP) is an important component in nuclear waste separation processes that has been used in nuclear projects since the Manhattan Project.[1] These processes use TBP dissolved in an alkane solution to extract uranium and plutonium from an aqueous acidic solution of dissolved fuel. Therefore, it is important to understand the radiolytic degradation pathways of TBP, since it absorbs high doses of ionizing radiation during the separation process.

Data and Results

The spin-trapped method allows for the identification of short-lived TBP radicals as spin-trap adducts. A spin trap, N-tert-butyl-α-phenylnitrone (PBN), was dissolved in TBP at various concentrations (2 mM, 10 mM, and 40 mM). To estimate the radiation-chemical yield (G-value) of TBP radicals, we measured the EPR kinetics *in situ* upon X-ray irradiation of TBP solutions with PBN. Figure 1 below shows the EPR spectra results of the experiments. Fricke dosimetry was performed to estimate a dose rate using iron (II) sulfate heptahydrate in sulfuric acid with thiocyanide, and the dose rate was calculated to be 211 mGy/s. After PBN was dissolved in TBP and saturated with argon, the solution was placed in BLAUBRAND® disposable micropipettes and sealed with hot glue to ensure no oxygen could penetrate the solution and reduce the signal. Using a Spellman DF3 high-voltage power supply (50 kV, 30 mA) and Thales THX X-rays, the solutions were irradiated. EPR spectra were measured using Bruker EMXplus spectrometer in X-band with ER4119HS standard resonator. This experiment produced spin adducts with $\alpha(N) = 13.6$ G and $\alpha(H) = 1.8$ G, which corresponds to alkyl TBP radicals. Signals from H-trapped adducts were noticeably lacking from the spectra, indicating PBN traps mainly alkyl radicals from TBP.

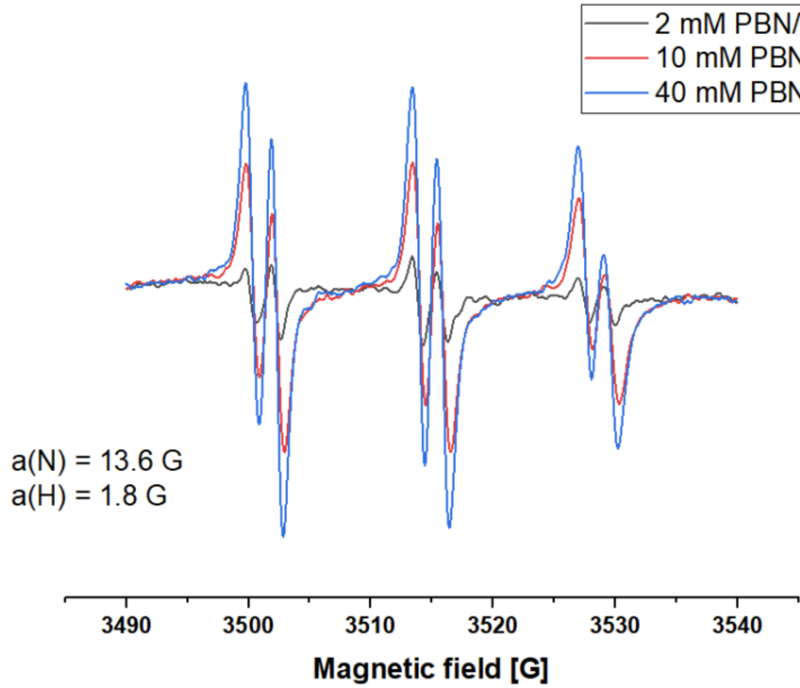

Figure 1. EPR spectra of X-rays irradiated PBN in TBP

The efficiency of TBP radiolysis was evaluated by measuring the *G*-value of radicals formed. The *G*-value derived from the experimental accumulation curves is related to spin-trapped adducts (PBN-TBP$^{\bullet}$). Figure 2 shows the spin adduct (PBN-TBP$^{\bullet}$) accumulation curves for 2 mM, 10 mM, and 40 mM PBN in TBP.

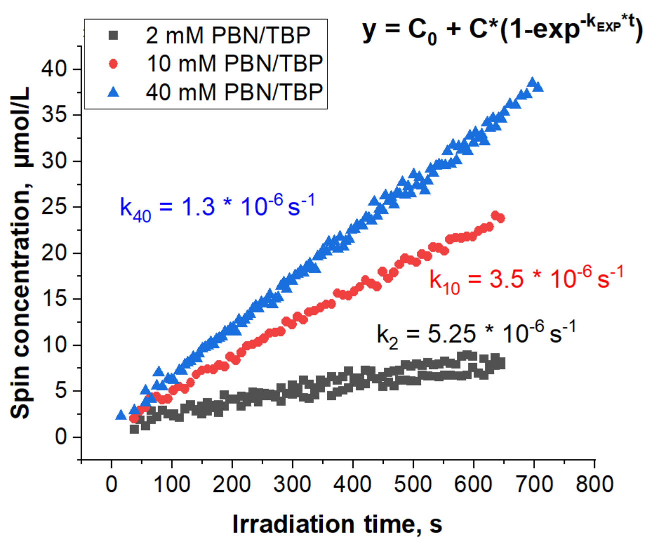

Figure 2. Formation curves of PBN-TBP adducts for 2 mM, 10 mM, and 40 mM PBN in TBP. Reaction rate constants from fitting shown in the figure with color code.

The corresponding G-value for the formation of TBP-derived radicals was 2.18 mol/J at room temperature. Previously, it was reported that the *G*-values of alkane-derived radicals from $C_5 – C_9$ hydrocarbons at room temperature, measured using the same approach, are in the range of 1-2 mol/J,[2] which agrees with our present results.

For low-temperature EPR experiments, TBP was degassed using a Freeze-Pump-Thaw method on a Schlenk line, sealed under vacuum, and frozen in liquid nitrogen. The frozen samples were then irradiated with ca. 15 ns 8 MeV electron pulses from an electron linear accelerator. After irradiating, the samples were placed in a Dewar flask filled with liquid nitrogen, and the EPR spectra were acquired at 77K, seen in Figure 3 below. The six lines of the spectra are consistent with previous literature values.[3, 4, 5] Irradiation of solid organic compounds at 77 K usually leads to the formation of H-abstraction radicals.

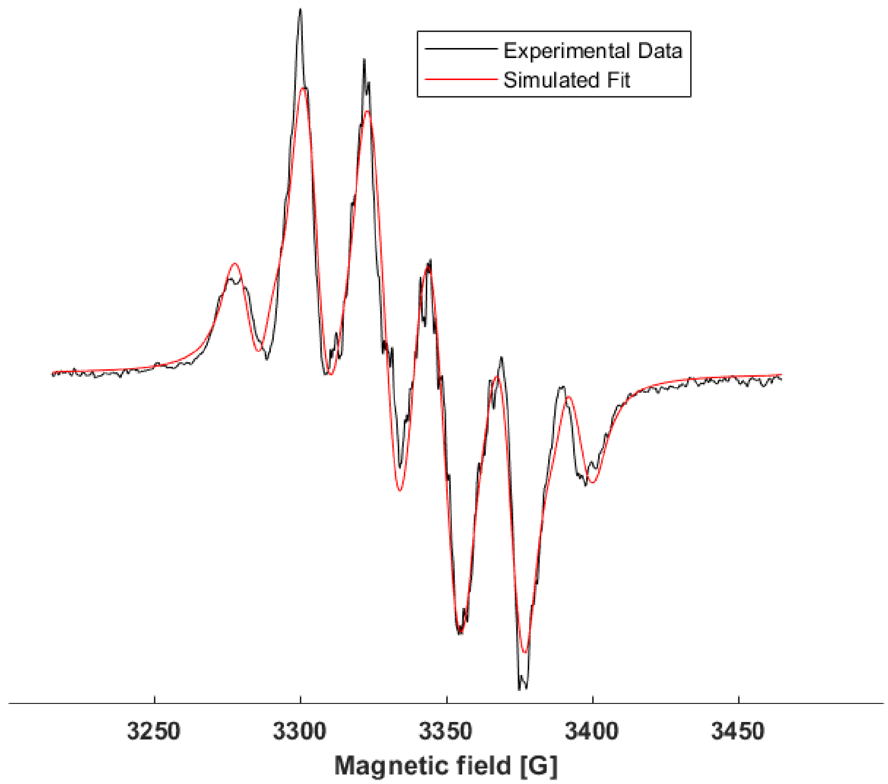

Figure 3. EPR spectra of irradiated TBP at 77 K. Fitting parameters: R2 - 58%, g = 2.002, a(1αH) = 22.6G, a(4βH) = 28.9, 22.7, 27.2, 11.1G; R3 - 20%, g = 2.0019, a(1αH) = 21.3G, a(5βH) = 24.9, 24.1, 22.5, 21.5, 4.4G.

The resulting spectra from irradiated TBP at 77 K were initially thought to be a combination of four different alkyl radicals (R1-R4, shown in Figure 4) derived from TBP during irradiation at different carbon atoms (C1-C4) in the alkyl chain. After careful spectrum processing, the simulated spectrum was fitted as a combination of R2 (58%) and R3 (20%).

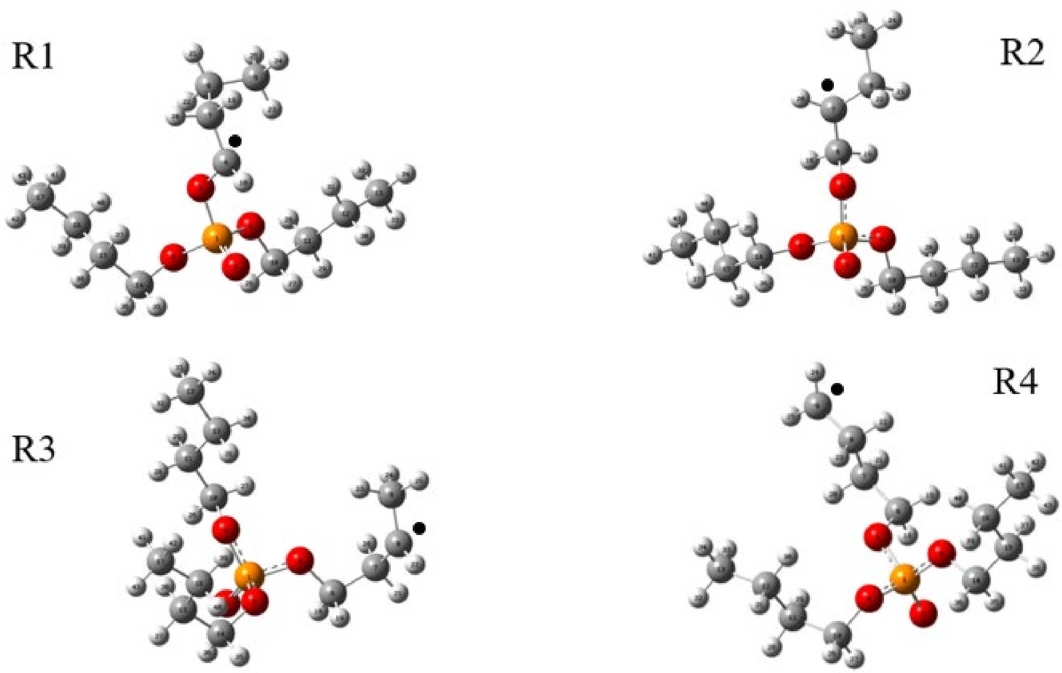

Figure 4. Structures of possible TBP-derived radicals

The last attempted experiment was to examine the radicals produced by TBP when it was mixed with *n*-dodecane at 77 K, as the PUREX process uses a TBP in kerosene solution to extract uranium and plutonium from spent nuclear fuel. Though samples were degassed and sealed under vacuum, the low-temperature EPR experiment showed an accumulation of additional *n*-dodecane radicals together with TBP radicals. Figure 5 below shows the comparison of the *n*-dodecane and TBP in *n*-dodecane spectra.

There are eight peaks total on the TBP in *n*-dodecane spectra, which is two more than that in the *n*-dodecane or TBP spectra. We also noticed that the EPR pattern and intensity change with and without the addition of TBP. We plan to continue our work on this experiment to quantitatively compare the yield of TBP radicals in solvent.

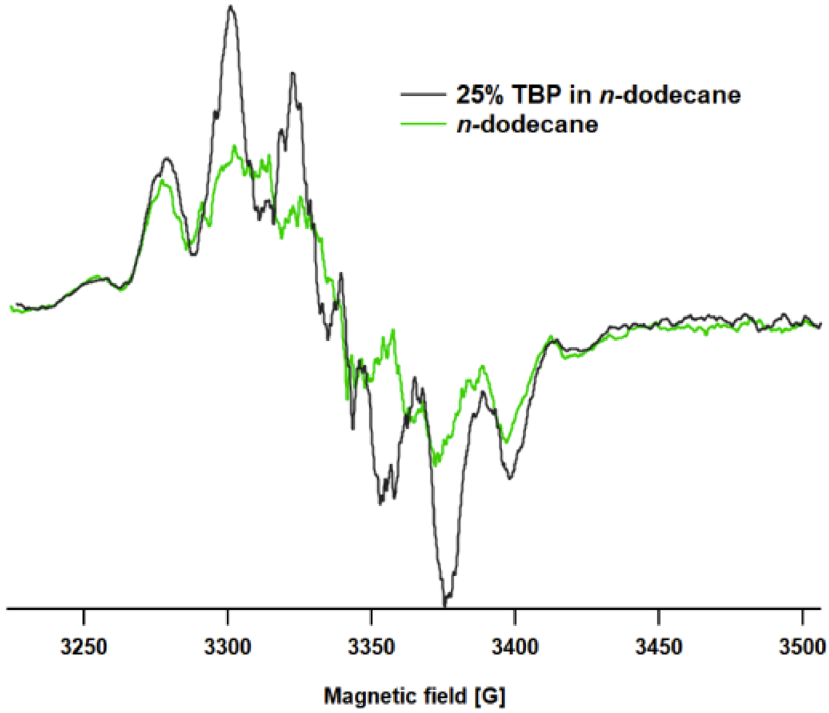

Figure 5. TBP in *n*-dodecane at 77 K

Conclusions

In this work, a systematic investigation of radicals derived from TBP was performed. The efficiency of radiation-induced radical formation at room temperature was for the first time evaluated by the PBN spin-trapping approach. The corresponding *G*-value for $TBP^{\bullet}$ is 2.18 mol/J, which is in reasonable agreement with literature data for alkanes at the same conditions.

The recorded EPR spectrum of neat TBP irradiated at 77 K displays signals from alkyl radicals in accordance with previous findings. Careful analysis of the spectrum indicates the main contribution of the carbon-centered radical with four beta-protons and one alpha-proton, formed upon H-abstraction from one of the two middle methylene groups of TBP. Thus, one can conclude that the EPR spectrum of irradiated TBP at 77 K corresponds to the conformer A of R2 TBP radical.

The results obtained are of great importance for the radiation chemistry of TBP for nuclear waste separation. These data make it possible to estimate the radiation resistance and determine the structure of radical conformers induced by irradiation with X-ray or electron beams.

References

1. Naylor, A.; Eccles, H. In Tri-n-butyl phosphate - the universal solvent for the nuclear fuel cycle, International solvent extraction conference Vol 1, USSR, USSR, 1988; pp 31-36.

2. Belevskii, V. N.; Belopushkin, S. I., Ion-molecule reactions of primary radical cations in the liquid-phase radiolysis of n-alkanes: An EPR study. *High Energy Chemistry* **2005,** *39* (1), 1-9

3. Kuruc, J.; Zubarev, V. E.; Bugaenko, L. T.; Macášek, F., ESR spectra of radicals at a low-temperature X-radiolysis of phosphates. Journal of Radioanalytical and Nuclear Chemistry 1988, 127 (1), 37-49.

4. Haase, K. D.; Schulte-Frohlinde, D.; Kouřím, P.; Vacek, K., Low-temperature radiolysis of organic phosphates studied by electron spin resonance. International Journal for Radiation Physics and Chemistry 1973, 5 (4), 351-360.

5. Huai-Yu, S.; Zhi-Zhong, W.; Yao-Huan, C.; Yong-Hai, H.; Qi-Zhong, W.; Jin-Tai, C.; Ren-Zhong, L., A study of the radiation chemistry of phosphorous compounds. International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry 1989, 33 (6), 585-597.

Characterization of tributyl phosphate radicals by electron spin resonance

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Introduction

- PUREX process – nuclear waste separation technique using tributyl phosphate (TBP) in kerosene solution to extract U and Pu from spent nuclear fuel
- TBP absorbs high doses of ionizing radiation during the separation process
- We capture TBP-derived radicals using both room-temperature spin-trapped and low-temperature electron paramagnetic resonance EPR spectroscopies

TBP at 77 K

- TBP samples were degassed using Freeze-Pump-Thaw and sealed under a vacuum in quartz tubes
- Samples were irradiated by 8 MeV electron linear accelerator at 77 K, the absorbed dose was ~180 Gy (1 Gy = J/kg)
- EPR spectra were recorded at 77 K in Dewar flask on an EMXplus Bruker spectrometer

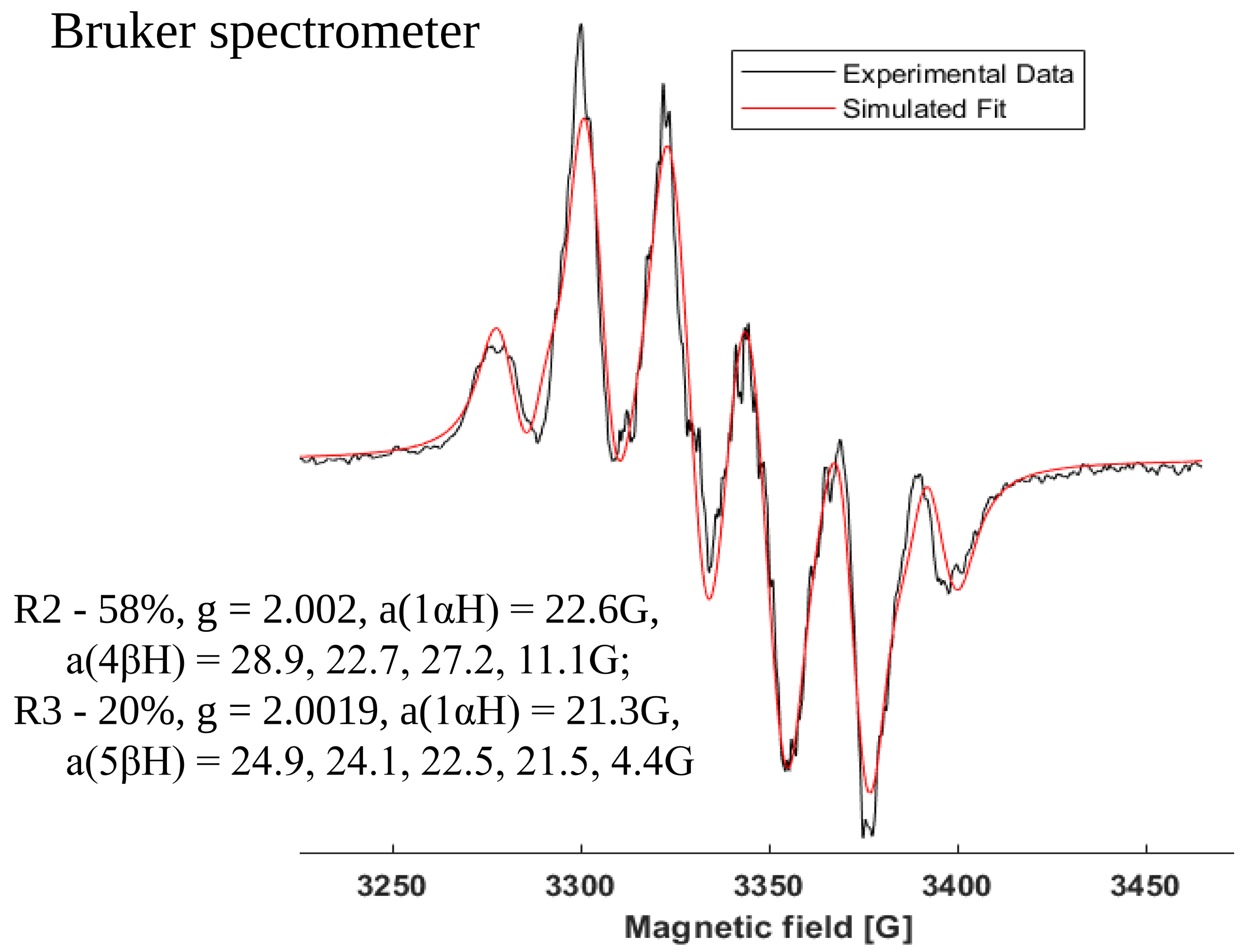

Figure 1. Experimental and simulated EPR spectra of irradiated TBP at 77 K

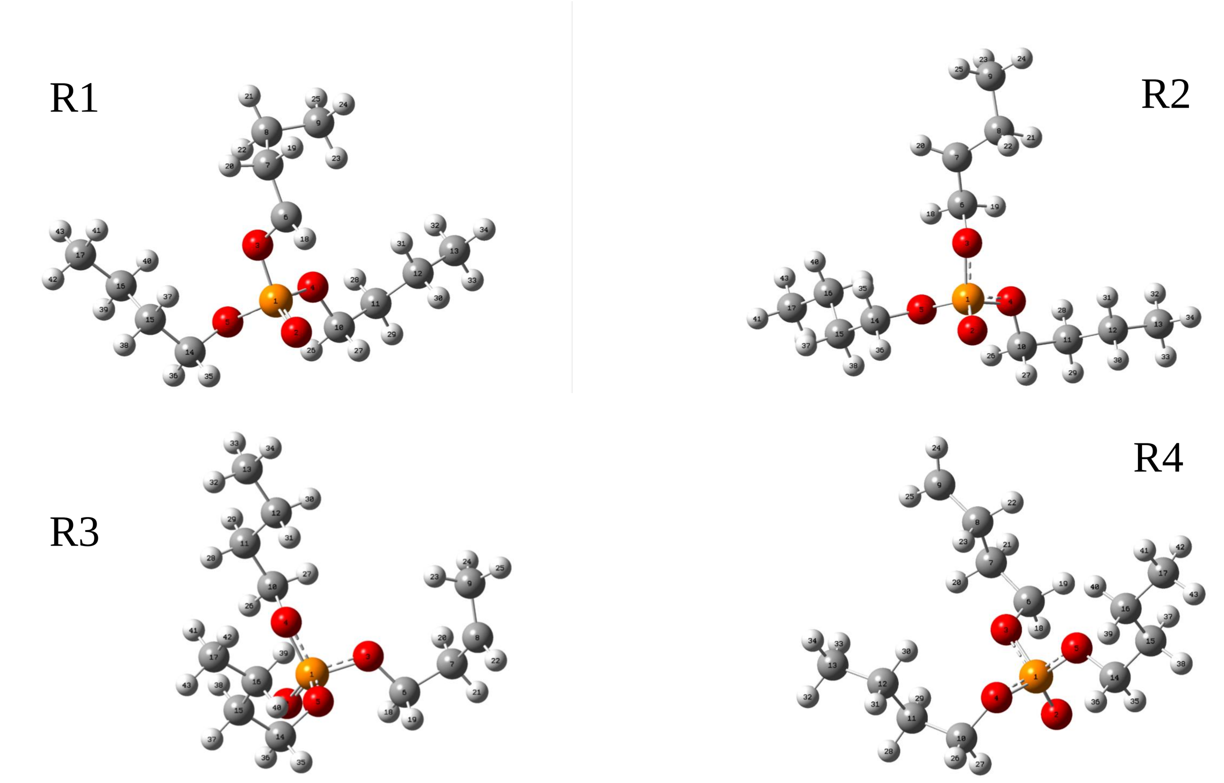

Figure 2. Structures of possible TBP-derived radicals

TBP in *n*-dodecane at 77 K

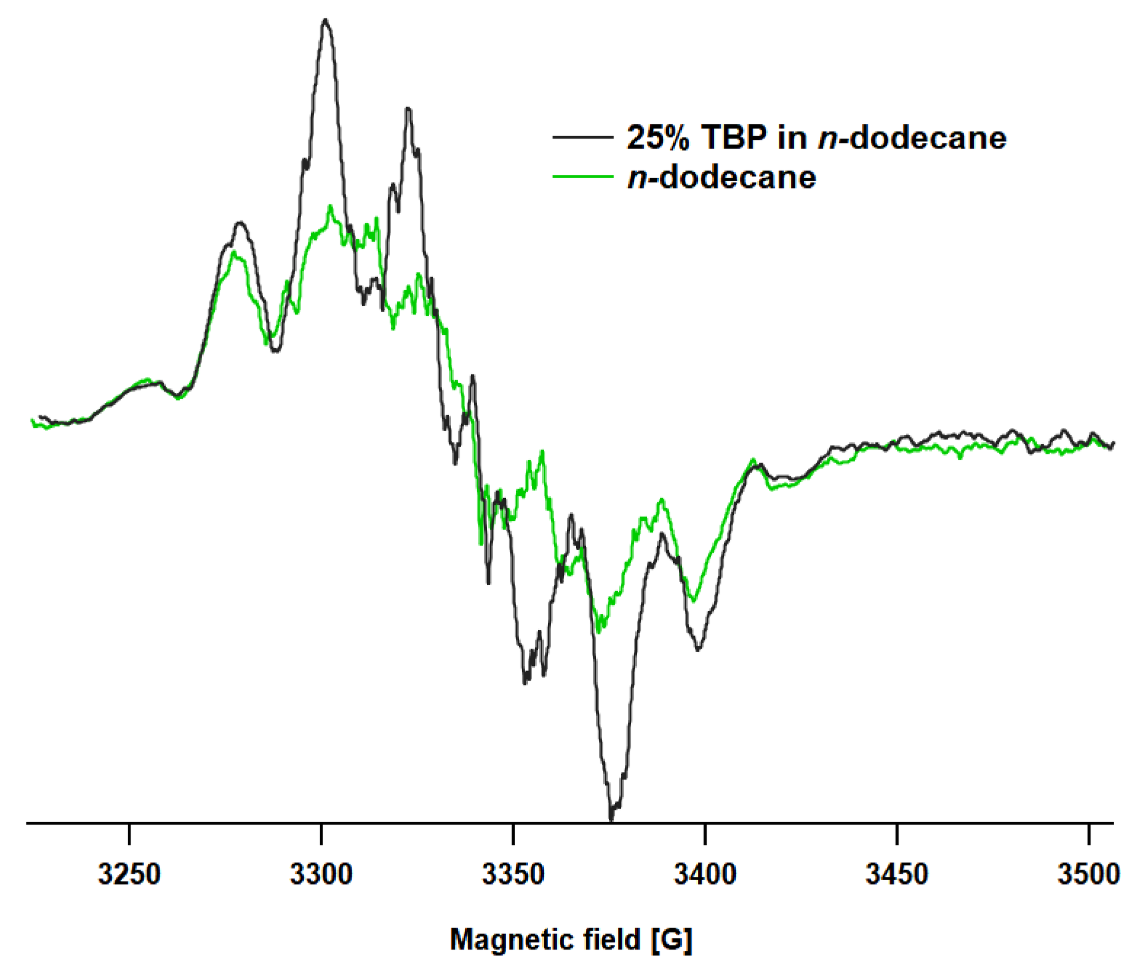

Figure 3. TBP in *n*-dodecane at 77 K

- In *n*-dodecane solution, the EPR spectra show the accumulation of additional n-dodecane radicals together with those from TBP
- EPR pattern and intensity change with and without the addition of TBP

N-tert-butyl-α-phenylnitrone (PBN) in TBP

- PBN solutions in TBP were saturated with Ar, placed in micropipettes, and sealed
- *In situ* irradiation was carried out with a Thales THX 160 X-ray tube in EPR cavity
- The dose rate measured by Fricke dosimetry using iron (II) sulfate heptahydrate in sulfuric acid yielded 211 mGy/s

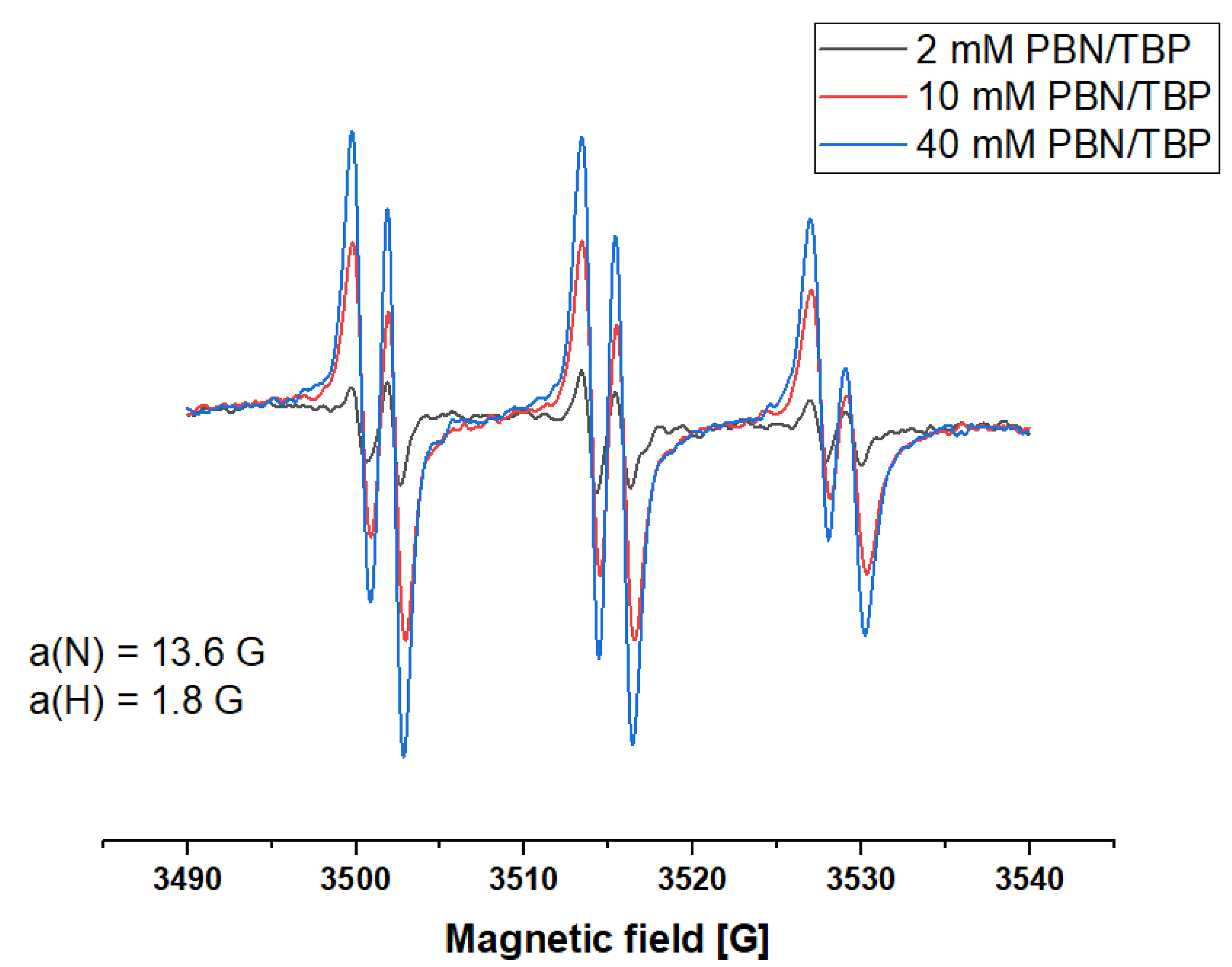

Figure 4. EPR spectra of X-rays irradiated PBN in TBP

Kinetics of PBN in TBP

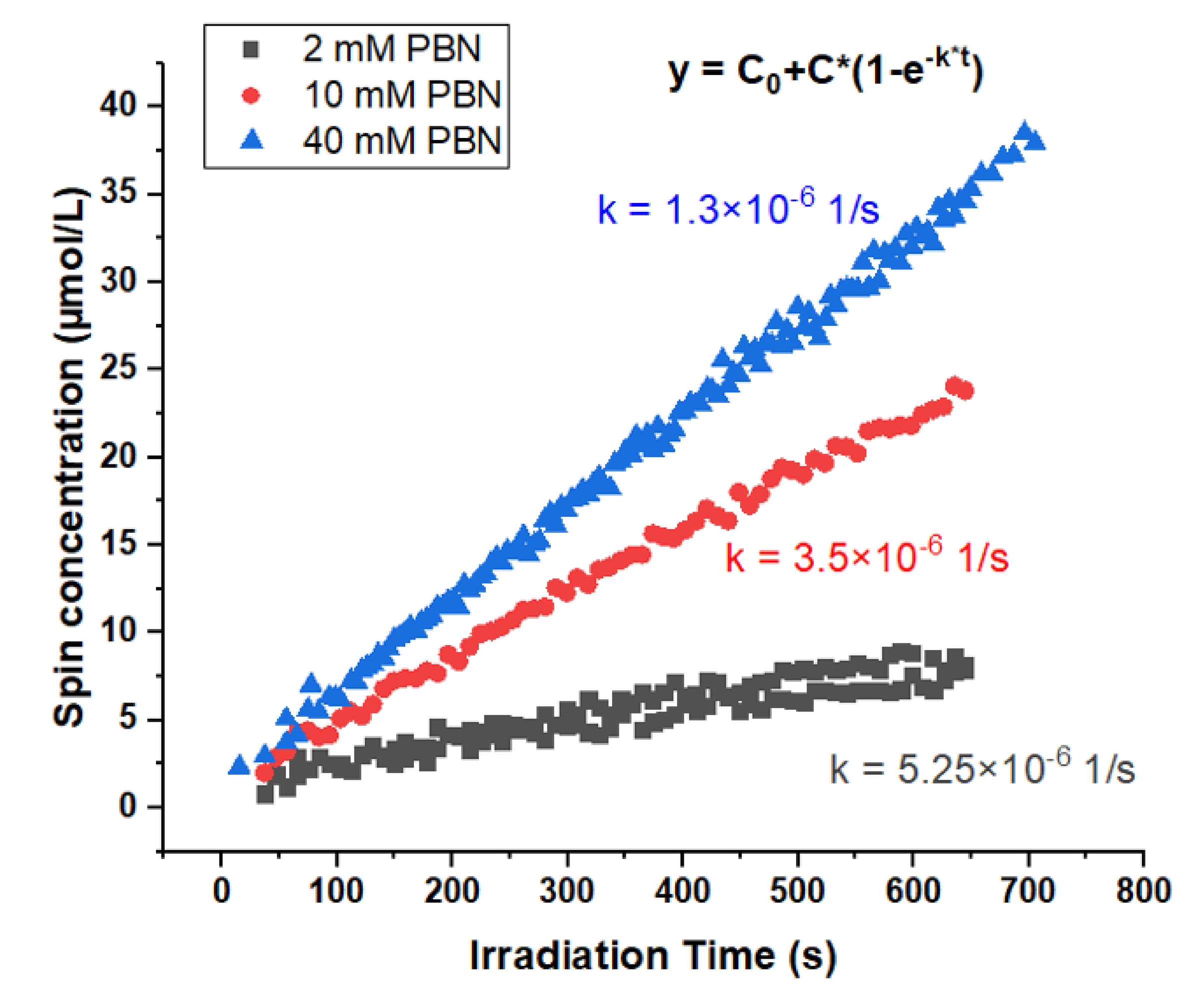

Figure 5. Formation curves of PBN-TBP adducts. Reaction rate constants from fitting 2 mM, 10 mM, 40 mM shown in the figure with color code

$$TBP \xrightarrow{\rho GI} TBP^{\bullet} \quad (1)$$

$$TBP^{\bullet} \xrightarrow{k_d} P\ (EPR\ silent) \quad (2)$$

$$TBP^{\bullet} + PBN \xrightarrow{k_t} A^{\bullet} \quad (3)$$

$$\frac{dA^{\bullet}}{dt} = \frac{k_d\,\rho GI}{k_d + k_t[PBN]}[PBN] \quad (4)$$

$$A^{\bullet} = [PBN](1 - e^{-k_{exp}\,t}) \quad (5)$$

$$b = \frac{k_{exp1} - k_{exp2}}{k_{exp2}[PBN]_2 - k_{exp1}[PBN]_1} \quad (6)$$

$$G = \frac{k_{exp2} + k_{exp2}[PBN]_2 b}{bI} \quad (7)$$

- Equations 1-3: simplest depictions of formation and decay of spin adducts
- Equations 4-5: show pseudo-first order steady-state kinetics simplification
- Equations 6-7: system of equations to express G-value

Conclusion

- ✓ EPR spectra of PBN-TBP• spin adducts are characterized by $a(^{14}N)$ = 13.6 G and $a(^{1}H)$ = 1.8 G that correspond to carbon-centered alkyl radicals
- ✓ Radiation-chemical yield for TBP radicals is 2.18 mol/J at room temperature
- ✓ Low-temperature EPR experiments confirmed the formation of R2 and R3 alkyl radicals derived from TBP after irradiation

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