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INFLUENCE OF SOLVENT ON THE STRENGTH OF CYCLIC OXYGEN-CONTAINING PHOSPHORUS ACIDS

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In the study of strength of cyclic oxygen-containing phosphorus acids (CPA) in various media, cases were observed of systematic deviations of 1,3-alkylenephosphoric acids from the general Brönsted dependences: $pK(S) = \alpha pK(H_2O) + \text{const}$, derived for "standard" phosphorus acids $ABPOOH$ (where A, B = H, Alk, AlkO, Ar, cyclo- C_6H_{11}) [1]. The reason for the deviations may be the anomalies of solvation of six-membered cyclic phosphoric acids, but it is still unclear how these anomalies are related to the nature of the solvent and the structure of the compounds studied.

In the present work, we selected absolute alcohol as a solvent in which acyclic phosphorus acids were studied previously [2-4], for measuring the dissociation constants of the CPA. Using 1,3-propylene- and 1,4-butylenephosphoric acids as examples, we examined the influence of size and conformational rigidity of the ring on the solvation of alkylene phosphoric acids in different media.

EXPERIMENTAL

The dissociation constants of the acids were determined by potentiometric titration in charge-transfer circuits, in absolute alcohol at 25°C [2]. The dissociation constants of 1,4-butylenephosphoric acid were also measured in water and in $MeNO_2$, as described in [1]. The acids studied were synthesized and purified as described in [1].

2-Hydroxy-2-oxo-1,3,2-dioxaphosphhepane was obtained by hydrolysis of the corresponding chlorophosphate, mp 128-129°C (benzene) (cf. [5]).

DISCUSSION OF RESULTS

We compared the values of $pK(S)$ of cyclic and acyclic phosphorus acids in water, absolute alcohol, and $MeNO_2$ (Tables 1, 2). On transition from water to ethanol and from water to $MeNO_2$, the strength of the acyclic acids changes in accordance with the Brönsted equations (1) and (2)

$$\begin{aligned} pK(EtOH) &= 4.90 + 1.18 pK(H_2O) * & (1) \\ n &= 8, r = 0.986, S = 0.16, Sp = 0.08 \\ pK(MeNO_2) &= 6.86 + 2.05 pK(H_2O) [1] & (2) \\ n &= 9, r = 0.993, S = 0.22, Sp = 0.09 \end{aligned}$$

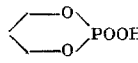
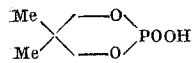
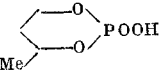
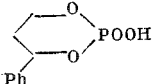
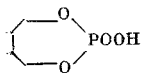
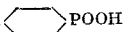
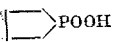
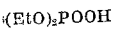
while for the six-membered CPA (I)-(IV) (see Table 2) these equations did not hold.[†] On Fig. 1, the points corresponding to acids (I)-(IV) deviate statistically reliably from the general linear dependences (1), (2). At the same time, 1,4-butylenephosphoric acid (V) and CPA (VI), (VII) in both cases (see Fig. 1) obey the corresponding equations (1), (2).

A question arises as to which of the solvents used, water, alcohol, or $MeNO_2$, causes the deviation from the Brönsted rule, and which structural features of the acids promote this? We

*Calculated according to the data in Table 2.

[†]The deviation of acids (I)-(IV) from the Brönsted dependence has been described in [1].

TABLE 1. Dissociation Constants (pK) of CPA in Various Solvents

Acid		H ₂ O	EtOH	MeNO ₂
	(I)	1.87 [1]	6.15	9.27 [1]
	(II)	1.67 [1]	6.06	9.14 [1]
	(III)	1.75 [1]	6.42	9.40 [1]
	(IV)	1.67 [1]	5.92	8.94 [1]
	(V)	1.58	6.51	10.02
	(VI)	3.18 [1]	8.54	13.87 [1]
	(VII)	2.84 [1]	8.09	12.80 [1]
	(VIII)	1.37 [6]	6.79 [4]	9.90 [1]

compared the pK (S) values of the acids studied (see Tables 1, 2) in the alcohol-MeNO₂ coordinates and obtained one single Brönsted dependence (see Fig. 2) general for all acids

$$\begin{aligned} \text{pK}(\text{MeNO}_2) &= -1.95 + 1.80 \text{pK}(\text{EtOH}) \\ n &= 16, r = 0.990, S = 0.27, S_p = 0.08 \end{aligned} \quad (3)$$

Hence, the anomalies of hypersolvation of six-membered cyclic phosphoric acids, compared with their acyclic and seven-membered analogs, are observed only on transition from water to anhydrous media. In other words, a change in the free energy of solvation of the anions and molecules of 1,3-alkylenephosphoric acids on transition from water to anhydrous solvents differs from that for "standard" acids, while on transition from alcohol to MeNO₂, these changes are similar for all acids.

We tried to make a quantitative assessment to determine in which of the solvents the free energy of solvation of these two groups of acids differs. For this purpose, we compared the strength of six-membered CPA (I)-(IV) and diethylphosphoric acid (VIII) in each solvent (see Table 1). In absolute alcohol and in MeNO₂, acids (I)-(IV) are stronger than (VIII), while, on the contrary, in water, the cyclic acids (I)-(IV) are weaker than the "standard" acid (VIII). It can be assumed that the acidity ratio of the compared compounds in MeNO₂ and absolute alcohol corresponds more to the ratio of the "internal" (i.e., not complicated by solvation) acidity, which is determined by the electronic influence of the substituents.

According to the quantum-chemical calculations [8, 9], in six-membered cyclophosphates, the positive charge on the P atom is higher than in acyclic phosphates. Accordingly, the acidity of six-membered cyclic phosphoric acids should be higher than that of dialkylphosphoric acids. This conclusion was reached from examination of the experimental data on the acidity of phosphorus acid esters in the gaseous phase [10]. The proton affinity is higher in trimethyl phosphite (222.3 kcal/mole) than in methyl 1,3-propylene phosphite (221.5 kcal/mole) [10]. Thus, the acidity ratio of six-membered cyclic and acyclic phosphoric acids in anhydrous media (absolute alcohol and MeNO₂) corresponds to the ratio of the internal acidities of these compounds, while the acidity ratio in water is contrary to this ratio and hence, is caused by specific hydration.

A second aspect of the problem consists in the influence of structural factors of the acids on the occurrence of anomalous hydration and deviations from the Brönsted rule. It was shown [1] that the solvation features of 1,3-alkylenephosphoric acids are related to the pres-

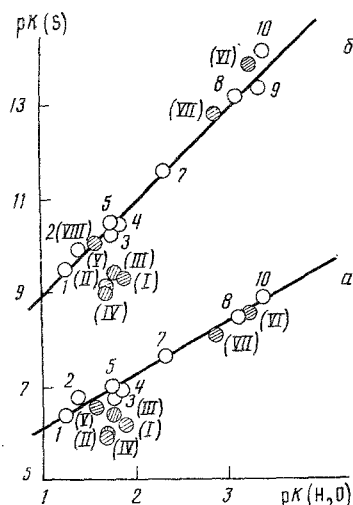


Fig. 1

Fig. 1. Comparison of $pK(S)$ and $pK(H_2O)$ values of acyclic and CPA. The numeration corresponds to that in Tables 1 and 2. $S = EtOH, MeNO_2$. Lines (a), (b) correspond to Brönsted dependences (1) and (2) for the $ABPOOH$ acids.

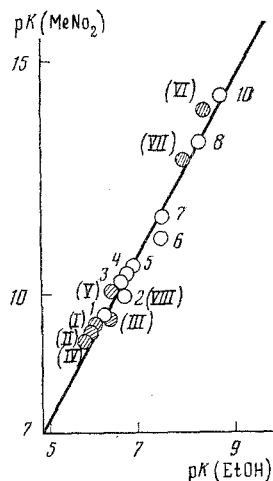


Fig. 2

Fig. 2. Dependence of $pK(MeNO_2)$ on $pK(EtOH)$ for acyclic and CPA. The line corresponds to Eq. (3), the numeration of the compounds corresponds to that in Tables 1 and 2.

TABLE 2. Dissociation Constants (pK) of Acyclic Phosphorus Acids $ABPOOH$ in Various Solvents

Ord. No.	A	B	H_2O	$EtOH$	$MeNO_2$
1	MeO	MeO	1,25 [6]	6,37 [4]	9,50 [1]
2	EtO	EtO	1,37 [6]	6,79 [4]	9,90 [1]
3	Ph	H	1,75 [7]	6,73 [4]	10,20 [1]
4	$p-CH_3C_6H_4$	H	1,83 [7]	6,89 [4]	10,41 [1]
5	$n-BuO$	$n-BuO$	1,72 [6]	6,97 [4]	10,49 [1]
6	Ph	Ph	—	7,61 [4]	11,12 [1]
7	Me	EtO	2,30 [1]	7,65 [4]	11,61 [1]
8	Me	Me	3,05 [6]	8,45 [4]	13,18 [1]
				8,33 [3]	
9	Et	Et	3,29 [6]	—	13,36 [1]
10	$n-Bu$	$n-Bu$	3,32 [3]	8,91 [4]	14,19 [1]
			3,41 [6]	8,73 [3]	

ence of O atoms in the ring. However, the data on the acidity of 1,4-butylenephosphoric acid (V) obtained in the present work show that in contrast with the six-membered (I)–(IV), the seven-membered acid (V) is solvated in all solvents in the same way as the acyclic acids.

According to x-ray diffraction analysis data [11–13], the geometry of the phosphorus tetrahedron practically does not change in 1,3-propylene-, 1,4-butylen- and diethylphosphoric acids. At the same time, the molecules of these acids have different conformational mobilities. 1,3,2-Dioxaphosphorinanes are conformationally more rigid systems than seven-membered cyclophosphates and even more so than acyclic phosphates [14]. The anomaly of hydration of six-membered cyclic phosphoric acids can possibly be related to the conformational rigidity of the 1,3,2-dioxaphosphorinane ring, in which the most convenient conformation for the hydration is not obtained. Consequently, these acids are weaker in water, as should have been expected from their "internal" acidity.

Thus, analysis of the influence of the solvent on the strength of cyclic and acyclic phosphorus acids led to the conclusion that the specific hydration is the reason for the deviations of the six-membered cyclic phosphoric acids from the general Brönsted dependences.

CONCLUSIONS

The dissociation constants of cyclic oxygen-containing phosphorus acids in absolute alcohol were measured by potentiometric titration in charge transfer circuits.

For acyclic phosphorus acids ABPOOH, there is a Brönsted dependence in $pK(\text{EtOH})-pK(\text{H}_2\text{O})$ coordinates, which does not apply to 1,3-alkylenephosphoric acids, while in the $pK(\text{MeNO}_2)-pK(\text{EtOH})$ coordinates there is a uniform Brönsted dependence for all the acids.

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REACTIVITY OF LANTHANIDE AND ACTINIDE IONS AT THEIR LOWEST OXIDATION LEVEL WITH Cl_2^- , Br_2^- , AND I_2^- IONS IN AQUEOUS SOLUTION AS DETERMINED BY PULSE RADIOLYSIS

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There has been relatively little research on the reactivity of metal ions with free inorganic radicals (Cl_2^- , Br_2^- , I_2^- , NO_3 , HSO_4 , SO_4^- , etc.) in aqueous solution, especially in concentrated solutions. Since such information is important in radiation chemistry, in the chemical kinetics of fast reactions, and for the prediction of radiochemical processes in some solutions that are employed in practice, we have made a systematic study of the problem. For this purpose, we have employed pulse radiolysis and recorded short-lived particles spectrophotometrically [1-4]. This paper presents data on the reactivity of Cl_2^- , Br_2^- , and I_2^- with lanthanide and actinide ions at their lowest oxidation levels [Eu(II), Yb(II), Sm(II), U(III), Np(III), and Pu(III)].

EXPERIMENTAL

Rate constants were measured with fast-response microsecond- and nanosecond-range spectrophotometric installations based on a U-12 linear electron accelerator (energy $E = 5$ MeV, pulse length $\tau = 2.3$ μsec) and an Elektronika linear accelerator ($E = 8$ MeV, $\tau = 15$ nsec).

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