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DISSOCIATION CONSTANTS FOR POLYFLUORO ACIDS OF PHOSPHORUS IN VARIOUS MEDIA

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UDC 541.124.7:547.1'118'161

The present work extended our earlier studies on the dissociation of the acids of phosphorus in various media (cf. [1]) to include the polyfluoro acids of the element. There is little information on the effect of polyfluoro substituents on the dissociation of the phosphorus acids [2, 3]. It is, at the same time, interesting to study the electronic effects arising from the presence of polyfluoro groups at the P atom, CF_3 being the only aliphatic group of this kind for which data are presently available ($\sigma^{\Phi} = + 0.7$ [4], with an error of ± 0.3 [5]). With a view to obtaining additional data in this field, we have synthesized the polyfluoro acids of phosphorus listed in Table 1, and measured their dissociation constants in 50, 80, 95, and 100% alcohol, and nitromethane.

Bis(2,2,2-trifluoroethyl)phosphoric acid (I) was prepared by alkaline hydrolysis of tris(2,2,2-trifluoroethyl) phosphate, and acidifying the reaction mixture. Bis(2,2,3,3-tetrafluoroethyl)phosphoric acid (II), bis-(1,1-dihydroperfluorobutyl)phosphoric acid (III), and bis(3,3,3-trifluoropropyl)phosphoric acid (V) were prepared through alkaline hydrolysis of the respective bis(polyfluoroalkyl) chlorophosphates. The potassium salt of bis(1,5-trihydroperfluoropentyl)phosphoric acid (IV) was obtained through alkaline hydrolysis of tris(1,1,5-trihydroperfluoropentyl) phosphate. Bis(3,3,3-trifluoropropyl)phosphonic acid (VI) was synthesized by the method outlined in [8]. Bis(pentafluorophenyl)phosphoric acid (VII) was prepared by the hydrolysis of tris(pentafluorophenyl) phosphate in air. The acids (II)-(IV) have been described in the patent literature (cf. Table 1), but have not yet been characterized in detail.

The fact that the direct and reverse titration curves of each of these acids were identical, while the calculated and measured neutralization equivalents were identical for each, was taken as an indication that each was stable toward hydrolysis under our working conditions.

EXPERIMENTAL

Bis(2,2,2-trifluoroethyl)phosphoric Acid (I). A mixture containing 17.2 g (0.05 mole) of tris(2,2,2-trifluoroethyl) phosphate, 3.4 g (0.06 mole) of KOH, and 10 ml of water was boiled for 30 min; at the end of this time 30 ml of water and 7 ml of concentrated HCl were added, and the mixture extracted with ether (4 × 25 ml). The extract was dried over anhydrous $MgSO_4$, and distilled. This procedure gave an 81.7% yield (10.7 g) of (I) in the form of a colorless viscous liquid.

Bis(2,2,3,3-tetrafluoropropyl)phosphoric Acid (II). A mixture containing 34.4 g (0.1 mole) of bis(2,2,3,3-tetrafluoropropyl) chlorophosphate, 14.0 g (0.25 mole) of KOH, and 20 ml water was stirred for 1.5 h, at the end of which time 20 ml of concentrated HCl, 40 ml of water, and 100 ml of ether were added to it. The resulting water layer was extracted with ether (3 × 15 ml). The extract and the organic layer were combined, dried over anhydrous $MgSO_4$, and distilled. This procedure gave a 91.7% yield (29.9 g) of (II) as a colorless viscous liquid.

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TABLE 1. Polyfluoro Acids of Phosphorus

Compound	Formula	bp, °C (p, mm Hg) or mp, °C	n^{20}_D	d_4^{20}	Found/Calculated, %				Found/Calculated		Empirical formula
					C	H	F	P	MR	neutralization equiv.	
(I)	$(CF_3CH_2O)_2POOH$	122–124(1)	1,3378	1,6257	18,17/18,33	1,93/1,92	43,61/43,50	11,73/11,82	33,59/33,39	262,0/262,1	$C_4H_5F_6O_4P$
(II)	$(HCF_2CF_2CH_2O)_2POOH$ [6]	163–165(0,5)	1,3539	1,6686	22,12/22,10	2,28/2,16	47,29/46,61	9,26/9,50	42,47/42,91	326,3/326,1	$C_6H_7F_8O_4P$
(III)	$(CF_3CF_2CF_2CH_2O)_2POOH$ [7]	143–144(0,5)	1,3206	1,7249	20,8/20,8	1,1/1,1	57,1/57,6	6,6/6,7	53,24/52,99	462,7/462,1	$C_8H_5F_{14}O_4P$
(IV)	$(HCF_2CF_2CF_2CF_2CH_2O)_2POOK$ *	Melted above 200°	–	–	21,50/21,29	1,14/1,07	54,02/53,83	5,44/5,49	–	564,0/564,2	$C_{10}H_6F_{16}KO_4P$
(V)	$(CF_3CH_2CH_2O)_2POOH$	147–149(10^{-3})	1,3624	1,5271	24,8/24,8	3,0/3,1	39,4/39,3	10,5/10,7	42,17/42,63	291,7/290,1	$C_6H_9F_6O_4P$
(VI)	$(CF_3CH_2CH_2)_2POOH$ [8]	66,5–68,5	–	–	–	–	–	–	–	258,2/258,1	–
(VII)	$(C_6F_5O)_2POOH$	137–138 (from hexane)	–	–	33,50/33,51	0,24/0,23	44,17/44,17	7,05/7,20	–	430,0/430,1	$C_{12}HF_{10}O_4P$

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* The boiling point of $(H(CF_2)_4CH_2O)_2POOH$ is 200°C (5 mm) [7].

TABLE 2. Dissociation Constants (pK) for R_2POOH Polyfluorophosphoric Acids

Acid	R	pK				
		EtOH				CH_3NO_2
		50%	80%	95%	100%	
(I)	CF_3CH_2O	2,42	2,70	3,78	4,05	6,38
(II)	$H(CF_2)_2CH_2O$	2,46	2,69	3,71	4,15	6,38
(III)	$F(CF_2)_3CH_2O$	2,47	2,69	3,69	4,18	6,35
(IV)	$H(CF_2)_4CH_2O$	2,43 *	2,70 *	3,74 *	–	–
(V)	$CF_3CH_2CH_2O$	2,45	2,68	3,82	5,68	8,48
	CH_3CH_2O	2,61 [1]	3,17 [1] 3,15 [13, 14]	4,66 [1]	6,79	9,90 [1]
(VI)	$CF_3CH_2CH_2$	3,04	3,76	5,06	6,66	10,76
(VII)	C_6F_5O	2,36	2,67	3,60	3,27	4,02
	C_6H_5O	2,28 [14]	2,71 [14]	3,58 [15]	4,81 [15]	7,31

* Potassium salt.

TABLE 3. Dissociation Constants for Certain ABPOOH Acids of Phosphorus in Various Solvents

A	B	pK			
		80% EtOH	95% EtOH	100% EtOH	CH_3NO_2
CH_3O	CH_3O	3,01 [13, 14]	4,58 [1]	6,37	9,50 [1]
C_2H_5O	C_2H_5O	3,15 [13, 14] 3,17 [1]	4,66 [1]	6,79	9,90 [1]
C_6H_5	H	–	4,76 [1]	6,73	10,20 [1]
p-$CH_3C_6H_4$	H	–	5,00 [1]	6,89	10,41 [1]
C_4H_9O	C_4H_9O	–	5,06 [1]	6,97	10,49 [1]
C_6H_5	C_6H_5	4,24 [14]	5,80 [1]	7,61	11,12 [1]
CH_3	C_2H_5O	4,41	5,60 [1]	7,65	11,61 [1]
cyclo-C_6H_{11}	C_6H_5	5,23	6,65 [1]	–	12,65
CH_3	CH_3	5,15 [14]	6,64 6,72 [15]	8,45 8,33 [15]	13,18 [1]
n-C_4H_9	n-C_4H_9	5,63 [14]	7,17 7,10 [15]	8,91 8,73 [15]	14,19 [1]
cyclo-C_6H_{11}	cyclo-C_6H_{11}	6,53	–	–	14,56 [1]

Bis(1,1-dihydroperfluorobutyl)phosphoric Acid (III). To a vigorously stirred solution containing 3.8 g (0.068 mole) of KOH dissolved in 60 ml distilled water, 15.3 g (0.032 mole) of bis(1,1-dihydroperfluorobutyl) chlorophosphate was rapidly added dropwise. This mixture was stirred, first for 2 h at ~ 20°C, and then for 2 h at 80-90°C; to it there was then added, still under agitation, 5 ml of concentrated HCl, the stirring continued for an additional 30 min, and the mixture extracted with ether. The extract was dried over anhydrous $MgSO_4$, and distilled. This procedure gave an 42% yield (6.2 g) of (III) in the form of a viscous oil.

Potassium Salt of Bis(1,1,5-trihydroperfluoropentyl)phosphoric Acid (IV). A mixture containing 148.0 g (0.2 mole) of tris(1,1,5-trihydroperfluoropentyl) phosphate, 11.2 g (0.2 mole) of KOH, and 40 ml of water was stirred for 3 h at 90-100°C. The volatile reaction products were pumped off, and the residue dried by azeotropic distillation of water and benzene. The resulting salt was purified by precipitation of the benzene from acetone solution, and dried in vacuum. This procedure gave a 98.9% yield (111.1 g) of the salt (IV) as a white, easily vaporized powder which did not melt, even when heated to 200°C.

Bis(3,3,3-trifluoropropyl)phosphoric Acid (V). To a stirred solution containing 4.9 g (0.088 mole) of KOH dissolved in 60 ml of distilled water, there was added dropwise 13.2 g (0.043 mole) of bis(3,3,3-trifluoropropyl) chlorophosphate, and the temperature of the mixture raised to 40°C. The mixture was stirred, first for 1 h at ~ 20°C, and then for another 1 h at 90-95°C, extracted with ether, and the extract acidified with 7.5 ml of concentrated HCl. The acid which separated out was extracted with ether, the extract dried over anhydrous $MgSO_4$, and distilled. This procedure gave a 67% yield (8.3 g) of (V).

Bis(pentafluorophenyl)phosphoric Acid (VII). A solution containing 1.4 g of tris(pentafluorophenyl) phosphate dissolved in 30 ml of hexane was filtered, and held in an open container for 6 h. The needle-like crystals which separated out were washed with hexane (2 × 5 ml), and vacuum dried. This procedure gave a 29.7% yield (0.3 g) of (VII).

Butylbis(1,1-dihydroperfluorobutyl) Phosphate. To a suspension containing 1.15 g (0.05 g-atom) metallic Na and 20 ml of absolute ether there was added dropwise and with constant agitation, 18.0 g (0.09 mole) of 1,1-dihydroperfluorobutanol, then 50 ml of absolute ether, and then dropwise a solution containing 4.8 g (0.025

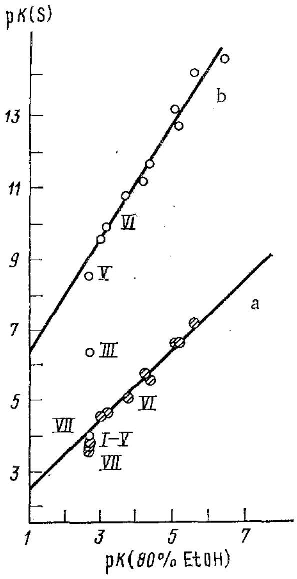

Fig. 1. Comparison of pK values for polyfluoro acids of phosphorus, (I)-(VII), in 95% EtOH and in CH_3NO_2 (S), and in 80% EtOH solution (numeration as in Table 1). The lines *a* and b are plots of the Brönsted equations (1) and (2) for nonfluorinated ABPOOH acids of phosphorus.

mole) of n-butyldichlorophosphate dissolved in 50 ml of absolute ether. The resulting mixture was stirred for 0.5 h, and then allowed to stand overnight. At the end of this time it was washed with water (3 × 50 ml), dried over anhydrous $MgSO_4$, and distilled. This procedure gave a 52% yield (7.1 g) of butylbis(1,1-dihydroperfluorobutyl) phosphate, bp 85-86°C (1 mm), n_D^{20} 1.3361; d_4^{20} 1.5041. Found: C 27.8; H 2.6; F 51.2%; MR_D 71.45. $C_{12}H_{13}F_{14}O_4P$. Calculated: C 27.8; H 2.5; F 51.3%; MR_D 71.46. (cf. [9]).

Tris(3,3,3-trifluoropropyl)phosphine Oxide. To a Grignard reagent containing 12.2 g (0.5 g-atom) of Mg, and 66.3 g (0.5 mole) of 3,3,3-trifluoro-1-chloropropane dissolved in 250 ml of absolute ether, there was added, dropwise under continuous stirring, 12.8 g (0.083 mole) of $POCl_3$ dissolved in 100 ml of absolute ether, addition being made at 0°C over a period of 45 min. The resulting mixture was stirred for 2 h at ~ 20°C, allowed to stand overnight, and then treated with 110 ml of 1:1 HCl. The white crystalline product was filtered off, washed with cold water and a small amount of ether, the resulting solution dried over anhydrous $MgSO_4$ and the ether eliminated from it under vacuum. This procedure gave a 96% yield (27.0 g) yield of tris(3,3,3-trifluoropropyl)phosphine oxide which sublimed above 130°C, and had a sealed-capillary mp of 195.5°C (from absolute benzene). Found: C 32.2; H 3.3; F 50.1; P 9.0%. $C_9H_{12}F_9OP$. Calculated: C 32.0; H 3.6; F 50.6; P 9.2%.

The syntheses of tris(2,2,2-trifluoroethyl) phosphate, tris(3,3,3-trifluoropropyl) phosphate, and tris(1,1-dihydroperfluorobutyl) phosphate have been described in [10].

The dissociation constants for the various acids were determined by potentiometric titration in transference cells, working in aqueous-alcoholic solution, nitromethane [1], or absolute alcohol [11]. Because of the low solubilities of the various compounds, no attempt was made to carry out measurements on aqueous solutions. Solutions containing HCl dissolved in the respective solvents at 0.5 N concentration were used for titrating the potassium salts in aqueous-alcoholic and alcoholic solution; in titrating the 50 and 80% alcoholic solutions, the initial concentration of the acid (salt) was built up to $5 \cdot 10^{-3}$ mole/liter so that the logarithmic dilution would not exceed the pK value [12]. The values of the dissociation constants obtained from titrating aqueous-alcoholic solutions of the acid and its salt were identical.

The IR spectra of the CCl_4 solutions of the phenol–phosphoryl compound complexes were obtained with a UR-20 spectrometer, using one-piece NaCl cells and working at a 10 ml layer depth with solutions of 10^{-3} mole/liter concentration.

DISCUSSION OF RESULTS

Analysis of the pK values of Table 2 indicated that the introduction of polyfluoroalkyl radicals into the various acids markedly increased the acid strength without, however, changing the general rules covering the effect of alterations in the P-atom environment, the strength of each fluorodialkylphosphoric acid, (I)-(V), being higher than that of the corresponding dialkylphosphonic acid, (VI), in each solvent.

Within the limits of experimental error, the pK value of each bis(polyfluoroalkyl)phosphoric acid, (I)-(IV), was the same, regardless of whether determination was based on the results of titration in one or the

TABLE 4. Estimated Values of the σ^{Φ} Constants for Polyfluoro-Substituents

R	$\sigma\Phi$ *					$\sigma\Phi$ †
	EtOH				CH_3NO_2	CCl_4
	50%	80%	95%	100%		
CF_3CH_2O	−0,15	0	+0,16	+0,90	+0,60	+0,51
$H(CF_2)_2CH_2O$	−0,16	0	+0,19	+0,85	+0,60	—
$F(CF_2)_3CH_2O$	−0,17	0	+0,20	+0,84	+0,61	+0,49±0,02
$H(CF_2)_4CH_2O$	−0,15	0	+0,18	—	—	—
$CF_3CH_2CH_2O$	−0,16	0	+0,15	+0,20	+0,11	−0,06
$CF_3CH_2CH_2$	−0,40	−0,43	−0,34	−0,22	−0,41	−0,42

* Calculated from pK (R_2POOH).

† Calculated from $-\Delta H_{as}$.

TABLE 5. Characteristics of the H-bonds in Phosphoryl Complexes with Phenol, in CCl_4 Solution, and Values of the σ^{Φ} Constants for Polyfluoro Substituents

Compound	$\Delta\nu$, cm^{-1}	$-\Delta H$, kcal/mole*	σ^{Φ}
$(CF_3CH_2O)_3PO$	168	3,75	+0,51
$(CF_3CF_2CF_2CH_2O)_3PO$	168	3,75	+0,51
$(CF_3CF_2CF_2CH_2O)_2P(O)OC_4H_9$	218	4,42	+0,47
$(CF_3CH_2CH_2O)_3PO$	258	4,90	−0,06
$(CF_3CH_2CH_2)_3PO$	328	5,63	−0,42

* Calculated from Eq. (4).

other of the various solvents. Thus, an increase in the length of the polyfluoroalkyl component of the R_FCH_2O substituent at the P atom had practically no effect on the acid strength. This was in line with the work of [16] on the effect of polyfluorination of the carboxylic acid and alcohols. Since the σ^* constants for the F atom and the CF_3 group are close in value (3.08 and 3.00; 2.85 according to [17]), the replacement of an F atom by a CF_3 group in a polyfluoroalkoxyl substituent, or the lengthening of the polyfluoroalkyl component of the substituent, could be expected to have only minor effect on the acid strength.

On the other hand, it could be anticipated that the elimination of a fluorinated group from the reaction center would lead to a reduction in the acid strength. In fact, acid (V) was some two orders stronger than acid (I) in nitromethane solution. The strengths of these two acids were, however, identical in 80% aqueous-alcoholic solution, and this despite the fact that a difference of 1.3 orders would have been predicted from Eq. (2) (vide infra) and the measured difference in strengths in nitromethane solution. The fact that differences in acid strengths tend to be less pronounced in aqueous-alcoholic solution than in aprotic dipolar solvents has also been reported in [18]. The effect in question seems, however, to be especially marked in the polyfluorophosphoric acids. Comparison showed that although acid (I) was stronger than its unfluorinated $(EtO)_2POOH$ prototype in each solvent, the difference varied from 3.5 and 2.6 orders in CH_3NO_2 and EtOH, respectively, to 0.2-0.5 orders in 50 and 80% EtOH. Similar relations were observed in the diarylphosphoric acids. The difference in the acid strengths of bis(pentafluorophenyl)-phosphoric acid (VII) and its $(PhO)_2POOH$ prototype was three orders in nitromethane solution, 1.5 orders in absolute alcohol, and essentially zero in aqueous-alcoholic solution. In distinction to the phosphoric acids, however, the difference in strength of (VI), a fluorophosphonic acid (cf. Table 2), and Bu_2POOH, an unfluorinated dialkylphosphonic acid (Table 3) was essentially the same, in alcohol (2.2 pH units) and in aqueous-alcoholic solution (1.9-2.1 pK units).

Figure 1, a plot of pK (95% EtOH) vs pK (80% EtOH), shows that each of the acids studied here followed the Brönsted equation: $pK(S_1) = \alpha pK(S_2) + \text{const}$, in the form applicable to the nonfluorinated phosphorus acids (Table 3), the latter serving as comparison "standards."

$$\begin{gathered} pK\ (95\%\ \text{EtOH}) = 1.57 + 0.98\ pK\ (80\%\ \text{EtOH})^{\dagger} \\ n = 7,\ r = 0.992,\ s = 0.14,\ s_{\rho} = 0.06 \end{gathered} \qquad (1)$$

Deviations from this type behavior were observed, however, when similar comparisons were set up using data on the fluoro acids in nitromethane and in absolute alcohol. By way of illustration, a pK (CH_3NO_2) vs pK (80% EtOH) plot is included in Fig. 1. Here, the points for the acids (I)-(III) and (VII) depart markedly from the line for (2), the "standard acid" form of Brönsted equation

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†Calculated from the data of Table 3.

$$pK\,(CH_3NO_2) = 4.95 + 1.53\,pK\,(80\%\ EtOH)^{*}$$
$$n = 8,\ r = 0.981,\ s = 0.42,\ s_{\rho} = 0.13 \qquad (2)$$

The data on the phosphonic acid (VI) and the phosphoric acid (V) did, however, satisfy this latter relation. This might be indication that the solvation of the standard acids and the polyfluoro acids, (I)-(IV), (VII), and/or their anions are affected differently on passing from aqueous solvents to anhydrous solvents such as nitromethane. Formally such difference could be expected from the presence of two polyfluoro groups, R_FCH_2O and Ar_FO, at the P atom. The result of removing the O atom from the molecule (phosphonic acid (VI)), or eliminating the fluoro group from a reaction center (acid (V)), should be that the change in polyfluoro acid solvation on passing from aqueous alcoholic solution to nitromethane or absolute alcohol would be exactly the same as that of the "standard" phosphorus acid.

Since the Hammett and Brönsted equations are interrelated, these same differences also appeared in the σ^{Φ} substituent constants calculated from the pK values of the various acids. Unfortunately, the available data are too limited to permit the calculation of completely trustworthy values of these constants. The σ^{Φ} values calculated from (3), and from the various forms of Hammett equation given in the literature† are therefore only provisional (Table 4). General tendencies did appear, however; when analyzed, these tendencies permitted certain conclusions concerning solvent effects to be drawn.

The form of Hammett equation shown as (3) below was developed from our measured pK_α (EtOH) values for nonfluorinated acids of phosphorus ("standard" acids) (cf. Table 3) and used for calculating σ^{Φ} values for solutions in absolute alcohol

$$pK_a\,(EtOH) = 6.15 - 1.17\Sigma\sigma^{\Phi\,\ddagger}$$
$$n = 9,\ r = 0.992,\ s = 0.14,\ s_{\rho} = 0.07 \qquad (3)$$

The effect of the solvent on the σ^{Φ} value of the polyfluoroalkoxyl substituent was studied by determining this value by the IR spectroscopy of CCl_4 solutions. This involved measuring the phenolic $\Delta\nu_{OH}$ in the IR spectra of the various $R_3(PO)$ H-complexes, followed by calculation of $-\Delta H$ and σ^{Φ} [19] through Eqs. (4) and (5)

$$(\Delta H)^2 = 0.11\,(\Delta\nu_{OH} - 40) \qquad (4)$$

$$-\Delta H = 4.78 - 0.67\Sigma\sigma^{\Phi} \qquad (5)$$

Measured and calculated values are given in Table 5.

It can be seen from Table 5 that the σ^{Φ} values for the polyfluoroalkoxyl substituents were not actually constant, their variation being particularly pronounced on passing from nonaqueous to aqueous media. In the case of the polyfluoroalkoxyl substituents, the σ^{Φ} value was found to rise continually as the concentration of alcohol in the solvent increased. This increase proceeded rather slowly, going from −0.15 to −0.17 in 50% alcohol solution, to 0 in 80% solution, to 0.15-0.20 in 95% solution. Passage from the 95% solution to absolute alcohol brought about a rapid rise of σ^{Φ} to 0.84-0.90. The σ^{Φ} values for these groups were considerably higher in the anhydrous solutions than in the aqueous solutions, varying from 0.49-0.51 in CCl_4 to 0.60-0.61 in nitromethane, and 0.84-0.90 in absolute alcohol. Despite the provisional character of the values in question here, it seems clear that the nature of the solvent was an essential factor in fixing σ^{Φ} for each substituent. It should be pointed out that a variation of σ^{Φ} with alteration of the solvent has been observed in the alkylenedioxide group [1, 20].

In distinction to the values given above, σ^{Φ} values for the $CF_3CH_2CH_2$ and $CF_3CH_2CH_2O$ groups calculated from the measured pK proved to be unaffected by a change in the solvent. The respective mean values of these groups in CCl_4 were −0.37 ± 0.10 and 0.04 ± 0.15.

CONCLUSIONS

1. Various polyfluoro acids of phosphorus have been synthesized. Potentiometric titration in transference cells has been used to determine the dissociation constants of these acids in nitromethane and in 50, 80, 95, and 100% alcohol solutions.

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*Calculated from the data of Table 3.

† For 50% EtOH: $pK = 2.05 - 1.24\ \Sigma\sigma^{\Phi}$ [4]; for 80% EtOH: $pK = 2.70 - 1.22\ \Sigma\sigma^{\Phi}$ [4]; for 95% EtOH: $pK = 4.20 - 1.27\ \Sigma\sigma^{\Phi}$ [1]; for CH_3NO_2: $pK = 8.97 - 2.16\ \Sigma\sigma^{\Phi}$ [1].

‡This differs only slightly from the equation given earlier in [15]: pK_a (EtOH) = $6.37 - 1.03\Sigma\sigma^{\Phi}$, n = 8, r = 0.989.

2. The differences in strength of the polyfluoro acids of phosphorus tend to be minimal in aqueous alcoholic solution.

3. The spectral characteristic ($\Delta\nu_{OH}$) of the H-bonds of phenol–polyfluorophosphoryl complexes have been measured in CCl_4 solution.

4. The σ^{Φ} values of polyfluoroalkoxyl substituents are radically different in aqueous and in water-free solvents. The companion values for 3,3,3-trifluoropropoxy and 3,3,3-trifluoropropyl groups are not affected by changes in the solvent.

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