

4-Acyl-5-Pyrazolones as an Analytical Reagent (II). Applicability of Halogen Substituted 4-Acyl-5-Pyrazolones to the Solvent Extraction of Metals

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Several 4-halogenated acyl derivatives of 1-aryl-3-methyl-5-pyrazolone were synthesized from 1-aryl-3-methyl-5-pyrazolone and the chlorinated acetyl chloride or perfluoroacyl anhydride, and their effectiveness as the solvent extracting agent of metals was evaluated. The replacement of halogen atom into the 4-acetyl group strengthened the acidity of the pyrazolones remarkably. A linear relationship was established between the dissociation constant of 1-aryl derivatives and Hammett σ constant. The derivatives had the extremely large extraction constant for the europium chelates, and for example, the pH value at half extraction by 0.02 M of 1-tolyl-3-methyl-4-trifluoroacetyl-5-pyrazolone went down to 1.1 when *n*-octanol was used as the extracting solvent.

KEY WORDS: 4-Acyl-5-pyrazolones/ Europium/ Solvent extraction/

INTRODUCTION

Fluoro-substituted β -diketone such as 2-thenoyltrifluoroacetone is one of the most proved extracting agents in solvent extraction analysis.¹⁾ One of the reasons for its widespread analytical applicability is that due to the electron-attracting effect of the trifluoromethyl group. The acidity of the enolate form is much more pronounced than those of related reagents containing no fluorine atoms, and this is the reason why metal ions can be extracted with the trifluoromethyl substituted β -diketones from more acidic solutions. On the other hand, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and its derivatives which are structurally similar to β -diketones (Fig. 1), was also proved to be a very versatile reagent for the solvent extraction of metals, because it extracted most of the metal ions at a lower pH region than β -diketones.¹⁻¹⁰⁾ In a

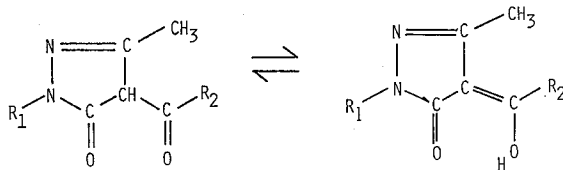


Fig. 1. 1-Aryl-3-methyl-4-acyl-5-pyrazolone.

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previous paper, we have synthesized eleven 1-aryl-3-methyl-4-aryl-5-pyrazolone derivatives and examined their applicability to solvent extraction of metal ions.¹⁷⁾ The present study intends to evaluate the applicability of halogen-substituted 4-acyl-5-pyrazolone derivatives as the solvent extracting agent of metals.

EXPERIMENTAL

Reagents

Several 4-halogenated acyl derivatives of 1-aryl-3-methyl-5-pyrazolone were prepared according to the method of Jensen¹⁸⁾ from 1-aryl-3-methyl-5-pyrazolone and the chlorinated acetyl chloride or perfluoroacyl anhydride. The crude compounds were recrystallized twice from dioxane-water or ethanol-water. The partial elemental analysis and melting point of the obtained compounds are reported in Table I.

Chloroform was purified by washing it with a dilute sodium hydroxide solution, water, diluted hydrochloric acid, and three portions of water, followed by distillation. Reagent-grade benzene was used without further purification. The radioisotopes of europium 152 and 154 were supplied from New England Nuclear, Boston, Mass., U.S.A.

The other chemicals were chemically pure or reagent grade materials.

Procedure

All extractions were carried out in 30 ml centrifuge tubes with the aid of a mechanical shaking device in a room at 25°C. Equal volumes (usually 10 ml) of aqueous and organic phases were equilibrated, and extraction times of 30 min were used in the present work. The aqueous phase contained europium carrier with an appropriate amount of radioisotope, sodium perchlorate (0.1 M), and acetic acid-sodium acetate (0.02 M) as the buffer solution. The organic phase contained 0.05 or 0.02 M of 5-pyrazolone derivatives in chloroform or benzene. After the solutions were centrifuged, the pH of the aqueous phase was measured. For the pH measurement a Hitachi-Horiba pH meter, Model F-7ss was used. Two milliliters of each of the two phases

Table I. Analytical Data

R ₁	R ₂	elemental analysis			mp. (°C)	
		calc. found	C	H		N
phenyl	cyclohexyl	71.81		7.09	9.58	75-76
		71.62		7.15	9.66	
ph	CF ₃	53.34		3.33	10.36	123
		53.55		3.30	10.56	
4-CH ₃ ph	CHCl ₂	52.19		4.04	9.36	215-7
		52.02		4.14	9.07	
4-CH ₃ ph	CCl ₃	46.81		3.32	8.40	130
		48.13		3.35	8.53	
CH ₃ ph	CH ₃	66.65		5.59	12.95	105
		65.65		5.99	12.33	
4-NO ₂ ph	CF ₃	43.58		2.66	13.85	138
		42.94		2.74	13.68	
4-CH ₃ ph	CF ₃	54.93		3.90	9.85	86
		55.31		3.82	9.63	

were pipetted into a vial. Radioactivity countings were made with a Metro Electronics NaI (Tl) (44.5 mm in dia. $\times$ 50.8 mm) well-type scintillation counter, Model PbW-6, connected with a Metro automatic scaler, Model SS-1061H.

Spectrophotometric measurements for evaluating the acid dissociation constant of 5-pyrazolone derivatives were carried out with a Model 323 Hitachi recording spectrophotometer with 1.0 cm cells and with a Model 139 Hitachi spectrophotometer with 1.0 cm cells.

RESULTS AND DISCUSSION

Acid Dissociation Constant

Since halo-substituted 4-acyl-5-pyrazolone derivatives were not very soluble in water, mixed solvent system of 10% dioxane-water was employed for the measurement of the acid dissociation constant, pK_a . The dissociation constant of these compounds were obtained by the same spectrophotometric method as that reported in the previous paper.¹⁷⁾ The values thus obtained are listed in Table II. A linear relationship was established for the dissociation constants of 1-aryl-derivatives of 3-methyl-4-trifluoroacetyl-5-pyrazolone and Hammett σ constants as shown in Fig. 2. The change of the acid constant was found in the case of the chlorine substituted 4-acetyl-5-pyrazolones; the introduction of chlorine atom into the 4-acetyl-group of 1-aryl-3-methyl-5-pyrazolone increases the acidity remarkably (Table II).

Solvent Extraction of Europium

The distribution ratio of europium is obtained from the usual formula

$$D = \frac{\text{total concentration of europium in the organic phase.}}{\text{total concentration of europium in the aqueous phase.}}$$

The log D values of europium obtained at a constant concentration of each 4-acyl-5-pyrazolone are represented as linear functions of pH with slopes near to 3 as shown in Figs. 3 and 4. As shown in Fig. 3, 4-fluorinated acyl-5-pyrazolones allowed the europium extraction to be made at lower pH values than the non-fluorinated reagents, because the former is more acidic than the latter. 4-Chlorinated acetyl-5-pyrazolones were also the useful reagent for solvent extraction as indicated in Fig. 4. However,

Table II. pK_a of 5-Pyrazolones and Extraction of Eu (III)

R_1	R_2	$pH_{1/2}$	$\log K_{ex}$	pK_a in 10% (V/V) dioxane
4-CH ₃ ph	CH ₃	3.59	-5.67	4.10
4-CH ₃ ph	CHCl ₂	2.20	-1.50	3.40
4-CH ₃ ph	CCl ₃	2.07	-1.11	3.05
4-NO ₂ ph	CF ₃	1.57	0.39	1.84
ph	CF ₃	2.52	-2.46	2.70
4-CH ₃ ph	CF ₃	2.72	-3.18	2.90

Organic phase: 2×10^{-2} M 5-pyrazolones in chloroform

Aqueous phase: 1×10^{-1} M NaClO₄

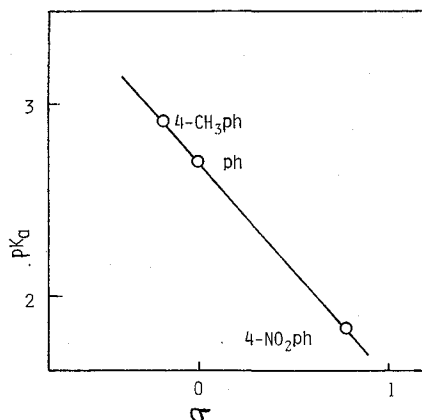


Fig. 2. Effect of substituents in 1-aryl derivatives of 3-methyl-4-trifluoroacetyl-5-pyrazolone.

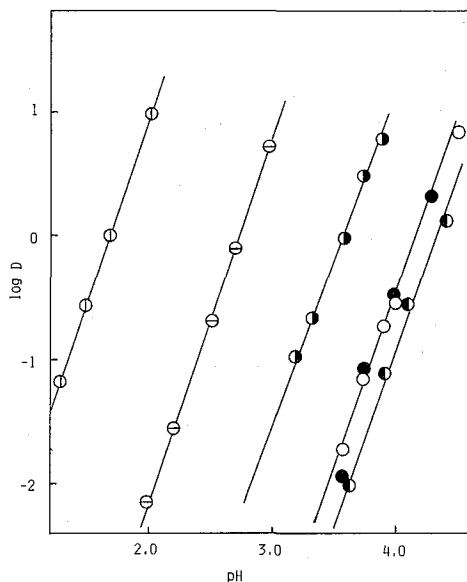
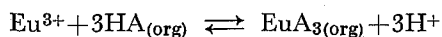


Fig. 3. Extraction of Eu with 4-acyl-5-pyrazolone derivatives.
Reagent: 2×10^{-2} M in benzene.
 R_1 : ph, R_2 : $\bigcirc$ C_2F_5 , $\ominus$ CF_3 , $\bullet$ CH_3 , $\bigcirc$ $n-C_3H_7$,
 $\bullet$ $iso-C_3H_7$, $\bullet$ $n-C_9H_{19}$

the introduction of chlorine atom into 4-acetyl group considerably lowered the solubility in such a non-polar solvent as benzene, and made difficult to purify the crude products which were synthesized by the method of Jensen.¹⁸⁾

The extraction reaction between europium and the reagent, HA, is



where the suffix "org" denotes the species in the organic phase. The extraction constant, K_{ex} , is obtained from the following relation.

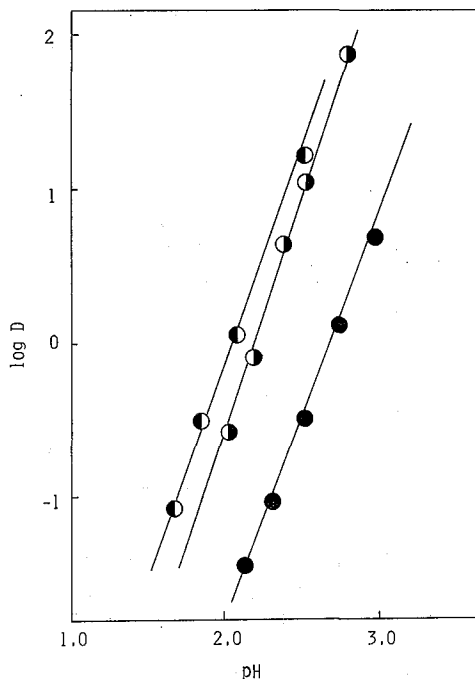


Fig. 4. Extraction of Eu with 4-acyl-5-pyrazolone derivatives.
Reagent: 2×10^{-2} M in chloroform
 R_1 : 4-CH₃ph, R_2 : ○ CHCl₂, ◐ CCl₃, ● CF₃

$$\log D = \log K_{\text{ex}} + 3\text{pH} + 3\log[\text{HR}]_{\text{org}}$$

where $[\]_{\text{org}}$ stands for the concentration in the organic phase. The pH value at half extraction by 0.02 M of each 4-acyl-5-pyrazolone, $(\text{pH}_{1/2})_{0.02}$, and the extraction constant, K_{ex} , calculated from the equation above are listed in Table II along with the pK_a value. Chloroform was used as solvent for the measurements of $(\text{pH}_{1/2})_{0.02}$ and $\log K_{\text{ex}}$, because 4-chloro-substituted acetyl-5-pyrazolones were poorly soluble for such an organic solvent as benzene and cyclohexane. The $\log K_{\text{ex}}$ values of halogen-substituted 4-acyl-5-pyrazolones in chloroform are in the range of about -3.2 to $+0.4$. These values are fairly large compared with the values for dibenzoylmethane ($\log K_{\text{ex}} = -18.9$)¹⁹⁾ and for thenoyltrifluoroacetone (-7.66).²⁰⁾ This indicates that the halogen substitution in the 4-acyl-group are exceedingly effective for the solvent extraction of some metals.

n-Octanol was fairly effective for the extraction of barium with 4-aryl-5-pyrazolones.¹⁷⁾ Consequently *n*-octanol as well as chloroform was chosen as the organic phase to examine the effectiveness for the europium extraction. 4-Trifluoroacetyl, and 4-dichloroacetyl derivatives of 1-(4-tolyl)-3-methyl-5-pyrazolone were used as the extraction reagent. Figures 4 and 5 show the plots of the $\log D$ vs. pH for the extraction of europium chelates using chloroform and *n*-octanol for the organic phase. *n*-Octanol enhanced the extraction of europium especially when the 4-trifluoroacetyl derivative was used. This suggests that the synergistic effect in solvent extraction appears

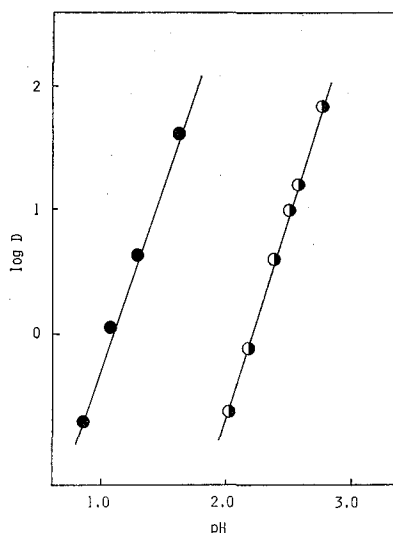


Fig. 5. Extraction of Eu using *n*-octanol as the organic phase.
 Reagent 0.02 M in *n*-octanol
 R_1 : 4-CH₃ph, R_2 : ○ CHCl₂, ● CF₃

remarkably in the chelates of the 4-trifluoroacetyl derivatives rather than those of the chloroacetyl derivatives.

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