EXTRACTION OF HAFNIUM BY MEANS OF SOME SUBSTITUTED 1-PHENYL-3-METHYL-4-BENZOYL-PYRAZOL-5-ONES

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Distribution between aqueous phase and benzene or chloroform was studied for 1-phenyl-3-methyl-4-benzoylpyrazol-5-ones with 2-chloro, 4-methoxy, 3-nitro, and 4-nitro substitution in the benzoyl group (ionic strength of the aqueous phase 0·1) and for hafnium in their presence (ionic strength 2·0). The distribution and dissociation constants of the reagents and the extraction constants of their hafnium complexes were determined. Hafnium was found to be extracted as the HfA_4 species. The extraction parameters of the derivatives in question do not differ substantially from those of the parent substance.

1-Phenyl-3-methyl-4-benzoylpyrazol-5-one has been for the first time practically applied to extraction by Jensen[1,2]. More recently, this substance has been demonstrated[3,4] to be a promising, very efficient reagent; the extraction constant values for a number of its complexes are very high, usually exceeding those for the complexes of 2-thenoyltrifluoroacetone. With a view to obtaining even more favourable reagent properties, attention has been paid to some derivatives of the compound, containing the substituents in the benzoyl group, *viz.* 4-bromo, 4-nitro (ref.[2]), 3,5-dinitro, 2,4,6-trinitro, 4-phenylazo (ref.[5]), 2-chloro, 4-chloro, and 2,4-dichloro (ref.[6]). The dissociation and distribution constants of these reagents are given in Table I.

The subject of the present work was some 1-phenyl-3-methyl-4-benzoylpyrazolones-5 (HA) with 2-chloro, 3-nitro, 4-nitro, and 4-methoxy substituents at the 4-benzoyl group; their distribution was examined between benzene or chloroform and aqueous solutions of $HClO_4$ and $NaClO_4$, ionic strength 0·1. The distribution of their complexes with hafnium between the same organic and aqueous phases was also investigated; the ionic strength of the latter was raised to 2·0 in this case.

EXPERIMENTAL

Chemicals and Apparatus

The method for preparation and purification of 4-acylpyrazolones has been described recently[1]. Their solutions in benzene or chloroform were prepared from precisely weighed amounts of the chemicals. The other chemicals used were reagent grade purity. The pH of the aqueous phase was adjusted with $HClO_4$, $NaClO_4$, and NaOH solutions so that for the study of the reagent distribution, the resulting ionic strength was 0·1.

Radioactive solution of $^{175+181}Hf(ClO_4)_4$ was prepared from commercial $^{175+181}HfCl_4$ by multiple heating and evaporation with $HClO_4$ and transfer into solution with 2M-$HClO_4$. Its concentration in the working solutions was $(1-5{\cdot}7) . 10^{-6}$ mol l^{-1}, activity $(4-6) . 10^3$ s^{-1} mol^{-1}. The gamma activity of the samples was measured by means of a Nuclear Chicago 1185 Automatic Gamma Counter scintillation detector fitted with a well-type NaI(Tl) crystal. The pH of the aqueous phase was measured potentiometrically by using an EIL instrument (Electronic Instruments, Richmond, England) equipped with a GHS 23 glass electrode and an RJ 23 saturated calomel electrode. The spectrophotometric measurements were performed on a Spektromom 201 spectrophotometer (MOM, Budapest) using 1 cm glass cells.

Working Procedure

Equal volumes (5 or 10 ml) of the aqueous and organic phases in glass test tubes were shaken on a thermostatted shaking machine at 20 ± 1°C for 6 h; as found by preliminary experiments, this period was sufficient for the extraction equilibrium to establish. After the extraction and phase separation, 2 ml of either phase were sampled in glass ampoules and their gamma activity

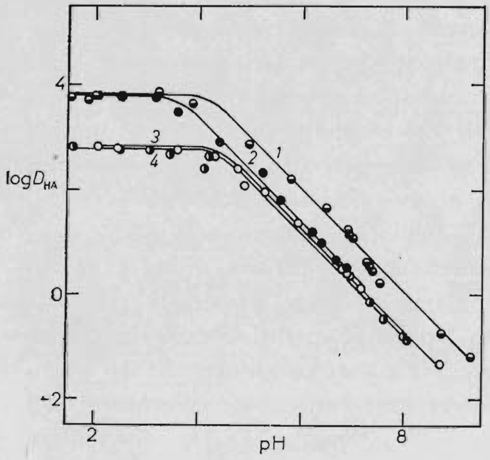

FIG. 1

Effect of pH on the distribution of the reagents between the aqueous and the organic phases. Aqueous phase: $HClO_4$ + NaOH, $I = 0{\cdot}1$. Reagent derivative (organic phase *1* 2-chloro (benzene); *2* 3-nitro (chloroform); ○ 4-nitro (chloroform); *3* 4-methoxy (benzene)

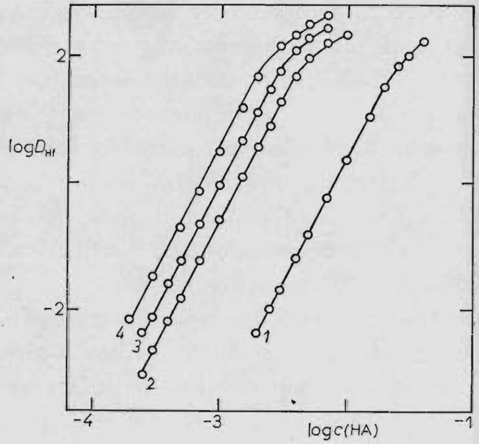

FIG. 2

Distribution of hafnium(IV) between solutions of the reagents in benzene or chloroform and 2M-$HClO_4$ aqueous solution. Reagent derivative (organic phase): *1* 4-methoxy (benzene), *2* 4-nitro (chloroform), *3* 3-nitro (chloroform), *4* 2-chloro (benzene); c(HA) in mol l^{-1}

was measured. The relative standard deviation of the radiometric measurements did not exceed 2%. In the remaining aqueous phase, the pH was measured. The distribution constants of the reagents $K_D(HA) = [HA]_{org}/[HA]$ and the dissociation constants $K_{HA} = [H^+][A^-]/[HA]$ were determined by extraction analogously as in the work[7] (the brackets denote the equilibrium concentrations; those with the subscript org refer to the organic phase, those without a subscript refer to the aqueous phase). The aqueous phase after alkalization with sodium hydroxide and the re-extract of the organic phase in 0·1M-NaOH (in which the reagent is converted into the dissociated form) were measured spectrophotometrically at 340 nm (2-chloro), 330 nm (3-nitro), 305 nm (4-nitro), and 320 nm (4-methoxy); the concentrations were read from calibration curves.

RESULTS AND DISCUSSION

Distribution of the Reagents between Aqueous Solution of 0·1M *Perchlorate and Benzene or Chloroform*

The distribution of the four derivatives studied between the aqueous phase, containing $HClO_4$, $NaClO_4$, and NaOH so that the resulting ionic strength was 0·1,

TABLE I

Values of the dissociation and distribution constants of 1-phenyl-3-methyl-4-benzoylpyrazol-5-ones substituted in the 4-benzoyl group. $I = 0·1$

Substituent	pK_{HA}	log $K_D(HA)$	Organic phase	Ref.
H	4·08[a]	3·66	benzene	7
4-Bromo		8·80[b]	chloroform	2
4-Nitro		7·6[b]	chloroform	2
3,5-Dinitro	2·65[c]	0·84	chloroform	5
2,4,6-Trinitro	1·60[c]	2·26	chloroform	5
4-Phenylazo	4·30[c]	2·04	chloroform	5
2-Chloro	3·26[d]	2·78	*o*-xylene	6
		2·56	MIBK[e]	
4-Chloro	3·74[d]	4·18	*o*-xylene	6
		3·02	MIBK[e]	
2,4-Dichloro	3·49[d]	3·39	*o*-xylene	6
		2·89	MIBK[e]	
2-Chloro	4·44[a]	2·76	benzene	this work
3-Nitro	3·62[a]	3·78	chloroform	this work
4-Nitro	4·48[a]	2·80	chloroform	this work
4-Methoxy	4·20[a]	3·80	benzene	this work

[a] $t = 20$°C, from the study of partition of the reagent between two phases; [b] $t = 22$°C, value of log $K_D(HA) + pK_{HA}$, ionic strength not reported; [c] water–dioxane system; [d] water–dimethylformamide system; [e] methyl isobutyl ketone.

and benzene or, for the nitro derivatives, chloroform are shown in Fig. 1. The use of chloroform as the solvent for the nitro derivatives as well as their hafnium complexes was dictated by their poor solubility in common aliphatic or aromatic solvents.

The distribution of the weak monobasic acids (HA) between the two liquid phases obeys the simple relation $D_{HA} = [HA]_{org}/(HA) + (A^-) = K_D(HA)/(1 + K_{HA}/[H^+])$, based on which both the $K_D(HA)$ and the K_{HA} values can be determined from the experimental data; their values are given in Table I. Apparently, the dissociation constant value is not affected appreciably by the presence of the substituents in question. The pK_{HA} value of the 2-chloro derivative found in the present work differs more than by unity from that given in[6], where, however, another technique has been employed; on the other hand, our value of the sum $pK_{HA} + \log K_D(HA)$ for the 4-nitro derivative is the same as that found in the study[2]. Comparing the two nitro compounds we find the 3-nitro derivative to be a stronger acid and less soluble in the aqueous phase.

The above facts, only supplementing the previous studies, do not allow new general conclusions to be drawn.

Distribution of Hafnium(IV)

The dependences of the logarithm of the hafnium distribution ratio on the logarithms of the initial concentrations of the reagents studied for 2M-$HClO_4$ solutions as the aqueous phase and benzene or chloroform as the organic phase are shown in Fig. 2. The higher acidity of the aqueous phase was applied in view of hydrolysis and polymerization of hafnium taking place in strong mineral acid as dilute as $c = 0{\cdot}1 \text{ mol l}^{-1}$. The slopes of the curves in their left, ascending parts are $4{\cdot}0 \pm 0{\cdot}1$. The distribution of hafnium between 2M-($HClO_4$ + $NaClO_4$) solutions and the organic phase was analogously investigated also in dependence on the concentration of hydrogen ions; the slopes of the curves attained in all cases the minimum values of $-4{\cdot}0 \pm 0{\cdot}2$.

These dependences evidence that for $c_{Hf} \leqq 6 \cdot 10^{-6} \text{ mol l}^{-1}$, $cH_{H^+} \geqq 1{\cdot}0 \text{ mol l}^{-1}$, ionic strength 2·0, the extraction of hafnium follows the scheme $Hf^{4+} + 4\,HA_{org} \rightleftharpoons HfA_{4org} + 4\,H^+$, with the corresponding extraction constant $K_{ex} = [HfA_4]_{org} \cdot [H^+]^4/[Hf^{4+}][HA]^4_{org} = D_{Hf}[H^+]^4/[HA]^4_{org}$. Its values for the derivatives used are as follows: 2-chloro (benzene) $10^{13 \cdot 8}$, 3-nitro (chloroform) $10^{13 \cdot 2}$, 4-nitro (chloroform) $10^{12 \cdot 6}$, and 4-methoxy (benzene) $10^{9 \cdot 6}$. Except for the last derivative, these values do not differ from the value for the parent 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (ref.[8]) more than by one order of magnitude.

It can be thus concluded that the derivatives studied in this work do not differ significantly in their properties from the parent reagent. The substituents do not affect appreciably the dissociation constant value; the presence of the nitro group, on the other hand, influences markedly the solubility in low polar organic solvents.

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