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DISSOCIATION CONSTANT OF SOME PESTICIDE DERIVATIVES

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PHTHALIMIDE derivatives are known to have biological effects and used as insecticide, fungicide and/or herbicide plant protecting agents. Their studies attracted the interest of many workers in the field of insecticides and toxicology. The present investigation is devoted to a spectrophotometric study of two phthalimide derivatives in aqueous buffer solutions at different pH values and in buffer solutions containing varying proportions of methanol, ethanol, ethylene glycol or glycerol. The pK_a are determined and are commented in the light of the nature of the medium.

Phthalimide derivatives under investigation are N-hydroxy phthalimide (I) and 4-carboxy N-phenyl phthalimide (II) and were prepared as recommended in the literatures^{1,2}. The buffer solutions used were components of the modified universal series of Britton and Robinson³. The UV and visible spectra were recorded on a Carl Zeiss PMQII spectrophotometer. The organic solvents used were purified according to the recommended procedures⁴.

Electronic Absorption Spectra of Pesticide (I):

The absorption spectra of N-hydroxy phthalimide (I) within 200–400 nm region in universal buffer sol-

utions with pH = 6 comprises one band with λ_{max} at 225 nm. This band is presumably due to absorption by the neutral molecules. The absorption of this band decreases gradually with the increase in the pH of the medium. At pH = 7, a new band appears at 250 nm. This band is due to the ionized form and its absorbance increases in the pH range 7–10.9.

In the presence of the organic solvent, the absorption of the two bands is affected by the amount and the nature of the organic solvent. Furthermore the band due to the ionized species acquires a blue shift in the case of methanol or ethanol and a red shift in the case of ethylene glycol or glycerol. This behaviour will be discussed later.

An isobestic point was observed at 235 nm. This reveals the existence of an acid-base equilibrium between ionic and nonionic forms of the type



The plot of absorbance at 225 nm or 250 nm as a function of pH is more or less an S-shaped relation. The dissociation constant for this pesticide is determined from the absorbance pH curves applying the following methods: (i) The half-height method⁵ where pK_a is equal to the pH at half-height of the absorbance pH curve, from which pK_a is evaluated by considering the activity coefficient term. (ii) The limiting absorbance method⁶ where (1) is used,

$$pH = pK_a + \log \frac{A}{A_m - A} + \log \gamma. \quad (1)$$

The plot of $\log (A/A_m - A)$ as a function of pH is linear from which pK_a can be determined.

The pK_a values obtained from the two methods are given in table 1.

Electronic absorption spectra of pesticide (II):

In the pH range 6–7.9, the spectrum of 4-carboxy N-phenyl phthalimide (II) possesses only one absorption band at 220 nm which can be assigned as due to the nonionized species. At pH 8.2, a new band due to the ionized form appears at 270 nm. With increase in the pH of the medium, the absorbance of the latter band increases while it decreases for the former one. An isobestic point was found at 260 nm.

The dependence of the pK_a values on the nature and the amount of the organic solvent is similar to that found for pesticide (I).

From the results of table 1, it is seen that the pK_a values for the two pesticides are higher in pure aqueous solution than in mixed solvents. This indicates that the

Table 1 Mean values of pK_a for the two pesticides, *N*-hydroxy phthalimide (I) and 4-carboxy *N*-phenyl phthalimide (II) in water-organic solvent mixtures.

Organic solvent	Org. solv. %	Dielectric constant	pK_a	
			I	II
Methanol	4.1	79.8	6.31	8.15
	8.2	78.12	6.46	8.28
	16.2	74.96	6.57	8.41
	25.1	71.47	6.71	8.49
	34.7	67.41	6.82	8.56
Ethanol	3.9	77.5	6.27	8.24
	7.8	76.6	6.48	8.38
	15.9	74.7	6.62	8.44
	24.6	72.7	6.69	8.60
	33.6	68.8	6.78	8.67
Ethylene glycol	5.6	80.22	6.86	8.00
	11.0	79.47	6.79	7.93
	21.7	77.92	6.64	7.90
	32.2	76.12	6.40	7.86
	42.5	73.91	6.33	7.67
Glycerol	6.3	81.06	6.87	7.83
	12.3	80.06	6.79	7.75
	24.0	78.80	6.72	7.59
	35.2	77.23	6.63	7.50
	45.80	75.51	6.47	7.43
Aqueous medium		74.42	6.91	8.86

presence of organic solvent increases the ionization of these compounds. The rate by which the ionic forms are produced is influenced by both the nature and the amount of the organic solvent added. The elimination of the proton is enhanced as the amount of glycol or glycerol increases whereas an increase in methanol or ethanol content decreases the ionization process. This behaviour may be explained⁷ on the basis that glycol and glycerol acting as proton acceptors, and facilitating the dissociation of the proton from the hydroxyl group in (I) and from the carboxylic group in (II).

The decrease in ionization in the presence of ethanol or methanol can be attributed to the blocking of π -electrons of the C=O group in the two compounds through intermolecular hydrogen bonding which renders excitation of π -electrons more difficult, thus resulting in higher pK_a values. The displacement of the absorption bands to shorter wavelengths by increasing methanol or ethanol concentrations at constant pH, can be attributed to the decrease in concentration of the ionized form as a result of association with the molecules of these solvents.

The variation of pK_a with dielectric constant (D) in solvent mixtures is given by the relation⁸

$$pK_a = pK_0 + \frac{0.43 Ne^2}{RT} \cdot \frac{Z_1 Z_2}{r_1 + r_2} \left(\frac{1}{D}\right)$$

where pK_a = acid dissociation constant in solvent mixtures, pK_0 is the dissociation constant in pure water, Z_1, Z_2 are the charges carried out by the ions in equilibrium, and r_1, r_2 are the radii of the ions involved in equilibrium.

The plots of pK_a as a function of $1/D$ however, do not strictly show linear relationships. This indicates that the changes in pK_a with the solvent proportion, though mainly governed by dielectric constant, yet solvolysis and solvent basicities play an important role.

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SYNTHESIS OF 1-[N-SUBSTITUTED ARYL, N-(4'-DIMETHYLAMINO-3-NITRO-BENZYL)AMINO]-2-[4''(IMIDAZOLIN-2-YL AMINO) BENZOYL]-ETHANE HYDROIODIDES AS ANTIHYPERTENSIVE AGENTS

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1-([N-SUBSTITUTED aryl, N-(4'-dimethylamino-3'-nitrobenzyl) amino]-2-[4''-(imidazolin-2-yl amino) benzoyl]-ethane hydroiodides (VI) have been synthesised by the Mannich reaction of N-substituted