

《Original》

The Solvent Extraction of Uranium(VI) and Other Metal Ions with Pyrazolone Chelating Agents

—The Studies on the Rad-Waste Treatment(1)—

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(Received March 22, 1983)

킬레이팅 화합물에 의한 우라늄의 용매추출

—방사성 폐기물 처리 처분 연구(I)—

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(1983. 3. 22 접수)

Abstract

The chelating agent with β -diketo functional group, 1-phenyl-3-methyl-4-acyl-pyrazolone-5-one, has been used in separating and extracting radionuclides in a waste solution. The derivatives of this pyrazolone compound, prepared by different acyl groups, were synthesized and examined to figure out the extracting ability for Uranium (VI) and Zirconium (IV). The product prepared with succinic anhydride, called succinyl pyrazolone, showed excellent extraction for uranium (VI) in a chloroform solvent system. This result indicates that acyl pyrazolones having carboxylic acid group as a functional group forming β -diketo functionality are very selective for uranium (VI) and generally other metal ions with high valency.

요 약

β -diketo의 관능기를 가진 1-phenyl-3-methyl-4-acyl-pyrazolone-5-one (acyl pyrazolone)이라고 이름지어진 킬레이팅 화합물은 오랫동안 동위원소 분리 및 추출에 이용되어 왔다. 새로운 acylating 물질을 사용해서 만들어진 succinyl, malenyl 그리고 phthalyl pyrazolone이 우라늄(VI)과 고가의 산화상태를 지니는 다른 중금속의 추출에 이용되었다. succinyl pyrazolone이 우라늄(VI) 추출에서 매우 뛰어나다는 것이 밝혀졌으며, 대체로 카르복실 관능기를 가진 킬레이팅 화합물이 우라늄(VI) 혹은 악티나이드 계열의 중금속 추출에 매우 효과적인 것으로 나타났다.

Introduction

A tremendous amount of liquid radioactive

waste containing rare-earth metal ions is being produced as the number of nuclear facilities increases. The elimination of rare-earth metal ions from waste solution has been regarded

to be important in the recovery of the useful metals and keeping pollutants out of the environment. Among numerous methods for this treatment, solvent extraction with chelating reagents has shown to be an effective method. One of the advantages using chelating reagents is their good selectivity for specific metals. This selectivity is very useful for the concentration and separation of metal ions of interest from bulk solutions.

Many chelating functional groups have been studied and used for the extraction of metal ions. The β -diketo group has been known as one of the most effective for the chelation of uranium (VI) and other polyvalent metals. Numerous molecules having β -diketo groups have been applied for the extraction of uranium (VI). Thenoyltrifluoroacetone (TTA) has been one of the most popular extractants for polyvalent metals, especially for uranium (VI). Acetylacetone and benzoylacetone have also been used as extractants for uranium (VI) for a long time. Many extractants having β -diketo groups were reviewed by Grindler⁽¹⁾.

One of the most interesting but not well-explored chelating reagents is 1-phenyl-3-methyl-4-acyl-pyrazolone-5 (acyl pyrazolone) and its derivatives. It was synthesized from 1-phenyl-3-methyl-pyrazolone-5 (pyrazolone) by Skitte Jensen in 1959⁽²⁾. Eleven different acyl pyrazolones were synthesized and tested for the extraction of uranium (VI), lanthanum (III), and zinc (II)⁽²⁾. To evaluate the extractive behavior of these acyl pyrazolones, the pH values for 50% extraction (pH_{50}) of metal ions by these reagents were compared⁽³⁾.

In terms of the pH_{50} values, acetyl pyrazolone is the best reagent for uranium (VI). The pH_{50} values of acetyl pyrazolone and TTA are -0.15 and 0.7, respectively, for uranium (VI). The other acyl pyrazolones also showed better extraction at relatively low pH, compared with

TTA. Capronyl pyrazolone was found to be an excellent extractant for thorium (IV), but TTA is better than capronyl pyrazolone in terms of the pH_{50} value. These acyl pyrazolones were found to be stable and selective chelating reagents, even in strongly acidic solutions⁽⁴⁾.

Zolotov and Mizra also indicated that acyl pyrazolones can extract metal ions from more acidic solutions than other chelating reagents^(5, 6). Zolotov showed that benzoyl pyrazolone extracts plutonium (IV) quantitatively even in 7 M-nitric acid⁽⁷⁾.

The advantage of the extraction in more acidic solutions is that competing hydrolytic reactions can be eliminated. This permits the chelating agents to compete effectively with other complex-forming reactions in the aqueous phase⁽⁸⁾.

Another great advantage of acyl pyrazolones is that different acyl groups can be introduced into the reagent through the proper choice of starting materials. Furthermore, these acyl pyrazolones are a useful class of compounds for studying the effects of physical and chemical properties on extraction and chelating behavior⁽⁸⁾. Both the size and functionality of the acyl group influence this behavior. Qualitatively, it appears that larger acyl groups can shield the coordinated ions. In the separation of thorium (IV) from uranium (VI), the separation factor was shown to decrease as the molecular size of the acyl groups became larger⁽⁸⁾. Although acyl pyrazolones were demonstrated to be excellent chelating reagents, only few derivatives have been used for extraction and separation.

All conventional acyl pyrazolones have simple aliphatic or aromatic groups as an acyl group. If new acyl groups, which contain carboxylic acids, can be introduced into the pyrazolones, the extractive behavior of the reagents may be influenced. The cooperative interaction of the

β -diketo group and the carboxylic acid group with metals should improve complexation.

The purpose of this report is to synthesize such new acyl pyrazolones and to compare their extractive behavior on uranium (IV) with conventional acyl pyrazolones.

Experimental

New acyl pyrazolones, 1-phenyl-3-methyl-4-acyl-pyrazolone-5-one, were prepared using the starting materials, 1-phenyl-3-methyl-pyrazolone-5-one and various cyclic anhydrides. The products derived were identified through elemental analysis, NMR, and the determination of molecular weight. These chelating agents were used in extracting various metal ions in various solvent systems. The concentration of metal ions used was in the range of $10^{-2}M$ to $10^{-4}M$.

Result and Discussion

The new acyl pyrazolones synthesized were named as succinyl, malenyl, and phthalyl pyrazolone according to the names of acyl groups substituted at 4-position in the pyrazolone ring. Forming β -diketo functionality, these new acyl pyrazolones have a carboxylic acid group in the acyl substituents. These carboxylic acid group were not found in the conventional acyl pyrazolones, shown in Table 2. These compounds were purified enough to get the best extraction for uranium (VI) and identified as compounds wanted through various analytical methods, including NMR spectrum, elemental analysis, and the determination of molecular weight with titration.

Table 1 shows the results of the extraction of uranium (VI) with these new acyl pyrazolones and conventional acyl pyrazolones. When chloroform was used as a solvent for the reagents, succinyl pyrazolone showed 99% ex-

Table 1. Extraction of Uranium(VI)^a by Acyl Pyrazolones in Chloroform^b and a Mixed Solvent^b

	Chloroform (%)	Mixed solvent (%)
Succinyl	99	50
Malenyl	81	55
Acetyl	88	66
Benzoyl	60	76
Phthalyl	75	70

^a The concentration of uranium (VI) was $10^{-4}M$ in 1M nitric acid.

^b The concentration of reagents was $5 \times 10^{-2}M$ in solvents.

traction and was regarded as the best extractant for uranium (VI). Acetyl pyrazolone showed 88% extraction, which was second to succinyl pyrazolone. Malenyl and phthalyl pyrazolones showed 81% and 75% extraction, respectively. Benzoyl pyrazolone showed the lowest extraction which was 60%. When a mixed solvent, 1 : 1 v/v iso-amyl alcohol and chloroform, was used as the solvent, the results of extraction were opposite to those obtained in pure chloroform. Succinyl and malenyl pyrazolones showed 50 and 55% extraction, respectively. Acetyl pyrazolone 66% extraction. Benzoyl and phthalyl pyrazolones showed 76 and 70% extraction, respectively.

Benzoyl pyrazolone appeared to be the most effective extractant. Phthalyl pyrazolone, among the new acyl pyrazolones, showed the best result in the mixed solvent and is comparable to benzoyl pyrazolone. The concentration of uranium (VI) used in this experiment was $10^{-4}M$ and the concentration of reagents was $5 \times 10^{-2}M$ in each solvent.

Figures 1 and 2 show the extraction curves of these reagents for uranium (VI) in chloroform and the mixed solvent, respectively. From Figure 1, the pH values for the half extraction of uranium (VI) (pH_{50}) using succinyl, acetyl, and benzoyl pyrazolones were -0.4, -0.2

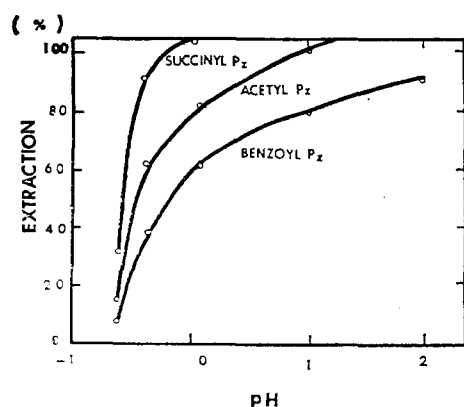


Fig 1. The Extraction of Uranium (VI) Whose Concentration is 10^{-4} M from Nitric Acid by Various Acyl Pyrazolones in Chloroform as a Solvent

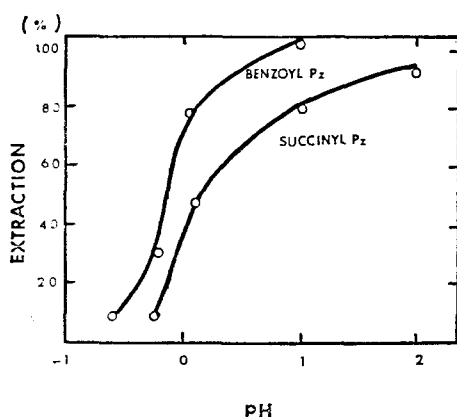


Fig 2. The Extraction of Uranium (VI) of 10^{-4} M from Nitric Acid by Succinyl Pyrazolone in a Mixed Solvent, 1:1 v/v Iso-amyl Alcohol and Chloroform

and 0.0, respectively. The pH_{50} value for each reagent indicates the extraction ability of the reagent in acidic solutions. The lower the value of pH_{50} , the more acid the reagent can tolerate. The pH_{50} values for the various acyl pyrazolones were provided by Jensen and are shown in Table 2. According to Table 2, acetyl pyrazolone whose value of pH_{50} is -0.15 was regarded as the best extractant for uranium (VI) in concentrated acid. The small difference in the pH_{50} values obtained from Figure 1 and Table 2 for acetyl pyrazolone is not significant,

Table 2. The Values of pH_{50} for Conventional Acyl Pyrazolones in the Extraction of Uranium(VI)

Acyl pyrazolones	pH_{50}
Acetyl	-0.15
Propionyl	0.05
Butyryl	0.52
Valleryl	0.24
Capronyl	0.7
Ethoxycarbonyl	1.00
Chloroacetyl	0.65
Trifluoroacetyl	0.8
Benzoyl	1.0
p-Bromobenzoyl	0.9
p-Nitrobenzoyl	—
TTA	0.70

considering experimental error.

The pH_{50} value for benzoyl pyrazolone is 1.0 from Table 2, while a value of 0.0 for pH_{50} is taken from Figure 1. Generally, the results in Figure 1 show higher extraction in concentrated acid in terms of the values of pH_{50} , compared with Jensen's results shown in Table 2. The extraction ability of all three was reduced extensively in a more concentrated acid solution. However, Zolotov reported that the extraction of plutonium (IV) by benzoyl pyrazolone was 100% even in 7M nitric acid⁽⁷⁾.

The most interesting observation from this information is that the extractive behavior of succinyl and malenyl pyrazolones was changed significantly by changing the solvents. The other reagents did not show such changes in their extraction behavior.

When studying the solvent extraction of metal complexes, the formula of the extracted complex can often be obtained from the dependence of the distribution ratio (D) on reagent concentration (C) and acidity. A plot of the $\log D$ vs. $\log C$ at constant pH gives a straight line whose slope is equal to the number of reagent molecules required for complexation.

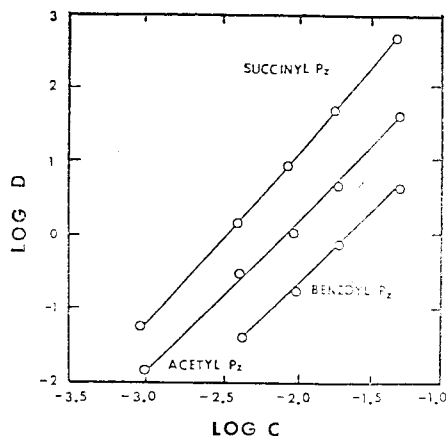


Fig 3. The Extraction of Uranium (VI) of $10^{-4}M$ in Nitric Acid by Various Pyrazolones in Chloroform

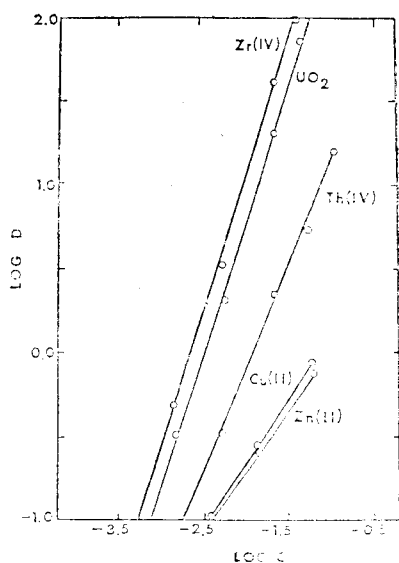


Fig 4. The Extraction of Zirconium (IV), Uranium (VI), thorium (IV) and Zinc (II) by Succinyl Pyrazolone in Chloroform

Similarly, a plot of $\log D$ vs. pH at constant reagent concentration gives a straight line whose slope is equal to the number of protons involved in the reaction. According to this theory, two molecules of succinyl pyrazolone are involved in the complexation of metal ions.

Figure 3 shows the plot of $\log D$ vs. $\log C$ for succinyl, acetyl, and benzoyl pyrazolones. Succinyl, acetyl, and benzoyl pyrazolones show

straight lines whose slopes are 2.2, 2.1, and 1.98, respectively. Figure 3 shows the superiority of succinyl pyrazolone as an extractant. From the slopes, it can be seen that two molecules of succinyl pyrazolone are involved in the complexation.

Figure 4 shows the plots of $\log D$ vs. $\log C$ for zirconium (IV), uranium (VI), thorium (IV), zinc (II), and copper (II) with succinyl pyrazolone as the extractant. Zirconium (IV) appears to be extracted to the same extent as UO_2^{2+} by succinyl pyrazolone. The extraction of thorium (IV) appears to be less than uranium (VI). The extraction of zinc (II) and copper (II) shows much lower extraction compared to the actinides. All the ions showed straight lines. The slopes of the two actinides and zirconium are parallel. The slopes of Zr (IV), Th (IV), and UO_2^{2+} (VI) are 2.2. The slopes of zinc (II) and copper (II) are 1.6 and 1.5, respectively. The slopes changed only slightly from metal to metal.

Summarizing the data, succinyl pyrazolone appears to be the best extractant for uranium (VI) when chloroform is used as a solvent. However, it was found to be a poor extractant in the mixed solvent. These results suggest that special factors, including a solvent effect, may be involved in the complexation by the new acyl pyrazolones, especially for the succinyl derivative. The fact that the slopes did not change very much from metal to metal also suggests that a different mechanism may be involved in the extraction of metal ions by succinyl pyrazolone when compared to pyrazolones without carboxylic acid groups in the acyl moiety.

It has been suggested that carboxylic acid group participation is a favorable process for acyl pyrazolones. While the results obtained with succinyl and malenyl pyrazolones can be reasonably explained, the results with phthalyl

pyrazolone are difficult to interpret. In Table 1, phthalyl pyrazolone showed not only less extraction, but also negligible change in extraction ability in both solvents, compared with other new acyl pyrazolones whose extraction abilities were solvent dependent. It is not known whether carboxylic acid group participation occurs in the complexation of phthalyl pyrazolone with metal ions. Unfortunately, the lack of intensive study of phthalyl pyrazolone limits further discussion of this point.

However besides these experimental results, the stability against radiation should be confirmed for the effective application of succinyl, malenyl pyrazolone to the radioactive waste treatment. Another thing to be done relating this acyl pyrazolone, the preparation of water soluble chelating agents should be tried for the better extraction and for the development of agents to be used in the decontamination.

Conclusion

1-Phenyl-3-methyl-4-acyl-pyrazolone-5 derivatives having carboxylic acid groups in the acyl moiety were synthesized from 1-phenyl-3-methyl-pyrazolone-5 and cyclic anhydrides and were identified using various methods. Among numerous acyl derivatives prepared, succinyl pyrazolone appeared to be the most effective extractant, especially, for uranium (VI) in chloroform as a solvent. Carboxylate participation in the complex was invoked and qualita-

tively discussed to help interpret the results of extraction using succinyl pyrazolone. These results indicate that the introduction of various functional groups in the acyl moiety may be useful in manipulating the molecule for the solvent extraction of various metal ions with high valency, contained in liquid radioactive waste.

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