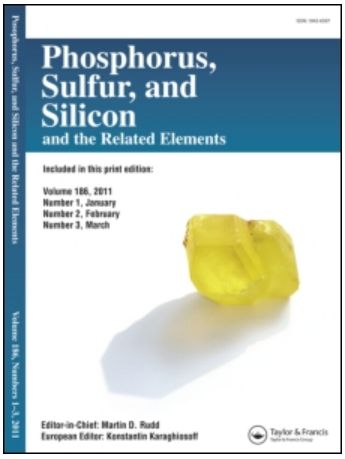

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PHOSPHORIC, PHOSPHONIC, AND PHOSPHINIC ACID AMIDES AS BASES

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PHOSPHORIC, PHOSPHONIC, AND PHOSPHINIC ACID AMIDES AS BASES

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Potentiometric titration in nitromethane, IR- and NMR-spectroscopy were used to study the processes of protonation and H-bonding for a number of phosphoric, phosphonic and phosphinic acid amides. [$(R^1_2N)_n P(O)R^2_{3-n}$ (R^1 = Me, Et; R^2 = EtO, Me, Et; n = 1–3) including 1,3,2-dioxa-, 1,3,2-oxazaphospholane and phosphorinane derivatives.] It was shown that in these compounds the center of the highest basicity is the oxygen of the phosphoryl group.

INTRODUCTION

The amides of phosphorus acids are solvents with good solvating properties due to their ability to enter into various acid-base interactions. At the same time, the acid-base properties of this important class of organophosphorus compounds have not been studied in much detail, and there is no reliable knowledge to date as to which of the atoms O or N, in the amide molecule is of the higher basicity. O-protonation[1-3] and N-protonation[4-6] of phosphoryl amides have been variously assumed in the literature to date; in some cases the parallel presence of both the N- and O-protonated forms in solutions is accepted.[7] The type of protonation for the amides of carboxylic acids is also uncertain, despite a large number of publications devoted to this problem; most researchers however favor O-protonation, as exemplified elsewhere.[8]

RESULTS AND DISCUSSION

The present work uses the methods of potentiometric titration in nitromethane,[9] IR- and NMR-spectroscopy to study the processes of protonation and H-bonding in a number of cyclic and acyclic amides of phosphorus acids. Table I lists the compounds under study, the protonation constants obtained, $pK_a(CH_3NO_2)$, the logarithm of the formation constants of the 1 : 1 hydrogen-bonded complex with p-FC_6H_4OH in CCl_4, lgK_{ass}, and O—H stretching frequency shift upon complexation, $\Delta\nu_{OH}$.

From the shape of titration curves, the amides under study can be divided into three groups (A, B, C).

A. Compounds **1–5** exhibit two potential jumps on the titration curves at 50 and 100% neutralization points (Figure 1). This suggests that in this case protonation occurs in two stages:

$$2B + H^+ \rightleftharpoons BHB^+ \text{ and } BHB^+ + H^+ \rightleftharpoons 2BH^+ \quad (1)$$

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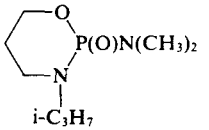
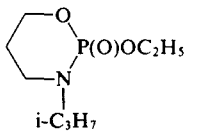
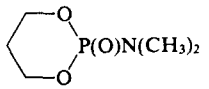
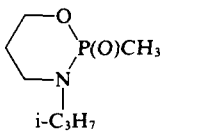
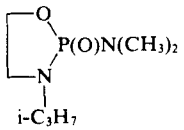
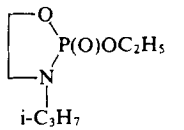
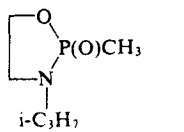
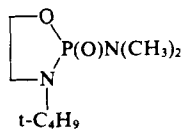
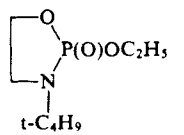
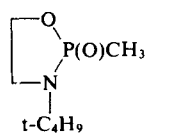
TABLE I

Values of $pK_a(CH_3NO_2)$ of the amides of phosphorus acids and the values of lgK_{ass} and $\Delta\nu_{OH}$ of H-complexes with *p*-fluorophenol in CCl_4

Group	Number	Formula of the compound	$pK_a(CH_3NO_2)$	lgK_{ass}	$\Delta\nu_{OH_{(cm^{-1})}}$
1	2	3	4	5	6
A	**1**	$(C_2H_5)_2P(O)N(C_2H_5)_2$	5.8	3.51	480
	2	$CH_3P(O)[N(C_2H_5)_2]_2$	5.7	3.54	490
	3	$C_2H_5OP(O)[N(CH_3)_2]_2$	4.5	3.18	435
	4	$[(CH_3)_2N]_3PO$	5.9	3.52	485
	5		4.1	3.26	440
B	**6**		<2	2.91	365
	7	$(C_2H_5O)_2P(O)N(CH_3)_2$	<2	2.81	385
	8		<2	2.85	365
C	**9**	$(CH_3)_2P(O)N(CH_3)_2$	(10.0)	3.32	460
	10	$CH_3P(O)[N(CH_3)_2]_2$	(8.9)	3.43	480
	11		(6.1)	3.18	420

12		(5.1)	3.06	410
13		(7.0)	2.74	350
14		(7.7)	2.99	390
15		(5.2)	3.09	405
16		(5.5)	2.77	350
17		(6.9)	2.99	385

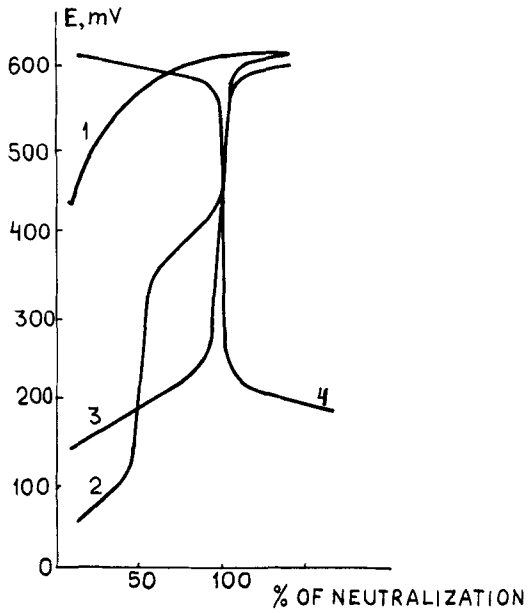
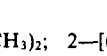


FIGURE 1 Titration curves in nitromethane

1—  P(O)N$(CH_3)_2$; 2—$[(CH_3)_2N]_3PO$; 3—$(CH_3)_2NP(O)(CH_3)_2$ (titrant—$HClO_4 \cdot 2H_2O$); 4—equimolar mixture of $(CH_3)_2P(O)OH$ + $(CH_3)_2NH_2^+ClO_4^-$ + $HClO_4$ (titrant—diphenylguanidine).

This is characteristic of oxygen bases of this class.[9,10] The values of $pK_a(CH_3NO_2)$ = 4.1–5.8 calculated for amides **1–5** are within the normal range of $pK_a(CH_3NO_2)$ values for phosphine oxides.[10] From this it is inferred that protonation of the oxygen atom occurs in compounds of group A.

For phosphine oxides and phosphinates we reported earlier the values of $pK_a(CH_3NO_2)$ and lgK_{ass} of H-complexes with para-fluorophenol[11] (Table II). These data when subjected to the least square treatment gave the linear relationship:

$$pK_a(CH_3NO_2) = (-16.4 \pm 0.2) + (6.2 \pm 0.4)\, lgK_{ass}, \quad (2)$$

with a correlation coefficient of 0.986. The points corresponding to amides **1–5** are located either on the straight line according to Eq. (2) or close to it (see Figure 2); this further favors their characterization as oxygen bases.

B. Compounds **6–8,** which contain two ester groups each, do not exhibit, any potential jumps on the titration curves (see Figure 1), due to their low basicity ($pK_a(CH_3NO_2) < 2$).

C. Amides **9–17** feature titration curves with one potential jump at the 100% neutralization point (see Figure 1), which may be a formal indication of N-protonation.[9] Moreover, the values of $pK_a(CH_3NO_2)$ and lgK_{ass} of these compounds deviate markedly from dependence 2 (see Figure 2), derived for the oxygen bases. At the same time, the potentiometric evidence alone cannot supply a conclusive judgement as to the behavior of amides of group B, since, the P—N bond in acid media is labile,[4,5] and the titration curves observed may possibly be assigned to the products of amide decomposition. The assumption that compounds **9–17** decompose during titration is justified by the discrepancy between the curves of "the direct" (perchloric

TABLE II

Values of $pK_a(CH_3NO_2)$ and lgK_{ass} of H-complexes of phosphonates and phosphine oxides with *p*-fluorophenol in CCl_4

Compound	lgK_{ass}		pK_a	
	2.98[11]		2.3[11]	
	3.13[11]		2.8[11]	
	2.94[11]		2.2[11]	
	3.10[11]		2.8[11]	
$(C_2H_5)_2P(O)OC_2H_5$	3.03[11]		2.6[11]	
$(4—CH_3C_6H_4)_2P(O)CH_3$	3.30		4.2[10]	
$(4—CH_3OC_6H_4)_2P(O)CH_3$	3.35		4.3[10]	
$(C_6H_5)_2P(O)CH_3$	3.20	this	3.2	this
$(C_6H_5)_3PO$	3.13	work	2.9	work
$(C_4H_9OCH_2)_2P(O)C_2H_5$	3.16		3.7[10]	
$(C_4H_9OCH_2)_2P(O)C_5H_{11}$	3.19		3.7[10]	this
$(C_4H_9)_3PO$	3.53		5.7	work

acid) and "back" (diphenylguanidine) titrations, as well as by the long time required for the electrode circuit potential to be established.

The interaction of amide **9** with perchloric acid in nitromethane was considered in detail by PMR-spectroscopy (Figure 3). This shows directly the cleavage of the P—N bond by the reduction in the intensity of the $N(CH_3)_2$ group proton signal (doublet, $\delta = 2.48$ ppm, $J_{NCNP} = 9.6$ Hz) and by the increase in the proton signal intensity of

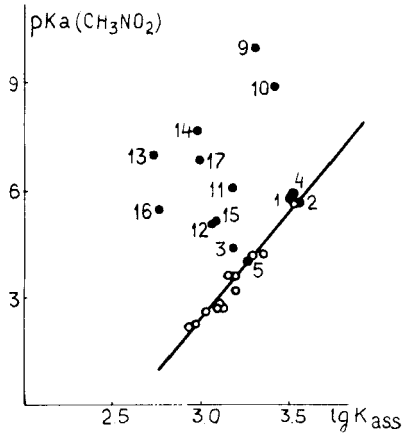


FIGURE 2 Relationship between the values of $pK_a(CH_3NO_2)$ and lgK_{ass} with *p*-FC_6H_4OH of phosphinates and phosphine oxides (○) and amides of phosphorus acids (●).

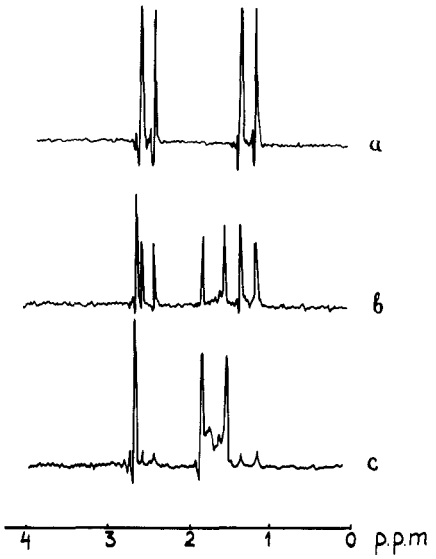


FIGURE 3 NMR-spectra in nitromethane (0.5 mol/l): a—$(CH_3)_2P(O)N(CH_3)_2$; b—$(CH_3)_2P(O)N(CH_3)_2$ + $HClO_4 \cdot 2H_2O$ (1 : 0.5 ratio); c—$(CH_3)_2P(O)N(CH_3)_2$ + $HClO_4 \cdot 2H_2O$ (1 : 1 ratio).

the methyl group of $(CH_3)_2NH_2^+ \cdot ClO_4^-$ (**18**), (singlet, δ = 2.6 ppm). The NMR-spectra show a parallel change in the intensity of the CH_3-group proton signal at the phosphorus atom. In this case the second doublet (δ = 1.63 ppm, J_{HCP} = 15 Hz) appears close to the doublet of the starting amide **9** (δ = 1.19 ppm, J_{HCP} = 13 Hz), which suggests the phosphorus atom substituent being replaced in the reaction product. The hydrolysis products of amide **9**, $(CH_3)_2P(O)OH$ **19**, and salt **18** were isolated from the reaction mixture. It is also important that the potentiometric titration curve for the equimolar mixture **18** + **19** + $HClO_4$ reproduces nearly exactly the curve of "the back" titration of amide **9** with diphenylguanidine (Figure 1).

Thus data obtained are consistent with the hydrolysis of amide **9** in the process of its titration with perchloric acid in nitromethane:

$$\underset{\mathbf{9}}{(CH_3)_2P(O)N(CH_3)_2} + HClO_4 \cdot 2H_2O \rightarrow \underset{\mathbf{19}}{(CH_3)_2P(O)OH} + \underset{\mathbf{18}}{(CH_3)_2NH_2^+ \cdot ClO_4^-} \quad (3)$$

This conclusion is probably legitimate for those other amides of group C, for which the same titration curves are observed. Their $pK_a(CH_3NO_2)$-values calculated from the titration results relate to non-equilibrium conditions, therefore they cannot be regarded as basicity constants (in Table I these values are parenthesized).

Hydrolysis of amides during titration is likely to be due to the small amount of water admitted to the solution under study together with the titrant (perchloric acid dihydrate).

To obtain data on the nature of the protonation of the hydrolytically unstable amides of group C, we made low-temperature measurements of the NMR-spectra of cyclic amides **12** and **15** in nitromethane and products of their interaction with perchloric acid at a 1 : 1.5 ratio. Hexamethylphosphoramide was used as the hydrolytically stable compound for comparison purposes, where protonation occurs at the oxygen atom of the phosphoryl group.[12] The spectra of cyclic amides **12** and **15**, measured at −30°C immediately after adding $HClO_4 \cdot 2H_2O$, do not contain any

new signals compared with the spectra of the starting compounds. This points to the absence of any noticeable hydrolysis under the experimental conditions. Protonation of amides **12** and **15** affects, primarily, the $N(CH_3)$-group proton signal, leading to an increase in the chemical shift and the coupling, J_{HCNP} (Table III). The same spectral changes are also observed on protonation of hexamethylphosphoramide (Table III).

Thus the NMR-spectral data for the reaction mixtures at low temperature (where the process of hydrolysis is markedly decelerated) indicate that protonation of hydrolytically unstable amides also occurs at the oxygen atom of the P=O group, (in the case of N-protonation J_{HCNP} would be expected to decrease[4,5]).

Consideration was also given to the interaction of amides with HCl in chloroform. The IR-spectra for the products of interaction of amides **4** and **5** are typical of the ion pairs $\geqslant POH^+ \cdots Cl^-$[13]. They feature a protonated phosphoryl group, $\nu_{POH^+} = 1010\ cm^{-1}$, and intense absorption with a complex structure (2450, 2060 and 1560 cm^{-1}) in the region of OH-vibrations. It should be noted that the spectra of the solutions remain unchanged, at least for a day. Thus amides **4** and **5**, judging by the spectral data obtained, are protonated with hydrogen chloride at oxygen:

$$R_2N-\underset{|}{\overset{|}{P}}=O + HCl \rightleftharpoons R_2N-\underset{|}{\overset{|}{POH^+}}\cdots Cl^- \qquad (4)$$

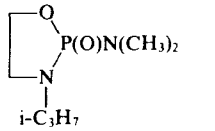
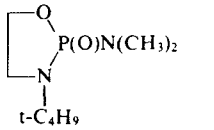
(a)

A different situation is observed in the interaction of HCl with amides **1,2,9–17**. Here, in the IR-spectra of freshly prepared solutions, an immediate appearance of the bands at 2980, 2770 and 2450 cm^{-1} of dialkylamine chlorohydrates takes place. It can be assumed that the interaction of HCl with the above compounds is accompanied by a fast cleavage of the P—N bond to give dialkylamine hydrochlorides (c) and corresponding phosphoric, phosphonic and phosphinic acid chlorides (b):

$$\underset{(b)}{\overset{O}{\overset{\|}{\geqslant P}}-NR_2} + HCl \rightleftharpoons \underset{(b)}{\overset{O}{\overset{\|}{\geqslant P}}-Cl} + \underset{(c)}{R_2NH_2^+\cdot Cl^-} \qquad (5)$$

TABLE III

Parameters of the NMR-spectra for the amides of phosphoric acid protonated with $HClO_4$ in nitromethane (a 1:1.5 amide-acid ratio, c = 1 mol/l).

Compound					$[(CH_3)_2N]_3PO$	
	δH_3CNP (ppm)	J_{HCNP} (Hz)	δH_3CNP (ppm)	J_{HCNP} (Hz)	δH_3CNP (ppm)	J_{HCNP} (Hz)
CH_3NO_2	2.61	10.3	2.63	10.3	2.53	9.3
$CH_3NO_2 + HClO_4$ (−30°C)	2.77	11.0	2.80	11.0	2.68	10.0

An interesting example of protonation with hydrogen chloride occurs for amide **3**. The initial IR-spectrum of the reaction mixture shows the protonated phosphoryl group, $\nu_{POH^+} = 1010\ cm^{-1}$, and intense absorption with a complex structure in the region of OH-vibrations (Figure 4), which suggests the formation of an O-protonated form (a). However, after some time, a set of intense bands at 2990, 2770 and 2450 cm^{-1} appears in the spectrum, characterizing $(CH_3)_2\ NH^+Cl^-$, which is accompanied by the disappearance of the OH-group absorption and the band ν_{POH^+} at 1010 cm^{-1} and appearance of the band $\nu_{P=O} = 1255\ cm^{-1}$ belonging to the acidolysis product of amide **3** (Figure 4). These spectral changes correspond to the following process:

$$[(CH_3)_2N]_2P(O)OC_2H_5 + HCl \rightleftharpoons [(CH_3)_2N]_2(C_2H_5O)POH^+ \cdots Cl^-$$

$$\xrightarrow[\text{slow}]{HCl} (CH_3)_2NP(O)Cl(OC_2H_5) + (CH_3)_2NH_2^+\ Cl^- \quad (6)$$

Thus the protonation studies of a number of cyclic and acyclic amides of phosphoric, phosphonic and phosphinic acids indicated in all cases O-protonation only, with no N-protonated form being spectrally detected. For H-bonding, all the amides under study give complexes with *p*-fluorophenol at the phosphoryl oxygen. For these complexes the following linear dependence was obtained:

$$lgK_{ass} = (0.80 \pm 0.06) + (0.55 \pm 0.03) \cdot 10^{-2} \Delta\nu_{OH},\ r = 0.980 \quad (7)$$

whose parameters agree completely with a similar correlation obtained for the H-complexes of the phosphoryl compounds with *p*-fluorophenol:[11]

$$lgK_{ass} = (0.79 \pm 0.06) + (0.55 \pm 0.02) \cdot 10^{-2} \Delta\nu_{OH},\ r = 0.983 \quad (8)$$

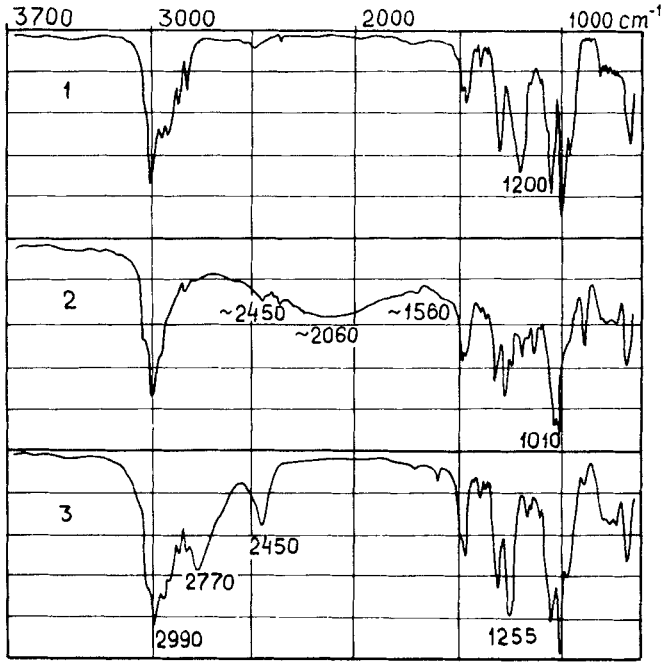


FIGURE 4 IR-spectra of solutions in $CHCl_3$ (0.07 mol/l): 1—$[(CH_3)_2N]_2P(O)OC_2H_5$; 2—$[(CH_3)_2P(O)OC_2H_5$ + HCl (freshly prepared solution); 3—the same (one day after preparation of the solution).

To conclude, the sum of the experimental data obtained suggests that the highest electronic density in the tetracoordinated phosphorus acid amides is exhibited by the oxygen atom of the phosphoryl group.

EXPERIMENTAL

The IR-spectra were measured with a UR-20 spectrometer (slit program 4, recording speed = 64 − 160 cm^{-1}/min) with the use of NaCl cells with a working layer thickness of 0.1 mm. The values of K_{ass} were measured with a Hitachi EPS-3T spectrometer in thermostatted quartz cells with a working layer thickness of 10 cm at 25 ± 0.1°C. These values were calculated according to the equilibrium:

$$\geqslant P = O + HOC_6H_4F - p \overset{K_{ass}}{\rightleftharpoons} \geqslant P{=}O \cdots HOC_6H_4F\text{-}p \qquad (9)$$

by the formula:

$$K_{ass} = x/(a - x)(b - x) \qquad (10)$$

where x = equilibrium concentration of the H-complex, calibrated from the peak intensity of the free OH-band of *p*-fluorophenol at 1420 mn; a and b = initial concentrations of the phenol ($1.5 \cdot 10^{-3}$ mol/l) and the base ($0.8–2.5 \cdot 10^{-3}$ mol/l), respectively.

The ^{1}H-NMR-spectra were recorded at 90 MHz with a Perkin-Elmer R-32 spectrometer in parts per million downfield from TMS.

The protonation constants of the bases, pK_a, were determined by potentiometric titration at 25 ± 0.1°C, using a pH-340 pH meter: electrodes—glass, type HHT, and calomel, manufactured by "Radiometer", type K 401. The electrode couple was calibrated by means of picrate buffers. A solution of a 72% $HClO_4$ (0.1 mol/l) in nitromethane was used as the titrant. The concentration of the compounds studied was $4 \cdot 10^{-3}$ mol/l.[14]

The phosphoryl compounds under study were synthesized by the usual methods, their physical constants agreeing with literature data; the compounds (as given by gas-liquid chromatography) were better than 98%.

Hydrolysis of Dimethylphosphinic Acid N,N-dimethylamide

To 2.5 g of amide in 20 ml of CH_3NO_2 was added a solution of 2.9 g of 72% $HClO_4$ in 5 ml of CH_3NO_2 at 20–25°C. After half an hour the solvent was distilled off in vacuo. The precipitated crystalline substance was dried over P_2O_5 and extracted with hot benzene (3 × 5 ml). 1.4 g (72%) of dimethylphosphinic acid were isolated from the cooled benzene solution m.p. = 89°C (Ref. 15: m.p. = 88.5–90.5°C). PMR— and IR—spectra identify the crystalline substance left after benzene treatment as dimethylammonium perchlorate.

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