

THE EXTRACTION OF ZINC WITH THE AID OF
1-PHENYL-3-METHYL-4-ACYL-PYRAZOL-5-ONES

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Received June 29th, 1970

1-Phenyl-3-methyl-4-acyl-pyrazol-5-ones (HL) were first used practically by Jensen^{1,2}. In his papers and in the subsequent ones³⁻⁶ it is pointed out that 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (*I*) and analogous β -diketones are powerful extractants; the extraction constants of a number of complexes with compound *I* are very high and generally exceed the constants determined for complexes of the frequently employed 2-thionyltrifluoroacetone. The synergic extraction of certain metals with the aid of agent *I* has also been studied^{6,7}. This type of extraction occurs with elements whose coordination numbers exceed twofold values of electrical charges of their ions and is intensely studied on metal β -diketone complexes⁸.

The distribution of various HL compounds between two liquid phases has been studied more or less generally². Special attention has been paid by Zolotov and coworkers³ to the distribution of compound *I*. These authors determined its values of $pK_1 = -0.28$ and $pK_2 = 4.11$ and its distribution coefficients Q for systems benzene-water ($\log Q = 3.01$) and *n*-isoamylalcohol-water ($\log Q = 2.33$) at a ionic strength of 1.0. With heavy bivalent metals the extraction of Mn, Zn and Co by means of this agent has been studied more intensely^{2,4,6,7}, in the case of Zn and Co the extraction has also been studied in the presence of synergic agents *S*. The composition of the extracted complexes was MeL_2 or $MeL_2.S$.

The present paper deals with the distribution of some HL agents between benzene and aqueous solutions of $HClO_4 + NaClO_4$ of a ionic strength 0.1, the 4-acyl in the molecule of HL being benzoyl (*I*), acetyl (*II*), ethoxycarbonyl (*III*), butyryl (*IV*), caproyl (*V*) and capryl (*VI*). The distribution of zinc complexes of these compounds between the same organic and aqueous phases has also been studied. Attention is also given to the synergic extraction of zinc into benzene with the aid of agent *IV* in the presence of some nitrogenous and oxygenous compounds.

EXPERIMENTAL

Chemicals and Apparatus

The preparation and purification of 4-acylpyrazolones was described previously¹. Their solutions in benzene were prepared from accurately weighed amounts. The other chemicals were of analytical reagent grade, isoquinoline was distilled prior to use. pH of the aqueous phase was adjusted with solutions of $HClO_4$, $NaClO_4$ and $NaOH$ in such a way that the final ionic strength was 0.1 in all cases. The working radioactive solution of $^{65}Zn(ClO_4)_2$ was prepared from a stock solution of $^{65}ZnCl_2$ by evaporation followed by dilution with perchloric acid. Its activity was 2 to 10 $\mu Ci/ml$ and the concentration of zinc was $5 \cdot 10^{-6} M$. γ -Radiation was measured with an apparatus Tesla NAQ 232, connected to an instrument VAM 15 D Vakutronik. pH of the aqueous phase was measured with a glass electrode on an apparatus OP-205 (Hungary). Spectrophotometric measurements were carried out with an apparatus Spectromom 201 (MOM Budapest) in 1 cm glass cells.

Procedure

Equal volumes of the aqueous and the organic phases (5 to 10 ml) were stirred for 12 hours. This time had been found sufficient for the establishment of an extraction equilibrium. After the separation of the phases aliquot portions (2 ml) were taken from each and measured in 5 ml glass ampoules in a Na(Tl)I well-type crystal. The distribution coefficients and dissociation constants of the individual agents were determined by extraction as in the case of Zn complexes, except that the metal was absent. The aqueous phases alkalinized with NaOH (conversion into the dissociated form) and the benzene phases were measured spectrophotometrically at λ_{\max} 385 nm (agent *I*) and 375 nm (agent *II* to *VI*) and their concentrations were read from calibration curves.

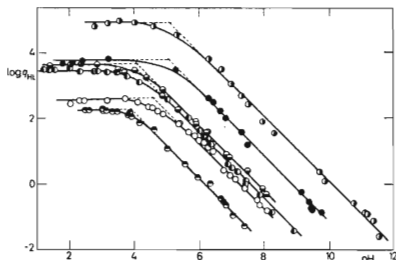


FIG. 1

Effect of pH on the Distribution of HL Agents between Aqueous Perchlorate and Benzene

The aqueous phases were prepared by mixing HClO_4 with NaOH, the final ionic strength was 0.1 in all cases. Agents HL: *I* ○, *II* ●, *III* ○, *IV* ●, *V* ● and *VI* ○.

TABLE I

Dissociation Constants and Distribution Coefficients of Agents HL

$I = 0.1$, the organic phases were benzene and/or chloroform.

Agent	$\text{p}K_{\text{HL}}$	$\log Q_{\text{HL}(\text{C}_6\text{H}_6)}$	$\log G_{\text{HL}(\text{CHCl}_3)}^a$
<i>I</i>	4.08	3.66	4.0
<i>II</i>	3.95	2.24	3.15
<i>III</i>	4.66	2.57	3.29
<i>IV</i>	4.15	3.45	4.02
<i>V</i>	5.10	3.77	4.3
<i>VI</i>	5.09	4.94	—

^a Calculated from $\text{p}K_{\text{HL}} + \log Q_{\text{HL}}$ in ref.².

RESULTS AND DISCUSSION

Distribution of the agents between benzene and aqueous perchlorate in the absence of zinc. Fig. 1 shows the distributions of the 6 substituted 4-acylpyrazolones between benzene and aqueous systems $\text{HClO}_4\text{-NaClO}_4$, ionic strength 0.1 in all cases, in relation to pH of the aqueous phase. From the distribution curves it is then possible to determine the values of $\text{p}K_{\text{HL}}$ (the dissociation constants of HL) and Q_{HL} (the distribution coefficients of HL). The compound HL as a weak monobasic acid is distributed between the two phases according to the simple relation

$$q_{\text{HL}} = \frac{[\text{HL}]_0}{[\text{HL}] + [\text{L}^-]} = \frac{Q_{\text{HL}}}{1 + K_{\text{HL}} \cdot 10^{-\text{pH}}} \quad (1)$$

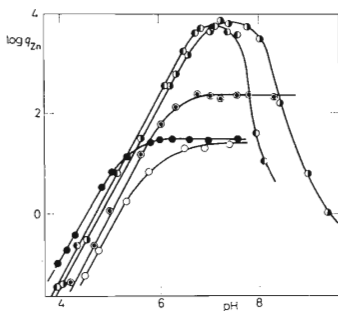


FIG. 2

Effect of pH on the Distribution of Zinc between Aqueous $\text{HClO}_4 + \text{NaClO}_4 + \text{NaOH}$ and Solution of HL Agents in Benzene

Agents HL: II, $5 \cdot 10^{-3}\text{M}$ (○) and $2 \cdot 10^{-2}\text{M}$ (●); III, $2 \cdot 10^{-2}\text{M}$ (◊); V, $2 \cdot 10^{-2}\text{M}$ (◐); VI $2 \cdot 10^{-2}\text{M}$ (◑).

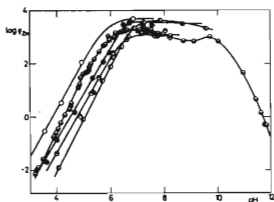


FIG. 3

Effect of pH on the Distribution of Zinc between Aqueous $\text{HClO}_4 + \text{NaClO}_4 + \text{NaOH}$ and Solutions of HL Agents in Benzene

Agents HL: I, $5 \cdot 10^{-3}\text{M}$ (◐), $1 \cdot 10^{-2}\text{M}$ (●) and $5 \cdot 10^{-2}\text{M}$ (○); IV, $1 \cdot 5 \cdot 10^{-2}\text{M}$ (◑) and $5 \cdot 10^{-2}\text{M}$ (◒).

which makes it possible to determine the two quantities from experimental data simultaneously. Their values generally depend on the polarity or polarisability of the molecule HL. The distribution coefficients Q_{HL} (Table I) express the solubilities of HL in benzene or CHCl_3 ; the values pK_{HL} are affected by various factors, such as the presence of oxygen in the principal chain. The value of pK for *I* well accords with that taken from ref.³, whereas the value of Q for *I* is higher by half-an-

TABLE II
Stability Constants of Zinc Complexes of Agents HL

$$\beta_n = \frac{[\text{ZnL}_n]}{[\text{Zn}][\text{L}]^n}; Q_{\text{ZnL}_2} = \frac{[\text{ZnL}_2]_0}{[\text{ZnL}_2]}; b = \text{computing parameter}^9.$$

Agent	$\log \beta_1$	$\log \beta_2$	b	$\log Q_{\text{ZnL}_2(\text{C}_6\text{H}_6)}$
<i>I</i>	2.94	6.56	-0.34	3.57
<i>II</i>	2.20	5.32	-0.46	1.49
<i>III</i>	2.05	5.52	-0.71	2.37
<i>IV</i>	3.03	6.06	0	3.27
<i>V</i>	3.82	7.36	0.14	3.84
<i>VI</i>	4.80	9.14	0.23	4.11

TABLE III
Effect of Organic Bases on the Extraction of Zinc with the Aid of HL Agents
Org. phase $1.5 \cdot 10^{-2}\text{M-HL}$ in benzene (HL = *IV*), pH of aqueous phase 4.0, $\log q_{\text{Zn}}$ in the absence of a base = -1.43.

Org. base	c_{Base}	$\Delta \log q_{\text{Zn}}$
1-Propanol	0.619	+0.19
1-Butanol	0.546	+0.54
1-Octanol	0.318	+0.47
Benzyl alcohol	0.483	+0.68
Acetophenone	0.430	-0.08
3-Methyl-2-pentanone	0.16	-0.17
<i>n</i> -Tributyl phosphate	0.074	+0.65
Benzimidazole	sat. solution	+0.18 ^a
Pyridine	0.62	-0.04 ^a
2,6-Lutidine	0.44	+0.28 ^b
<i>n</i> -Trioctylamine	0.051	-0.70 ^c
Quinoline	0.10	+2.18

^a pH 6.7, ^b pH 7.3, ^c pH 6.8.

order of magnitude. The values of Q_{HL} for the system water- CHCl_3 were not determined experimentally. The high values of Q_{HL} for the individual derivatives suggest that even the extractibilities of the arising chelate complexes with metals will be high.

Extraction of the Zinc Complexes into Benzene

Figs 2 and 3 show the extraction plots of $\log q_{Zn}$ vs. pH. After recalculation into the plots of $\log q_{Zn}$ vs pL, where pL is related to the equilibrium concentration of the free ligand $[\text{L}^-]$ by the equation

$$\text{pL} = -\log [\text{L}^-] = \text{pK}_{HL} + \log (Q_{HL} + 1 + K_{HL}/[\text{H}^+]) - \log c_{HL} - \text{pH}, \quad (2)$$

it is evident that the aqueous phase contains complexes ZnL^+ and ZnL_2 , the latter being extracted into benzene. The symbol c_{HL} in equation (2) is the analytical concentration of HL. It is only with compounds V and VI that the extraction curves exhibit a decrease of q_{Zn} with further increase of pH, from which it can be inferred that even negatively charged complexes, e.g. ZnCl_3^- , are formed.

Employing the Dyrssen-Sillen method of two parameters⁹ we calculated the stability constants of the two arising complexes in the aqueous phase. These values along with those of Q_{ZnL_2} are listed in Table II. It is evident that the extractibility and stability of the complexes ZnL_2 increases with the length of the chain in the 4-acyl group. The 4-benzoyl derivative is not the highest member of this series, but it does not form non-extractible or little extractible complexes, as compounds V and VI do. This is obviously why the benzoyl derivative has been used most. From the data in Tables I and II it can further be judged that similar advantageous properties will be observed with compound IV. On the other hand, the probable extraction asset of compounds V and VI will be a better selectivity.

Effect of Added Bases on the Extraction of Zinc

The Effect of various organic bases on the extraction of zinc was studied in the system HClO_4 - $+$ NaClO_4 - $1.5 \cdot 10^{-2}\text{M}$ solution of agent IV in benzene. The results show (Table III) that quinoline exhibited the strongest synergic effect on the extraction ($\Delta \log q_{Zn} = 2.18$); the other bases had a negligible synergic or even antagonistic effect, which can be ascribed to their probable interaction with HL. A moderate synergic effect was observed with some alcohols and n-tributyl phosphate.

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Translated by J. Salák.