STUDIES OF DIFLUOROPHOSPHORIC ACID AND ITS ALKALI METAL SALTS

by

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ABSTRACT

Difluorophosphoric acid was purified by a double distillation technique. Alkali metal difluorophosphates were prepared by reaction of the metal chlorides with purified difluorophosphoric acid; x-ray powder photographs and infra-red spectra of the salts were obtained.

Electrical conductivity measurements were made on solutions of the alkali metal difluorophosphates in difluorophosphoric acid as solvent. The order of mobility of the alkali metal cations in this solvent was found to be Li>Na>K>Rb>Cs. Results indicate that the difluorophosphate ion does not conduct by a proton transfer process in this solvent.

Conductimetric studies on solutions of a number of other compounds in difluorophosphoric acid are also reported.

:1

TABLE OF CONTENTS

	PAGE
INTRODUCTION	
(a) Historical	1
(b) Purpose of this work	7
EXPERIMENTAL	
I. PREPARATION AND PURIFICATION OF MATERIALS	
(a) Difluorophosphoric acid	8
(b) Difluorophosphates	9
(c) Other materials	15
II. PHYSICAL METHODS	
(a) Electrical conductivity	17
(b) Infra-red spectra	20
(c) X-ray powder photography	22
RESULTS AND DISCUSSION	
(a) Electrical conductivity	23
(b) Infra-red spectra	35
(c) X-ray powder photography	39

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LIST OF FIGURES

FIGURE		PAGE
1	Difluorophosphoric acid distillation apparatus	10
2.	Fraction collector used on distillation apparatus	11
3.(a)	Dropping funnel used for acid addition for distillation	12
(b)	Weight dropper used for addition of fluorosulphuric acid to the cell	
4.	Apparatus used for the preparation of alkali metal difluorophosphates	13
5.	Drying-train tester	16
6.	Difluorophosphoric acid conductivity cell	18
7.	Injector used for solute additions to conductivity cell	21
8.	Specific conductances of some difluorophosphates at 25°	25
9.	Specific conductances at low concentrations at 25°	28
10.	Specific conductances of some electrolytes at 25°	31
11.	Conductimetric titration of HSO_3F against $NH_4PO_2F_2$ at 25°	° 32
12.	Infra-red spectra of CsP02F2 and NaP02F2	38
13.	X-ray powder films of some difluorophosphates	40

LIST OF TABLES

TABLE		PAGE
I	Analysis results for P and F in the difluorophosphates	14
II	Specific conductances of some difluorophosphates at 25°	.24
III	Specific conductances of some electrolytes at 25°	30
IV	Infra-red data of the difluorophosphates	37

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V

INTRODUCTION

As no previous survey on difluorophosphoric acid and its salts has been made it was felt that a review of the literature would prove valuable.

(a) Historical

Difluorophosphoric acid was first prepared by Lange¹ in 1927 phosphoryl trifluoride was hydrolysed in cold water to give difluorophosphoric acid, the hydrolysis taking place in three stages:^{2,3}

$$0=P \xrightarrow{F} F \xrightarrow{OH} 0=P \xrightarrow{OH} 0=P \xrightarrow{OH} 0=P \xrightarrow{OH} 0=P \xrightarrow{OH} 0H$$

If the hydrolysis of POF_3 is carried out in a weakly basic solution it is possible to isolate the compounds HPO_2F_2 and H_2PO_3F in the form of their salts. The fluorine substitution products⁴ of meta- and orthophosphoric acids are stable to water in much the same way as fluorosulphuric acid⁵. However, even in neutral aqueous solution hydrolysis slowly occurs, the rate being much more rapid in the presence of acid or alkali⁶.

No further studies were reported on this acid for almost fifteen years. In 1941 Tarbutton, Egan and Frary⁷ examined the reaction,

 $CaF_2 + P_2O_5 \longrightarrow POF_3 + Ca(PO_3)_2$

and found that when they varied the ratio of the reactants varying amounts of difluorophosphoric acid as a volatile by-product were obtained. The presence of the acid was explained by the partial hydrolysis of POF₃ by small amounts of water present. The volatile by-products were separated and the boiling point of the acid was given as 108-111°. This appears to have been the first isolation of the acid contrary to the view of Sidgewick that the free acid does not exist³.

Lange⁸ investigated the reaction between phosphoric oxide and hydrogen fluoride to yield monofluorophosphoric acid.

$$P_2O_5 + 2HF + H_2O = 2H_2PO_3F$$

Difluorophosphoric acid or a mixture of H_2PO_3F and HPO_2F_2 were produced depending on the HF concentration. The same products were obtained when 100% orthophosphoric acid was allowed to react with aqueous hydrofluoric acid containing 41% HF.¹⁰ When liquid, anhydrous hydrogen fluoride was used⁹ in a 1:1 molar ratio with H_3PO_4 , 67% of the H_3PO_4 was transferred into the fluorinated derivative. However, the monofluorophosphoric acid, formed in the reaction, entered into a new equilibrium reaction with unreacted HF, forming difluorophosphoric acid.

> $H_3PO_4 + HF \implies H_2PO_3F + H_2O$ $H_2PO_3F + HF \implies HPO_2F_2 + H_2O$

Analysis of the equilibrium product showed that 33% H₃PO₄ was unchanged, 60% was transferred to the monofluorophosphoric acid but only 7% to the difluorophosphoric acid.

Variations on previous methods were attempted in order to synthesize the acid. Anhydrous monofluorophosphoric and difluorophosphoric acids were prepared¹¹ by allowing orthophosphoric acid and phosphoryl trifluoride to react at $70^{\circ}-80^{\circ}$. However, the usual problem of a mixture of products was obtained¹². Further work by Lange and Livingston¹³ consisted of a study

of the fluorophosphoric acids and a preparation of anhydrous difluorophosphoric acid. The hydrolysis of phosphoryl trifluoride was investigated and it was found that pure acid could be obtained by the reaction:

$$POF_3 + POF(OH)_2 \longrightarrow 2POF_2(OH)$$

Experimental details are given in the article together with various properties of the acid $(d^{25^\circ} = 1.583, \text{ m.p.} = -96.5^\circ \pm 1^\circ \text{ and b.p.} = 115.9^\circ).$

The system $H_2O-HF-P_2O_5$ was further examined by Shaposhnikova¹⁴; difluorophosphoric acid was prepared by adding P_2O_5 to an ice cold solution of HF in fluorosulphuric acid. The product was distilled in vacuo and fractionated; difluorophosphoric acid was found to decompose at its boiling point of 108°, its molecular heat of evaporation is given as 9125=360 cals. and Trouton's constant as 23.7-24.6. The acid was found to attack silicates at room temperature, the rate increasing with rise of temperature.

Nuclear magnetic resonance studies of solutions in the homogeneous region of the system $H_2^{0-HF-P_2^{0}}$ confirm the presence of a mixture of acids. Ames, Ohashi, Callis and Van Wazer¹⁵ detected the presence of HPO_2F_2 , HPF_6 , H_3PO_4 and H_2PO_3F in the system and estimated their relative concentrations by examining the F^{19} and P^{31} nuclear magnetic resonance spectra. An actual total of nine structural entities were found; in addition to the above acids, free water, end- and middle-phosphate structure units and a new structure unit containing one fluorine per phosphorus atom which is believed to be a monophosphate end group, were also found.

Various other workers have investigated the fluorophosphoric acids by nuclear magnetic resonance; multiple magnetic resonance lines have been observed for F^{19} and P^{31} nuclei in HPO_2F_2 , PF_3 , PH_3 , H_2PO_3F and HPF_6 in the

liquid state. At a field strength of 6385 gauss a splitting of 0.244 gauss was obtained by Gutowsky, McCall and Slichter¹⁶ for the F^{19} resonance in HPO₂F₂. Quinn and Brown¹⁷ measured the nuclear magnetic resonance splittings for F^{19} in HPO₂F₂ in weak fields. At a magnetic field strength of approximately 550 gauss they obtained a splitting of 0.240 gauss, but the doublet structure observed for the F^{19} resonance in HPO₂F₂ coalesced as the field was decreased until a single broad resonance was obtained at approximately 200 gauss. However, Roux and Bene¹⁸ obtained spectra at 35-15 gauss and found a doublet; the results were in general agreement with experiments at higher fields (at a field strength of 37 gauss a splitting of 0.245 gauss was observed), but as no singlet was observed it was concluded that the singlet observed by Quinn and Brown in the field of 200 gauss cannot be explained in terms of the size of the main field only.

Further information regarding indirect coupling of nuclear spins in molecules containing P-F and P-H bands has been reported by Frank^{19} ; the relative magnitude of J_{P-P} and J_{H-P} are given for HPO_2F_2 and other phosphorus compounds. For the series (i) F_3PO , (ii) $F_2PO(OH)$, (iii) $\text{FPO}(OH)_2$ and (iv) $PO(CH)_3$ Gutowsky and McCall²⁰ found phosphorus resonance in (ii) and (iv), with phosphorus shielding greater in (ii); the fluorine shielding increases with F-substitution.

Several salts of difluorophosphoric acid are known; the ammonium salt²¹ can be prepared by the fusion of phosphoric oxide with ammonium fluoride, the product being extracted with dry alcohol to remove the ammonium difluorophosphate which is then recrystallized from hot water. Dilute solutions of the ammonium salt treated with a soluable salt of nitron give a crystalline precipitate of nitron-difluorophosphate. Lange² prepared a number of salts

by treating hot aqueous solutions of nitron difluorophosphate with metallic nitrates, nitron nitrate was filtered off and the solution evaporated to dryness to recover the difluorophosphate. Most of the salts were found to be very soluble in water but the potassium and the cesium salts only moderately so. The difluorophosphates are stable in neutral solution, but less so in alkaline or acid solutions. Their general behaviour is similar to that of the perchlorates (and also the fluoroborates and fluorosulphates), the less soluble salts of both acids being the potassium and cesium salts. The alkali salts are isomorphous with the perchlorates, fluorosulphates and fluoroborates; this resemblance is due to these all being strong monobasic acids with tetrahedral anions of nearly the same size³. Jonas²² was able to prepare difluorophosphates by allowing salts of hexafluorophosphoric acid to react with oxides such as: SiO_2 , B_2O_3 , WO_3 ? CaO or sodium metaphosphate. Quantitative yields were obtained. Ryss and Tul'chinskii²³ investigated a new method to prepare the sodium salt free from other fluorophosphates. NaHF, and P20, were allowed to react in a platinum crucible, the product being extracted with absolute methanol. Rates of hydrolysis of the sodium salt were investigated and it was found that in neutral aqueous solution, hydrolysis was slow even at 100°. However, on heating in 0.1 N NaOH solution at a 3:1 ratio of OH^- to $NaPO_2F_2$ for 10 minutes at 70° quantitative hydrolysis occurred by the reaction:

$$PO_2F_2^- + 20H^- = PO_3F^{2-} + F^- + H_2O$$

On heating with excess of 0.1 N. NaOH in a stainless steel ampoule for about 2 hours at 160° complete decomposition occurred by the reaction

 $PO_2F_2^-$ + 30H⁻ = HPO_4^{2-} + 2F⁻ + H₂O

Of the salts, only the potassium and the ammonium salt have been investigated spectroscopically; Corbridge and Lowe²⁴ examined the infra-red spectra of ammonium difluorophosphate in the region 5,000 - 650 cm.⁻¹, and an assignment of the frequencies was made. Bühler and Bues²⁵ investigated the vibration spectra of fluorophosphate melts and crystals; the infra-red and Raman spectra of crystalline KPO_2F_2 , KPF_6 and K_2PO_3F are reported and assignments made. The force constants and bond orders in these and in related anions are discussed.

The only conductivity studies on difluorophosphoric acid have been made by Barr, Gillespie and Robinson²⁶, who measured the electrical conductivity of solutions of $HC10_4$, $HS0_3F$, $HP0_2F_2$, and $HS0_3C1$ in sulphuric acid. They found that $HS0_3F$ and $HS0_3C1$ behaved as acids, whereas $HP0_2F_2$ and CH_3S0_3H were bases in the H_2S0_4 system.

Difluorophosphoric acid has found little use in inorganic chemistry; however, Stolzer and Simon^{27,28} have used the acid extensively in organic reactions. Hood²⁹ has shown that the treatment of difluorophosphoric acid with aliphatic alcohols yields alkyl hydrogen phosphorofluoridates;

 $HPO_2F_2 + ROH \longrightarrow (RO) (OH) POF_2$

The fluorophosphoric acids have been used as polymerisation^{30a,b}, condensation and alkylation catalysts, and also as anhydrous acids in the non-oxidising refining of-oils.

The salts of difluorophosphoric acid have been used industrially: Na, K, Li, Ba and Pb salts stabilize chloroethylene polymers³²; Zn, Co, Pb, Fe and Cd salts are used as catalysts in the preparation of β -lactones³³, and, substituted aluminium chlorides, e.g., AlCl₂PO₂F₂ serve as alkylation catalysts³⁴.

(b) Purpose of the present work

The purpose of this work is to investigate the properties of solutions in difluorophosphoric acid and in so doing extend the range of studied protonic solvent systems. As no complete study of all the alkali metal difluorophosphates has ever been made by a single author these compounds have been investigated further by infra-red and x-ray powder diffraction methods.

EXPERIMENTAL

I. Preparation and purification of materials

(a) Difluorophosphoric Acid

Commercial difluorophosphoric acid, supplied by Ozark-Mahoning Chemical Company, was purified by five double distillations at 9.0 cms. of mercury and a temperature range of 45°-49°C. (Gillespie²⁶ used 15 mms and 44°-46°) in the apparatus³⁵ shown in Fig. I. The procedure was as follows. The apparatus was evacuated and flamed out with a hot bunsen flame. Dry air was allowed to enter through tap H until atmospheric pressure was attained. A dry, dropping funnel (Fig. 3a) was filled, in a dry box, with difluorophosphoric acid and was then fitted into the distillation apparatus at L. The acid was allowed to drain into the flask A. The dropping funnel was removed and the thermometer well replaced. The system, which was connected to a vacuum pump at N via liquid nitrogen traps and an acetone-dry ice trap, was evacuated to about 9 cms. of mercury. The acid was then refluxed for about 30 minutes to remove hydrogen fluoride which was condensed out in the liquid nitrogen traps. The acid was distilled into tube C until a temperature of 45°C. was reached. At this temperature the distillate was directed into flask B by the fraction collector E (E is shown in more detail in Fig. 2). Tap M was then closed and the vacuum pump was disconnected from N and attached to O.

The second distillation was carried out under the same conditions, but in this case separation was achieved by rotating F within the B.19 ground glass socket at G so that the acid could be directed into either D or J as

desired. Flask D containing the required acid was quickly detached and capped; it was then transferred to the dry box and the acid poured into the dropping funnel. Clean, dry apparatus was set up and the distillation repeated. In the first two or three double distillations considerable attack of glass occurred. In an attempt to reduce this, the acid was first refluxed under vacuum at temperatures slightly above room temperature for 24 hours in a stainless steel condenser and flask; however, on subsequent distillation in the glass apparatus no improvement was observed. Carrying out the same procedure as above but at room temperature had no effect on the result.

Periodic checks of acid purity were made by examination of the fluorine nuclear magnetic resonance spectrum¹⁴.

(b) Difluorophosphates

Ammonium, lithium, sodium, potassium, rubidium and cesium difluorophosphates were prepared by the reaction:

 $M C1 + H PO_2F_2 \longrightarrow M PO_2F_2 + H C1$

where M is the metal cation. Fig. 4 shows the apparatus used. The dry metal chloride was placed in the reaction vessel D which was then attached to the acid distillation apparatus at K in Fig. 1. The apparatus was evacuated and then flamed out in the normal manner. Difluorophosphoric acid was distilled at the usual pressure and temperature onto the chloride which immediately reacted with the acid resulting in the evolution of HC1. When sufficient acid had been added to dissolve all of the solid the reaction vessel was removed from the distillation apparatus and a ground glass B 19





FIG. 3(a) DROPPING FUNNEL (b) WEIGHT DROPPER



cap was quickly placed on Q. Tube R was then removed and the reaction vessel was attached via S to the vacuum pump. The excess difluorophosphoric acid was removed at a pressure of about 0.5 mms. of mercury, with occasional warming of the vessel D with a bunsen flame. When all the acid had been removed the product was washed with ether and then recrystallized from dry methanol (except the sodium salt which was found to be exceedingly soluble and was, therefore, recrystallized from dry ethanol). Finally the difluorophosphates were washed with ether, dried and stored over phosphoric oxide in a vacuum desiccator.

Aqueous solutions of the salts showed no precipitation on addition of silver nitrate solution (negative test for chloride) and no precipitation on addition of lead and barium nitrate solutions $\frac{36}{6}$ (negative tests for monofluorophosphate and fluoride).

Fluorine and phosphorus microanalysis were obtained in the A. Bernhardt Microanalytical Laboratories, Germany, and the results are shown in Table I below.

TABLE I

	Li		Na		К	
	calc.	obt.	calc.	obt.	calc.	obt.
%P	28.81	28.7	24.99	24.82	22.12	22.1
%F	35.21	35.5	30.65	30.80	27,14	27.29
	R	b	с	S	NI	ł
	calc.	obt.	calc.	obt.	calc.	⁴ obt.
% ₽	16.61	16.53	13.24	13.14	26.03	25.83
\$F	20.38	20.42	16.25	16.42	31.93	32.23
				kN m	11.76	11.63

(c) Other Materials

sodium monofluorophosphate: Commercial Na₂PO₃F obtained from Alfa Inorganics Inc. was recrystallized once from water.

sodium fluoride: Chemically pure NaF was dried in a drying pistol at 80° and a pressure of 10 mms. of mercury for three days.

<u>fluorosulphuric acid</u>: Commercial HSO₃F obtained from the Allied Chemical Co. was double-distilled at 164[•].

potassium fluorosulphate: KSO_3F was prepared by the method used by Gillespie et al.³⁷

dry air: The air allowed to flow into the vacuum distillation system was passed first through calcium chloride, then magnesium perchlorate and finally through a liquid nitrogen trap followed by an acetone/dry ice trap. As some compounds, as well as the acid, were handled in the dry box, compressed air was passed first through three gas wash-bottles containing concentrated sulphuric acid, then through a tube containing calcium chloride and finally through a tube containing magnesium perchlorate. The air, dried in this way, was always tested for traces of water by means of the""drying-train" tester, shown in Fig. 5. The air was allowed to enter the tester at A from the outlet of the dry box, then pass over 30% oleum contained in B and exit via C. If the air caused no fuming in the vessel it was considered to be dry enough for use. Air, dried in this manner was passed through the dry box for several hours before use. Several dishes of phosphoric oxide were placed at various locations in the dry box to ensure as dry an atmosphere as possible.



II. Physical Methods

(a) Electrical Conductivity

The design of the cell used to measure the conductivities of solutions in difluorophosphoric acid is shown in Fig. 6. The cell could be attached to the distillation apparatus at K by means of the B.19 ground glass cone L. The cell has three electrodes and was designed so that the cell constant, when using electrodes B and C, was approximately 5 while the constant, when used electrodes B and A was approximately 15. Thus, accurate conductivity measurements could be made on weakly conducting solutions using the electrodes A and B, while measurements on more strongly conducting solutions were made using electrodes B and C. The capacity of the cell was about 400 mls.

The cell was cleaned with aqua-regia and the electrodes were plated with platinum black by electrolyzing a chloroplatinic acid solution prepared according to Jones and Bollinger³⁸. The solution consisted of a 0.3% solution of chloroplatinic acid in 0.025N. hydrochloric acid with 0.02% lead acetate added. A current of 10 milliamps. was passed for 15 mins. with a reversal of current every 10 seconds. The cell was steamed out, dried and then calibrated using aqueous potassium chloride solution according to the method of Lind, Zwolenik and Fuoss³⁹. The cell was replated and recalibrated after every four or five experiments.

All measurements were made with the cell immersed in an oil bath regulated by means of a mercury-thallium regulator at 25[±] 0.002°. The temperature of the thermostat was measured by Beckmann thermometers which had been calibrated against a platinum resistance thermometer.



18 %

X

The apparatus used to make solid additions to the cell is shown in Fig. 7. It consisted of a "T"-shaped glass tube with B.19 ground glass sockets at the ends O and P, and a B.24 ground glass cone with an extension at M. The corks at O and P were made of teflon and they were tightly fitted with stainless steel pistons A and B respectively. The flat "runners" which were also made from teflon interlocked at Q and lay on the bottom of the tubes. The compound to be added to the cell was weighed into small, preweighed, dry, glass boats which were inserted through O of the sidearm. Approximately eight boats could be accommodated in the sidearm. The loaded injector was then connected at M tr a rotary vacuum pump via liquid nitrogen traps, warmed and evacuated. This was done to remove any water absorbed during the weighing-out process. After several hours the injector was detached from the pump and stored until use in the dry box.

A conductivity run was carried out in the following manner; the conductivity cell was attached by means of a B.19 inner ground glass joint directly to the distillation apparatus at K and flushed out with dry air. Difluorophosphoric acid was distilled directly into the cell; acid obtained in this way usually had a conductivity between 2.41 x 10^{-4} and 2.51 x 10^{-4} ohm. $^{-1}$ cm. $^{-1}$. At all times in handling the acid great care was taken to exclude water. It was found that there was a gradual increase in the specific conductivity with time; over a period of 4-5 hours a 1% increase in K was observed. Solutions for conductivity measurements were prepared as follows: difluorophosphoric acid was distilled directly into the cell which was weighed before and after addition of the acid. The B.24 stopper was removed and the injector was quickly inserted into the cell at F. Mercury was poured into the glass tubes holding the platinum electrodes, care being taken

to remove all the air bubbles. The cell and the injector were then placed on a support in the oil bath. To make an addition, a glass boat was pushed by the piston A from the sidearm into the main tube, the boat was then moved by piston B along N and pushed into the acid.

After each addition of solute the cell was well shaken to ensure good mixing, and returned to the thermostat. After sufficient time had elapsed to allow for temperature equilibrium (15 to 20 minutes) the resistance measurements were made. The cell was then removed from the thermostat, shaken again, and the resistance measurements repeated. In this manner errors due to insufficient mixing were eliminated.

Fluorosulphuric acid was added to the cell by means of the weight dropper shown in Fig. 3b. As both acids hydrolyze in air, the weighed sample was added to the cell in the dry box. The cell was returned to the thermostat and the above procedure for measuring resistance was followed.

Resistances of solutions were measured on a precision a-c resistance bridge which has been previously described by $Daggett^{40}$. A 2,000 c/s oscillator was employed as the source and a telephone headset was used as the null-detector.

Throughout this work, specific conductance will be referred to by the symbol K.

(b) Infra-red spectra

All spectra were recorded from 4,000 to 250 cm.⁻¹ on a Perkin-Elmer 421 Double Beam Spectrophotometer under "normal" operating conditions. The materials were examined as fine powders spread on cesium iodide plates. This was accomplished by finely grinding the sample and then dissolving it in dry



methanol. A thin layer of the resulting solution was obtained on the cesium iodide, which was then placed on a hot plate to drive off the methanol. Specimens were obtained as a thin layer, thicker samples being used when searching for weak absorption. A decrease in transmittance above about 2,000 cm. $^{-1}$ due to scattered radiation was observed in many spectra; this was not removed on decreasing the particle size. By taking spectra with Nujol mulls in the higher frequency region, sharper absorptions were obtained.

(c) X-ray powder photographs

X-ray powder samples of the difluorophosphates were prepared in 0.3 mm. quartz capillaries by the method described by Azaroff and Buerger⁴¹. The x-ray photographs were taken using a General Electric Camera of 14.32 cm. diameter. This camera employs Straumanis loading. Nickel filtered (using a 0.089 cm. thick Ni-foil) Cu-Ka radiation ($\lambda = 1.5418$ Å) was used as the source. The x-ray tube was operated at 35 kilovolts and 15 milliamps. The camera employed a slit collimator, for which the exposure time required was between 3-6 hours depending on the sample.

RESULTS AND DISCUSSION

(a) Electrical Conductivity

The results of the conductivity measurements on solutions of metal difluorophosphates in difluorophosphoric acid at $25\pm 0.002^{\circ}$ are given in Table II. As all the solutions were made up by weight the concentrations are expressed in molal units (m); due to the lack of accurate density data no attempt was made to express the concentrations in molar units. In each case a plot of κ against molality was made (Fig. 8). By analogy with other protonic solvent systems HPO_2F_2 would be expected to undergo autoprotolysis according to the equation:

 $2HPO_2F_2 \implies H_2PO_2F_2^+ + PO_2F_2^-$ ------1 In this system then, bases may be defined as substances which, when dissolved in difluorophosphoric acid, increase the concentration of the difluorophosphate anion $PO_2F_2^-$, and acids may be defined as any substance which increases the concentration of the difluorophosphoric acidium ion $H_2PO_2F_2^+$. It is, therefore, expected that the alkali and alkaline earth difluorophosphates will behave as strong bases in this system.

 $M PO_2F_2 = M^+ + PO_2F_2^-$ -----2

In solvents where the mobilities of the autoprotolysis ions are very much greater than the mobilities of other ions (due to a proton transfer mechanism of conduction for the former ions), strong bases exhibit almost identical conductivity curves at low concentrations with small deviations noticeable only in the more concentrated solutions³⁷. As the conductivity curves for the alkali metal difluorophosphates deviate from each other at even the lowest concentrations measurable, it must be concluded that $PO_2F_2^{-1}$ ion does not show abnormal conduction.

TABLE II

SPECIFIC CONDUCTANCES OF SOME DIFLUOROPHOSPHATES AT 25°C.

LiP	0,F,	KPO,	F ₂	RbPC	P_2F_2	
10^{2} m	10^{4} K	10^{2}m^{2}	² 10 ⁴ κ	10^{2} m	10 ⁴ к	
10	ohm. $^{-1}$ cm. $^{-1}$		ohm. ⁻¹ cm. ⁻¹		ohm. $^{-1}$ cm. $^{-1}$	
0.000	2.482	0.000	2.410	0.000	2,499	
0.306	2.673	0.158	2.557	0.639	2.662	
1.020	3.464	0.566	2.740	2.051	3.318	
2.190	4.528	1.326	3.153	4.056	4.314	
4.429	6.379	2.485	3,889	7.084	5.825	
6.773	8.086	4.043	4.925	11.22	7.829	
9.733	10.15	6.054	5.939	16.84	10.56	
13.91	12.73	9.310	7.658	23.63	13.81	
19.69	16.59	13.83	10.10	31.88	17.72	
27.66	20.46	18.53	12.79			
37.20	24.48	23.88	15.21	CsPC	D ₂ F ₂	
49.84	29.18	29.65	17.77	· · 2	2 2 104	
60.08	32.21	34.37	19.82	IU m	10 K	
70.55	34.56	40.28	22.46		ohm. cm.	
		48.26	24.27	0 000	2 443	
				0.000	2.445	
NaP	0,F,	NH_PO	2F2	1 409	2.303	
10 ²	² ² 10 ⁴	10^{2}	10 ⁴ r	3 191	3,708	
TO IU	10 K	ТОШ		6 155	5,041	
	ohm. cm.		ohm. cm.	9.751	6,665	
0 000	2.503	0.000	2.473	13.48	8,395	
0.000	2.557	1.977	3,546	17.92	10.51	
0.761	2.868	5.864	5.851	24.29	13.64	
2.859	4,500	11.44	9.110			
6.008	6.794	18.75	13.35	NH	PO ₂ F ₂ (at low concer	ntration)
8.220	8.266	27.15	18.71	102-4	2 2 104	
11.16	10.12	35.60	23.91	IU M	$\frac{10}{-1}$ K -1	
15.13	12.26				onm, cm,	
20.95	15.15	•	•	0.000	2,499	
25.36	17.96			0.380	2.693	
31.37	20.67			1.090	3.088	
36.88	22.81			1.842	3.546	
42.46	24.75			2,724	4.076	
47.79	26.40			3.758	4.691	
				4.834	5.507	
•				6.718	6.619	
				8.940	7.740	



The conductivity of the alkali metal difluorophosphates at any given concentration decreases in the order Li>Na>NH₄~K>Rb>Cs. As all these salts have the common anion $PO_2F_2^-$ the difference in conductivity must be due to differences in the mobilities of the cations. This order of cation mobility is opposite to that found by Gillespie et al. in their conductance measurements in HSO_3F^{37} and $H_2SO_4^{42}$ in which they found the order Cs>Rb>NH₄~K>Na>Li prevailed. Gillespie⁴³ has suggested that the lighter members have the larger solvated ion size, therefore, accounting for their lower mobilities. Our results suggest that solvation of cations in HPO_2F_2 is weak and, therefore, the mobility is determined by the unsolvated ion size. As may be seen the potassium and the ammonium salts give conductance curves which are almost collinear at low concentrations (Fig. 9). This agrees with other workers' findings that the potassium and ammonium ions are of similar size and hence have similar mobilities^{37,42}.

On extrapolation of the linear portion to zero concentration the curves do not pass through the origin nor through the initial point corresponding to the solvent conductivity. There must, therefore, be some curvature of the conductivity curve at the lowest concentrations and this appears to be substantiated on close examination (Fig. 9). The conductivity of the acid may be attributed at least partly to its autoprotolysis. However, if the conductivity of the pure solvent is due only to the ions produced in the autoprotolysis reaction the linear portion of the conductivity curve should pass through the origin on extrapolation. It appears that on extrapolation the conductivity at zero concentration is approximately 2.3×10^{-4} ohm. $^{-1}$ cm. $^{-1}$ This may be attributed to ions other than those produced in reaction (1).

These ions presumably arise from impurities such as monofluorophosphoric acid, hydrogen fluoride and water. Small traces of water would cause hydrolysis of the acid as given by the following equations:

$$HPO_{2}F_{2} + H_{2}O \implies HF + H_{2}PO_{3}F$$
$$H_{2}PO_{3}F + H_{2}O \implies HF + H_{3}PO_{4}$$

Ions would arise from the ionization of HF which would be expected to behave as a weak acid:

$$HPO_2F_2 + HF \implies H_2PO_2F_2^+ + F^-$$

and from the ionization of H_2PO_3F which would be expected to behave as a weak base:

$$H_2PO_3F + HPO_2F_2 \implies H_3PO_3F^+ + PO_2F_2^-$$

No evidence of any impurity was obtained on examination of the fluorine nuclear magnetic resonance spectra (a doublet with a splitting of 0.241 gauss (969.5 c.p.s.) was obtained which agrees well with that of Gutowsky¹⁶, Quinn¹⁷ and Roux¹⁸). The original acid appeared to contain 50% monofluorophosphoric acid and although the final acid showed no monofluorophosphoric acid impurity in the N.M.R. spectrum the concentrations of impurity with which we are concerned in conductivity work are too low to be detected by N.M.R.

In order to investigate salts which contain anions other than PO_2F_2 solutions of NaF, Na₂PO₃F, KSO₃F and HSO₃F were studied (Table III). Potassium fluorosulphate is insoluble; however, conductance results were obtained for the other solutes and these are given in Fig. 10.

At low concentrations the slope of the κ -m curve for Na₂PO₂F is more



than twice that of $NaPO_2F_2$ and this may be explained by assuming that Na_2PO_3F reacts as is given by equation below:

 $Na_2PO_3F + 2HPO_2F_2 \longrightarrow 2Na + 2PO_2F_2 + H_2PO_3F$ As a result of this Na_2PO_3F should have a conductivity curve with twice the slope of the curve for $NaPO_2F_2$. The fact that it is slightly more than twice can be explained by assuming that monofluorophosphoric acid is a base in this solvent and is protonated by the difluorophosphoric acid:

$$H_2PO_3F + HPO_2F_2 \longrightarrow H_3PO_3F^+ + PO_2F_2^-$$

The slope of the conductivity plot for sodium fluoride is considerably lower than that of $NaPO_2F_2$, while this could be due to a much lower mobility of the F⁻ ion compared to that of the $PO_2F_2^-$ ion it is more probably due to incomplete dissociation of NaF through ion pair formation

$$Na^+F^- \implies Na^+F^-$$

This idea is supported by the fact that at low concentration where ion pair formation is weakest the slope of the NaF curve is very similar to the curve for $NaPO_2F_2$, while at higher concentrations the slope of the NaF curve decreases whereas that of $NaPO_2F_2$ remains essentially constant. This tendency for ion pair formation is consistent with the apparent low solvating power of the medium. It is not immediately obvious why the difluorophosphates themselves show less tendency to form ion pairs than other salts in difluorophosphoric acid.

Conductivity data for solutions of fluorosulphuric acid in HPO_2F_2 are also given in Fig. 10. Solutions of HSO_3F may be neutralized by addition of the base $NH_4PO_2F_2$ giving rise to precipitation of the salt NH_4SO_3F and a resulting decrease in conductivity (Table III, Fig. 11) of the solution. These results prove that HSO_3F is an acid in this system, probably ionizing according to the equation:

TABLE III

Na_PO_F		HSO _z F	
10^{2} m ²	10 ⁴ κ	10^2 m	о 10 ⁴ к
	ohm. $^{-1}$ cm. $^{-1}$		ohm. $^{-1}$ cm. $^{-1}$
0.0000	2.443	0.000	2.580
0.0754	2.455	11.81	5.02
0.1990	2.567	17.70	7.46
0.5426	3.216	23.62	9.79
1.131	4.280	29.50	12.19
2.064	6.368	41.35	18,86
3.684	8.896	53.10	24.60
6.908	14.38		
11.83	21.30		

Addition of $NH_4PO_2F_2$ to the 0.531 molal. HSO_3F/HPO_2F_2 solution - conductimetric titration

Nal	2	NH P	0,F,
10^2 m	10 ⁴ к	10 ² m 4	10 ⁴ κ
	ohm. $^{-1}$ cm. $^{-1}$		ohm. $^{-1}$ cm. $^{-1}$
0.0000	2.300	6.79	19.33
0.4115	2.441	22.9	10.25
1.811	3.239	45.6	4.48
4.166	4.263	61.8	8.16
8.315	5.685		,
13.81	7.520		
30.15	11.68		

30

SPECIFIC CONDUCTANCES OF SOME ELECTROLYTES AT 25°C.





$$HSO_{3}F + HPO_{2}F_{2} \longrightarrow H_{2}PO_{2}F_{2} + SO_{3}F$$

The κ versus m curve for HSO₃F shows an initial flat portion followed by a linear increase in conductivity with concentration. On extrapolation of the linear portion to zero concentration the curve does not pass through the initial point corresponding to solvent conductivity but appears to pass through the origin. If the impurity in the solvent is in fact basic then addition of HSO₃F should neutralize this impurity. In fact the flat portion of the HSO₃F curve may be attributed to titrating the impurity. Since the slope of the linear portion of the HSO₃F curve is similar to the slopes of the curves for the difluorophosphates it may be concluded that fluorosulphuric acid is undergoing dissociation to roughly the same extent as occurs with the alkali metal difluorophosphates. Hence fluorosulphuric acid appears to be a strong acid in this solvent, a result which is consistent with the conclusion of Gillespie et al.²⁶ that HSO₃F is a very much stronger acid than HPO₂F₂.

Gillespie⁴⁴ has suggested that the strengths of inorganic oxyacids are determined largely by the number of equivalent oxygen atoms in the anion over which the negative charge may be spread. The strength of the acid increases with the number of equivalent oxygen atoms, therefore, HSO_3F , HSO_3Cl and HSO_3OH are of the same type, having the anions FSO_3^- , $ClSO_3^-$ and $HOSO_3^-$ with three equivalent oxygen atoms. ClO_4^- should, therefore, be the anion of the stronger acid $HClO_4$, which has four equivalent oxygen atoms, and $(HO)_2PO_2^$ and $F_2PO_2^-$ anions of weaker acids, having only two equivalent oxygen atoms. However, it seems reasonable to suppose that some of the charge on the anion is accommodated on the halogen atom and if the sharing of the charge between the oxygen atoms and halogen are equal HSO_3F and HSO_3C1 would be in the same class as $HC1O_4$. A similar effect for $PO_2F_2^-$ would put the acid in the same class as $HC1O_4$ and it would be expected to be stronger, rather than weaker, than H_2SO_4 . Gillespie et al.²⁶ have made comparisons of acid strengths of dilute solutions of various acids with that of H_2SO_4 in bulk, and obtained the order: $H_2S_2O_7$ >HSO₃F>HSO₃Cl>HC1O₄>HPO₂F₂; they have indicated that the acid strength of H_2SO_4 in bulk may, because of co-operative hydrogen bonding, be considerably greater than that of H_2SO_4 in dilute solution. This suggests that HPO_2F_2 may in fact be a stronger acid in bulk but our results do not substantiate this, since even in bulk HPO_2F_2 is a very much weaker acid than HSO_3F

Conclusions

Difluorophosphoric acid is a solvent of weak solvating ability as shown by the low solubility of salts such as KSO_3F and the order of mobilities of the alkali metal cations.

Since one of the requirements for proton transfer conduction in a solvent is association between the autoprotolysis ions and the solvent molecules through strong hydrogen bonds, then the absence of proton transfer conduction in this solvent may be due to a large extent to the inability of the solvent to solvate the ions strongly. Indeed the relative low boiling point of difluorophosphoric acid compared to the boiling points of $HSO_{r}F$ (163°) and $H_{2}SO_{4}(290-317°)$ for example indicates that hydrogen bonding in this solvent is very weak.

(b) Infra-red spectra

Results of measurements of the infra-red spectra of the difluorophosphates in the region 4,000-300 cm.⁻¹ are given in Table IV. The position of the peaks is in good agreement with the reported spectra for difluorophosphates; the absence of any absorption in the monofluorophosphate region indicates little contamination of the compounds used in this work by monofluorophosphate impurity. The spectrum for the lithium salt differs from that of the other salts studied; this could be due to a basic difference in the crystal structure. Spectra of CsPO₂F₂ and NaPO₂F₂ are given in Fig. 12 as typical spectra.

P-O stretching vibration region:

The ionic phosphate vibration has already been connected with absorption at 1040-1000 cm. $^{-1}^{44}$, 1110-1050 cm. $^{-1}^{45}$, and 1,170-1,000 cm. $^{-1}^{46}$. In the series of compounds studied only absorption in the last range of values was observed. The difference in position of the ionic phosphate absorption bands of the difluorophosphates compared with other phosphates has been connected with the presence of highly electronegative F atoms bonded to the phosphorus atom⁴⁷. Corbridge and Lowe²⁴ examined the spectra of annonium difluorophosphate in the region 5,000-650 cm. $^{-1}$ and their values are given in the table. It can be seen that they obtained an extra peak at 1,005 cm. $^{-1}$ and it appears likely that this may be due to monofluorophosphate (which absorbs in the region 1,070-1,000 cm. $^{-1}$) as no peak was detected in any difluorophosphate studied in this work. A difference of 30 cm. $^{-1}$ was found for the asymmetric PO stretching frequency from that found by Corbridge. However, the value obtained by Buhler and Bues²⁵ for the asymmetric PO stretch

in KPO_2F_2 agrees well with that found in this work. Their values for KPO_2F_2 are also given in the Table; it is felt that the peak they report at 535 cm.⁻¹ is due to monofluorophosphate which absorbs at 530 cm.⁻¹ in $\text{K}_2\text{PO}_3\text{F}$.

Robinson⁴⁸ has recently discussed P-O stretching frequencies in a number of phosphorus compounds. He found a linear relationship existed between the symmetric and asymmetric stretching frequencies of the PO₂ group. In ammonium difluorophosphate 1,125 cm.⁻¹ was assigned to the symmetric PO stretching frequency and 1,262 cm.⁻¹ to the asymmetric. However, Robinson used only the ammonium difluorophosphate in his plot of symmetric against asymmetric PO stretches; the straight line correlation is given by the equation:

$$v_{sym.} = 0.65 v_{asym.} + 270$$

Making use of the information obtained here on the difluorophosphates a better value for the straight line correlation is:

 $v_{\rm sym.} = 0.70 v_{\rm asym.} + 210$

P-F stretching vibration region.

P-F stretch has been assigned to the region 990-840 cm.⁻¹ in PF₃, POF₃ and PF₅⁴⁹ and 980-740 cm.⁻¹ in organophosphorus compounds⁴⁷. The absorption at 835-720 cm.⁻¹ found in all the monofluorophosphates has been assigned by Corbridge and Lowe²⁴ as probably due to P-F stretching; they also found that ammonium difluorophosphate absorbs in this region. However examination of Table IV indicates that the P-F stretch of the difluorophosphates lies in the region 940-818 cm.⁻¹. It⁵⁰ has been shown that the symmetric PF₂ deformation occurs around 500 cm.⁻¹ and this agrees well with the values obtained. However Buhler and Bues²⁵ have also assigned the symmetric PO₂ deformation to about the same region, namely 535 cm.⁻¹.

S.

TABLE IV

INFRA-RED DATA OF THE DIFLUOROPHOSPHATES

(FREQUENCIES IN cm.⁻¹)

LiP02F2	NaPO2F2	KPO2F2	RbP02F2
1273 s	1309 s	(1332 s	{ 1330 s
1164 s	1152 s	1310 s	[1310 s
940 s	(868 s	1148 s	1145 s
890 s	844 s	∫850 s	∫846 m
(525 s	(502 s	832 s	827 s
498 s	1458 m	∫503 s	(505 m
(426 s	360 w	1495 s	(492 s
415 5-			-
(357 5			
342 s			

CePO2F2	NH ₄ PO ₂ F ₂ 3,380-2,2680 m,vb.	NH4 ^{PO} 2 ^F 2 (Corbridge and Lowe ²⁴) 2,900-2,550 mw,bv.	KPO2F2 (Buhler 25) and Bues 25)
∫1321 s	∫1443 s	∫1445 w,sh	1330 w
1299 s	1410 s	1414 s	1311 s
1137 s	1292 s	1262 s	1145 s
{843 m.sh	1138 s	1125 s	£857as
818 s	(860 m,sh	1005 vvw	834 s
(503 m	1842 s	{870 w,sh.	535 w
1489 s	500 s	1832 s	∫512 m
•			481 s
			286 w

Note: Brackets indicate incompleted resolved bands (see Fig.12)

s = strong; m = medium; w = weak; sh = shoulder



The influence of the cations on the spectra do not appear to be very marked, except in the case of the lithium salt. A pronounced shift of all peaks to lower frequency was observed, excepting the asymmetric PO stretching frequency which occurs at 1,273 cm.⁻¹. These shifts are probably bound up with the tendency of lithium salts to exhibit some covalency. With the remaining alkali metal salts, a tendency for the shift of certain peaks to higher frequency with increasing mass is noticeable. The progressive shift is most evident with the symmetric PO stretching frequency, i.e. in LiPO_2F_2 it is 1,164 cm.⁻¹, and drops gradually to 1,137 cm.⁻¹ in CsPO₂F₂.

(c) X-ray powder photographs

Inspection of the x-ray powder films (Fig. 13) indicates that with the exception of LiPO_2F_2 and possibly NaPO_2F_2 the alkali metal and ammonium difluorophosphates are isomorphous. The anomality of the lithium salt may be due to the tendency of the lithium atom to attain only 4 co-ordination in the crystal while the other larger alkali metal cations attain 6 co-ordination.

The presence of numerous lines in the NaPO₂F₂ powder film indicates either that considerable impurity occurred in the sample used or that the NaPO₂F₂ is in fact not isomorphous with the other salts.



X-ray Powder Films

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