

γ -Radiolysis of Trioctyl Phosphine Oxide and Its Emulsification Phenomenon

Bo Qu, Wei Zeng and Qihui Wu*

Department of Chemistry, College of Chemistry and Life Science, Quanzhou Normal University, Quanzhou 362000, China

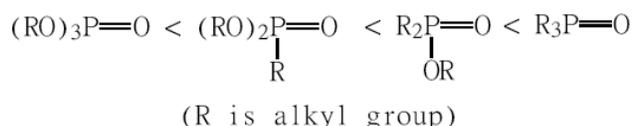
Abstract: In this article, the γ -radiolysis of trioctyl phosphine oxide (TOPO) regarded as the typical representative of trialkyl phosphine oxide (TRPO) composites has been studied. The irradiated sample solutions were extracted with 5% Na_2CO_3 aqueous solution, then washed with triply distilled water. The emulsification phenomenon was found during the washing process. The extent of emulsification was dependent on the absorbed dose and the pH value of the system. IR and UV spectroscopy as well as elemental analysis were used to determine the structures of the final products. The results indicated that the main scrubbed products were phosphinic acid, its ester and an oligomer of TOPO which induced emulsification and produced permanent damage on TOPO.

Keywords: Trioctyl phosphine oxide, γ -radiolysis, extraction, emulsification, oligomer.

1. INTRODUCTION

Trialkyl phosphine oxide (TRPO) composites are usually used as co-extractants for gold and uranium [1]. Although the chemical components of TRPO made from different sources are different, their physical properties are similar [2, 3]. In this case, there are no obvious effects on the extract processes when TRPO produced from different sources is used.

Compared with other neutral phosphorous extractants, the extracting ability of TRPO is much better, which is demonstrated as following,



It was reported [4, 5] that TRPO is effective extractant for transition metal ions, especially for actinide ions with +4 and +6 oxidation states and lanthanide ions because the electronic cloud is repelled to phosphoryl group due to the three alkyl groups and the oxygen atom which has a lone electron pair. The reaction mechanism of TRPO on the extraction of transition metals is similar with other neutral organic phosphorus extractants, i.e. tributyl phosphate (TBP). Special attentions have been paid on the research field of industrial TRPO at home and abroad, which is used to treat the high level radioactive waste (HLRW) owing to its perfect complexing ability, better radiation stability, higher load capacity, lower price, and its liquid

state at room temperature. Additionally, TRPO is miscible with kerosene that is used widely in the process of the treatment of HLRW [6].

A lot of researches [7] on the TRPO extraction system have been carried out. In addition to its extraction performance for lanthanide and actinide metal ions, its co-extraction and stripping extraction in the organic phase were studied. The design of the process of the extraction of HLRW was performed [8]. Even after several years of efforts on cold experiment, the preparation stage of hot experiment was achieved. However, compared with TBP extraction system, TRPO system still exists two shortcomings. The third phase [9] will appear if HLRW is extracted directly with 30% TRPO- kerosene due to the high concentration of salts in HLRW. There are many disputes on the origin of the third phase. Another disadvantage of TRPO is the emergence of emulsification which makes the extraction and separation much more difficult in the process of the treatment of HLRW and will cause permanent damage to the extractants. But, unfortunately, the emulsification phenomenon was ignored, and few researchers [10] paid their attention on the radiolytic stability of TRPO.

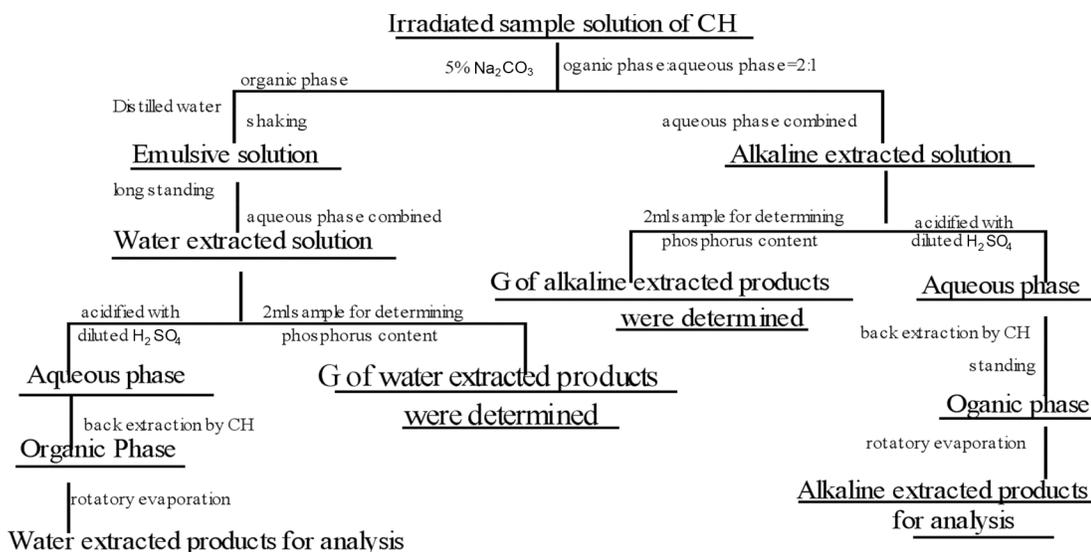
Therefore, it is necessary to further investigate the radiation chemistry of TRPO in order to be used practically. In this work, TOPO was used as the model of TRPO [12]. The γ -radiolysis and emulsification in the extraction processes were studied and the structures of final products were analyzed.

2. EXPERIMENTAL

2.1. Irradiation

All the reagents were A.R. grade. Samples were saturated with air and irradiated at 20 ± 5 °C with Co-60

*Address correspondence to this author at the Department of Chemistry, College of Chemistry and Life Science, Quanzhou Normal University, Quanzhou 362000, China; Tel: +86-595-22937909; Fax: +86-595-22919563; E-mail: qhwwu@qztc.edu.cn



γ ray irradiator. The dose rate was determined with the Fricke dosimeter.

2.2. Separation and Analysis

After irradiated, the samples were dissolved in cyclohexane (CH). The solutions were extracted with 5% Na₂CO₃ aqueous solution, subsequently followed by extraction with distilled water, according to the above flow sheet.

As the acidity of final radiolytic products is very weak, the method of titration of acid is insensitive especially in case of low dose irradiation. Therefore, phosphomolybdate method is used to determine the content of phosphorus.

3. RESULTS AND DISCUSSION

3.1. The Determination and Identification of Final Radiolytic Acid Product of TOPO.

After irradiated, TOPO (836.50 mg) was dissolved in 40 ml CH, which was extracted with 5% Na₂CO₃ solution, and the G values of acid products were determined as shown in Figure 1. In the process, clear demixion reached quickly. TOPO is insoluble in 5% Na₂CO₃ solution, but after irradiated, it produced acidic products which could be extracted by Na₂CO₃ solution.

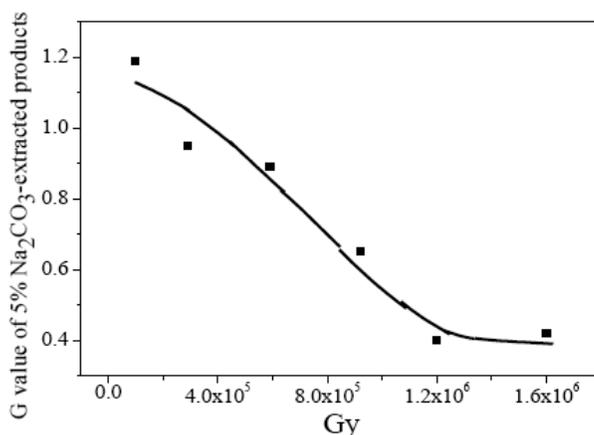


Figure 1: Dependence of G value of 5% Na₂CO₃ extracted products on the dose absorbed.

The irradiated TOPO dissolved in CH was extracted with distilled water directly and the variations of pH values of aqueous phase were list in Table 1. The values lie in 2.9~3.5. If the unirradiated sample solution of CH was washed directly with water, the pH value of the aqueous phase was about 7. It demonstrates that the products extracted with 5% Na₂CO₃ are acidic. The potentiometer titration of irradiated TOPO solution of methanol showed that they were weak acids. Their structure was identified with IR and UV spectroscopy and elemental analysis. Its IR spectra were shown in Figure 2.

Table 1: The pH and G Values of Acid Product in the Extraction with Distilled Water Directly after Irradiated (Dose=7×10⁵Gy)

Number	1st	2nd	3rd	4th	5th	6th	7th	8th
G	0.044	0.033	0.046	0.034	0.039	0.024	0.002	0.008
pH	2.91	3.06	3.17	3.22	3.28	3.34	3.41	3.44

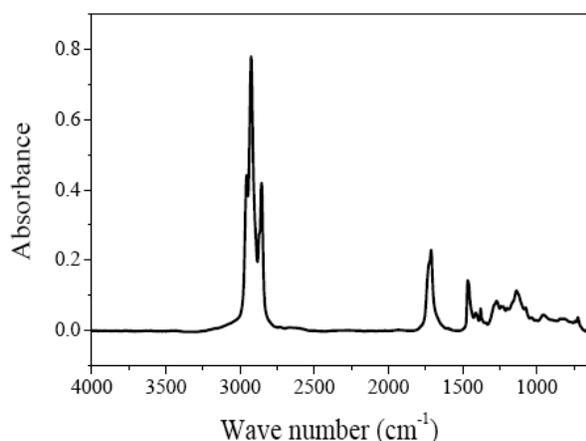


Figure 2: IR spectra of products extracted with 5% Na_2CO_3 .

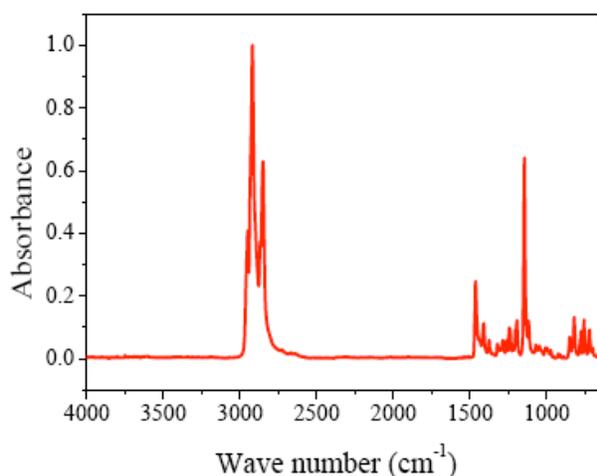


Figure 3: IR spectra of TOPO.

Compared with the spectra of pure TOPO, the peaks of $-\text{CH}_3$, $-\text{CH}_2$, and long carbon chain skeletons (Figure 3) were almost the same. However, the two spectra have following dissimilarity: there is a peak of $\text{C}=\text{O}$ at 1710 cm^{-1} in the spectra of products; the peak of 1140 cm^{-1} is absorbance of $\text{P}=\text{O}$ and peak of 966 cm^{-1} is contributed to $\text{P}-\text{OH}$, which suggests that the products have the structure unit of $\text{O}=\text{P}-\text{OH}$; Among three peaks of $\text{P}-\text{C}$, 776 cm^{-1} and 757 cm^{-1} disappear in the products spectra and the peak of 821 cm^{-1} becomes much weaker. So the PC_3 structure of TOPO was destroyed. Therefore, the products extracted with 5% Na_2CO_3 solution were mainly phosphinic acid.

Elemental analysis of carbon, hydrogen, and phosphorus was performed. The composition of the acid product extracted by alkaline solution was C 72.2%, H 12.3%, P 8.7%, and O 6.8%. So the empirical formula was calculated to be $\text{C}_{24}\text{H}_{49}\text{PO}_{1.7}$, which was close to that of phosphinic acid $\text{C}_{24}\text{H}_{51}\text{PO}_2$.

The UV spectra are shown in Figure 4. There is a strong absorbance band at 280~330 nm. The maximum absorbance of $n\rightarrow\pi^*$ of $\text{O}=\text{P}$ is at about 280~330 nm. On the other hand, the absorbance of $n\rightarrow\pi^*$ of carbonyl group is also at about 280 nm. It agrees with the results of IR spectra.

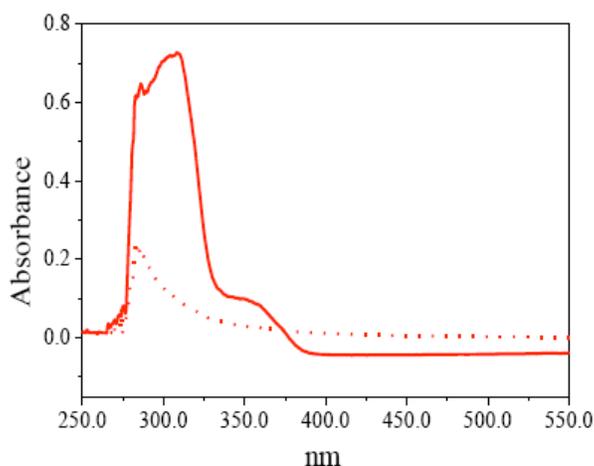


Figure 4: UV spectra of TOPO and its radiolytic acid product.

3.2. Emulsification and Structure Analysis of the Emulgent

After 5% Na_2CO_3 extraction, the organic phase was washed further with distilled water. In this process, emulsification was observed, which induces demixion slowly. When washed with 5% Na_2CO_3 solution, the concentration of sodium ions was relatively high and the sodium salts of weak acids with long carbon chains were forced into organic phase because of the salting-out effect. But in the subsequent water extraction process, a part of sodium salts diffuse into the aqueous phase and induce emulsification consequently. The pH variation of the aqueous phase of two emulsifying samples was measured and listed in Table 2. While the pH value approaches to 7, the time of demixion becomes longer.

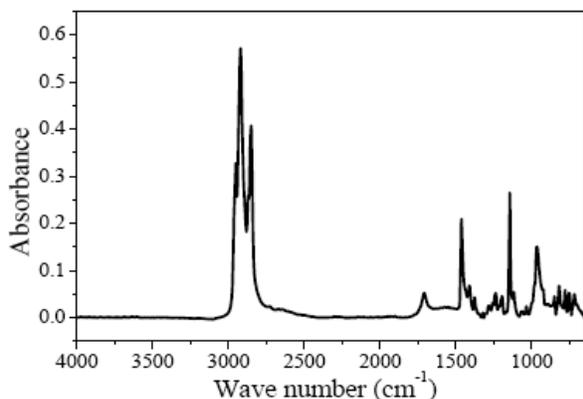
Table 2: pH Values of Aqueous Phase of Two Emulsifying Samples in Water Extraction Process (dose of Sample 1 is 1200 kGy, dose of Sample 2 is 1600kGy)

Number of Times	First 3	4 th	5 th	6 th	7 th	8 th
Sample 1	9.59	8.12	7.83	7.34	7.48	7.16
Sample 2	9.70	8.18	7.97	7.26	7.46	7.28

Table 3: G Values of Acidic Products and the Dependence of Emulsification Extent on dose Absorbed

Dose (kGy)	97.9	290	590	920	1200	1600
G of 5% Na ₂ CO ₃ extracted products	1.19	0.95	0.89	0.65	0.38	0.42
G of water extracted products	1.42	1.58	0.95	1.1	1.2	1.3
Emulsification after 6 times water extraction	Disappeared		Weakened		Violent	

The dependence of emulsification on the absorbed dose was also studied. Results are list in Table 3. The G values of products extracted with 5% Na₂CO₃ solution increase apparently with the decreasing of absorbed dose, while the G values of products extracted with distilled water changed irregularly. However the total G values decrease with the dose increasing. The G values of emulsifying compounds vary from 0.9 to 1.6, but that of emulsifying agent from TBP radiolysis in Wei's work [13] was only 0.1. It demonstrates that emulsification extent of TOPO radiolysis products is much higher than that of TBP, which coincides with its longer carbon chains in TOPO and the formation of weak phosphinic acid. In addition, the type of emulsification was studied with dilution method, which suggests as oil-in-water type. Further research demonstrates that emulsification does not happen when pH is higher than 12 and the optimum pH to destroy emulsification was about 10~11.

**Figure 5:** IR spectra of product extracted with water.

IR spectrum of the obtained emulsifying agent is shown in Figure 5. Its absorbances of -CH₃, -CH₂, the long carbon chain skeleton and carbonyl group are the same as those of products extracted with alkaline solution. The peaks at 1140 cm⁻¹ and 966 cm⁻¹ suggest that the emulsifying agent also has O=P-OH structure unit, but the peak at 966 cm⁻¹ is much more stronger than that of products extracted with 5% Na₂CO₃ solution, which demonstrates that it probably has P-O-C structure unit. The peaks of P-C at 821 cm⁻¹, 776 cm⁻¹, and 757 cm⁻¹ are the same as those of TOPO, which

reveals that its PC₃ structure unit still exists. Therefore the product consisted of three structure units: TOPO, Phosphinic acid, and its ester. It agrees well with the results of Wei's work [13] that the emulsifying agent from TBP radiolysis was detected to be 2TBP·DBP.

Results of elemental analysis of product extracted with water are C 70.4%, H 12.6%, P 6.0% and O 11.4%. Its empirical formula is calculated to be C₃₀H₆₅PO_{3.68}. Its UV spectra are similar to the products extracted with alkaline solution. Their complicated structures will be studied further

4. CONCLUSION

After irradiation, TOPO produced phosphinic acid and an acidic emulsifying agent containing phosphorus, which was analyzed to be an oligomer of TOPO, phosphinic acid, and its ester. The emulsification extent was dependent on the dose absorbed and the pH values of the system. It increased with the dose absorbed, while the total G values decreased with the increasing of the dose. At the same time, the G values of emulsifying agent were more than 1, which was much higher than the 0.1 of TBP.

REFERENCES

- [1] Zhou L, Li M. Extraction of Au (I) from Alkaline Cyanide Solution by TRPO-TBP Mixed System. Mining and Metallurgical Engineering 2010; 30 (3): 86-92.
- [2] Duan W, Cao P, Zhu Y. Extraction of rare earth elements from their oxides using organophosphorus reagent complexes with HNO₃ and H₂O in supercritical CO₂. J Rare Earth 2010; 28 (2): 221-226. [http://dx.doi.org/10.1016/S1002-0721\(09\)60084-3](http://dx.doi.org/10.1016/S1002-0721(09)60084-3)
- [3] Xin R. Study on Composition and Properties of Mixed Trialkyl Phosphine Oxide. Chin J Spectro Lab 2001; 18 (5): 685-688.
- [4] Ma J. Preparation and Characterization of ZrO₂ Nanoparticles Capped by Trioctyl-phosphine Oxide (TOPO). J Wuhan Univ Technol-Mater Sci Ed 2011; 26(4): 611-614. <http://dx.doi.org/10.1007/s11595-011-0277-2>
- [5] Duan W, Zhu L, Jing S, Zhu Y. Properties of TRPO-HNO₃ complex used for direct dissolution of lanthanide and actinide oxides in supercritical fluid CO₂. Sci China Ser B-Chem 2007; 50 (6): 759-763. <http://dx.doi.org/10.1007/s11426-007-0081-1>
- [6] Wang J, Zhang L. Determination of Ru, Rh and Pd in 30% Trialkyl Phosphine Oxide (TRPO)-Kerosene by Inductively Coupled Plasma- Atomic Emission Spectrum (ICP-AES). Chin J Spectro Lab 2013; 33 (7): 1957-1960.

- [7] Li Y, Wang Y, Dai Y. Effect of Diluents on the Extraction of Oxalic Acid by Trialkyl Phosphine Oxide. *Chin J Chem Eng* 2004; 12 (1): 143-148.
- [8] Liu X, Xiao X, Liang J, Xu J. Technology on Re-extraction of U, Np and Pu by Hydrazine Carbonate in TRPO Process. *Atomic Energy Sci Technol* 2005; 39 (5): 399-403.
- [9] Chen J, Li C, Liu X, Jiao R. Extraction Behavior of Actinides, Eu, Tc, Zr and Fe by TRPO. *J Nuclear Radiochem* 2002; 24 (4): 218-222.
- [10] Xin R, Liang J, Song C, Jiao J. FT-IR Spectra Study of Gamma Irradiated Trialkyl Phosphine Oxide. *Chin J Spectro Lab* 2000; 17 (6): 625-630.
- [11] Zhang P, Liang J, Xin R, Song C. Radiostability of extractants Containing Phosphorus Used in Nuclear Recycling. *Nuclear Techniques* 2003; 26 (12): 940-945.
- [12] Yang T, Shui C, Bin W. The Synergistic Mechanism of Solvent Extraction of Gold in HCl Media with Toa and TOPO. *J Cent South Univ Technol* 1999; 6 (1): 28-31. <http://dx.doi.org/10.1007/s11771-999-0026-2>
- [13] Wei G, Wu J. Investigation on the formation of trimer of dibutyl acid phosphate and tributyl phosphate in ⁶⁰Co-irradiated TBP system. *J Nuclear Radiochem* 1984; 6 (3): 161-167.

Received on 09-11-2014

Accepted on 29-11-2014

Published on 23-12-2014

[DOI: http://dx.doi.org/10.15377/2410-4701.2014.01.01.1](http://dx.doi.org/10.15377/2410-4701.2014.01.01.1)© 2014 Qu *et al.*; Avanti Publishers.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.