

## STUDY OF THE ACID-BASE SPECIES OF DI-*n*-BUTYL N-(4-ANTIPYRYL)AMIDOPHOSPHATE

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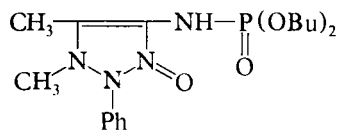
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The acid-base species of di-*n*-butyl N-(4-antipyril)amidophosphate present in aqueous solutions of perchloric acid were studied. The compound was observed to protonate as far as the second step in this medium, with protonation constants  $\log \beta_{H1} = 0.49 \pm 0.02$  and  $\log \beta_{H2} = -1.34 \pm 0.07$ . The distribution of the solute between chloroform and aqueous solutions of perchloric acid was also investigated, and the value of  $\log K_{ex} = 2.55$  was obtained.

A new extracting agent involving functional groups of the frequently used pyrazolone derivatives<sup>1,2</sup> and dialkyl phosphates, di-*n*-butyl N-(4-antipyril)amidophosphate (*I*)\*



*I*

has been synthesized and characterized in our laboratories<sup>3</sup> and used for the extraction of mercury from iodide solutions, in the presence of perchloric acid, into chloroform<sup>4</sup>. This investigation of the extraction of mercury has shown that the complexes passing into the organic phase involve *I* in various acid-base forms. In the present work the acid-base species of *I* are examined in more detail.

### EXPERIMENTAL

#### Chemicals and Apparatus

Chloroform and perchloric acid were chemicals of reagent grade purity (Lachema, Brno). Substance *I* was synthesized<sup>3</sup>, dissolved in chloroform, and purified by repeated agitation with 5% aqueous Na<sub>2</sub>CO<sub>3</sub>, 0.1M-H<sub>2</sub>SO<sub>4</sub>, and finally with distilled water. Solvent was then removed by evaporation and the substance was dissolved in CCl<sub>4</sub> and precipitated carefully with *n*-hexane

\* In equations *I* is denoted as L.

to obtain fine crystals of *I*. The composition was confirmed by elemental analysis and by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR measurements. No impurities were detected.

Samples for spectral measurements of the acid-base species were prepared by diluting stock solution of *I* in  $\text{HClO}_4$  with water.

The extraction experiments were carried out by shaking in ground-in test tubes on a rotary shaking machine for 10 min at  $20 \pm 1^\circ\text{C}$ . Phase volumes of 10 ml were used. The organic phase was solution of *I* in chloroform, the aqueous phase contained perchloric acid. Aliquots of the organic phase were taken for absorbance measurements.

The spectrophotometric measurements were performed on a Superscan<sup>3</sup> instrument (Varian, Switzerland) combined with an HP 9815A computer (Hewlett-Packard, USA). The absorbances were measured in 1 cm quartz cuvettes; the reading accuracy was 0.0001, but the overall absorbance precision for the entire sample preparation and measurement procedure was  $\pm 0.002-0.003$ .

### Data Processing and Calculations

*Calculation of the rank of the absorbance matrix.* The SPECIES program<sup>5</sup> based on the FA 608 procedure<sup>6</sup> was used. The method consists in the calculation of the eigenvalues of the second moment of the absorbance matrix, *M*:

$$\mathbf{M} = (1/n_s) \mathbf{A}\mathbf{A}^T, \quad (1)$$

where *A* is the absorbance matrix,  $\mathbf{A}^T$  is the corresponding transpose, and  $n_s$  is the number of solutions treated.

Let  $s_{\text{inst}}(A)$  be the experimental error of the absorbance measurement and  $s_k(A)$  the estimate of the standard deviation of absorbance, calculated by factorial analysis. Then the rank of the matrix is the first *k* for which

$$s_k(A) < s_{\text{inst}}(A), \quad (2)$$

where *k* is the number of eigenvalues arranged by magnitude.

The SPECIES program also computes the percentage relative variance and overall (cumulative) variance. Eigenvalues whose variance is less than 0.01% of the matrix trace are disregarded (considered to be zero). The rank of the matrix, determined by the number of absorbing species in solution, thus equals the number of nonzero eigenvalues.

*Calculation of the dissociation (association) acidity constants from spectrophotometric data.* The general minimization program for matrix analysis<sup>7</sup>, SQUAD, was used in the SQUAD-G version<sup>8</sup>. The validity of the Bouguer-Lambert-Beer law is assumed; the absorbance for solution *i* at wavelength *k* then is

$$A_{ik} = \sum_p \sum_q [\text{H}_p\text{L}_q] \varepsilon_{pq}, \quad (3)$$

where  $[\text{H}_p\text{L}_q]$  are the equilibrium concentrations of the acid-base species of reagent L and  $\varepsilon_{pq}$  are the corresponding absorptivities. The program minimizes the sum of squares of differences between the observed and calculated absorbances,

$$U = \sum_{i=1}^{n_s} (A_{\text{obs}} - A_{\text{cal}})^2 w_i, \quad (4)$$

where  $w_i$ 's are statistical weights — unity was used for them by us — and  $n_s$  is the number of solutions. Values of dissociation (association) constants and molar absorptivities are sought such

that the  $U$  value is minimum. The following criteria of adequacy of the chemical model suggested were applied: *a*) the absorbance standard deviation estimate  $s(A)$  should be lower than or equal to the experimental error of absorbance measurement; *b*) the standard deviation of the equilibrium constant should satisfy the criterion  $s/s(\beta) < F_s$ , where  $F_s$  is at least 3; and *c*) the molar absorptivity values obtained must be reasonable (for instance, they must not be negative).

*Extraction data processing.* The dependences of the distribution ratio of  $I$  on the acidity of the aqueous phase were evaluated by the EXLET program<sup>9</sup>, a modified version of the EXT-DISTR-LETAG program<sup>10</sup>. This program finds values of the parameters (distribution constants, distribution ratios, dissociation and extraction constants) such that the sum of squares of differences between the observed ( $D_{\text{obs}}$ ) and calculated ( $D_{\text{cal}}$ ) distribution ratios

$$U = \sum_{i=1}^{N_s} (D_{\text{obs}} - D_{\text{cal}})^2 \quad (5)$$

is minimum; the summation is carried out over all the  $N_s$  experimental points. The program is also capable of minimization of the function

$$U = \sum_{i=1}^{N_s} (A_{\text{obs}} - A_{\text{cal}})^2, \quad (6)$$

where  $A$  is the absorbance of the organic phase. This latter approach was used throughout the present work.

The calculations were performed on a EC 1033 (500 k) computer (USSR) at the Department of Computing Technique of Purkyně University, Brno.

## RESULTS AND DISCUSSION

### *Distribution of the Extracting Agent*

The UV spectrum of substance  $I$  in chloroform is shown in Fig. 1. The absorption maximum lies at 280 nm, the corresponding molar absorptivity is  $\epsilon = 1.23 \cdot 10^4 \text{ cm}^2 \cdot \text{mol}^{-1}$ . At this wavelength the absorbance of solution of  $I$  in chloroform was measured in dependence on the acidity of the aqueous solution of perchloric acid with which the solution measured had been in contact. The results are shown in Fig. 2. The acidity is expressed by the Hammett acidity function<sup>11,12</sup>  $H_0$ . The absorbances obtained were entered into the computer using EXLET program to calculate the extraction constant of  $I$  for the reaction



( $\bar{\text{L}}$  is the species in the organic phase), for which

$$\log K_{\text{ex}} = \log \left( \frac{[\bar{\text{L}}][\text{H}^+]}{[\text{LH}^+]} \right). \quad (7)$$

A value of 2.55 was obtained for  $\log K_{\text{ex}}$ .

Spectra of *I* were also measured in water and in weakly alkaline solutions. The spectrum of *I* in water is virtually identical with that in weakly acid solutions. The spectrum in 0.01M-KOH, however, is different and exhibits a maximum at 208 nm, which further shifts to 220 nm in 0.1M-KOH. The distribution of the reagent in alkaline systems was not measured and the dissociation constant was not determined because the reagent is intended for metal extraction from acid solutions<sup>4</sup>.

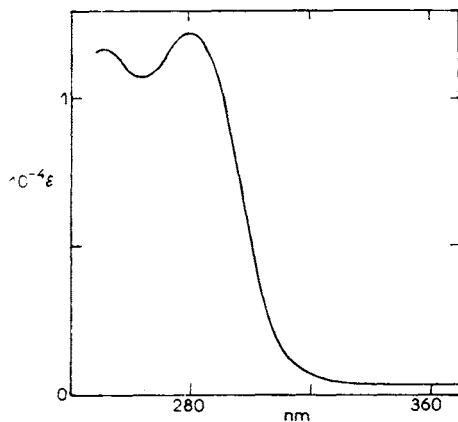


FIG. 1  
Ultraviolet spectrum of substance *I* in chloroform ( $c_I = 0.1 \text{ mmol l}^{-1}$ )

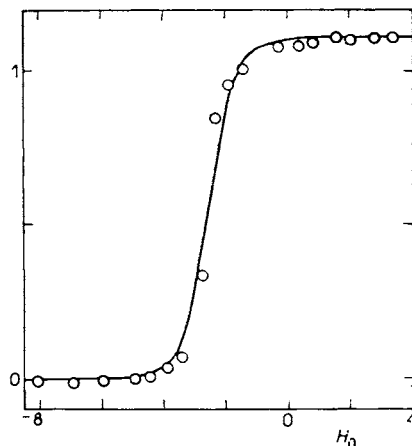


FIG. 2  
Dependence of absorbance of substance *I* in chloroform on acidity of aqueous solution of perchloric acid;  $\lambda$  280 nm.  $\circ$  experimental values, — calculated curve

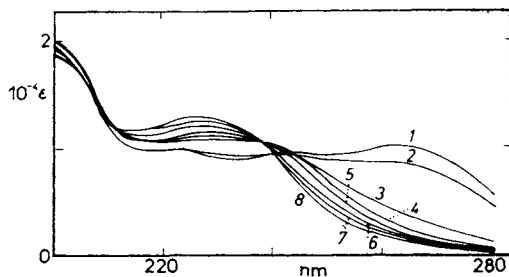


FIG. 3  
Ultraviolet spectra of substance *I* in aqueous solutions of perchloric acid.  $c_{\text{HClO}_4}$  ( $\text{mol l}^{-1}$ ): 1 0.01, 2 0.1, 3 1, 4 2, 5 4, 6 8, 7 9.4, 8 11

*Acid-Base Equilibria of the Extracting Agent*

It has been shown that substance *I* can protonate in acid solutions. In view of the several basic centres in the reagent molecule, multiply protonated forms can be expected to exist. UV spectra were therefore measured in perchloric acid solutions of different acidity (Fig. 3). The spectral patterns reveal the occurrence of a minimum of two protonated species of *I*. This is also borne out by the calculation of the rank of the absorbance matrix performed by factorial analysis using SPECIES program (Table I).

TABLE I

Data for the determination of the number of absorbing species by factorial analysis of the absorbance matrix of substance *I* by means of the SPECIES program: eigenvalues  $r_i$ , relative variance RV, cumulative variance CRV, standard deviation estimate for absorbance  $s_k(A)$  (for  $k$  species); matrix trace  $\text{tr}(\mathbf{A}) = 5.549076$

$k$	$r_i$	RV %	$\sum_{i=1}^k r_i$	CRV %	$s_k(A)$
1	5.370929	99.936	5.379028	99.936	0.0922
2	0.167823	3.024	5.546851	99.959	0.0108
3	0.002184	0.039	5.549035	99.999	0.0015
4	0.000026	0.005	5.549061	100.00	0.0009
5	0.000009	0.000	5.549069	100.00	0.0005
⋮	⋮	⋮	⋮	⋮	⋮
20	0.000000	0.000	5.549072	100.00	0.000

TABLE II

Protonation models for substance *I* and results obtained with SQUAD-G program

Model	Reaction	$\log \beta_{H_n} \pm s(\log \beta_{H_n})^a$	$s(A)^b$
a	$L + H^+ \rightleftharpoons LH^+$	$0.309 \pm 0.042$	0.160
b	$L + H^+ \rightleftharpoons LH^+$	$0.488 \pm 0.021$	0.0057
	$L + 2H^+ \rightleftharpoons LH_2^{2+}$	$-1.338 \pm 0.074$	
c	$L + H^+ \rightleftharpoons LH^+$	$0.556 \pm 0.022$	0.0041
	$L + 2H^+ \rightleftharpoons LH_2^{2+}$	$-0.315 \pm 0.133$	
	$L + 3H^+ \rightleftharpoons LH_3^{3+}$	$-5.465 \pm 0.247$	

<sup>a</sup>  $s(\log \beta_{H_n})$  is the standard deviation estimate for the logarithm of the protonation constant;

<sup>b</sup> standard deviation estimate for absorbance, calculated by general regression.

The standard deviation of absorbance was lower than the experimental error for  $k \geq 3$ ; hence, at least three absorbing species with different spectra can be assumed to be present in perchloric acid solutions.

The experimental absorbances together with the values of the Hammett function,  $H_0$ , for the perchloric acid concentrations used were entered to be processed by SQUAD program for the various protonation models. The results are given in Table II.

The adequacy of the models was tested in terms of the standard deviation of absorbance,  $s(A)$ , as a quantity characterizing the agreement of the calculation with the experiment. This value decreases with increasing number of protonation equilibria from models *a*) to *c*); however, the decrease from model *b*) to model *c*) is little significant and moreover, it is accompanied by a high increase in the error of the constants

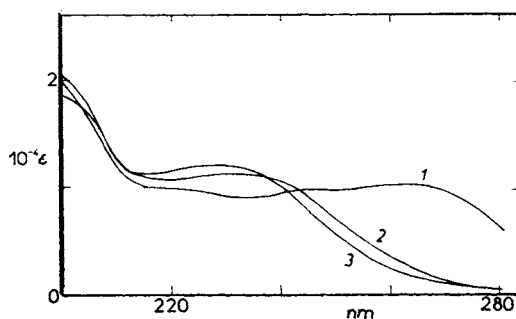


FIG. 4

Calculated spectra of the individual acid-base species of substance *I*: 1 L, 2  $\text{LH}^+$ , 3  $\text{LH}_2^{2+}$

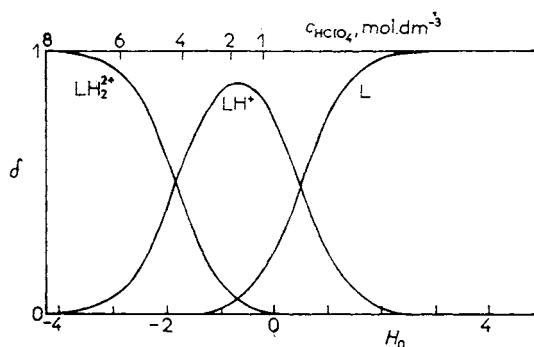


FIG. 5

Distribution diagram for the acid-base species of substance *I*

of protonation for the second and third steps. It can be concluded that the model of protonation in three steps (model *c*) can be ruled out. The difference between the constant of protonation in the second step in models *b*) and *c*) also bears out the above conclusion. The results are consistent with the determined number of absorbing species, *viz.*, three species of which one is the neutral form and two are protonated.

Fig. 4 shows the calculated spectra of the individual acid-base species of substance *I*. Only the spectrum of the neutral form is experimentally accessible. The calculated spectrum of this form agrees well with spectrum No 1 in Fig. 3, where this neutral form can be assumed to predominate.

The protonation constants for model *b*) (Table II) were employed to calculate the distribution diagram of the acid-base species of di-n-butyl N-(4-antipyryl)amidophosphate (Fig. 5). In the range of negative  $H_0$  values, perchloric acid concentrations are also given.

In conclusion, it can be suggested that the new extracting agent under study, which exists in various protonated forms in acid solutions, can serve as a convenient reagent for the extraction of univalent and divalent anions. This is also borne out by the results obtained previously for the extraction of mercury<sup>4</sup>. The first protonation of the agent is supposed to take place at the amide group nitrogen. The second protonation site is difficult to assess because the molecular structure of the compound is too complex to enable the requisite quantum-mechanical calculations to be performed. Most likely, this site will be at some of the pyrazolone ring nitrogens.

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